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SPECIAL SESSIONS

SpS 1 Special Session

Contaminated Land in the EU Accession Countries

LIQUIDATION AND RECULTIVATION OF REPOSITORIES CONTAINING UNWANTED PESTICIDES IN POLAND: CURRENT STATUS AND PERSPECTIVES FOR SOLVING THE PROBLEM

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Introduction

The repositories containing unwanted pesticides are a serious geoenvironmental problem in Poland. Foundation of special objects, later called "tombs", has began in 1965, when in the regions of southern Poland a relatively small amount of unwanted pesticides as well as their packages were buried directly in the ground. These places were commonly located nearby the stores of the agricultural co-operatives. Because the amount of unwanted pesticides successively increased, in 1971 a special "Instruction", which precised the type of constructions in which such products should be stored, was prepared. The recommended repository included up to several tens of concrete wells with a diameter 1-2 m and 3-4 m deep. Moreover, various military fortifications were used as repositories, from the bunkers of the IInd World War to the Prussian and Russian forts of XIXth century.

In the "tombs", besides the unwanted pesticides, were also collected the overdue drugs and small amounts of chemical reagents from school laboratories.

Location of "tombs" has never been proceeded by any geological recognition. Most often the repositories were located outside villages but there are also known cases of the "tombs" placed near inhabited areas. Foundation of new repositories was stopped at the beginning of the 80-ties but till the end of that decade the unwanted pesticides and their packages were stored in the existing constructions. These "tombs" pose a serious threat especially to ground waters and soils and less – for the atmosphere. Fires being the result of auto-ignition or arson were noticed in several of them.

In the 90-ties the "tombs" began to be considered as objects dangerous to the natural environments. It was soon found out that locations of some of these repositories became completely forgotten and the administration changes of the 70-ties caused dispersion of their technical documentations and liquidation protocols of unwanted pesticides. So, it was necessary to catalogue the "tombs" and to estimate their influence on the surrounding grounds and waters. The first catalogues were prepared in 1993 by the National Inspection of Environmental Protection. In 1994, the detailed cataloguing of "tombs" and other repositories containing unwanted pesticides, was started, accompanied with field inspections and detailed studies on selected most dangerous objects. The finish of these works, realised by the Polish Geological Institute, is planned for 2003.

After taking into consideration the hitherto collected data, it was concluded that ca. 300 "tombs", including also ca. 50 simple ground holes dated mostly at the 60-ties were located in Poland (Fig.1). Most of them were placed in the regions dominated by giant national farms, which obtained the pesticides for special lower prices and used them without a rational management. Because the data concerning the about amount of deposited pesticides is incomplete and unsure, it is difficult to estimate the volume of the pesticides stored in the “tombs”. Basing on the field observations, the number and volume of chambers in each repository and results of hitherto liquidated “tombs”, the amount of still stored pesticides (and their packages) is calculated as ca. 12-15 thousand tons.

Pesticides deposited in “tombs”, usually become a mixture whose components cannot be segregated. Here segregation is unnecessary because such type of waste is combusted in special incinerating plants. Moreover, it is expensive and it slowed the liquidation procedure. The liquidation processes produce also other harmful wastes, such as contaminated concrete elements of “tomb” infrastructure and contaminate soils. Considering that contamination of natural environment by ‘tombs” was generated before 30 September 1980, after the acts: on introduction of the Law of the Protection of Natural Environment, the Act on Wastes, and on changes of some acts from 27 July 2001 (Acts Monitor No 100, pos. 1085), the recultivation could concentrate on liquidation of hazard to the human health and life. Because actual liquidation procedures produce ca. 4 tons of wastes (contaminated concrete and soils) per 1 ton of unwanted pesticides, the amount of produced wastes, remaining after liquidation of existing “tombs”, is calculated as ca. 60 thousand tons. These by-products should be neutralised in the repositories of industrial dangerous wastes.

Methodology of liquidation

In the end of the 90-ties the “tombs’” liquidation was initiated. During the first stage of such works the Institute of Plant Protection had removed the unwanted pesticides to the new founded “tombs” (objects in Sośnicowice and Niedźwiady), but such method, which is very expensive, does not solve the problem and creation of only new and better protected repositories, was stopped soon. In 1999, the real liquidation works have began in the area of the Lublin voivodeship, after methodology proposed by the Polish Geological Institute. This procedure includes:

- excavation and re-packing of unwanted pesticides, stored in the “tombs”, into special containers, their transport and incineration outside Poland, with storing of produced wastes in the dumps of incinerating plants,
- complete liquidation of stable „tomb” infrastructure, with sorting of concrete elements, which – depending on the contamination intensity – are stored in the communal dumps or in the repositories of dangerous wastes;
- determination of contamination rate of ground and water environments, excavation of most polluted soils and their neutralisation in the repositories of dangerous wastes;
- recultivation of the area of the liquidated “tomb”;
- location of monitoring system of groundwaters.

A different liquidation method is applied for repositories located in the military fortifications. There only the chamber walls are cleaned without the liquidation of a “tomb” stable infrastructure.

Programs of “tombs” liquidation

Local authorities of voivodeships initiate mainly the programs of “tombs” liquidation. The area of Poland area is subdivided into 16 voivodeships and in each of them there exist from several up to several tens of such objects. In regions with numerous "tombs" their liquidation is realised in several stages and is preceded with studies, which attempt to define their menaces for the natural environment.

The "tombs" located in the following positions are liquidated in the first pace:

-nearby the buildings,

- in areas where the Main Groundwater Aquifers are located,

- nearby the intakes of ground waters,

- nearby rivers and lakes,

- in areas consisting of permeable deposits (sands and gravels), fractured and karsted,

- in areas of shallow occurrence of ground waters, so the chambers with unwanted pesticides are located within the ground water horizon and are flooded by these waters.

Till now, the following works were finalised (Fig. 1):

- in the area of Lublin voivodeship all (16) existing "tombs" were liquidated, as well as all unwanted pesticides stored in repositories. This province is the only one in Poland now being free of the "tombs problem";
- in the area of Lubusko voivodeship 7 of 8 existing 'tombs" were liquidated;
- in the area of Fore-Carpathian voivodeship the 1st phase of liquidation processes of "tombs" and repositories with unwanted pesticides. The complex works were done in 6 objects and now the 2nd phase of planned works is realised, which should completely solve the "tombs problem" in this province;
- in the area of West Pomerania voivodeship the 1st phase of works is finished, which included liquidation of 11 most dangerous repositories located there;
- in the area of Kujawy-Pomerania voivodeship, 5 existing "tombs" were liquidated (1st phase of planned works).

Presently, the liquidation works in the areas of following voivodeships are continued: Wielkopolskie, Pomerania and Świętokrzyskie, which should finish in the year with liquidation of all "tombs", hitherto located in these regions.

Geological studies

Menaces valuation and qualification are based on preliminary geological studies, which focuse on recognition of geological structure in the "tomb" area and hydrogeological conditions as well as definition of the vertical and horizontal extents of contamination.

Geological structure of basement nearby the "tombs" may be estimated by the standard method of geoelectric sounding (SGE). Commonly, it is enough to realise ca. 10-20 soundings on the single object located along 2 perpendicular profiles. Obtained curves are interpreted with data of the characteristic borehole profile, for instance, the piezometric well drilled nearby the "tomb". This method is relatively quick and is applied with good results for recognition of geological structure of areas with the Quaternary cover.

Studies of contamination aureole around the "tombs" are successfully realised with two methods: multilayered profiling of electric resistance and atmogeochemical analyses of hydrocarbons content of a xylene group in a soil gas. Multilayered profiling of electric resistance is a modification of electro-resistance soundings but the rock resistance is measured at the defined depths. During interpretations of sounding results it was stated that a resistance of deposits contaminated with pesticides is lower, being the lowest at the top of the first aquifer. It results from the pesticides transportation by surficial waters from the "tombs" when part of them infiltrate down being absorbed by deposits of the aquifer. While evaluating the "tombs" influence on grounds and waters a multilayered profiling of electric resistance was commonly applied. The first, shallow interval of penetration aimed to define a resistance of deposits beneath the chambers base from where pollutions are expanded. The second, deeper interval enabled determination of resistance deposits at the supposed depth of occurrence of first aquifer, which could be responsible for redistribution of contaminations around the repository (Fig. 2).

Atmogeochemical measurements focuse on determination of a selected element of soil gas using the appropriately calibrated apparatus. Since many years this method is applied for determination of mercury (mercurometry) and radon (emanometry) contents. To determine a content of organic compounds the photoionic detector is used, containing and calibrated for various gases.

To valuate the influence of repositories with unwanted pesticides on the environment, the photoionic detector PID OVM 580S is applied, calibrated for a xylene group. The compounds of that group were commonly used for pesticides production. Measures are done in the field that allows to quickly contour the atmogeochemical anomalies. Single measurement lasts ca. 15 seconds and the soil gas is taken from the hole ca. 80 cm deep.

Liquidation and recultivation works

An integral part of liquidation works is a recultivation of "tomb" area after excavation and removing of stored wastes. This recultivation procedure includes: decomposition of stable "tomb" infrastructure, removing of the most contaminated grounds, infilling of resulted empties with clay materials with sorption and hydro-isolating properties and with unpolluted grounds. In the final phase of this activity the recultivated area is commonly forested. The enclosed photos illustrate phases of liquidation procedure on the "tombs" mentioned above (Fig. 3).

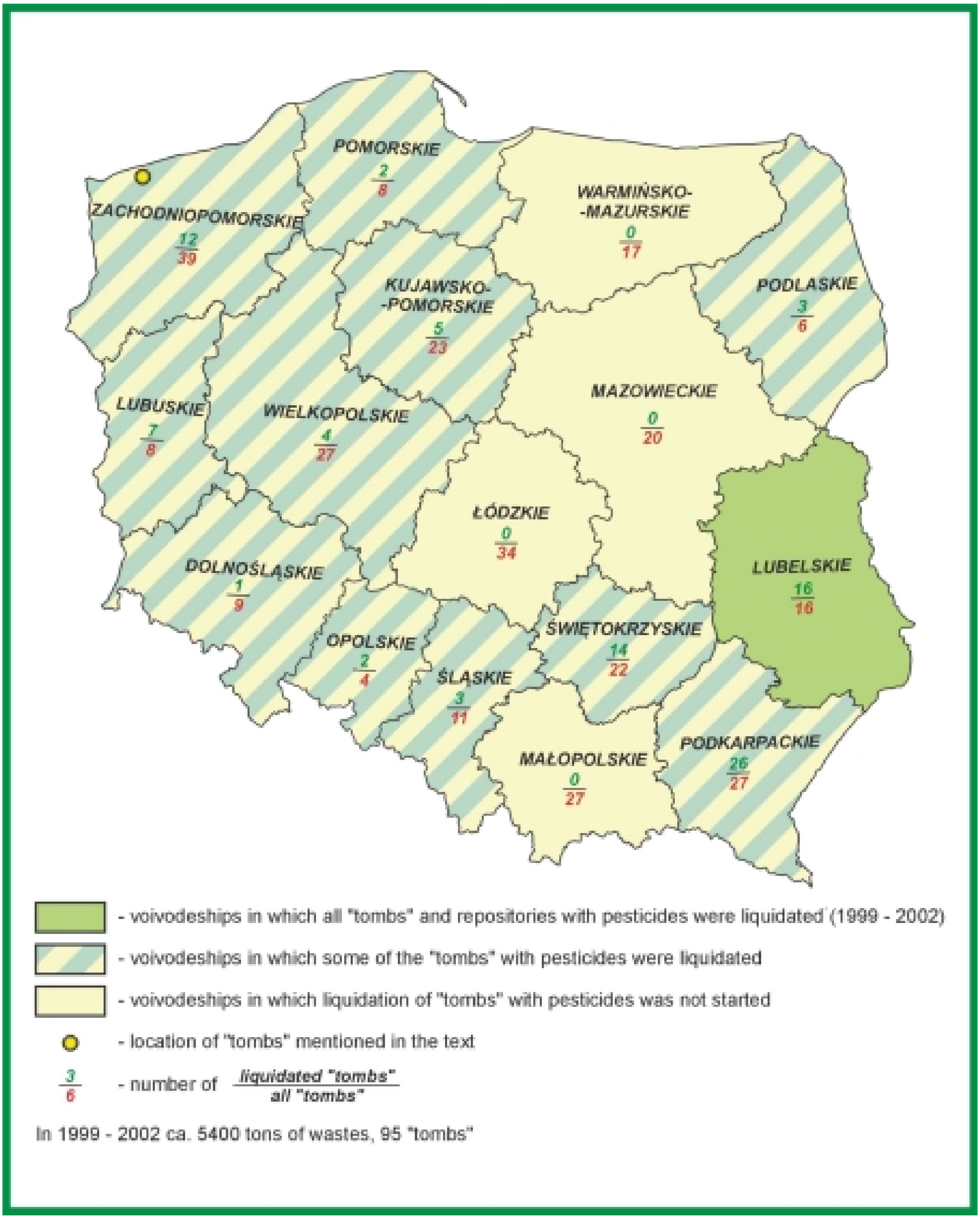
The most important problem of recultivation is determination of volume of contaminated grounds which should be removed from the liquidated object. The legislation in force in Poland, comparable with the regulations in countries of the European Union, is very rigorous and accepted values of contamination by pesticides (mainly by chlorine-organic compounds) are very low. But geological recognitions documented ground contamination at the depth of 40 m – at the top of aquifer. Ground waters, especially those concentrated within porous deposits (a. e. in sands), transported the dissolved substances from the "tombs" polluting grounds to the depth of a dozen or so meters and in a zone up to 1-2 km from the repository. In such situation it is almost impossible to excavate all contaminated grounds, because of technical difficulties and economically groundless. The cost of neutralization of 1 ton of highly contaminated ground, being a dangerous waste, is calculated in Poland for ca. 120 Euro. So the realised recultivation works are the result of comparison of technical and economical potential with determinations of a contamination scale of individual object. Normally the highest pollution is noticed at the depth interval 0,5-1 m beneath the chambers bases and the grounds located there should be utilised in the repositories of dangerous wastes. The bottoms of remaining excavations are covered with the 0,5 m thick layer of compacted clays, which should protect the underlain less polluted grounds against water infiltration. These grounds are still a real, secondary source of contaminations. Fig. 4 presents a scheme of recultivation procedures, applied for the "tomb" in Chrząstowo (West Pomerania Voivodeship). To consider a total scale of contamination the samples of concrete infrastructure are also analysed and depending on the results these concrete elements are neutralised in the repositories of dangerous wastes or in the communal dumps. Seldom they are used, for instance, for hardening local roads.

The liquidation and recultivation works are very expensive and they are financed by the National Fund of Environmental Protection and Water Management and its voivodeship equivalents, in proportion: 50 to 50. Till now, Poland has used none financial supports from the European Union. The average cost of liquidation per 1 ton of waste varies from 3 000 Euro to 3 500 Euro in 1999 – 2002. The structure of costs is presented on Fig. 5.

Prognosis of the tombs' liquidation rate

If the actual rate of „tombs" liquidation is maintained, then all such objects in Poland will be closed during 5-7 years. Process of liquidation could be accelerated but it is limited by the financial possibilities of Poland. Total cost of liquidation of all "tombs" – according to actual prices – is estimated as ca. 50 mln Euro. During last 4 years the prices have stabilized and their future distinct lowering is not predicted, because it may be realised only by a lowering of quality of continued liquidation-recultivation works.

Fig. 1


POMORSKIE
2
8
ZACHODNIOPOMORSKIE
12
39
WARMIŃSKO-
-MAZURSKIE
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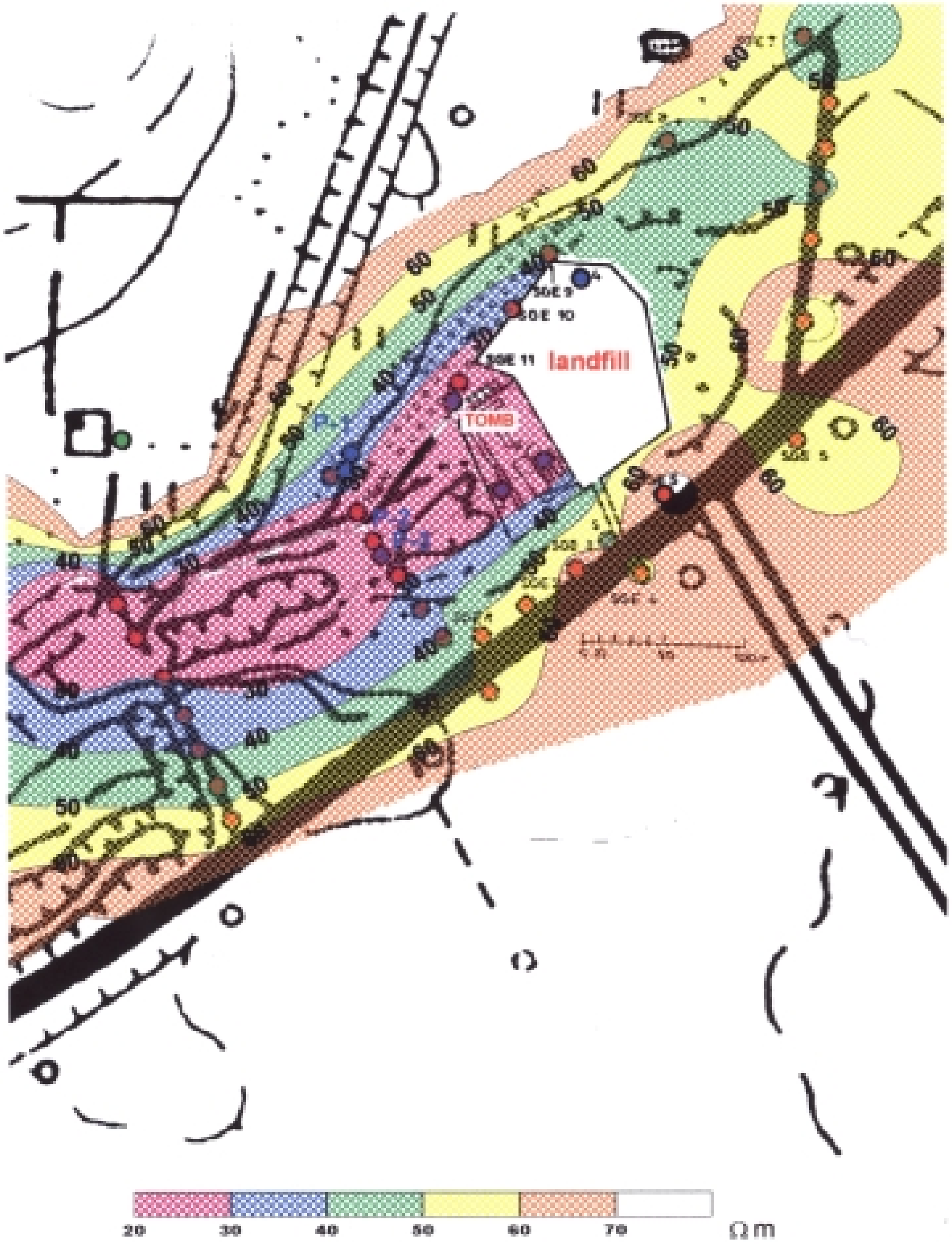
17
PODLASKIE
3
6
KUJAWSKO-
-POMORSKIE
5
23
MAZOWIECKIE
0
20
LUBUSKIE
7
8
WIELKOPOLSKIE
4
27
ŁÓDZKIE
0
34
LUBELSKIE
16
16
DOLNOŚLĄSKIE
1
9
ŚWIĘTOKRZYSKIE
14
22
OPOLSKIE
2
4
ŚLĄSKIE
3
11
PODKARPACKIE
26
27
MAŁOPOLSKIE
0
27
- voivodeships in which all "tombs" and repositories with pesticides were liquidated (1999 - 2002)
- voivodeships in which some of the "tombs" with pesticides were liquidated
- voivodeships in which liquidation of "tombs" with pesticides was not started
- location of "tombs" mentioned in the text
3
6
- number of
liquidated "tombs"
all "tombs"
In 1999 - 2002 ca. 5400 tons of wastes, 95 "tombs"

Fig. 2

A TOMB IN CHRZĄSTOWO (KAMIEŃ POMORSKI REGION)

A MAP OF THE GROUND RESISTIVITY AB/2 = 30 m

(depth ca.10 m)



Legend:

- geoelectrical sounding
- piezometer
- well

Fig. 3

A view of "tombs" prior to liquidation

Recultivation works - exchange of grounds

Tomb's contents

Post - recultivation tomb - area

CHAMBERS LOCALIZATION IN THE CHRZĄSTOWO "TOMB" AND SCHEME OF EXCAVATION AND NEUTRALIZATION PROCEDURES

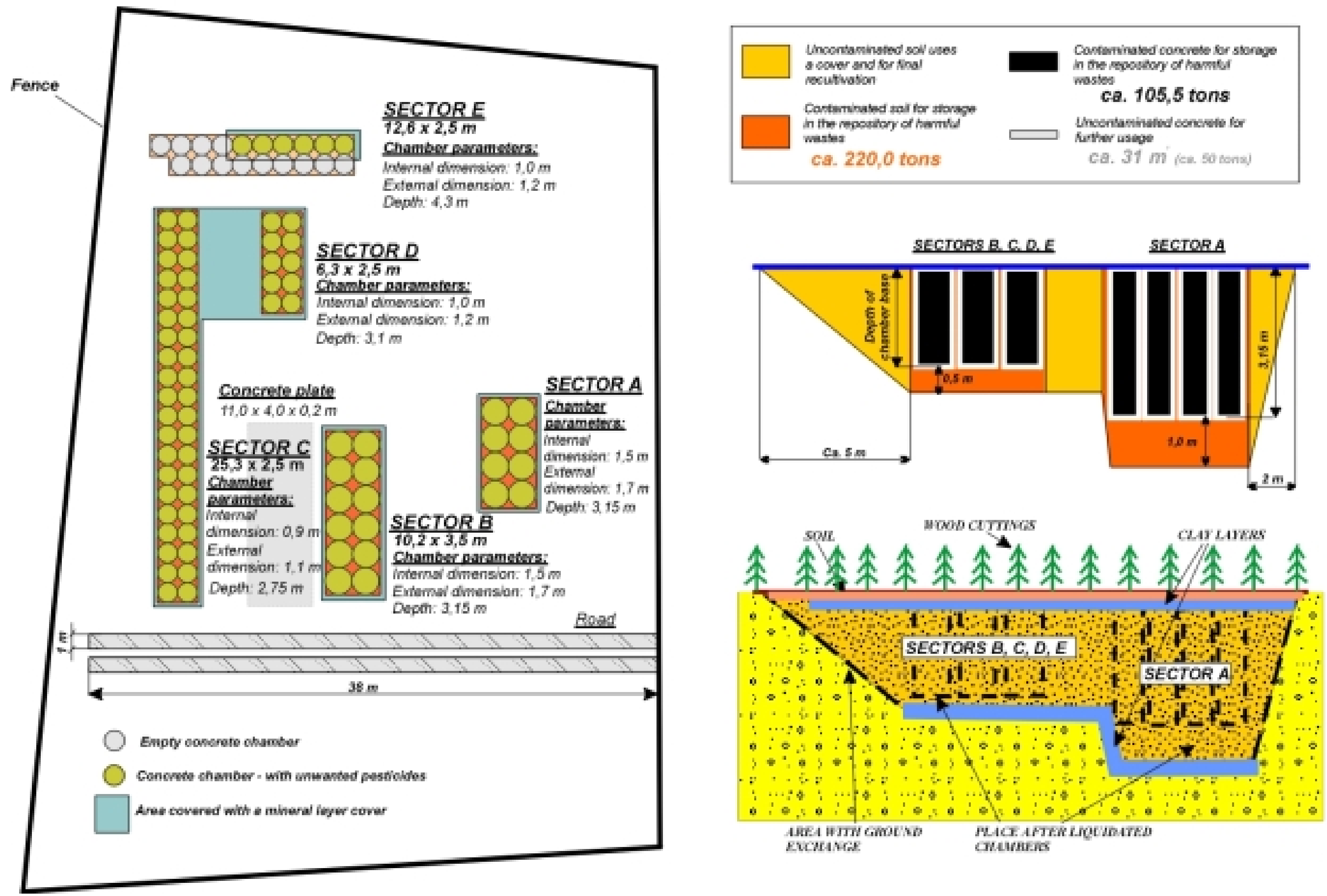
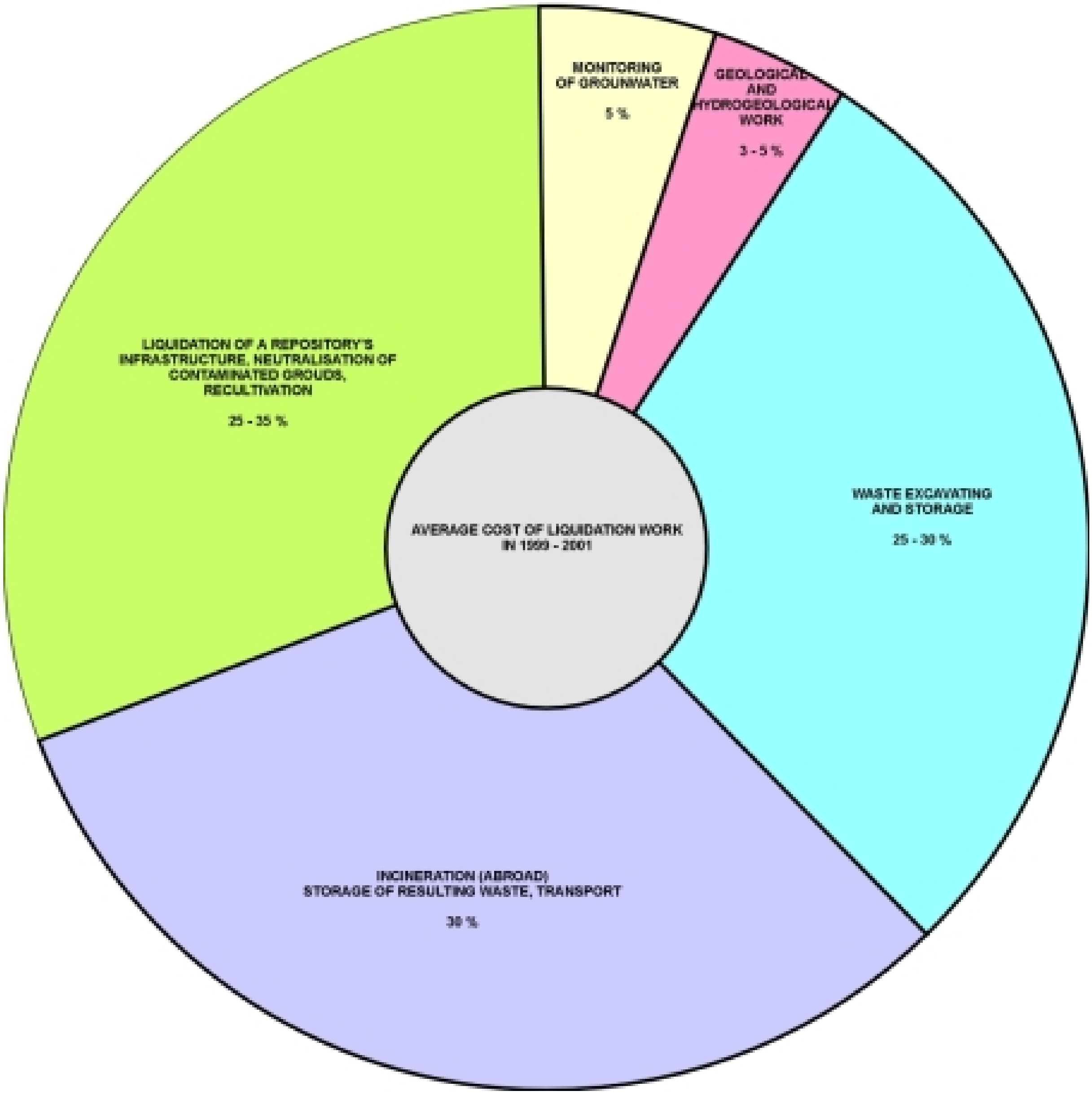


Fig. 4

Fig. 5

LIQUIDATION WORK COST



SpS 2 Special Session

Risk Based Land Management (RBLM)
Kempen Case

SIX KEY FACTORS IN SOLVING A SERIOUS ENVIRONMENTAL HEAVY METAL PROBLEM IN THE NETHERLANDS

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What is the problem?

Due to the production of zinc by the smelting of zincores in Belgium and the Netherlands, the Kempen area, located in the southeastern part of the Netherlands, is heavily contaminated with the elements zinc, cadmium, lead and arsenic. The contamination is caused by atmospheric deposition, the use of zincslags and the discharge of waste water. The soil, the groundwater and the sludge in the surface water are affected. Several hundreds of square kilometres are polluted. The effects of the pollutants are enlarged by the general presence of acid, sandy soils.

What is the solution?

Excavating all polluted soil, pumping and treating all polluted groundwater and dredging all polluted sludge would be not realistic, because of the enormous costs. Therefore another approach had to be developed. Six key factors have been nominated:

1 Stopping of further pollution

The zinc smelting factories in both countries have polluted their own sites. Polluted groundwater is not under control at every site. It may enter the surface water system, which results in polluted sludge and polluted surface water. The rivers spread the polluted sludge and the polluted water over the banks. The stopping of further pollution has been accepted as a first priority.

2 Removing of zincslags

About 1000 km road and about 1000 properties in the Netherlands have been paved with zincslags, which are subject to leaching resulting in a serious groundwater problem. For this reason it has been decided to remove the zincslags. Mixing with additives results in a harmless mass which can be used as construction material.

3 Removing of sludge

The polluted sludge is removed from the watersystem. The sandfraction is separated from the sludge and can be reused. The remainder of the sludge will be dumped at a controlled site. Investigations have been started to develop sites in the riversystem where the sludge can settle down, in order to protect the downstreams area for the polluted sludge.

4 Managing the groundwater

A special program has started to learn how the groundwater situation can be improved at regional and local level. Options include classical pump and treat methods for problems at a local scale and integrated groundwater system management at a regional level. Examples will be shown how the natural adsorption capacity of more clayey layers can be used.

5 Limiting the risks

For the different forms of landuse the risks must be determined and measures must taken to lower the risk to an acceptable degree. These measures vary from change of landuse to immobilisation of the pollution or to excavate the soil. My Belgian colleague Victor Dries will focus on this subject.

6 Promoting good administration

The barriers within the soil and watersystem seldom coincide with the administrative barriers (countries, provinces, towns, waterboards). A good cooperation between these administrations and agreement about funding is indispensable.

Results and prospects

The authorities involved agree with the six key factors approach and are willing to pay for it. A start has been made with the removing of zincslags and the removing of sludge. Pilots have been started to develop the other key factors. It’s the aim to have removed the zincslags and the sludge before the year 2015. From that year on the environment in the Kempen should be actively managed, in the knowledge that a significant part of the metals will remain for centuries in the soil and watersystem.

SpS 5 Special Session

Site Specific Ecological Risk Assessment: Where are we now?

INTRODUCTION TO SPECIAL SESSION 5: SITE SPECIFIC ECOLOGICAL RISK ASSESSMENT; WHERE ARE WE NOW?

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In spring 2001 the CLARINET workshop (CLARINET, 2001) on ecological risk assessment agreed on an outline of an EU-framework on site specific ecological risk assessment (SS-ERA). The main final conclusion of this workshop was: 'On the one hand there agreement on the outline of an EU-framework on ERA. On the other hand much details are not filled in yet or have not been discussed yet. From these two facts it can be concluded that there is a good basis for filling in the ERA in future and ongoing discussion is recommended.'

As important common elements for an European framework for SS-ERA were identified:

- Generic values in the first tier;
- Bioassays;
- Bioavailability;
- Land use specific;
- Negotiable with stakeholders.

Although the workshop agreed on a tiered approach, no final conclusion was drawn about the elements of each tier. One of the proposals consisted of:
Tier 1: informative, cost effective, broadly applicable, easy to handle, screening tools (chemical or biological).
Tier 2: site specific information (easy verifiable), checklist targets/routes/tools, to define tier 3 activities.
Tier 3: check it out, bioassays, monitoring, field research, uncertainty analysis, risk or impact? Effect? Damage?

The first and second tier should conclude with a go/no go decision for the following tier. In going through the tiers one should be aware of a 'conceptual' model of the ecosystem, which refers to contamination, exposure routes and ecological receptors. There was much discussion about the position of bioassays; pleas were made for using them in the first or second or third tier. What to measure and investigate was considered to be dependent on negotiation between all interested parties (site owners, (risk) managers, authorities, others). This negotiation should take place before and during the actual risk assessment.

In this special session of ConSoil we will continue the discussion about use of SS-ERA and the possibilities for a European framework. We will start with introductionary presentations that will focus on four main topics for SS-ERA:

- Implementation of site specific ecological risk assessment as a regulatory tool: what to take into consideration (Trudie Crommentuijn, Ministry of Housing, Spatial Planning and Environment, The Netherlands);
- The feasibility of bio-assays in site specific ecological risk assessment (Jörg Römbke, ECT-Ökotoxikologie GmbH, Germany & Jason Weeks, National Centre for Environmental Toxicology WRc-NSF Ltd, United Kingdom);
- Bio-availability (John Jensen, National Environmental Research Institute, Denmark);
- Higher tier field research in ecological risk assessment: a case study (Jack Faber, Alterra, The Netherlands).

The session will not deal with the development of screening tools (for instance trigger - or intervention values).

In the discussion you are invited to give your view on SS-ERA, especially regarding the questions:

- When and where to apply SS-ERA?
- What is the strength/weakness of SS-ERA results?
- How to come to a European framework for SS-ERA?

Bioavailability

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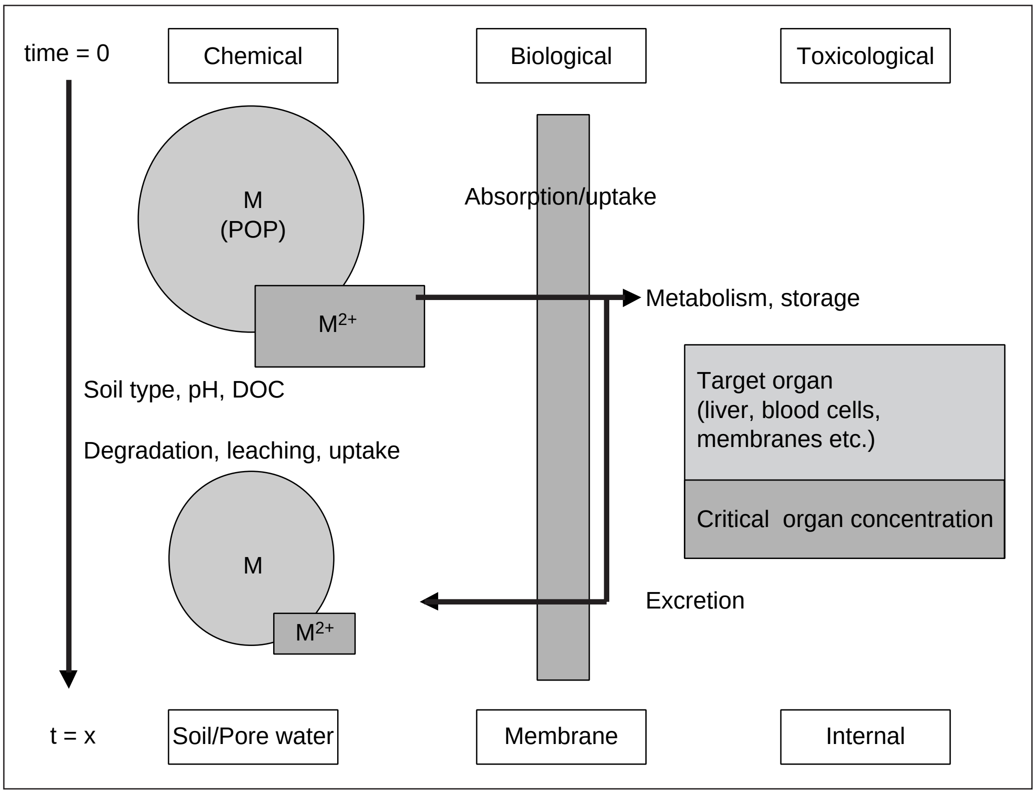
Introduction.

The last number of years terms like ageing, natural attenuation and bioavailability has been used regularly in connection to risk assessment of contaminated soil and sediments. A common feature for these terms is the absorption and slowly sequestration of contaminants into soil particles. The ageing process leads to a situation were more and more contaminants gradually adsorb to high surface areas of organic material or interact with high-affinity nano-pores in the soil or sediment material where desorption is slowed down by limited diffusion. This leads to lower toxicity for soil organisms and reduced leaching of contaminants. However, it will also lead to a slow down in degradation and hence limiting the possibility of a successful or complete natural attenuation. It has been demonstrated that soil characteristics and desorption characteristics in many cases are more important factors in controlling bioavailability than the actual contact or ageing time between contaminants and soil and sediment. Metal adsorption by soil for example is highly pH dependent. The surface charge of soil and sediments are strongly dependent on the reaction of protons with hydroxide minerals and charged groups of humic substances, as metals and protons generally are competing for the same binding sites. The number of binding sites and hence the absorption of heavy metals also depends on the soil texture as clay minerals for example have far more binding sites than sandy soil. A better understanding of the retention and ageing mechanisms and prediction of the contaminant availability is valuable for the setting of environmental standards, and crucial for the ranking of sites according to risk and monitoring of different remediation techniques or processes like natural attenuation.

Although commonly discussed and debated, the scientific basis for adequately using bioavailability in ecological risk assessment is still relatively weak. One of the first obstacles to solve is to define the term properly. It must be recognised that bioavailability is dynamic processes comprising several distinct phases. One is the physico-chemical driven adsorption/desorption process (chemical availability) controlled by parameters like pH, clay, CEC and organic matter. Another one is a physiological driven uptake process (biological availability) controlled by species-specific parameters like anatomy, feeding strategy, preferences in micro-habitat etc. The last one is an internal allocation process (toxicological availability) controlled by species specific parameters like metabolism, detoxification, storage, excretion, energy resources etc. Internal concentration is hence most relevant when target organs have been identified and their critical levels estimated. A simplified diagram of different phases is found in Figure 1.

Figure 1. Diagram over different phases of bioavailability. M = Heavy metal. POP = persistent organic pollutant. See text for further explanation.



The influence of soil characteristics and ageing on toxicity

Already in the late 50's it was reported that ageing of chemicals in soils reduced toxicity (Edwards et al 1957). There exist numerous examples of how toxicity of specific compounds differs according to soil characteristics such as pH, soil texture and organic matter. When exposed to freshly spiked soils Smit and van Gestel (1998) for example showed that zinc toxicity was correlated to both the clay content but also to the organic matter content. Lock and Janssen (2001) found that pH, CEC and organic matter content mainly determined the toxicity of copper and lead. Vijver et al (2001) found on the other hand no influence of the soil characteristics of 16 field soils on Cd and Zn uptake in springtails as the insects apparently maintained a fixed internal body concentration.

Similar observations of the influence of soil characteristics have been made for organic contaminants (e.g. van Gestel and Ma 1990, White et al 1997, Gevao 2002, Chung and Alexander 2002).

The time needed to observe changes in toxicity or uptake is nevertheless dependent on properties of the contaminants as well as soil characteristics. Pedersen and van Gestel (2001) showed for example that increasing the ageing time between spiking and exposure were not - in the case of copper – very useful for obtaining field like conditions, as ageing of up to 12 weeks did not affect the toxicity to springtails. It seems likely that the primary adsorption processes happen within the first hours after spiking. Further significant changes may take months or years. This observation was confirmed by Sverdrup et al (2002) who did not find any effect on the toxicity of pyrene and phenanthrene when ageing soil samples up to 120 days. Robertson and Alexander (1998) on the other hand observed a significant reduction in DDT toxicity after 30 days of ageing. Also Sae-Mae et al (1998) saw a reduction in cadmium toxicity when sediment was aged for 31 days.

These very few examples taken from a vast amount of publications on this issue illustrates the complexity of the bioavailability aspect in ecological risk assessment. There seems no straight forward way how to handle bioavailability in the risk assessment procedure. Nevertheless, what almost all people – from scientists to problem holders and responsible authorities - agree upon is that there is a need for alternatives to the common use of the "total concentration approach".

Methods for assessing bioavailability

It has long been recognised by industry and regulators that it will be technically and financially unfeasible to clean up the sites to pristine levels suitable for most sensitive land and ground water uses, as the costs runs up in billions of Euro. Tools for ranking the sites according to risks and for prioritisation of clean up measures for brown field redevelopment need to be established. Tools for assessing the relevant bioavailable fraction of contamination is crucial for such a ranking and prioritisation.

From an ecological perspective, biological tools would be preferred when assessing risk to ecosystems. However, due to the lower cost and higher reproducibility chemical tools may often be the best suitable solutions. The outcome of mild extraction procedures like $CaCl_2$ have been shown to be relatively well correlated to ecotoxicological effects of heavy metals (Spurgeon et al 1994, Spurgeon and Hopkin 1995, Pedersen et al 2000, Pedersen and van Gestel 2001).

Bioavailability of organic pollutants has less frequently been correlated to ecological effects of organisms within the soil compartment and adjacent water systems. On the other hand biodegradability and/or microbial activity as well as uptake in plants and earthworms is shown to be relatively predictable by different extraction procedures. Tang and co-workers concluded that extraction with as well C18 membrane as 25% aqueous solution of tetrahydrofuran was useful to predict the uptake of DDT (Tang et al 1999) and PAHs (Tang et al 2002) in earthworms. Although slightly less correlated also extraction with ethanol was found useful for assessing the bioavailability of PAHs. It is also documented that mild extractors like *n*-butanol, propanol, ethyl acetate and acetonitrile are useful in predicting the uptake of PAHs in earthworms and crop species like wheat and barley and microbial toxicity (e.g. Tang and Alexander 1999, Liste and Alexander 2002, Gong et al 1999).

Recently also other extraction techniques have been suggested useful for estimating the bioavailable fraction of contaminants in soil and sediment. Supercritical fluid extraction (SFE) may be used to investigate the sorption / desorption behaviour of organic contaminants in soil and sediments. Sequentially stronger SFE conditions produce selective extraction of PAHs associated with "fast", "moderate," "slow," and "very slow" sites for desorption within the soil matrix. It may therefore determine the level of sequestration and hence the bioavailable fraction in a matrix (Björklund et al 2000, Harkey and Young 2000, Loibner et al 2000).

Solid phase micro-extraction technique is based on a negligible depletion extraction technique to measure the freely dissolved concentrations. This method has already successfully been applied to measure binding to proteins, microsomes and humic acids and to measure freely dissolved concentrations in sediment-water systems, e.g Verbrugen et al 2000, Hermens et al 2002, Mayer et al 2000, King et al 2003. Little experience is, however, available for the soil compartment.

How is bioavailability implemented in an ecological risk assessment framework?

It is obvious from the above that there exist a number of more or less suitable extraction measures that are relatively successful in estimating the bioavailable fraction of as well heavy metals as persistent organics. Despite the fact that most people recognise the importance of bioavailability and there has been substantial technically development in the last decade, bioavailability measures have so far not been directly incorporated in any national or international framework or guideline for ecological risk assessment. The guidelines or protocols from national agencies still rely on vigorous extraction methods, which has as its primary aim to extract as much of the contaminants as possible, so it is possible to determine the total concentration in soil and sediments. What needs to be done before authorities, and the public, who have to live with or on contaminated soils, will trust the outcome of less harsh extractions? First of all for many new techniques more evidence is needed. Secondly a complete new set of quality standards, guideline or screening values are needed as these tools currently are the dominating instrument in the generic risk assessment procedure throughout Europe. In stead of expressing the values as total concentration they need to be recalculated and expressed as for example $CaCl_2$, butanol or SPME extractable concentrations. This calls for a substantial amount of new experiments. It is therefore not very likely that guideline values for soil and sediments will be expressed by other means that total concentrations in the near future. However, in the case of site specific assessment it is already now possible to include alternative chemical measures.

Two new European research projects on bioavailability

In 2002, the European Commission – within in the FP5 programme - funded two new European research projects dealing with bioavailability. One focuses on sediment and another one on soil.

ABACUS (Co-ordinator : John Parsons, Amsterdam University, jparsons@science.uva.nl)
Evaluation of availability to biota for organic compounds ubiquitous in soils and sediments.

The overall aim of ABACUS is to provide methods to determine the actual bioavailable concentrations of chemicals in sediment in such a way that they may be compared to quality criteria for soil, sediment and water as part of a site-specific assessment of risks. The mechanistic basis of the formation of fast and slow sorbing fractions of contaminants in relationship to the role of fractions of particulate and dissolved organic matter will be investigated. The structural characteristics of natural organic matter and contaminants that are important for sorption will be determined, in part using new computational chemical methods such as molecular modelling. New techniques such as the Tenax method will be further developed to quantify desorption rates from fast and slow sorbing fractions. Desorption rates will be related to the uptake by organisms and biodegradation of fractions of sorbed contaminants. Structure-activity relationships and kinetic models will be developed relating the kinetics of these processes to properties of sediment organic matter and contaminants. The results of experimental work and modelling will be applied to develop protocols for the measurement of bioavailable contaminant concentrations in contaminated soils and sediments.

LIBERATION (Co-ordinator : John Jensen, National Environmental Research Institute – Denmark, john.jensen@dmu.dk) (www.liberation.dk)
Development of a decision support system for sustainable management of contaminated land by linking bioavailability, ecological risk and ground water pollution of organic pollutants

Processes underlying sorption, ageing and bioavailability are the key soil parameters controlling dispersion of pollution to ground water and exposure of fauna and plants within in the soil environment. It is therefore the overall aim of LIBERATION to improve ground water protection and assessment of ecological risk of contaminated land and connective freshwater by developing and validating a novel decision support system for sustainable management of contaminated land that includes measures of bioavailability. LIBERATION will study the underlying mechanisms affecting the bioavailability and mobility of contaminants in soils and identify key parameters controlling sorption, desorption, mobility, leaching and ecotoxicity in soil and aquatic receptors. It will assess changes in the bioavailable fraction of model compounds in different soil types using various biological assessment tools and chemical extraction methods, including solid phase micro extraction, Supercritical fluid extraction, microbial degradation, earthworm accumulation. The project will measure and monitor changes in the bioavailable fraction during ageing processes. The usefulness and ecological relevance of these measures of bioavailability will be evaluated by correlating them to ecotoxicological studies with soil and water organisms and with changes in ecosystem structure observed at field sites with mixed pollution.

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HIGHER TIER FIELD RESEARCH IN ECOLOGICAL RISK ASSESSMENT: A CASE STUDY

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Approach to ecological risk assessment

As a result of recent changes in the Dutch soil protection policy, the need for site specific risk assessment has increased through a number of options. Soil clean-up and remediation projects may be prioritized over various polluted sites by the use of site specific risk assessment techniques, and soil remediation and management measures at polluted sites can be adjusted in view of land use on the basis of such techniques. Also, land use can be adjusted according to soil quality on the basis of site specific risk assessment. A procedure for site specific ecological risk assessment and the principles behind have been described elsewhere (Rutgers *et al*., 2000). This basic approach focuses on effects rather than risks, and includes multidisciplinary parameters from environmental chemistry, toxicology and ecology to provide multiple weight of evidence. The type of land use largely affects the selection of parameters, as a particular use may demand specific services from the ecosystem, which requires relevant testing methods. Moreover, the approach is characterized by repetitive interactions between stakeholders and researching consultants, in particular with respect to the choice of parameters and criteria to assess the results. As a result of these interactions, site specific risk assessments and the decisions based upon them may be more acceptable to these stakeholders and the public.

Case study Krimpenerwaard

In practice this basic approach was followed for the first time in an ecological risk assessment against a background of testing the assumptions underlying a soil management plan for a rural area polluted at large scale. The area in question is called 'Krimpenerwaard', and comprises an extended polder area in the Dutch province Zuid Holland (South-Holland) forming a substantial part of the "Green Heart' of Holland. It is a large area with predominantly agriculture (85%, mostly dairy farming) and nature (2% at present, 20% in future), together with roads, waterways and settlements. In this peat meadow polder landscape some 5000 ditches have been filled with an array of wastes in the 50'ies to late 80'ies of the last century. The sources of these wastes range from local households and waterway sludge to industrial wastes and car shredders. Some of these wastes have been shown to contain excessive concentrations of heavy metals, cyanides, PAH or chlorinated hydrocarbons, and according to law several sites must be qualified as seriously polluted and requiring remediation or clean up. However, the distribution of these waste types in the individual ditches over the entire area is mostly unknown, and the Krimpenerwaard as a whole is treated as a single case of serious soil pollution.
Two rural redevelopment planning programs aimed at conservation and reinforcement of green functions, such as nature, agriculture and recreation, were largely obstructed as a result of soil pollution, as were private land and soil transactions. As much as 13 stakeholding parties constructed a soil management plan, and a foundation was formed to facilitate its implementation. The soil management plan aims at a 'functional clean up' in view of land use, by means of covering "suspected" categories of wastes with a 30-cm layer of local type soil. In support of this management, an extensive research has been started to verify the assumptions in the soil management plan regarding the existence of possible undesirable effects induced by the various waste categories and cover materials.

This study addresses effects to agriculture, "ecology", and environmental transport of contaminants, and is made up of 3 consecutive phases and a monitoring phase. The ecological risk assessment itself follows a tiered approach, including a screening for bioavailable contaminants, a testing for general effects by use of standardized bioassays and field inventories, and a survey of specific effects on natural and agricultural ecosystem services. Further, site specific effects, if demonstrated in lower tiers, will be scaled up to the entire region in higher tiers.

At present, third and higher tier field studies are in preparation, since contaminants were shown to be present in bioavailable concentrations in all suspected categories of waste and effects have been demonstrated in standard bioassay tests. This paper will not discuss these lower tier results, however, but rather focus on the process of defining these higher tier studies and the iterative discussions with stakeholding parties that are involved. It will be discussed how research goals were set in view of land use, and how suitable parameters in the consecutive tiers were derived. Also, some experiences will be presented with respect to the determination of agreeable criteria to assess forthcoming results in a multi-stakeholder situation.

Ecological aspects and assessment parameters

There is no such thing as "the ecological risk" of soil pollution. From a society point of view specific ecological risks may be recognized in relation to land use at the site and in the immediate surroundings. The functioning of the local ecosystem may be threatened in such a way that the quality or quantity of ecosystem services to society (if not ecosystem values *per se*) is reduced. As a result, damage would be experienced by the stakeholding parties to a particularly affected ecosystem service, either in terms of economic losses, or risks to health and wellbeing of the individual. It would therefore make sense in ecological risk assessments to make use of study parameters with direct interpretability to ecosystems services of relevance. Land use may therefore be a key factor for the type of tests and inventories to be selected for risk assessment.

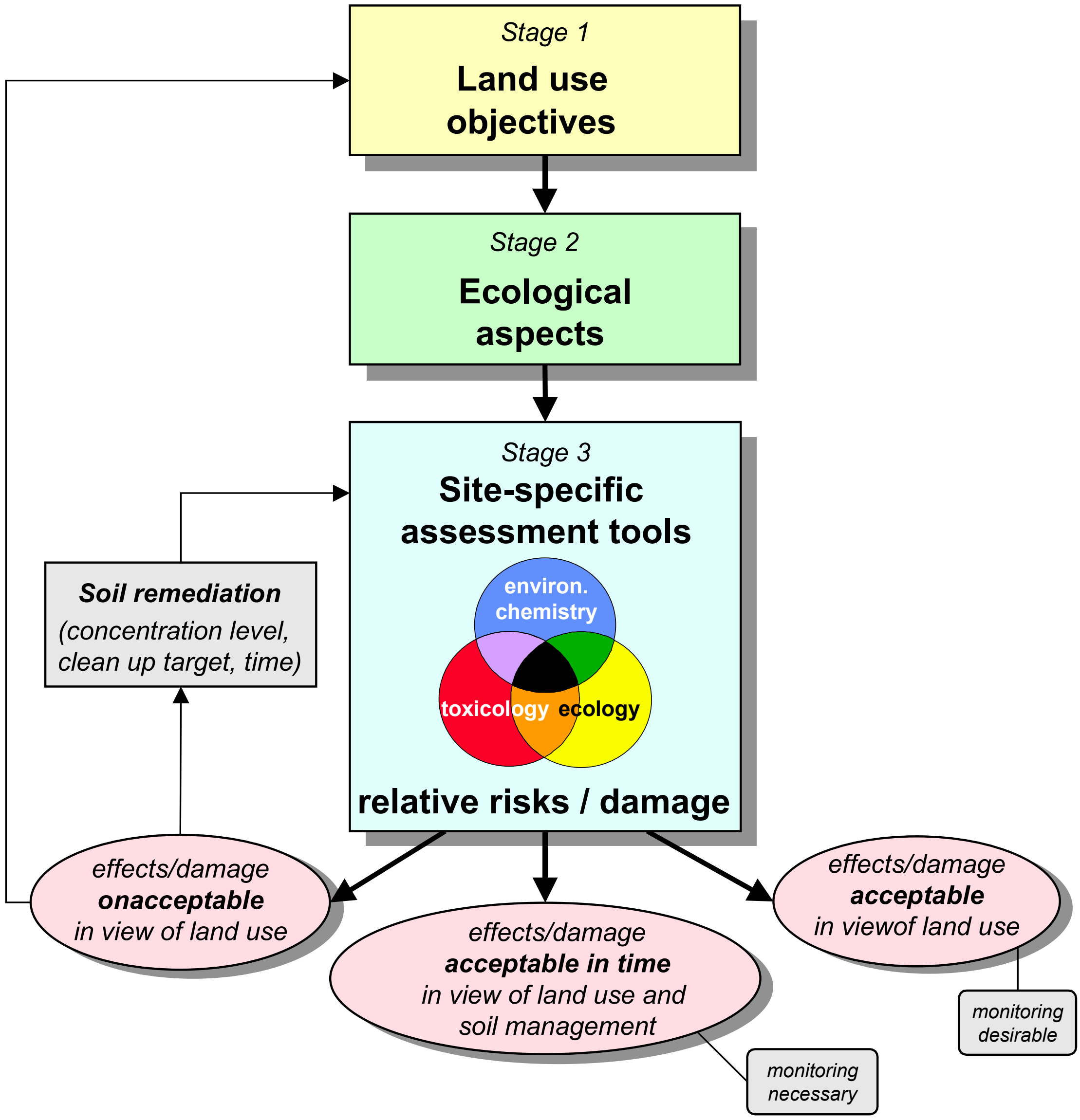

Figure 1. Basic approach to site-specific ecological risk assessment. The derivation of ecological assessment tools is developed in three stages in interaction between risk assessor and stakeholding parties. (After Rutgers et al.*, 2000)*

Given a particular use of a polluted site (either in the present or in the future), ecological aspects of the local ecosystem can be derived that are conditional to the particular targets of land use, as desired by the stakeholder. Such ecological aspects usually comprise soil processes or the presence and interactions between particular species, as these may largely determine the life support functions of the soil ecosystem. The recognition of relevant ecological aspects is a recommended step of interaction between the risk assessor and the stakeholder (figure 1). In The Netherlands, this is usually the first stage at which a risk assessor becomes involved. Government parties and other stakeholders have already taken the decisions on land uses and their specific objectives at an earlier stage. Ideally however, risk-assessing consultants would be involved earlier in the process. From stage 2 a further step is then taken towards the definition of a set of tools appropriate for the ecological aspects, which will enable the evaluation of the risks to ecological functioning in view of the desired ecosystem services. A tool set will ideally consist of several measurable or calculable indicators and parameters for soil quality, in order to establish present and future effects through site-specific assessment studies (rather than use of non-specific data). The results of the site-specific studies will then be assessed on the basis of previously determined criteria, thus facilitating clear-cut policy and management decisions whether to accept any demonstrated extent of effects in view of the intended land use (figure 1).

In the case of the Krimpenerwaard, the above generic approach was worked out to test the suitability of the intentional measure for soil management; *i.e.* coverage of suspected waste categories by 30 cm soil. It was questioned whether this measure would be sufficient to acceptably reduce harmful effects to the ecosystem in terms of ecological aspects for nature and agricultural and recreational land use. It was thought that two mechanisms could potentially cause a reexposure of the aboveground ecosystem after soil management measures would have been taken:

a. uptake by deep rooting plants and allocation to aboveground parts;
b. bioturbation and mixing of contaminants into cover layer.

In reflection of these mechanisms for recontamination two routes of exposure of the ecosystem were considered relevant to be studied:

a. soil – plant – insect herbivores – bird predators;
b. Soil – burrowing earthworms – meadow birds.

Ecological aspects were then derived from land use targets in interaction with stakeholders in the Krimpenerwaard region (table 1). Aspects were preferred if derived from multiple targets and land use types, for economical reasons of time and budget. Therefore, not every aspect was chosen for assessment studies eventually, even if so proposed by a stakeholder. The table is focused on biological parameters in higher tier risk assessment; chemical information (such as substance concentrations and “bioavailability”) has been left out. These have been applied predominantly in earlier tiers for screening purposes.

Assessment criteria

In the Krimpenerwaard case, assessment tools have been selected and at present preparations are made for field studies in the coming season. Meanwhile, a set of criteria will be conceived for the quantitative interpretation of results of these tests. A selection of research parameters with a preliminary set of criteria still under development is shown in table 2. It is expected that during the ConSoil 2003 meeting further developments can be presented.

In relation to the development of assessment criteria, it will be discussed what references should be used. A site-specific definition and, if possible, measurement of reference values is preferred over some generic values. This is related to the complexity of ecosystems in general and local variability in particular. Any framework for the level at which ecological processes have to be protected in relation to a particular land use is presently lacking. Research in this direction is still at an exploratory stage (Faber 1997, Van Hesteren *et al*. 1998).

In the Krimpenerwaard case, stakeholders in nature development and agricultural land use showed preference for *in situ* field references sampled in meadow grassland adjacent to disposal sites or partial regions within the Krimpenerwaard region, rather than determining a region specific reference value, still rather than using a reference value derived from some other peat meadow region.

Table 1. Land use targets and ecological aspects, and outlines for potential indicators and parameters in the Krimpenerwaard case. Parameters selected for assessment studies are presented in bold typing.

LAND USE	Stage 1 **LAND USE TARGETS**	Stage 2 **ECOLOGICAL ASPECTS**
Nature	Nature policy target types (including nature type target species such as flower-rich peat meadows)	Meadow bird densities and breeding success (**Black-tailed Godwit,** *Limosa limosa*)
		Peat meadow flower diversity
	"Wet-moist gradients" (with willow shrubs with avian breeding habitats)	Willow and **nettle** phytotoxicity and **bioaccumulation**
	Rare or protected species	Habitat species (**Black-tailed Godwit**)
		Red list species
	Top predators	**Bioaccumulation in birds** and mammals
	Soil keystone species	**Earthworm bioaccumulation** and **ecological functioning**
	Soil ecosystem processes	**Nitrification rate** and **microbial populations**
		Nematode community structure and **maturity**
		Litter decomposition rate
Agricultural use	Nutrient cycling and soil fertility	**Nitrification rate** and **microbial populations**
		functional groups of soil mesofauna
	Functional diversity in soil food web	**Nematode community structure** and **maturity**
	Litter degradation and incorporation	**Earthworm bioaccumulation** and **ecological functioning**
	Disease suppression	**Nematode community structure** and **maturity**
		Predator and competitor diversity
	Natural attenuation	Contaminant and pesticide biodegradation rates
	Sensitive crops and cattle	Copper toxicity in sheep
	Plant growth	Cattle fodder quality
		Mycorrhizal establishment
Recreational use	Landscape diversity (including "wet-moist gradients")	Phytotoxicity
	Flora and fauna diversity and typical species	Meadow bird densities and breeding success (**Black-tailed Godwit population size**)
		Willow and **nettle** phytotoxicity and **bioaccumulation**
		Peat meadow flower diversity

Furthermore, these stakeholders have indicated that for decision making on the basis of ecological risk assessment only ecologically relevant aberrations from the reference would be taken in consideration, even when not statistically significant, but minor differences to a reference (ecologically irrelevant) would not be taken into account however statistically significant (table 3). One party indicated to accept α=0.10 for type I errors in statistical analyses. Results for field tests and inventories should be assessed against their windows of natural variation. Reference and criteria setting therefore require a thorough knowledge of these study parameters, particularly if these should be studied over a single season. Monitoring may then be desirable or even necessary for future feed back on the decision based on the ecological risk assessment (figure 1).

Table 2. *Land use and some examples of indicators and parameters for higher tier ecological risk assessment, and preliminary criteria for assessment of research data as compiled in discussion with stakeholders in the Krimpenerwaard region.*

LAND USE	INDICATORS and PARAMETERS	CRITERIA
Nature	Black-tailed Godwit population size and breeding success	1000 birds per 5x5 km square;
		1 complete nest per 5 ha
	Nitrogen mineralization rate	100% of reference
	Nettle (*Urtica dioica*) root-shoot allocation of heavy metals	100% of reference (no bioconcentration)
	Nematode community structure and maturity	Maturity Index (cp2-5) > 2.30 (?)
Agricultural use	Nitrogen mineralization rate	80% of reference
	Nematode community structure and maturity	Maturity Index (cp2-5) > 2.15 (?)
Recreational use	Willow shrubs	No phytotoxicity

Table 3. *Approval of the use of data for the determination of minimal soil quality in view of the significance and ecological relevance of effects, as judged by stakeholders in nature development and agricultural land use in the Krimpenerwaard region.*

	Ecologically relevant	Ecologically irrelevant
Effect statistically significant	✔	✘
Tendency, not significant	✔	✘

Conclusions

1. In ecological risk assessment a greater relevance of results and greater acceptability to the stakeholders can be achieved by deriving research parameters directly from land use objectives and underlying ecological aspects.
2. Standard tests remain necessary, especially for screening of presence and general toxicity of contaminants at the site in lower tier assessments;
3. It seems possible to differentiate effect criteria in view of land use; in our case effect criteria for any particular test parameter were chosen less protective for agricultural land than for nature development and conservation areas.
4. In a multi-stakeholder situation the assessment can be complicated by different views on criteria for ecologically acceptable effect limits;
5. Some higher tier field studies may require special attention in setting references and criteria, given a relative high natural variability and a limited timeframe to establish results.

Acknowledgement

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IMPLEMENTATION OF SS-ERA AS A REGULATORY TOOL
WHAT TO TAKE INTO CONSIDERATION

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Introduction
In the cycle of policy development, earlier or later the question arises which instruments can be used in order to reach the aim of the policy. In the case of soil protection often the answer was found in the development of quality objectives (QO). In most cases, these QO are based on scientific information. If used in policy as generic values, the application of these QO is straightforward and as a consequence they are not appropriate to evaluate the "ecological quality" on a specific site. As such, at this moment the attention of ecological risk assessment in different EU-countries is focusing on developing techniques for Site-Specific Ecological Risk Assessment or SS-ERA.

When considering generic values a lot of experience is available how to deal with the translation from scientific values into values as a tool in policy. When considering SS-ERA not much experience is available how to deal with the translation from these techniques into a broadly applicable policy-instrument. On the other hand a lot of experience is available on the use of SS-ERA in practice. Results of projects in the context of prioritising contaminated sites and land management/potential of contaminated land deliver information on how existing techniques can be used to base decisions on. In this presentation an analysis will be made of the translation of science into policy when considering SS-ERA, on the basis of the experience when considering generic QO. The discussion will focus on points of attention to take into consideration when implementing SS-ERA as a broadly applicable policy-instrument.

From science to policy instrument; generic values, the process
The implementation of quality objectives like the target and intervention values into the soil remediation policy is a Dutch example of how to deal with implementation of science into policy. The figure beneath illustrates the process ending in the implementation of generic QO in soil remediation policy.

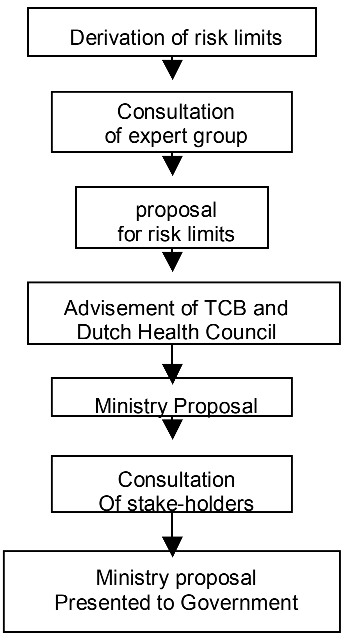

Figure 1: Outline of process to derive generic quality objectives

From this figure factors that have to be taken into account when implementing science into policy can be deducted. At the start of the process scientific knowledge is the leading theme. On the basis of the data and knowledge available at that moment risk limits are derived on the basis of the values asked for by policy. Advisement of expert groups and advisory boards is essential to come to values as scientifically sound as possible. In the following steps risk limits are translated into proposals for QO taking into account the scientific soundness, the manageability and practicability of the proposed values. In case there is already a system of QO embedded in policy the consequences of replacing old values by new values for existing policy are also of interest. All these factors determine together the ultimate proposal for the QO.

From science to policy; SS-ERA; The CLARINET-ECORISK framework as an example, what is different compared to generic quality objectives.
The process and factors of interest described above could be adjusted for the implementation of SS-ERA in policy as well. To decide whether the same process could be followed and whether the same factors should be taken into account, the SS-ERA approach as developed in CLARINET is outlined beneath.

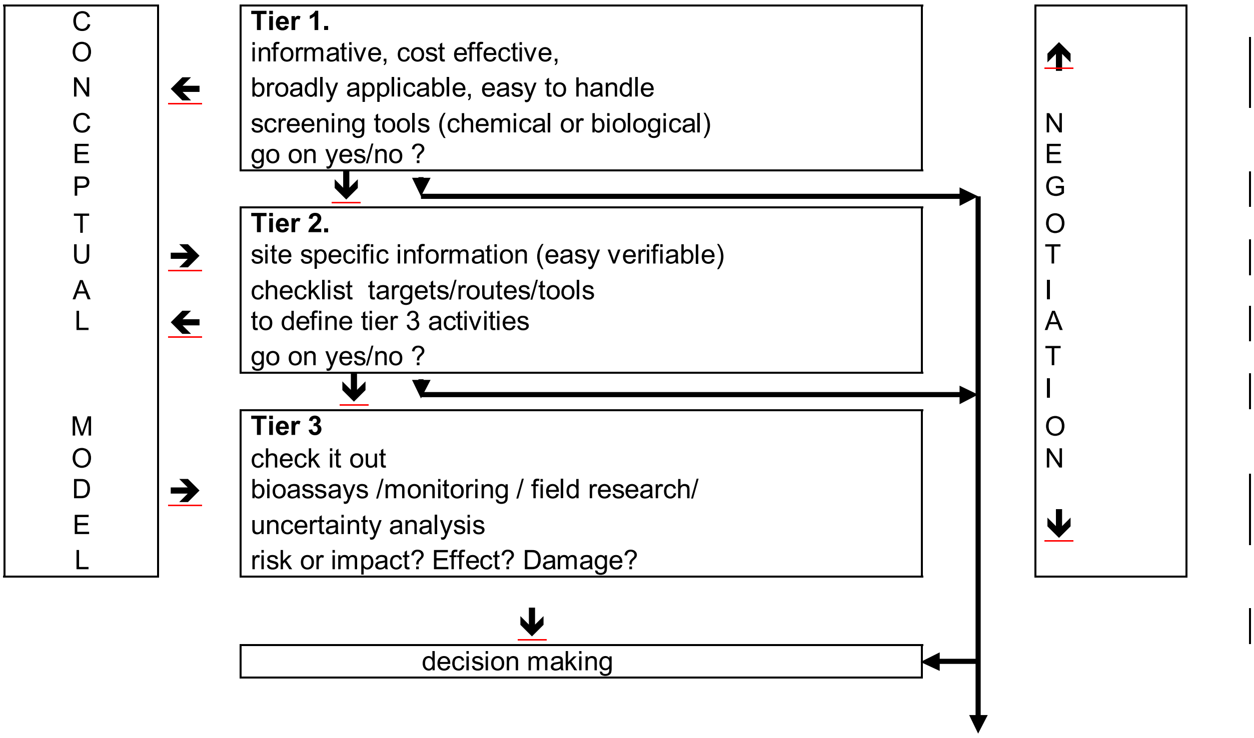

Figure 2: Outline of the SS-ERA framework as developed in CLARINET

From this figure it can be concluded that SS-ERA as tool in risk assessment is quite different from generic QO. First of all SS-ERA is a process in which the results of different tools should be combined into an answer for the question asked. The framework should provide a decision-oriented approach based on the application of scientific knowledge. Science is included as a conceptual model and in the individual measurements and techniques adapted. A conceptual model, describing the potential threats, exposure routes and impacted ecological targets, is considered as an important aspect of the framework.

At the basis of each ERA historical research should be carried out (which pollutants, which comparable accidents are known etc.). After that a tiered approach can be followed. Public communication is considered important because the public perception of risk is crucial to the final approval of ERA. A scheme for interpretation of results from the different tools in terms of ecological impact is important and lacking at the moment.

Points of attention when implementing SS-ERA into policy
Specific for SS-ERA is that the instrument is not one single value that is used as a threshold or trigger in policy. Beneath this value there is no problem, beyond this value there is a problem and actions can

be prescribed. In the case of SS-ERA a set of results from measurement and the discussion with stakeholders have to lead to an answer. The combination of results should give an objective judgement of the ecological quality of the site in the context of the policy the SS-ERA is used for. The factors mentioned above, scientific soundness, the manageability and practicability, combined with the specific character of SS-ERA dictate that a balance should be found on the following points:

Fixed approach versus flexible approach;
As simple as possible versus as sound as possible;
A simple, fixed approach in which the measurents/tools to be used are prescribed is from the point of manageability and practicability to be preferred; from the point of scientific soundness however, a flexible and to the characteristics of the site adapted approach is preferred. Because of the diversity in soil ecosystems one fixed approach would not result in realistic risk assessments. The tools used should be adapted to the characteristics of the site in question.

Fixed interpretation of results versus expert judgemement
It was concluded by CLARINET that a scheme for interpretation of results from the different tools in terms of ecological impact is important but lacking at the moment. Before it is possible to make SS-ERA a broadly applicable policy tool attention should be paid to this aspect. Attention should be paid to the way decision-making on the basis of SS-ERA should be designed. Fixed interpretation schemes are simple and from the point of the manageability and practicability to be preferred. Justifying the diversity of ecosystems expert judgement may be desired to give a more scientific sound answer. The latter from a point of manageability and practicability less preferred.

Conclusions
-A lot of tools for site-specific ecological risk assessment have already been developed.
-Also several frameworks exist how different types of tools can be used.
-What is missing is the guidance how to set-up a system providing an objective answer on the ecological quality of the site and the actions to be taken to reach the policy-aim aiming for.
-What is difficult and is missing is the guidance on how to interpret results from the parts of the tools in SS-ERA and combine this into an answer to the question asked by policy.

THE FEASIBILITY OF BIOASSAYS IN SITE-SPECIFIC ECOLOGICAL RISK ASSESSMENT (SS-ERA)

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Soil is a vital and complex environment. In Europe, it is necessary to evaluate the ecotoxicological hazard potential of chemicals (and in particular pesticides) to soil. Until recently, only a small number of standardised (mainly acute) tests with earthworms and plants were available, but during the last few years various new methods (especially with chronic endpoints such as reproduction) have not only been forthcoming but have been standardised. Moreover, beyond measuring structural aspects (for example, the effects of a chemical on individuals) in the soil matrix, questions concerning the influences of chemicals in soils on the general ecological function of a soil (such as litter decomposition rates) have been raised. These functional endpoint measurements have with time developed into biological test methods initially in the laboratory but latterly many have also been adapted for the testing of field soils. Results of biological tests are now considered as part of the ecological risk assessment process of potentially contaminated sites in some European countries as well as in the USA and Canada. However, it is important to remember that there is no single bioassay available to monitor soil quality. When choosing a specific soil test, the purpose of the test must be clear.

Tests involving terrestrial vertebrates such as shrews, voles and amphibians have not been included in this presentation, due in part to the ethical issues surrounding their use. They could, however, be important when the interrelationships between surface water, soils, and groundwater is a management issue for a particular habitat or site. Soil extract tests are generally restricted to mechanistic evaluations for specific exposure pathways or for assessing the retention function of the soil. Occasionally, but not routinely, they are conducted to assess 'soil' toxicity. Therefore aquatic tests such as the *Daphnia* test for the testing of groundwater or soil elutriates will not be covered here.

Site-specific ecological risk assessment

Ecological risk assessment involves qualitative and/or quantitative analysis of the actual or potential effects of contamination on ecological receptors other than humans and domesticated species. Unlike human health risk assessment, which is based on protecting individuals, ERA tends to be concerned with communities, populations and ecosystems and the effect of contamination on mortality and fecundity. ERA has to address a multitude of organisms, all with varying sensitivities to contaminants and different exposure scenarios.

Data from bioassays can provide a basis by which to derive site-specific values that protect specified ecological receptors. However, because of the difficulty in obtaining toxicity data on all organisms in an ecosystem, and the uncertainty in extrapolating laboratory data, the recognised practice is to test selected representatives of major taxonomic groups and use these as surrogates for the whole system. This approach is questionable, as it may not protect the most sensitive species exposed in the environment. Failure to identify the effects of a contamination on a potential receptor can result in widespread damage to that receptor and the ecosystems that they inhabit.

Nowadays, a broad battery of ecotoxicity tests accredited to international standards is available within Europe. Acute exposure of ecological receptors to contamination at a site can be estimated within 24 hours while chronic exposure requires at least 21 days. Ecotoxicological tests provide a direct measure of ecotoxicity (avoiding the need to model harm to receptors) and account for all known or unknown toxic components in a soil.

A range of laboratory and field-based biological test methods are also increasingly commercially available in Europe for use on projects involving land contamination. These tests are based on biological components, such as microorganisms, plants, invertebrates or vertebrates, which directly or indirectly provide information relating to site contamination. Data are obtained by exposing the biological components to site contamination and measuring the uptake into tissues or the response. There is a broad spectrum of responses from indistinguishable genetic mutations to clearly defined impacts such as mortality of individual organisms and loss of communities.

Such ecotoxicological test methods offer the scope for cost savings on contaminated land projects by using relatively cheap biological tests to screen for contamination and help focus subsequent more expensive chemical sampling and analysis. It may also be possible to demonstrate that a contaminated site does not need remediation by showing that the bioavailability of the contaminants to receptors is low.

Soil and water samples from contaminated sites can be tested for toxic, hazardous substances as part of a combined biological and chemical analytical approach to site characterisation. Biological test methods may be used, for example, to screen for soil toxicity prior to undertaking chemical sampling and analysis. This integrated approach ensures that toxicity, which chemical analysis alone may fail to reveal, is detected and its source identified. It also enables the chemical analysis to be targeted at specific locations of concern.

Assessment of remediation potential and monitoring of treatment progress

Many of the biological test methods outlined in this section can also be used to assess the potential feasibility of bioremediation, and to monitor the progress of a bioremediation treatment process. Soil microbiological parameters, such as soil respiration and soil microbial biomass, can be measured as a surrogate of the continuing biological activity of a treatment process such as biopiles. Monitoring remediation through toxicological methods can also be useful in detecting possible alterations in contaminant bioavailability and/or the formation of more toxic metabolites.

The figure below summarises the range of biological test methods that can be used to assess ecological risks on contaminated sites. This figure does not represent the full range of tests, but highlights those that are currently available either as a commercial product or as a research tool. The vast majority of tests are used on research projects for *in situ* and *ex situ* analyses. Some methods, such as the *lux* assay, may only be used *ex situ* due to restrictions on the use of genetically modified organisms (GMOs) in the real environment. The following subsections provide an overview of the broad categories of biological tests available.

SOIL TOXICITY TESTS

Existing standardised ecotoxicity tests were originally designed to assess the toxic effects of new and existing chemicals, particularly pesticides, added to soils and water as part of a generic risk assessment. In contrast, biological tests use soil and water samples from contaminated sites to generate a more site-specific risk assessment.

Numerous single-species toxicity tests (bioassays and biomarkers) are available to measure contaminant exposure and its effects on different components of soil ecosystems. Whole-soil toxicity tests using terrestrial invertebrates including tests with earthworms, springtails, mites and nematodes etc, plants and microorganisms (bacteria, protozoan, or bioluminescence assays).

Single and multiple species assays and test systems

Although single species laboratory assays can provide a measure of relative toxicity of land contamination, they may not be the most accurate or efficient means of predicting ecosystem responses to contaminant stressors. Single tests may fail to assess the effect of contamination on sensitive and important species in the ecosystem. They also do not take into account interactions between populations of individual organisms and their environment, and are conducted under chemical and physical conditions unlike those in the real environment.

A battery of tests can improve the accuracy and relevance of the risk assessment by providing information on the effects of contamination on organisms with different sensitivities at different organisational levels of the food chain. However, this approach still fails to consider complex community dynamics in the field. Multispecies test systems (microcosms and mesocosms) conducted *in situ* may provide a means of providing more accurate risk assessment data at en ecosystem level.

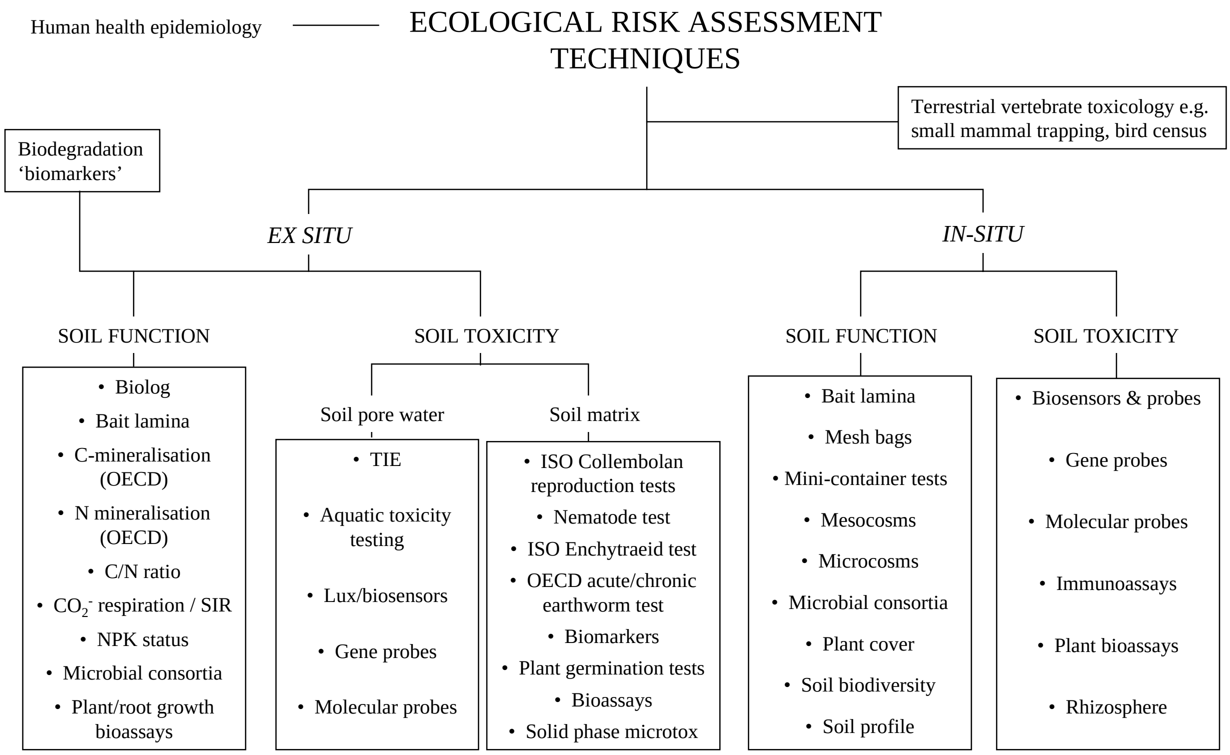

Figure 1 Categories of ecological risk assessment techniques

Microcosms and mesocsoms

Microcosms and mesocosms are experimental subsets of naturally occurring environments in which the response of more than one biotic species to contaminants is measured. The principal difference between microcosms and mesocosms lies in the scale / proportion of contained soil used in the experiment. Micro/mesocosms should be replicable and contain at least one biotic species at a higher trophic level than a microorganism.

Unlike bioassays that test the effects of contaminants on single species, mesocosm and microcosm studies allow observation of the effects of contamination at a population and community level. Microcosms can be structurally simple or complex, large or small, synthetic or natural. They are limited in size, time, soil mass and in biotic and abiotic components. The boundaries of microcosms restrict interaction with the rest of the ecosystem. Microcosms do not exactly mimic natural systems at all levels of organisation, and are incapable of self-perpetuation over long periods.

Chemical toxicity can be tested using two basic microcosm designs: small Integrated Soil Microcosms (ISM) with sieved soil, selected indigenous invertebrates and single plant species which require significant replication to simulate field conditions; or larger Terrestrial Model Ecosystems (TME) with intact soil cores, indigenous invertebrates and mixed plant flora with greater biodiversity, which are designed to simulate field conditions with minimal replication.

Tests of soil functions

Maintaining soil quality, fertility, and structure is essential for protecting and sustaining biodiversity and ecological integrity in terrestrial ecosystems. Central to achieving this goal is the need for a greatly improved understanding of the potential effects of chemical contaminants on the structure, i.e. the species, and function of ecosystems at contaminated sites. In practice, soil organisms and carbon and nutrient cycling processes are so intimately linked that the effects of contaminants on any one of these aspects are likely to impact on the others. Furthermore, the intensity and duration of the environmental effects of chemicals may strongly depend upon those processes that influence the activity, fate, persistence and movement of chemical contaminants through the soil ecosystem and into soil organisms and plants. Ultimately, these effects can interfere with key soil processes that may be important to the regulation, flow, and internal cycling of carbon and nutrients in ecosystems.

In excess of two thirds of soil biomass consists of microorganisms. Microbial communities have an important function in mediating the natural cycles of carbon, nitrogen, phosphorus and sulphur, which are crucial to maintaining sustainable soil quality for soil fauna and flora. Changes in the microbial activity and rate of mineralisation may be indicative of the effect of a contaminant. Effects may also be identifiable from changes in the biomass composition and diversity, extractable biomass and health of soil microflora and fauna.

Mineralisation of organic matter and carbon and nitrogen cycles have to date been the most commonly tested microbial processes. This is due to their sensitivity to pollutants and the fact that the processes determine the availability of nutrients through the food chain. Examples of specific contaminant effects that have been studied include inhibition of soil respiration, nitrification and enzyme activity.

Community structure

Concepts for the assessment of soil quality by using the soil community (biotic) structure including the linkage between the presence of particular species or groups or soil invertebrate organisms and the functioning of that soil system will be discussed. Such concepts have already be developed for surface water ecosystems. They are routinely used for evaluating the biological quality of surface waters in several countries (e.g. called RIVPACS in the UK or BEAST in Canada).

Summary

In summary the methods discussed in the presentation will include the use of a range if biological/ecotoxicological tests such as BIOLOG (to test soil bacteria), bait lamina test-strips (microbiotic, zoological baits), mini containers and litter bags (measuring kinetics of decomposition of organic material). All these tests may be used to determine the risks posed by a potentially contaminated land site using the SS-ERA process. The continued development and evaluation of new experimental techniques, methods and tools (using ecological receptors like earthworms and non-target arthropods) will further improve this SS-ERA process. Also as refinement and clarification of the European regulatory guidance continues an appropriate and consistent risk assessment scheme for the protection of soil systems may be realised that integrates the developed (and developing) biological tools.

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SpS 7 Special Session

Permeable Reactive Barriers or Zones

Permeable Reactive Barriers: a multidisciplinary approach of a new emerging sustainable groundwater treatment technology

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Abstract

Permeable reactive barriers have been under development since the early ninety's. The first PRBs were designed for the reductive dehalogenation of chlorinated solvents by zero valent iron granules. Since the beginning questions arose about the possible clogging due to inorganic or organic precipitates. More than ten years later more knowledge exists concerning the long term performance of these barriers. It has been observed that the clogging is not that problem as foreseen and that iron barriers are not just based on a chemical process but can be a combination of chemical, physico-chemical and biological processes. Also much more information does exist on the different organic processes that can occur and the transformation of certain precipitates by e.g. iron reducing bacteria. This introduces an *in situ* biological renewal of the iron granules. It seems that the hydrogen, produced by the anaerobic corrosion of the iron, can be used as electron donor by a wide variety of microbial phenotypes, including denitrifying bacteria transforming nitrates in the groundwater into nitrogen gas.

Based on these observations PRB technology is now extended to the development of an *in situ* treatment technology applicable for remediation of all kind of pollutants. PRBs are developed for the sorption (on zeolites, silicates, compost etc.) and *in situ* bioprecipitation of heavy metals (as in soluble metal sulphides). Sorption on granular activated carbon can be used for the removal of all kinds of hydrophobic contaminants as PAHs.

Permeable barriers are restricted in their use by the depth (10 – 15 m) as construction costs and technical problems will be to high in case of larger depths. Therefore an increasing interest is going into the direction of the development of virtual barriers or *in situ* reactive zones. These barriers are induced by creating specific conditions that induce pollutant removal processes. These can be obtained by the induction of biological processes in so called bioscreens (sulphate reduction, denitrification, biodegradation or biodehalogenation) or by the injection of nano-materials (e.g. nano-iron, or ultramicrobacteria) that migrate with the same velocity as the groundwater flow rate. Further a combination of these activities with zerovalent iron systems (or adsorption systems) can lead to the treatment of mixed pollution in a so called 'Multibarrier' system. This allows to treat mixtures of pollutants as is e.g. the case when landfill leachates are entering the groundwater.

1. Introduction

Permeable treatment walls installed as permanent, semi-permanent, or replaceable units across the flow path of a groundwater contaminant plume, allow the plume to move passively through while precipitating, sorbing, or degrading the contaminants. These mechanically simple barriers may contain metal-based catalysts for degrading volatile organics, chelators for immobilizing metals, nutrients and oxygen for micro-organisms to enhance bioremediation, or other agents.

Degradation reactions break down the contaminants in the plume into harmless byproducts. Precipitation barriers react with contaminants to form insoluble products that are left in the barrier as water continues to flow through. Sorption barriers adsorb or chelate contaminants to the barriers surface. The reactions that take place in barriers are dependent on parameters such as pH, oxidation/reduction potential, concentrations, and kinetics. Thus, successful application of the technology requires characterization of the contaminant, ground-water flux, and subsurface geology. Although most barriers are designed to operate *in situ* for years with minimal maintenance and without an external source, the stability of aging barriers is still under study.
The development of treatment technology for the clean up of contaminated groundwater resources has expanded in the past few years. The main perceived advantage of this technology over *ex situ* and other *in situ* ground-water remediation approaches is reduced operation and maintenance costs.
Although, considerable design details have already been developed through field- and pilot-scale applications of this technology, some critical issues still remain to be solved (e.g., establishing tested and proven design procedures, improving construction technologies, documenting long-term performance, and evaluating synergy with other groundwater remediation technologies). Currently planned field-scale tests and any ongoing laboratory studies are designed to address these issues and facilitate wider implementation of this technology.

2. Results and discussion

2.1. Long term performance of PRBs in North America

Since the inception of permeable reactive barriers, there has been considerable speculation as to the long-term performance of each and every PRB that has been installed. This speculation was attributed to the apparent simplicity of the technology, basically placing a wall of granular metal across the plume and destroying the contaminants. The technology has undergone a lot of scrutiny, probably more than any groundwater clean up technology ever! Has this been brought about by the fact that people are leery to try an innovative technology based on the past ineffective groundwater technologies, or is it merely based on cost, and the fact that these systems may have slightly higher capital costs than other clean up systems and therefore the overall savings are dependent on low operating costs.

In the early 1990's, it was suggested that if these systems lasted for a minimum of 5 years then they would more than pay for themselves. PRB applications have provided direct evidence of long-term performance with a 10+ years at the very first research site in Borden, Canada (Reynolds and Gillham, 2002) and an 8 year track record at the first commercial site in California (Sorel, et al., 2001). The technology has more than proven itself.

The key to an effective PRB application is to understand both the groundwater chemistry and flow characteristics of the system, by completing adequate site characterization along the line of the PRB installation. The PRB design is dependent on having adequate dimensions to both provide sufficient residence time within the reactive zone and to ensure complete plume capture. The primary issue associated with PRBs has been with hydraulic performance. Factors such as variation in flow velocity, variable seasonal flow direction, and inadequate plume delineation have all caused hydraulic issues at some sites (i.e. by pass of VOCs). Unforeseen conditions have been encountered during PRB construction. These conditions can pertain to unexpected complexities in geological formation, buried utilities, or complications resulting from the construction technique itself. Issues such as compaction or densification of the aquifer material during vibration of equipment, flowing sands and the smearing of clay materials along the PRB walls are some examples. These factors have been addressed during PRB construction on a site specific basis, but have added time and cost to system installations. However these lessons learned have helped improve the design and cost effectiveness of subsequent PRB installations, making the technology an even more attractive remedial alternative.

Organic monitoring data show all installed systems are performing as designed. Systems that have monitoring wells installed within the iron zones show direct evidence that the anticipated concentrations have been achieved or indicate better performance than predicted. Most PRB installations occur within a plume and as the clean water emerges from the PRB formation, it flushes the contaminated downgradient aquifer. Consequently, downgradient concentrations persist due to the compounds desorbing from the aquifer solids. The rate of desorption is dependent upon the aquifer properties such as fraction organic carbon content and the presence of the low hydraulic conductivity horizons, but the most important fact is the flow velocity. In low flow systems, complete desorption may take many years, while other high velocity sites will clean up faster.

In most environments these PRBs will last a long time, due to the amount of iron present. However, depending on the inorganic geochemistry, issues arise related to the long term impact of the inorganic precipitates on the iron surface. Initially, it was thought the these precipitates would cause significant losses in permeability, however recent research (Gillham et al., 2001) indicates that only slight permeability losses will be observed over time. Based on laboratory predictions, the greatest factor with respect to precipitate formation now appears to be the loss of reactivity on the iron surface (Gillham et al, 2001; Battelle, 2002). This reactivity loss will be very dependent upon the groundwater flow velocity and the inorganic constituents of the site water, especially the calcium, magnesium and alkalinity concentrations. Based on these observations and the site specific groundwater chemistry, some sites may require refurbishing every 10 years or so. To date no iron PRB has required rejuvenation with respect to precipitate formation. The use of technologies such as ultrasound, to rejuvenate granular iron surfaces appears promising. These rejuvenation techniques represent less costly alternative to partial PRB replacement, and will therefore improve the technologies cost effectiveness even further.

2.2. Iron-based bioremediation: an example on RDX groundwater remediation

RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) is an explosive compound that is gaining notoriety as one of the most recalcitrant and toxic groundwater contaminants in military installations. We are developing a promising technology to treat RDX-contaminated aquifers, based on combining a novel chemical process (reductive treatment with zero valent iron [Fe^0]) with an emerging bioremediation approach (in situ reactive zones). This integrated Fe^0-microbial system is more than a mere juxtaposition of two technologies because Fe^0 and some microorganisms interact synergistically to mineralize RDX to CO_2 and N_2O (Oh et al., 2001)

Batch and column studies suggest that microorganisms are responsible for RDX mineralization, and that Fe^0 provides a favorable reducing environment and electrons (via cathodic H_2 produced by Fe^0 corrosion), which stimulate anaerobic bioremediation processes. We also observed that RDX is toxic to some bacteria at the ppm level, and that Fe^0 may degrade RDX below inhibitory levels and transform it to byproducts that facilitate microbial participation in the clean-up process (Wildman and Alvarez, 2000)

Several different groups of microorganisms are likely to be important for RDX removal in biologically-active PRBs. In addition to hydrogenotrophic bacteria that use RDX as electron sink or nitrogen source, dissimilatory iron(III)-reducing bacteria (DIRB) may enhance PRB efficiency by reductive dissolution of passivating layers of Fe(III)-oxides, by generating reactive surface-associated Fe(II) species, and by biodegrading RDX. Batch studies showed that biogenic minerals produced by DIRB can degrade RDX, by sequential reduction of the nitro groups. The biogenic production of reactive minerals (confirmed by Mössbauer spectroscopy) suggests that DIRB could also contribute to process robustness by enhancing the reactivity of iron-bearing minerals in the downgradient aquifer for enhanced natural attenuation of reducible byproducts that could break through. Another group of microorganisms that could enhance process performance is the homoacetogenic bacteria (Oh and Alvarez, 2002). Such bacteria were shown to cometabolize RDX (using H_2 as primary substrate) and could comensalistically support heterotrophic activity and Fe(III) reduction through acetate production ($4Fe^0 + 2CO_2 + 5H_2O \rightarrow CH_3COO^- + 4Fe^{+2} + 7OH^-$). These examples illustrates that multiple bacterial species could act in concert to enhance RDX removal in PRBs.

Overall, this work suggests that permeable reactive iron barriers should effectively intercept and degrade RDX plumes, and that treatment efficiency could be enhanced by some biogeochemical interactions resulting from bioaugmentation..

2.3. PRBs for remediation of heavy metal containing groundwaters

Permeable Reactive barriers (PRB) are being developed and in many cases demonstrated to be efficient for the treatment of dissolved metals and dissolved non-metallic species typically associated to metal pollution problems as could be sulfur containing species (mainly SO_4^{-2}), arsenic (III, V) containing species ($HAsO_4^{-2}$, $HAsO_3^{-2}$), selenium (IV, VI) containing species (SeO_3^{-2} and SeO_4^{-2}) (Blowes, 2000; Sherer, 2000).
Selection of the treatment technology for those type of pollution scenarios depends upon the type, water flux and pollutant concentration reduction or removal requirements. Attending to the chemical properties of the target pollutants different physico-chemical processes have been selected to develop the suitable reactive materials. Fryar and Schuartz (Fryar, 1998) classified them into the following types:

- inducing the precipitation of a relatively insoluble mineral phases
- promoting adsorption onto mineral and adsorbent phases
- supplying carbon sources and nutrients for biodegradation
- modifying the redox potential and acidity to promote any the previous processes.

2.3.1. Reactive barriers based on pollutant immobilization by formation of low solubility solid phases

Several remediation projects have used calcareous surface barriers to neutralize acidity and remove metallic species, generated by the oxidation of sulfidic minerals in mines however limited success was achieved when applied to sub-surface barrier. The reduction in hydraulic conductivity resulting from metallic oxy-hydroxide precipitation has been viewed as an impediment in sub-surface streams because flow is diverted around, rather than continuing through the calcareous barrier. The chemical evolution within a ferric-calcareous barrier, proceeds with the hydrolysis of Fe^{3+} generating H^+, which is neutralized by reaction with calcite, causing poorly crystalline ferric oxy-hydroxide to precipitate via the simplified reaction:

$$Fe^{3+} + 3\,H_2O + 2\,CaCO_3(s) \Leftrightarrow Fe(OH)_3(s) + HCO_3^- + H_2CO_3 + Ca^{2+}$$

The deposition of ferric oxy-hydroxide peaked the precipitate front, where the neutralization of acidity generated by hydrolysis was completed and the hydraulic conductivity decrease achieve up to a factor of 100 to 1000 times (Fryar, 1994) .

Phosphate-Induced Metal Stabilization (PIMS) has been presented as a technology that can be applied to clean up metal and radionuclides contaminated soils and groundwater, and works especially well for lead (Pb), uranium (U), zinc (Zn), cadmium (Cd) and copper (Cu) (Wright, 1995; Conca, 1997). PIMS uses a special form of mineral apatite, called Apatite II, that is the least expensive but most reactive form available, to stabilize a wide range of metals, *in-situ* or *ex situ*, by forming new stable phosphate phases (apatite minerals) and other low-solubility phases. PIMS can be placed as down-gradient permeable reactive barrier, can be mixed in with contaminated soil or waste, or can be used as a disposal liner (Conca, 2000).

2.3.2. Reactive permeable barriers based on co-precipitation

Typically, waters, from landfills or mining operations often contain high concentrations of iron and other metals at low pH. As the pH is neutralized, multivalent metal ions tend to hydrolyze and polymerize, and precipitate poorly crystalline or amorphous hydrous oxides, such as oxy-hydroxides (AFO). Because of their relatively disordered structure and high surface area, iron oxy-hydroxides can incorporate other metals through co-precipitation or adsorption, a feature exploited in the use of ferric chloride as an additive in water treatment systems. Because iron oxy-hydroxides from hydrous aggregates capable of reducing porosity and permeability, their precipitation along the front of a contaminant plume is potentially useful in slowing the spread of the plume.

Almost all the materials that have been suggested to be used in chemical barriers are particles (e.g. zero valent Fe(Gillham, 1994), anoxic limestone (Hedin, 1994), and peat (Longmire, 1991). These materials require emplacement in an excavation such as trench because injection would clog the aquifer causing flow to be diverted around the chemical barrier. Because aqueous ferric chloride ($FeCl_3$) will react with naturally occurring carbonate minerals to form AFO, it was investigated the possibility of injecting $FeCl_3$ into the subsurface through wells. A chemical barrier emplaced through wells could be used to treat deep contaminated aquifers and at sites where surface disturbances (such as trenching) are unacceptable. AFO could be emplaced beneath structures or landfills by horizontal drilling wells.

Typically, natural and synthetic materials have been used for depolluting acid mine waters in off-site applications, however scarce data on the application of these type of materials on in-situ applications are available. The use of adsorption and ion-exchange of ion exchange materials of highly cost when compared to natural materials has been made to show different ways to remove a specific pollutant not solved by other barrier materials. Brown coal char, metallurgical coke, hardwood sawdust and other cellulose like materials acted as good adsorbents for metals achieving in the case of brown coal up to 15% to 50% of its own weight on the metals (Cu(II), Ni(II) and Pb(II)). Coal is pre-conditioned with lime prior to sorption of the metals, and the lime requirement depends on the metal concentration and pH of the solution being treated (Ritcey, 1985). Recently, laboratory studies to investigate the feasibility of using ion-exchange resins in PRB applications for removal of Cd, Pb and Cu (Vilensky, 2002).
The use of surfactant modified zeolites (SMZ) as anion adsorbents in permeable barriers is an effective way to remediate groundwater polluted with multiple types of contaminants, for example, cationic and anionic heavy metals as well as organic contaminants (Bowmann, 1995). In any case, the application of those materials is overseen when using removable cassettes for the reactive material, however this technological approach postulated in the last decade and widely used for PRB development is being classified as not economically feasible.

2.3.3. Barriers based on the combination of biological and precipitation steps.

In the last decade an extensive work have been focused on above ground-surface treatment of oxidized mine drainage water characterized by low pH and elevated concentrations of dissolved SO_4^{2-}, Fe(III) and other metal ions. Under favorable conditions sulfate-reducing bacteria (SRB) convert sulfate to sulfide by catalyzing the oxidation of organic carbon coupled with the reduction of sulfate as described by the following reaction:

$$SO_4^{2-} + CH_2O \Leftrightarrow H_2S + 2HCO_3^-$$

where CH_2O represents a simple organic carbon. Sulfate-reduction reactions consume SO_4^{2-}, produce H_2S and result in an increase in alkalinity and pH. Increases in dissolved H_2S concentration enhance the precipitation of metal (M^{n+}) as metal sulfides M_2S_n(s). Additionally the increase of total alkalinity will produce the precipitation of the metal carbonates and hydroxides, and also the dissolution of gypsum

$$CaSO_4 + 2(CH_2O) \Leftrightarrow H_2S + CaCO_3(s) + CO_2 + H_2O$$

Recently, Benner et al. (2002) critically summarized the critical performance data on the changes of the sulfate and iron reduction rates. Factors as temperature, organic matter ageing as well as the hydrodynamic aspects of creation of slow and fast flow lines were critically discussed. After 3 years of installation, the overall rate of sulfate reduction within the barrier is 40 mmol/L·a, 30% of the initial value, removing <1000 mg/L sulfate (Benner et al. 1997, 1999, 2002). However, due to the high levels of sulfates and iron in the groundwater to be treated PRB could provide long-term treatment efficiency and ultimately remediate the aquifer. The potential importance of variations in hydraulic conductivity and temperature fluctuations has shown as key parameters for the design of the PRB.

2.3.4. Permeable reactive redox walls

Permeable-reactive redox walls provide an alternative remediation approach for removing electroactive chemicals from contaminated groundwater. Conventional pump-and treat treatment programs for groundwater contaminated by redox-sensitive inorganic species, such as chromium, iron, sulfate, molybdenum, uranium, technetium, selenium and arsenic, have been substituted by PRB concept (Mackay, 199; 1993, Blowes, 1995).

Fe-bearing solids, siderite ($FeCO_3$), pyrite (FeS_2), coarse-grained elemental iron (Fe(s)), were assessed for their ability to remove dissolved (Cr(VI)) from solutions at flow rates typical of those encountered at sites remediation (Blowes, 1997). The removal mechanism for Cr(VI) by fine-grained Fe(s) is through the reduction of Cr(VI) to Cr(III), coupled with the oxidation of Fe(s) to Fe(II) and Fe(III) and the subsequent precipitation of sparingly soluble Fe(III)-Cr(III) oxy(hydroxide) phase.
Reduction of Cr(VI) to Cr(III) is waste water treatment using dissolved Fe(II) and adding base to favor precipitation of the resultant Cr(III) is a common practice. The overall reaction can be written as:

$$8H^+ + CrO_4^{2-} + 3Fe^{2+} \Leftrightarrow Cr^{3+} + 3Fe^{3+} + 4H_2O$$

This reaction can be driven by several Fe(II) sources, both Fe(II) containing solutions and Fe(II) containing solids. Examples of aqueous solutions include $FeSO_4$ or $FeCl_2$ solutions. Examples of solid-phase reductants include elemental iron, biotite, hematite, pyrite, magnetite and other Fe(II)-bearing minerals (Blowes,1994; Bostick, 1990, Powell, 1995). Whereas the rate of reduction is important, of greater interest for applications in porous-wall settings is the rate of removal of Cr(III) through precipitation of a sparingly-soluble solid. This second step is often the rate-limiting step for removal from solution. Under moderate pH conditions, removal of Cr(III) can occur through the precipitation of $Cr(OH)_3$(s) or through precipitation of mixed iron(III)-chromium(III) hydroxide solid Cr_xFe_{1-x} $(OH)_3$(s), Cr_xFe_{1-x} OOH(s). Mineralogical analysis of the reactive material used indicates that Cr is associated with goethite (α-FeOOH), suggesting that Cr(III) is removed either through the formation of a solid solution or by adsorption of Cr(III) onto the goethite surface. The effective removal of Cr(VI) by Fe(s) under dynamic flow conditions suggests porous-reactive walls containing Fe(s) may be a viable alternative for treating groundwater contaminated Cr(VI).

The first PRB for Cr(VI) was installed at a US Coast Guard Facility in Elizabeth City, North Carolina (Benner et al., 1997). The same reductive principle has been extended to other oxy-anions as TcO_4^-, UO_2^{2+}, AsO_4^{-3} / AsO_3^{-3} , SeO_4^{-2} / SeO_3^{-2}. Large treatment of TcO_4^- and UO_2^{2+} was evaluated at the US Department of Energy, Oak Ridge National Laboratory Y-12 Site using iron aggregates, with incomplete removal of some of the contaminants due to insufficient residence times on the barrier. Mixtures of apatite, amorphous iron oxide and iron aggregates were assayed to remove UO_2^{2+} in a pilot field scale reactive barrier at Fry canyon, Utah (Naftz et al. 1999). Finally, preliminary promising results on AsO_4^{-3} / AsO_3^{-3} , SeO_4^{-2} / SeO_3^{-2} removal were shown by Mc Rae et al. (Mc Rae, 1997) using iron aggregates.

2.4. PRBs based on sorption processes with granular activated carbon

At many contaminated sites groundwater has been found to be contaminated with hydrophobic **n**on-**a**queous **p**hase **l**iquids (NAPLs). These contaminants, typically are characterised by low water solubility and high octanol-water partitioning coefficients. It is understood that these contaminants accumulated in the subsurface either as separate phase blobs or pools or they are sorbed on the organic matter in the aquifer. The time frame for remediating sites therefore depends on the dissolution rates and also on the desorption rates. Dissolution rates are controlled by the interfacial area between the mobile water phase and the immobile NAPL phase, the solubility of the contaminant in water and the groundwater flow velocity. Desorption rates however are diffusion limited, i.e. this process cannot be accelerated by increasing groundwater flow rates. It is therefore not surprising that groundwater remediation efforts based on pump-and-treat techniques have been found to fail particularly in cases where strongly sorbing compounds such as PAHs are present. Due to long time scales necessary for full remediation, passive groundwater remediation using permeable reactive barriers (PRBs) is considered to be more cost effective than active methods.
At a number of sites in North-America and Europe PRBs which are based on sorption rather than degradation have been installed during the last five years. At most of these sites **g**ranular **a**ctivated **c**arbon (GAC) is used as the "reactive" sorbent material. GAC has been used for above-ground water treatment in numerous cases, therefore a huge data base is available in the literature with regard to the sorption capacity of GAC for a large number of organic contaminants.
The sorption capacity of GAC for organic contaminants mainly depends on the chemo-physical properties of the various compounds and also on the type and concentration of dissolved organic carbon in general (usually determined as DOC). K_d-values, which are determined from sorption

isotherms, can be used to quantify the sorption behaviour of organic contaminants. Especially PAHs but also PCBs and compounds can be eliminated from the water phase very effectively over many years without changing the sorbent.
However there are significant differences between above-ground and in-situ application of GAC which have to be considered for PRB applications. Most important, above-ground treatment using GAC in many cases is performed under aerobic conditions, i.e. dissolved iron or manganese either are removed before the sorption filter or they are not present at significant concentrations. In contrast, contaminated groundwater to be treated in-situ typically contains considerable amounts of dissolved iron which may precipitate within the GAC barrier. This does not only reduce the sorption capacity but more important such precipitates reduce the permeability of the barrier.
Other processes which have to be considered for *in-situ* applications can be summarised under the term "biofouling". This may occur in particular when groundwater from different parts of a site containing different amounts of oxygen or e.g. nitrate mixes within the barrier. Microbiological activity then may develop within the barrier leading to sliming and clogging.
For the design of GAC based PRBs therefore pilot scale testing in the field using site water is highly recommended in order to determine the significance of bio- and chemo-fouling processes for in-situ GAC filtration of contaminated groundwater.
The presentation given within this session will concentrate on the experience from several sites where GAC based PRBs are applied. The results obtained from laboratory and field testing will be compared with monitoring results obtained after installation of the PRB.

2.5. Long-term monitoring of PRB activity

The overall purpose of monitoring is to demonstrate whether the PRB is effective as a remedial measure for the polluted groundwater and that its application does not cause additional pollution or harm (M.A. Carey et al. 2002). A typical monitoring network includes:
A. Monitoring points up-gradient of the contaminant source and PRB to determine background water quality and any changes in this reference during operational life of the PRB;
B. Monitoring points up-gradient of the PRB to provide information on groundwater quality/contaminant flux. These boreholes can be located within a few metres of the PRB to provide accurate data on the contaminant flux;
C. Monitoring point within the PRB to provide information on processes within the reactive material. As the majority of changes in a PRB tend to occur within the first few centimetres of the reactive material, the installation of minitroing points in this zone will be extremely important.
D. Monitoring points down-gradient of the PRB to provide confirmation of the effectivieness of the PRB in treating contaminated groundwater, i.e. there is no unacceptable breakthrough of the contaminant (or metabolites) and that the PRB does not result in a detrimental change in groundwater quality. These boreholes are likely to be located within a few metres of the PRB;
E. , F. Side-gradient monitoring points to provide assurance that contaminated groundwater does not flow around the PRB and monitoring points below the PRB to provide assurance that contaminated groundwater does not flow under the PRB;
G. Boreholes located between the plume and the identified receptors, for which exceedence of an operational control level will require implementation of additional mitigation measures.

A high frequency of sampling would be required during the first year of monitoring to confirm the treatment process and to establish trends. Thereafter, the frequency could be reduced, subject to agreement with the authorities. Annual monitoring or even less frequent for particularly slow-moving groundwater) may be acceptable for some sites, once baseline conditions and trends in the PRB behaviour have been established with confidence. The design should also consider whether the use of field measurements coupled with less frequent laboratory measurements is an effective approach. The monitoring information will need to b e reviewed routinely against the objectives set for the monitoring scheme.

In summer 1998 two zero valent iron PRBs were constructed in Germany (Rheine: Nordrhein-Westfalen; Tübingen: Baden-Württemberg). The monitored time series of contaminant concentrations as well as major inorganic ground water constituents show somewhat confusing results in both cases. An extended monitoring was initiated as a part of the RUBIN R&D network aiming at the detailed investigation of possible reasons for performance limitations and the development of new monitoring techniques for reactivity assessment of PRBs.

The Rheine site PRB was constructed using two different reactive fillings, i.e. an iron sponge (ISPAT, Hamburg, Germany) and a mixture of 30 vol.% cast iron (Gotthart-Meyer AG, Rheinfelden, Germany) and gravel. The actual monitoring results indicate a proper function of the iron sponge section of the PRB. Initially after installation the down gradient contaminant concentrations were higher than expected from laboratory experiments performed with iron sponge before the PRB was constructed. After a couple of month the PCE concentrations along the iron sponge monitoring transect became coincident with the forecast from the column experiments. This lack in response time can be easily explained by desorption processes down gradient of the PRB. Actually the down gradient contaminant concentrations were below 10 µg/l. Furthermore, the overall degradation efficiency of the iron sponge was > 99.5% and up to now a decreasing reactivity is not indicated. The time series of major inorganic groundwater constituents indicate several expected geochemical reactions within the PRB as well as down gradient of the PRB. For example the concentration profiles of nitrate, sulfate and ammonia indicate the colonisation with microbes during the first half year of operation. The determined loss in total inorganic carbon (TIC) concentration, calcium as well as magnesium concentration due to increasing pH and precipitation reactions was also expected. The down gradient concentration time series indicate pH-buffering and ion exchange reactions. However, some problems and questions regarding the monitoring results still persist. One of the major problems concerning the efficiency assessment of the PRB is the groundwater velocity. The groundwater flow can only be roughly estimated within one order of magnitude due to small hydraulic gradients and uncertainties in permeability determination. Furthermore, high methane concentrations along the monitoring transect may indicate an overestimation of carbonate precipitation calculated from TIC concentration profiles. If this should be validated, the life time of the PRB should be longer than expected because carbonate precipitation is one of the main passivation mechanisms within an iron PRB.

In contrast to the efficiently working iron sponge section, the section containing a mixture of gravel and cast iron showed a significant decrease in reactivity half a year after PRB construction. The initial degradation efficiency was > 98% and decreases to ~80% one year after installation. The performance was stable between 70% and 80% during the last four years. The remediation efficiency was smaller than expected from known material properties, though no column experiments were performed to characterise the reactivity of this particular mixture. The usual performance monitoring techniques are insufficient to identify probable reasons for the observed concentration patterns. Concentration measurements alone do not approve a distinction between hydraulic problems, i.e. over- or underflow, and passivation problems. New monitoring approaches were applied to identify the problem, i.e. the first application of reactive tracers combined with a pumping test at an iron PRB as well as by our knowledge the first field application of stable carbon isotope fractionation. First evaluation of results indicate that the higher down gradient contaminant concentration is mainly caused by a loss in system reactivity and not by hydraulic problems. However, other investigations including solid phase characterisation and column experiments using material excavated from the PRB show no significant passivation of the cast iron itself. Therefore an inhomogeneous mixture of cast iron and gravel caused by construction technique probably combined with heterogeneities in contaminant load are the favourite reasons for decreasing remediation efficiency in this part of the PRB.

The monitoring results of the funnel and gate system at the Beka site in Tübingen show a proper function of the three gates during the first 6 to 12 months after construction. Later on contrary concentration profiles were measured along the monitoring transects. A typical concentration profile along a compliance transect shows contaminants at the upper as well as down gradient monitoring points but not within the PRB. The composition of the groundwater ~0.5 m down gradient of the reactive filling does not indicate any iron contact neither in contaminant concentrations nor in inorganic groundwater constituents even if a broad hydraulic gradient indicates a flow through the gate. In fact, the geochemical patterns of the groundwater are nearly equal down and upper gradient of the PRB. Similar to the Rheine site, the usual monitoring techniques do not really result in explanations. First results of a forced gradient tracer test using reactive and conservative substances were show the existence of at least two flow paths, one is a flow bypass with only minor reactivity and one is through the gate. Actually the interpretation of the incomplete tracer breakthrough curves is imperfect because a validated transport/reaction model is required for full interpretation. Nevertheless, the results point to preferential flow problems which were not considered in the past.

The comparison of the extended monitoring results from the Rheine site PRB and the funnel & gate system in Tübingen hint to constructional problems which are more responsible for performance limitations than passivation of iron reactivity. Furthermore, usual ground water monitoring techniques are not able to indicate these problems and further investigations are required to develop more significant tools for performance monitoring. This may lead to a better understanding of factors that effect the longevity of iron PRBs at field conditions.

2.6. Multibarriers tackle mixed pollution

Groundwater is the main source of drinking water in Europe. The contamination of this groundwater by contaminated soils or as a result of landfill leaching is one of the major concerns for the European society in the beginning of the 21th century. Since hundred years landfills were installed for domestic and industrial waste dumping. Landfill technology was not designed for longterm performance which means that most of the old landfills are leaching into the groundwater and threatening drinking water resources in the neighborhood of large and small cities. Recently, *in-situ* treatment is becoming more interesting for aquifer treatment as the technology is developing and becoming more reliable and accepted. A very attractive *in-situ* system is the concept of the “permeable barrier technology” in which a trench is made perpendicular to the groundwater flow. This trench is filled with a coarse material and induced to treat the pollutants in the passing groundwater. The coarse material can consist of iron fillings (reactive material) to induce reductive dechlorination of VOCLs (reactive barrier) or it can be suitable for the development of a biofilm able to degrade organic compounds like BTEX or mineral oil (biobarrier). In the latter case, substrates or electron acceptors are infiltrated in the barrier material to stimulate bacterial activity. Finally, the coarse material can be a sorbing material (for example compost) to remove heavy metals or some other compounds.

Mostly, reactive walls and biobarriers are designed to abate specific pollutants. However in many cases, polluted groundwater (especially in case of contamination by landfill leachates) contains a mixture of both organic and inorganic contaminants. The abatement of such pollutant mixtures is not possible with a simple barrier based on removal of the pollutants by either physico-chemical or biological way. However, such pollutant mixtures might be treated using a combination of both systems. Such a Multifunctional Permeable Barrier (MULTIBARRIER) concept will be based on the combination of a chemical reduction system to dechlorinate the AOX compounds and a biological system to further degrade the organic skeleton of the dechlorinated pollutants and other non-chlorinated pollutants. Furthermore, it can be combined with adsorbing materials such as carbon to remove traces of pesticides and other pollutants (like PCBs). Such an approach requests the efficient synergistic interaction and compatibility of the microbial and physico-chemical key-components of the system, i.e., the biofilm community and the coarse material which can function both as the biofilm support and as reactive material.

3. Conclusions

A Permeable Reactive Barrier (PRB) is an engineered zone of reactive material(s) that is placed in the subsurface in order to remediate contaminated fluids as they flow through it. A PRB has a negligible overall effect on bulk fluid flow rates in the subsurface strata, which is typically achieved by construction of a permeable reactive zone, or by construction of a permeable reactive ‘cell’ bounded by low permeability barriers that direct the contaminant towards the zone of reactive media.

In most environments these PRBs will last a long time. However, depending on the inorganic geochemistry, issues arise related to the long term impact of the inorganic precipitates on the iron surface. Initially, it was thought the these precipitates would cause significant losses in permeability, however recent research indicates that only slight permeability losses will be observed over time. The knowledge of processes occurring in the reactive material and interactions with microbiology and inorganic elements allowed to understand and design the barriers that they could work for a longer period than expected until now. The combination between bacterial activity and the chemical processes on the iron surface or the physical processes of adsorption on the GAC surface seem to play an important role in the longevity of the barrier. This knowledge also lead to the understanding that the combination of different chemical, physical and biological processes must make that also mixed pollutants (inorganics and organics) could be treated in one single measure in a MULTIBARRIER.
Almost all the materials that have been suggested to be used in chemical barriers are particles (e.g. zero valent Fe (Gillham, 1994), anoxic limestone (Hedin, 1994), and peat (Longmire, 1991). These materials require emplacement in an excavation such as a trench because injection would clog the aquifer causing flow to be diverted around the chemical barrier. Therefore several attempts are going on to introduce compounds that are either soluble or can be transported at the water flow rate. In this was the possibility of injecting $FeCl_3$ into the subsurface through wells was investigated. A chemical barrier emplaced through wells could be used to treat deep contaminated aquifers and at sites where surface disturbances (such as trenching) are unacceptable. AFO could be emplaced beneath structures or landfills by horizontal drilling wells.
For the chemical barrier to be effective, AFO must spread throughout the aquifer during injection and must remain immobile after emplacement to prevent the transport of contaminants. Excessive clogging of the subsurface will hinder injection by decreasing hydraulic conductivity and may cause groundwater to be diverted around the chemical barrier.
An other way is the injection of nano-iron particles. These can be injected in the wells and will proceed with the water flow rate. At the moment no information exists about the behavior of such iron particles in the aquifer (possible aggregation, co-precipitation and clogging).

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The Industrial Waste Landfill at Bonfol (Switzerland)

THE INDUSTRIAL WASTE LANDFILL AT BONFOL (SWITZERLAND)

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0. Summary

The landfill for industrial waste in Bonfol (Switzerland) was installed in 1961 in a waterproof clay pit and was run until 1976 by the **bci, the Basel chemical industry**, to dispose off their industrial waste originating from chemical production. For the first time in Europe chemical wastes were deposited in a special area selected according to geological criteria. Groundwater and surface waters have been continuously supervised since the beginning of the activities in Bonfol in 1961. After the landfill was totally filled up, it was covered by a clay layer.

114'000 tons of industrial wastes are stored below the surface on an area of approximately 20'000 square meters. To the largest part the waste was generated in the production of colouring agents, pharmaceuticals, detergents and agrochemicals, including the intermediate products involved. Besides waste from the industry of the former canton of Berne and the Swiss army were disposed off, too.

Roughly 70 % of the wastes were deposited in drums. Most of these 300 to 400 thousands of drums were damaged upon deposition and storage. It was not usual at that time to log detailed data about the composition of the wastes or the exact place of deposition and no analytic controls were applied.

1976 the landfill was totally filled up and was covered by a clay layer and reforested. Since its deactivation the site is subject to a long-term monitoring program that has been installed together with the authorities based on a risk analysis. Since that time bci is responsible for the Bonfol site with its own expert team.

In the years 1980/81 the monitoring program discovered that the cover of the landfill was leaking and that the pit slowly filled up with water. Some exfiltrations resulted. It was important to overcome the critical situation by the implementation of immediate measures, e.g. pumping and removal of leachate. Different remediation options were studied at that time, among others the excavation and final disposal of the contents of the landfill.

Given the legal framework and missing technical possibilities bci agreed on a containment solution. A large and sophisticated new cover and a biological purification plant for the treatment of the leachate were installed between 1986 and 1995. The investment ran up to 28 millions of Swiss francs (approx. 20 mio. Euros).

In October 1998, a new regulation on contaminated sites came into force in Switzerland. As a result, bci was asked by the authorities to perform a total clean up of the industrial landfill of Bonfol. bci explained that the situation of the landfill complied with the requirements of the new regulation and that there were no signs of mobilization of contaminants into the environment.

From 1999 up to now the authorities and some non-governmental organizations in Switzerland and France tried to inflict considerable pressure on the bci through the media with the aim to get a promise for the total clean up.

In May 2000, bci decided to study options for a final clean-up, because the long-term stability under reasonable economical conditions can only be guaranteed by the total remediation of the site. At the same time, Greenpeace occupied the area of the former landfill and started some actions on site.

On October 17, 2000, a voluntary agreement between the authorities and bci was signed. The latter committed itself to finance a study of options for the total clean up carried out by an independent team of consultants.

Since 2000 some new instruments have been introduced to explain bci's position and to help information interchange in the project:

- the bci Internet homepage (www.bci-info.ch), in operation since August 2000
- bci is publishing newsletters for the French speaking population of the villages around Bonfol, including France
- a committee of information was founded with members of the authorities, communities and NGOs of Switzerland and France

On May 15, 2001, bci presented the result of the study of remedial options. Excavation/ incineration in European incinerators or in-situ vitrification, with a suboption excavation/on-site vitrification, were seen as the most promising ones.
At the end of 2001 the option of the in-situ vitrification was dropped because of the resulting public and political resistance towards this technology.
In 2002 on July 2, bci announced a new organization for managing the whole project (bci Betriebs-AG).
The remaining options are being evaluated thoroughly at the moment to prepare the basis for a decision on the clean-up project.
Meanwhile Swiss and French NGOs and politicians are keeping up their high pressure on bci to force it into a full takeover of its financial responsibility.

1. Historical overview

1.1. The bci, a Society of the Basle Chemical Industry

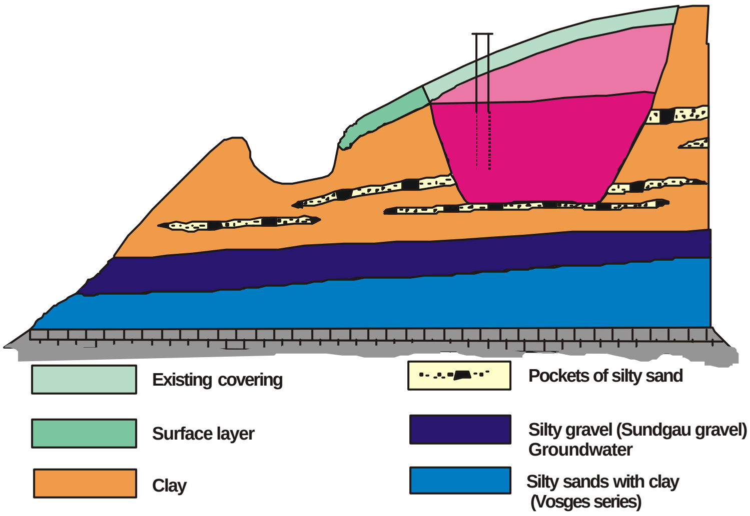
With the increase in chemical production end of the 1950s, the Basle Chemical Industry was confronted with the need to find an appropriate site for the disposal of its wastes. A society named **bci** (Basle Chemical Industry) was founded by the predecessors of the following companies: Novartis, Roche, Ciba Specialty Chemicals, Clariant, SF-Chem, Syngenta, Henkel and Rohner.

1.2. Evaluation and situation of the landfill

The most important selection criteria for the construction of a landfill were a flat site and an impermeable subsurface, i.e., consisting of loam or clay. The former clay pit used by the ceramic industry at Bonfol, in the North-Eastern part of Switzerland, with a 6 – 8 m thick clay layer met these criteria. For the first time in Europe, chemical wastes were disposed of in a landfill based on the evaluation of appropriate geologic criteria. From the beginning of the landfill activities, groundwater and surface waters were regularly monitored.

1.3. Operation from 1961 to 1976, Contents of the landfill

From 1961 to 1976, a total of **114,000 tons** of wastes were disposed of by the bci, over an area of approximately 20,000 m^2. The majority of the wastes consisted of residues from the production of dyes, pharmaceutical products, detergents, agrochemicals as well as corresponding intermediate products. Relatively minor quantities of products and wastes from the Swiss Army and the industries of the former Canton of Berne were also disposed of in the landfill.



Approximate Geological Profile State 1981

A detailed characterization of the composition of these wastes was not common at that time and thus not recorded during this period. The composition of the wastes present in the landfill is estimated as follows:

Parameter	Expected values averaged over the entire contents of the Bonfol-pit	Expected (local) extreme values
Combustible Fraction	10-30%	0-100%
Inorganic Salts	1-5 %	
Metal drums (Fe)	100’000 – 400’000 pcs.	
Heavy metals	?	
Halogens	2-6%	
Sulfur	= 1% (as Sulfate)	
Water content	10-30%	

In 1976, the landfill was closed and the clay pit covered by a 1.5 - 2 m thick layer of clay and revegetated.

1.4. <u>Supervision and first remedial activities 1981 to 1995</u>

In parallel to the waste deposition, a long-term monitoring program was initiated in collaboration with the regulatory authorities. The program was designed to identify potential emissions from the landfill as quickly as possible and to take the appropriate measures if needed.

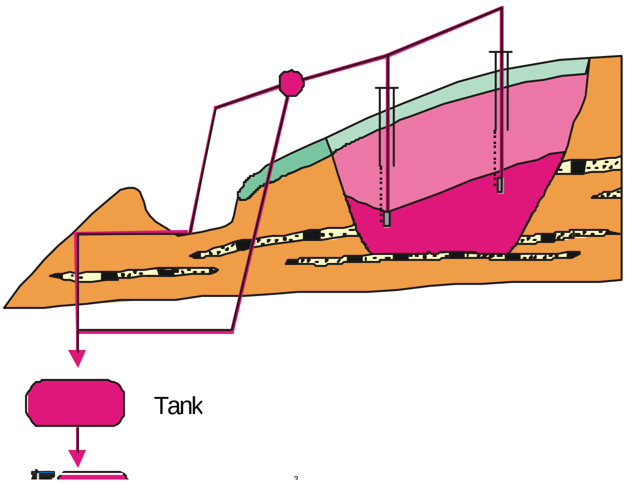
Events

Based on the data generated from the landfill-monitoring program, it became apparent in 1981 that the landfill cover was not completely water tight. The former clay pit was filling up with infiltrated rainwater. This infiltration resulted in low rates of lateral leachate migration in the direction of the former railway cut close to the landfill. Based on this phenomenon, it was believed that the stability of the clay pit could not be entirely guaranteed.

An extensive investigation was conducted, indicating that the soil in the vicinity of the landfill was slightly contaminated in certain areas. However, no contamination was detected in the gravelly aquifer underlying the landfill.

Immediate Measures

In order to reduce the critical risk of landfill instability as well as to stop as quickly as possible the migration of contaminants from the landfill, the water level in the landfill was lowered. Leachate was syphoned, pumped and transported to industrial wastewater treatment facilities in Basel.



Pumping of leachate from the landfill

Due to these immediate measures, sufficient time was available for a detailed evaluation of potential risks, for the planning of measures to assure the long-term landfill safety, for obtaining the regulatory permits from the Canton and for the required contractual negotiations with the property owner, the municipality of Bonfol.

Remedial Actions

Several remedial actions and treatment options were evaluated, including excavation and incineration of the wastes. The option of a complete site clean-up was not viable due to the lack of appropriate waste treatment facilities and the requirements of the regulatory authorities. Therefore, a long-term containment option was selected.

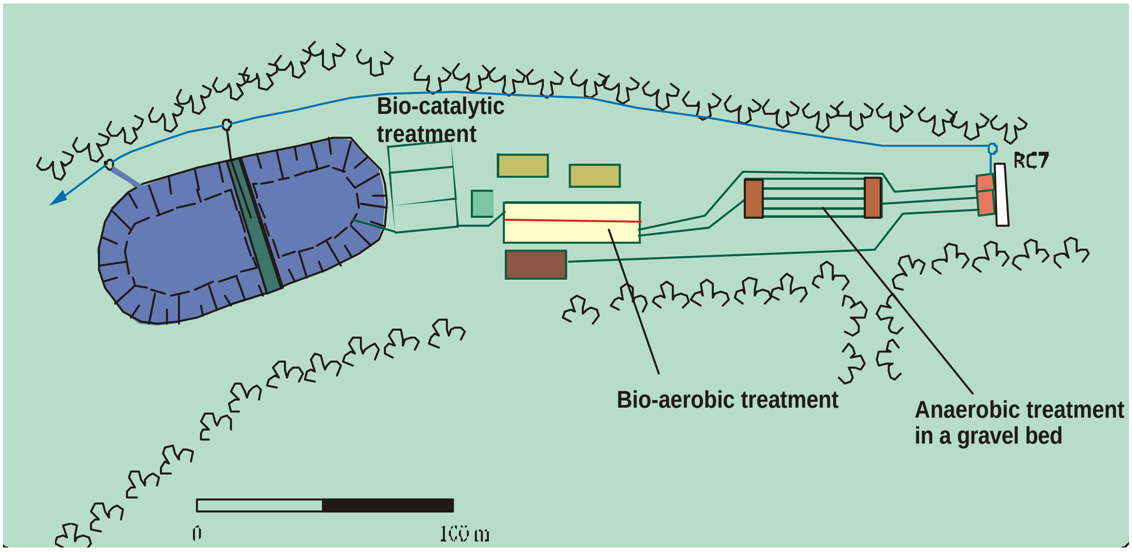
During the first phase (1986-1989), the following remedial measures were implemented:

- Construction of a drainage system to lower the level of water in the landfill to a pre-determined level in order to minimize the hydraulic gradient and thus a lateral migration of leachate from the landfill

- Filling of the railroad cut and reestablishment of the original level of the groundwater table to the north of the landfill in order to guarantee long-term stability and minimize the hydraulic gradient
- Construction of a biological treatment system for the leachate

Leachate Treatment

The process for treating the landfill leachate was developed in the laboratory of the Environmental Technology group of the former Ciba-Geigy Inc. Due to the high concentration of salts and organics, the leachate needs to be diluted approximately by a factor of 10 before treatment in an anaerobic gravel filter (in the absence of oxygen). In this step heavy metals are precipitated and a fraction of the organic matter is eliminated by biological degradation. The second treatment step consists of a two-stage aerobic activated sludge process. The used air is purified in a biofilter. In order to improve the overall treatment efficiency and nitrification during the cold period of the year, a complementary treatment step consisting of a sand and activated carbon bed had to be subsequently added. The treatment efficiency increased to >95% for organic carbon as well as for ammonia. The quality of the treated water complies with the current requirements for discharge into surface waters.



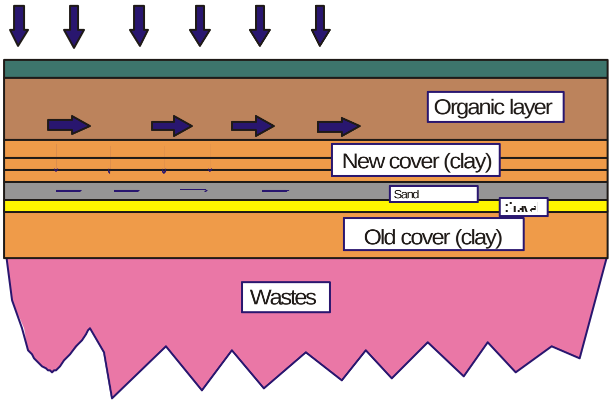
Water treatment at the industrial waste landfill in Bonfol

Landfill Cover

In the period from 1991 to 1995, a new 2.5 m-thick cover was placed on top of the landfill. The multi-layer cover was constructed with the aim to minimize rainwater infiltration into the landfill. The cover consists of (from top to bottom):

- Organic soil layer
- Cover layer - composed of sandy soil-material permitting the development of plant root systems
- Clay layer – poor in oxygen, acting as a barrier for plant root systems
- Water-impermeable layer – 40 cm of clay
- Capillary Drainage layer – consisting of a sand layer
- Capillary Barrier – consisting of a gravel layer

The old clay cover of the landfill is located underneath this new cover.



Cover

Safety and Monitoring Concept

In the same period, the risk analysis was reevaluated a third time and a new safety and monitoring concept was defined in collaboration with the regulatory authorities. The document establishes the duties and responsibilities regarding operation and maintenance of approximately 100 monitoring points (groundwater, natural springs, streams and landfill surface), of the drainage system and of the leachate treatment installations. The periodical analytical results of the monitoring program confirm the expectations of the risk analysis. The remedial measures implemented have led to a situation where acute risks associated with the landfill can be excluded. The short- to mid-term safety of the landfill is assured by a periodic evaluation of the situation on site. The results of the monitoring program are presented in annual reports.

2. Present situation

2.1. Safety and supervision concept: Monitoring, Survey and groundwater modelling

The third risk analysis in 1991 demonstrated that the long-term safety option (containment) had reduced the risk associated with the presence of the landfill. This residual risk was evaluated as acceptable. However a long-term monitoring of the landfill and the hydrosphere is necessary. It is important to detect as quickly as possible releases from the landfill and take all necessary corrective measures. As water is the main pathway for the propagation of the contamination in the environment, the monitoring of the hydrosphere is of fundamental importance.

An improved safety and monitoring concept was developed in collaboration with the regulatory authorities in 1994. The concept takes into account the following elements:

- Detection of a contamination in the environment of the landfill
- Monitoring of any discharge of the drainage system
- Prevention of accidents
- Control of the long-term safety
- Information and relations (regulatory authorities, municipality of Bonfol, French authorities, bci, etc)

An annual report is issued on the basis of new data acquired during the monitoring. It permits to judge if the situation is normal or abnormal. This information is also used for the update of the risk analysis.

The monitoring concept divided the landfill system in four parts: the landfill, the drainage system, the water treatment and the environment.

A monitoring program is in place for each of the definite parts with specific indicators. For the landfill these parameters are water levels, discharge of drainage systems, packing of clay cover and vegetation. For the drainage systems these parameters are discharges and sludge. For the water treatment system and the surrounding waters these parameters are chemical and physico-chemical parameter concentrations. In 2002, the analyzed parameters have been reevaluated and adapted.

The risk analysis showed that the quality of the groundwater in the Sundgau gravels situated directly below the clay layer under the landfill is a good indicator of the impact of the landfill on the environment.

New Investigations

In May 2000 bci proposed to do some additional investigations on the site of Bonfol. These would supplement the safety and monitoring concept that is already in force.

The strengthening of the safety and monitoring concept is divided into three domains:

- complete chemical and physico-chemical analyses in the present monitoring points (groundwater, sources, stream and surface water)
- field investigations of clays around the landfill
- Improvement of knowledge on Sundgau gravels

The aim of these investigations is to detect a possible pollution that would escape the monitoring boundaries. As long as no emissions are detected close to the landfill, it is not reasonable to investigate the regional hydrogeology. For this reason the works concentrated essentially on a better knowledge of the Sundgau gravel. A leak of contaminated water must necessarily pass through this formation and it would be possible to stop this pollution with a pumping system.

Until now, there is no evidence of a new pollution except of a weak contamination in the North-Western part of the landfill, which has propagated further than formerly known. Any new piezometers will be usable for monitoring and as pumping wells in case of accidental pollution of the groundwater during the total clean-up.

The different investigations are discussed below.

Analyses in the present monitoring network

Since 1995 the monitoring of the environment is based on a network of sample points and parameters that would allow to observe any new contamination. Over the years a vast set of data has been collected.

It has been decided to do some complete analyses of the monitoring network based on a risk assessment (see 2.2.). These investigations are performed on a half year basis and results of analyses showed no sign of pollution.

Geoelectric investigations in clays and Sundgau gravels around the landfill

The determination of the best locations for new piezometers that would allow to control the quality of the Sundgau waters must be made with complementary hydrogeological data. For this reason investigations with geophysical methods like the RMT-R method (Radio Magneto Telluric - Resistance) and tomography (Geoelectrical Imaging System) have been carried out.

Some pockets of silty sand were detected by RMT-R. This method however is not suitable to investigate depths superior to 10 m in clays and to define the depth of the basis of the Sundgau gravels.

Tomography has been successfully tested in the field with investigations going up to 60 m in depth, allowing the different geological layers to be determined. Sometimes however there exist deviations between the results obtained by tomography and the corresponding piezometer profiles.

Improvement of knowledge on Sundgau gravels

If an exfiltration of contaminated water propagates itself towards the environment, it must cross the groundwater in Sundgau gravels. For this reason it is important to really know the hydraulic system of this layer in order to be able to intervene in case of an accident.

Hydraulic modeling was done during the risk analysis of 1991. This model has been recalculated in July 2000 and 2002 using the latest data and confirmed the results already obtained.

Pumping tests in the different piezometers situated in the Sundgau gravels have been done. These tests allow to drain and to analyze waters on a bigger surface. They also give access to a better knowledge of the hydraulic conductivity of the Sundgau gravels. These informations are important to plan intervention measures.

With the first results of the geoelectric investigations, 7 new piezometers have been installed in 2001 and 10 new ones will be put in place in 2003 to improve the monitoring and intervention concept.

All these investigations aim towards improving the calibration of the model and so enhancing the knowledge on the hydraulic system of the groundwater around Bonfol.

2.2. Risk assessment

BMG Engineering Ltd. was retained by the bci for a chemical risk assessment of the deposited wastes, including present and potential future impacts.

The base and lateral barrier system of the landfill is formed by the natural Bonfol clay formation, which is underlain by a local gravel aquifer. Both the Bonfol clay formation and the gravel aquifer are accessed by numerous piezometers. The water from these piezometers as well as the waste water collected by the drainage system are monitored for a large number of compounds.

The compound classes relevant for an evaluation of chemical risks were identified based on site history and available data on leachate and off-gas composition:

- Chemical index parameters with regard to the potential risk for man and the environment were selected based on the toxicity, mobility, and biological degradability of the landfilled substances. The most significant risk was found to be associated with methylated anilines, selected volatile halogenated hydrocarbons and benzenes. Toxicity tests were performed to verify that relevant compounds had no been overlooked in the chemical analyses.
- Compounds that occur specifically in the landfill, and whose environmental mobility and/or persistence would allow an early detection of potential emissions were defined as tracers. This group comprises 1,1,2,2-tetrachloroethane, butylbenzene, THF, dioxane, selected anilines, nitrobenzene, and bromide.

The potential emission pathways were evaluated. Losses of dissolved constituents vi a leachate turned out to be the only relevant route for emissions. Significant losses in the form of gaseous emissions or DNAPLs are unlikely. In particular, the present concentration levels of relevant contaminants directly downstream of the SMDB give no evidence for an accumulation of DNAPLs on the underlying aquifer.

The natural wells and surface waters, which might be exposed in case of emissions from the landfill, were identified based on the current knowledge on regional groundwater circulation systems.

The monitoring program was adapted in order to sample the (potentially) exposed waters and to analyze the above mentioned chemicals. Significant levels of volatile halogenated hydrocarbons were only observed in groundwater monitoring wells in the North-East of the landfill. Although the corresponding pollutant load was estimated to only 1-5 kgs/a, the groundwater was pumped to limit the spreading of contaminants. No significant impact was observed on the waters further downstream from the site.

Since the halogenated hydrocarbon concentrations in the groundwater directly downstream of the site exceed threshold values of the Swiss Ordinance for Contaminated Sites, the Bonfol lnadfill may be classified as a site where remediation is definitely required. However, the known pollution is limited and the sources downgradient of the sites can be used at present without restrictions. There is no evidence for a significant increase of emissions from the landfill in the near future. Therefore, there is no urgent need for remediation.

To further quantify and curtail chemical risks emanating from the Bonfol landfill, a continuation of the monitoring program, an extension of the monitoring grid, and a better characterization of the groundwater circulation system are recommended.

2.3. Legal situation and political development; events since November 1998

In October 1998, a new ordinance on contaminated sites came into force in Switzerland. As a result, bci had a first discussion with the responsible minister of the government of the Canton of Jura. The minister asked for the total clean up of the industrial landfill of Bonfol. bci explained that they had just completed in 1995 the new containment with costs of about 30 Mio Swiss Francs in 1995 and that the situation of the landfill complied with the requirements of the new regulation.

At the end of December 1998 the minister contacted the media (newspapers, radio, TV) and asked again for the total clean-up of the industrial landfill of Bonfol. bci responded in different media, mainly of the French speaking part of Switzerland, that they were in legal compliance.

At a meeting held in January 1999 with the federal and Canton of Jura authorities, bci again stated that the situation of the landfill was in legal compliance but as this could change in future a feasibility study for the total clean up would be started. bci would not rush this study, the situation was stable and there were no signs of mobilization of contaminants into the environment.

Without informing bci, the government of the Canton of Jura and the federal authorities of Switzerland held a press conference on 13 January 2000. They strenuously attacked bci and demanded the total clean up of the landfill within a time frame of 5 years. They presented a team of experts who had done a feasibility study that showed that a total clean up could be possible in 3 - 5 years (none of these experts had any experience in landfill remediation). A major media event resulted. bci's response was that the landfill was in compliance with the legal requirements and that the situation was safe.

At the end of February 2000 the green non-governmental organizations of France held a press conference and demanded the total clean up, because the landfill is directly on the border with France. The issue had became international.
On March 27 bci had their first meeting with the team of experts named by the Canton of Jura.

On April 17 the French minister for the environment met her Swiss colleague and discussed the situation of the industrial landfill of Bonfol.

On May 13 Greenpeace occupied the site and started different actions, so the pressure on bci increased again.

On May 15 the first meeting between the government of the Canton of Jura and bci took place.

On May 16 bci organized a press conference and explained its position.

On July 7 Greenpeace stopped the occupation. bci only offered that the NGOs would be periodically informed about the next steps. One week later bci discussed this item with all the interested groups of NGOs.

On August 1, a bci-homepage in the Internet was installed (www.bci-info.ch). At the end of August, bci published a newsletter informing the French speaking population of Bonfol.

On October 17, 2000, the agreement between the Canton of Jura and the bci was signed. The important point was that bci would finance a study of options for the total clean up. This study would be done on the basis of the already existing feasibility studies carried out by the Canton of Jura and by the bci. This study is directed by bci but will be carried out by an independent consultant. The study has to be overseen by a group of experts named by the bci and the Canton of Jura and has to be completed within a timeframe of 7 months.

On April 27 2001, a committee of information was founded. Members are Canton of Jura, bci, authorities of Switzerland and France, communities around the landfill und NGOs of Switzerland and France.

On May 15 bci presented the result of the study of options. The favorite solutions were excavation/incineration in European incinerators (capacity in Switzerland is too small) or in-situ vitrification. A suboption is excavation/on-site vitrification. These options have to be evaluated seriously by the end of 2003 to prepare the basis for a decision on the clean-up project.

On November 27 bci dropped the option of in-situ vitrification because the political and public resistance to this technology was too strong.

In 2002 on July 2 bci announced a new organization for managing the project (bci Betriebs-AG).

In July and October 2002 Swiss and French NGOs and politicians held 2 press conferences in Bonfol and Basel to once again claim that the bci shall take full responsibility and financial liability for the whole activities in the total remediation of the Bonfol landfill. bci answered in October 2002 in a press statement that it will accept its responsibilities but would not be willing to pay for additional activities not directly linked to the cleanup.

3. Evaluation of remedial methods

On October 17, 2000, representatives of the Canton Jura and bci signed an agreement regarding the total remediation of the industrial waste landfill of Bonfol. The agreement envisaged the completion of a 'remedial investigation/feasibility study' "Final remediation of the Industrial Waste Landfill Bonfol" within 7 months. BMG Engineering Ltd. (BMG) was retained to perform this feasibility study.

The study's goal was the evaluation of possible solutions for eliminating the potential risk originating from the approx. 114'000 t of wastes deposited in the Bonfol landfill. The proposed remediation options have to satisfy the following criteria, according to a "4 pillars principle":

- technical feasibility
- legal compliance and socio-political acceptance
- resource and cost efficiency
- minimization of overall environmental impact.

The study was completed in three phases:

1. Compilation and update of available data and information on the landfill characteristics, as well as evaluation of the urgency for remedial measures
2. Description and first evaluation of possible remediation technologies
3. Comparison of feasible remediation options according to the criteria defined above (4 pillars principle).

The Swiss Environmental Protection law (1997) and the Swiss Ordinance on Contaminated Sites (1998) provide the legal frame for the evaluation of the remediation options.

For the feasibility study, a large quantity of existing data and many reports were evaluated. Simultaneously, data from the hydrogeological investigations of the year 2000 were integrated into the study.

After the evaluation of numerous possible remedial options, the following processes were identified as technically feasible:

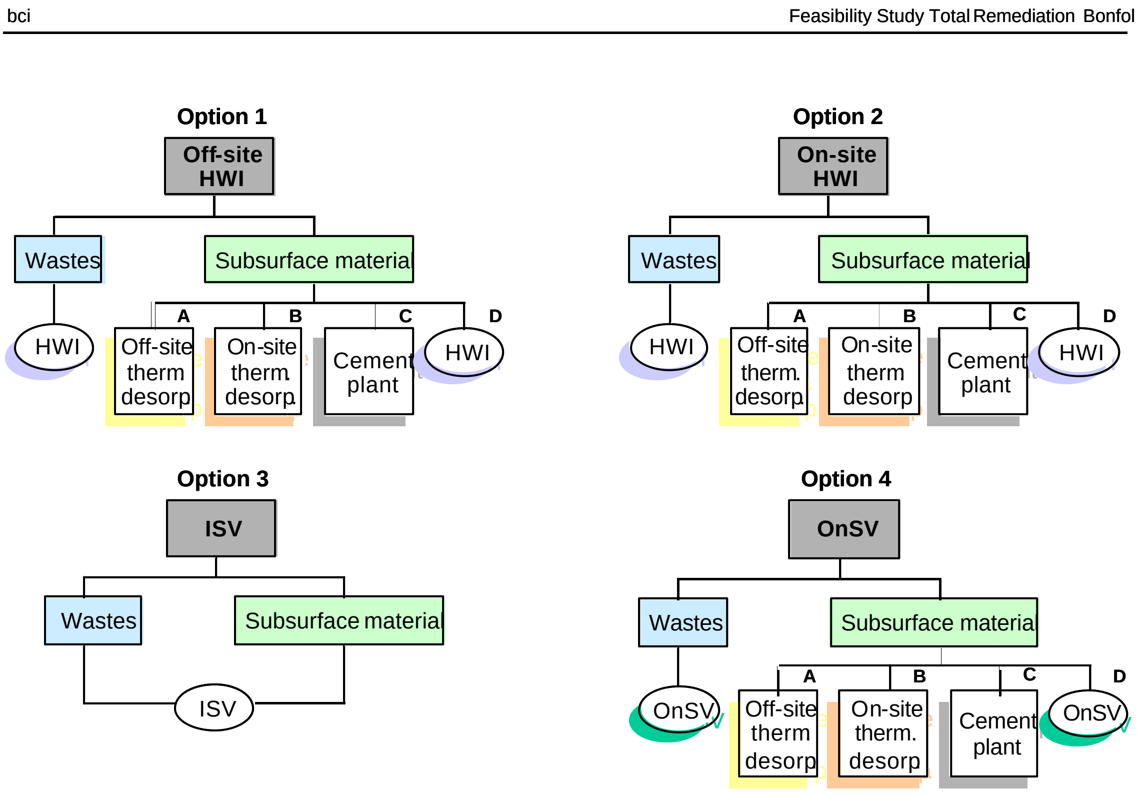
For the <u>treatment of the actual waste</u>:

- **Option 1**: Off-site incineration in existing hazardous waste incinerators (off-site HWI)
- **Option 2**: On-site incineration after construction of an on-site HWI (on-site HWI)
- **Option 3**: In-situ vitrification (ISV)
- **Option 4**:On-site vitrification in corresponding reactors (OnSV)

For the <u>treatment of subsurface material</u> (earthen dams and borders of the landfill):

- Off-site thermal desorption
- On-site thermal desorption
- Thermal treatment and recycling in an existing cement plant (rotary kiln)
- Similar options as for the treatment of the wastes.

The evaluated options are illustrated in the following figure.



Schematic representation of evaluated, technically feasible remediation options

In comparison to the subsurface (soil) material that has to be treated, the waste material represents a significantly larger volume and requires a technically more complex and sophisticated solution. Hence, the establishment of treatment options for the wastes is of highest priority. Treatment options for the subsurface material can subsequently be defined as a function of the treatment process for the wastes, in order to ensure the best compatibility.

Discussion of options 1 to 4 (see detailed schematic representation of options in the figure above):

Remediation option 1: Off-site incineration (A/B/C or D)

This option envisages the excavation of the wastes, followed by a separation/ classification and conditioning. Subsequently, the materials are transported to one or more existing, commercially operated hazardous waste incineration plants.

Remediation option 2 with the construction of an on-site HWI was not identified as feasible and dropped due to

- significant technical problems
- the long time requirement for the implementation and remediation
- the long planning and permitting phases anticipated
- significant local and regional impacts (disturbances and nuisances)
- significantly higher total costs

Remediation option 3: In-situ vitrification (ISV)

With this option, wastes and subsurface material are heated simultaneously, without prior excavation, up to their melting points (1'400-2'000°C). This is accomplished by introducing electrodes into the landfill. The high temperatures will induce the desorption of organic substances, and their subsequent destruction in the gas phase. Released gases are collected by a hood and subjected to a multi-stage off-gas treatment process. Heavy metals are either immobilized within the melt or removed in the off-gas treatment. The vitrified glass-like matrix that remains after cooling is inert.

Remediation option 4 consisting of on-site vitrification (OnSV) was also identified as a feasible method with the advantage of allowing a more consistent check of the vitrification-efficacy.

Detailed Evaluation of Prime Options

Following the completion of the feasibility study, a project-oriented engineering partnership of two consulting companies (BMG and CSD) was commissioned by bci in late summer 2001 to conduct a detailed evaluation of the remaining options 1, 3 and 4.

The in-situ vitrifcation (ISV) option required an initial in-depth verification of its feasibility for the application in Bonfol, as this technology is less known and has only been commercially applied for remediations of a scale about an order of magnitude smaller than Bonfol. In November 2001 bci had to drop ISV (option 3), because the political and public resistance became too high.

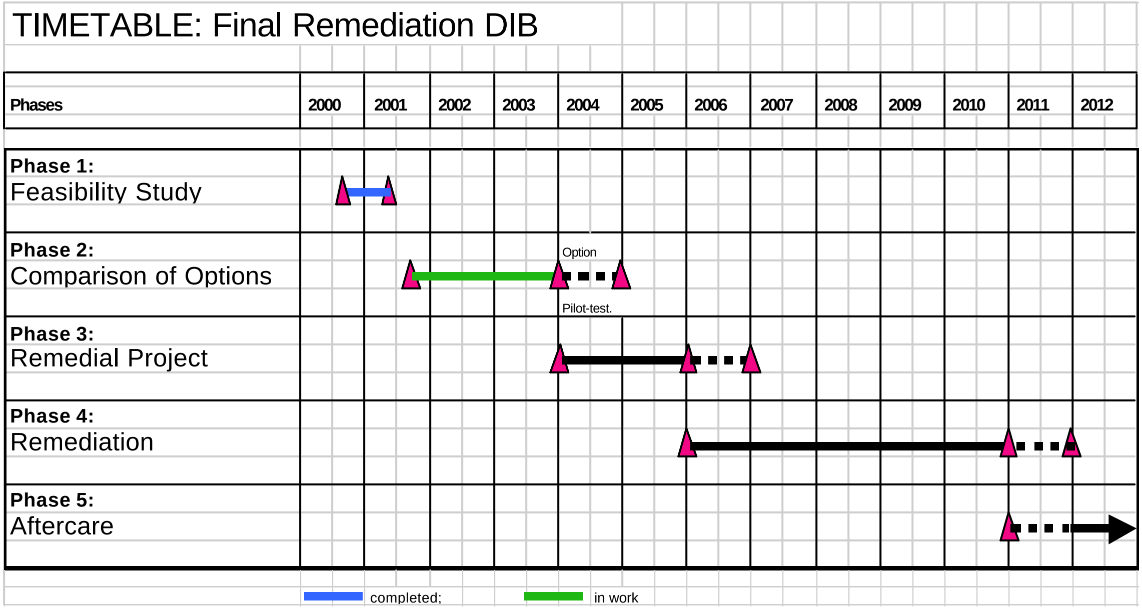
Therefore only options 1 and 4 are left. Current activities in the frame of a detailed assessment of the two options, off-site incineration and on-site vitrification, include the following:

- Evaluation of existing European facilities for hazardous waste incineration (Switzerland has no capacity for treating the expected 150'000 tons of special wastes)
- Evaluation of approaches for excavating, partially segregating and transporting the wastes
- Evaluation of appropriate containers for safe and secure transportation by rail and road
- Assessment of civil engineering options to cover the landfill (area 150 by 200 m) with an appropriate control of emissions and precipitation
- Needs and options for on-site waste pretreatment (segregation, shredding, conditioning)
- Characterization of likely emissions at all stages (excavation, pretreatment, transportation) and assessment and evaluation of required health and safety measures
- Definition and preliminary design of required infrastructure (access, transportation, area requirements, buildings for conditioning, site personnel, other treatment units, fuels and electrical energy, water, etc)
- Evaluation and preliminary design of processes (off-gas treatment, wastewater treatment, secondary waste streams)
- Evaluation of logistics and procedures
- Feasibility study for an on-site “in-container vitrification” option
- Evaluation of thermal desorption plants for treating approx. 50'000 tons of contaminated clayey soils (mobile units for on-site treatment vs. existing commercial units)
- Permitting procedures (local, regional, transportation, export/import)
- Risk assessment for defining appropriate remediation goals (“how clean is clean enough?”)

This detailed evaluation is scheduled to be completed towards the end of 2003. Shortly thereafter bci shall choose the preferred option for the final remediation of the Bonfol landfill based on this evaluation.

4. Timeframe

The timetable of the remedial project is presented in the following graph:



5. Abbreviations

bci	Basle Chemical Industry; this society was founded by the predecessors of the following companies: Novartis, Roche, Ciba Specialty Chemicals, Clariant, SF-Chem, Syngenta, Henkel and Rohner
BMG	BMG Engineering Ltd. Schlieren, Switzerland
CSD	CSD Ingenieure und Geologen AG, Berne, Switzerland
DNAPL	Dense Non Aqueous Phase Liquid
HWI	Hazardous waste incinerator
ISV	In-situ Vitrification (a vitrification directly in the pit, without excavation and any pretreatment)
NGO	Non Governmental Organization
OnSV	On-site Vitrification (a vitrification in the vicinity of the landfill, without excavation and possible pretreatment
RMT-R	Radio Magneto Telluric – Resistance; a geo-physical method to explore the environment of the landfill
THF	Tetrahydrofurane

SpS 10 Special Session

Agriculture as Source of Contamination: Bioremediation and Risk Assessment

MICROBIOLOGICAL DEGRADATION OF PRODUCTS FO DETOXICATION OF CHEMCIAL WEAPONS AND ORGANOPHOSPHORIC HERBICIDES

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1. Introduction

The pace of development of modern industry resulted in a vast anthropogenic pollution of the environment, which is a real menace of ecological crisis. In this connection, one of the primary tasks of the modern ecology is development of the most efficient methods of decontamination of hazardous industrial waste and purification of polluted territories and water areas.

Various methods for destruction and decontamination of solid and fluid industrial wastes and for cleaning of polluted soils from toxic hard-to-degrade compounds have been proposed. Physical, chemical and mechanical methods are predominant (burning, neutralization, adsorption, extraction, coagulation, ozonization, fast electron and UV irradiation, bituminous grouting and burial, mechanical collection, etc.). However, the available technologies are very energy and material consuming and, above all, not quite effective. Such cleaning yields great amounts of mud and by-products whose utilization causes serious ecological problems.

The analysis of progress trends in the study of environmental protection shows that, along with the improvement of the available physical and chemical methods, much attention is paid to biotechnological methods, which are recognized as undoubted priority by efficiency and economy. These methods are ecologically safe and compare favorably with other methods by the absence of secondary waste, because they allow a complete mineralization of chemical compounds discharged into the environment as industrial waste.

The degrading activity of microorganisms towards natural organic compounds, which enables the circulation of substances in the biosphere, is a basis of the biotechnological methods of environmental protection from technogenic pollution. The case with the circulation (mineralization) of unnatural compounds synthesized by modern chemical industry is much more difficult. Toxic chemicals, otherwise called xenobiotics, began to be intensively discharged into the environment not long ago (in the last 50 years). As a result of microevolution, microorganisms not only resistant to such chemicals but also capable of their degradation have appeared in the nature. These microorganisms may be a basis of biotechnologies for environmental protection and cleanup from different pollutants.

Bioremediation is the most efficient and ecologically safe method for cleaning of the environment from different pollutants. There are two fundamental approaches to biodegradation of xenobiotics in the natural environment: stimulation of aboriginal microflora by creation of the optimal conditions for its activity and introduction of effective microorganisms-degraders into a polluted ecosystem along with the addition of mineral salts. Biopreparations for bioremediation are based on selected microorganisms, actively utilizing certain xenobiotics. Such approaches to bioremediation need a comprehensive study of microorganisms engaged in biodegradation processes. This concerns first of all the study of their degrading activity, optimization of biodegradation processes depending on environmental conditions, and maintenance of stability of biopreparations.

The development of ecologically safe technologies is an up-to-date problem also for the program of CW destruction in accordance with the Chemical Weapons Convention. Russia has accepted the conception of a two-step destruction of chemical warfare agents, which envisages their chemical detoxification at the first step followed by destruction of the formed reaction solutions at the second step. The reaction solutions, although do not possess the toxicity of the initial chemical warfare agents, contain substances of the 2nd and 3rd classes of toxicity, which are not subject to discharge into the environment. The proposed physical chemical methods of destruction of chemical warfare agents detoxification products (burning, bituminous grouting) do not satisfy the ecological safety requirements, thus making it necessary to develop alternative methods for their destruction.

CW destruction implies also a problem of the cleanup of territories, which may be polluted with toxic agents or products of their detoxification in the places of CW storage, transportation and destruction as a result of possible leaks and accidental emissions.

The current methods of decontamination of soils polluted by ecotoxicant, which include a number of sequential procedures (excavation followed by thermal treatment of soil, delivery of new soil and recovery of fertility), are very energy consuming, whereas bioremediation reduces the cost of this procedure approximately 1000-fold. A method of phytoremediation of soils polluted with mustard detoxification products has been developed by now. This method uses a number of plants, which are able to accumulate sulfur-containing compounds from soil and thereby to reduce their content 3-5-fold without treatment and 20-25-fold at additional treatment of such plantations with phytohormone solutions (Zakharova et al., 2000). Introduction of microorganisms capable of bioutilization or transformation of chemical warfare agents and their detoxification products into such soils may increase the cleanup efficiency tenfold, exposing these substances to a complete mineralization or transformation into less toxic compounds.

The search of microorganisms, which are able to utilize TDG, the non-chlorinated product of mustard hydrolysis, with a rather stable C-S bond (Harvey et al., 1998), is in progress. Mustard (bis(2-chloroethylsulfide) is a vesicant, slightly soluble in water, hydrolyzable in an alkaline medium. TDG is a stable product, well soluble in water and less toxic than mustard, however it was included in the list of precursors of vesicants that should be destroyed in accordance with the Chemical Weapons Convention. TDG can be a product of hydrolysis of mustard in soil, accumulate and remain in the environment for a long time. The development of soil bioremediation methods using the introduction of TDG degrading microorganisms in combination with agrotechnical approaches is an optimal solution for the problem of cleaning the soil contaminated with mustard or its detoxification products.

One of the most important problems is development of an ecologically safe technology of the cleanup and bioremediation of soils polluted with POs. They include methylphosphonic acid (MPA), which is in the list of precursors for the synthesis of neurotoxic CW agents and is subject to destruction in accordance with the Chemical Weapons Convention. Intensive pollution of the environment with POs is a result of a wide and uncontrollable use in agriculture of a number of pesticides, herbicides, and insecticides. At present, the most significant problem in purification of the environment from POs is the degradation of POs with a hard-to-hydrolyze direct C-P bond. This bond is resistant to photolysis, chemical hydrolysis, thermal degradation, and occurs in a wide range of both natural and anthropogenic POs (MPA and its analogs, glyphosate or “round-up”, phosphonolipids, methylphosphonylfluoride, etc.).

Destruction of POs and remediation of contaminated territories involve physical, chemical and biological methods. Biological technologies are the most preferable due to ecological safety, low cost of work, and rather high efficiency, which has been more than once demonstrated at solution of other ecological problems (Zharikov et al., 2000; Boronin et al., 1997).

The ability to utilize POs with the direct C-P bond as a sole phosphorus source has been known for a comparatively long time. The biocatalytic methods for detoxification of organophosphorus CW by uncoupling of P-O and P-F bonds using organophosphate hydrolase have been developed (Zhang et a., 1999, Dave et al., 1993). Microorganisms possessing high activity of C-P lyase, which splits the C-P bond of MPA and its analogs (the products of enzyme-based hydrolysis of neurotoxic CW agents – sarin and soman), were revealed (Yakovleva et al., 1998), but their activity was very low.

The goal of the current work was the search and selection of highly effective strains of microorganisms – destructors of mustard detoxification products, as well as strains hydrolyzing the C-P bond of organophosphorus compounds (detoxification products of neurotoxic CW agents, herbicides), and the study of their degrading activity with the purpose of their further use in technologies for bioremediation of contaminated soils.

2. Results and discussion

2.1 Bioutilization of MLM detoxification products

In accordance with the technology of neutralization of MLM developed in Russia, alkaline hydrolysis is used to obtain reaction solutions containing mustard detoxification products: TDG, diglycosulfoxide (DGSO), sulfanol, as well as the salts of arsenic component of lewisite. The biological methods cannot be applied to utilization of the organic components of such solution because of the high content of arsenic. A two-step method has been developed for purification of reaction solutions from arsenic and conversion of the organic products of mustard destruction into bioutilizable compounds. The first step includes electrochemical pre-treatment, electrolysis and electrocoagulation, which almost completely removes arsenic from a solution (its concentration decreases from 14.1 to 5×10^{-5} g/l). After sedimentation, toxic arsenic residues may be disposed in the form of a secondary raw material used for the production of arsenic-containing compounds, specifically metallic arsenic for electronic industry.

At this stage, the organic components of mustard destruction are oxidized in the process of electrolysis, mainly to low molecular organic acids: acetic, formic, isethionic, tartaric. At the second stage, the above substances are utilized as carbon sources by a selected association of microorganisms. The biological stage proceeds in a fluidized bed reactor (FBR) with activated carbon as a carrier for immobilization of microbial cells. The mixed microbial culture used in the FBR was isolated from long-stored reaction solutions of mustard and primarily composed of *Pseudomonas putida* and *Alcaligenes eutrophus*. Biological activity of the microbial association in the FBR was estimated by the extent of carbon source utilization and the intensity of oxygen consumption by adsorbed cells. The efficiency of bioutilization was calculated from the initial concentration of carbon sources in the medium, since the sorbed chemical substances could be utilized by the microorganisms both on the surface of the carrier and from liquid medium after their desorption. High-resolution proton magnetic resonance spectroscopy (^{1}H-NMR) was used to analyze the organic products in the initial reaction solution and during its treatment. The dissolved oxygen concentration was measured in the liquid prior to input and immediately after its exit from the reactor using an oxygen electrode.

The intensity of oxygen uptake in the FBR as a result of endogenous cell respiration without a substrate was 0.2-0.4 mg/l. The respiration activity sharply increased up to 3.2-3.5 mg/l, when carbon sources were added to the medium. Up to 93% of organic substances were utilized by the microorganisms at a continuous circulation of the medium for 96 h. Their consumpion could be increased by adapting the mixed microbial culture to the carbon sources. A low specific growth rate of the mixed microbial culture on these substrates (0.015-0.021 h^{-1}) restricted the biomass increment in the FBR.

2.2. Bioutilization of TDG, the mustard detoxification product

TDG-degrading microorganisms were isolated from soil samples contaminated by the mustard detoxification products. These samples were incubated with TDG and mineral salts for 3 months at 30°C. The isolated strains were selected by repeated re-inoculation into the medium with TDG concentrations increasing from 1 to 3 g/l. Within a 6-month period, using this method some strains were selected with a lag-phase of 4-8 h (instead of 40-50 h) and a specific growth rate of 0.04-0.045 h^{-1} (instead of 0.01 h^{-1}). One of them, *A. xylosoxydans* TD2, was used to study the cultivation conditions and growth characteristics on TDG, as well as the mechanism of TDG oxidation.

The efficiency of TDG utilization is affected by pH value in the medium. The pH drops precipitously due to accumulation of SO_4^{2-} ions. The culture growth and TDG utilization stop when pH drops to 5.5, whereas in the medium with glutamate as a sole carbon source this strain grows at pH 5.2. With pH 7.0-7.5, the culture growth stops only after TDG has been consumed completely. These results point to the significance of pH in TDG metabolism.

Specific substrate loading (g TDG/g biomass) in the initial period of cultivation is a very important factor for the growth dynamics of *A. xylosoxydans* TD2. The reduction of specific substrate loading in the medium with TDG from 125 t? 5 promotes the shortening of both the lag-phase from 20 to 3 hours and the duration of biodegradation process as a whole from 160 to 42 hours. The maximal specific growth rate and biomass yield did not depend on specific substrate loading. In these experiments their values were 0.037-0.04 h^{-1} and 0.28-0.3 g/g TDG, respectively. The data obtained allow to calculate the optimal amount of the inoculum culture according to the initial substrate concentration. This parameter can be used for regulation of the efficiency of TDG biodegradation process.

?. xylosoxydans TD2 can grow at rather high TDG concentrations in the medium, but the maximal values of specific growth rate (0.042-0.045 h^{-1}) and biomass yield (0.28-0.24 g biomass/g TDG) were observed at the TDG concentrations not over 10 g/l. No cell propagation was observed at the TDG concentration of 39.3 g/l, however the cells remained metabolically active and oxidized TDG, thus reducing its concentration in the medium. The growth started when TDG concentration decreased to 25 g/l. Under these conditions, the specific growth rate was 0.004 h^{-1}, i.e., several times lower than that with the initial TDG concentration of 26.4 g/l (0.015 h^{-1}).

The results of HPLC analysis showed the presence of DGSO and thiodiglycolic acid (TDGA) in the culture liquid of *A. xylosoxydans* TD2 growing on TDG as the sole carbon source. These compounds were presumably the products of biological TDG oxidation, since they were absent in the mineral medium with TDG incubated in the same conditions without bacterial cells or with inactivated cells. Their maximal amount increased with the increase in initial TDG concentration. Along with DGSO and

TDGA, the concentration of SO_4^{2-} ions (containing 80-90% of sulfur being a part of the consumed TDG) has also increased.

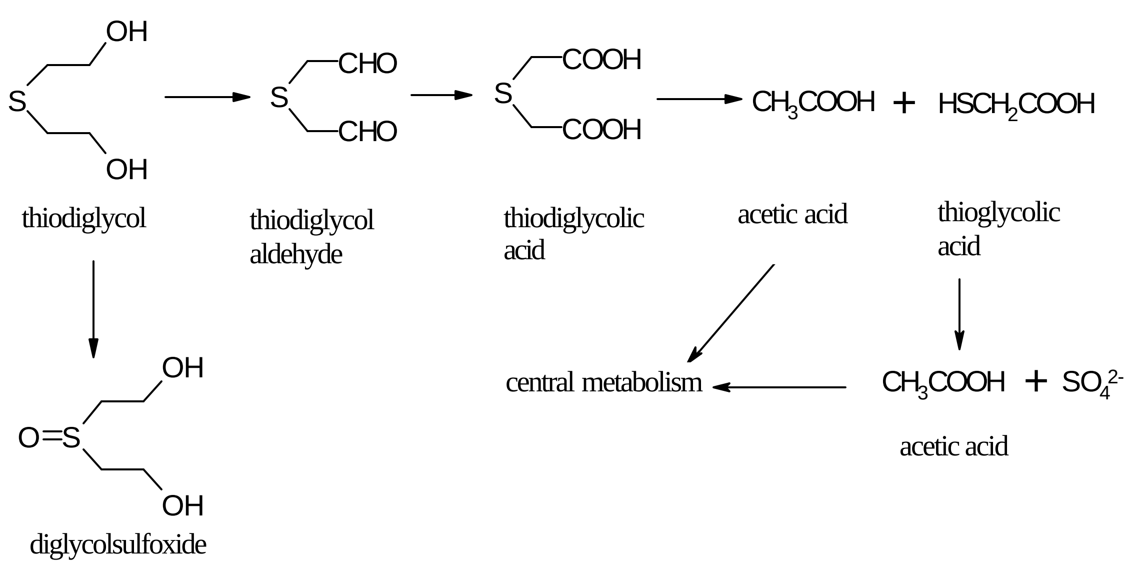
Chromato-mass-spectrometric analysis of intermediates of TDG oxidation by intact cells (native and diasomethane-methylated samples) showed the presence of thioglycolic acid, thiodiglycolic aldehyde, diglycolsulfoxide, dimethyl ether of thiodiglycolic acid and methyl ether of acetic acid.

The presence of DGSO and TDGA in the medium suggests that TDG can be exposed to a microbial attack by two independent pathways. One of them is oxidation of the sulfur atom with the formation of DGSO. Otherwise, TDG can be metabolized via the oxidation of primary alcohol groups to TDGA and subsequent uncoupling of C-S bonds of TDGA and thioglycolic acid (TGA). The uncoupling of this rather stable bond (the energy of C -S bond is equal to 64 kcal/mole) is the key reaction in degradation of sulfur-containing compounds, since the final products of this process are readily assimilated by microorganisms in the reactions of peripheral or central metabolism.

The results suggest that the oxidation of TDG to DGSO by *A. xylosoxydans* TD2 is most probably catalyzed by oxygenase with a wide substrate specificity. However, this enzyme seems to be inactive with respect to DGSO containing the sulfur atom in the higher oxidation degrees. DGSO is neither utilized as the sole carbon source for growth nor inhibits the bacterial growth on TDG, when both substrates are present in the medium simultaneously. DGSO was accumulated in the medium with TDG only in a growing culture because resting cells grown on TDG did not oxidize it. The comparison of the results for both *A. xylosoxydans ssp. xylosoxydans* (SH91) (Pham et al., 1996) and *A. xylosoxydans ssp. denitrificans* TD2 has shown that the transformation of TDG to DGSO by these cultures is a metabolic deadlock. Such processes occur during biodegradation of xenobiotics and are realized due to a wide substrate specificity of different enzymes.

The processes of accumulation and utilization of TDGA by *A. xylosoxydans* TD2 are largely determined by cultivation conditions (pH, pO_2, and TDG concentration). The acid is accumulated in the medium and not utilized under unfavorable growth conditions such as low pH and high substrate concentration. However, it is not accumulated under the controlled optimal growth conditions in fermenter. The rate of TDGA accumulation in a medium with high TDG concentration (39.3 g/l) in the lag-phase was 0.045 g/l/h whereas it decreased 4.5-fold in the period of active bacterial growth and was 0.01 g/l/h. This means an increase in the flow of this metabolite for the following oxidative reactions in the growing culture. These results imply that TDG destruction is realized in subsequent reactions of TDGA transformation.

Thus, the results of this work allow to present the TDG degradation pathway in *A. xylosoxydans ssp. denitrificans* TD2 as follows:



According to the scheme, the main catabolic reactions are TDG oxidation to TDGA with subsequent uncoupling of C -S bonds in TDGA and TGA resulting in the formation of acetate. The latter is assimilated in the reactions of central metabolism providing bacterial cells with carbon and energy sources. This suggestion is supported by the fact that sulfate ions are produced in the course of TDG biodegradation in equimolar amounts.

?. xylosoxydans ssp. denitrificans TD2, which actively degrades TDG, the product of mustard detoxification, can be used for bioremediation of soils contaminated by this CW agent as well as in the technologies for biological cleaning of solutions formed during the degassing of containers by alkaline hydrolysis of residual mustard.

2.3. Bioutilization of PO s

Microorganisms able to hydrolyze the C-P bond of POs were isolated from soil samples taken from the territories polluted with detoxification products of organophosphorus CW agents (sarin, soman) and from rice fields that had been treated with herbicide glyphosate for a long time. Samples were incubated for a long time (up to 6 months) with the addition of MPA, the product of sarin hydrolysis, or glyphosate for adaptation and activation of microorganisms able to degrade these compounds. The activity of isolated microbial strains was assessed by the amount of growing biomass and by specific growth rate in the media with the above phosphorus sources and glutamate as a carbon source. The most active bacterial strains have been selected, which grew with the maximal specific rate of 0.12-0.15 h^{-1} and accumulated biomass of 2.0-2.5 g/l.

The effect of concentration of the POs under study on the growth of selected cultures and efficiency of their biodegradation has been determined. It was shown that the level of utilization of the phosphorus source decreased from 95% to 33% with the increase in MPA concentration from 0.05 to 0.5 g/l (C:P ratio, 247:1 – 24.7:1), at the initial concentration of the carbon source in the medium (glutamate) of 10 g/l.

High concentrations of MPA and glyphosate (up to 10 g/l) do not inhibit the bacterial culture growth. With the same concentration of the carbon source (10 g/l) and MPA concentration increasing from 0.5 to 10 g/l, the amount of growing biomass consecutively increases from 1.9 to 3.7 g/l. At the same time, specific growth rate decreases from 0.13-0.15 h^{-1} to 0.1 h^{-1} and the lag-phase becomes much longer (from 4 to 24 h). The limiting factor of bacterial growth in these experiments is depletion of the carbon source. Introduction of 10 g/l glutamate in the stationary phase at the initial MPA concentration of 2.0 and 5.0 g/l results in a 1.7-2.0-fold increase in the biomass growth, although the specific growth rate decreases to 0.017 h^{-1} (as compared with 0.1 h^{-1} in the beginning of cultivation), which evidently results from oxygen limitation with the increase in biomass. Introduction of 1 g/l MPA at the stationary phase with the initial MPA concentration of 0.5 g/l does not increase the level of biomass.

The study of gas phase composition by gas chromatography, at cultivation of the bacteria with MPA, showed the presence of methane. The culture activity was 400 nmol CH_4/g biomass/day, and the level of substrate utilization was 83.2% in 96 hours. Cultivation of the bacteria in the medium with MPA resulted in accumulation of inorganic phosphate, 20-30 mg/g biomass in the range of concentrations of the introduced phosphorus source from 1.0 to 10 g/l. The presence of methane and inorganic phosphate in the medium evidences that MPA destruction in the bacteria under study is carried out by C-P lyase due to the C-P bond uncoupling.

3. Conclusion

1. The effective method for destruction of mustard-lewisite mixtures detoxification products has been developed. It includes two sequential stages: electrochemical pretreatment of the detoxification products and bioutilization of the formed organic products. The levels of organic compounds and arsenic in waste after these procedures meet the environmental standards.
2. Possibility for biodestruction of detoxification products of mustard, neurotoxic CW agents – sarin and soman, and organophosphorus herbicides using microorganisms isolated from the areas polluted with these substances and adapted to their bioutilization has been shown.
3. The pathway of metabolism of TDG, the product of mustard hydrolysis, utilized by microorganisms as a carbon source – has been established and the conditions of the highest efficiency of TDG biodegradation have been determined.
4. The cultures of microorganisms degrading methylphosphonic acid via the uncoupling of direct C-P bond have been isolated and selected. The efficiency of biodegradation is to a great extent determined by C:P ratio in the medium and by concentration of organophosphorus substrates.
5. Selected active strains-destructors can be used as a basis of biopreparations in the technologies for remediation of soils polluted with the products of CW agents detoxification and organophosphorus herbicides.

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DEMONSTRAION TRIALS OF THE TECHNOLOGY FOR BIOREMEDIATION "IN SITU" OF SOILS CONTAMINATED BY POLYCHLORINATED BIPHENYLS

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1. INTRODUCTION

The goal of the given project is to conduct demonstration trials of ecologically sound technology for bioremediation of soils contaminated by polychlorinated biphenyls on the territory of Serpukhov.

According to the WHO data polychlorinated biphenyls (PCBs) are among twelve most dangerous and hardly decomposed environmental pollutants. Till recently they had been broadly used for the electrotechnical and chemical industries because of extreme persistence in the environment. They can not be decomposed photolytically, chemically, and biologically. Polychlorbiphenyls are highly-toxic, accumulate in human organism and have carcinogenic effect.
Processes of soil self-cleanup are slow due to high PCB concentrations and their high persistence in the environment, and they need active human interference. In our opinion, biotechnological methods have a number of advantages in comparison with physical-and-chemical ones: ecological soundness, harmlessness of final degradation products for the environment, high adaptability and specificity towards different pollutants, acceptable labor expenditures and work cost, keeping of natural state and fertility of soils under bioremediation.

As a result of investigations on the ISTC Project #228–96, 2 natural strains of microorganisms-PCB degraders – *Hansenulla californica* strain *? ?* and *Alcaligenes latus* strain *TCD–13* – were obtained from soils contaminated by polychlorbiphenyls nearby "Condensator" plant in Serpukhov. Isolated microorganisms are aerobes and can be applied directly in upper soil layers *in situ*. According to the results of laboratory and field trials on PCB degradation in soil, as well as toxicological trials, the given microorganism strains have been recommended for biotechological purposes.

The microorganisms were deposited to All-Russian Collection of industrial microorganisms for international depositing (Mosciw). 2 international patent applications ? ? ? – RU/98/00036, and ? ? ? – RU/98/00037, as well as Russian (? 2155803 ? 2155804) and American patents (? 6,284,521 ? 6,287,842) have been drawn up on them.

1.1. Selection and determination of territory where bioremediation is required. Sanitary-and-hygienic and soil-and-agrochemical description of the selected territories.

The work was implemented on the territory of Serpukhov, "Zaborie" district. 14 commercial PCB preparations such as Arochlor 1242 and 1254 (USA), Kanchlor (Japan), Pyralen and Fenochlor (France), Klofen (Germany), Trichlordiphenyl, Sovol, and Sovtol (Russia) have been used at Scientific-and-Production Association "Condensator" for 30 years. Most part of contaminated zone is occupied by private houses with farmlands, which are actively used for growing crop production – traditional food of the population.
8 sites having total area 2 hectares were chosen for bioremediation. 4 of them are located on the plant territory, and another 4 sites are on adjoining living zone. Each site was divided into 3 sub-sites. On these sub-sites, averaged soil samples were taken commissionally from the most contaminated upper soil layer (0-20 cm).

Determination of concentration and congener composition of polychlorinated biphenyls in soil was conducted at chemical-and-analytical laboratory SPA "Taifun" (Obninsk) certified according to international standards.

Analysis of contamination by PCB was conducted by:

- Total pollutant concentration,
- Congener profiles (38 congeners),
- Amount of low - and highly chl orinated biphenyls,
- Content of toxic isomers.

The chosen sites differed by distinctive contamination by polychlorinated biphenyls. PCB contamination varied from 1.01 mg/kg up to 1,545.12 mg/kg. Maximal xenobiotic content was registered in soil on the territory of the plant in the area of waste disposal plants, minimal contamination was registered at the top of the site in Bezyimyanni lane, 17.
The sites differed by qualitative composition of PCB contamination as well. Sites as with low-chlorinated biphenyl domination, so with paramount content of highly chlorinated biphenyls, stood out by specific weight of low - and highly chlorinated biphenyls. Soil nearby impregnation department of SPA "Condensator" contained 62.1-83.5% of biphenyls with low content of chlorine atoms, and their content in soil nearby waste disposal plant was 73.4-89.7% of total contamination. Highly chlorinated biphenyls dominated nearby the metalware department (60-76%). In swampy soil (Strelkov str., 16) content of low-chlorinated toxicants was up to 75-79%. Soil from a private site (Kondensatornaya str., 8) contained 59-65% of highly chlorinated biphenyls. On former scrap-heap (Bezyimyanni lane, 17) at the bottom of the site nearby Borovlyanka stream there were 78-84% of low-chlorinated biphenyls, and highly chlorinated biphenyls dominated at the top of the site (65%).
Heterogeneity of PCB contamination on the bioremediation sites appeared on level of isomers with the same amount of chlorine atoms as well. Isomers with 4 chlorine atoms dominated (39-55% of total PCB amount). Trichlorinated and pentachlorinated biphenyls occupied the second and the third place in pollutant composition.
Specific weight of toxic congeners in composition of biphenyl contamination is one of criterion of its toxicity. It is determined that the sites differ from each other by content of toxic congeners. Toxic congeners came to 4-37% in total PCB content, and 39-48% in composition of highly chlorinated biphenyls.

Investigations on assessment of soil integral toxicity showed that soil on the territory under bioremediation was highly toxic for biotests. Dependence between percent of died daphnia and concentration of pollutant in soil was noted. That allowed to control bioremediation processes by biotesting in daphnia.

1.2. Study of relative risk and population attributive risk to health of population living in PCB-contaminated zone

To determine relative risk and population attributive risk to health of children of preschool age, living in the zone of extremechronic PCB effect, copying out data from individual health cards, Russian forms ? 26 («Individual card of a child going to child preschool institution (CPI) and school»), and ? 112 («Children health card») of children on sickness rate for the period from 1996 to 1999. Children sickness rate was registered by Russian form ??? -?. 438 individual health cards were considered, i.e. data was collected on 219 children from pilot (kindergarten ? 17, "Zabor'e" district) and control CPI (kindergartens ? 41 and ? 47 in ecologically favorable regions of Serpukhov). Information on tension of post-vaccinal immunity in children from kindergarten ? 17 (26 children) and kindergarten ? 47 (16 children) was taken from SCSES laboratory journals. To study physical development, anthropometric measuring of 208 children according to generally accepted methods was conducted. Additional information was obtained by polling of parents of 132 children.
Conducted was statistical processing of data on health status of pre-school age children with different extent of exposing to PCB. Analysis of children health was conducted with determination of somatic and infectious sickness rate, as well as intensity of post-vaccine immunity and physical development. Somatic sickness rate was studied with respect to 17 disease classes ICD 10 (International Classification of Diseases of the 10th revision). Infectious sickness-rate was characterized by the total sickness incidence of uncontrolled infections, e.g., German measles, chicken pox, and scarlet fever. To assess physical development, several indices have been used, namely, group simple average body parameters (weight, length of a body, thorax circle), and sex-age indices (Ketle, Pinie, Rorera Livie); the method of sigma deviations, percentile scales, and regression scales.
To determine individual and population cancerogenic risk to population, eating crop production contaminated by polychlorinated biphenyls, information on those (110 people) growing vegetables in bioremediation zone on 1.5 hectares (cooperative society "Yurievka") was collected.

1.3. Bioremediation work

In June 2001 sites for bioremediation were prepared (scavenging, ploughing and harrowing).
On the base of RCT&HRB accumulated was microbial biomass (100 litres per each strain) of two strains of microorganisms-PCB degraders (strain ?? and strain TCD–13 with concentrations 10^7 and 10^9 respectively).
From July 2 degrader microbial biomass was introduced in contaminated soil on the sites with the help of farming machinery. During July and August, due to extremely high temperature for this region and rain absence, soil was mostened with the help of washing machinery.
In a month after bioremediation start, soil samples for investigation were taken from the sites. Microbiological assay showed that concentration of microorgansims-degraders lowered considerably because of unfavorable weather condition.
In connection with that repeated growing of microbial biomass and its introduction in contaminated soil were performed in August.

1.4. Bioremediation result registration

In two months of bioremediation soil samples were taken commissionally to register bioremediation results. The results of chemical analysis of soil samples, conducted at chemical-and-analytical laboratory SPA "Taifun" certified according to international standards, showed that during summer microorganisms actively decomposed PCB being in soil.
Level of polychlorbiphenyl decomposition varied in dependence on PCB initial concentration in soil, as well as on soil humidity during bioremediation. At that, not only polychlorbiphenyls in soil solution, but also those sorbed on soil particles were subjected to decomposition. Thus, according to the chemical analysis data, on some sites in one bioremediation month PCB concentration considerably increased at the expense of released by microorganisms PCB part bounded in helate complexes with humic acids of soil particles. The fact is in good correlation with literature data on bioremediation.
It should be noted that bioremediation *"in situ"* has always been a quite difficult technological method, as it is hard to create equal conditions for technological process due to differences in place relief, temperature-and-humidity differences, soil nature, etc. on vast territories. Nevertheless, we managed to get satisfactory results even under such conditions.

<u>On the territory of "Condensator" plant</u>, where most contaminated soils were revealed, PCB concentration (site #7) at constant moistening lowered from 1,600 down to 160 mg/kg, and decomposition degree amounted to 90%. According to the congener analysis data, mainly 3-, 4-, and 5-chlorinated biphenyls were subjected to degradation. At this, decomposed were not only polychlorbiphenyls in soil solution, but also those sorbed on humic acids.
On some sites, where soil was not watered (site #8), only partial PCB decomposition was observed, and PCB concentration lowered by 20-30%.
<u>On the territory of the scrap-heap</u> (slightly contaminated site), which was watered constantly, PCB concentration lowered from 12-14 mg/kg of soil down to practically maximum permissible values (to 0.1 mg/kg).
<u>On the territory on garden cooperative society "Yurievka"</u>, where soil contains highly-chlorinated biphenyls, microorganism decomposed not only 2-, 3-, and 4-, but also even 5- and 6-chlorinated biphenyls. At this, upper part having area 0.5 hectares was completely cleaned from PCB, and 2 others (having total area 1 hectare) were cleaned only partially. Also, as on the plant territory, release of PCB from soil colloids by microorganisms-degraders followed by partial pollutant decomposition was revealed. It is necessary to continue bioremediation here.

Investigations on assessment of integral toxicity of soil showed that after bioremediation soil integral toxicity on all sites lowered considerably and reached permissible level.

Microbiological investigations of soil samples revealed that during bioremediation there is practically no change in concentration of aboriginal soil microflora. On the contrary, after introduction in soil, microorganism-degrader concentration, as PCB decompose, lowers considerably and reaches ecologically sound level.

1.5. Assessment of efficacy of taken measures on lowering risk to health of population living in bioremediation zone.

Efficacy of taken measures on lowering risk to health of population living in bioremediation zone was assessed on the basis of data of chemical analysis of soils on PCB.
Farming cooperative society "Yurievka" (points #22-24) was taken as an example for **calculation of carcinogenic risk** related to the use of PCB-contaminated vegetative production. The calculations were performed in accordance with the existing techniques for qualitative evaluation of risk related to the use of contaminated foodstuff, EPA "RISK ASSESSMENT" [*PCBs: Cancer Dose-Response Assessment and Application to Environmental Mixtures// EPA/600/P-96/001F. – National Center for Environmental Assessment. Office of Research and Development. USEPA, Washington D.C., September 1996*].
Estimation of affecting PCB doses was conducted on the basis of comparative analysis of data on soil contamination and PCB examination data in foodstuff in "Zaborie" area (where "Condensator" plant is located and soil is most contaminated). As it was determined by the analysis, the use of corresponding coefficients for PCB migration from soil into vegetative production allows to obtain the values of biphenyl content in foodstuff (vegetables, potatoes, and greens), comparable with real data of monitoring of agricultural product quality. This allowed to calculate mean values of PCB concentrations in vegetative foodstuff grown in "Yurievka" cooperative at different levels of soil contamination.

To evaluate individual risk, it was assumed that up to a half of daily ration of "Yurievka" cooperative society members is foodstuff grown on individual sites contaminated by PCB. We used the following scenario: daily consumption of foodstuff is 1.5 kg, including 0.75 kg of products grown in "Yurievka" cooperative society: 500g of potatoes, 100g of beet and 100g of carrot roots, and 50g of greens. In this case, the given group of Serpukhov population can get from 0.09 up to 1.55 mg of PCB per day. As a result of bioremediation, reliable lowering of PCB concentration in soil occurred on 1/3 of the territory of "Yurievka" cooperative society (0.5 hectares out of 1.5 hectares). The concentration lowered 28.5 times on average. At corresponding lowering of the given pollutant concentration in soil, daily intake of PCB by this group of Serpukhov population can comprise 0.003-0.05 mg per day.

Individual carcinogenic risk at corresponding lowering of PCB concentration will reduce for exposure at maximal contamination (point #24) from 48 ? 10^{-3} down to 1.3 ? 10^{-3}, and for exposure at minimal contamination (point #22) from 2.8 ? 10^{-3} down to 0.1 ? 10^{-3} (or 1.1 ? 10^{-4}), Table 2. Unfortunately, even at such (practically 30-fold) lowering of contamination, individual risk remains quite high.
In some countries permissible carcinogenic risk is considered to be 10^{-4}-10^{-6}. According to accepted in Russia "Standards of radiation safety" (SRS-99) the limit of individual life risk level is $5x10^{-5}$. Target risk level to be achieved as a result of sanitary measures is 10^{-6}, as a rule. According to recommendations of the US Environmental Protection Agency and some other organizations, emergency measures to lower the risk are required at level of life carcinogenic risk being more than 10^{-3}.
It should be noted that lowering of individual carcinogenic risk is attended by lowering of minimal toxicity as well. Risk lowering from 3.0–4.0 ? 10^{-3} down to 1.1–1.4 ? 10^{-4} is conditioned by decrease of minimal toxicity from 7.7 ? 10^{-4} down to 2.6 ? 10^{-5}.

2. DISCUSSION OF THE OBTAINED RESULTS

It should be noted that the goal of the Project was not profound scientific study of PCB microbial decomposition processes and determination of degradation biochemical schemes. It was related to limitation of work terms (summer of 2002) and funding, and impossibility to conduct large amount of expensive chemical analyses for monitoring of the territories under cleanup for a long time. In connection with that, PCB sorption on soil particles and formation of complexes of PCB with humic acids were not studied, as well as introduced microorganism-degrader effect on these processes (PCB bioavailability, biosurfactant properties, etc.) was not determined.
As analysis of literature data on soil bioremediation from toxic pollutants shows, such theoretical-and-practical studies should last for quite a long period (from 2 to 5 years). During the first year determined are the following points on the basis of great amount of chromatographic and mass-spectrophotometric chemical analyses: study of PCB zonal distribution in soil on the experimental site, migration in soil and water levels, and determination of concentration and congener composition of polychlorinated biphenyls in soil. Besides, general agrochemical analysis to assess sorption properties and type of soil under cleanup is realized.
Only after comprehensive study of soil contamination by PCB, microbial bioremediation is started. Simultaneously with soil detoxication, soil samples are taken and chemical processes in soil are studied. Soil integral toxicity is controlled as well.
Correspondingly, during the third year, studied is residual PCB concentration in soil, as well as their sorption on soil agglomerates and distribution in soil and water levels.
This allows to study bioremediation processes and to assess role of microorganisms-degraders quite profoundly and with high reliability.

<u>The basic goal of the conducted trials in Serpukhov</u> was to demonstrate that with the help of isolated natural aerobe microorganisms-degraders, it is quite easy and efficient to conduct detoxication of soil, contaminated by polychlorinated biphenyls in different concentrations, during summer *"in situ"* (i.e. directly on the place), and to determine terms of microbial degradation. Presently, in the world practice, there are no quite high efficient technologies for bioremediation of soil, contaminated by PCB. That is why the field trials of the technology form microbial bioremediation of soils (developed under ISTC project #228) had to show possibility of ecologically sound 10-fold reduction of PCB concentration in contaminated soil during summer.
As it was mentioned above, insufficient funding and implementation terms limited the research. Rightful desire of Serpukhov Administration to conduct soil detoxication in the area of SPA "Condensator" had to be taken into account. The ground for such desire is that about 14 thousand people, growing foodstuff (potatoes, vegetables, fruits, berries, etc.) on their farmlands, live in the

given area. It is natural that anxiety about people health limited the period of research and required real results of contaminated soil detoxication, PCB concentration in which exceeded permissible values hundreds and thousands times, on large territories (several hectares).
Besides, people presence in bioremediation zone toughened requirements to ecological-and-toxicological and medical harmlessness of the applied biotechnology. That is why one of research basic directions was assessment of sickness rate risk in population living in the given area. The studies were conducted on the basis of summarizing of data from population health cards and study of health of children attending kindergartens in “Zaborie” microdistrict. The calculations were performed in accordance with the techniques of US EPA “RISK ASSESSMENT” [*PCBs: Cancer Dose-Response Assessment and Application to Environmental Mixtures// EPA/600/P-96/001F, 1996*]. It was necessary to demonstrate that the biotechnology had no toxic effect on people, and it lowered sickness rate risk. Otherwise, the biotechnology could not be recommended for further practical application. For the given purposes computer database on health of population living in bioremediation zone was created, and risk was assessed according to US EPA methods by SCESE medical employees. Based on these data, risk was calculation by EPA techniques.
The mathematical calculations showed 30-fold reduction of individual carcinogenic risk for population living in bioremediation zone. Under all ambiguous evaluations of detoxication processes revealed was lowering of PCB concentration in soil, and, consequently, reduction of toxicant getting in the growing agriculture production, what is certainly favorable for health of population in “Zaborie” region.
Notwithstanding limited amount of chemical analyses and their ambiguous assessment related to complicated PCB conduct in soil under cleanup, the results of Serpukhov demonstration trials showed that introduction of the isolated microroganisms and complex of bioremediation measures led to 10-fold reduction of concentration of polychlorinated biphenyls in soil and lowering of its integral toxicity. It is the fact that bioremediation with the use of microorganisms-degraders leads to lowering of soil contamination and toxicity, that allows to recommend the developed biotechnology for further practical use.

Unfortunately, when performing demonstration trials of the biotechnology, some unpredictable mistakes were made. Thus, control (non-treated) sites were placed between two experimental soil sites. The results of the trials showed that microorganisms-degraders actively migrate in soil within 10-meter range in subsoil waters and at watering. They were found in control site soil in great concentrations. In connection with that, it was impossible to compare monthly change of PCB concentrations on experimental and control sites and to assess bioremediation results. That is why PCB congener destruction was registered on each of 24 sites.
Besides, insufficient attention was paid to technical issues concerning keeping necessary moisture of soil during summer. As practice showed, a number of sites were hard to reach by watering machinery due to absence of roads or unequal profile. In connection with that, soil moisture during summer went down to 5-14 % because of the heat, and the value is quite lower than that required for successful bioremediation. At further field trials it will be necessary to provide for soil watering with the help of hose system or automatic sprayers.
In connection with late funding of the project the work was started in the beginning of July. By that time soil was quite dry and had temperature 30-35º. These were conditions unfit for microorganisms. Besides, bioremediation was conducted for 2 months only, what was evidently not enough. Optimal bioremediation term for the middle zone of Russia is from the end of May till the end of September (i.e. 4-month period).

In case there is funding, further studies should be directed at more detailed studies of processes of aerobe microbial degradation of polychlorinated biphenyls in soil “*in situ*”, biodegradation schemes, and determination of final products of PCB decomposition.
For these purposes it is necessary to select an experimental PCB-contaminated site in Serpukhov having area of about 100 m^2. During first 2-3 years it is necessary to analyze in-depth soil contamination by polychlorinated biphenyls: heterogeneity of contamination, PCB concentrations in soil levels, sorption properties and bioavailability of PCB for microorganisms and plants; migration with the help of subsoil waters; change of PCB concentration during several seasons under effect of climatic factors, saprophytic soil microflora, and physical factors (aeration, re-ploughing, and moistening), etc.
Then, during 3-4 months of summer it is necessary to perform soil bioremediation with the help of microorganisms-degraders. Basing on the available data on distribution of pollutant in soil and obtained during bioremediation new data on PCB congener composition in soil, it will be possible to consider the treatment results, and products of PCB microbial decomposition. Besides, at the same

time with studying chemical composition of the pollutant during soil cleanup, assessed will be soil integral toxicity, microbiological composition of saprophytic soil microflora and concentrations of introduced microorganisms-degraders.

Data on proper ties of undecomposed PCB (their toxicity and bioavailability, sorption properties, distribution in soil levels, and coefficients of their getting into different agricultural plants) are of great practical and theoretical interest.

Studying of effect of microorganisms-degraders on PCB found in soil solutiona and in silt at the bottom of Borovlyanka and Oka rivers is worth detailed attention.

The results of demonstration tests conducted in Serpukhov evidence that the developed biotechnology and microorganisms-degraders can be recommended for bioremediation *"in situ"* of soils contaminated by polychlorinated biphenyls.

On the basis of conducted work the following conclusions can be drawn:

1. Microorganisms-degraders AT and TCD-13 strains are recommended for industrial application at bioremediation "*in situ*" of soils contaminated by PCB in concentration from 1 to 1,600 mg per kg of soil.
2. Different methodical approaches at conducting demonstration trials in Russia and USA do not allow to assess uniquely the results of the demonstrtion trials performed in Serpukhov (sample purity and depth of sampling, distance between them, sample weight, residual moisture under drying, etc.). these studies should be continued and broadened.
3. Summer of 2002 was not typical of middle Russia. According to meteorological service data it was a unique one for the last 120 years of observations. Rain absence and unprepared for such unequal non-typical conditions experimental sites (absence of special machinery and no road approach) were sure to impact the results of the experiment. Upper layers of soil warmed up to 60–65^0? . Increased temperature and low humidity decreased survival of microorganisms introduced in soil, that is why they were introduced repeatedly. It is clear from the obtained data that bioremediation was most efficient on moistened or shadowy sites of the experimental field, where there were more "comfortable" conditions for microorganism introduction.
4. Basing on data of laboratory and field investigations, the main optimal factors at bioremediation are high humidity (60–80 %) and temperature (15–30$^?$?) of soil.
5. The results of chemical analysis of soil samples showed that during bioremediation 2-, 3-, 4 -, and 5 -chlorinated biphenyl compounds with no generation of toxic products of PCB decomposition.
6. Medical information on sickness rate of Serpukhov population, living on PCB-contaminated territory, was collected and analyzed. Mathematical calculations conducted in accordance with US EPA "RISK ASSESSMENT" method showed 30-fold lowering of individual carcinogenic risk to health of population living in bioremediation zone.

3. PUBLICATIONS.

The results of the developments and studies within the framework of the project are given not only in ISTC reports, but in scientific publications in major Russian and foreign journals, as well as in the materials of foreign meetings.

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THE NEED FOR REMEDIATION OF PESTICIDE-CONTAMINATED SOILS IN KAZAKHSTAN

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Pesticide Use in Kazakhstan

The increasing problems in Kazakhstan's environment are due not only to industrial wastes and irradiation, but also to pesticide contamination of soil.

Kazakhstan has considerable land resources for agricultural development. From a total land area of 2.7 million square kilometers, 223 million hectares are suitable for agriculture as cultivated land or pasture. There are 300 types of agricultural weeds of which 120 are very widespread and reduce harvests. In 1996, according to the regional monitoring stations for the protection of wildlife and plants, out of 18727.2 thousand hectares inspected, 15245.7 thousand (81.4%) had weed problems. Of this area, 7848.6 thousand hectares were infested with deep-rooted perennial weeds, 2975.2 thousand had wild oats, and 605.4 thousand were infested with invasive or quarantined weeds such as dodder, ambrosia, and bitters. There has been an increase in invasion of pastures with bitters. The average reduction in yield due to the weeds is 250 kg per hectare for cereal grains, 500 kg per hectare for maize, 4000 to 6000 kg per hectare for forage, and up to 6000-8000 kg per hectare for sugar beets. In 1996, in the Republic of Kazakhstan, 1,267 thousand hectares were treated with herbicides by ground application and 374 thousand hectares were treated by aerial spraying. In recent years, there has been an increasing problem due to locusts. Locusts have been observed in more than 1.5 million hectares (1). There is no doubt it is necessary to use pesticides to help manage the increasing number of diseases, pests, and weeds.

There are 243 foreign-made pesticides registered for use in Kazakhstan to control pests, diseases, and weeds, as well as for use as defoliants and plant growth regulators. These chemicals were approved for use in agriculture and forestry in Kazakhstan for the period of 1997-2001. Of these pesticides, 54 are used as insecticides and acaricides, 90 herbicides, 58 fungicides, four antibiotics, two rodenticides, 22 fumigants, two nematicides, four defoliants/dessicants, and seven plant growth regulators. Pesticides are imported primarily from the United States of America, England, Israel, Germany, and Russia (2). In 1999, Kazakhstan imported 44,000 tonnes of pesticides valued at 40 million US dollars.

In Kazakhstan, the main requirement to receive approval for state registration of imported pesticides is to develop regulations for their use including quantitative sanitary-hygienic standards and methods to control use (3). State registration of pesticides containing unknown substances, is certified by the Ministry of Agriculture. The required state hygienic registration is performed in the Health and Hygiene Agency of the Republic of Kazakhstan. This includes rules for conducting registration trials, government registrations, and re-registration of methods of plant protection permitted for use in Kazakhstan (4). In Kazakhstan, as well as neighboring countries of the CIS, laws have been established for the regulation of pesticide use, national programs for pesticide registration have been established, and there is a list of registered pesticides. However, to the disappointment of many, there are no national normative documents prohibiting the production and use of pesticides considered persistent organic pollutants.

Pesticide Contamination Problems

Kazakhstan, as well as neighboring republics of the CIS, has a severe problem with salvaging and destroying unsafe and obsolete pesticides that are no longer usable. This has resulted in accumulation and migration of pesticides in soil and groundwater, the disruption of soil microorganisms, and the gradual destruction of natural ecosystem processes. Historically, during the last 30 to 50 years in Kazakhstan and other countries of the CIS, more than 700 chemicals from many classes of compounds have been used in agriculture (5). The capacity for storing these pesticides has not corresponded to the need. Currently in Kazakhstan, out of 563 pesticide storage sites, 411 are in an emergency condition. It is estimated that 574 tonnes of pesticides and 54 thousand container-units are stored open to the air and in danger of polluting the local environment (6). Solutions to this problem are severely limited by financial resources.

The danger of pesticides in comparison with other chemical compounds is that pesticides possess high biological activity, the ability to circulate in the biosphere, they can accumulate in food sources, and they can be dangerous for agricultural workers. To address these problems environmental hygenists are developing methods to take precautions with these acute and chronic toxins. This includes developing regulations for effective use of pesticides and taking measures to protect the surrounding areas where pesticides are used. It is important to understand the long-term toxicological effects of pesticide pollutants and their effects on ecosystems at different levels of organization.

Many pesticides are highly stable to chemical and biological degradation and are capable of maintaining toxic properties for a long time. A good example is DDT (dichlorodiphenyltrichloroethane). It is a chlorinated organic pesticide with high pesticidal activity and was widely applied in agriculture and household activities. Although most countries have permanently eliminated or severely restricted the use of DDT in agriculture, DDT and its metabolites accumulated in many places in the environment and can still be detected. Application of DDT was prohibited in the Soviet Union in 1971. Despite this, pesticide residues can still be detected. One ecological report from locations in the Aral Sea region of Kazakhstan (7) showed the concentration of chlorinated organic pesticides in cereal grains maintained at a level of 20.0 to 45.4 mg/kg, exceeding sanitation standard doses by 1.5 to 2 times (PDK-20.0 mg/kg).

For recent decades including, most recently, a period with large locust infestations, use of pesticides has been widespread. Potential pesticide contamination of food supplies and the environment is a concern. There has been some success in controlling locusts, but the problem with repeated pesticide applications to the same land can result in increased of residual quantities of pesticides in the treated plants and in soil (8). Government sanitary inspections in Kazakhstan have shown pesticide contamination of farm-potable water supplies in 1986 was 0.4% and in 1996 was 0.5%. In some locations these parameters are higher. For example, in Kyzylorda and Almaty regions, contamination of potable water supplies exceed a marginal concentration level 2.7% and 2.5% of the time. In some situations, contamination of air exceeds acceptable levels by 3 - 10 times (6).

Remediation of Pesticide Contaminated Soil

There are two main approaches for cleanup of pesticide-contaminated soils, physical-chemical methods and biological methods. Physical-chemical methods include approaches that separate fluid fractions (settling methods, filtration, cetrifugation, etc.); or process the waste (extraction, desorption of contaminants, reverse osmosis, ultra filtrating, formation of precipitates, or chemical oxidation) (9). The use of physical-chemical methods of remediation usually involves excavation and treatment of the contaminated soil. The efficiency of these methods is usually high and often depends little on the characteristics of the contaminated media or the local climatic conditions. The remediation process is often rapid depending on the quantity of material to be treated. However cost of these methods is very high (10).

In recent years, the new bioremediation technologies have offered new soil cleanup methods. During bioremediation, contaminants are detoxified and biodegraded as a result of biological processes often involving microbial activity. Bioremediation technologies help increase the volume and speed of natural microbial degradation of contaminated media by providing nutrient sources or electron donors that limit microbial activity. Under these conditions, indigenous microorganisms or introduced cultures are capable of rapidly reducing contamination. Bioremediation can take place at the site of contamination, *in situ*, or the contaminated material can be removed and treated, *ex situ*. *Ex situ* bioremediation includes bioreactors, biofilters, and some composting methods. *In situ* methods include biostimulation, bioaugmentation, and other composting methods (11).

Bioremediation methods of treating contaminants are often more cost-effective to reach similar objectives as physical-chemical methods. By some estimates, bioremediation may cost less by 10-40% in the USA market (11). Bioremediation methods have been most intensively designed in western countries. In the USA, for example, more than 200 companies in the USA are engaged in marketing remediation technologies to large corporations, government agencies or others ordered by regulatory agencies (10). The costs of these remediation approaches are still prohibitive for use on a large scale in Kazakhstan and many other countries. Due to the limitations of financial resources, new remediation and risk reduction approaches need to be developed for countries like Kazakhstan.

Expensive technologies for cleanup of pesticide-contaminated soils are unacceptable for Kazakhstan. Therefore, there is a critical need to find inexpensive methods to clean local sites contaminated with pesticides. Sites of particular concern include deserted pesticide storage sheds located in agricultural areas.

Phytoremediation

Phytoremediation or phytotechnologies are a new set of bioremediation methods for contaminated soils that is receiving increased attention in the scientific literature. Phytoremediation uses plants to enhance degradation or stabilization of environmental contaminants to reduce risk to humans and the environment posed by contaminated soil and water. This technology is especially promising for restoring small, local sites with low to moderate levels of contamination. If effective, phytoremediation techniques may be low cost. Phytoremediation has been applied to a range of contaminants including organic chemicals and heavy metals. There are many different mechanisms of interaction between plants and environmental contaminants depending on the plant species, the chemical and physical properties of the contaminants, and characteristics of the contaminated media.

In some cases, plants can accumulate or extract contaminants from soil. This is called phytoaccumulation or phytoextraction. Phytoextraction has been investigated for use to cleanup heavy metals and radionuclides using plant species such as *Brassica* sp., *Helianthus* sp., and others (12). In the case of phytoremediation of heavy metals, it is expected that metals accumulated within plants would be harvested and disposed. In some cases with organic compounds including pesticides, plants may selectively take up the compounds and the compounds may be degraded or detoxified within the plants.

Another important mechanism of interaction between plants and contaminants is called rhizosphere degradation. The region of soil under the influence of plant roots is called the rhizosphere. In this region, there are typically higher populations of microorganisms that are capable of accelerating biodegradation of pollutants. Biodegradation of pesticides in the rhizosphere has been investigated for a number of pesticides. For example, the plant genus *Kochia* was shown to enhance degradation of the herbicides atrazine, metalochlor, and trifluralin (13). Tree species in the genus *Populus* have been investigated for many potential phytoremediation applications due to the rapid root growth of *Populus* sp. and its ability to produce deep roots that can reach the groundwater. *Populus* as been investigated for treatment of atrazine, arochlor, and nitrates in field tests (14). In some cases phytoremediation may help degrade contaminants while in other cases the contaminants may accumulate in plant tissue or the rhizosphere. This may help reduce migration of mobile contaminants.

Although phytoremediation offers many potential methods for addressing pesticide contamination problems, it is important to note that it may not completely address contamination problems. For example, plants that accumulate toxic substances in their tissues may not be safe as food for humans, livestock, or wildlife. Phytoremediation processes may also be slow and take a long time to address contamination problems. These issues need to be considered when investigating phytoremediation as a strategy to address Kazakhstan soils that have been contaminated with persistent organic pollutants for 30 to 50 years.

The Institute of Plant Physiology, Genetics, and Bioengineering of the Republic of Kazakhstan, the Department of Agronomy of Kansas State University, and the Technology Innovation Office of the United States Environmental Protection Agency are cooperating on research to develop phytoremediation strategies for pesticide-contaminated soil in Kazakhstan. This applied research project is designed to identify pesticide tolerant plant genotypes from contaminated locations. These plants will be studied for their ability to reduce risk and restore contaminated soils and to understand their mechanisms of detoxification of pesticides. On the basis of the research results, techniques will be developed for use of plants to help restore pesticide-contaminated sites.

The first stage in the research has been to identify and characterize several "hot spots" in Kazakhstan that are contaminated with chlorinated organic compounds. Plant species surveys at these locations have identified plants representing more than 19 angiosperm families. These sites will be studied for accumulation and biodegradation of pesticides by plants.

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ELECTROKINETIC SOIL REMEDIATION. ENHANCEMENT BY COMPLEXANTS

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1. INTRODUCTION

Contamination of soils with hazardous organic waste, specially with polychlorinated organic compounds, heavy metals and radionuclides is a serious problem for the world community. Volatile polychlorinated organic compounds such as perchloroethylene (PCE), trichloroethylene (TCE), dichloroethylene (DCE) and vinyl chloride (VC) have been used extensively as industrial solvents, reagents and cleaning agents and have become common ground water contaminants throughout the world [1-18].

Known soil remediation methods could be classified as follows:

a. Soil Removal method, The contaminated upper layer of soil is scraped and transported offsite for soil washing [1,2], combustion of contaminants or ex-situ bioremediation [3-5].
b. Pump and treat method, [6,7],
c. Thermal desorption & vapor extraction method, [3,8],
d. In-situ bioremediation, [3, 9,10],
e. Pollutant selective extraction, either in-situ (electrokinetic treatment [11-17]) or ex-situ (surfactant enhanced soil washing [7,18].

Because of the wide diversity of site conditions, organic contaminant identities and concentrations, and intended use of reclaimed site none of the methods mentioned above could be treated as universal ones, Table1. One has therefore to have a variety of remediation technologies to choose from in particular cases.

Rehabilitation technologies focused on complete removal of polluted soil lead to formation of large amounts of waste, which must be transported and stored. More comprehensive technologies (*ex situ* soil washing, electrokinetics) assume some special reagent enhanced soil treatment to minimize secondary waste. In these cases various surfactants are intensively studied. However, the general consensus is that any economically viable process must eventually provide for recycle of surfactant. Technologies for separating the surfactant together with the contaminant from the leachate solution have been advanced, however, recovering the surfactant in some reusable form remains a problem for these technologies.

The principle of the soil washing technology is to concentrate the contaminants in a small residual fraction by separation. The soil is mixed with water into a
slurry and then several separation/classification techniques, such as screening, hydrocyclonic, gravity separation, magnetic separation and froth flotation are used to remove the contaminants. The sand product can and must be reused, the residue has to be landfilled or treated as possible. Soil washing is applicable to a wide variety of contaminants, such as heavy metals, PAH, mineral oil, pesticides, cyanides (CN) and others. Limitations are found to be in the type of soil. When the texture of the soil is fine, a higher percentage of residue will be produced resulting in a lower percentage of clean material for reuse [20].

Solubilization of organic and heavy metal compounds in water with the aid of surfactants and other additives is well known. In treatment of contaminated soil in the laboratory, it is generally possible to achieve any target level of separation by adjusting the concentration of additives, increasing the wash liquid to soil ratio, repeated washing, etc. In industrial operation, however, there is a problem with disposing of the wash and rinse liquids, which contain hazardous organics. The volume of the wash and rinse liquids may be 10-20 times as large as the volume of the treated soil.

* Experimental part has been done in cooperation with RDIPE, Arzamas-16, Dokuchaev Soil Institute and ISOTRON Co. (New Orleans) within the frames of ISTC and DOE Grants

Table 1. Advantages and Disadvantages of different Technologies for Soil Cleanup

Soil Treatment	Advantages	Disadvantages
Thermal treatment	-Fast decontamination - Removal of any organics	- Subsequent gas-phase treatment - Possible accidents of gas-phase leaks are irreversible - Moderate acceptance by population - High costs -Difficulties with explosive organics - Suitable only for organics, but not for radionuclides and heavy metals
"in situ" Soil washing.	- Fast decontamination - No transport costs due to mobile facilities	- Suitable only for extractable organics; - Hardly suitable for fine particle matter (clays) - Power consuming step of solvent purification;
Electrokinetics "in situ"	- Treatment of clayey soils - No transport costs due to mobile facilities - Possibility of "in situ" remediation (important for city-areas) - Possibility of deep soil layers "in situ" treatment;	- Power consuming step of solvent purification; - Suitable mostly for local areas. - Preliminary research and the daily process control are needed; -Not suitable for oils and other pollutants with high viscosity - Time consuming process
Bioremediation	-Low costs - Natural process well accepted by public; - Possibility of "in situ" remediation (important for city-areas)	- Suitable only for restricted number of substances and pollutant concentrations; - Time consuming process - Preliminary research and the daily process control are needed -Residual pollution is possible - Suitable for organics, but not for radionuclides and heavy metals

Biological remediation is performed preferably in greenhouses and as land-farming. Only soils with contaminants such as mineral oil can be treated, preferably in sandy soils. This is the least costly method [20]. Bioremediation *in situ* is hardly capable to treat the deep subsurface layers of reclaimed site. At the same time not all the contaminants especially taken in high concentration are suitable for bioremediation. In particular this is the case of TCE taken in amounts 2.6 mg/kg of soil [21].

The texture of the soil is not so critical for thermal remediation. It is reasonable to mention here, that *in situ* pump-and-treat thermal treatment is suitable mostly for volatile organics and could cause secondary air pollution [20]. An attempt to use soil vapor extraction at 23 ^{o}C for TCE removal demonstrated very little efficiency due to the low-permeable layer and estimated cleanup time of more than one year [8].

None aqueous phase liquids and explosive wastes are non-polar and they have very low solubility in water. Methods that have been proposed for remediation of such species include incineration and bioremediation. However, these techniques have their own shortcomings. Incineration, although well established and the only proven technique to date, in the case of explosive waste will cost between $400 to $1500 per ton to be incinerated [22]. Bioremediation has been successful in laboratories but pilot-scale field tests demonstrated several problems associated with short-circuiting and the difficulty to supply nutrients and electron acceptors to the deposit due to heterogenities [22].

Electrokinetic remediation is a relatively new technology that uses low-level direct current between electrodes placed in the ground to extract contaminants. Application of an electric field across a soil mass causes transport of ionic species and pore fluid through the soil medium. Such electric field-induced transport process provides a means to introduce changes to the chemistry of the soil/pore water, ultimately leading to the contaminant mobilization. The mobilized contaminants are then collected at corresponding electrodes resulting in an eventual reduction in contaminants concentration at the site. **Electrokinetics is a unique tool for clayey soil remediation**.

Application of electrokinetic technique for the purpose of decontamination of soil polluted with heavy metals has been very promising [11,12], but required mobilization of pollutant by some chelating agents (Complexants). Isotron Corporation (New Orleans, Louisiana) in collaboration with Russian scientists had demonstrated in pilot scale tests that complexants could be very effective in electrokinetic removal of Uranium (VI) from soil (DOE Project no. 70K-EKQ-72C, Oak Ridge K-25 soil, 1993-1996) [13b; 23-26]. The uranium content of soil was reduced from 400-500 ppm to 25 ppm within 477 hours (see Part 5.4.) This result is now used even as an illustration in IUPAC sponsored tutorials "Solution Equilibria: Principles and Applications" [27].

The efforts to use electrokinetic technique for removal of organic matter has been less successful, because of the difference in electrokinetic phenomena governing heavy metals and organics mobility in soils. The former can take place due to both electromigration and electroosmosis, while neutral molecules of hydrocarbons could be driven in soil only via electroosmotic flow. Normally the zeta-potential of soil particles is small and the corresponding electroosmotic flow is very weak. Therefore, the efficiency of electroosmotic cleanup is low.

Within the frame of ISTC Grant 95-16 it was demonstrated that this obstacle could be eliminated by addition of appropriate complexants [24-26]. It was found that small concentration of chelating reagents like citric acid or diaminoethanetetraacetic acid (EDTA) could result in a 10-fold increase in both zeta potential and electroosmotic flow velocity [24-26].

Addition of surfactants and use of microemulsions of chlorinated hydrocarbons have attracted special interest based on their potential use to remediate sites contaminated with chlorinated hydrocarbons. By some change of lipophilic linker of a surfactant, the solubilization was increased 4 to 5 folds [27-33].

The perchloroethylene reduction rate with surfactant modified zeolite/zero-valent iron pallets (SMZ/ZVI) were three times higher than the reduction rates with unmodified pallets (Z/ZVI) in laboratory tests conducted to evaluate the performance of the pallets for perchloroethylene (PCE) sorption/reduction under dynamic flow through condition [35].

Current report is devoted to basic aspects of complexant application in the electrokinetic cleanup. It should be noted that several alternative soil-remediation technologies, such as soil washing, organics/heavy metal mixed waste treatment could also benefit from the development of organic pollutant-complexant-surfactant-soil-electric field interaction mechanism.

Within the ISTC Projects [36,37] the development of practical and theoretical grounds of efficient electrokinetic remediation technology for soils, polluted with polychlorinated organic waste was started. These are the interdisciplinary Projects combining experimental and theoretical approaches in the fields of Surface Science, Hazardous Waste Management, Co-ordination Chemistry of Chelating Compounds, Equilibrium speciation, Soil Science and Environmental Chemistry.

The main objectives included a development of an industry acceptable methodology based on the selection and application of chelating agents and surfactants for drastic decontamination process enhancement. Another objective was to develop the theoretical grounds for an advanced understanding of basic mechanisms involved in complexant enhanced reclamation of soils contaminated with polychlorinated organic wastes.

2. GENERAL THEORETICAL GROUNDS FOR ELECTROKINETIC PAH REMOVAL IN PRESENCE OF COMPLEXANTS

For non-soluble PAH it should be used in combination with surfactants, Fig.1, 2.
Clay particles are negatively charged, therefore electroosmotic flow is directed to cathode. PCE and TCE are water insoluble and have no electric charge. Therefore contaminants are not moved neither by electroosmotic flow, nor by electromigration flow, Fig.1. The electroosmotic flow itself is normally weak. The situation changes if one introduces nonionic surfactants, Fig 2. (anionic surfactants would move in a counter-flow with electroosmotic one, while cationic would be strongly adsorbed by negatively charged surface). Now TCE and PCE are solubilized, and removed by electroosmotic flow that is still weak.

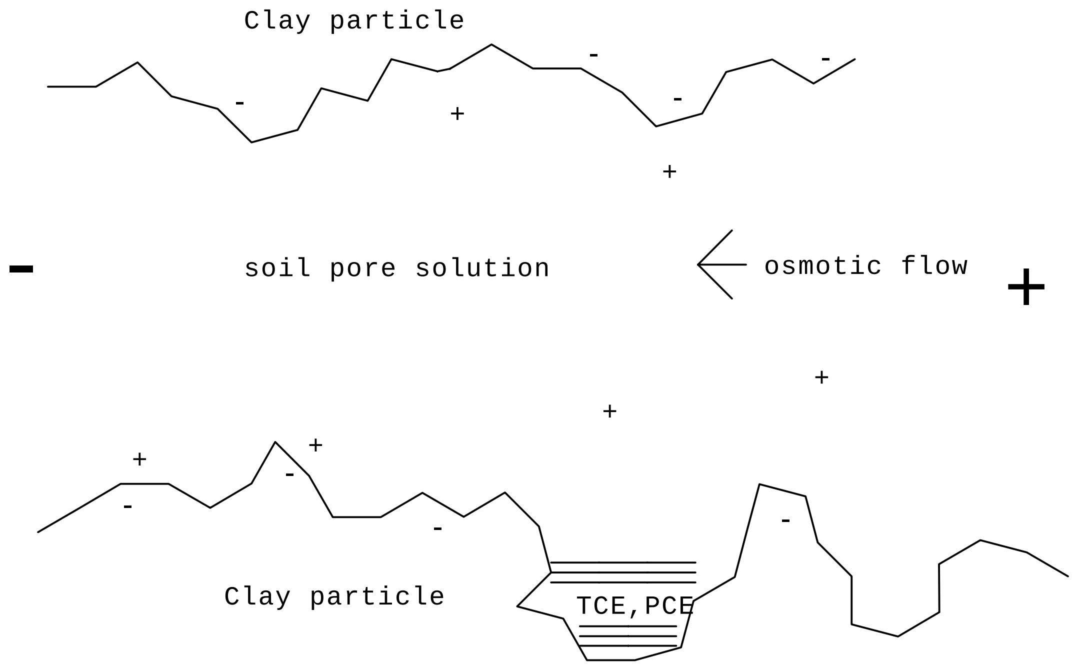


Fig.1. Tentative scheme of electroosmotic flow in soil.

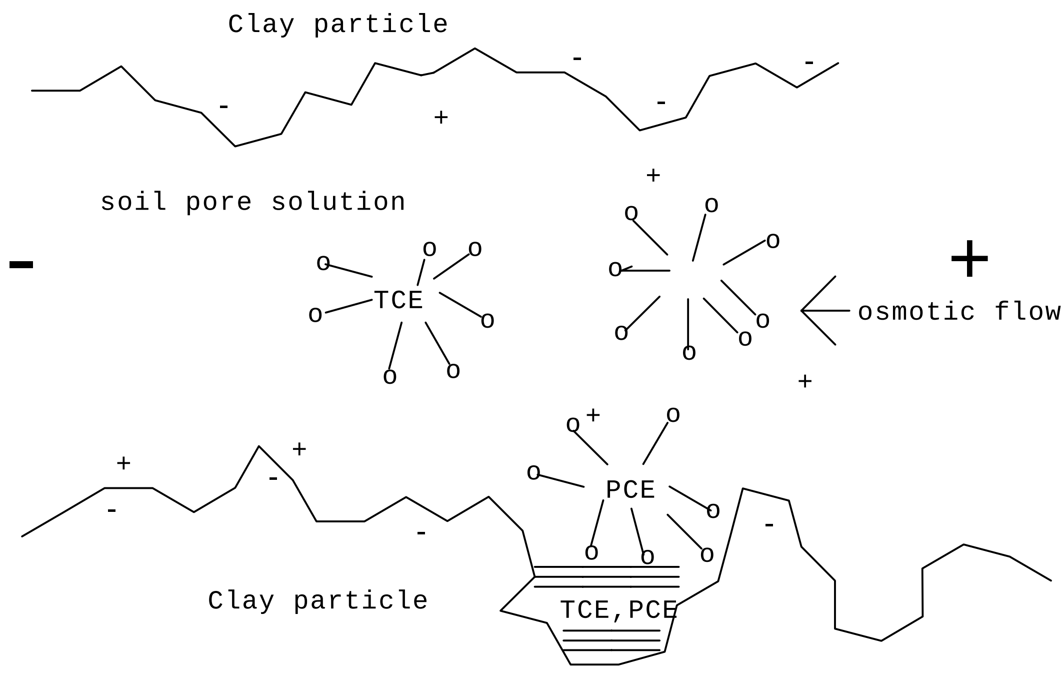


Fig. 2. Tentative scheme of PCE, TCE removal by electroosmotic flow in presence of non-ionic surfactants

The situation changes with addition of both non-ionic surfactants and complexants. The former solubilize contaminants, while the latter are increasing an electroosmotic flow, Fig.3. Complexants interact with surface (adsorption, dissolution of ferrous hydroxy-oxides) and **DRASTICALLY** increase negative charge of surface clay particles:

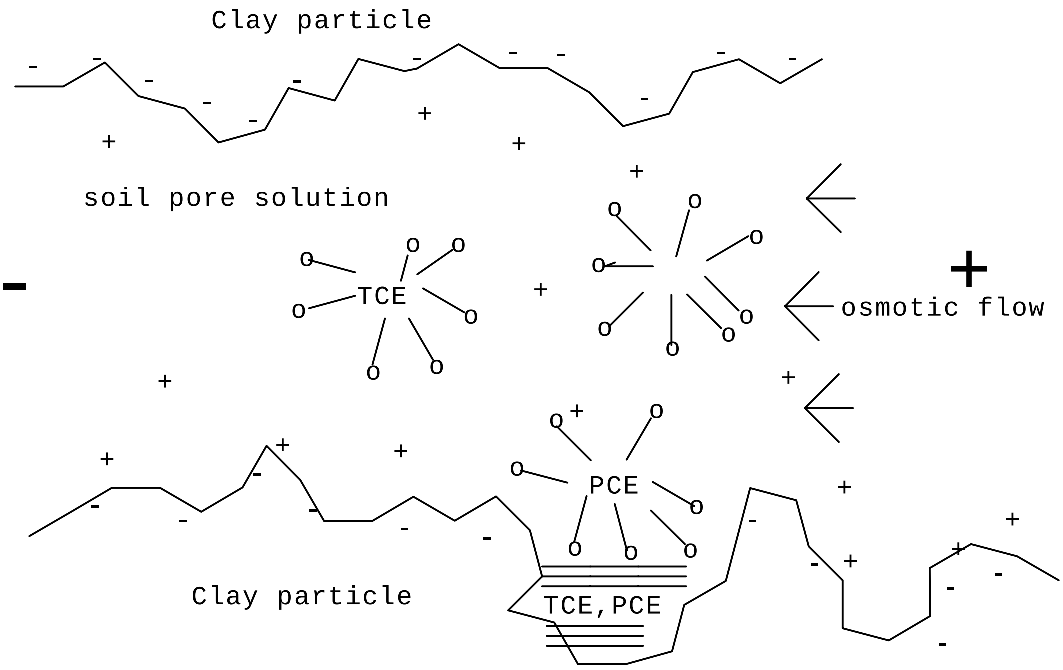
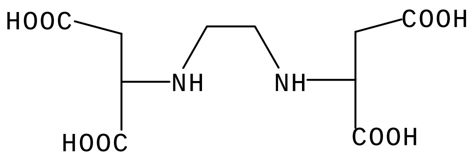
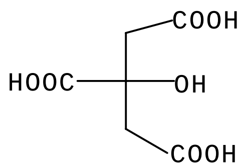
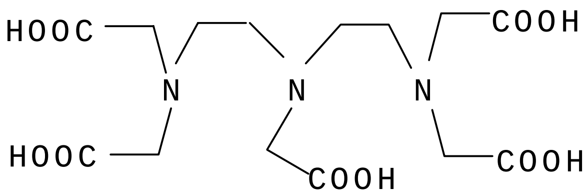
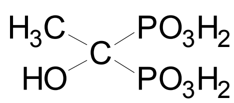
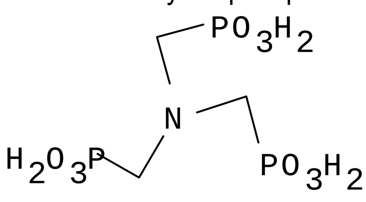
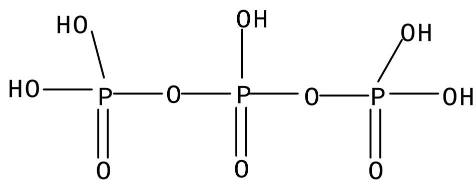


Fig. 3. Tentative scheme of PCE, TCE removal by electroosmotic flow in presence of non-ionic surfactants and complexants.

3. COMPLEXANT SELECTION AND USE

The reagents tested have met the following requirements:
- Complexants have to be readily soluble in water, commercially available and environmentally friendly, although some of them (taken for reference) could be moderately hazardous.
- Reagents to be tested should have well defined protonation and stability constants with background soil cations (Fe, Al, Ca, Mn) to permit the computer speciation experiments.
- Complexants should have different (none uniform) selectivity against background soil cations.
- Soil - Complexant equilibration time should be not less then one week.
- pH Range of reagent enhanced extraction is expected to be "mild": 4<pH<9

Based on the experiments the following complexants could be recommended:

Diaminoethane-N,N-bissuccinic acid (EDDS) 	Citric acid 
Diethylenetriaminepentaacetic acid (DTPA) 	1-Hydroxyethane-1,1-bisphocphonic acid (HEDPA) 
Nitrilotrismethylenephosphonic acid (NTPH) 	Tripolyphosphoric acid (TPP) 

EDDS is known to decompose with formation of environmentally friendly substances. Citric acid and TPP are environmentally friendly compounds themselves. DTPA is not retarded by soil, while HEDPA is a medical drug. NTPH was used as reference. All acids have been used as K-salts at pH 5-7, therefore they have not been aggressive.

4. GENERAL THEORETICAL GROUNDS FOR ELECTROKINETIC REMOVAL OF HEAVY METALS AND RADIONUCLIDES IN PRESENCE OF COMPLEXANTS

For heavy metals and radionuclides the situation is much more complicated, than for organic pollutants. It is expected that cationic species would be driven in soil via both elctromigration and electroosmotic flow with destination in cathode chamber. Normally cationic species are strongly absorbed by clay particles and do not exist in soil moisture, Fig.4. Therefore and application of electric field does not affect the contaminants. This problem could be eliminated by the use of strong acids (pH~1), but then the soil structure and biota become completely destroyed. Compexants represent a reasonable alternative to strong acids. The pH of treatment could be therefore increased. The mechanism of interaction could be illustrated for U(VI) – EDTA systems. EDTA is an acid: H_4edta. At pH 7 it exists in the form of anion H_2edta^{2-}, which interacts with uranium to form soluble species by a simplified scheme:

$$\text{Clay-}UO_2^{2+} + H_2\text{edta}^{2-} \rightarrow [UO_2\text{edta}^{2-}] + 2H^{+} + \text{Clay}$$

But here another problem arises. The side effect of EDTA administration is an increase of soil zeta-potential. Therefore electroosmotic flow increases. At the same time the charge of uranium species changes from positive (UO_2^{2+}) to a negative one ([UO_2edta^{2-}]). Thus electromigration flow moves uranium to anode, while an increased elctroosmotic flow acts in an opposite direction, Fig.5.

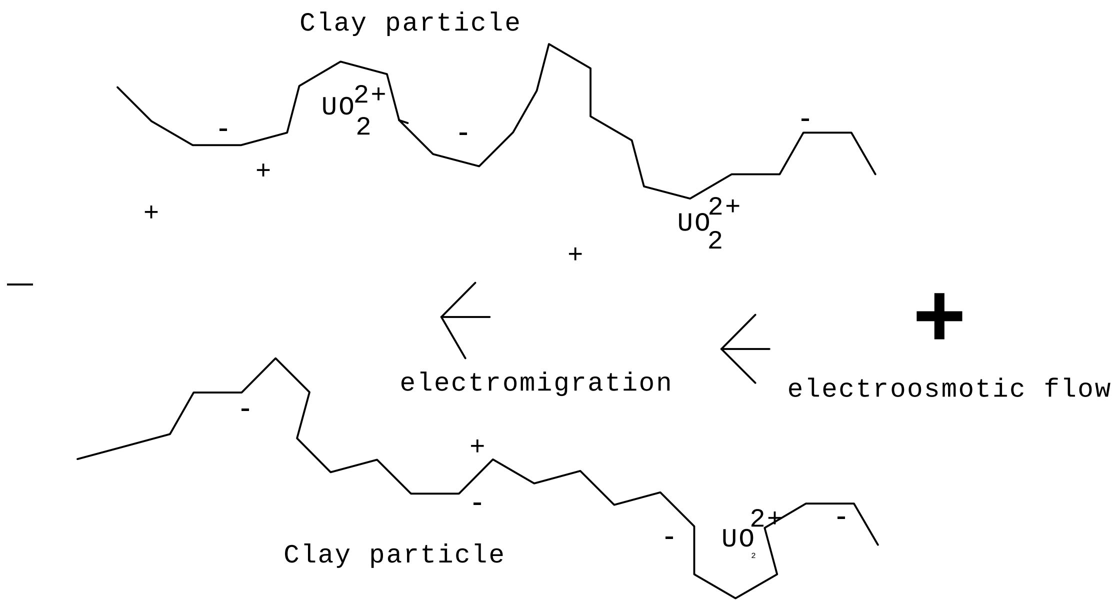


Fig.4. Tentative scheme of electrokinetic process in soil contaminated with U(VI).

Therefore both streams could neutralize each other and solubilized contaminant remains in soil or moves very slow either to cathode or to anode. Thus a very fine attenuation of pH based on chemical equilibrium speciations is needed in order to get the positive result: uranium removal.

In both cases of organic matter and radiunuclides electrokinetic removal in presence of complexants, the negative charge of clay particles increases as well as electroosmotic flow intensity. Thus the complexants do **not interact with contaminants,** but enhance elctroosmotic flow. The contaminants are collected at cathode and are decomposed there.

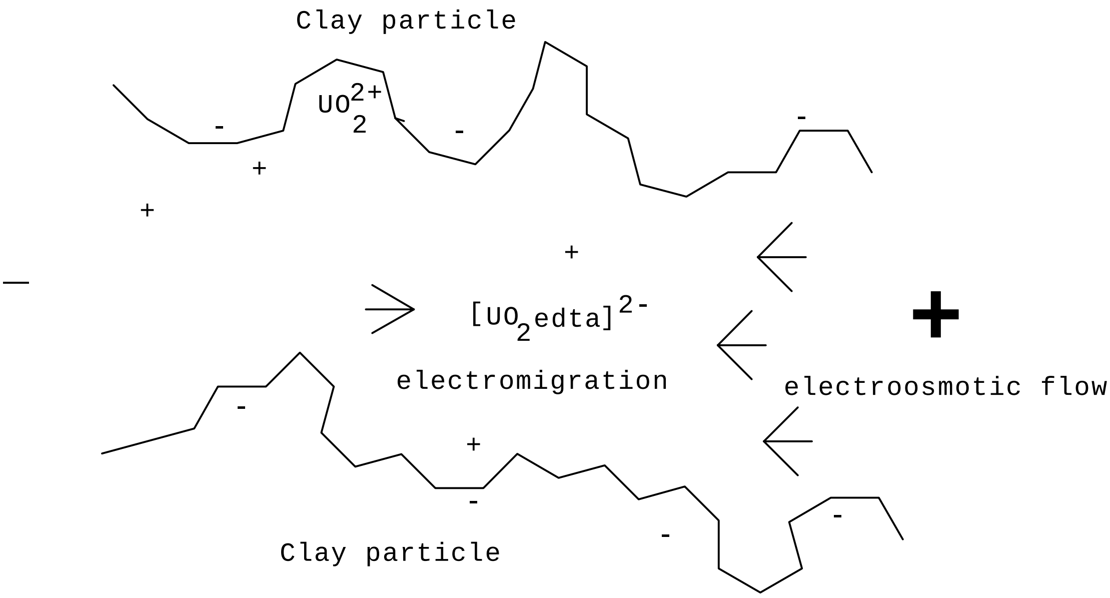


Fig. 5. Tentative scheme of electrokinetic process in soil contaminated with U(VI) in presence of EDTA.

5. EXPERIMENTAL

5.1. Electrokinetic Cell Design

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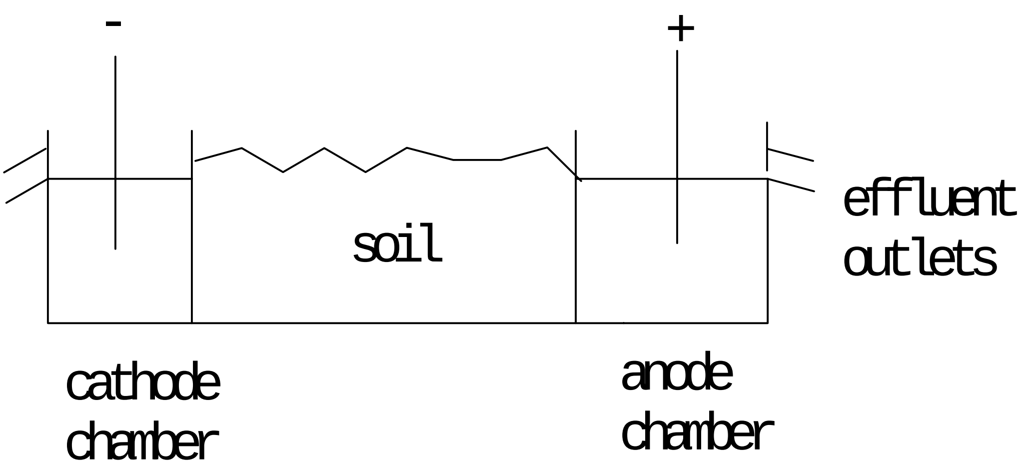
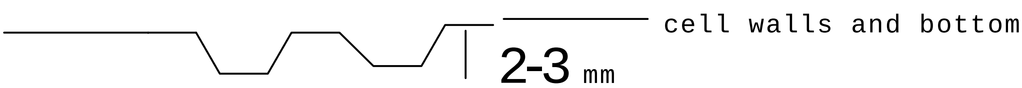
The electrokinetic cell was shaped in such a way that the level of soil is 2-3 mm higher than the level of effluent. This shall eliminate possibility of any overflow of washing liquid along the surface of the soil. The walls and the bottom of the cell shall also have 2-3 mm projections to avoid channeling between the two electrodes along the walls and the bottom of the cell.





The effluent was collected from the cathode chamber, while the corresponding amount of surfactant solution was added in the anode chamber. A manual neutralization of liquids in anode and cathode chambers by strong base and acid correspondingly has been done periodically. During each test an electric current and electroosmotic flow under constant voltage was periodically monitored and recorded .

4. GENERAL METHODOLOGYIES & APPROACHES USED

4.1. Soil sampling

Artificial contamination samples are intended to represent various (at least three) types of soil. At least 40 – 50 kg of each soil have been prepared for the studies

4.2. Soil Characterisation before and after the treatment with chelating reagents included:

(i) Place of sampling, identification of soil type, depth (cm), pH (KCl), total organic content, moisture content, exchangeable acidity, exchangeable cations (Ca & Mg); extractable iron,

(ii) Soil texture and Soil separates (Granulodensimetric fractionation),

(iii) Natural Background Soil Cations (Fe, Mn, Ca) content, Total metal content - Aqua regia digestion (referring to DIN 38414,Teil 7, 1983) followed by AAS (Atomic Adsorption Spectrometry)

Two different types of natural soils have been used in the study. One was sampled from the top layer of arable land (0-15 cm) at Moscow site (Pushkinskij District, experimental site of Dokuchaev Soil Institute) and classified as soddy-podzolic soil. This sample represents a heavy clay soil with the following size fractions: sand 50-40%, silt 10%; clay 40-50%. Mineral content: kaolinite+chlorite 38-48%; mica: 24-49%; smektite - 8-21%. Other soil properties are given in Table 2.

Another type of the heavy clay soil (black soil) was sampled from the top layer of arable land (0-25 cm) at Kursk City site (Petrinskij experimental site of Dokuchaev Soil Institute), Table 2.

Table 2. Soil Properties

Soil Properties.	Soddy-podzolic Soil	Black Soil
pH (aqueous)	6.7	7.9
pH (KCl)	5.3	6.7
Hydrolytic acidity, mg-equivalent/kg of soil	17	6
Exchangeable Ca, mg-equivalent/kg of soil	160	300
Exchangeable Mg, mg-equivalent/kg of soil	70	45
Mobile Phosphorus, mg P_2O_5/kg soil	115 (Kirsanov)	110 (Chirikov)
Exchngeable Potassium mg K_2O/kg soil (Maslova)	170	160
“Free” Iron (Jackson),%	0.17	0.12
Mobile Iron (Tamm), %	0.05	0.07
Organic carbon, %	1.2	3.4

All research groups used one and the same soil samples.

4.3. Soil Preparation for Electrokinetic Tests.

Soil pretreatment included separation of soil mass from large stones and plant roots. Then the soil was spread over a large surfaces in the form of 1 cm layer and let to equilibrate on the opened air for about one week in order to reach an air-dry state. During this period some large particles have been pounded manually and the whole mass has been mixed several times. The uniform soil mass (c.a. 50 kg) was then sieved with 2 mm sieves and stored.

Injection of pollutants has been done with a syringe in a way to provide uniform distribution of toxic organic compound in a soil matrix. Depending on the aims of experiment and pollutant properties several modes have been used:

(i) injection to the air dry soil in a closed vessel followed by 10 minutes manual mixing and from 24 to 48 hour equilibration;

(ii) injection to the air dry soil placed in the electrokinetic cell with an immediate addition of water or an aqueous solution of surfactant/complexant followed by 24 hour equilibration. Within this scheme the soil compartment of the cell was protected from evaporation (the top and inter-chamber surfaces), while electrode chambers remained empty.

When an air dry polluted soil is placed in the electrokinetic cell, then the DI water or complexant/surfactant solution is added from the top unless soil saturation takes place. Both electrode chambers are filled in by either DI water, or complexant (surfactant) solution. Initial concentrations of surfactant are taken in amounts 10-100 times higher than its critical micell concentration. Concentrations of complexants are taken in such a way that the final pore solution concentration should be within 0.01-0.0001 mol/l. Complexant solutions are neutralized to get pH 5-8.

4.4. Electrokinetic leaching is done generally:

(i) with an air dry soil samples in three replicates under particular soil/(complexant solution) extraction ratio followed by centrifugation and determination of PCE content in both aqueous and solid phases (with pollutant mass balance) in presence of complexant solutions and surfactants.
(ii) with two sets of blank experiments with DI water.

4.5. Computer simulations

Simulations of background cations (Al(III), Fe(III), Ca(II), Mn(II)) and complexants forms in soil moisture during the electrokinetic treatment have been done on various levels of approximation operating with existing computer Stability constants data bases and supplementary software programs in relation with particular chemical analysis of corresponding cation content in effluent

4.6. Risk assessment

The following illustrates the basis for studying the "environmental risk" of various soil decontamination options.

A. First it may be possible to classify the complexant using a classification called "environmental compatibility", i.e., the complexant that poses no environmental consequences. For example, complexants like citric acid, gluconic acid, tannic acid are prone to be environmentally innocent. The presence of residual of such species are actually complementary to agricultural land use.

B. There may be a second category of complexants that could be environmentally acceptable if its quantum is carefully controlled. For example, such as 1-Hydroxyethanediphosphonic acid (known as medical drug) or ethylenediaminedisuccinic acid (EDDS) which easily biodegrades into environmentally innocent compounds.

C. A third category would be those complexants, which have inherent in their structure the potential for the environmental consequences, for example EDTA, DTPA. Such complexants would be considered potentially useful, however, subsequent removal to some specified level would be necessary.
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5. RESEARCH RESULTS

5.1. Electroosmotic flow enhancement with complexants.

Influence of chelating agents was studied for K-25 soil (Oak Ridge, USA) and for Soddy-podzolic Soil, Moscow area, Tables 3-5. For Soddy-podzolic Soil also the distribution of background cations was studied, Table 6.

Table 3. Influence of chelating agents on electroosmotic flow in K-25 Soil at 25^{o}C and 1 V/cm voltage

Reagent solution	Final soil moisture Content,%	pH anode chamber		pH cathode chamber		Average osmotic flow, ml/hour
		initial	final	initial	final	
0.2 M Citric acid, pH 2.2	24	2.3	2.2	2.2	2.4	2.7 (0.2)
0.2 M Sodium citrate, pH 6.6	29	6.6	4.5	6.6	10.9	11.3 (0.1)
0.2 M EDTA, pH 6.1	27	6.1	4.0	6.1	1.5	**14.7** (0.1)
0.2 M EDTA, pH 10.8	28	10.8	6.3	10.8	12.3	**13.8** (0.1)
0.2 M HEDPA, pH 2.2	28	2.2	1.8	2.2	2.0	5.2 (0.2)
0.2 M HEDPA, pH 7.5	25	7.5	6.4	7.5	7.7	**15.3** (0.1)
0.8 M HEDPA, pH 7.3	18	7.3	6.9	7.3	7.8	6.1 (0.2)
DI Water, pH 7.6	25	7.6	6.0	7.6	8.5	1.2 (0.2)

Table 4. Influence of chelating agents on electroosmotic flow in Soddy-podzolic Soil at 20^{o}C and 1.5 V/cm voltage

Reagent solution	Initial soil pH	Final soil pH	Average osmotic flow, ml/hour
0.01 M EDTA	7.5	7.9	**5.2** (0.2)
0.01 M HEDPA	7.4	7.2	**5.6** (0.2)
DI Water	5.0	4.9	1.8 (0.2)

Table 5. Influence of HEDPA on the electroosmotic flow in K-25 and Soddy-podzolic soil (SP) within 7 hour electrokinetic tests.

Soil	Complexant	Soil pH init. final	Voltage, V/cm	Average Osmotic flow, ml/hour per 100 g soil and 1V/cm	Increase in Osmotic flow per 100 g under 1 V/cm; ml/hour (%)
K-25	HEDPA, 0.2 M	7.5 7.0	1	2.20	2.03 (1290)
K-25	DI water	7.6 7.0	1	0.17	-
SP	HEDPA, 0.01 M	7.4 7.2	1.5	0.93	0.6 (300)
SP	DI Water (0.001 KCl)	7.5 7.9	1.5	0.3	-

Conclusions:

(i) Although the experiments are done using different HEDPA concentrations and different temperatures, the effect evidently depends on the soil type.

(ii) The data reveal a drastic increase of electroosmotic flow.

Influence of elctrokinetic treatment on the soil background ions mobility was studied with both surfactant and complexant (HEDPA) in order to estimate possible side effects of the complexant/surfactant electrokinetic treatment on the mobility and transport directions of main natural soil background cations.

Basic experimental conditions:

Soil:	soddy-podzolic	Cell:	E-1
Surfactant:	Triton X-100, 18 g/l	Voltage:	1.5 V/cm
Complexant:	HEDPA, 2.1 g/l, (0.01M), pH 7.	Aver.elctroosmotic flow:	3.5 ml/hour
Electrokinetic treatment time:	7 hours	Air dry soil mass:	250 g

Air dry soil sample (250 g) was placed in E-1 cell, then 170 ml of an aquous solution of Triton/HEDPA was added. Both electrode chambers have been filled with the same Triton/HEDPA solution. The system equilibrated hours before voltage was applied and pH in the chambers was periodically adjusted manually to 7 by an appropriate addition of NaOH or H_2SO_4. After 7 hours the soil was separated from the cell, dried at room temperature on the air, mixed and then 1 g of it was treated with 50 ml of 0.05 M H_2SO_4 centrifuged and analyzed for metal content by ICP.

The blank experiments included:
a. Acidic leaching of electrically untreated initial air dry soil sample
b. Acidic leaching of soill sample that equilibrated with Triton/HEDPA solution for 5 days without voltage supply. Then the soil was converted to an air dry state without any separation of liquid Triton/HEDPA phase and 1 g of it was leached by 50 ml of 0.05 M H_2SO_4.

Table 6. Influence of elctrokinetic treatment on the soil background ions mobility.

Cation	cation content leached from 250 g of chemically untreated soil, mg	cation content leached from 250 g of chemically treated soil, mg	cation content in electrochemically treated soil, mg cathode	soil	anode
Fe	192	504	0.16	460	0.85
Al	261	390	0.12	345	1.2
Mn	26	37	0.05	34	0.04
Mg	113	140	35.4	135	0.35
Zn	1.5	3.5	0.01	2.3	0.02
Cu	0.3	0.4	not detected	0.4	not detected
Ba	3.8	3.0	0.04	2.4	0.01
Ca	>80	625	64.0	540	0.41
K	43	54	8.64	51	0.35

Remarks: anode solution got colored (pale brown) and slightly untransparent. This observation is attributed to the electrophoretic migration of fine clay particles and an electromigration of humic/fulvic acids.

Conclusions.

(i) HEDPA interacts with most of soil background metals and increases ion leachability.
HEDPA is therefore likely to form negatively charged complexes with d-elements which get sorbed at the surface increasing its negative charge and therefore increasing electroosmotic flow.
(ii) The mobility of Fe, Al, Mn, Zn, Cu under electrokinetic treatment is low. Migration of Fe and Al mostly towards anode could be associated rather with corresponding movement of soil organics than with HEDPA complexes migration.
(iii) The mobility of Ca, Mg and K is rather high and is definitely directed towards cathode. As far as complexes of these metals with HEDPA are negatively charged at pH 6-7, this mobility could not be explained by complex formation. These cations are therefore likely to electromigrate in an uncomplexed form.

In all three soils effluent was collected in cathode chamber indicating permanent negative charge of soil particles within the applied pH and chelating agent concentration range. The results presented in Tables 3-5 clearly indicate a large increase in electroosmotic flow (EF) for the soil treated with complexants in comparison with untreated soil in equilibrium with DI water. This effect is more pronounced for K-25 soil, which has higher clay content, than for soddy-podzolic and black soils. Experimental data reveal that irrespectively of the high ionic strength of the liquid phase, the overall negative zeta-potential of the soil surface increases up to more than one order of magnitude due to the specific influence of complexants, even at 0.2 M concentrations.

The intensity of EF depends on the character, concentration and pH of complexant solution, the character of soil and voltage applied. EF passes maximum when HEDPA concentration changes from 0 to 0.8 M. It decreases at low pH of complexant solutions in comparison with high pH range.

As far as we know the reported increase of EF in soil caused by complexants has not ever been described. This effect could be the result of a threefold interaction of complexant with soil surface:
(i) Negatively charged complexants and their complexes with metal ions could be specifically adsorbed on the surface of clay minerals, silicates and Fe/Mn oxides increasing negative charge of soil particles;
(ii) Natural Fe(Al)/Mn amorphous oxides being adsorbed onto clay minerals could suppress an original permanent negative charge of clay particles. Complexants in turn could dissolve oxides and remove iron(III) and aluminum(III) from crystal lattice of soil minerals restoring the original negative charge of the clay surface.
(iii) Complexants are able to mask all multivalent cations present in liquid phase including electric double layer. Then all multivalent cations are converted into negatively charged complexes and are substituted by univalent ones, which are less effective in diffusion layer compression. Zeta-potential therefore increases.

Processes based on mechanisms (i-iii) are generally known, although they are normally not associated with electric double layer consequences. In fact EDTA dissolves magnetite at pH 3-4 and hematite even at pH 9. Adsorption of metal-EDTA complexes, citric acid and organophosphonates onto hydrous oxides, clay minerals and soils is also well studied. The low mobility of organophosphonates in soils favor mechanism (i) for HEDPA. At the same time low retarding effect and high mobility of EDTA complexes reported make the first mechanism (i) unlikely to dominate for this complexant.

A unique masking ability of all three ligands studied is widely used in detergents and is well known in soil chemistry. This fact indicates that mechanism (iii) should be also accounted for all the ligands used. The detailed theory of this effect is a matter of further research.

The possibility of specific ligand - surface interaction should be taken into consideration by the interpretation of the complexants apparent leaching ability. The new effect of a complexant's enhanced osmotic flow in soil should be treated as undesirable when used for the removal of heavy metals and radionuclides in electrokinetic decontamination technologies. It should also be taken into account in reagent selection for chemically enhanced soil washing technologies due to an undesirable effect of stable colloid formation. On the other hand the same effect could become a unique powerful tool in electrokinetic remediation of soils contaminated with organic nonionogenic compounds. The combination of surfactants, complexing agents and electric fields seems to be extremely promising. An observed ability of complexants to affect electroosmosis evidently offers a possibility to govern remediation technologies by an appropriate choice of the reagent, its concentration, and pH.

Influence of complexant enhanced electrokinetic treatment on soil properties.

A combined intensive influence of electric field surfactants and complexants requires a thorough investigation of corresponding consequences for agricultural properties of treated soil. Thus a present chapter represents one of the first attempts to get some preliminary information in this field.

Three replicates has been done operating with not polluted soil. All other conditions (voltage, complexant and surfactant concentrations) have been kept the same as in remediation tests. Both electrode compartments have been filled with surfactant/complexant solutions and pH has been adjusted by an appropriate addition of NaOH (anode chamber) or H_2SO_4 (cathode chamber).

Basic experimental conditions:

Soil:	soddy-podzolic	Cell:	E-1
Surfactant concentration	0.018 g/ml Triton X-100	Voltage:	2.1 V/cm
Complexant concentration:	0.010-0.014 M HEDPA, pH 7	Temperature:	20 C
Electrokinetic treatment time:	6-7 hours	Humid soil mass:	370 g

After the treatment was completed, the soil is removed from the cell, dried at room temperature, milled manually and sieved with 1 mm sieves. Results are presented in Tables 7 and 8.

Table 7. Influence of the electrokinetic soil treatment on soddy-podzolic soil properties

Charachteristics	untreated soil sample	treated soil replicate I	treated soil replicate II	treated soil replicate III
Averaged electroosmotic flow, ml/hour	0	4.5	4.5	4.5
Treatment time, hours	0	6.3	6.5	7.5
HEDA concentration, mol/l	0	0.014	0.010	0.010
pH (KCl)	5.3	6.1	5.9	5.6
Free Iron (By Jackson),%	0.17	0.40	0.31	0.27
Mobile Iron (By Tamm), %	0.05	0.30	0.25	0.26
Organic carbon, %	1.2	2.0	1.8	0.7

***Comments*:**

(i) pH of soil slightly shifts towards higher pH what could be attributed to the buffering effect of HEDPA solution (pH 7) ;

(ii) both pH adjustment in the electrode compartments and buffering properties of HEDPA in soil provide no negative consequences for soil pH (acidification of soil cathode zone and basification of the anode one);

(iii) increase in organic carbon content takes place due to organic reagents added: Triton X-100 and HEDPA. This tendency is superimposed on some natural soil organic carbon removal to a cathode chamber. The observed values indicate therefore some difference in both processes.

(iv) with an exception of Ca and Mg most of the other soil natural background cations content (Fe, Al, Mn, Zn) is not affected by the electrokinetic treatment (Table 10). At the same time the chemical forms of iron in soil undergo a serious changes: relative content of "free" iron (normally associated in agricultural tests with hydroxide forms) increases by 1.5-2.5 and a "mobile" iron (inorganic gels) - by 5-6. This fact could be explained by a complex formation of d-elements with HEDPA. Complexes are negatively charged ant therefore migrate towards anode. An electroosmotic flow towards cathode moves them in an opposite direction. As the result all these elements stay in soil. Mg and Ca are not complexed by HEDPA at pH 4-6 and are therefore moved via both electromigration and electroosmosis towards cathode.

Table 8. Changes in Soddy-podzolic Soil particle size speciations within the electrokinetic treatment.

Sample	soil density g/cm^3	soil humidity %	Fraction content, % 1-0.25 mm	0.25-0.05 mm	0.05-0.01 mm	0.01-0.005 mm	0.005-0.001 mm	silt <0.001	clay <0.01
untreated soil	2.63	1.90	2.9	13.9	60.6	11.3	7.8	3.5	22.6
treated soil, replicate I	2.63	1.50	1.2	5.6	60.7	13.3	14.8	4.4	32.5
treated soil, replicate II	2.63	1.55	1.3	8.8	62.7	12.4	11.1	3.7	27.2
treated soil, replicate III	2.63	1.58	1.2	8.6	58.3	11.1	14.8	6.0	31.9

Initial soddy-podzolic soil particle size speciation indicates that fraction with sizes 0.05-0.01 mm dominates. After the treatment an air dry soil humidity decreases. This effect could be caused either by specific surface decrease or by decrease of surface hydrophility. At the same time a significant decrease in a middle size sand and a fine sand fractions content as well as a relative increase of dust takes place. This indicates a destruction of large soil particle aggregates which in turn leads to general change for a worse of agricultural properties of the soil.

5.2. Electrokinetic remediation of soil, polluted with phenol in presence of complexants.

Phenol represents a unique water soluble volatile organic pollutant, capable to interact with bases and even with soil background cations, e.g. Fe(III), Al(III). Depending on pore solution pH phenol can therefore exist both as anions ($C_6H_5O^-$) , cations (positively charged iron(III) complexes) or neutral molecules (C_6H_5OH). Therefore, it is very important to keep pH constant during electrokinetic treatment.

Soil pretreatment. Experiment No.99.03.1. 350 g of air-dry soddy-podzolic soil has been mixed with 56 ml of phenol aqueous solution (16 g/l) in an air-isolated vessel. One hour later 140 ml of an aqueous solution of HEDPA (0.0033 g/l, pH 7) was added and the mixture equilibrated in a closed vessel for 28 hours. Then a 420 g sample was taken to fill in a soil compartment of E-1 cell. Electrode chambers have been filled with the same HEDPA solutions (pH 7). Soil compartment was covered by a wooden non-hermetic cover in order to reduce evaporation.

Basic experimental conditions:

Soil:	soddy-podzolic	Cell:	E-1
Soil pH	pH 6-8	Voltage:	2.1 V/cm
Complexant concentration:	0.01M HEDPA, pH 7.	Temperature:	20 C
Electrokinetic treatment time:	33 hours	Humid soil mass:	420 g

A blank experiment (No.99.03.2) included the same soil equilibration in E-1 cell without voltage supply and without any change of electrode chamber solutions. Results are presented in Tables 9 and 10. Accumulation of pollutant in a cathode compartment indicates that electroosmotic flow is a predominant phenomenon responsible for remediation.

Table 9. Electrokinetic treatment of soddy-podzolic soil, polluted with phenol.

No.exp.	Voltage V/cm	Effluent, ml	Aver. Flow, ml/hour	Treatment Time, hours	Initial content of Phenol in soil, g	Final content of Phenol,g Cathode	Soil	Anode

99.03.1	2.1	163	5*	33	0.7	0.46	0.14	0
99.03.2	0	0	0	32	0.7	0.07**	0.38	0.01**

* Electroosmotic flow varied from 7 to 3 ml/hour, depending on the frequency of fresh solution addition: every 20 minutes in the day time, and every 3 hours during the night. At the same time pH was adjusted to pH 7 by an appropriate addition of concentrated NaOH (anode chamber) or H_2SO_4 (cathode chamber). **Figures indicate conventional "cathode" and "anode".

Table 10. Mass-ballance of 99.03.1 and 99.03.2 experiments.

No.exp.	Number of pore Volumes passed	Final mass of phenol found in E-1 cell, %	Phenol Collected in Cathode Chamber, %	Residual amount of Phenol in soil, %	Remediation Coefficient
99.03.1	1.1	85.7	65.7	20	3.3
99.03.2	0	65.7	11.4*	54.3	0.2

The data presented in Table 9 evidently reveal an efficiency of complexant enhanced electroosmotic remediation technique for soils polluted with phenol. At the same time the supplementary experiments indicated a key importance of pH adjustment in electrokinetik process. When no pH corrections are done, then pH in cathode camera and therefore in cathode layers of soil increases to pH 10-11. That makes phenol to dissociate in cathode soil layer and hence to move back towards anode *via* electromigration. On the other hand an uncontrolled electrode process in anode compartment makes pH acidic. When phenol crosses the acid/base front in soil its dissociation in turn is suppressed and phenol again moves towards cathode via electroosmotic flow. Thus the electric field indicates a cyclic rotation of phenol in soil sample without its removal. It should also be mentioned here, that low pH suppresses an electroosmotic flow as well. The acidified part of soil is therefore inactivated from the point of view of electroosmotic remediation mechanism. The lack of pH adjustment in the case of phenol and other weakly acidic organics is therefore strongly undesirable. An automatic correction of pH by an acidic complexant self-buffering is possible although it is not uniformly acceptable for different soils. A non-stop process should be used for volatile organics, otherwise up to 80% of pollutant is lost in atmosphere and the pollution is merely redistributed from soil into air.

Conclusions:

- in presence of HEDPA electroosmosis is the dominating remediation mechanism. Diffusion is one order of magnitude weaker, while the evaporation from the soil surface seems to be comparable with electrokinetics although still less effective;

- electrokinetic method provides a good opportunity for phenol removal from contaminated soil. This method gives 65% removal of pollutant within 33 hour treatment and only one pore volume of liquid flow. Moreover, elctrokinetic accumulation of phenol in an aqueous phase decreases its losses in atmosphere via soil surface evaporation.

5.3. Electrokinetic remediation of soil, polluted with chlorbenzene in presence of complexants.

Phenol represents a unique water non-soluble organic pollutant. Therefore a combination of surfactant and complexant has been used for electrokinetic remediation, Table 11.

Table 11. Electrokinetic treatment of soddy-podzolic soil, polluted with chlorbenzene (CB) in presence of HEDPA and surfactant (ALM-10).

Treatment time – 45 hours; Initial CB content – 0.46 g.

Voltage, V/cm	Number of pore Volumes	Final mass of CB found in E-1 cell, %	CB Collected in Anode Chamber, %	CB Collected in Cathode Chamber, %	Residual amount of CB in soil, %	CB removed, %
2	1.6	100	14	47	39	61

5.4. Electrokinetic remediation of soil, polluted with Uranium(VI) in presence of complexants.

A pilot scale testing has been completed for removing Uranium(VI) from soil taken from Oak Ridge Diffusion Plant (K-25)*. Uranium(VI) is strongly bonded with soil matrix and its concentration in soil pore solution is very low. Therefore effectiveness of exclusive electroreclamation is not satisfactory. The solution of the problem has been found in complexants application.

Basic experimental conditions:

Soil pH (ASTM D 48872)	5.5	Cell	ISOTRON Pilot Cell
Soil natural moisture content	7.7%	Voltage	0.7-1.8 V/cm
Initial Uranium(VI) content	566 ppm	Av. Current density	2.0-3.0 amps/ft^2
Complexant	Citric acid	Dry soil mass	19.4 kg
Electrokinetic treatment time	477 hours	Humid soil mass	23.3 kg

The success of the process was strongly dependent on appropriate pH adjustment based on chemical speciations (details would be presented within the frames of ConSoil special Session). Effectiveness decreased when pH was either lower or higher than 3. The main electrokinetic transport in this particular case was electromigration, but not electroosmos.The results are presented in Tables 12, 13.

Table 12. Electrokinetic treatment of K-25 soil, polluted with Uranium(VI) in presence of Citric acid.

Parameters	**Near Anode**	**Average**	**Near Cathode**
Soil pH	**2.9**	**3.0**	**3.0**
Final Uranium content in Soil, ppm	**56.6**	**41.3**	**22.8**

Table 13. Mass Balance of Pilot Scale test

Initial Uranium content, %	100
Uranium extracted at anode, %	85.2
Uranium extracted at anode, %	2.5
Residual Uranium in soil, %	7.3
Mass Balance	95

6. CONCLUSIONS

- Depending of the soil type compexants are capable to increase electroosmotic flow in soils from 300% up to 1200%. This in turn provides 3-10 fold shortening of treatment time.
- Surfactants can either increase or decrease complexant efficiency. Even the worst complexant/surfacatnt combination still provides twice higher electroosmotic flow than chemically untreated soil.

* Results obtained by Dr. Val Yachmenev (ISOTRON Co.) in collaboration with ISTC stuff.

- Complexant HEDPA demonstrates a high efficiency in phenol removal from 400 g soil sample: 65% within 32 hours. Estimated complete remediation time varies from 50 to 60 hours.
- An unappropriate use of electrokinetic treatment conditions (complexant concentration, pH) could completely destroy all advantages of this method which in turn could be misleading in the choise of remediation technology in a particular field application.
- Chemically assisted electroremediation of soil has some negative side effects for agricultural properties of soil, yet not very dramatic.

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DEVELOPMENT OF METHODS FOR REMEDIATION OF SOILS WITH INCREASED CONTENTS OF HEAVY METALS, TAKING INTO ACCOUNT THE POPULATION HEALTH INDICATORS

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Introduction

On the global scale Kazakhstan is a large unfavorable for human life territory. Ecosystems of the Republic due to the economic activities are considerably changed and deteriorated. Some of them are in a critical state. Especially crucial is the problem of the technogenic pollution of the environment near everywhere in Kazakhstan (5, 15).

On problems related to influence of biogeocenoses components contamination on population health it is envisaged to carry out a hygienic evaluation of soils and vegetation; to determine mechanisms of the influence on the population health condition; to study main parameters of social - demographic situation; to investigate health condition dynamics of inhabitants in the zone influenced by the technogenic contamination; to determine main problems and to give a multi-alternative prognosis of population health rehabilitation.

The investigations were supported by ISTC and modern methods were used.

Sources of contamination, priority contaminants and paths of their migration

The researches were carried out in the landscapes limits of the river Karatal valley from its sources up to a modern delta. The mountain areas of Dzhungarskiy Alatau are characterised by presence of polymetallic ore fields. Extraction and enrichment of lead-zinc ores on Tekely deposit being developed since 1936, has been causing environment contamination in the river Karatal valley. In region of researches priority contaminant among heavy metals (HM) is lead.

The main contamination source of the environment by lead and other heavy metals in the upper reaches of the river Karatal valley was submitted by "beach" of a tailing storage of the Tekely Lead-Zinc Combine (TLZC). After lead-zinc ores enrichment a liquid component of the pulp was dried up in the tail storage cup. During pulp drying up the significant masses of lead and other concomitant metals is taken out by wind. Comparison of lead and zinc contents in slime before and after wind processing demonstrates the following. In air at forming small-sized ripple on dried surface from one kilogram of pulp about 5 mg of lead and 15 mg of zinc are taken out (13, 14).

Other sources of heavy metal emission into region environment components are: Industrial site of the Karabulak sugar plant, Industrial zone of Taldykorgan city, including the plant of lead accumulators and railway junction of Station Ushtoby.

The conducted expeditionary researches have allowed to reveal a high pollution level by heavy metals of atmospheric air. The zones of the greatest pollution placed around the tail storage of TLZC Enrichment Plant, settlement of GREK expedition, pioneer camp "Orlenok" and rest house "Baldyrgan". Considerable air pollution was marked in settlements Karatalskoe and Malinovka.

The aerial masses play a role of “solvent of emissions” of industrial plants. Due to their involvement the aerosols are carried away on significant distances. The distances and bulk of transferred matters depend on a direction and wind velocity. The orographical territory features bring a significant correction into this regularity. In case of close location of high mountain sites from the pollution sources, at foot of declines the zones of the heavy metal heightened contents are formed.

The motor vehicles make certain contribution into the pollution of the investigated territory. Mostly lead gets onto soil surface with exhaust gases. As a result along highways at a distance of 200 m zones of heightened lead contents in soils are forming.

In water of the Karatal river section from Tekely to Taldykorgan cities there is a noticeable decrease of heavy metal sink in comparison with the background (mineralization of the water above sewage inflow from biological ponds of tail storage). The sink of lead on the average decreases on 4 tons. Further down the river to the Balhash Lake the refinement of water is marked. This happens due to heavy metal deposition into river bottom sediments and formation of complex organic-mineral compounds (12).

In the modern Karatal river delta the heavy metal contents in water do not exceed Standard Concentrations (SCs), frequently they do not find out. In bottom sediments their contents are low too.

In the upper reaches of the Karatal river valley the HM potential supplier in soils is irrigation water.

The heavy metals fall into soil together with fertilizers. They enter into fertilizer’s compounds as admixtures. However fraction of this source is minute.

The main transfer of lead and attendant HM in the Karatal river valley ecosystems takes place by eolian way. Mainly HM gross forms are transferred. The minor part of lead migrates by water way with dominating of its mobile forms.

For revelation of biogeocenosis component pollution extent determination of total β- and γ-activity have been carried out. At investigated soils the maximal values as γ-activity, and β-activity of separate extracts does not exceed a level of global pollution by radioactive fallout.

Confirmations of such conclusion are also the measurement results of a background radiation in the sampling points of the contaminated soils. In the sampling points at altitude 0,5 m from a ground surface the gamma - background was within the limits of 18 - 25 microroentgen/per hour, and the beta-ray at altitude 2 - 3 cm above a ground surface has been changed within the limits of 5 - 12 fragments/??^{2}/per minute. These data are corresponded to the background indexes of the investigated region.

For improvement of the region ecological conditions it is necessary to develop a special program and introduce effective measurements on decreasing industrial emissions of Tekely and Taldykorgan cities and also railway station Ushtoby.

Soil pollution maps of Tekely-Taldykorgan biogeochemical province.

For revealing of priority contaminants and general regularities of heavy metals distribution in soils of the river Karatal valley soil pollution maps were performed. For diagrams compiling soil-geochemical surveying of Tekely proluvial-alluvial cone, Taldykorgan proluvial-alluvial cone, Ushtoby alluvial cone and modern Karatal river delta were carried out.

The mining and enrichment of polymetallic ores in the Karatal river basin have resulted in an aggregate of technogenic-geochemical processes going on in the region natural-territorial complexes. One of results of such processes is the accumulation of heavy metals in soils.

Almost half of the soils of the Tekely and Taldykorgan proluvial-alluvial cones of the Karatal River are polluted with the total forms of lead from low up to high degree. Low polluted soils are occupied 32,6 %, middle polluted soils - 10,8 %, highly polluted soils - 2,7 %; very highly polluted soils - 1,4 % of the territory. The greatest pollution of the territory is coincided with the Tail Storage of Tekely Lead-Zink Combine and in the southwest direction from it (13).

The anomaly of the highly polluted soils (more than 6 SC of the total lead forms) is adjacent to the southern border of Taldykorgan city. Apparently, it is connected with the industrial center located here, including the Lead Accumulators Factory. Soils polluted by lead surround the Oblast Center from all directions. In the southwest direction a wide strip of low polluted soils stretches for 12-15 km from the city border. In the river Karatal middle flowing the soils polluted by lead are located near Ushtobe industrial complex and railway station. Only not polluted and low polluted soils (1-2 SCs) are revealed.

Small by the size, but characterized by the high lead contents (up to 292 mg/kg) the polluted soil plot is located to the west of Karabulak settlement downwards (along the current) from the sugar factory sedimentation tanks. The local nature of pollution proves that sedimentation tanks play a main role in its occurrence.

A significant by territory and complex in configuration outline is located in the Taldykorgan industrial zone. Within it the three centers of the heightened lead contents in soils have been observed. The first center soils contain lead up to 180-210 mg/kg. It is located around the industrial zone with westward asymmetry. As it was mentioned above, this evidences a wind genesis of the center. The second south-east center is located at the foothills of the western declines of Lobashoky mountains and is connected with their barrier influence on the north-east wind. The large values of lead concentration in the soils of this center (100-110 mg/kg) and in soils located between it and the first center (up to 100 mg/kg) are the result of heavy metals dry sedimentation. The third center is located on a distance of 7-9 km westwards from the Taldykorgan lead accumulators factory. The lead contents in the soils of its central part achieve 132 mg/kg of soil. On the Ushtoby alluvial cone low polluted soils are occupied 37,5 % of investigated territory. In the river Karatal lower course, including modern delta, heavy metal contents both in superficial soil horizons and on profile do not exceed existing Standard Concentration levels (total forms).

It is necessary to note, that transfer of lead from soils into plants occurs through mobile lead forms (4). In the areas with the increased lead content in soils the food products usually are polluted with this element and lead quantity, entering with food into man's organism, by two - five times and more exceeds the average level. Such lead quantities can make an adverse influence on population health, since lead is a toxic element of the first danger class.

Diagram of soils zonal division by level of complex pollution

??? investigations were conducted in Southern and Southern Eastern Kazakhstan in the plantings and gardens.

For the purpose of zoning the Kazakhstan territory is subdivided into natural-reclamation zones, oblasts, suboblasts and regions based on the conditions for cultivation of main agricultural crops, and also types and complexity of land reclamation. The earmarking of soils contaminated by heavy metals is carried out at last stage of zoning at the level of soil-melioration groups and subgroups.

The factor of interaction between the elements reduces toxic effect of the joint influence of lead, zinc and cadmium. To a minor extent the antagonistic relations are observed between lead and cadmium, and to a greater extent - between lead and zinc, and they are especially strong between zinc and cadmium, i.e. zinc acts as an antagonist of lead and cadmium.

While determining the combined toxicological effect of the priority contaminants, the factor of the elements interaction is taken into account, which was not used until now in practice of mapping of the contaminated territories. The survey of soils and vineyards of the Tarazskaya biogeochemical province has allowed to draw up a scheme of contamination of the soils and plants by the priority contaminants taking into account the factor of their interaction and the extent of toxicological influence on productivity and quality of grapes berries. Unlike earlier divisions of territories of the contaminated provinces made according to the extent of pollution by a single contaminant, we suggest to calculate the combined toxicological effect.

Considering the values of the elements individual SCs in the soil it is convenient to make zonal division of the soils by the level of pollution and plan the placement of the breeds

and sorts of the agricultural plants on the contaminated territory taking into consideration their resistance to the contaminants.

The following zones are subdivided according to the pollution levels:

Uncontaminated zone, where it is possible to grow without limitation, all breeds and sorts of the agricultural plants.

Low contaminated zone, where it is possible to grow the sorts resistant to the priority contaminants.

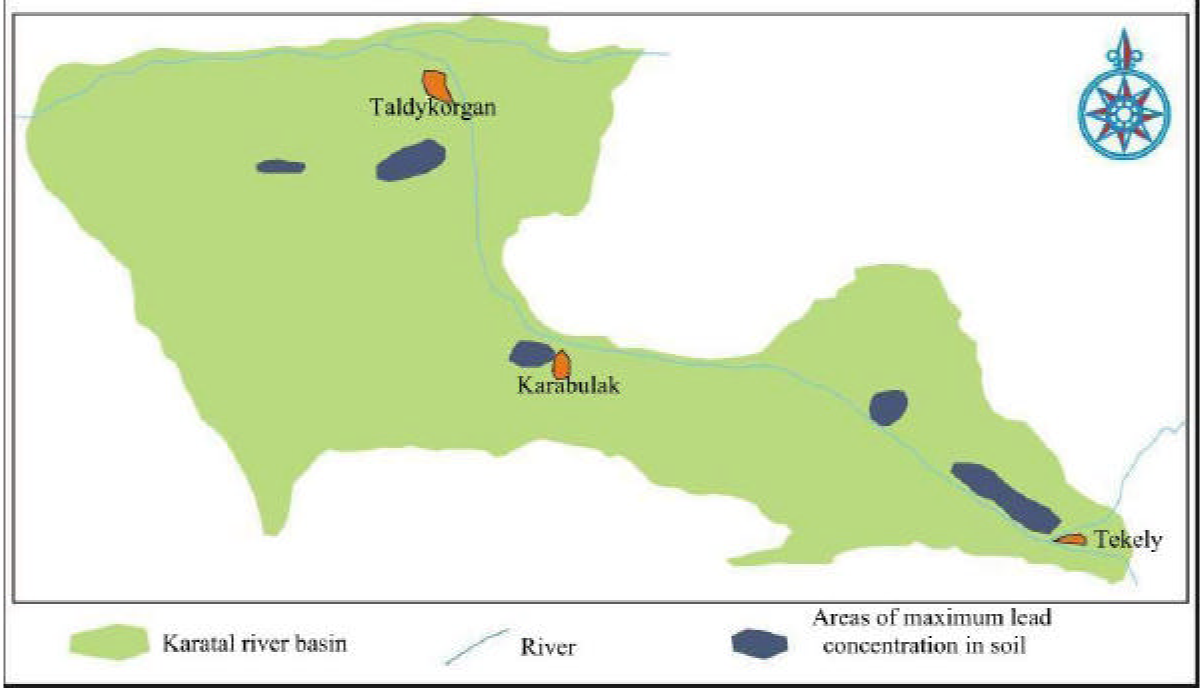
Middle contaminated zone, where preliminary land reclamation is required.

Highly contaminated zone, where radical land reclamation is required.

Zone of very strong contamination, where cultivation of the agricultural plants is not possible due to constant emissions of the contaminants.

The highly contaminated zones and zones of very strong contamination require preliminary land reclamation (1).

Fig. 1. Lead distribution in soils of the river Karatal upper basin



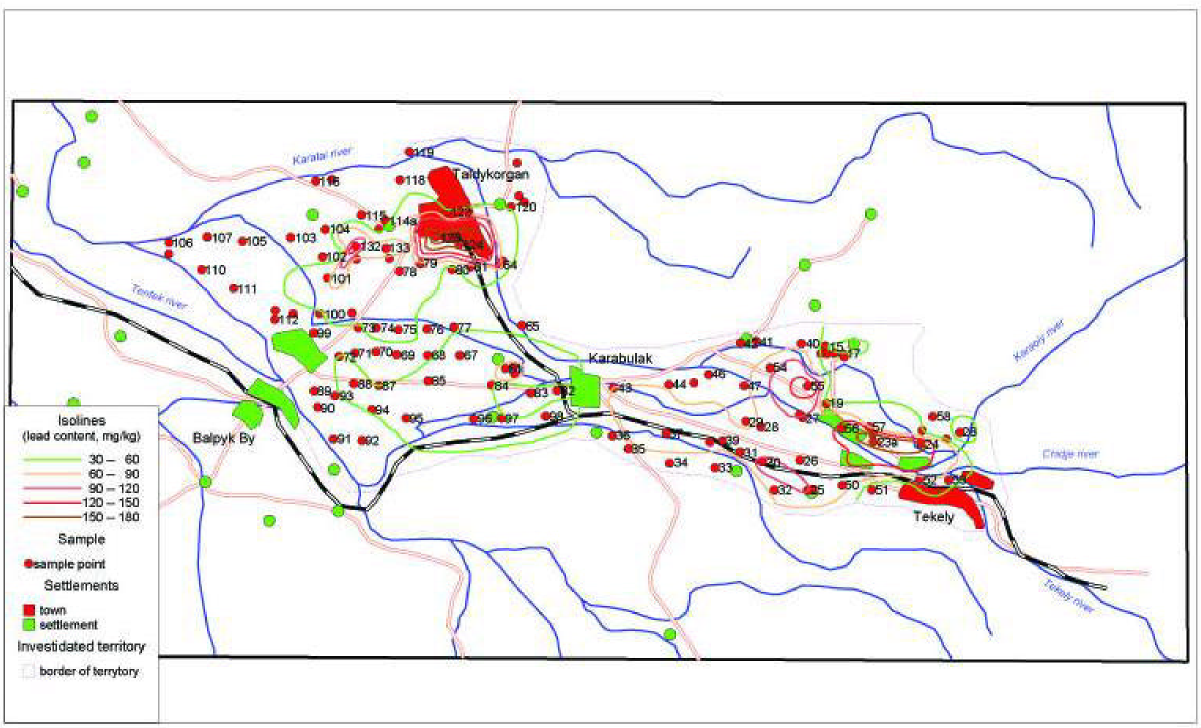


Fig. 2. Lead soil pollution map of the river Karatal upper basin

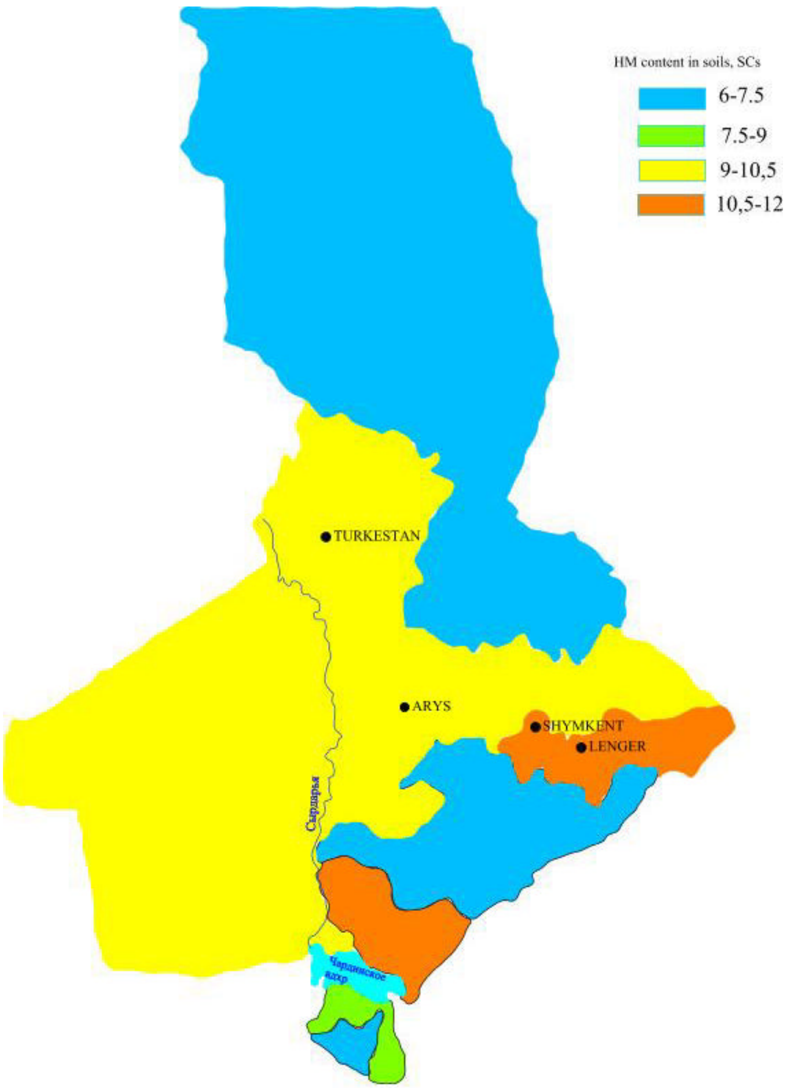


Fig. 3. Southern-Kazakhstan oblast

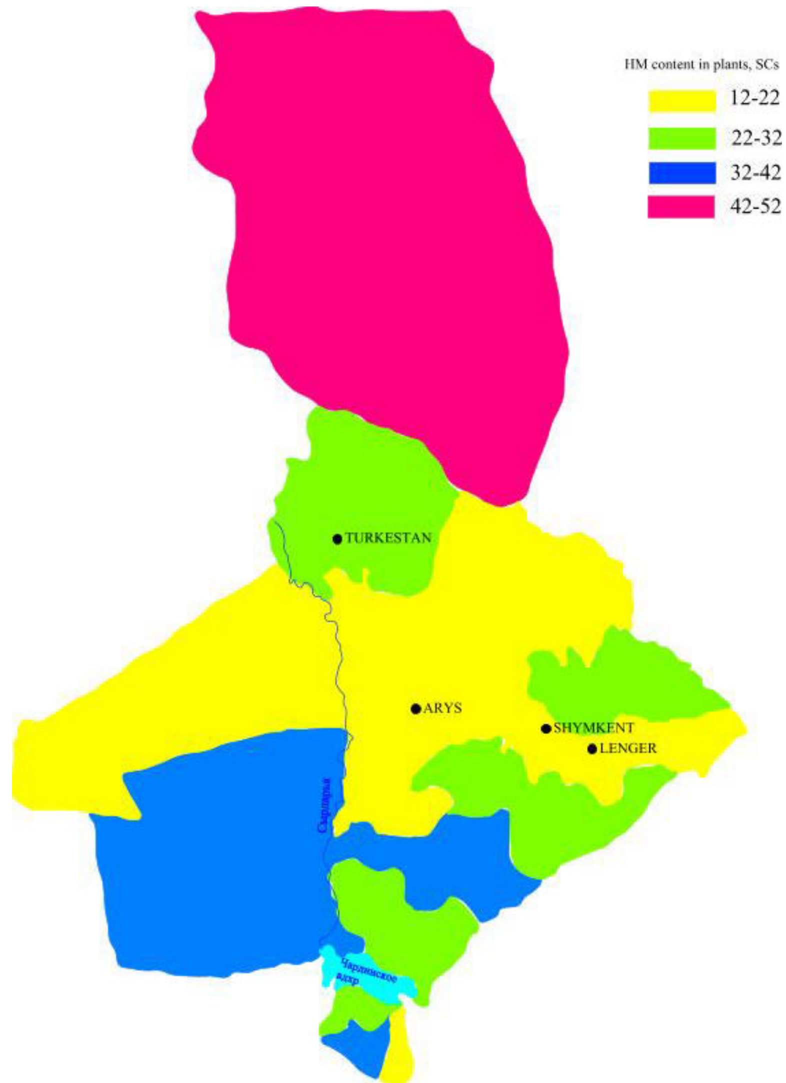


Fig. 4. Southern-Kazakhstan oblast

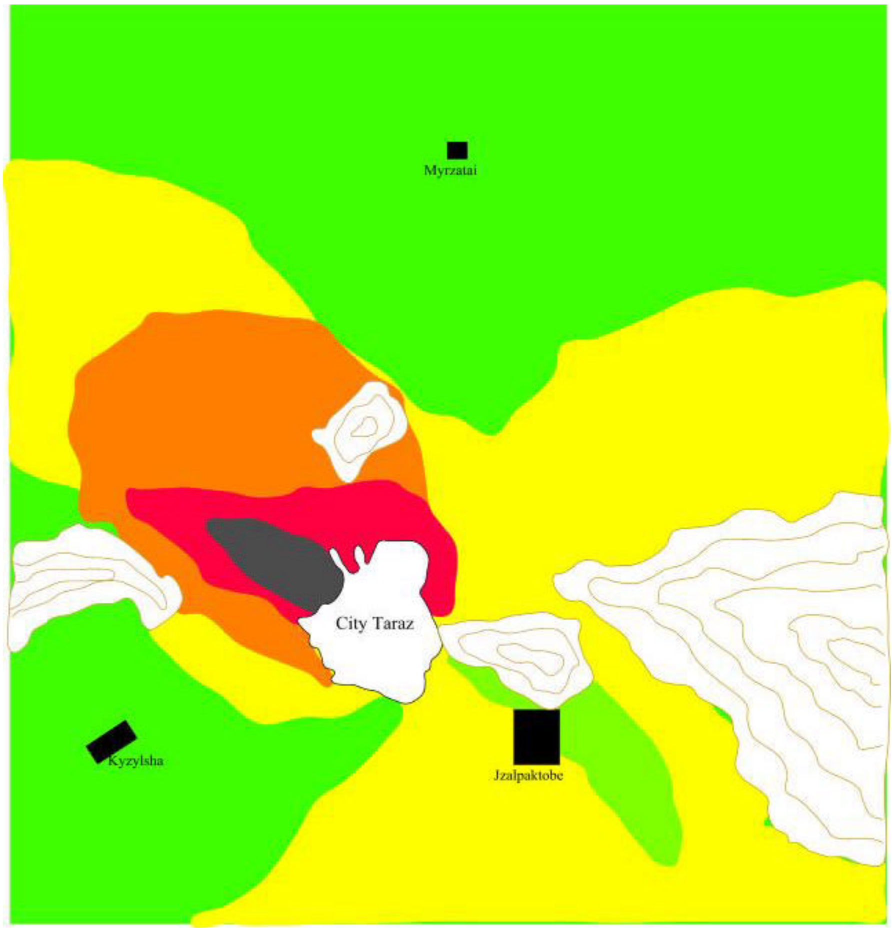


Fig. 5. Complex content of fluorine, lead and cadmium in layer of soil 0-60 cm (SC)

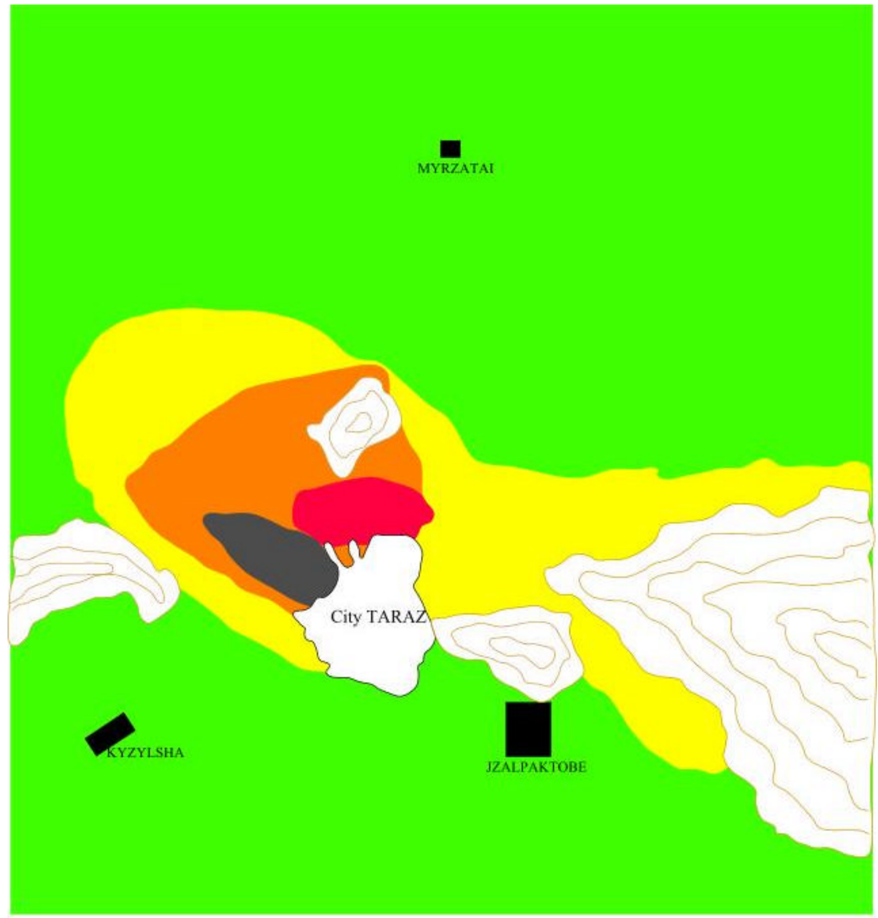
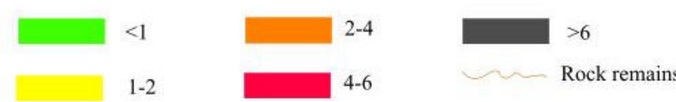


Fig. 6. Complex content of fluorine, lead and cadmium in grape berries, SCs



Considering the results of the researches carried out a wide scope examination of the most contaminated part of the Tekely-Taldykorgan province landscape was made, i.e. of the gardens and orchards of the Tekely population: the gardening societies “Samal”, “Almagash STsK”, “Shakhtostroitel”, “Obogatitel”, “Uchitel”, “Geolog”, nursery KKP. The gardening societies “Shakhtostroitel” and “Obogatitel” are located in the conditions of severe contamination, since they are directly adjacent to operating tailings storage. The increase of the heavy metals contents in the soil is detected on the sites adjacent to cattle passes. While receding from the tailings storage the lead content in the soil decreases from 9 to 2-2,7 SC on the territory of the gardening societies “Geolog” and “Uchitel”. As regards to the contents of the lead mobile forms in the soil, they vary a lot depending on peculiarities of the sites orography and depths of subsoil waters stratification.

As a whole, the soil on these sites has a middle level of contamination. In order to obtain quality products in such conditions, melioration technologies have been developed: to apply elements-meliorants, spray the plants with antioxidants, optimize nutrition and irrigation regimes.

Lists of agricultural plants tolerance to the priority contaminants

The tolerance of various breeds and sorts of fruit plants to heavy metals is different. According to lead contents in fruits and its mobile forms in the soil the coefficients were calculated and rows of biological accumulation of elements in the fruits were drawn up (2, 7, 9).

Lead

Apple tree – Renet Burkhard (0,07), wild apple tree (0,08), Golden Delicious (0,16), Kirghizskoe Zimnee (0,23), Aport (0,32), Starkrimson (0,37), Aidared (0,39), Bystritsa (0,41), Proton (0,41), Zarya Alatau (0,45), Saltanat (0,77), Rashida (1,07).

Plum - Stenly (0,12), Vaneta (0,14), Ispolinskaya (0,16).

Pear – Lesnaya Krasavitsa (0,08), Talgarskaya Krasavitsa (0,28).

Grapes - Olesya (0,04), Taifi Rozovyi (0,04), Chaush Kirghizskiy (0,05), Vartan (0,01), Zarif (0,02), Zhemchug Saba (0,02), Zarrin (0,03), Predgornyi (0,05), Chaush Muscatnyi (0,05), Almatinsky (0,33), Koroleva Vinogradnikov (Queen of Vineyards) (0,35), Arman (0,66).

Berry bushes - Strawberry (0,7), raspberry (4,16), currant (5,07), sea buckthorn (16,09).

Cadmium

Apple tree - Aidared (0,07), Rashida (0.07), Zarya Alatau (0,07), Saltanat (0,07), Bystritsa (0,07), Renet Burkhard (0,08), Starkrimson (0,1), Kirghizskoe zimnee (0,1), Proton (0,1), wild apple tree (0,2), Aport (0,28), wild apple tree (0,39), Golden Delicious (0,72).

Plum - Ispolinskaya (0.089), Vaneta (0,1), Stenly (0,107).

Pear – Lesnaya Krasavitsa (0.07), Talgarskaya Krasavitsa (0,07).

Grapes – Chaush Kirghizskiy (0,03), Arman (0,1), Vartan (0,1), Taifi Rozovyi (0,1), Chaush Muscatnyi (0,12), Zhemchug Saba (0,16), Koroleva Vinogradnikov (Queen of Vineyards) (0,17), Zarrin (0,19), Almatinsky Ranny (1,76).

Berry bushes - currant (0,03), strawberry (0,15), sea buckthorn (0,23), raspberry (0,31).

Fluorine

Grapes – Olesya (0,24), Chaush Muskatnyi (0,28), Chaush Kirgizskiy (0,29), Vartan (0,54), Zarrin (0,7), Arman (0,73), Taifi Rozovyi (0,76), Zarif (0,77), Zhemchug Sabo (0,79), Predgornyi (0,81).

The obtained results are necessary for clone breeding, sort agro technical cultivation of garden cultures on the technogenic polluted areas. And also it’s necessary for rational distribution of kinds, sorts and plant clones taking into account component pollution degree of biogeocenoses.

Conclusion on nature of aberrations causes.

Among medical and ecological problems, the affect of lead is to be regarded as the most grave. Despite of the fact that in the environment a number of heavy metals is present the levels of lead concentrations arouses the serious anxiety.

The most of children exposed to a lead influence suffer due to subclinical effects. Due to this, it is proposed to regard lead as the main criterion of the effectiveness of a preventive program in the Tekely-Taldykorgan region.

As researches of the lead content in the blood of the adult population in the region show that the levels above 20 mkg/dl had 66% of the examined, higher than 30 mkg/dl – 21%, above 35 mkg/dl – 7%. International regulations (in particular, the EU directive of 27 March 1977) require that these proportions be reduced to 50%, 10% and 2%, accordingly. Such criteria must be a basis for the Tekely-Taldykorgan region. It is necessary to meet these standards in the term of 5 – 10 years (3, 11).

Based upon an expert evaluation we have found that priority ones among them are: the soil contamination (45%), contamination of vegetable products (20%), lead content in painted surfaces (toys, dishes, household items, etc., 18%), pollution of the air and dust (15%), other sources (2%).

Recommendations on soil remediation, plantation placing on the polluted territories, and on preventive maintenance of the population diseases

A positive influence of the evolved antagonist elements of heavy metals accounts for the change of the chemism of soils, which will drive heavy metals into inaccessible compounds or difficultly accessible ones. Magnesium fixes lead in soil and suppresses the move of zinc and cadmium. Sulfur, acidifying the soil, will favour accelerated release of the magnesium, calcium and aluminium, which fix lead in soil. Besides, heavy metals can fix themselves into such difficultly accessible inorganic compounds as sulphates and sulphides. Under the influence of sesquioxides of aluminium the ingress of zinc and lead to plants will abruptly decrease. Boron is antagonist to zinc and also drives this heavy metal to difficultly accessible form for plants.

The most perspective in terms of the practice and economic expediency we recommend the introduction of zinc sulphate calculated at 80 g/plant against a background of a biohumus. Dry table wines made of Aligote grapes grown in saline soils showed an optimal biochemical composition and high degustation evaluation (7,4-7,6 scores) in all experiment variants.

For the effective influence on the productivity of fruits and grapes, increase in the stability of garden cenosises and obtaining ecologically safe products in technogenically contaminated and saline soils it is necessary to rationally use fertilizers and irrigation.

On low contaminated soils, improvement of mineral nutrition may be achieved by optimization of a ratio of elements. The optimal ratio of a mineral nutrition ratio may be received at a low, optimal or high level of the element content. In soils with a low excess of heavy metals, a calculation of required doses of fertilizers may be made in accordance with an equation of the optimal balance in a proportion with the actual balance of elements in the soil.

In the low contaminated soil, introduced elements including microelements optimize mineral nutrition of plants. The more elements are brought to optimum; the best is the end effect. In soil with a higher level of contamination, it is impossible to get positive results by optimization of the elements' relationship as the concentration of a soil solution will increase till toxic. In that case, optimization of nutrition regimes may be reached at the expense of the use of antagonistic elements which decrease a negative affect of contaminators on plants. For a practical application of meliorants we propose the following technology (6, 16).

At strawberry plantations with a low contaminated soil it is recommended in bring in 540 kg/ha of zinc sulphate and 144 kg/ha of magnesium sulphate; with a medium contaminated soil - colloid sulfur in the quantity of 500 kg/ha. Colloid sulfur may be replaced with boric acid (40 kg/ha) in combination with aluminium sulphate (600 kg/ha). All meliorants are introduced against a background of a biohumus in the quantity of not less than 3 t/h?. The biohumus may be replaced with a manure in the quantity of 20 t/h?. In the heavy contaminated soil it is recommended to put in colloid sulfur in the quantity of 500 kg/h? or H_3BO_3 (100 kg/h?) in combination with $MgSO_4$ (1440 kg/h?).

To improve the resistance of plants to heavy metals it is best to spray low and medium contaminated soils with salicylic acid of 150 mg/l with 50 mg/l of vitamin «?», vitamin «?» 100 mg/l, ?scorutine 50 mg/l, epin 0,2 mg/l.

In a young garden in low contaminated soils are best added 540 kg/h? $ZnSO_4$ and 1450 kg/h? of $MgSO_4$ or applied colloid sulfur in the quantity of 500 kg/h?. In the medium contaminated soils it is used boric acid – 110 kg/h? and $MgSO_4$ – 1450 kg/h? or boric acid of 15 kg/h? with sulfate aluminium in the quantity of 1200 kg/h?; in heavy contaminated soils - 15 kg/h? of boric acid with sulfate aluminium or 40 kg/h? of boric acid with 600 kg/h? of sulphate aluminium. All meliorants are introduced against a background of a biohumus. In a young garden recommended doses of meliorants by be reduced by 3 times.

In vineyards growing on medium and heavy contaminated soils it is recommended to add 140 kg/ha of boric acid and 2000 kg/ha of sulphate magnesium. As an alternative in the heavy contaminated soil it is also possible to enter colloid sulfur in the quantity of 700 kg/h?.

In vineyards growing on saline soils with the excess of boron and soluble sulphates, 180 kg/ha of sulphate zinc should be introduced. All meliorants are added one time in 4-5 years and their using is justified by an increment of the harvest and improvement of a quality of products.

There is a certain differentiation of territories within the limits of the region as regards the level of risks of the heavy metals affect on a human being. The highest lead levels have been found in Tekely and villages adjacent to it. The levels in Taldykorgan are somewhat lower. However, these differences have not an expressed statistical reliability. As a whole, all territory of the region including Tekely and Taldykorgan and villages should be considered as a risky zone. Unified measures must be taken in the region.

For these purposes it is necessary to carry out a comprehensive ecological audit at each large industrial facility in the region. At each of them, a system of a nature protection administration should be set up in accordance with international standards ISO 14001.

As it was established, people employed in the production in Tekely and Taldykorgan have the highest lead concentrations in the blood (up to 40 mkg/dl).

Recommendations on improvement of the soil quality proposed in this report should be implemented and monitoring and control over states of the soil cover at sites where vegetable products are grown established.

Since till present the ban on the use of leaded gasoline in the region does not work, it must be sought as an important factor which facilitates the improvement of health of the population.

The population of the region should follow a number of hygienic requirements:

- change clothing and shoes while ente ring homes;
- adults and children have to wash their hands more often, especially before meals and after coming homes from the street;
- cut nails short;
- do not use painted ceramic dishes;
- daily wet cleaning of premises, etc.

These measures will allow to reduce risks of affect of heavy metals at least by 30-40%.

Those who contact with lead at the production or who have an elevated level of lead in the blood can take individual preventive measures. In order to avert a deficit of iron in the diet and take up to 1g of calcium per day.

The summary efficiency of the said measures may make up USD13-16 mln at the cost of the reduction in a sickness rate of the population, increase in ability to work and prevention of intellectual development of the growing up generation.

Conclusion

During investigations the pollution sources, priority contaminants and their ways of migration were established in Tekely-Taldykorgan technogenic-polluted province. The map of polluted soils by lead was compiled.

Principally new system of technogenic-polluted soils melioration was developed. This system is based on the principals of element antagonizim-sinergizm, and also on changing base regimens of nutrition and irrigation of the plantings.

Proposals on technogenic-polluted soils remediation were given. Also proposals were made on rehabilitation of health population of the environment unfortunate regions of the South and Southeast Kazakhstan. The summary efficiency of the said measures may make up USD 13-16 mln.

These investigations have a tremendous social, environment and economic significance. It's only the first essential stage. Such investigations must be developing in future.

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SOIL PROTECTION AND REMEDIATION: USING NATURAL MATERIALS AGAINST TECHNOGENEOUS CONTAMINATION *

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Kazan State University (KSU) was established in 1804 and for a lot of years remained Russia's easternmost higher education establishment. At present it is a large educational and research complex. About 11000 students are trained in 32 specialties and directions at 16 faculties. There are 1075 professors including 562 candidates and 192 doctors of science, 172 researchers on staff (154 candidates, 18 doctors of science) that work at 86 departments.

For over thirty years the staff of the Research Laboratory of Organic Compounds Structure, along with the theoretical studies, have been working intensively on the development of new types of industrial products and the technologies of their production. In the last few years in co-operation of this Laboratory with the Laboratories of Soil-Plant System (Faculty of Geography) and Soil Physics (Faculty of Mathematics) the new direction in the field of environmental protection is being developed. The main research problems here are the investigation of migration of contaminants - exogenous low-water-soluble organic substances (aliphatic and aromatic hydrocarbons, halogen-substituted organic compounds, etc.) in soils and development of new technologies of soil protection and remediation from contamination with products of chemical and petroleum industry and animal farming wastes.

The main directions of these investigations are: *i)* The conversion of animal farming wastes (manure, litter) into organic fertilizers of 2 kinds: granulated (drying of litter in "boiling" layer) and pounded (composting of wastes in bio-reactors). The addition of natural meliorants (limestone, dolomite, zeolite-containing rock) and nitrogen into prepared fertilizers. Hereby one can obtain organic fertilizers with wide sphere of action. *ii)* The study of physical-chemical characteristics of soils and clays of various types and composition and selection of those that possess the highest barrier functions. Such soils can be used for the creation of protective shields for petroleum- and product-storage facilities; sites of great ecological risk (on places oil recovery wells and petroleum pipes); gas stations etc. *iii)* The search of the ways to strengthen the barrier functions of soils in relation to hydrocarbon contamination via the inserting of natural minerals. This aspect is being developed in 2 directions: the creation of water barrier with the purpose of increasing of hydraulic resistance of porous medium to the infiltration of hydrocarbons and the modification of natural minerals, placed into the soil. *iiii)* The development of phytoremediation technologies of soils, contaminated with hydrocarbons. It includes directions of the resistance of traditional and non-traditional agricultural plants and their influence on the residual hydrocarbon content in soil, on the number and activity of soil microflora. *iiiii)* The development of technologies of remediation of soils by the combination of phytoremediation (use of plants)

* *The work was supported by Russian Foundation of Basic Research*

and augmentation (use of fertilizers). The final result of all these investigations will be the creation of new complex technology of protection and remediation of soils through the joint application of physical-chemical and biological methods.

Further we will discuss more detailed the results of our investigations concerning the study of hydrocarbon filtration and sorption processes (as the most important ones by the solution of the problem of protection and remediation of soils contaminated with hydrocarbons) and also phytoremediation study. These problems are very actually in Russia, especially for regions with intensive petroleum recovery and refinery, such as Tatarstan Republic. About 1.420.000 hectares of its territory are suffering from their influence. The most widespread soils here are leached chernozems containing sufficient amounts of clay and organic matter.

The search for the ways to increase barrier functions of leached chernozem was followed by the investigations of main processes that influence transport and accumulation of hydrocarbons in soils: 1) hydrocarbon filtration and 2) their sorption retention by various organic and mineral soil sorbents.

1. TRANSPORT AND DISTRIBUTION OF HYDROCARBONS IN SOIL

Technogeneous hydrocarbons flows are formed in the presence of extraction, transportation and conversion of the combustible raw materials, especially oil and gas. They play a significant role in antropogeneous change of the natural rotation of matters and cause an intense contamination of the nature environment, soils and groundwaters in particular. This does the great ecological and economical damage. Among all of soil contaminants, even the most toxic ones, oil is the most widespread and has the greatest number of the sources of contamination. The localized hydrocarbon flows upon the floods of oil and petroleum products affect the landscape in an especially bad way (or with a special strength). Hydrocarbons become degraded very slowly when reaching the soil surface and then the aerated soil environment. They are sorbing in separate soil horizons and they also can vertically migrate in the soil profile with the water flow. But further they migrate in to the groundwater **[19-21, 27].**

In the Republic of Tatarstan oil recovery spreads all over 1420 thousands hectares of the territory (more than 1/5 of the overall soil fund), including 909 thousands hectares of agricultural area, 724 thousands hectares out of them are plough-lands. According to the tentative calculations made during the period from 1943 to 1995, in Tatarstan the recovery of 1 ton of oil was accompanied by the destruction and contamination of 1-1,3 m^3 of soil **[13].** The territory of the oil recovery is characterized by the temperate-continental climate with the average annual temperature (+2)-(+3)^oC and by the average annual amount of sediments of 440 mm. The most widespread soils here are chernozems which form 88%. From these the leached and podzolic chernozems form 40%. More over these soils are ploughed up.

The remediation of soils and quality of the oil-polluted groundwater is quite a difficult task. It is a complicated and prolonged process that demands a strictly scientific grounds and therefore carrying out of fundamental research investigations. The search of the fast and economical way of remediation is especially difficult because of the complexity of the processes of transport and distribution of hydrocarbons in soils and also because of the poor studied mechanisms of filtration of immiscible liquids in porous media **[11, 22, 23, 28].**

The character of hydrocarbon filtration in various geochemical and agro-landscapes depends on many factors **[1-3, 10, 16, 26].** The main factors (those that control hydrocarbon distribution in soil profile) are particle size and water regime of soil. Under the influence of the floods of hydrocarbons onto the landscape, the structure and the water-air regime of soils modify, their fertility decreases too. The chromatographic distribution of oil and consumption of hydrocarbons on the sorption barriers are present in the soil profile. Among all the factors that influence the filtration of hydrocarbons, the most important one is the soil moisture **[32].** It creates the capillary barrier on the way of hydrocarbon movement and it also has a significant influence on the structure and therefore on the sorption capacity of soil (the last one is connected with the total porosity and the pore size).

The most detailed, exact and statistically reliable information, connected with the questions of filtration and accumulation of hydrocarbons in soil, can be received in experiments in laboratory columns packed with the soil. However, data on the influence of structure and moisture of soil on the mechanism of these processes are found very seldom. The number of authors suggests to use various soil meliorants (mineral and organic fertilizers combined with the additions – lime, surfactants and others) for the recultivation of soils contaminated with oil **[23, 27].** But the high effectiveness of such a way is not yet proved experimentally and the mechanism of their action is poorly studied.

The aim of this work was the intensification of the accumulating ability of soil as mineral-sorption barrier against the spread of hydrocarbons into the soil and further into the ground waters. *The basic tasks* of the first step of these investigations were formed:

1) To study the structural dynamics of soil and to define the conditions (moisture of soil, duration of moistening) for which the structure is most closely to the natural soil monolith arranges in soil columns;

2) To investigate the hydrocarbon filtration in 0-40 cm layer of leached chernozem with homogeneous structure and high clay content.

The great amounts of technogeneous hydrocarbons that accumulate on soil surface during the long winter period are very dangerous in spring for soils with high water content ("field capacity"). Therefore the soil in our experiments has been wetted up to "field capacity".

Objects and methods of investigations

The choice of the composition of model mixture of hydrocarbons was made on the basis of the results of study of the composition of kerosene and the main petroleum products (which are used as the fuel and solvents) by the methods of gas-liquid chromatography and infrared spectroscopy. Nonane, tetradecane, decaline and 1-methylnaphtalene formed the mixture. This composition corresponds to the contents of the main types of hydrocarbons in kerosene and is also common with the composition of the other known types of petroleum products (diesel fuel, benzene fuel and others). In the mixture all the components were taken in the equal weight quantities. This way it is easier to carry out experimentally the control of the change of hydrocarbons composition during their filtration in soil. We studied the migration of the mixture of hydrocarbons in the upper horizons of the leached chernozem (0-40 cm). It contains 38% clay, 40% silt, 22% sand. Upper layer (0-20 cm) contains 4,41% organic matter and has a pH_{KCl} of 5,60. Lower layer (20-40 cm) contains 3,26% organic matter and has a pH_{KCl} of 5,31.

For the decision of the first task the experiment in soil columns on the definition of the speed filtration of distilled water through the 0-40 cm layer of leached chernozem was carried out. Soil columns are glass tubes with the diameter of 40 mm, length of 600 mm, filled with pounded and sieved (16 mesh) chernozem (sieve 1 mm). The lower layer of soil in tubes (20-40 cm) was taken from under the arable soil horizon, the upper layer (0-20 cm) from the arable soil horizon. During the experiment on the surface of soil the constant level of distilled water (5 cm) was maintained during 60 days. The volume of infiltrate was defined after every day. Repetition of the experiment was double multiplied (2 columns were used).

For the decision of this task the vacuum-capillary installation was also assembled. It allows to investigate the samples of soils and grounds of the various structure – as distorted (pounded samples), as not distorted (complete samples taken with the drill). With its help the pore size distribution (separately in the soil layers of soil 0-20 and 20-40 cm) was estimated quantitatively. This characteristic of the soil structure was used as the main indicator of the structural changes in leached chernozem. The definition of the soil pore size using this method is based on the connection between the capillary retention of water and their sizes. Capillary powers are estimated by the value of strength (the degree of exhaustion created in installation) applied to the water-saturated sample of soil, placed on the porous membrane. The amount of water discharged with the definite value of exhaustion characterizes the volume of pores of the corresponding size. The duration of the experiment was 1, 6, 40 and 60 days. Repetition of the experiment was 4-multiplied for every soil layers (8 columns in total).

For the decision of the second task experiments in other soil columns were carried out. The soil was saturated with the distilled water till the constant speed of filtration. Then the mixture of hydrocarbons was placed on the surface of soil (2 cm) and after its imbibition the saturation with water was continued. The duration of experiments was 2, 4, 7, 9, 11, 12, 15, 19, 24, 30, 32 and 36 months. Repetition of each experiment was 2-multiplied (2 columns were used). Therefore we studied in columns: 1) the primary contamination of soil (the absorption of hydrocarbons into the soil occurred, then the remainder of the mixture was removed and the content of hydrocarbons and moisture in soil were determined layer by layer in columns); and 2) secondary contamination (the already contaminated soil was saturated with distilled water - the water post was equal to 5 cm - and the redistribution of hydrocarbons after the end of experiments was studied with layered soil analysis in columns).

Analysis of the content of hydrocarbons in soil profile: After the completion of every experiment the soil from the columns was taken out by layers with step 2 cm. The received samples of soil were extracted by tetrachloromethane (4 ml of distilled water and 6 ml of tetrachloromethane on 6 g of damp soil), centrifuged and the solution was separated. The analysis of the content of hydrocarbons in extract was carried out using the gas-liquid chromatograph Biochrom-1 equipped with a filled column of 3-m length and flame ionization detector. The medium for column Inerton AW-HMDS with the liquid phase SE-30 in the amount of 5% was used. The conditions of separation: the gas-carrier – hydrogen, the flow rate - 30 $ml \cdot min^{-1}$, the temperature of the column – (70-170)^oC, the speed of the rise of temperature – $4^oC \cdot min^{-1}$, the temperature of sampler - 220^oC. The threshold of detection of hydrocarbons by this method forms 0,001 %.

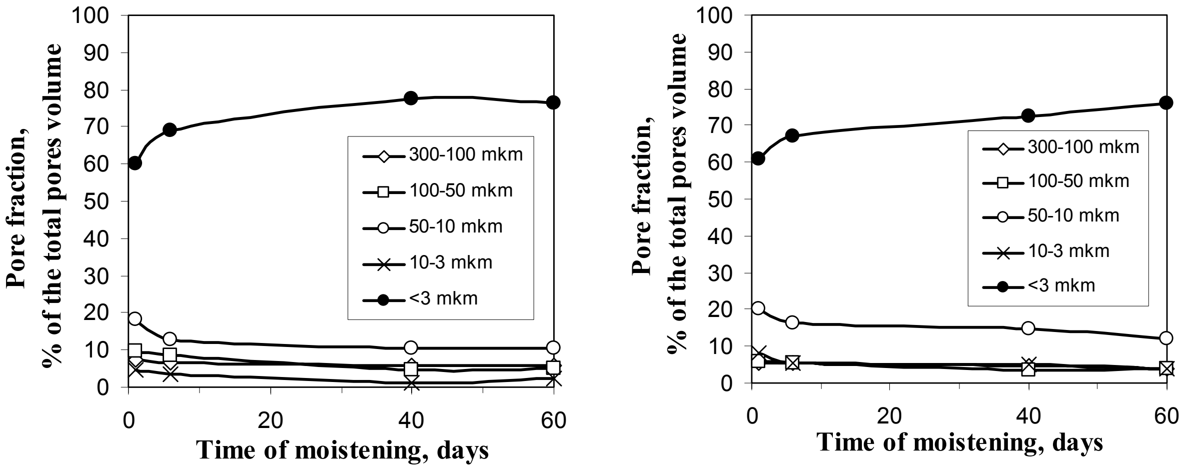
The content of moisture in chernozem were defined after the drying of soil at 105^oC.

The received experimental data were statistically analyzed with the help of Statgraph and MS Excel software.

Results and discussion

a) The investigation of the structural dynamics of soil during its movement to the state of 'field capacity'

The results of experiment on the accumulation dynamics of water infiltrate from the leached chernozem showed that during the experiment the speed of water infiltration decreased but irregularly. Graphs have shown two bends of the curve, which characterize its uneven decreasement: on 6-th and 40-th days of the experiment. Therefore during the first 6 days the speed of filtration of water decreased sharply, further till 40 days – gradually and after 40 days – reached practically constant value up to 60 days. Constancy of the speed (and therefore of the resistance of filtration) pointed on the



a b

Fig.1. Dynamics of soil pore size distribution during soil moistening of pounded samples (leached chernozem, a – layer 0-20 cm, b – layer 20-40 cm)

stabilization of the soil structure: after 6 days – non-complete, after 40 days – complete. Such stabilization is connected with the complement of processes of swelling and sedimentation of soil particles and aggregates.

On **Fig. 1** are shown the results of the experiment that was carried out in a vacuum-capillary installation for 0-20 and 20-40 cm of layers of chernozem. The time of moistening of the samples (after expiration of which the soil pores size distribution was determined) was taken from the previous experiment: 1, 6, 40 and 60 days. From the received data is clear that during the period of moistening the structure of the soils pores was gradually changing. The most significant changes were connected with the increase of volume of the smallest pores (less than 3 μm) in an overall pore volume. The degree of the porous volume of all other (bigger) groups of soil pores decreased upon the moistening of the chernozem. These regularities were shown in both layers of soil: 0-20 and 20-40 cm. In the upper soil layer these changes were observed in a great degree after first 6 days. In the lower layer the same changes but slower relaxation of soil structure were observed.

When carrying out the experiments on filtration in filled columns, it is necessary to know exactly what kind of soil structure we deal with. The comparison of air-dry pounded samples with soil monoliths prior moistening showed that the latter contained more large pores (100-300 mkm and more than 300 mkm) but during the moistening, the porous space structures for pounded samples and monoliths chummed in. **Fig. 2.** The complex of the received on the first question data allowed to draw a conclusion that during the process of moistening, soil structure changes from distorted (particles of the pounded soil are smaller than 1 mm) to the structure corresponding to the real soil monolith. The main occurring structural changes here are the increase of the degree of small pores in an overall porous volume. Therefore we determined time intervals necessary for the recovery of the soil structure after the moistening of its pounded samples in soil columns. This method gives us the possibility to estimate the soil pore structure used in next experiments. Taking this into account, the following experiments on the hydrocarbon migration we began after 6 and 40 days of soil wetting in columns.

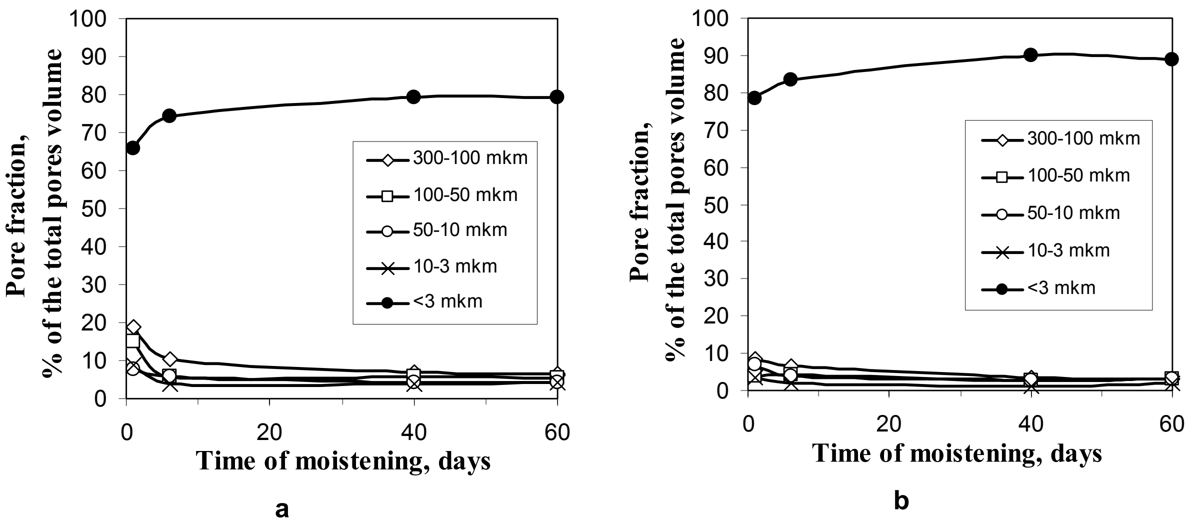
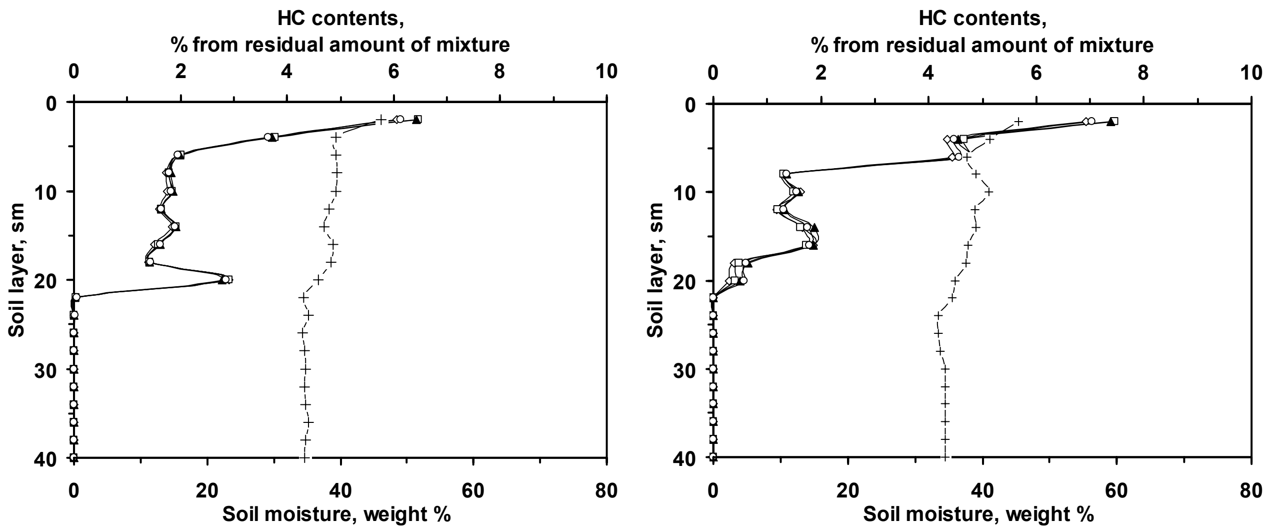


Fig.2. Dynamics of soil pore size distribution during soil moistening of monolyte samples (leached chernozem, a – layer 0-20 cm, b – layer 20-40 cm)

b) Study of the infiltration processes of hydrocarbons in soil

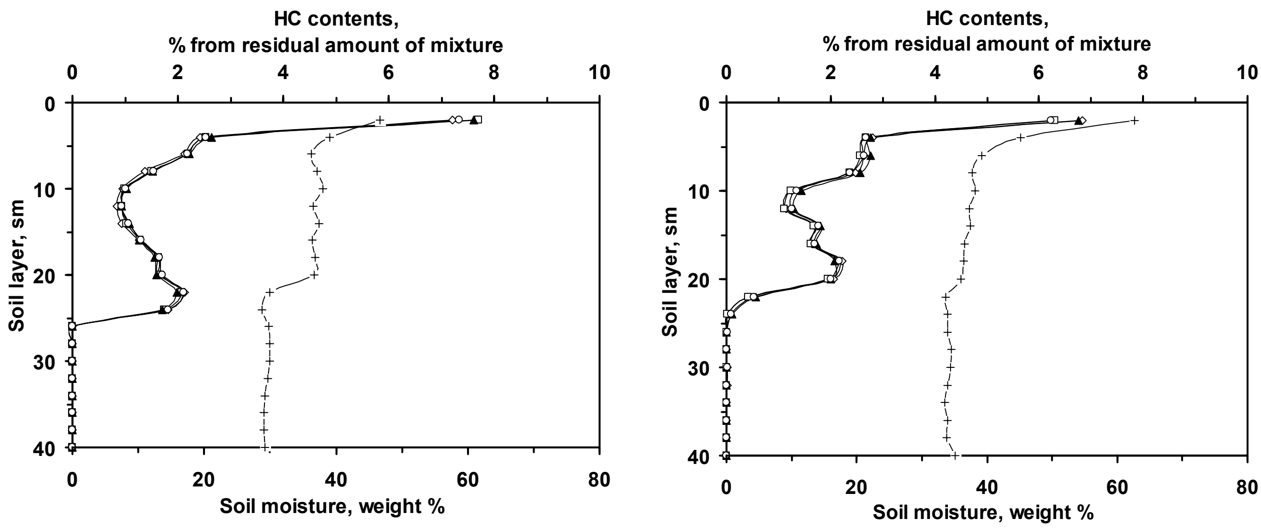
The hydrocarbon imbibition and distribution in soil (primary contamination). It was found that the amount of hydrocarbons soaking into chernozem, moistened beforehand over 6 and over 40 days, was limited. However, the speeds and volumes of hydrocarbons soaked were significantly higher in columns with 6 days moistening. This fact is in accordance with different structure of soil porous space under different times of moistening (see Section 1a). In **Fig. 3** is shown the distribution of the residual hydrocarbons and water in these two variants (for the convenience of comparison of profiles of hydrocarbon distribution in columns, their amount is stated in normalized mode). In both variants the hydrocarbons front was shifted up to 22 cm and two maximums of hydrocarbons amount were noted in profile: in variant with prior moistening over 6 days the second maximum was shifted further and had a higher value.



a **b**

Fig.3. Contents of hydrocarbons (HC) and water in profile of leached chernozem (layer 0-40 cm) after hydrocarbon imbibition into the soil moistened up to its 'field capacity' during 6 days (a) and 40 days (b) - (Primary hydrocarbon contamination).
◇ n-Nonane, □ Decaline, ▲ 1-Methylnaphtalene, ○ n-Tetradecane, ✖ Water

On a **Fig. 4** is shown the distribution of hydrocarbons in the soil profile after the completion of the experiment on the secondary contamination of soil (after 7 months of model mixture migration in leached chernozem with 'field capacity'). From the figures it is evident that as a result of water drainage upon secondary contamination in both variants front and lower maximum of hydrocarbons content were slightly shifted inland into the soil (2-3 cm). The received data show that during the migration of hydrocarbons mixture in root-inhabited layer (0-40 cm), there were no significant changes in their ratio. In layer 18-20 cm after 7 months of filtration the contents of decaline and methylnaphtalene was approximately two times lesser than in the upper layer. The presence of nonane and tetradecane was not detected. Starting from the layer 22-24 cm hydrocarbons in soil were not observed. Therefore we determined that the layer of chernozem of homogeneous structure (not distorted with cracks and frac-



a **b**

Fig.4. Contents of hydrocarbons (HC) and water in profile of leached chernozem (layer 0-40 cm) after 7 months of distilled water drainage in soil with hydrocarbon-contamination originally moistened up to its 'field capacity' during 6 days (a) and 40 days (b) - (Secondary hydrocarbon contamination).
◇ n-Nonane, □ Decaline, ▲ 1-Methylnaphtalene, ○ n-Tetradecane, ✖ Water

tures, with maximum of water saturation) practically completely stops the hydrocarbons entrance from root-inhabited horizons into the lower layers.

Conclusions. The results of our studies have shown that the upper layer of leached chernozem with homogeneous structure that has been wetted up to the condition of 'field capacity' practically completely restrains hydrocarbon migration into the lower soil layers.

2. SORPTION OF HYDROCARBONS ON ORGANIC AND MINERAL MATERIALS

Hydrocarbons sorption is one of the key processes impacting hydrocarbons movement in soil-plant systems. In soils it represents the primary act in hydrocarbon interactions with soil sorbents possessing different nature, structure and chemical composition. Consequently, the sorption much determines the following distribution and fate of hydrocarbons – the degree of their accumulation and/or degradation in soil profile and the arrival into the overgrown plant bio-mass **[6-8, 23, 25, 31, 34]**. The failure to take sorption into account can result in a significant underestimation of the amount of a contaminant at a site as well as the time required for it to move from one point to another.

For low-polarity contaminants, including hydrocarbons, in soil-water systems it was ascertained the sorption isotherm linearity. The strong suppression by water of solute vapours adsorption on soil mineral surfaces (this effect is characteristically for different mineral adsorbents) leads to a relatively linear solute uptake by soil over a wide range of solute concentrations, most evident for non-polar solutes, benzene for example, at moderate to high relative concentrations. Contrariwise there exist very little experimental data about hydrocarbon sorption from vapour phase (on the dry soil). Consequently it is difficult to draw conclusions about soil moisture influence on the hydrocarbon sorption processes**.** As a result of some studies on dry soils sufficiently great hydrocarbon sorption capacity and non-linear sorption isotherms were found **[15].**

Soil, in its natural state, is primarily composed of sand, silt, clay, water and a highly variable amount of natural organic carbon. The latter profoundly complicates sorptive properties of soil. The extent to which sorption proceeds is dependent upon how receptive the soil matrix is to the organic molecule, which is a function of the organic content. Humic acids are a major fraction of soil organic matter, and sorption of hydrophobic organic chemicals by humic acids influences their behaviour and fate in soil. A clear understanding of the sorption of organic chemicals by humic acids can help to determine their sorptive mechanisms in soil. But even when the organic carbon content is very low, some sorption of the most hydrophobic molecules continues because of the soil's mineral surfaces.

In the area of hydrocarbon sorption on plants less experimental information is available.

The sorption of hydrocarbons on over-ground plant biomass was studied mainly from water solutions - as well as on soil. Davis et all **[9]** have studied sorption of trichloroethylene, trichloroethane, chloroform and dichloromethane on aspen wood splints and crushed dried alfalfa by static equilibration techniques. Contaminant retention in the thin segments of poplar stem was there also studied. It was shown that contaminant sorption on plant material is proportional to octanol-water distribution coefficient and that hydrocarbons are sorbed worse on plants than on soil organic matter. As the check experiment with pure cellulose showed sorption depends on content of other plant components and on lignification process also.

Sorption of hydrocarbons on plant roots was studied less and in water solutions too. Naphthalene sorption on fescue and alfalfa roots was described by Freundlich isotherm during a few growth stages **[29].** On the later growth stages the sorption was four times more intensive than early cause by higher surface and biomass of roots. Independently of growth stage sorption on alfalfa roots was at least two times greater in comparison with fescue despite of less surface of alfalfa roots. It was assumed lipid content might affect the naphthalene sorption on roots.

Especially little is the information about hydrocarbon vapour-phase sorption on plant materials. Using static headspace gas chromatography Welke et all **[33]** studied physical-chemical properties between the vapour and the isolated plant cuticles or aqueous phase, respectively in order to characterize the sorptive properties of plant cuticles for a diversity of 50 volatile organic compounds including n-heptane, o-xylene et all. Over a wide range of concentrations linear sorption isotherms were obtained.

The sorption processes can be studied by various methods (manometric, gravimetric, dynamic and static chromatography methods). The later of them provides reliable results in more wide range of sorbate concentrations and also permit to study sorption processes with long-lived equilibrium time.

The aims of this work were the comparative estimation of character and magnitude of sorption interactions of hydrocarbons with organic and mineral sorbents and the revelation of mechanisms of hydrocarbons vapor sorption.

The basic tasks of investigation were formed:

1. To determine the main soil sorption parameters for different classes of hydrocarbons.
2. To estimate the type of hydrocarbon sorption on soil and the structure of its sorption surface.
3. To estimate the effect of sorbent humidity on hydrocarbon sorption.
4. To compare the magnitude and parameters of hydrocarbon sorption on different organic and mineral sorbents.

Objects and methods of investigations

Chemicals: Hydrocarbons - n-octane, n-nonane, n-decane, decaline ([4,4,0]-bicyclodecane) and p-xylene - were chosen as representatives of typical components of oil and petroleum products. Aliphatic alcohols (methanol, ethanol, propanol-2 and 2-metil-propanol-2) were also used. The purity of all compounds used was 99%.

Sorbents: Soil (leached chernozem), zeolite containing material (ZCM), bentonite clay, limestone, soil humic acids extracted from leached chernozem and plant materials (leaves and roots of maize) were chosen as sorbents. Leached chernozem (upper 0-20 cm layer was used) was the same as in Section 1 (the most prevalent soil type for oil recovery regions of Tatarstan Republic). Also typical for the Republic soils were used (with different sand, silt and clay fractions and organic matter contents) - soddy podzolic, light- and dark-gray forest ones.

Here the natural adsorbent (local ZCM) was used. In Russia there are more than 10 main deposits of Zeolite, which are situated mainly in Siberia and Far East. One of the well-known Russian big deposits of the Zeolite-containing raw material is situated in Tatarstan. Local ZCM are characterized by the stable technological parameters, including high sorption and cation-exchange ability. The content of ZCM (Tatarstan deposit) was opal-cristobalite (28%), heulandite-clinoptilolite (19%), clay minerals (25%), calcite (22%), quartz (4%) and glauconite (2%). Limestone contained 99% $CaCO_3$. Humic acids were prepared by the traditional alkaline extraction method **[24]**; their chemical composition was following: (C) – 39,5%, (H) – 40,3%, unburned residue – 5,9%. As plant materials roots and leaves of maize *(Zea mays L.*) were used. Protein content estimated by Kjeldall method in roots and leaves was 5,1% and 3,8% respectively.

Sample preparation: Dried sorbents (soil at 378 K; ZCM and limestone at 573 K; plant materials at 273 K over P_2O_5, vacuum) were weighed (equal portions at 0,200-1,000 g) in glass vials (volume 14,5 ml). Then into the each vial ampoule with sorbate dosed by Hamilton microsyringe was placed and immediately the vial was hermetically sealed with fluoroplaste (0,2 mm) and silicon linings. In experiments where hydration effect was studied sorbents were previously wetted. Further vials were equilibrated in thermostat at 298 K during from 48 to 120 h.

Static Headspace Gas Chromatography: Gas chromatograph Chrom-5 was equipped with a specially constructed injector **[14]** and flame ionisation detector (sample temperature 298 K, detector temperature 423 K). Separation was achieved using a fused silica capillary column (30 m length, 0,4 mm inner diameter, stationary phase SE-54) isothermally at 373 K with He as carrier gas (inlet pressure 2,4 bar). He, H_2 and air rates were 0,1 ml/s, 0,6 ml/s and 9,0 ml/s respectively. The dosing time was 0,5 s; the volume of headspace sample was 0,5% of the total volume of the vial **[4].**

Experimental data analysis: The thermodynamic activity of organic sorbat vapours (P/P_0) was determined as a ratio of the area of its chromatographic peak for vapour phase over sorbent (P) and over sorbate pure liquid (P_0) at 298 K by headspace gas chromatographic analysis method. The precision of the sorbat activity determination was in the interval from 5% (for P/P_0 > 0,5) to 10% (for P/P_0 < 0,1). Uptake of sorbat by sorbent (V_S) was calculated from the difference between the initial quantity of a sorbat in the system and its quantity in the vapour phase at equilibrium. Estimation error of V_S determination was 5%.

Vapour sorption isotherms were made on the basis on gas chromatographic headspace method data as a dependency of the sorbate uptake on its activity and represented graphically as a set of experimental points. On this basis the approximation of isotherms was made with the help of Brunauer – Emmett – Teller (BET) equation **[5]** by non-linear least square method:

$$V_S = (P/P_0)\left[\left(\frac{1}{V_m c} + \frac{c-1}{V_m c}\frac{P}{P_0}\right)\left(1 - \frac{P}{P_0}\right)\right]^{-1},$$

where V_m - sorbat monolayer volume, c - sorption constant.

Using V_m value the specific surface (S) for each sorbent were calculated by equation:

$$S = (V_m / V_0) N_A \sigma \ ,$$

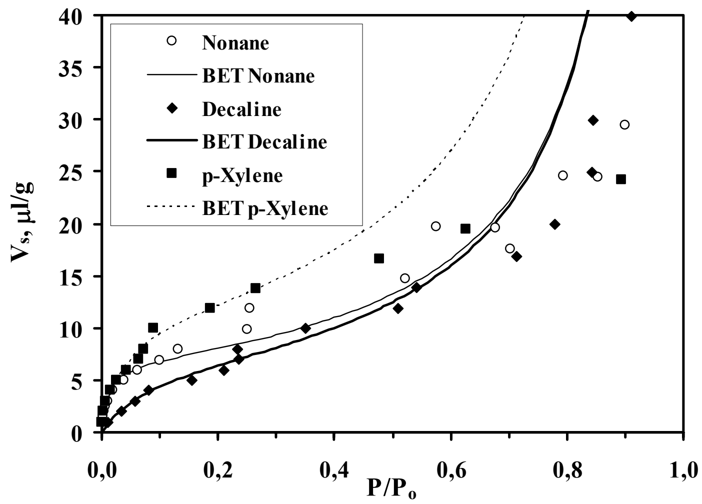
where V_0 - molar volume of sorbat, N_A - Avogadro constant, □ - area of surface occupied by sorbate molecule. The received experimental data were statistically analysed with the help of Statgraph and MS Excel software.

Results and discussion

a) Hydrocarbon sorption on dry whole leached chernozem

Sorption isotherms are widely used to characterize retention of chemicals, including hydrocarbons, in soils. The isotherm equations are incorporated into chemical speciation programs; transport models for assessing the mobility of hydrocarbons also require isotherm parameters as input. To describe sorption data simple equations, such as the Freundlich isotherm are commonly used **[15].** Often these equations do not accurately describe the data and more complicated expressions have to be used. Lack of an accurate description of sorption data may yield serious errors when applied to transport modelling. Hence, it is crucial that sorption data are described adequately with appropriate equations.

We have received sorption isotherms of n-heptane, n-octane, n-nonane, n-decane, p-xylene and decaline on leached chernozem. The determined sorption isotherms are the dependencies of solid phase composition on the sorbate thermodynamic activity at 298 K (P/P_0) and have a similar type for all studied hydrocarbons. On **Fig.5** the isotherms of representatives of different classes of hydrocarbons (from aliphatic hydrocarbons only nonane is shown as isotherms of four aliphatic hydrocarbons were practically the same) are compared. All sorption isotherms were of S-type, which characterises polylayer sorption described by BET model **[5, 15].** On **Fig.5** sorption isotherms that have been calculated according to the BET equation are also shown.



Nonane: C = 91,3
V_m = 6,7 ml
S = 11,0 m^2/g

Decaline: C = 12,6
V_m = 6,7 ml
S = 11,5 m^2/g

p-Xylene: C = 29,5
V_m = 11,.0 ml
S = 20,4 m^2/g

Fig.5. Isotherms and parameters of n-Nonane, Decaline and p-Xylene sorption on dry leached chernozem. C - sorption constant, V_m - sorbat monolayer volume, S - specific sorbent surface

From data analysis it was evident that hydrocarbon sorption isotherms were not described by the BET equation in all range of activities. This may have to do with the heterogeneity of sorption centres of leached chernozem as soil is a complex porous multi-component media. This accords with idea about soil as a 'double' sorbent which possesses both mineral and organic parts **[6-8, 25].**

On Figures are also presented sorption isotherm parameters that characterize hydrocarbons and soil interaction: hydrocarbon sorption constant and sorbat monolayer volume, calculated from BET equation. We have evaluated the magnitude of leached chernozem surface that was active for interaction with hydrocarbons. For this the specific surface of sorbent was calculated on the basis of V_m of each hydrocarbon studied. Upon the definition on nonane it formed 11 m^2/g. This value was later compared with *S* values received by us for low-porous limestone (1 m^2/g) and high-porous ZCM (44 m^2/g). The comparison showed a presence of a significantly large soil surface available for the interaction with hydrocarbons.

The values of sorption constants for all hydrocarbons studied were of the same order which suggests a closeness of hydrocarbon sorption activity in relation to leached chernozem. However, the sorption value for aromatic p-xylene in the activity range from 0,1 to 0,5 was 30-40% higher than that of saturated hydrocarbons. This difference in sorption capacity was mainly connected with a bigger sorbat monolayer volume found for p-xylene. Because of the same reason the value of specific surface of leached chernozem that we have calculated from V_m for p-xylene has also turned out to be higher than for other hydrocarbons. It was almost two times higher than *S* value determined from V_m of non-aromatic hydrocarbons. One can suggest that overhigh values of *S* and V_m in case of p-xylene point at non-coplanar location of flat of aromatic molecule relatively to the sorbent surface upon the formation of hydrocarbon monolayer (if sorption occurs on the interface between phases) or they show more greater sorption capacity of the soil organic phase (if hydrocarbon sorption passes in a volume of soil organic matter).

b) Fractal dimension of soil surface

For the evaluation of structure of soil sorption surface and of sorption type, we have determined the fractal dimension of leached chernozem surface. The calculations were carried out according to the formula $D = 3(1 - a)$ where *D* – fractal dimension of surface, *a* - angular coefficient in the equation $\ln V_m = a \ln V_0 + b$ that connects the value of sorbat monolayer volume with the molar volume for sorbents of close nature.

Due to the fact that the sorbat monolayer volume in homologous row of aliphatic hydrocarbons does not change significantly, the estimation of fractality based on their sorption data may lead to great mistakes. That is why we have gathered the experimental data on sorption on leached chernozem of aliphatic alcohols (methanol, ethanol, propanol-2, 2-methyl-propanol-2) for the evaluation of soil fractality. The received D value formed 5,4 and has significantly exceeded the fractality value for sorbents that have 'rigid' structure (not changing in the process of sorption interaction). This abnormally high fractality value for leached chernozem suggests that the molecules of organic sorbent distribute ('dissolve') in the organic phase of soil during the interaction with sorbent.

It is possible that the same reason has caused sharp increase of sorption affinity of studied hydrocarbons when P/P_0 were lower than 0,05, **Fig.5.** This type of isotherms was distorted only in the case of decaline. That can be due to the bicyclical structure of its molecules (in comparison with other hydrocarbons) that troubles diffusion of decaline into the sorbent volume. The observed phenomenon is in accordance with Chiou ideas about soil organic matter ability to sorb organic compounds into the volume of organic phase.

The illustration of sorbat 'dissolving' in soil organic matter can be fractality data for sorbents that do not have organic matter. According to the literary sources, the fractality of silica gel and highly porous kaolinite soil does not exceed *D* = 3 (*D* respectively is equal to 2,94 и 2,92 **[12]).** Thus, the value of fractality of sorbents that are characterized by highly developed surface but do not contain organic matter did not exceed 3 - the limit value.

So we have established that leached chernozem has a highly developed and heterogenous sorption surface that exhibits low selectivity upon the interaction with hydrocarbons. Leached chernozem is capable not only of sorbing organic compounds on outside and inside soil surfaces but also of 'dissolving' them into the soil organic phase.

c) Effect of humidity on hydrocarbons sorption on leached chernozem and zeolite containing material

Diverse humidity is typical for soils. That is why it is important to take it in consideration when the hydrocarbon contamination problem is solved. An especially large amount of hydrocarbons goes into soils during spring melting of snow when soil humidity reaches a state of 'field capacity'. It is known that in humid soils hydrocarbon sorption occurs competitively with water. For the evaluation of the competitive sorption effect we have received sorption capacity values for leached chernozem with different humidity for nonane, decaline and p-xylene. On **Fig.6** the appropriate sorption isotherms of nonane are presented. The evident decrease of nonane sorption was found already with the 1% moisture content of soil. With further increase of humidity (5%) the value of sorption continued to lower steadily, and with 33% humidity ('field capacity') it reached the limit value that was the same as the sorption of nonane from the water phase. Because in the latter case the sorption of all three studied hydrocarbons turned out to be practically the same (it was equal to their sorption from water), the greatest differences in sorption on soil with different humidity were found for p-xylene which had maximum sorption values on dry soil.

For the comparison of humidity effect on sorption capacity of soil (as a bioinert sorbent) with mineral sorbents the sorption of aliphatic nonane on ZCM has been also studied, **Fig.7.** In this case a different type of humidity effect was established. The 1% moisture content in ZCM did not influence the sorption of nonane: sorption isotherms on absolutely dry and on ZCM moistured were completely the same. This pointed at the presence of micro pores in ZCM structure, which are totally inaccessible to hydrocarbons. On the other hand, for leached chernozem probably there are no sufficient limitations in structure of the internal porous soil space that would make hydrocarbon sorption difficult.

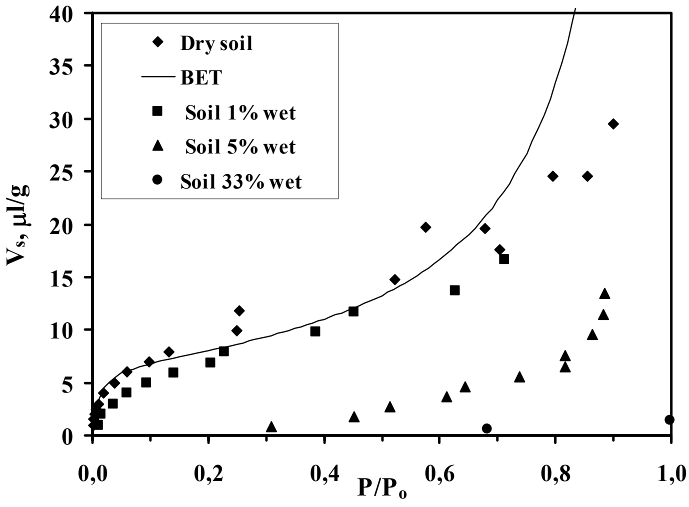


Fig.6. Effect of leached chernozem humidity on n-Nonane sorption

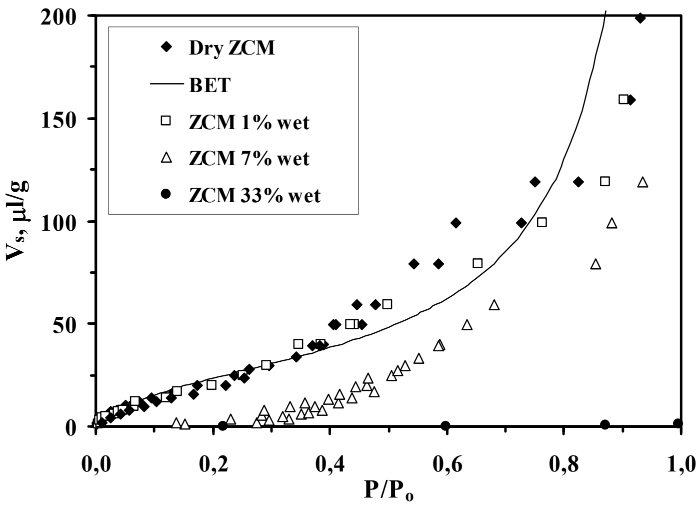


Fig.7. Effect of zeolite containing material (ZCM) humidity on n-Nonane sorption

d) Sorption on humic acids

Soil is a complex system containing organic and inorganic components. Organic matter in soils can be divided into humic and non-humic substances. Humic substances are brown to black polyelectrolytes formed by the profound alteration of non-humic substances. They are divided into three operationally-defined fractions based on their solubility as a function of pH: humic acid is soluble in basic solutions but insoluble in acidic solutions, fulvic acid is soluble at any pH value, and humin is insoluble at all pH values. Each of these fractions has been shown to play a significant role in the fate of hydrophobic organic contaminants introduced into a natural system.

In work of **[34]** the sorption of α-naphthol on lignin, collagen, chitin, cellulose and collagen-tannic acid mixture as on model organic sorbents have been studied. A very strong (on some orders higher) influence of model sorbent nature on sorption process was found. This demonstrates the principal importance of the choice of sorbent during such modelling. Because there are no arguments in favour of sorbent preference, we have thought it would be most expedient not to imitate the soil organic matter but to extract its components and to study sorption using them.

In accordance with this approach we have prepared humic acids, which present the main component of humus of leached chernozem. The sorption of nonane on absolutely dry humic acids turned out to be significantly lower (almost eight times) than on the soil, **Fig.8.** Naturally humic acids change their spatial configuration upon the selection from soil. Hence it is possible that native humic acids hold a higher sorption activity towards hydrocarbons than that of humic acids extracted in an individual state. The results of studies **[17, 18],** demonstrating that humin (an organic-mineral component of soil and non-hydrolysed residue) represents the main sorbent of hydrocarbons in soil, agree with such a suggestion. In all probability the greatest number of optimal sorption centres develops in soil upon interactions of organic with mineral components. To resolve the above question we plan to carry out additional experiments.

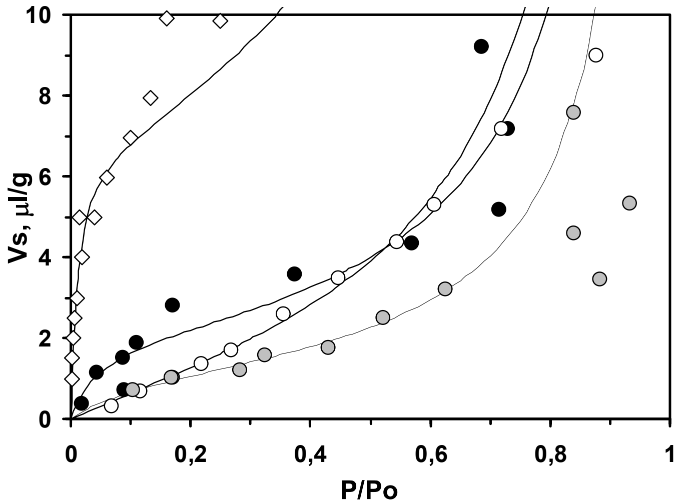


Fig.8. The comparison of isotherms of n-Nonane sorption on dry soil and different organic sorbents.
Sorbents: ◇ Leached chernozem, ● Humic acids, ○ Leaves of maize, ● Roots of maize

e) Sorption on plant materials

On **Fig.8** the obtained sorption isotherms of nonane on roots and leaves of maize are compared with isotherms on leached chernozem and humic acids extracted from it (all sorbents were absolutely dry). The sorption value for humic acids by P/P_0 = 0,4 was 1,8, for leaves it was rather greater (2,8) and for roots – nearly two times greater. In comparison with plant materials, sorption value of nonane on soil was even greater – 4-6 times as large. Taking an increased (above on 40%) protein content in maize roots compared to leaves into the account, one can suggest that differences in sorption values are caused mainly by hydrocarbon sorption on plant proteins. This lies in accordance with the idea of a key role of proteins in hydrocarbon detoxification. However, studies exist that demonstrate the important role in hydrocarbon sorption of also lipids **[18].** But the above works have been carried out with soil lipids, when plants in this aspect are less studied.

f) The influence of soil mechanical content and soil humus content on hydrocarbon sorption

Table 1. Parameters of n-Nonane sorption on different dry natural sorbents
(V_m - sorbat monolayer volume, V_S – sorption capacity, S - specific sorbent surface)

Natural sorbent	V_m, mkl/g	V_S, mkl/g (P/Po=0,4)	RSD*	S, m^2/g
Soddy podzolic soil	0,89 ± 0,05	1,31 ± 0,07	1,04	1,4
Light-gray forest soil 1	5,63 ± 0,22	9,25 ± 0,46	0,57	9,2
Light-gray forest soil 2	4,64 ± 0,10	7,52 ± 0,38	0,25	7,6
Leached chernozem	8,20 ± 0,40	13,2 ± 0,7	0,74	13,4
Humic acids extracted from leached chernozem	1,28 ± 0,06	1,78 ± 0,09	0,14	2,1
Bentonite clay	26,5 ± 1,3	43,0 ± 2,1	6,20	42,4
Limestone	0,60 ± 0,10	1,10 ± 0,10	1,08	1,1
Zeolite-containing material	107 ± 15	165 ± 8	22,1	175
Leaves of maize *(Zea mays L.)*	2,82 ± 0,17	2,82 ± 0,14	0,15	4,6
Roots of maize *(Zea mays L.)*	2,09 ± 0,20	3,25 ± 0,16	1,29	3,4

* For V_m and V_S standard deviations are presented. RSD is residual standard deviation by approximation of V_S experimental data using BET equation.

In **Table 1** the main thermodynamic parameters of n-nonane sorption on different oven-dry natural (organic and mineral) sorbents are summarized. The obtained values of sorption capacities for monoaromatic p-xylele on soddy podzolic, light- and dark-gray forest soils and leached chernozem we have putted together with ones presented in literature for toluene and benzene sorption on soils with different mechanical and humus content **[7, 25, 31]**. On **Fig.9 a,b** all these data are correlated with clay particles (< 0,002 mm accordingly to ISSA) content in soil. The existence of good correlation testifies the crucial contribution of highly dispersed clay soil fractions in the sorption. This result is justified by high magnitudes of n-nonane sorption capacity of mineral sorbents in comparison with organic ones, **Fig.10.** The conclusion of the main contribution of mineral sorption processes in the common hydrocarbon sorption on the soil attests also the absence of correlation between sorption capacities and soil organic carbon content **(Fig.9 b)** and also abject magnitudes of n-nonane sorption parameters on humic acids extracted from chernozem, **Table 1.**

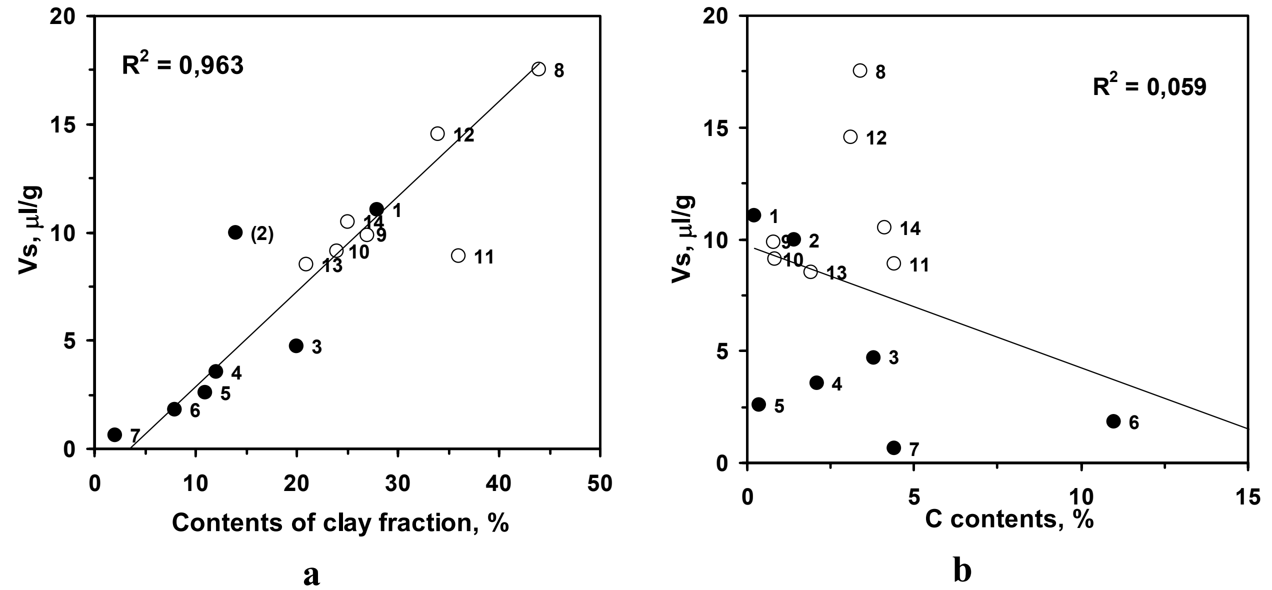


Fig.9. The dependence of sorption capacity of alkyl benzenes on different soils from their clay fraction **(a)** и organic carbon **(b)** contents
Hydrocarbons: ● Toluene, ○ p-Xylele, ● Benzene.
Soils: 1 – Marcus hook **[31]**; 2 – Adelphia **[31]**; 3 – Quakertown **[31]**; 4 – Pequest **[31]**; 5 – Plainfield **[31]**; 6 – Great Meadows **[31]**; 7 – Cohansey **[31]**; 8 – Leached chernozem; 9 – Light-gray forest soil 1; 10 – Light-gray forest soil 2; 11 – Soddy podzolic soil; 12 – Dark-gray forest soil, layer 3-10 cm; 13 – Dark-gray forest soil, layer 10-20 cm; 14 – Dark-gray forest soil, layer 20-30 cm; 15 – Woodborn **[7]**; 16 – Webster **[25]**.

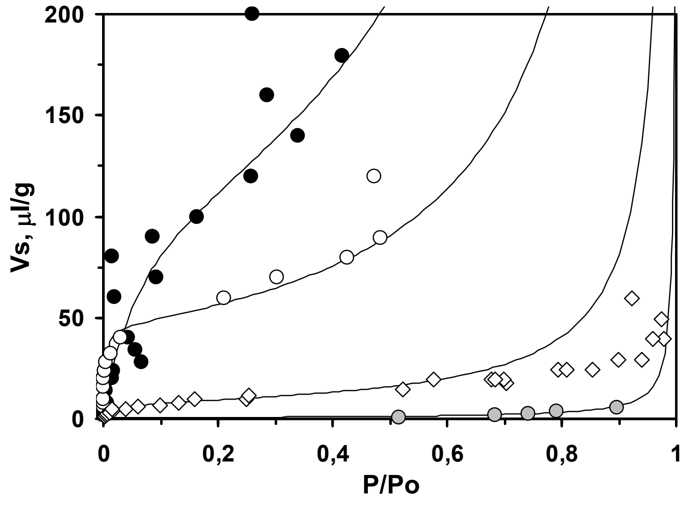


Fig.10. The comparison of isotherms of n-Nonane sorption on dry soil and different mineral sorbents.
Sorbents: ◇ Leached chernozem, ● Limestone, ○ Bentonite clay, ● Zeolite-containing material

Conclusions

1. The values of sorption of hydrocarbons on soil depended on their chemical nature. Aliphatic hydrocarbons were sorbed weaker than aromatic ones.
2. Hydrocarbon sorption occurred not only on the soil surface but also in a volume of soil organic matter.
3. The increase of sorbent humidity sharply inhibited hydrocarbon sorption.
4. In the absence of water the main contribution in the hydrocarbon sorption on soils is their interaction with mineral soil components.
5. The sorption activity of soil-plant sorbents (including the different soil types) essentially differs. The highest activity possess minerals - zeolite containing material and bentonite clay. Essentially less active are absolutely organic sorbents, the range of sorption activity for them is: roots > leaves > humic acids.

3. TRANSPORT AND DISTRIBUTION OF HYDROCARBONS IN SOIL WITH MOISTURE OF 'FIELD CAPACITY' UPON PLACING THE ZEOLITE-CONTAINING MATERIAL INTO IT

Taking into account that the soil moisture is a barrier for the infiltration of hydrocarbons in soils, we attempted to increase its content by placing natural Zeolite-containing material (ZCM). It is known that Zeolite have high sorption ability with regards to the water also **[30].**

The aim of this section was to study the processes of migration of hydrocarbons in soil with the maximal residual moisture upon placing the natural adsorbent (ZCM) into the soil.

For the decision of this task experiments were carried out analogous to the stated above, in soil columns analogous to ones described above in Section 1. The duration of experiments was 9 and 11 months, repetition was 2-multiplied. The difference from the stated above experiment (See Section 1) was that during the filling of the column into the upper 20 cm layer of soil, ZCM was placed here. Into two columns ZCM was placed on the basis of the ratio – (mass of the soil : mass of the ZCM) = 10:1 (5%), and into two columns – 1,6:1 (25%). In addition, three experiments in soil columns were carried out on infiltration and distribution of distilled water in soil profile till the placement of hydrocarbons (the duration 6 - 8 days). In these experiments chernozem was used without the placement and with the placement of the same amounts of ZCM.

The distribution of moisture in soil profile after the completion of experiments (soil without ZCM and with ZCM) on infiltration of distilled water in chernozem before placing hydrocarbons have shown that in chernozem not containing ZCM moisture of the lower (20-40 cm) layer was only 2,5% lesser than of the upper layer (0-20 cm). Upon placing ZCM into soil dampness of its upper layer increased. When the ratio (soil : ZCM) was 10 : 1, this increase formed 6% , when it was 1,6 : 1 – 7%. In all three experiments values of the moisture of chernozem within each soil layer were approximately constant. Only the upper 2-4 cm soil layers in columns were characterized by significantly higher moisture. Thus we have demonstrated sufficiently high water retention by local ZCM.

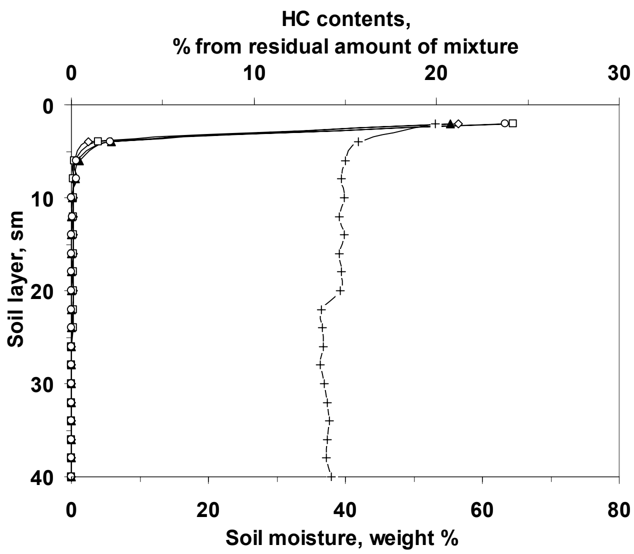


Fig.11. Contents of hydrocarbons (HC) and water in profile of leached chernozem (layer 0-40 cm) containing 5% of the inserted Zeolite-containing material (Secondary hydrocarbon contamination - after 11 months of distilled water drainage in soil with hydrocarbon-contamination originally moistened up to 'field capacity' during 6 days).
◇ n-Nonane,
□ Decaline,
▲ 1-Methylnaphtalene,
○ n-Tetradecane,
✖ Water

Taking this result into account, the experiments on migration of the mixture of hydrocarbons in leached chernozem (contained placed ZCM) with the 'field capacity' moisture were carried out. The received after the end of experiments data on hydrocarbon distribution in soil profile are presented on **Fig.11**. From these regularities is obvious that in chernozem containing placed ZCM, all hydrocarbons of the model mixture were found only in the close to surface 0-4 cm soil layer. In deeper layers their content decreased sharply (on 95-99%). In a soil profile without ZCM, 95-99% decrease of hydrocarbons concentration was detected only after 18 cm.

Conclusions. Therefore we determined that the placement of ZCM into a upper (0-20 cm) layer of chernozem of homogeneous structure with the maximal moisture, led to the sharp increase of the protective action of soil against their hydrocarbons entrance deep into on profile. This ability of ZCM allows to increase the water barrier on the way of migration of hydrocarbons in soil profile. The more considerable effect we have received using this ZCM after its physical-chemical modification.

4. GREENHOUSE-SCALE EVALUATION OF PHYTOREMEDIATION OF FUEL-CONTAMINATED SOIL USING FODDER PLANTS

The using of plants for remediation of soils contaminated with less-water-soluble materials, such as petroleum hydrocarbons, is still under development **[27, 28].** It is known that plants directly (by overgrown biomass and/or roots uptake) or indirectly (by increase of processes of their biodegradation in the rooting zone) may influence the dissipation of contaminants in soils.

The aim of this investigation was the selection and optimization of application of plants, most suitable in phytoremediation projects. The investigated plant types were 5 fodder crops - 4 monocotyledones cereals (main in the Middle Volga Region) and amaranth - dicotyledone, not traditional for Russia plant type. The plants were grown in plastic pots filled with leached chernozem, upon placement of 0 - 50000 mg diesel fuel (DF) /kg soil. First, two-weeks plants were grown in 200-g plots with 0, 5000, 10000, 20000 and 50000 mg DF /kg soil. Then, during the period from June to September, two consecutive experiments (N1 and N2) were carried out in 6-kg planting plots (in the experiment N2 there was the repeated sowing into the same plots) with 0, 5000 and 20000 mg DF /kg soil.

In the experiments the relative depression of plant growth and biomass after soil contamination was defined. In the experiment N1, the crops that were most (maize - *Zea mays*) and least (millet - *Panicum miliaceum*) tolerant to DF were found. For overgrown organs and roots of the investigated cultures, parallel inhibition of biomass accumulation in the soil with DF was established. The DF dose that was higher than 20000 mg /kg soil was lethal after 10-15 days for all the cultures apart from maize. On the contrary DF dose 5000 mg /kg soil showed only not very significant inhibiting action on plants.

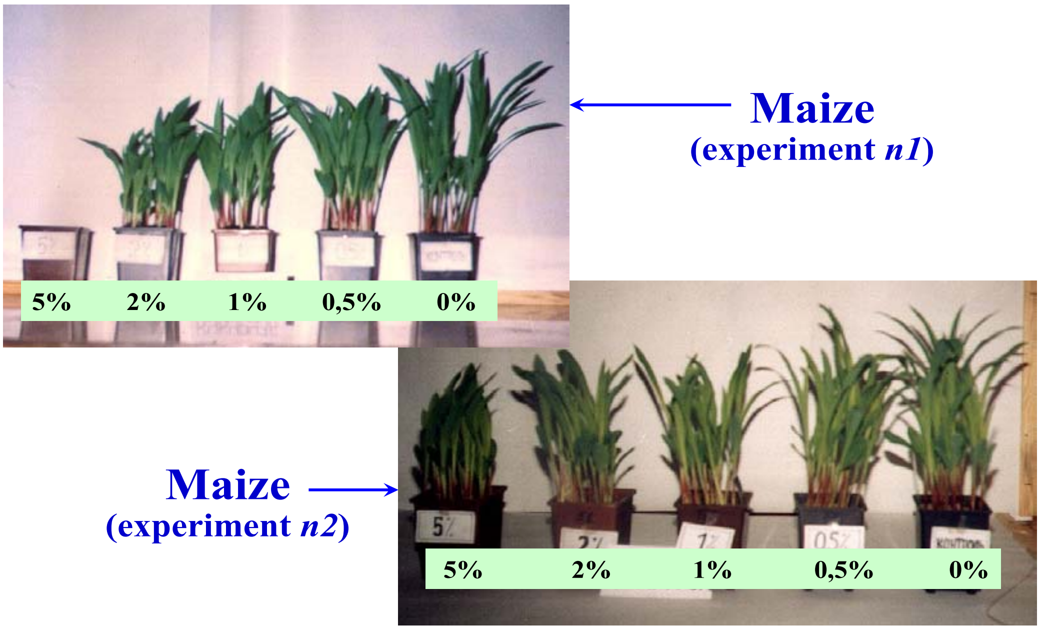


Photo 1. The tolerance of 15-days seedlings of *Zea mays* to hydrocarbon (diesel fuel) contamination

The increase of DF content induced the proportional increase of soil microbe respiration coefficient (Q_R) - that characterizes the relation of basal respiration speed (V_{basal}) to substrate-induced respiration speed (V_{sir}) - to 0,5-0,7. This showed the distortion of soil microorganisms consortium stability. The total amount of heterotrophic microorganisms increased with the increase of DF dose by a factor of 10^2-10^3. However, the same rise of their total metabolic activity (V_{basal}) was not observed. When DF content was higher than 20000 mg /kg soil the toxic effect for the soil microflora was observed. The majority of investigated plants in greater or lesser degree restored the soil microbiocenosis stability.

During the repeated sowing in the experiment N2 the significant decrease of contaminants action on both biomass and height of all plants was observed upon 20000 mg DF /kg soil. For oats (*Avena sativa*) the greatest difference between the results of experiments N1 and N2 was noted.

Using the method of gas-liquid chromatography, the accumulation levels and transformation times of petroleum hydrocarbons in overgrown biomass and roots of the plants, and at the same time the content of the residual DF in soil, were determined.

Conclusions. In the Middle Volga region among main fodder crops phytoremediation with *maize* is most suitable for recent DF soil contamination and *maize* and *oats* - for the aged contamination.

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SURFACTANT PRODUCING TNT-DEGRADING MICROORGANISMS FOR BIOREMEDIATION

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In general the biodegradation of nitroaromatic hydrocarbons is influenced by their bioavailability. 2,4,6-trinitrotoluene is very poorly soluble in water. TNT is easily adsorbed to clay or humus fractions in the soil, and pass very slowly to the aqueous phase, where microorganisms metabolize it. Biosurfactants that increase TNT solubility and improve its bioavailability can thereby accelerate degradation.

Pure cultures of microorganisms-TNT degraders were isolated by the method of enrichment cultures from samples of different-type soils contaminated by TNT (soddy-podzol, black earth, and gray forest ones). From 28 soil samples 35 isolates of microorganisms degrading TNT were taken.

The soil samples had been picked at TNT-producing sites:

- Chapaevsk city, Samara region, Russia.
- Rubezhnoye city, Lugansk region, Ukraine.

TNT-contaminated spots have been available at the specified sites for a long time. TNT-production at Ivashchenkovo settlement (called Trotsk since 1921 and Chapaevsk since 1929), Samara region, has been initiated since 1909 and still is under way. The city is located on the right bank of Chapaevka river, which is a left tributary of Volga river, 45 km south-west Samara city. The “Zarya” enterprise in Rubezhnoye city is a leading Ukrainian TNT manufacturer.

The soil had been sifted through sieves with ∅ 0.5cm cells for removal of coarse particles, then packed in plastic containers and stored at 4°C before starting experiments.

The isolated soil samples had been tested for availability of microbial activity towards TNT. By 10 g of air-dried soil, 10 ml of distilled water, and 2 mg of TNT were placed into 750 ml shaken flasks. The flasks were incubated at 150 rev/min and 24°C. Glucose, sodium succinate or sodium acetate had been used as co-substrates.

The ability of the strains to produce surfactants was studied by drop collapsing test and direct measuring of surface tension of cultural liquid after cultivation with TNT. Cells of the strains were cultivated on solid and liquid nutrient media. For drop collapsing test the cells were cultivated on solid nutrient media; then separated colonies were suspended in distilled water. Drop sustainability test was conducted on a standard 96-well plates coated with a thin layer of vaseline oil [1].

Surface tension of cultural liquid was measured after cultivation of strains in the presence of TNT with the use of a ring tensiometer. Before measuring of surface tension microbial cells were collected from liquid culture by centrifugation.

Availability of microorganisms-TNT degrader cells growth was determined in 96-well plates. Into each well of the plate was added defined medium containing 100 mg/l TNT as well as the samples taken from flasks with enrichment culture. The plates had been incubated during 7 days at 24°C, after each 1-2 days one checked changing optical density by UNIPLAN scanning.

As biological test-systems for integrated toxicity assessment daphnia in soil water extracts and earthworms in TNT-contaminated soil samples had been employed.

The soil containing 112 mg/kg TNT was mixed with equal portions of control soil samples to reduce the contaminant’s concentration. Mature earthworms were introduced to vessels with soil (1 kg); their death rate was assessed in 7 and 14 days. The possible TNT degradation had not been considered in the experiment.

For getting soil extract from water the sterile tap water had been used. 1 liter of water was added to 1 kg of soil, the filtered water extract was used for biotesting in daphnia.

The Ames test was used for examination of genotoxicity of TNT-contaminated soil [2]. Water extracts of the samples under test were examined using *Salmonella typhimurium* TA98, TA100 taken from the RCT&HRB collection of microorganisms. The genotoxic effect was revealed in water extracts of soils picked from TNT production: Chapaevsk city, Samara region and Rubezhnoye city, Ukraine.

Identification of taken isolates to genus was done according to Bergey’s manual. Of 35 TNT-degrading isolates identified to genus were 14 strains that were referred to *Alcaligenes, Bacillus, Pseudomonas, Rhodococcus, Serratia,* and *Staphylococcus* genus.

TNT degradation by strains-degraders in liquid culture was carried out on a shaker in the presence of glucose, sodium acetate and sodium succinate. TNT vanishing in cultural liquid (CL) was evaluated by color reaction on a spectrophotometer. 18 strains were studied including those producing biosurfactants. Biosurfactant-producing strains and the most active TNT-degraders are presented in Table.

Strains	Surface tension decrease	TNT degradation in liquid culture
CH 3	+++[1]	+++[2]
CH 4	?	++
CH 7	++	+
CH 12	-	++
R 5	++	+
R 10	+	++
R 12	-	+
AR 1	+++	+
AR 6	-	++

[1] CL surface tension decrease: up to 30 dynes/cm (+++), 40 dynes/cm (++), 50 dynes/cm (+).
[2] TNT concentration lowering in liquid culture on the 6th day: TNT is not detected (+++), TNT concentration lowering by 50% and more (++), TNT concentration lowering by less than 30% (+).

Among the selected strains in 5 cases only liquid surface tension decrease following cultivation in TNT-containing medium was noted. However, a part of strains-degraders that did not exhibit surface-active features were considered promising to be used in combination with biosurfactant-producing strains.

In model experiments in soil microcosms strains-TNT degraders are able to effectively reduce contaminant concentration and weaken toxic features of the environment.

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CONTAMINATION AND REMEDIATION OF SOIL OF THE TOWN KARABASH (URAL, RUSSIA)

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Chelyabinsk region is one of the unsafe territories in Russia in terms of environmental conditions and the town of Karabash located in Soimanovskaya valley is the hottest spot in the Chelyabinsk region. The territory of the town bears:

- traces of ferrous, gold, copper mine workings;
- submerged mines of shipping Karabash polymetallic deposit and sludge valley deposited by neutralized mine water flowing;
- pyrite sediments valley deposited by wasted tailings flowing from Karabash concentrating mill and tailing ponds of this mill;
- working copper smelting plant which during as long as a hundred years have released an estimated 12 million tons of hazardous substances;
- about 18.5 million tons of metallurgical wastes.

About 12,4% of the town territory is near-desert area where there are practically no soil coating and plants.

Man-caused impact on the environment is complicated by hydrographic and hydro-geological situation. As far as there are no big natural reservoirs in the vicinity of the town, the problem of water supply for copper smelting production in Karabash ("Karabashmed" JSC) was resolved by regulating a drain of two left tributaries of Miass river (that surround the town from the north and south) into the ponds and water storage within the town. Surface waters penetrate the zone of mine underworking via numerous cracks and downfalls where they are connected with water carrying horizons, forming single technogenic water carrying horizon. Sufficient changes in the old pit water circulation led to the swamping of the valley as well as to the soil contamination. Open excavation and open pit coexistence leads to the additional technogenic burdens on the territory such as soil erosion and gully formation

The town of Karabash was selected as a territory for RFNC-VNIITF researches under the 2nd stage of the ISTC project #500 «The Assessment of Priorities for Middle Urals` Environmental Pollution Prevention». The project was funded by European Community. During the second local stage of activities under the Project a methodology of the environmental priorities assessment for the Karabash (as example) was developed and applied in order to minimize the hazardous impact on the public health.

The project goals were achieved thanks to cooperation of many organizations:

- First of all those are organizations responsible for monitoring and control of environmental conditions and population health:
  - The State Center for Sanitary and Epidemiological Inspection of the Chelyabinsk region and the town of Karabash;
  - The Chelyabinsk Regional Center for Hydrometeorology and Environmental Monitoring;
  - The State Committee for Environmental Protection of the Chelyabinsk region and the town of Karabash;
  - The Committee for Natural Resources of the Chelyabinsk region;
- Karabash and Chelybinsk region Administration participated the project;
- Tree institutes of the Ural Branch of Russian Academy of Sciences have fulfilled concrete environmental investigations at the territory of the town (the Institute of Solid State Chemistry, the Institute of Mineralogy and the Institute of Industrial Ecology).

It was implied within the project that the environmental conditions in the town were to be evaluated (i) on the basis of the activities of official Russian organizations, (ii) taking into account the approaches widely used in the world, and (iii) using advanced information technologies. A four-level methodology was applied. On the first and second levels the environmental parameters of Karabsh town averaged over the town were being considered. Third and forth levels included:

- ecological and geochemical analysis of the processes of transport, spreading and accumulation of microelements in the individual object of the town ecosystem, and
- multimedia risk assessment,

dealt with the variables though detailed for the concrete points of the above territory.

A geo-information system (GIS) of Karabash was created as a part of general ecological investigation. Data of the previous studies were collected, analyzed and entered into the corresponding databases. The Center for Environmental Monitoring handed at the project team's disposal the data of Karabash soil contamination. Another sets of the data were assessed as unsatisfactory for the project tasks. To understand the causes and mechanism of chemical pollutions in the system “metallurgical process – air – soil – subsoil waters– plants – population” within the town ecosystem an additional experimental study was pursued within the whole town territory aimed at chemical and geochemical analysis of hazardous substances in such objects as :

- snow fallen on the town,
- well water,
- the potatoes grown at the town territory,
- hair of children 4-7 years old.

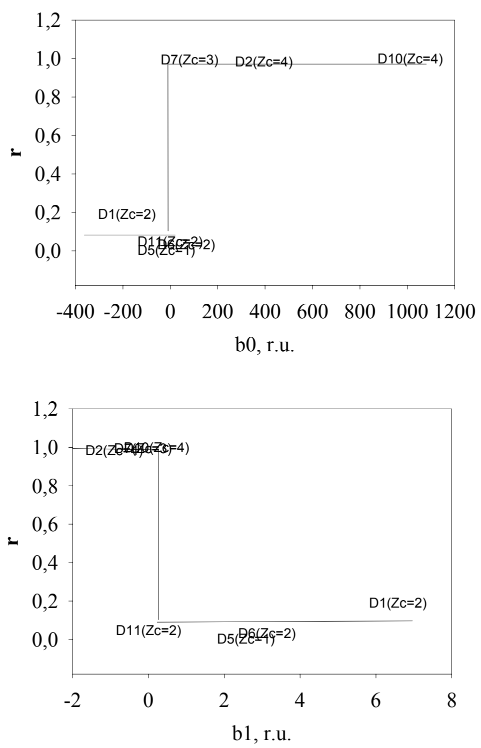

Figure. Bifurcation of correlation coefficients (**r**) as a function of the coefficients b0 and b1 of linear correlation equation C(Hairs)=b0+b1C(well), which describes connection between the levels of concentration of microelements in well water (C(well), mkg/l) and hair (C(Hairs), mkg/g).
The data are estimated by ICP-MS. D1-D11 are numbers of the town districts; Zc denotes relative total soil contamination index.

Due to the lack of measurements, the spread of the contaminants in the town atmosphere was simulated by using the inputting data on the inventory of the contamination sources of “Karabashmed” JSC, and the measurements of regional meteorological service.

Databases has been created also which included inventories of the sources of environment contaminates, of water consumption system, of sampling sites, of chemical elements abundance in the different objects of the ecosystem “air - soil – well water – plant growing – childhood hair” and of the demographic data. To estimate numerical correlation in the levels of chemical elements in different objects of the environment additional measurements have been carried out using ICP-MS, AAS and ISP-AES analytical methods. Following environmental objects have been analyzed: drinking water (~60 samples), potato, grown and collected within the territory of the town (~100 samples), hair of children at the age 4-7 years (~200 samples).

Thermodynamic simulation of metallurgical processes in the system “copper matte – copper melt – metal vapor” was carried out which shown that impurity metals vaporization is principal process in consequential spreading of chemical elements in such stratums of the ecosystem of Karabash town as snow cover, soil, well-water. Differences in dispersion and precipitation of mobile forms of chemical elements as well as non-mobile pollutants are detected in the considered ecosystem. Significant impact of the landscape on that dissipative processes in the given ecosystem is also estimated. Determined and proved are men-caused origin of soil and water bodies contamination on the territory of the town. That fact is allowed us to trace the key role of contaminants accumulation in the soil and well water upon involvement of the same contaminants into the food chains and their following assimilation by the population. Estimated was that the soil at the territory of the town is now near saturated with heavy metals and admittedly couldn’t play a role of natural geochemical barrier. Thus, the contamination of the environment leads inevitably to the corresponding rise of the chemical contaminants abundance in the well water. The last factor enhance involvement of heavy metals into the food chains.

Analysis of chemical elements distribution in the system “soil – plants” has shown that the plants differ significantly in their ability to accumulate chemical elements. It is shown that potato is the most “harmless” crop the population uses. In contrast, the onion is detected as the most harmful crop due to intensive accumulation of traces of heavy metals from the soil.

Hair bioassay analysis has indicated strong correlation between abundance of such elements as As, Hg, Pb, Cd in the well water on the territory of the town and in the hair of children at the age of 4-7. It was proved statistically that the mentioned correlation reflects an overall impact of the principal contamination source (“Karabashmed” JSC) on the ecosystem of the town (see the figure). In contrast, at the territory of districts with centralized water supply the above factor is statistically negligible.

The investigations fulfilled in the framework of the local project is allowed one to formulate concrete countermeasures aimed at the immediate protection of the population. Significant changes in general water-supply system of the Karabash town as well as radical modification of gas-purifying system of the copper smelter were proposed as the countermeasures.

Risks to public health

To assess risks to human health which follow from the detected industrial pollution the territory we followed the methodology of EPA (USA). In accordance with that methodology the individual lifetime carcinogenic risks, the annual population carcinogenic risks and risks of the excessive deaths caused by airborne particulate suspension and sulfur dioxide were obtained.

The GIS developed for Karabash in the framework of the project now allows estimate individual risk at any point of the town and the population risk at any specified district of the town. The Administration of Karabash, the State Center for Sanitary and Epidemiological Inspection and the project team jointly specified 11 districts of the town to assess and compare the population risks. The results of carcinogenic risks assessment are depicted at the tables 1 and 2.

Table 1. Ways of impact and substances included in the carcinogenic risk assessment.

	Inhalation intake	Oral intake		
Ingredients	**Air**	**Soil**	**Water**	**Potatoes**
Cadmium	+	+	+	+
Arsenic	+	+	+	+
Nickel	+			
Lead	+	+	+	+
Chloroform			+	

Table 2. Average individual lifetime carcinogenic risk induced through different contamination paths in the Karabash districts and total annual population risk in the town.

District	Air	Soil	Water	Potatoes	Total risk
1	0,000148	2,11E-05	0,000199	0,000802	0,00117
2	0,000128	6,23E-05	0,000243	0,000864	0,001297
3	6,49E-05	3,45E-05	0,001595	0,000916	0,00261
4	0,000101	3,08E-05	0,000747	0,00059	0,001468
5	7,19E-05	4,55E-05	0,001595	0,000201	0,001913
6	0,000104	4,66E-05	0,000252	0,000788	0,001191
7	3,05E-05	2,2E-05	0,0002	0,000322	0,000574
8	3,84E-05	2,66E-05	0,000277	0,000268	0,00061
9	3,27E-05	4,02E-06	0,00034	0,000208	0,000585
10	0,000175	2,97E-05	0,00065	0,000756	0,00161
11	0,000124	3,76E-05	0,001097	0,000757	0,002015
By the town	2,27E-02	6,09E-03	8,95E-02	1,35E-01	2,54E-01

The Tables 1,2 actually present the ranking of environmental problems by the town districts and by the impacting environments. Risk from air contamination is caused by the neighborhood of the

"Karabashmed" JSC and by wind rose specific for the town. It should be noted that the assessed risk in District 4 distant from the JSC is relatively high. The reason is in the different spread pattern of the dust component and soluble metal forms. Next to District 4 is Serebry Lake which play the role of water supply source for Districts 3, 5, and 11. Since there is no water purification plant here, a higher risk due to drinking water is to be expected in these districts, and that is what is observed in practice.

Arranging the districts in order of decreasing the risks due to potatoes consumption one can see on the map of the town that the territory is being divided onto the two parts. One part includes the districts which surround the "Karabashmed" JSC as a ring (a group of a highest risk districts) and another one includes the districts beyond this ring. The same division was observed when assessing the risk due to dwelling on the contaminated soil. Nevertheless the District 5 fells in the higher risk group due to soil factor, which shows that other contamination sources may exist at the territory. Main contribution to individual and population carcinogenic risk induces potatoes consumption. Since potatoes accumulates less toxic substances than other local agricultural products, a conclusion was drawn that it is better to avoid eating traditional local agricultural products grown within the Karabash territory. As a part of ISTC project ranking of the substances on carcinogenic risk rate at the territory is performed. In decreasing order they include arsenium, cadmium, lead, nickel and chloroform. The risk for arsenium impact is determined mainly by:

- Drinking water consumption from the Serebryanskiy water-supply in the districts 3, 5, 11 ;
- Consumption of potatoes being grown in districts 1, 2, that requires an additional analysis.

The results of carcinogenic and non-carcinogenic risks assessment show that total annual population risk in the town implies 2.52 excessive cases due to suspended particles, 0.695 — due to the sulfur dioxide, 0.254 — due to the intake the carcinogenic substances through all media.

Most effective measures for reducing risks.

A high priority measure to reduce the hazardous impact on the environment and public health is construction of the purification plant for "Karabashmed" JSC. Top-priority countermeasures for reduction the carcinogenic risk imply:

- to "switch off" the mechanism of well water consumption and to built centralized tap water supply system at the town,
- to construct water purification facilities for the Serebryansky water pipe or switch the water pipe onto Kialimskaya line, and
- to provide allotments of gardening for the local population at the clean districts of the town.

In the result, the technique of environmental priority assessment was developed and demonstrated on the Karabash example. The conclusions which were worked out in the framework of the project are nowadays supported by both the administration of "Karabashmed" JSC which undertake construction of sulphuric acid production plant and authorities of Karabash who plan to change existing system of residential water consumption. The Chelyabinsk region Administration is stressed that the fulfilled ecological investigation has already shown what are to be the start points of future Karabash rehabilitation program. Because the territory and human health rehabilitation measures require significant funding, during ISTC Project # 500 implementation an idea was brought up to use the internal resourcers of the territory as a source of the funding. Karabash dumps contain considerable amounts of valuable substances including copper, zinc, gold, silver, platinum metals, rare-earth elements. The value of these useful components depends on commercial treatment. No one of metallurgical works in the Ural region provides integrated cost-effective treatment because of high power and capital demand. However, some innovative proposals exist which demonstrate feasibility of such reprocessing based upon ferrous and non-ferrous metallurgy technologies.

The team of scientists is nowadays carrying a new ISTC project № 1872 **"**Working-out a Program of Remediation and Development of the Town of Karabash by Implementing Technologies for Recovery of Its Technogenic Resources"**.** Objective of this project is to create an informational, scientific and technological framework for investment projects aimed at the remediation and development of the town of Karabash by using its internal and external resources. The above project implies to:

- fully investigate all wastes accumulated in Karabash (composition, physicochemical properties and amounts);
- search out and to assess already existing and innovative technologies of copper smelter wastes treatment and remediation of the territory;

- experimentally prove that some of them can be used specifically for Karabash.

Consistent criteria will be developed to assess technologies. They will address a diversity of factors including

- performance,
- easy maintenance,
- end product marketability,
- secondary waste generation,
- risks to public safety and health,
- damage to environment,
- regulatory and legal basis,
- economic effectiveness and other.

It is planned to consider competitive interests and ways of cooperative interaction with the authorities on the municipal and regional levels and with small and medium business. The planned research will exploit Russian and worldwide experience of earlier activities in remediation of areas contaminated with radioactive and toxic substances. On the basis of obtained results we are planned to define a consistent set of technologies for waste handling and for the rehabilitation of public health and the environment in the town. The program “Karabash Remediation” should be developed under the project the elements of which will allows:

- for governing bodies of the area to concentrate investments in the most critical activities related to remediation and development of the town;
- for local government to promote the development of internal resources of the town rather than to try for external funds;
- to demonstrate available resources and their possible commercially effective use to potential investors;
- for local people to improve their lives.

Resources recovery could provide both economic and environmental benefits for the town. It also has the potential to spur the local, endogenous development of resources recovery technology for broader application within Ural and Russia and elsewhere, particularly if done in collaboration with the significant human and technological resources of the region (e.g. the technological capacities of the Institutes of the Ural Branch of the Russian Academy of Sciences, The Technical Universities, the State Center for Sanitary and Epidemiological Inspection, and the Chelyabinsk Regional Center for Hydrometerology and Environmental Monitoring, and the Russian Federal Nuclear Center). There is significant potential, therefore, for reducing some of the heavy burden of environmental contamination through the Program and, under the right conditions, for generating a set of technological assets within Karabash that may become the basis for future economic development.

Now the project team have prepared a new project ”Improving Economy and Environment at Karabash via Resource Recovery: Enhancing Access to Environmental Information and Technology Transfer” as a part of the International Program “Sustainable Development of Chelyabinsk and Region”. This project is deemed to be a frame for the practical application of the obtained and expected results of ISTC Project #1872. The goal of this new project is to promote economic development and environmental remediation in the town Karabash by providing information and assistance for resource recovery efforts. Specifically, based upon the pre-existing environmental assessments and current scientific studies of the resources of Karabash we are planning to build (i) a system which allows to transfer freely information and technologies associated with resource recovery and environment and population remediation from the State institutions to the private business, and (ii) a business incubator to assist this transfer. The projects results and the experience gained in the course of the projects implementation can be useful for finding solution of the similar problems in other parts of the Ural region and Russia.

ASSESSING CONTAMINATION OF SOIL WITH PCBs AND ITS HEALTH EFFECT IN SERPUKHOV (MOSCOW REGION)

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Up to the mid 80s there was nothing special about the epidemiological indicators in Serpukhov, as compared with other industrial cities of Moscow region. The first indication that something was wrong was the increasing incidence of diathesis in infants. In 1988 the atopic dermatitis rate in the city was 45.4 cases per one thousand of children, which was by 2.6 times higher than the average in the Moscow region (Pleskachevskaya & Bobovnikova, 1992). Diathesis was registered primarily in children whose mothers lived in the vicinity of the science and production association (SPA) "Capacitor" or were employers of this enterprise. In many cases, the disease was cured only by abandoning breast-feeding. This led to a hypothesis that the reason of diathesis was the presence of toxicants in the breast milk of mothers, which, in turn, was due to the unsatisfactory sanitary situation at the SPA "Capacitor" and on the adjacent territory.

The experimental plant "Capacitor" that was part of the whole enterprise manufactured electric capacitors for different purposes. Starting from 1960 they were using PCBs as insulating liquid for filling capacitors. The toxicity of these chemicals and in particular their ability to cause dermatitis in infants was already widely acknowledged in the 80s. Therefore, considering the inadequate technology and low industrial culture, lack of laboratory control and treatment plants at the "Capacitor" it was fair to assume that PCBs were responsible for the detected adverse effects. The first analyses of environmental and breast milk samples for PCBs were carried out in 1986 in SPA "Typhoon" at the request of the State Committee on Sanitary Epidemiological Surveillance in Serpukhov, Serpukhov district and Puschino of Moscow region (SCSES), and they confirmed the soundness of this assumption.

High levels of snow contamination with PCBs were revealed not only in the sanitary zone, but also in different directions at a distance of several kilometers from the plant. The concentrations of PCBs in water samples collected in different places of the city were as high as 14 maximum permissible levels (MPL) equal to 1 µg/l for water reservoirs. The analysis of breast milk in women living in the vicinity of the plant and working there revealed abnormally high levels of PCBs: in some samples the concentrations were as high as 990 to 2390 µg/l, while the tolerable level equals 25 µg/l (WHO, 1988). The concentrations of PCBs in breast milk of women working at a plant, but living in other parts of the city were somewhat lower (180 to 657 µg/l). These, however, were also above the tolerable level by tens of times. Thus it was established that the operations of the "Capacitor" plant resulted in significant releases of PCBs to the environment and a significant impact on human health in Serpukhov.

The results of breast milk analysis in 1986 showed that apart from working at the plant, living near the plant is another important factor responsible for elevated levels of PCBs in people. That is why, the primary purpose of the wide scale studies initiated by the SCSES in 1987 was to evaluate the environmental contamination (soil, water, air) and contamination of foodstuff produced both within the city and outside (vegetables, eggs, sour cream, milk). The results of the performed studies showed that the most contaminated area in the city was the neighborhood of private houses bordering the plant site in the south. Over many decades people had been growing in their gardens agricultural products for their needs and for the local market. The maximum levels of soil contamination were reported at a distance from 300 m to 2.5 km from the plant on the banks of the Borovlyanka rivulet flowing in the ravine and dividing the neighborhood of private houses into two parts. Outside of the city, downstream of the point of confluence with the Oka River, the allotments of the "Yurievka" cooperative are located. The rivulet is the receiver of wastewater of the plant. In 1987 the PCBs concentrations in the discharged wastewater were found to exceed MPL by 1270 times. Below the discharge point the PCBs concentrations in the rivulet water were exceeding MPL by 80 times. During spring floods the rivulet water enters the floodplain, which leads to additional yearly contamination of soil with PCBs. Furthermore, the owners of the allotments and gardens were actively using the water from the rivulet for irrigation, which resulted in formation of localized areas with abnormally high contamination. The PCBs content in soil along the rivulet banks was hundreds and thousands MPLs and the contamination level of the produce grown there (vegetable root crops, dill, parsley) was the highest in the city, with carrots being contaminated most of all: up to 9.5 mg/kg. The contamination levels for other vegetables were also high. The concentrations of PCBs in parsley, dill, spring onion were several mg/kg wet weight. The PCBs concentration in yolk of eggs collected in contaminated private yards was 100-200 times higher than in eggs bought in stores and originating from other regions. Similar to 1986, the breast milk samples of those living in the vicinity of the plant showed high concentrations of PCBs. Estimation suggests that an infant is exposed to PCBs levels exceeding the tolerable one (WHO, 1988) by tens and hundreds of times.

The studies conducted in Serpukhov in 1986-1987 demonstrated that the operations of the capacitor plant pose a major hazard for the plant workers and city residents, among them infants in the first place. As a consequence, the sanitary service of the city and of the Moscow region, with the support of the municipal authorities and the Committee on environmental protection, banned the use of PCBs for impregnation of capacitors.

After PCBs were no longer used, the study of the scale and implications of environmental contamination in Serpukhov was continued in 1988-1992. Soil samples were collected in different parts of the city in children nurseries, hospitals, parks and holiday homes, flowerbeds and agricultural lands. In all 85 samples collected in 1988 the PCBs concentrations were higher than MPL (0.06 mg/kg). In other words, over the time of plant operations almost the whole city was affected by contamination to a greater or lesser extent. Further investigation in 1989-1992 showed that only about 10% of the city territory can be regarded as conventionally clean, while the MPL is exceeded at least by ten times on 50% of the territory. It may be worth noting that strongly contaminated spots were discovered in quite unexpected places and there was no homogeneity in the contamination.

In order to estimate PCBs intake by humans, the PCBs content was determined in foods available on the city market and in drinking water. In some samples of drinking water the PCBs concentrations were found to be above MPL of 1 µg/l (Drinking water, 1996). In addition to plant crops, the study objects included milk, sour cream and cottage cheese produced by the nearby diary firms. The PCBs concentration in milk was not high (up to 20 µg/l), but increased by tens of times when milk was reprocessed into sour cream and to a lesser degree with reprocessing into cottage cheese. The estimates of the municipal sanitary service showed that the daily intake of PCBs with food was several times above the norm. High concentrations of PCBs were discovered in blood of the plant workers. As might be expected, the higher levels of about 1000 µg/l were found in the workers engaged in impregnation operations. Thus, the studies conducted in 1988-1992 showed that the decision to stop using PCBs at the capacitor plant was justified and timely.

The investigation of the environmental contamination and epidemiological situation were resumed in Serpukhov in 1997 and are continued up to the present time within several international projects. Analysis of several tens of soil samples for PCBs shows that the contamination levels have not decreased significantly since the plant was closed. The impact of this contamination on human health was also studied. For the most contaminated areas adjacent to the plant site there is evidence of the increased disturbance of reproductive health of women, reduced hemoglobin level and erythrocytes in blood. Also post vaccination immunity in children and adolescents and increased mortality in the population in general were detected (Khakimov et al., 2000; Popova, 2000; Revich et al., 2000). It may be considered to be proved that all these adverse manifestations are results of high levels of PCBs in the environment and agricultural produce grown on the contaminated areas. Specifically, it was demonstrated that the likelihood of infertility increases with certainty with increase in PCBs level in blood of women. (Revich et al., 2000)

The data available in SPA “Typhoon” on contamination of the environment and biological materials were entered in the database in Microsoft Excel. This database contains a total of 1000 results of PCBs determinations in samples of different type. The database contains results of 360 determinations of PCBs in soil, 16 in air, 83 in water, 50 in snow and 70 in root vegetables, 14 in fruit, 33 in leaf vegetables, 33 in tree leaves and needles, 73 in eggs, 109 in breast milk and 20 in blood. The majority of the data were obtained in 1987-1992, and also in 1997 and 1999. The following sections provide analysis of the derived data of each type from the standpoint of their use for the project purposes and necessity of additional measurements.

An important feature of PCBs contamination in Serpukhov is high heterogeneity of contamination. As demonstrated by the data of Table 1, the contamination of the surface soil layer can differ by five orders of magnitude or so within one yard. The contamination is less heterogeneous on cultivated lands than on virgin ones, but even there a ten-fold difference may be expected. That is why, when a program of field experiments on the selected experimental plots is designed, particular attention should be given to representativeness of collected soil samples.

The discovered high heterogeneity of PCBs content in soil is indicative of the occurrence of localized contamination sources. Of them the principal sources are:

- leakage of PCBs during storage, transportation and use
- irrigation of agricultural lands with contaminated water from the Borovlyanka rivulet and from tanks used earlier for PCBs transportation and storage;
- sewage and waste waters from the site;
- inundation of the floodplain of the Borovlyanka rivulet during floods.

Table 1. PCBs content in soil in selected places of Serpukhov (SPA “Typhoon” database)

Location	Year	Sampling location	Layer, cm	PCBs, mg/kg
Kondensatornaya,10	1988	Virgin land, 1 m of the right bank of the Borovlyanka rivulet	0-5	35700
		Virgin land the upper point	0-5	119,5
		Garden, middle of the plot	0-5	3,9
		Garden upper point	0-5	11
		Virgin land, entrance to yard	0-3	0,3
		Virgin land, left bank of the Borovlyanka rivulet	0-3	23
		Virgin land, right bank of the Borovlyanka rivulet	0-5	11
		Virgin land, left bank of the Borovlyanka rivulet	0-5	8,1
Moskovskaya, 85	1988	Garden	0-5	0,22
		Garden	0-5	2,4
		Garden	0-5	2,6
Uglovaya, 8	1989	Garden	0-10	3,4
		Garden	0-10	8,5
		Garden Garden	0-10 0-10	2,6 4,39
		Garden	0-10	1,4
Around the plant	1991	Virgin land	0-10	108
		Warp	0-10	1836
		Virgin land	0-10	260
		Virgin land	0-10	6,4
		Virgin land	0-10	0,19
Strelkova, 16	1995	Garden	0-20	40
		Garden	0-20	54
		Garden	0-20	200

The available data on the long-term dynamics of PCBs content in the soils of Serpukhov are rather conflicting. Some samples collected in 1999 in the same non-agricultural areas as those studied in 1992 showed somewhat decreased concentration of PCBs, but in other places it was practically unchanged or increased (Bobovnikova et al., 2000). This suggests that the redistribution of PCBs across the territory of Serpukhov continues up to the present time and secondly, no major increase in the total contamination level due to natural reasons should be expected in the near future. The last conclusion is confirmed by the measurements of PCBs in two places of the most contaminated areas of Serpukhov on different years presented in Table 2. The high contamination levels registered in 2001 indicate that, possibly, there were additional PCBs entering the soils under study in the last few years. Most likely, the source of these inflows is the nearby Borovlyanka rivulet.

In the most of the sampling points the vertical distribution of PCBs was determined. The data in Table 3 show that PCBs are distributed by the soil profile in a complicated way and even in 1988 not only the surface soil was affected by contamination. The PCBs level was significant to the depth down to 60 cm and, possibly, even lower, which indicates that, most likely, groundwater on the plant site was subjected to significant contamination too. This guess is supported by the data on well water contamination.

Table 2. Long-term dynamics of PCBs content in the surface soil layer in some places of Serpukhov (SPA “Typhoon” database)

Location	Year	Month	Layer, cm	PCBs, mg/kg
Strelkova, 16	1987	October	0-50	267
	1988	August	0-5	24
	1988	August	0-5	9,1
	1995	September	0-20	40
	1995	September	0-20	54
	1995	November	0-20	200
	1999	July	0-10	172
	1999	July	0-10	182
	1999	July	0-10	13,6
	2001	May	0-20	120
	2001	June	0-20	1342
Kondensatornaya, 8	1988	August	0-5	11
	1997	September	0-10	14
	2001	June	0-20	28

Table 3. Vertical distribution of PCBs in soils sampled in 1988 near the houses ? 8 and 10 on Kondensatornaya street (SPA “Typhoon” database)

Layer, cm	PCBs, mg/kg					
	Point 1*	Point 2	Point 3**	Point 4	Point 5	Point 6**
0-5	35700	119,5	3,9	8,1	11	11
5-10	18300	356	3,6	20,8	0,4	96
10-20	2350	89,9	1,9	13,6	1	146
20-30	2740	7,1	4,7	10,5	0,7	9,7
30-40	29,4				3,8	
40-60	50,6				4,1	

*The point is 1 km of the Borovlyanka rivulet
** Tilled areas

The PCBs level was determined in 23 agricultural plant species. However, no parallel determination of air contamination was done, which makes impossible to estimate quantitative characteristics of distribution of gaseous PCBs between leaf vegetables and the air. In order the parameters of this distribution be estimated, additional experiments are required. Results of such experiments can be used for calculation of contamination of those kinds of agricultural produce, which accumulate hydrophobic organic substances primarily from the air.

They are also useful for solving the reverse problem: estimation of air contamination based on PCBs levels in leaf vegetables, fruit, tree leaves and needles. In some cases, plants were analyzed simultaneously with the soil on which they had been grown. This allows deriving the bioconcentration factors (BF) equal to the ratio of PCBs concentrations in plants (or its edible part) and in soil. Results of calculating BFs for some crops are shown in Table 4. For potatoes the spread in BFs is several orders of magnitude, while in other cases the difference in the values for different areas is not more than several fold. There is no trend for decrease in PCBs accumulation with time. Vegetable leaf crops tend to accumulate organic substances primarily from the air. The values of BF for parsley indicate that no major changes occurred from 1988 to 1997 in the quantitative parameters of PCBs transfer from soil to plant leaves through the air. Accumulation of PCBs in vegetable root crops in 1997 was lower that in 1988. This can be due to PCBs aging effect and a decline in biological bioavailaibility as a result. However, in this case the PCBs concentration in the air above the soil should be decreasing with time too and, accordingly, contamination of leaf vegetables.

Table 4. The values of BF for selected products grown in Serpukhov

Agricultural produce	Address	Year	Month	BF*
Potato (peeled root)	Kondensatornaya, 8	1988	August	1,86E-02
	Strelkovaya,16	1988	August	1,70E-01
	Strelkovaya,16	1988	August	1,91E-02
	Tsentralnaya, 19	1988	August	1,43E-01
	"Yurievka" cooperative, allotments 1-3	1997	June	1,41E-04
	Raboche-Krestyanskaya, 43	1997	June	3,33E-03
Parsley	Kondensatornaya, 10	1988	August	3,91E-02
	Yurievka" cooperative, allotments 1-3	1997	June	2,77E-02
	Raboche-Krestyanskaya, 43	1997	June	1,08E-01
Tomato(fruit)	Kondensatornaya, 10	1988	August	2,60E-02
	Uglovaya, 8	1989	September	2,64E-02
Beans	Kondensatornaya, 8	1988	August	2,07E-03
	Raboche-Krestyanskaya, 15	1988	August	8,46E-03
Turnip (peeled root)	Kondensatornaya, 10	1988	August	8,28E-02
	Raboche-Krestyanskaya, 43	1997	June	3,75E-03
Carrots (peeled root)	Kondensatornaya, 10	1988	August	7,07E-02
	Yurievka" cooperative, allotments 1-3	1997	June	4,37E-02
	Yurievka" cooperative, allotments 1-3	1997	June	2,77E-02
	Raboche-Krestyanskaya, 43	1997	June	4,14E-02

*The total concentration of PCBs in plant was estimated in wet weight and concentration in soil in dry weight.

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EVALUATION OF THE POTENTIAL HEALTH RISKS RESULTING FROM WORKER AND PUBLIC EXPOSURES TO TOXIC AND RADIOACTIVE SUBSTANCES IN THE CHELYABINSK REGION
(Project # 60)

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The main objective of the project is to evaluate human health effects of radiation with an example of selected worker and public cohorts.

From potential objects of the Chelyabinsk region two towns Ozyorsk and Snezhinsk were chosen.

The town of Ozyorsk with the population of about 90 thousand most of whom has been living there from the first years of PA MAYAK operation fits mostly the study on effects of low doses of radiation upon members of the public.

The town of Snezhinsk founded in 1957 and now populated by about 50 thousand people was chosen as a control for Ozyorsk in epidemiological studies.

As critical groups of the public the project considered cohorts of children of 1974-1988 years of birth who were born in the town (Ozyorsk or Snezhinsk) or moved to the town at age of 0-14 years and had lived there a year at least.

Environmental monitoring was taken for the areas under PA MAYAK impact including the town of Ozyorsk itself, monitored zone of PA MAYAK, and agricultural lands of specialized PA MAYAK's farms - "Burino", "Kuluevo", "Ozyorskoye" (ESRS). Square of the area under survey is about 1,800 km^2.

Monitored territory also includes the town of Snezhinsk, the "Beregovoy" farm and private kitchen-gardens of Snezhinsk residents. Snezhinsk is 50-60 km to the north from PA MAYAK's source of releases. Minimum distance from the EURT axis is about 20 km.

In the course of the project implementation more than 2,000 samples of the environmental objects and agricultural products were taken for analytical determination of their specific activity. To measure specific activity of ^{90}Sr and Pu in samples radiochemical methods were used. Specific activity of ^{137}Cs was measured by scintillation methods.

Sources of Contamination in the Study Region:

The following major factors contributed to radioactive contamination of the environment in the past:

⇒ intensive discharges of radioactive liquid wastes into the Techa river in 1949-1956 that resulted in high-level, still existing contamination of the river along its entire length. Flowing in latitudinal direction from PA MAYAK the river is not now a source of additional exposure of children in Ozyorsk and Snezhinsk, however its radioactive contamination burdens the entire radiation environment in the region and in some cases may lead to appearance of small batches of foodstuffs highly contaminated with radionuclides;

⇒ chemical explosion of a repository with high-active waste in 1957 that resulted in the contamination of an area of about 20 thousand square kilometers (Eastern Ural Radioactive Trace) with long-lived ^{90}Sr and ^{137}Cs. A significant part of the contaminated area is included in the study being an actual source of additional exposures for the Ozyorsk and Snezhinsk residents;

⇒ airborne suspension of radioactive substances (silt sediments) from dry bed of the Karachai lake in 1967 (the lake was a depositary of radioactive liquid wastes) that additionally contaminated the study region with ^{90}Sr and ^{137}Cs;

⇒ regular releases of gases and aerosols to the atmosphere in the 50-s from PA MAYAK's plants. Residual contamination of the study region with long-lived radionuclides accumulated before the 70-s is of rather high level. Against this background the contribution of current atmospheric releases to the areal contamination prove to be insignificant.

Almost simultaneously with the PA MAYAK construction a central heating-and power plant (Argayash CHPP) was put into operation in the settlement Novogorny. The plant uses brown coal the Chelyabinsk coal-field with ash to 43 %. In the period from 1976 to 1986 the Argayash TPP (**ATPP**) every year released into the atmosphere to 85 t of ashes with high NRN content (see Table1 and Table 2.)

Table 1.

Average annual atmospheric release of NRN with ashes of ATPP in the period of 1982 - 1985

Radionuclide	**U** t/y	**Th** t/y	**^{210}Po** Ci/y	**^{210}Pb** Ci/y	**^{226}Ra** Ci/y	**^{228}Th** Ci/y	**^{40}K** Ci/y
Release	0.44	1.1	0.3	1.2	0.17	0.13	1.5

Table 2.

Average annual specific activity of SO_2, NO_x, volatile ash in near ground air nearby the ATPP mg/m^3

Distance from ATPP	**Number of samples**	**maximum one-time concentrations**			**average daily concentrations**		
		SO_2	**NO_x**	**volatile ash**	**SO_2**	**NO_x**	**volatile ash**
5	31	0,14	0,06	0,43	0,07	0,03	0,23
25	12	0,04	0,09	0,25	0,03	0,015	0,13
average		0,19	0,07	0,38	0,06	0,04	0,18

Together with radioactive releases of PA MAYAK atmospheric releases of NRN from the Argayash CHPP contribute to the natural background of the region under study.

Density of Soil Contamination

Earlier radiation monitoring and that one additionally performed in the course of the project implementation within the area under PA MAYAK impact and VNIITF inspected area allowed reliable estimation of levels of residual contamination of soil with long-lived ^{90}Sr, ^{137}Cs and Pu. Moreover, the estimates were confirmed by official maps (fig. 1. -2) on current (as of 1977) levels of surficial contamination with ^{90}Sr and ^{137}Cs in the South Ural region resulted from the accidents of 1957 and 1967 at PA MAYAK that were developed with the participation of the project participants.

The data presented in Table 3 contain generalized levels of radioactive contamination within the areas. Analysis of the data shows that for residential areas of Ozyorsk and Snezhinsk moderate levels of contamination are typical now.

Area of the middle part of EURT is a nature management territory for the residents of Snezhinsk. Outlying areas of the trace are used as farming lands and private kitchen gardens of the residents of the settlements who supply cities with agricultural products.

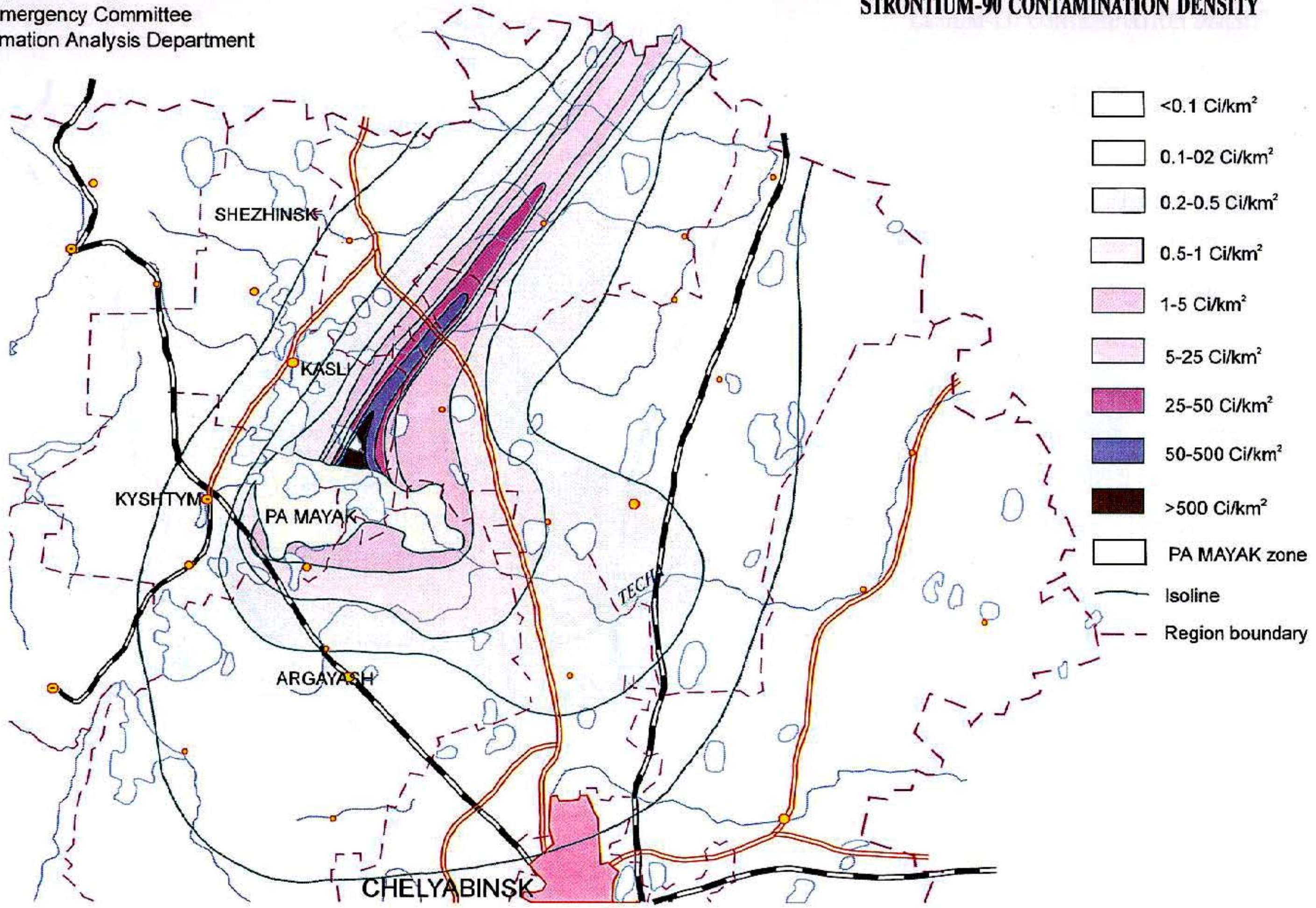
Involvement of contaminated territories at the trace axis into agrarian use is a source of secondary contamination of private kitchen-gardens at the remote territories, in particular, within RAA Snezhinsk.

Implemented scheme of profile observations consisting of 6 profiles (fig. 3.) allowed using limited number of observation points to detail distribution of radionuclides, and obtain generalized spatial characteristics of the trace over a stretch of ~40 km in the direction of radioactive cloud propagation.

Fig. 4 presents contamination levels in the middle part of EURT in 1957 (a) and 1997 (b).

RADIOACTIVE CONTAMINATION OF SOILS IN THE NORTH OF THE CHELYABINSK REGION

Chelyabinsk Region Administration
Emmergency Committee
Infomation Analysis Department



The map is based on data provided by
the Chelyabinsk Regional Center for Hydrometeorology
and Environmental Monitoring

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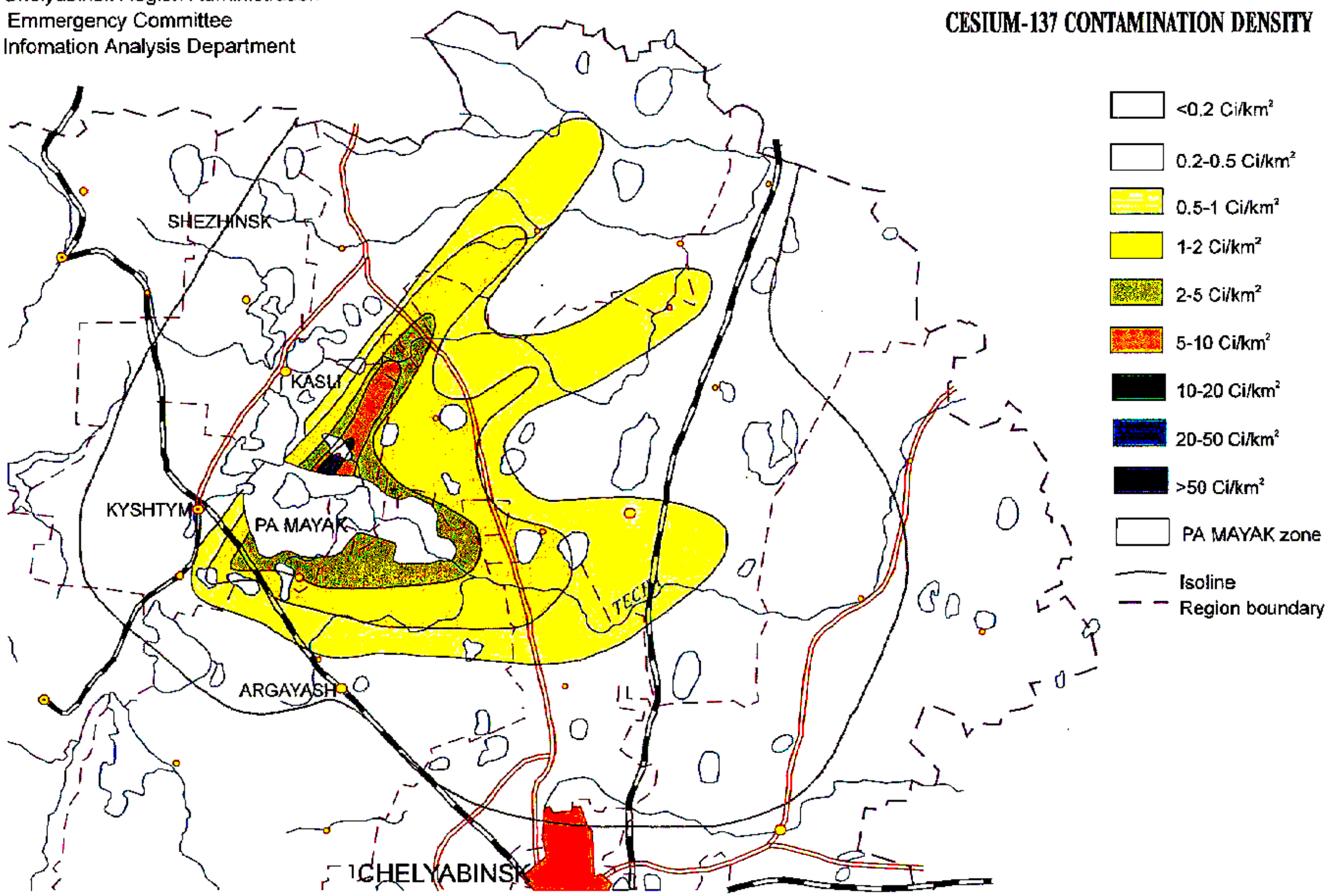

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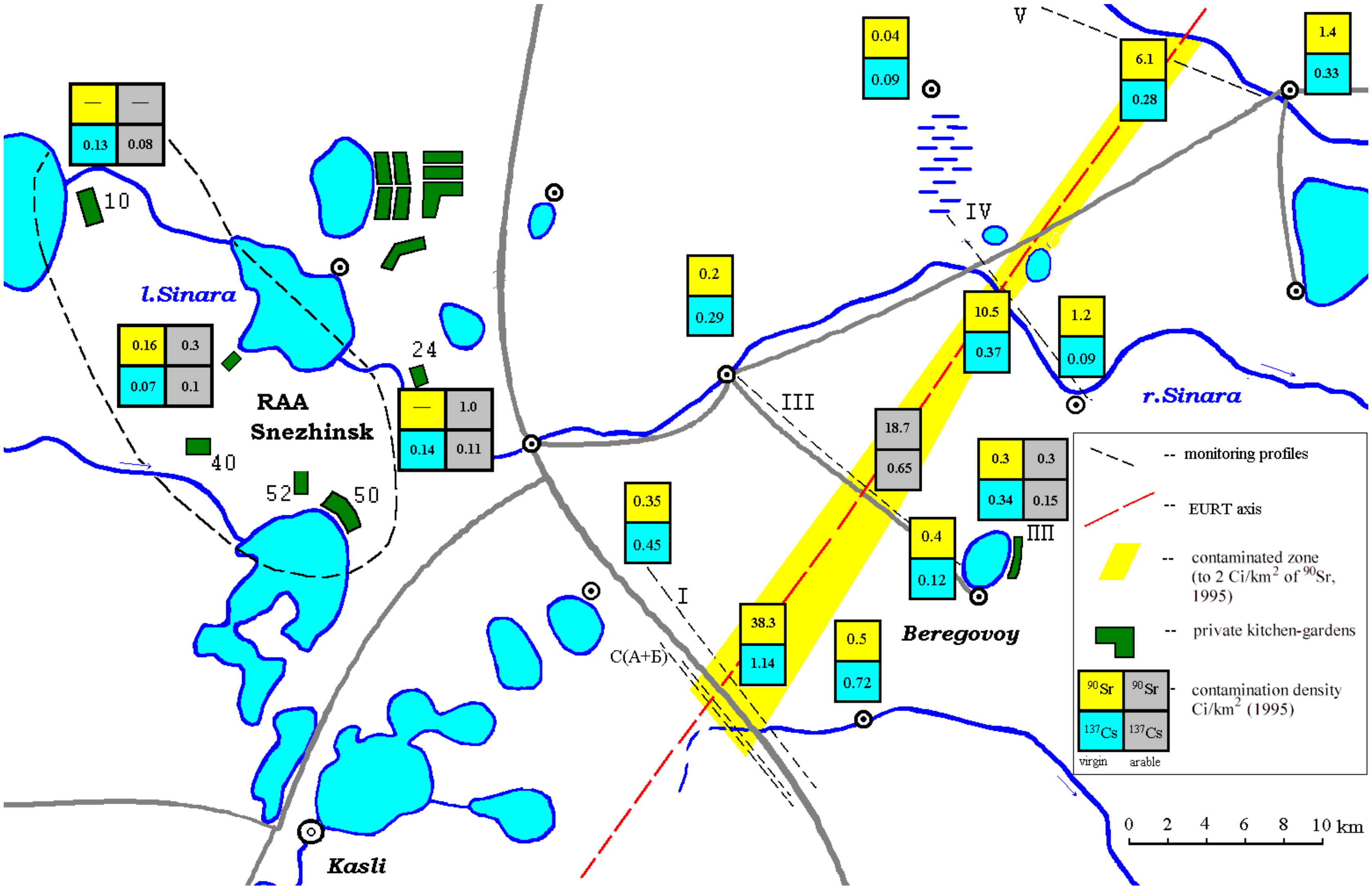
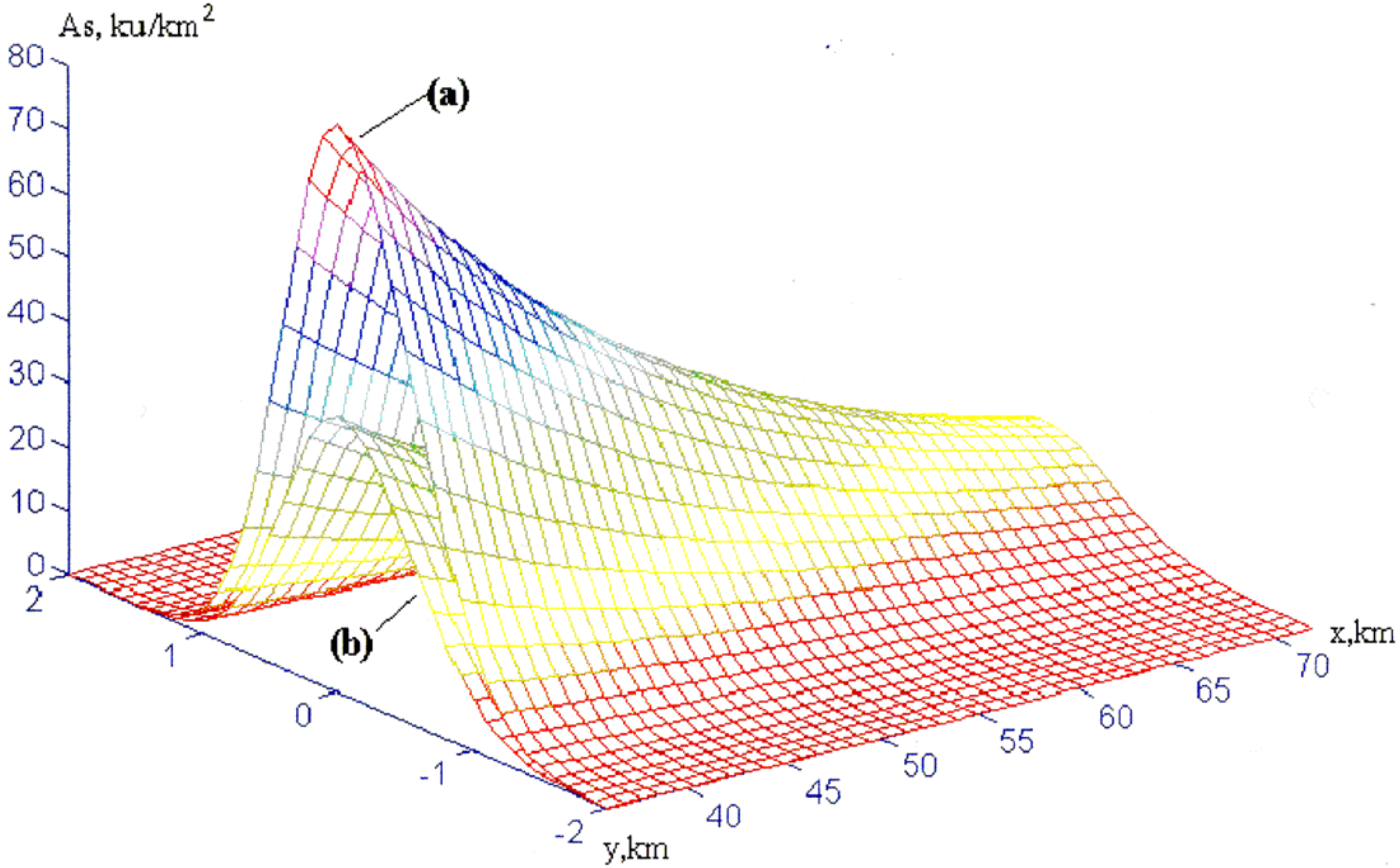


Fig. 3. Sketch map of monitoring taken for the middle part of EURT and RAA Snezhinsk.



(a) -1957 (b) - 1996

y - distance from EURT axis

x - distance along EURT axis

Fig. 4

Radionuclide Content of Water in Surficial Reservoirs

Within the scope of the project estimations were made of ^{90}Sr, ^{137}Cs and ^{3}H contents of water in the lakes that are sources of drinking water for Ozyorsk (the Irtyash lake) and Snezhinsk (the lakes Sinara and Itkul). All the reservoirs are beyond the official boundaries of Eastern Ural Radioactive Trace (EURT). The presence of ^{90}Sr and ^{137}Cs in water of the lakes is stipulated by the catchment from the area impacted by all factors including global radioactive fallout and residual, though not high, radioactive areal contamination resulted from earlier activity of PA MAYAK. The presence of ^{3}H in the environment is a result of production activities of PA MAYAK and VNIITF.

The investigation into the radiation environment in the reservoirs that are sources of drinking water shoed the following.

Studied reservoirs are within the area with levels of ^{90}Sr up to 3.7 kBq/m^2. The initial contamination was a result of radionuclide deposition to water table of the lakes. In next years added the secondary contamination due to the catchment from areas contaminated with radionuclides. The increase of radionuclides in the reservoir caused by the catchment is not higher than 50% of the initial contamination in a running reservoir. The catchment area adds from 1 to several per cent of current radionuclide content each year. Catchment coefficient depends upon landscape of the area and differs hundreds times for forest and meadow or field. Far less amount of radionuclides is derived to the reservoir from ground water and global fallout. Integral inventory **Q** of radionuclides in a reservoir is mostly determined by its amount in water and sediments.

Qlake = **Q** silt + **Q** water + **Q** biomass

100% 90% 9.9% 0.1%

The distribution is typical for strontium-90 and cesium-137. Table 3 contains data on radionuclide redistribution between lake components.

As it seen from Table 3, redistribution of uranium and tritium oxide between aqua components differ from that of ^{90}Sr and ^{137}Cs that should be taken into account when estimating radionuclide intake via ingestion pathway.

Table 3.

Radionuclide content of lake components,Bq/l(kg), uranium-10^{-6} g/l(kg)

Nuclide	Reservoir	Water	Sediments	Water Vegetation	Fish
Strontium-90	Sinara	0.048	-	-	-
1993	Itkul	0.09	-	46.0	15.3
	Irtyash	<0.1	-	-	-
Cesium-137	Sinara	0.051	-	-	-
1993	Itkul	0.04	-	16.0	4.6
	Irtyash	<0.1	-	-	-
Uranium	Sinara	0.7	3450	510	2.2
1987,1988, 1993	Itkul	0.7	1040	128	5.9
Tritium	Sinara	122	137	204-337	100
1993	Itkul	55	81.4	122-233	96.2
	Irtyash	200	-	-	-

Radionuclide Content of Diet Components

In the course of the project implementation estimates were made of ^{90}Sr and ^{137}Cs content of main food products consumed by the Ozyorsk ands Snezhinsk residents. Three groups of food products were considered given the following delivery sources:

⇒ centralized state delivery of foodstuffs to the towns;

⇒ dedicated agricultural enterprises of Ozyorsk and Snezhinsk - main providers of marketable potato, fresh milk and vegetables;

⇒ non-centralized delivery from backyards of inhabitants of neighboring settlements.

Radionuclide contents of food products from centralized delivery were estimated on data of sanitary radiation control being practiced by local offices of State Committee for Sanitary Epidemiological Inspection. In Ozyorsk the control is performed in the fullest scope. Data from Tables 4- 5 show average levels of ^{90}Sr in products over appropriate time periods for the whole amount of foodstuffs form centralized delivery.

Table 4.

Average annual specific activity of ^{90}Sr in main food products from centralized delivery in Ozyorsk in 1974 - 1995, Bq/kg*

Survey period, year	Milk and milk products	Meat, meat products, fish	Bread, bread products, cereals	Potato	Vegetables (fruit and root crops)	Greens	Drinking water
1974-1975	0.81	0.25(0.23-0.27)	0.34(0.33-0.13)	0.67(0.52-0.81)	1.41(1.22-1.59)	11.84(7.40-16.28)	0.37
1976-1980	0.6 (0.44-0.8)	0.22(0.18-0.34)	0.27(0.18-0.35)	0.78(0.59-0.81)	1.48(0.85-2.29)	8.51(6.29-10.36)	0.24(0.22-0.26)
1981-1985	0.52 (0.41-0.85)	0.23(0.19-0.29)	0.24(0.22-0.27)	0.81(0.48-1.33)	2.04(1.6-2.33)	5.55(1.33-14.43)	0.19(0.18-0.22)
1986-1990	0.3 (0.23-0.41)	0.13(0.09-0.18)	0.12(0.10-0.15)	0.89(0.37-1.30)	0.70(0.37-0.93)	4.07(0.74-6.66)	0.16(0.15-0.18)
1991-1995	0.24 (0.2-0.27)	0.20(0.11-0.19)	0.16(0.11-0.20)	0.56(0.30-1.18)	1.11(0.67-1.55)	5.18(3.18-8.14)	0.11(0.07-0.15)

* - In brackets - ranges of average annual values of specific activity.

Table 5.

Average annual specific activity of ^{137}Cs in main food products from centralized delivery in Ozyorsk in 1974 - 1995, Bq/kg*

Survey period, year	Milk and milk products	Meat, meat products, fish	Bread, bread products, cereals	Potato	Vegetables (fruit and root crops)	Greens	Drinking water
1974-1975	0.89	0.85	0.59(0.56-0.67)	1.33(1.0-1.63)	1.04(0.59-1.52)	1.70(0.85-2.55)	0.07
1976-1980	1.11 (0.70-2.0)	1.15(0.52-2.0)	0.48(0.34-0.63)	1.59(0.78-2.11)	1.44(0.44-3.07)	1.81(1.0-4.81)	0.04
1981-1985	1.15 (0.70-1.5)	0.63(0.37-1.11)	0.27(0.15-0.41)	1.48(0.96-2.41)	1.92(0.93-2.44)	0.96(0.63-1.52)	0.04
1986-1990	0.48 (0.2-0.74)	1.11(0.74-1.41)	0.37(0.21-0.44)	0.93(0.67-1.30)	0.48(0.33-0.67)	1.26(0.48-1.48)	0.05(0.04-0.07)
1991-1995	0.32 (0.26-0.41)	0.85(0.59-1.78)	0.21(0.19-0.24)	0.63(0.22-1.41)	0.93(0.33-2.52)	1.0 (0.59-1.85)	0.03(0.02-0.04)

- - In brackets - ranges of average annual values of specific activity.

Table 6.

Average specific activity of ^{90}Sr and ^{137}Cs in products from dedicated farms in 1974 - 1995, Bq/kg

Product	1971-1975		1976-1980		1981-1985		1986-1990		1991-1997	
	^{90}Sr	**^{137}Cs**	**^{90}Sr**	**^{137}Cs**	**^{90}Sr**	**^{137}Cs**	**^{90}Sr**	**^{137}Cs**	**^{90}Sr**	**^{137}Cs**
Farm "Ozyorskoye"										
Potato	1.07	2.11	1.67	1.30	4.07	2.63	1.92	0.52	0.67	0.70
Vegetables	4.81	1.22	5.55	0.85	3.03	0.74	2.37	1.37	2.15	1.26
Milk	3.11	4.44	6.29	1.30	3.40	2.04	1.92	3.63	1.67	2.67
Farm "Burino"										
Potato	0.41	0.81	0.20	0.81	0.19	0.20	0.19	0.18	0.15	0.11
Vegetables	1.18	0.30	1.0	0.25	0.93	0.16	0.70	0.13	0.59	0.16
Milk	0.70	0.89	0.59	0.59	0.37	0.52	0.22	0.37	0.16	0.24
Farm "Kuluevo"										
Potato	0.44	0.52	0.35	0.41	0.17	0.28	0.16	0.26	0.12	0.10
Vegetables	0.81	0.89	0.70	0.70	0.35	0.48	0.34	0.41	0.18	0.10
Milk	0.81	1.0	0.81	1.0	0.26	0.52	0.14	0.22	0.13	0.21
Farm "Beregovoy"										
Potato	0.35	0.95	1.10	1.10	0.45	1.05	0.30	0.75	0.13	0.41
Vegetables	1.05	0.85	1.50	0.75	1.15	0.95	0.45	1.15	0.70	0.22
Milk	0.25	0.65	2.20	1.35	0.35	1.40	0.14	0.70	0.48	0.24

A comparative analysis was taken on levels of ^{90}Sr and ^{137}Cs in agricultural products provided by dedicated farms for Ozyorsk ("Ozyorskoey", "Burino", "Kuluevo") and Snezhinsk ("Beregovoy") (Table 6.). It was found that main foodstuffs (milk, vegetables, potato) produced in "Beregovoy" have almost the same specific activity of ^{90}Sr as the products from "Burino" and "Kuluevo". The products from "Ozyorskoey" has 2-4-folded the above activity. However, due to relatively small fraction of products from "Ozyorskoey" (approximately 10%) in the total amount foodstuffs delivered to Ozyorsk from "Burino" and "Kuluevo", average annual intake of ^{90}Sr with the products is almost equal in Ozyorsk and Snezhinsk.

Results of Dose Assessment

Accepted Assumptions and dose calculation methods

The project estimated annual effective and equivalent doses to tissues for children of Ozyorsk and Snezhinsk born in 1974 to 1995, as well as the doses accumulated from the birth to 1995 at permanent residential living in the towns.

The doses were estimated resulted form external exposures to technogenic radiation of the Ozyorsk and Snezhinsk environment (minus natural background) and airborne radionuclides from atmospheric releases of PA MAYAK. The doses of external exposure to atmospheric releases were calculated for radioactive noble gases (^{41}Ar, ^{85m}Kr, ^{87}Kr, ^{88}Kr, ^{133}Xe, ^{135}Xe, ^{135m}Xe, ^{138}Xe and ^{131}I.

To estimate annual equivalent doses of external exposure resulting from atmospheric releases (calculations for submersion into radioactive cloud), we used dose coefficients relating dose to specific activity of radionuclides in air

Doses of internal exposure to the whole body, tissues and organs were estimated for the radionuclides mostly contributing to the resultant dose of internal exposure (T, ^{90}Sr, ^{131}I, ^{137}Cs, Pu). As initial data for calculating doses of internal exposure we used:

- ♦ average annual specific activity of T in urine;
- ♦ average annual specific activity of ^{131}I in near ground air;
- ♦ annual ingestion intake of ^{90}Sr and ^{137}Cs;
- ♦ annual increment in Pu content body.

Equivalent Doses of Combined Exposure

The highest doses were accumulated in bone tissue (20mSv in Ozyorsk and 7.6 mSv in Snezhinsk), thyroid (6 and 5 mSv, respectively), red bone marrow (4 and 3 mSv). Doses to gonads, lungs and liver are approximately equal in each of the town (2.2 - 3.6 mSv in Ozyorsk and 1.6 - 1.9 mSv in Snezhinsk).

Effective Doses of Combined Exposure

Estimated annual effective doses to young people of Ozyorsk and Snezhinsk display that in the period of 1974 - 1995 annual effective doses to the public of the two towns distinctly reduced: from 0.25 mSv/y to 0.05 mSv/y in Ozyorsk and from 0.17 mSv/y to 0.03 mSv/y in Snezhinsk.

The estimates give the evidence that levels of cumulative effective doses of technogenic radiation are insignificant compared with equivalent doses of external exposure to natural sources. The dose accumulated during 1974 - 1995 from natural sources is about 11mSv. Hence, the dose increment due to past and current PA MAYAK activities to the dose of natural radiation is no higher than 30% in Ozyorsk and 18% in Snezhinsk.

Registry Structure and Mortality Rates among Children of Ozyorsk and Snezhinsk

Within the scope of the project an epidemiological study was performed on the basis of Children Registry of the towns of Ozyorsk and Snezhinsk. Ozyorsk and Snezhinsk are the towns located at the restricted access area, they are similar in infrastructure, provision with medical personnel and quality of medical care, living standard, etc. They differ in a distance from PA MAYAK and, therefore, in the doses of technogenic radiation people receive due to residence within the territory affected by the operating atomic facility.

Table 7 describes the structure of the Registry. The Registry comprises 20,983 children of Ozyorsk and 11,994 children of Snezhinsk. Of those children 18,630 and 11,017 were born in Ozyorsk and Snezhinsk, respectively, the rest came there in childhood and had lived a year or more. Totally the Registry contains data on 32,977 children.

To compare rates in the primary and control cohorts we used probabilistic approaches being conventionally exploited in epidemiology. On data of the cohort study based on use of mortality rates a standardized relative risk (SRR) is calculated which relates to the effect of the exposure factor under study and is a ratio between the actual number of deaths and the expected one estimated on the basis of a chosen standard.. The research used the age-specific death rates for the Snezhinsk children.

SRR is not the only measure of exposure effects. One can consider a difference between mortality rates, as well. In any case it is necessary to specify accuracy of the effect measure chosen. This can be done either by applying a significance criterion with preset level *p*, or by designing a confidence interval with the confidence level ***P***.

Table 7

General Characteristics of Children Registry

	Town, sex, number of children					
	Ozyorsk			**Snezhinsk**		
	male	female	total	male	female	total
Number of children in Registry	10719	10264	20983	6207	5787	11994
Of them with known vital status	10558 (98.5%)	10144 (98.8%)	20702 (98.7%)	6075 (97.9%)	5666 (97.9%)	11741 (97.9%)
person-years of follow-up	129266	124768	254034	76415	71200	147615
Died of all causes at age of 0 - 15 * by December 31, 1996	227	159	386	112	64	176
Died in the first year of life (infant mortality rate**)	166 17.6	109 12.1	275 14.9	83 14.5	45 8.6	128 11.7
Died at age above 1 to 15 number of deaths per 10^5 person-years	61 47.2	50 40.1	111 43.7	29 38.0	19 26.7	48 32.5
Average effective dose of technogenic radiation due to residence, mSv	1.6			1.0		
Dose range (min- max), mSv	0.05-3.4			0.04-2.0		

* - including children died at age of 14 years and 364 days, but not including those died at age of 15 and above

**- number of cases per 1,000 live-born children

In Ozyorsk parents of about one third of children were subjected to occupational external γ-radiation at PA MAYAK. Having data on the doses, we were able to analyze the role of parental exposures. The analysis seemed to be important because when comparing mortality rates in Ozyorsk and Snezhinsk, certain differences were found only in rates of deaths of congenital malformations which clearly cannot be a result of technogenic exposure of children to radiation (since they appear prior to birth), bur may be the effect of occupational exposures of parents at PA MAYAK. Therefore the comparison of mortality rates between groups of children with exposed and non-exposed parents might provide more definite information about the role of radiation factor in the study cohorts. Table 8 characterizes two subcohorts of children born in Ozyorsk: primary subcohort of children whose parents worked in contact with sources of ionizing radiation, and the control subcohort of children whose parents were not subjected to occupational exposures.

Table 8.

Characteristics of subcohorts of children born in Ozyorsk

Characteristics	Children of exposed parents	Children of non-exposed parents
Number of children in subcohort	5303	13196
including those with known vital status	5294 (99.8%)	13081 (99.1%)
Persons-years of follow-up	67401	165756
Average dose (cGy)of occupational exposure prior to conception, (min-max) *in fathers* *in mothers*	 6.0 (0.01-486) 2.2 (0.01-83)	
Died of all causes at age of 0 to 15 by December 31, 1996	93	292
Died in the first year of life per 1,000 live-births	$\frac{66}{12.4 \pm 1.5}$	$\frac{209}{15.8 \pm 1.82}$
Died at age of above I year to 15 * per 10^5 person-years	$\frac{27}{40.1 \pm 7.7}$	$\frac{83}{50.1 \pm 5.5}$

*- numerator -absolute number of cases, denominator - mortality coefficient ± error (in cases per 10^5 person-years of follow-up)

So, the investigation into mortality rates and structure of causes among children at age of 0-15 has not revealed significant differences between the group of children whose parents were subjected to occupational exposure at PA MAYAK and the group whose parents did nor work in contact with sources of ionizing radiation.

To judge on health status of children living in the settlements located nearby an operating atomic plant, it was interesting to compare results of our research with data of national statistics. In the available literature there are only age-specific overall rates of deaths among children in Russia in 1970-1986 and of most important causes in 1986. To compare our data with those in Russia we chose the rates among urban population of Russian Federation.

STUDY OF REGULARITIES RULING RADIONUCLIDES TRANSITION FROM DIFFERENT SOILS OF KAZAKHSTAN TO MEADOW GRASSES AND CROP PLANTS

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In the Republic of Kazakhstan substantial portion of the territory is polluted with radionuclides and heavy metals in the result of the ground A-bomb tests in Semipalatinsk and functioning of plants dealing with nuclear fuel, as well as with mining and processing of rich raw material resources.
The problem of using contaminated soils in Kazakhstan has no rational solution till now. There are no scientifically based recommendations on the effective countermeasures in agricultural production systems on such territories.
For development of methods to reduce radionuclide transition to plant products on polluted territories of Kazakhstan it is necessary to study regularities governing their transition from soils to plants. Due to this we have tried to get more exact information on regularities of ^{137}Cs and ^{90}Sr transition to meadow grasses and some crops during their growth on soils prevalent in Kazakhstan.

Materials and Methods

The research work was carried out on 15 prevailing in Kazakhstan soils with dosed radionuclide pollution. A long-term model-field experiment was initiated; alfalfa and tomato plants were grown in the course of it in 1997. In 1998 the trial was expanded with three soils transported from the area of the Semipalatinsk A-bomb Test Site. These soils were used in the experiment in two variants. In the first one the soil was used as a monolith with growing plants and water solution of the radionuclide was evenly applied to the surface of soil. In the other variant application of the radionuclide was accompanied with thorough mixing of an arable layer. The plots of the second variant were sown with garden radish, after its harvest carrot was sown. In early spring (February – March) of 1999 wild meadow plants were sown and planted at the plots. Calculated density of soil pollution in lysimeters in 2000, when the bulk of plant samples was analyzed for radioisotope content, was 113.687 KBq of radiostrontium and 249.9877 KBq of radiocesium per 1 m^2.
For developing countermeasures against radionuclide transition impact of various fertilizers on ^{90}Sr and ^{137}Cs transition from soil to barley plants was studied on ordinary sierozem and light chestnut soil.
Two vegetation trials were carried out, in one of them 1.0 MBq of ^{137}Cs was applied to 1 kg of soil, in other 0.5 MBq of ^{90}Sr was applied to 1 kg of soil. Nutrient elements under study were introduced into soil as follows: N and P in 71.4 $mg \cdot kg^{-1}$, K in 42.9 $mg \cdot kg^{-1}$, Ca in 20.0 $mg \cdot kg^{-1}$, humus was applied in dose 20 g to 1 kg of soil. The experiments were implemented for 3 years in vegetation vessels containing 5 kg of absolutely dry soil in 4 repetitions.
Prior to radiometric assay the obtained vegetation samples were wet ashed in mixture of HNO_3 and $H_2Cl_2O_5$ acids (v/v 3:1) supplemented with H_2O_2. In samples obtained on soils that have been polluted both with ^{137}Cs and ^{90}Sr the radionuclides were separated by sedimentation of oxalates at pH 4. Radiometric analysis was carried out by γ-counter MINI GAMMA 1275 of LKB and alpha-beta multidetector MINI 20 of Eurisys Mesures.

Results and Discussion

Taking into consideration that the most part of the territory in Kazakhstan is used as a pasture, that there is no sufficient data on peculiarities of radionuclide transition from various soils to meadow grasses to develop effective measures for rational use of soils contaminated with radionuclides we have made an attempt to supplement the missing experimental data by our own studies.
For the most part the soils under study gave alkali reaction (pH saline – 7.5-8.0) with the exception of ordinary chernozem from Vostochno-Kazakhstanskaya oblast' with merely neutral (pH 6.9). Other parameters of soils were significantly different, ratio factors for some of them were several tens, e.g. for cation absorption capacity the ratio factor was from 0.7 (solonchak) to 51.0 (ordinary chernozem) mg-equivalents in 100 g of soil. These differences in soil characteristics provided different biological availability of introduced radionuclides to plants through root system. On fertile soils rich in humus and

potassium (all types of chernozem) the content of radionuclides in most plant species was low, on lean soils (sierozem, gray-brown, some chestnut soils) this index was high (Table 1).
Two years' (1999 and 2000) observation has shown the factors of ^{137}Cs transition (transition factor (TF) = $Bq \cdot kg^{-1}$ of plant/$KBq \cdot m^2$ of soil) to wheat-grass plants on chernozem soils to be within 0.47-0.82, to wormwood plants within 0.39-0.85 and to differ little for different soil varieties (Table 1). For dark chestnut and chestnut soils this factor is slightly higher (by 0.25-1.08) in comparison with chernozems. Marked increase in this coefficient was registered for gray-brown soil from Zhezkazganskaya oblast'. It was 1.95-2.38 that is 3-4-fold higher than for chernozems. The highest transition factor (2.34-2.76) was shown for wheatgrass plants grown on sod-podzolic soil. It should be noted that the radionuclides transition from soils of the Semipalatinsk Test Site (solonchak, light chestnut, chestnut) with higher content of potassium (117.8 mg/100 g of soil) was similar to that from chernozems.
Comparison of the rate of ^{137}Cs accumulation by meadow plants allows noting a tendency of lower radionuclide accumulation in wormwood plants and of higher accumulation in brome-grass and feather-grass in comparison with wheat-grass. The results of experiments on ^{90}Sr transition to plants evidence that in soils under study its availability to plants is higher than of ^{137}Cs (Table 2). The coefficients of its transition to meadow grasses are in 2.2-6.5 higher. But like cesium radiostrontium is absorbed by plants grown on chernozems in smaller quantities than by plants grown on sierozem, gray-brown and light chestnut soils. The differences are 1.7-4.7-fold. The influence of soil parameters on the radionuclide transition to plants has also been observed.
Correlation of the radionuclides accumulation by meadow grasses to parameters of soils under study demonstrates existence of correlation dependence between ^{137}Cs concentration in wheatgrass and wormwood plants and content of mobile forms of potassium and calcium, content of humus in soil has been demonstrated (correlation coefficients were respectively -0.662 ± 0.04 and -0.674 ± 0.04) (Table 3).
Transition of ^{90}Sr to plants from soils under study depends on content of Ca and humus in them, as well as on their absorption capacity. The correlation coefficients for these parameters of soils and the radionuclide accumulation in plants of wheatgrass, wormwood and alfalfa were within (-0.691) – (-0.820).
The results of observation on radionuclide transition to vegetable plants have shown that the regularity ruling transition of radiocesium from different soils to plants of garden radish, carrot and tomatoes was approximately the same as that for meadow grasses. But different species of vegetable plants on the same soils vary in the value of the radionuclide absorption. Thus, ^{137}Cs content in roots and leaves of carrot grown on all soils was relatively low in comparison with the same parts of a garden radish plant. Still less the radionuclide was accumulated in tomatoes.
Radiostrontium was adsorbed by vegetable plants as well as by meadow grasses more intensively and the rate of dependence of this process on soil properties was higher than it was shown for radiocesium. The coefficients of ^{90}Sr transition from soils to plants of garden radish and carrot on soil parameters differed 3.9-4.9 times, whereas for radiocesium they differed in 1.5-1.7 times only.
The presented findings confirm the published data on close relationship between the rate of ^{37}Cs and ^{90}Sr accumulation and the parameters of soils on which they are grown as well as biological peculiarities of plants [1-11].
The radionuclide transition from soils to plants depends not only on soil properties and biological peculiarities of plants but on their distribution in soil profile as well. In our experiments on studying regularities ruling ^{137}Cs and ^{90}Sr transition from different soils to meadow plants there were variants with application of water solutions of radionuclides to soil surface and into plough-layer. Ways of ^{137}Cs application were tested on chestnut, light chestnut and solonchak soils delivered from the region of the Semipalatinsk Test Site. When the radionuclide was applied to the surface of soil the process of its transition from all soils under study to meadow plants was more intensive in comparison with the experiments where the plough-layer was mixed. The transition factor was in 1.4-3.4 times higher.
The ways of applying ^{90}Sr were tested on mountain chernozem, ordinary chernozem, on chestnut and gray-brown soils. There is also a tendency of lower radionuclide transition to meadow grasses from soils under study when it is applied with mixing of the plough-layer.

Table 1

^{137}Cs transition factors (TF) from various soils to meadow plants

Soil Variety	Region of Soil Sampling	TF (Bq/kg of plant) / (KBq/kg of soil) in grass species and years										
		alfalfa		wheat-grass		wormwood		feather-grass		bromegrass		other
		1997г	1999г	2000г	1999г	2000г	1999г	2000г	1999г	2000г	1999г	2000г
Mountain chernozem	Zhambylskaya	0,39	0,68	0,48	0,52	0,40	1,01		0,78	1,37	0,92	
Common chernozem	Vostochno-Kazakhstanskaya	0,42	0,82	0,47	0,85	0,70	1,45		1,39	0,64	1,01	1,26
Common chernozem	Kokshetausskaya	0,39	0,59	0,62	0,39	0,70	1,06		1,49	0,60	1,83	
Common chernozem	Akmolinskaya	0,38	0,62	0,64	0,47	0,57	0,71		0,48	1,28	1,40	0,69
Dark chestnut	Zhambylskaya	0,49	1,19	1,01	1,04	0,94	1,69	1,68	1,24		1,83	2,54
Dark chestnut	Almatinskaya	0,58	0,98	0,86	0,64	0,95	2,29			1,79	1,92	
Chestnut	Zhambylskaya	0,97	1,39	1,22	1,23	1,14	2,61	1,96	1,33	1,08	1,88	
Chestnut	Karagandinskaya	1,09	1,34	1,10	1,25	1,48	1,83	1,62	1,98	2,40	2,72	
Chestnut	Zhezkazganskaya	1,00	1,53	1,19	1,14	1,08	2,65		1,71		2,02	1,85
Light chestnut	Almatinskaya	1,23	1,58	1,59	1,39	0,57	1,90	2,33	2,17		1,21	0,69
Common sierozem	Zhambylskaya	1,38	1,50	1,43	1,30	1,85	2,59		2,03	2,21	1,30	
Gray-brown	Zhezkazganskaya	1,39	2,38	2,13	1,95	1,99	2,24			1,62	2,16	1,59
Solonchak	Semipalatinskaya		1,02		0,75	1,06	1,21	1,35	0,98	1,10	0,30	0,46
Light chestnut	Semipalatinskaya		0,64	1,22	0,67	0,72	0,84	0,86	0,69	1,38	0,58	0,66
Chestnut	Semipalatinskaya		0,50	0,42	0,61	0,44	0,74	0,94	0,54	0,92	0,49	0,45
Sod-podzolic	Kaluzhskaya	1,74	2,76	2,34	1,97	1,64	2,43		1,96		2,01	1,44

Table 2

^{90}Sr transition factors (TF) from various soils to meadow plants

Soil Variety	Region of Soil Sampling	TF (Bq/kg of plant) / (KBq/kg of soil) in grass species and years										
		alfalfa	wheat-grass		wormwood		feather-grass		bromegrass		other	
		1997	1999	2000	1999	2000	1999	2000	1999	2000	1999	2000
Mountain chernozem	Zhambylskaya	2.48	1.39	1.03	2.09	1.16	4.19	2.67	3.04	2.15	3.30	2.88
Common chernozem	Vostochno-Kazakhstanskaya		1.73	1.31	1.47	1.65	4.42		3.04	2.56	5.31	4.47
Common chernozem	Kokshetausskaya		1.49	2.20	1.19	1.34	5.55		4.47	3.13	3.26	
Common chernozem	Akmolinskaya		1.03	0.60	1.70	1.60	6.27		2.52	2.36	1.95	1.95
Dark chestnut	Zhambylskaya		4.48	2.68	1.89	1.82	8.71	6.80	5.57	5.04	8.80	3.32
Dark chestnut	Almatinskaya		2.99	2.09	2.86	1.82	8.00				5.78	
Chestnut	Zhambylskaya		3.91	3.61	2.20	1.78	7.92	7.87	6.24	6.51	4.94	
Chestnut	Karagandinskaya		5.69	3.85	2.56	1.97	8.03	4.61	6.02	3.09	3.90	
Chestnut	Zhezkazganskaya	3.79	3.34	2.02	3.41	2.50	5.84	4.11	5.96	2.76	3.28	2.95
Light chestnut	Almatinskaya		5.22	3.93	4.20	3.94	6.02	5.67		5.01	6.61	8.17
Common sierozem	Zhambylskaya	6.41	5.49	5.28	3.50	2.82	6.27	6.00	5.75	3.72	5.30	3.78
Gray-brown	Zhezkazganskaya	6.19	6.93	5.12	5.54	5.04	7.58	7.20	5.06	4.66	5.21	4.75
Solonchak	Semipalatinskaya		5.01	4.69	5.50	4.97	7.43	6.80	5.17	2.68	8.31	
Light chestnut	Semipalatinskaya		4.19	4.75	3.63	3.19	7.34	4.99	5.81	5.13	6.01	2.68
Chestnut	Semipalatinskaya		2.39	2.05	2.73	3.03	5.30	4.65	4.71	4.38	7.01	11.95

Table 3

Correlation coefficients (r) between the values of radionuclide accumulation in plants of various species and quantitative characteristics of some agrochemical parameters of soils

Plant species	Agrochemical parameters of soils						
	K_2O content mg/100 g of soil	Ca content, mg-equi/100 g of soil	Absorption capacity, mg-equi/100 g of soil	Total content (Ca+ K_2O)	Humus content, %	Clay content, %	pH
^{137}Cs accumulation							
Wheatgrass	-0,662	-0,640	-0,389	-0,738	-0,485	-0,305	-0,043
Wormwood	-0,674	-0,536	-0,273	-0,723	-0,400	-0,303	0,068
Feather-grass	-0,849	-0,332	-0,057	-0,868	-0,147	-0,022	0,020
Bromegrass	-0,684	-0,419	-0,196	-0,737	-0,249	-0,276	0,013
Alfalfa	-0,777	-0,379	-0,892	-0,854	-0,840	-0,175	-0,281
^{90}Sr accumulation							
Wheatgrass	-0,334	-0,820	-0,710	-0,519	-0,758	-0,322	0,135
Wormwood	-0,005	-0,775	-0,730	-0,193	-0,750	-0,055	0,362
Feather-grass	-0,381	-0,348	-0,196	-0,572	-0,267	-0,182	-0,356
Bromegrass	-0,460	-0,501	-0,385	-0,372	-0,250	-0,260	0,070
Alfalfa	-0,336	-0,691	-0,831	-0,713	-0,826	-0,836	-0,254

One of the most widely used methods of reducing radionuclide transition to plants is fertilization. In our experiments we attempted to specify the rate of influence of various fertilizers on ^{137}Cs and ^{90}Sr transition to plants from sierozem and light chestnut soils that are common for Kazakhstan and the Semipalatinsk Test Site. The results of determining cesium-137 content in the barley plants grown on sierozem for three years show that substantial reduction of the yield pollution has been registered when humus is introduced into soil. The radionuclide content in barley grain was 14.4 on average for 3 years and 9.4% in straw (Table 4). Separate application of phosphate or potash fertilizer did not virtually influence the rate of ^{137}Cs transition. Joint application of phosphate and potash fertilizers promoted reduction of grain pollution by 12.5% and straw pollution by 11.5%.

Introduction of mineral nitrogen increased the radionuclide absorption by plants. In the variant of experiments with use of this element the average pollution of grain was by 20.9% higher, pollution of grain by 20.6% higher. Increase in the isotope transition to grain and straw by 7.4 and 11.1% respectively was registered also when nitrogen was added to soil with humus. But introduction of this element to soil in complex with phosphorus and potassium in weight ratio 1:1:0.5 promoted reduction of ^{137}Cs concentration in grain (by 6.1%) and in straw (by 11.8%). This fact, in our opinion, may be explained by favorable influence of balanced use of fertilizers on plants. Higher content of nitrogen that is not balanced with other nutrient elements stimulates higher transfer of radiocesium to barley plants. The fact that introduction of potassium as an analogue of radiocesium does not lead to essential effect may be explained, in our opinion, by rather high content of its available forms in the soils under study. That is why a relatively small dose of this element does not cause considerable change in its ration with other elements. Introduction of calcium to ordinary sierozem does not influence transition of ^{137}Cs to barley plants.

Impact of fertilizers under study on ^{90}Sr transition to barley plants was more substantial in comparison with ^{137}Cs. The results of studies for three years evidence that application of fertilizers to ordinary sierozem leads to lower transition of radiostrontium to barley grain and straw. Ammonium nitrate was an exception since its introduction did not show any effect. The greatest reduction of the radionuclide transition to barley grain and straw (by 36/6 and 46.1% respectively) resulted from joint application of humus with complete mineral fertilizer (NPK). Separate introduction of humus, phosphate-potash or complete mineral fertilizer had equal effect on the radionuclide transition to plants reducing the concentration by 22.6-34.4%. Significant influence was recorded after application of calcium (20.0-21.2%) and phosphorus (17.7-24.6%). Potash fertilizer caused reduction of the radionuclide accumulation in barley grain and straw only by 6.8-11.3%.

Similar experimental data have been obtained on light chestnut soil, since after application of humus and complete mineral fertilizer transition of radiostrontium to barley grain and straw lowers on average in 1.6-1.9 (Table 5).

Table 4

Impact of various fertilizers on ^{137}Cs and ^{90}Sr transition to barley plants from ordinary sierozem (average for 3 years), Bq/g

##	Trial variant	^{137}Cs				^{90}Sr			
		grain	%	straw	%	grain	%	straw	%
1	^{137}Cs	12.88±504	100.0	27.83±0.53	100.0	123.4±18.1	100.0	1405.3±218.9	100.0
2	^{137}Cs +N	15.58±0.84	120.9	33.56±1.21	120.6	125.8±19.9	101.9	1569.3±288.0	111.7
3	^{137}Cs +P	12.34±0.39	95.8	26.44±0.93	95.0	101.6±11.6	82.3	1059.8±155.9	75.4
4	^{137}Cs +K	11.91±0.27	92.5	26.52±0.70	95.3	115.0±22.8	93.2	1246.0±201.2	88.7
5	^{137}Cs +Ca	13.00±0.46	101.0	27.89±0.93	100.2	98.7±13.1	80.0	1121.5±151.5	79.8
6	^{137}Cs+humus	11.03±0.30	85.6	25.21±0.73	90.6	94.8±15.8	76.8	971.5±256.9	69.1
7	^{137}Cs+humus+NK	13.83±0.30	107.4	30.92±1.01	111.1	78.2±11.0	63.4	757.8±258.3	53.9
8	^{137}Cs +PK	11.27±0.23	87.5	24.64±0.52	88.5	95.5±6.6	77.4	926.5±86.2	65.9
9	^{137}Cs +NPK	12.09±0.28	93.9	24.53±0.71	88.2	94.4±10.3	76.5	942.8±156.6	67.1
10	Control - without fertilizers	0.13±0.03		0.28±0.06		12.4±5.4		81.0±32.2	

Table 5

Influence of various fertilizers on ^{137}Cs and ^{90}Sr transition to barley yield from soils of the Semipalatinsk Test Site (average for 3 years), Bq/g

№	Trial variant (applied to soil)	^{137}Cs				^{90}Sr			
		grain	%	straw	%	grain	%	straw	%
Light chestnut soil									
1	^{137}Cs	10.55±1.98	100.00	24.84±3.21	100.00	134.7±28.6	100.0	1323.3±147.7	100.0
2	^{137}Cs +N	10.88±1.05	103.08	24.65±3.46	99.22	144.3±22.2	107.1	1367.9±90.3	103.4
3	^{137}Cs +P	8.56±0.64	81.06	21.41±1.35	86.20	115.8±17.3	86.0	1038.3±159.3	78.5
4	^{137}Cs +K	9.73±1.59	92.20	22.22±3.18	89.46	129.3±22.7	96.0	1110.8±156.3	83.9
5	^{137}Cs +Ca	9.71±1.29	91.97	23.49±1.64	94.57	117.9±13.0	87.5	1043.7±95.1	78.9
6	^{137}Cs + humus	7.28±0.76	68.95	18.06±1.63	72.72	70.8±7.1	52.6	839.9±77.9	63.5
7	Control (without fertilizers)	0.28±0.05		0.84±0.20		77.5±11.1	57.5	813.3±44.1	61.5
Chestnut soil									
1	^{137}Cs	10.55±0.64		24.38±4.63		143.2±43.7		1156.0±76.3	
2	Control (without fertilizers)	0.11±0.07		0.31±0.12		22.8±6.3		78.3 ± 13.6	

Application of fertilizers to light chestnut soils has appeared to be more effective in reducing ^{137}Cs transition in comparison with sierozem. Introduction of phosphorus to soil provided lower ^{137}Cs transition to barley grain on average by 18.9%, to straw by 13.8%. Application of potassium also leads to reduction of the radionuclide accumulation in grain by 7.8% and in straw by 10.5%. Lower radionuclide accumulation (by 8.0% in grain and 3.4% in straw) resulted from application of calcium as well. The greatest effect has been registered after introduction of humus to soil: radiocesium concentration in grain and straw lowered by 31.0 and 27.3% respectively. Contrary to sierozem nitrogen fertilizer introduced to light chestnut soil does not influence radiocesium transition to plants.
It is worthy to note that our results, in general, agree with published data [10 - 21].

Conclusion

The results of the research activity and analysis of publications on study of regularities ruling radionuclides transition from different soils to plants and on influence of various fertilizers on this transition allows concluding the following.
There is a linear dependence between pollution density and size of radionuclide accumulation in plants on soils prevalent in Kazakhstan.
Agrochemical parameters of soils where plants are grown are one of the main factors specifying radionuclides accumulation in plants. High degree of correlation between size of ^{137}Cs accumulation and content of exchangeable forms of calcium and humus as well as adsorption capacity of soils prevailing in Kazakhstan has been demonstrated. Close inverse relationship of ^{90}Sr transition to plants and content of exchangeable calcium and humus, adsorption capacity of soils has been shown.
Under conditions of Kazakhstan the largest transfer of radionuclides to plants may take place on polluted sandy, brown, gray-brown soils and sierozems in desert, semidesert and piedmont areas, the smallest - on chernozems and chestnut soils.
It has been shown that size of radionuclides accumulation by various species of plants grown on one and the same soil may differ in tens of times. Cultivation of crops characterized by low accumulation of isotopes is one of the economically sound methods to limit the rate of radionuclides transition from soils to plant produce.
Application of fertilizers (organic – humus, mineral – complete or phosphate-potassium, as well as mixture of organic and phosphate-potassium) is an effective method of reducing radionuclide transition from soils prevalent in Kazakhstan to agricultural plants. Among agrotechnical ways the most acceptable one is improvement of pastures, radical or superficial, with fertilization and undersow of grasses, which accumulate radioisotopes in relatively small quantities, such as alfalfa, wheatgrass, bromegrass, etc.
The submitted experimental data may be used in developing "Recommendations on effective use of radionuclide polluted territories in Kazakhstan" and in improving the database, which is requisite in solving radioecological problems.

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THE NEED FOR REMEDIATION OF PESTICIDE-CONTAMINATED SOILS IN KAZAKHSTAN

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Pesticide Use in Kazakhstan

The increasing problems in Kazakhstan's environment are due not only to industrial wastes and irradiation, but also to pesticide contamination of soil.

Kazakhstan has considerable land resources for agricultural development. From a total land area of 2.7 million square kilometers, 223 million hectares are suitable for agriculture as cultivated land or pasture. There are 300 types of agricultural weeds of which 120 are very widespread and reduce harvests. In 1996, according to the regional monitoring stations for the protection of wildlife and plants, out of 18727.2 thousand hectares inspected, 15245.7 thousand (81.4%) had weed problems. Of this area, 7848.6 thousand hectares were infested with deep-rooted perennial weeds, 2975.2 thousand had wild oats, and 605.4 thousand were infested with invasive or quarantined weeds such as dodder, ambrosia, and bitters. There has been an increase in invasion of pastures with bitters. The average reduction in yield due to the weeds is 250 kg per hectare for cereal grains, 500 kg per hectare for maize, 4000 to 6000 kg per hectare for forage, and up to 6000-8000 kg per hectare for sugar beets. In 1996, in the Republic of Kazakhstan, 1,267 thousand hectares were treated with herbicides by ground application and 374 thousand hectares were treated by aerial spraying. In recent years, there has been an increasing problem due to locusts. Locusts have been observed in more than 1.5 million hectares (1). There is no doubt it is necessary to use pesticides to help manage the increasing number of diseases, pests, and weeds.

There are 243 foreign-made pesticides registered for use in Kazakhstan to control pests, diseases, and weeds, as well as for use as defoliants and plant growth regulators. These chemicals were approved for use in agriculture and forestry in Kazakhstan for the period of 1997-2001. Of these pesticides, 54 are used as insecticides and acaricides, 90 herbicides, 58 fungicides, four antibiotics, two rodenticides, 22 fumigants, two nematicides, four defoliants/dessicants, and seven plant growth regulators. Pesticides are imported primarily from the United States of America, England, Israel, Germany, and Russia (2). In 1999, Kazakhstan imported 44,000 tonnes of pesticides valued at 40 million US dollars.

In Kazakhstan, the main requirement to receive approval for state registration of imported pesticides is to develop regulations for their use including quantitative sanitary-hygienic standards and methods to control use (3). State registration of pesticides containing unknown substances, is certified by the Ministry of Agriculture. The required state hygienic registration is performed in the Health and Hygiene Agency of the Republic of Kazakhstan. This includes rules for conducting registration trials, government registrations, and re-registration of methods of plant protection permitted for use in Kazakhstan (4). In Kazakhstan, as well as neighboring countries of the CIS, laws have been established for the regulation of pesticide use, national programs for pesticide registration have been established, and there is a list of registered pesticides. However, to the disappointment of many, there are no national normative documents prohibiting the production and use of pesticides considered persistent organic pollutants.

Pesticide Contamination Problems

Kazakhstan, as well as neighboring republics of the CIS, has a severe problem with salvaging and destroying unsafe and obsolete pesticides that are no longer usable. This has resulted in accumulation and migration of pesticides in soil and groundwater, the disruption of soil microorganisms, and the gradual destruction of natural ecosystem processes. Historically, during the last 30 to 50 years in Kazakhstan and other countries of the CIS, more than 700 chemicals from many classes of compounds have been used in agriculture (5). The capacity for storing these pesticides has not corresponded to the need. Currently in Kazakhstan, out of 563 pesticide storage sites, 411 are in an emergency condition. It is estimated that 574 tonnes of pesticides and 54 thousand container-units are stored open to the air and in danger of polluting the local environment (6). Solutions to this problem are severely limited by financial resources.

The danger of pesticides in comparison with other chemical compounds is that pesticides possess high biological activity, the ability to circulate in the biosphere, they can accumulate in food sources, and they can be dangerous for agricultural workers. To address these problems environmental hygenists are developing methods to take precautions with these acute and chronic toxins. This includes developing regulations for effective use of pesticides and taking measures to protect the surrounding areas where pesticides are used. It is important to understand the long-term toxicological effects of pesticide pollutants and their effects on ecosystems at different levels of organization.

Many pesticides are highly stable to chemical and biological degradation and are capable of maintaining toxic properties for a long time. A good example is DDT (dichlorodiphenyltrichloroethane). It is a chlorinated organic pesticide with high pesticidal activity and was widely applied in agriculture and household activities. Although most countries have permanently eliminated or severely restricted the use of DDT in agriculture, DDT and its metabolites accumulated in many places in the environment and can still be detected. Application of DDT was prohibited in the Soviet Union in 1971. Despite this, pesticide residues can still be detected. One ecological report from locations in the Aral Sea region of Kazakhstan (7) showed the concentration of chlorinated organic pesticides in cereal grains maintained at a level of 20.0 to 45.4 mg/kg, exceeding sanitation standard doses by 1.5 to 2 times (PDK-20.0 mg/kg).

For recent decades including, most recently, a period with large locust infestations, use of pesticides has been widespread. Potential pesticide contamination of food supplies and the environment is a concern. There has been some success in controlling locusts, but the problem with repeated pesticide applications to the same land can result in increased of residual quantities of pesticides in the treated plants and in soil (8). Government sanitary inspections in Kazakhstan have shown pesticide contamination of farm-potable water supplies in 1986 was 0.4% and in 1996 was 0.5%. In some locations these parameters are higher. For example, in Kyzylorda and Almaty regions, contamination of potable water supplies exceed a marginal concentration level 2.7% and 2.5% of the time. In some situations, contamination of air exceeds acceptable levels by 3 - 10 times (6).

Remediation of Pesticide Contaminated Soil

There are two main approaches for cleanup of pesticide-contaminated soils, physical-chemical methods and biological methods. Physical-chemical methods include approaches that separate fluid fractions (settling methods, filtration, cetrifugation, etc.); or process the waste (extraction, desorption of contaminants, reverse osmosis, ultra filtrating, formation of precipitates, or chemical oxidation) (9). The use of physical-chemical methods of remediation usually involves excavation and treatment of the contaminated soil. The efficiency of these methods is usually high and often depends little on the characteristics of the contaminated media or the local climatic conditions. The remediation process is often rapid depending on the quantity of material to be treated. However cost of these methods is very high (10).

In recent years, the new bioremediation technologies have offered new soil cleanup methods. During bioremediation, contaminants are detoxified and biodegraded as a result of biological processes often involving microbial activity. Bioremediation technologies help increase the volume and speed of natural microbial degradation of contaminated media by providing nutrient sources or electron donors that limit microbial activity. Under these conditions, indigenous microorganisms or introduced cultures are capable of rapidly reducing contamination. Bioremediation can take place at the site of contamination, *in situ*, or the contaminated material can be removed and treated, *ex situ*. *Ex situ* bioremediation includes bioreactors, biofilters, and some composting methods. *In situ* methods include biostimulation, bioaugmentation, and other composting methods (11).

Bioremediation methods of treating contaminants are often more cost-effective to reach similar objectives as physical-chemical methods. By some estimates, bioremediation may cost less by 10-40% in the USA market (11). Bioremediation methods have been most intensively designed in western countries. In the USA, for example, more than 200 companies in the USA are engaged in marketing remediation technologies to large corporations, government agencies or others ordered by regulatory agencies (10). The costs of these remediation approaches are still prohibitive for use on a large scale in Kazakhstan and many other countries. Due to the limitations of financial resources, new remediation and risk reduction approaches need to be developed for countries like Kazakhstan.

Expensive technologies for cleanup of pesticide-contaminated soils are unacceptable for Kazakhstan. Therefore, there is a critical need to find inexpensive methods to clean local sites contaminated with pesticides. Sites of particular concern include deserted pesticide storage sheds located in agricultural areas.

Phytoremediation

Phytoremediation or phytotechnologies are a new set of bioremediation methods for contaminated soils that is receiving increased attention in the scientific literature. Phytoremediation uses plants to enhance degradation or stabilization of environmental contaminants to reduce risk to humans and the environment posed by contaminated soil and water. This technology is especially promising for restoring small, local sites with low to moderate levels of contamination. If effective, phytoremediation techniques may be low cost. Phytoremediation has been applied to a range of contaminants including organic chemicals and heavy metals. There are many different mechanisms of interaction between plants and environmental contaminants depending on the plant species, the chemical and physical properties of the contaminants, and characteristics of the contaminated media.

In some cases, plants can accumulate or extract contaminants from soil. This is called phytoaccumulation or phytoextraction. Phytoextraction has been investigated for use to cleanup heavy metals and radionuclides using plant species such as *Brassica* sp., *Helianthus* sp., and others (12). In the case of phytoremediation of heavy metals, it is expected that metals accumulated within plants would be harvested and disposed. In some cases with organic compounds including pesticides, plants may selectively take up the compounds and the compounds may be degraded or detoxified within the plants.

Another important mechanism of interaction between plants and contaminants is called rhizosphere degradation. The region of soil under the influence of plant roots is called the rhizosphere. In this region, there are typically higher populations of microorganisms that are capable of accelerating biodegradation of pollutants. Biodegradation of pesticides in the rhizosphere has been investigated for a number of pesticides. For example, the plant genus *Kochia* was shown to enhance degradation of the herbicides atrazine, metalochlor, and trifluralin (13). Tree species in the genus *Populus* have been investigated for many potential phytoremediation applications due to the rapid root growth of *Populus* sp. and its ability to produce deep roots that can reach the groundwater. *Populus* as been investigated for treatment of atrazine, arochlor, and nitrates in field tests (14). In some cases phytoremediation may help degrade contaminants while in other cases the contaminants may accumulate in plant tissue or the rhizosphere. This may help reduce migration of mobile contaminants.

Although phytoremediation offers many potential methods for addressing pesticide contamination problems, it is important to note that it may not completely address contamination problems. For example, plants that accumulate toxic substances in their tissues may not be safe as food for humans, livestock, or wildlife. Phytoremediation processes may also be slow and take a long time to address contamination problems. These issues need to be considered when investigating phytoremediation as a strategy to address Kazakhstan soils that have been contaminated with persistent organic pollutants for 30 to 50 years.

The Institute of Plant Physiology, Genetics, and Bioengineering of the Republic of Kazakhstan, the Department of Agronomy of Kansas State University, and the Technology Innovation Office of the United States Environmental Protection Agency are cooperating on research to develop phytoremediation strategies for pesticide-contaminated soil in Kazakhstan. This applied research project is designed to identify pesticide tolerant plant genotypes from contaminated locations. These plants will be studied for their ability to reduce risk and restore contaminated soils and to understand their mechanisms of detoxification of pesticides. On the basis of the research results, techniques will be developed for use of plants to help restore pesticide-contaminated sites.

The first stage in the research has been to identify and characterize several “hot spots” in Kazakhstan that are contaminated with chlorinated organic compounds. Plant species surveys at these locations have identified plants representing more than 19 angiosperm families. These sites will be studied for accumulation and biodegradation of pesticides by plants.

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NEW APPROACH TO NATURAL WATER GENOTOXICITY ASSESSMENT - DEVELOPMENT OF THE SYSTEM OF ECOTOXICOLOGICAL CONTROL IN THE TERRITORIES SUBJECTED TO RADIOACTIVE AND/OR CHEMICAL CONTAMINATION

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1 Introduction

Acting monitoring systems of observation and control of anthropogenic effects, connected with toxic pollutant emissions are limited, as a rule, by measuring content of limited number of priority substances in environmental objects, human and animal food chain elements and its comparison with standard requirements. However, the list of toxicants can not been limited in principal. Moreover many of pollutants, being in an Environment, are capable to be transformed to derivatives, many times more toxic, than initial substance. For example, at photolysis of polychlorinated phenols under action of solar light polychlorinated dibenzo-dioxines and dibenzo-furanes are formed (Skurlatov et al. 1995 [1]). So only analytical methods aren't able to give garantee of safety of the environment objects.

More adequate estimation of influence of antropogeneous sources of emission of polluting substances on the man and natural Environment can be received only in view of effect of all set controlled and uncontrollable toxic substances present in an environment in small, and sometimes in supersmall concentrations. From integrated methods of an assessment of environment state methods of bioindication and biotesting are most informative. First are based on an estimation of changes in biological objects on territory subjected to antropogeneous impact, in comparison with background territories. Second are based on the analysis of the selected samples toxicity with use the test–organisms of various trophic level and model functional test-systems. At the same time only in case major accidents the pollution content can exceed concentrations, at which an acute response of biological objects is possible.

In real situations the prolonged response of biological systems to cumulative effect of a large number of toxicants and/or radiation even in "extremely low doses" can be no less serious than consequences of high single doses.

According to official data, approximately 20% of diseases are connected with injurious influence of environmental contamination. Prolonged exposure to chemical pollutants results in the development of pathological changes in internal organs and nervous system, induces malignant tumors, anomalies in the development of progeny, and genetic diseases. It is clear from the above that the search for methods for early recognition of toxic contamination of environment, and tools for predicting early and remote toxic effects becomes more and more important.

Analysis of published data on methods for toxicological monitoring of the environmental objects allows to conclude that cytogenetic methods are more promising in this field (e.g. WHO 1989 [2]; Swierenga et al., 1991[3]; Galloway et al., 1994 [4]; Scott et al., 1991[5]). In world practice there is saved enough wide experience of the control of genotoxicity of individual chemical substances by methods of biotesting on cell and organism level. In a basis of these methods the ability of the various adverse factors lays to influence on DNA, changing its structure, that results to cancerous and hereditary diseases.

It is considered, that the genetic changes in somatic cells represent an integrated parameter both environment mutagenicity, and efficiency of organism's immune system. Rather simple and high-sensitivity cytogenetic methods are based on an evaluation of structural and numerical chromosome changes (including micronuclei test, sister chromatid exchange aberrations e.a.) in somatic cells.

Structural chromosomal lesions is one of common and adequate high sensitiv short-term *in vitro* biotesting method using mammalian cells for evaluation of carcinogenic hazards of chemicals (e.g. Ishidate and Odashima, 1977 [6]; Ishidate et al., 1988 [7]; Skurlatov et al., 2000 [8]). However, the experience of application of these methods to ecological environmental monitoring is very poor. All natural objects have the natural biotic component, which presents, probably, the greatest difficulty for their biotesting with cell systems. At the same time, it is the biotic component that takes an active part in formation of qualities of natural water as the aqueous habitat and the most common food product (Skurlatov and Ernestova, 1998 [9]). The number of works on evaluation of genotoxicity in drinking, natural and waste waters is very small, which renders their results especially interesting (e.g. Vartiainen and Liimatainen, 1986 [10]; Wigilius et al., 1988 [11]; Waters at al., 1989 [12]; Tuomico and Vartiainen, 1990 [13]; Antoschina et al., 1995 [14]; Ernestova et al., 2000 [15]). However, even under the methods that are most similar to the cytogenetic technique, not water samples themselves are analyzed but mainly their organic extracts. There is a coordinated protocol for evaluation of genotoxicity of separate chemicals under *in vitro* short-term tests using mammalian cells as the test-objects (WHO, 1989 [2]; Scott at al., 1991 [5]; Whitehead et al., 1983 [16]), but there is no such a protocol for evaluation of genotoxicity of native water samples.

Thus with the purposes of an estimation of the remote consequences of pollution of environment the methods based on an estimation of genotoxicity of analyzed native samples of water and water extracts are especially essential.

One of the most widespread short-term tests for an evaluation of potential mutagenic and carcinogenic hazard of chemical compounds is the definition of structural chromosome lesions damages in the cell test-cultures. The experience accumulated in many laboratories in the field of genetic toxicology allows to recommend as the main test-objects for cytogenetic studies two clones of Chinese hamster (CH) cells, namely Chinese hamster ovary (CHO) cells and Chinese hamster lung cells (V79), and also the culture of human peripheral lymphocytes obtained from healthy donors (Swierenga et al. 1991 [3]).

The purpose of the project ISTC # 547 was to represent a new high-sensitive method for genotoxicity assessment of native water samples without any treatment, on the basis of the analysis of frequency and types of structural mutations in cell cultures of CH. We also comparise sensitivity of the suggested method and other biotesting methods, including Ames test, in relation to some the most famous toxicants (in particular, benz(a)pyrene, 3,3',4,4'-tetrachlorobiphenyl).

2 Materials and Methods

2.1 Water Sampling

Samples of natural water from Protva River and some small rivers (Kaluga Region), Tsymliansk reservoir and the Rostov NPP reservoir-cooler (Rostov Region) and samples of cleaned waste water taken at an outlet from the municipal collector (town Obninsk) have been analyzed. Water samples were taken with the aid of standard equipment and corresponding sampling facilities.

Immediately after the sampling, temperature, conductivity, pH and the content of dissolved oxygen were measured in each water sample.

In addition, samples of surface waters from rivers in Zhizdra and Oulianovo districts of Kaluga Region have been used. These districts have been radioactively contaminated with long-lived radioisotopes as a result of the ChNPP accident.

To evaluate the contribution of various components of aquatic environment into the cytogenetic effect, the following water samples were tested: native water samples (without any preliminary treatment), samples passed through the membrane filter with pore diameter 0.22 or 0.45 μ, and also extracts obtained from the samples with mixture of organic solvents. Organic compounds for mutagenicity testing were extracted with diethyl ether/hexane mixture (1:1). Water samples were acidified to pH 2 - 3 (Variatinen and Liimatainen, 1986 [10]).

2.2. Ames' test

Salmonella/microsomes mutagenic activity test (the Ames' test) with the TA97, TA98 and TA100 strains was used, both without and with addition of microsomal activation mixture. S9-fraction (the mixture of rat liver enzymes) was made according to the protocol of Ames et al. 1975 [17], to induce production of microsomal enzymes was used phenobarbital suspension. The inducer (80 mg per kilogram of body weight) was injected intraperitoneally to male rats daily for 3 days. After the last injection, the rats were given neither feed nor water. The next day, they were decapitated. The supernatant (S9 fraction) from the rat liver was frozen immediately and stored at the temperature of liquid nitrogen during 3-4 months.

1 ml of microsomal activation mixture are 0.3 ml of the S9 fraction, 4 mM NADP, 5 mM glucose-6-phosphate, 8 mM $MgCl_2$, 33 mM KCl and 100 mM phosphate buffer (pH 7.4). The mixture was prepared *ex tempore* and kept on ice during 1 day.

Versions with metabolic activation contained, in addition to the culture and the sample to be tested, 0.5 ml of the activation mixture. To check the S9 fraction activity, an experiment was performed with a reference pro-mutagen (aminoanthracene) that revealed mutagenic activity only under metabolic activation with the S9 fraction.

All following experimental procedures are standard and are described (D.M. Maron, B.N. Ames 1983 [18]).

The experimental scheme included analyses with addition of different doses of toxicants or water samples, and both with and without addition of the microsomal activation mixture. Versions with addition of distilled water and microsomal activation mixture served as the net controls. Three Petri dishes were used per each experimental and control version.

The results are presented as ratios of the mean number of revertant his^+ *Salmonella* colonies per dish to that observed in the control. If this ratio was less than 2, no mutagenic activity was registered; mutagenic activity was recorded, correspondingly, as weak, medium and strong, for the ratio values in 2 to 10 range, 10 to 100 range, and exceeding 100.

2.3. Test with mammalian cell cultures

Monolayer cultures of Chinese hamster cells (CHO and ?II-d-ii-FAF28, line 237, with modal chromosome numbers 22 and 18, correspondingly; (e.g. Christian and Galloway, 1993 [19]; Zakharov et al., 1966 [20]) and human peripheral blood lymphocytes were used for the short-term *in vitro* test for evaluation of mutagenic activity of environmental samples.

The CHO cell line was obtained from the cell culture bank of the Medical Genetics Center, RAMS (Moscow). The 237 cell line was obtained from the cell culture bank of the Institute of Molecular Genetics, RAS (Moscow). In both cases, the cells had been checked against mycoplasma contamination. The cultures were stored in a Dewar vessel with liquid nitrogen and thawed before usage.

Chinese hamster cells were grown at 37 °C in glass Carrel flasks in Eagle's medium with 10% bovine serum and antibiotics (all the reagents produced by *PanEco*, Moscow). At each reseeding, cell suspension was diluted to low density in order to get rid of mutant cells that could arise under prolonged culturing. To prepare the cells for the biotesting, approximately 10^6 cells were taken from the maintained culture, placed in fresh medium with 10% serum, and grown for 7 days. Immediately before the testing, approximately 10^6 cells (per flask) were transferred into medium with 20% serum, and incubated for 24 hours. Then the culture medium was poured out of the flasks (and saved), and the cell monolayer was washed with Hanks' solution preheated to 37 °C.

Natural water samples and/or their filtrates were mixed with physiological solution of sodium chloride (PS), dry organic extracts of water samples were dissolved in methanol, mixed with PS and the resulting solution were added to the flasks with culture. The same amount of methanol (≤10%)

without additions of extracts used as control. The physiological solution without additions also used as a negative control.

Cultures were incubated with the mixtures to be tested for 2 h at room temperature. Then the mixture was discarded, the cells were washed twice with Hanks' solution, and returned to the initial (saved) medium for additional 8 h. Colchicine was added to the cultures for 2 last hours of incubation. Then the medium was removed, the cells were detached from the glass with 0.25% trypsin, transferred to centrifuge tubes, and fixed with methanol/acetic acid mixture (3:1).

Mutagenic activity of organic extracts was assessed both with and without metabolic activation (S-9 fraction).

Percentage of cells with chromosome aberrations, total aberration frequency (per 100 cells), as well as frequencies of chromosome and chromatid aberration types were registered; deletions and exchanges were scored separately. Mitotic index was calculated as the number of mitoses per 1,000 nuclei.

To characterize mutagenic activity of a water sample, two values were used, the total number of chromosome aberrations per 100 cells ($MA_{test.\ med.}$), and the coefficient of mutagenic activity ($K_{MA}^{test.\ med.}$) calculated by the excess of aberration frequency induced by the sample over the frequency observed in the control solution:

$$K_{MA}^{test.\ med.} = (MA_{test.\ med.} - MA_{control}) / MA_{control},$$

where $MA_{test.\ med.}$ is aberration frequency in the tested sample, and $MA_{control}$ is the base aberration level.

3 Results and Discussion

3.1 Cell cycle stage for water solution genotoxicity assessment

Experimental substantiation of the cell cycle stage for aqueous medium biotesting was carried out on an example of chemical substances direct genotoxic action (sodium nitrite, hydrogen peroxide, 3,3',4,4'-tetrachlorobiphenyl (PCB 77)), as well as on the example of pro-mutagenic agent – benz(a)pyrene both in absence, and at the presence of metabolic activation system. The experiences carried out on secondary cultures of CH 237 and ??? cells, as well as on cultured human peripheral blood lymphocytes. The revealing of the most sensitive cell cycle stage was carried out with the aid of multiple fixations of cultured cells with definition of frequency chromosomes aberrations in each term of cells fixation and in comparison to the time-table of the mitotic cycle [8].

For all studied pollutants with different physico-chemical and toxic properties a stage of replicative synthesis DNA has appeared the most sensitive. At short-term (2 hours) impact of chemical compounds on cells which are taking place in the S-stage it appeared possible to register (at fixing cells in 10-12 hours) the mutagenic effects of genotoxic agents in concentration below than the level of the health standard requirements, which has not been possible under traditional schemes of bioassay.

In particular, in comparision to traditional schemes of genotoxicity assessment sensitivity offered method in relation to nitrite -ions is 3 order higher.

In case of ??? 77 consedered usually as toxicant of direct action the distinct dependence a doze - effect in a range of concentration, since 10 ng per liter is observed (Table 1).

Table 1. Dose dependence of tetrachlorbiphenyl PCB 77 cytogenetic effect on CH 237 cells fixed in 10 h after the treatment

Composition of the solution under the testing	Damaged cells, %	Chromatid aberrations per 100 cells		
		fragments	exchanges	total
Spontaneous level	2±1,4	2	0	2±1,4
PS [a]	5±2,2	4	1	5±2,2
PCB 77 0.01 µg/l	13±3,4*	11	6	17±4,1*
PCB 77 0.03 µg/l	17±3,8*	17	7	24±4,9*
PCB 77 0.1 µg/l	28±4,5*	34	10	44±6,6*
PCB 77 0.3 µg/l	31±4,6*	38	14	52±7,2*
PCB 77 1.0 µg/l	38±4,9*	48	22	70±8,4*
PCB 77 3.0 µg/l	45±5,0*	62	34	96±9,8*

[?] Physiological solution (0.9% NaCl). * Significant difference from the control at $P<0.05$.

Unexpected result was obtained in case of benz(a)pyrene. With application of the offered technique it was possible authentically to fix its genotoxic effect in supersmall concentration as a mutagenic agent of direct action (Table 2).

Table 2. Cytogenetic effect of 2 hours exposure to various BP doses in CH 237 cells cultured in physiological solution and fixed 10 hours after the exposure (without microsomal metabolising system addition)

BP dose, µg/l	Studied metaphases	Damaged cells, %	Chromatid aberrations per 100 cells

		%	Fragments	Exchanges	total
Spontaneous level	200	1.0±0.7	0.5	0.5	1.0±0.7
0.01	200	5.0±1.5 *	6.0	2.0	8.0±2.0 *
0.1	200	10.0±2.1 *	9.5	3.5	13.0±2.5 *
1.0	100	12.0±3.2 *	12.0	1.0	13.0±3.6 *
10	100	14.0±3.5 *	16.0	0.0	16.0±4.0 *
2500	100	7.0±2.6 *	12.0	6.0	18.0±4.2 *

- Significant difference from spontaneous level at P<0.05

Before BP was considered only as pro-mutagenic agent revealing genotoxic properties after metabolic activation procedure with microsomal S9-fraction isolated from the rat liver induced by Arachlor or phenobarbital.

3.2 Water samples analysis

We carried out approbation of the offered method of biotesting for an evaluation of genotoxicity of natural and waste water samples, and also water soil extracts.

As a result of these studies it was shown, that the offered method can be applicated to assessment of genotoxicity of native samples of natural or waste waters without its preliminary treatment or sterilization, another words - without loss of native properties of analyzed water objects.

Special experiments were performed to evaluate contribution of water-soluble components into the cytogenetic effect of water samples. Filtration of a water sample through the membrane filter with the pore diameter 0.45 μ or 0.22 μ removes from the sample practically all suspended particles of mineral and biological origin, keeping mainly water-soluble ingredients. The contribution of these components to genotoxicity of natural aqueous medium usually is not regarded as significant. However, our long-term experience in the analysis of critical ecotoxicological situations in natural aqueous objects (Ernestova et al., 1992 [9]; Skurlatov and Ernestova, 1998 [21]) evidences that water-soluble compounds may play important role in formation of water toxicity. The results obtained for samples of river water and wastewater are shown in Table 3.

Table 3. Comparison of cytogenetic effects of natural and filtered through the membrane filter (∅ 0.45 μ) water samples in CHO cells (sample 1 was taken in spring; sample 2 and the wastewater sample, in summer)

Type of water	Sample type	Number of scored cells	Damaged cells, %	Chromatid aberrations per 100 cells		
				fragments	exchanges	total
Protva (sample 1)	Natural	200	5.0±1.5*	3	2	5.0±1.6*
	Filtered	200	4.5±1.5*	2.5	2	4.5±1.5*
Protva (sample 2)	Natural [1)]	100	25±4.3*	20	14	34±5.8*
	Filtered	100	13±3.4*	11	8	19±4.4*
Protva (sample 2)	Natural [2)]	100	28±4.5*	22	13	35±5.9*
	Filtered	100	16±3.7 *	10	11	21±4.6*
Wastewater	Natural	100	24±4.3*	16	14	30±5.5*
	Filtered	100	11±3.1*	9	6	15±3.9*
Spontaneous level		100	1±1.0	1	0	1±1.0
Physiological solution		100	1±1.0	1	1	2±1.4

- * Significant difference from spontaneous level at P<0.05.
- [1)] Water was analyzed one hour after the sampling.
- [2)] The sample was stored in frozen state and tested four days after the sampling.

Represented data shows that the contribution of water-soluble components, both of natural water and of wastewater, can be significant. For example, the genotoxicity of the sample 1 of river water exceeded the control level significantly, the contribution of water-soluble ingredients making up 90 %. In the cases when water samples revealed expressed cytogenetic toxicity (the sample 2 of river water, and wastewater), the contribution of soluble substances made up at least 50%.

The value of the toxic effect in cell culture practically did not decline after storage of the frozen sample for four days and then decreased (Table 4).

Table 4. Effect of duration and conditions of storage of water samples on the biotesting results

Type of water	Duration of storage, days	Number of scored cells	Aberrant cells, %	Chromatid aberrations per 100 cells		
				deletions	exchanges	total
Protva	0,04	100	25±4.3*	20	14	34±5.8*
Protva	4 [2)]	100	28±4.5*	22	13	35±5.9*
Protva	16 [1)]	200	4.0±1.4	4.0	0	4.0±1.4
	16 [2)]	200	2.5±1.1	2.5	0	2.5±1.1
Protva	20 [1)]	100	3±1.7	1	2	3±1.7
Wastewater	0,04	100	24±4.3*	16	14	30±5.5*
Wastewater	4 [2)]	100	23±4.2*	18	17	35±5.9*

Physiological solution	100	1.0±1.0	0.5	0.5	1.0±1.0

* Significant difference from the control at P<0.05

1) The sample was stored in a refrigerator (4°C)

2) The sample was stored in frozen state (-18°C)

It is interesting to note, that the same effect was found in the water samples (the Protva River) taken in background dam locations. This means that mutagenic activity of native aquatic environment can be formed not only under the influence of antropogenic factors, but also as a result of natural intra-reservoir processes.

It is known that natural water and wastewater contain a lot of organic solvent-extractable compounds that are capable of exerting direct and mediated cytogenetic effects. This is why the contribution of components extracted with the mixture of organic solvents (diethyl ether/hexane) to the total cytogenetic toxicity of natural water and wastewater was studied more detail in literature.

We found that the contribution of the organic compounds extracted from water with the help of organic solvents into the total genotoxicity of natural waters can be negligible.

The procedure for biotesting dry residues of extracts of ether-soluble substances (ESS) on their mutagenic activity includes the following stages. The initial sample to be analyzed is treated with an organic extracting agent, for example, with hexane/diethyl ether mixture; the obtained dry residue is dissolved in methanol. For the biotesting, the dry residues of the organic extracts dissolved in methanol were added to physiological solution. Simultaneously, the control version was prepared with the same volume of methanol.

As an example, in the Table 5 data on effects of various concentrations of an extract obtained from water of the Protva River is given.

Table 5. Yield of chromatid aberrations in 237 CH cells incubated for 2 h with methanol solution of river water extract and harvested after 10 h

Composition of tested medium**	Number of meta-phases scored	Aberrant cells, %	Chromatid aberrations per 100 cells		
			Fragments	Exchange	Total
ESS (50)	100	3±1.7	2	1	3±1.7

ESS (100)	100	14±3.5*	7	9	16±4.0*
ESS (300)	100	30±4.6*	38	19	57±7.5*
Native water sample	50	28	18	16	34
Filtered sample, ∅ 0,22 µ	50	20	12	14	26
Control	100	2±1.4	2	0	2±1.4
PS	100	1±1.0	0	2	2±1.4

*Significant difference from control at $P<0.05$

** In parentheses, amount of the ESS dry residue in tested medium, µg

It can see that the analysis of ESS dry residues reveals proportional dose-effect dependence. Interestingly, the spectra of chromosome rearrangements show that the frequency of fragments increased to a more extent than that of exchanges, with increase of the extract's content in the medium under the testing.

If genotoxic effect of a native water sample had been connected only with the presence of ESS, as it is often believed in literature, this would have corresponded to 200 µg of the ESS dry residue in the tested sumple. But real content of ESS in this sample is only 3 µg. Thus, the observed genotoxic effect of the native water sample cannot be explained by the presence of ESS. Relative contribution of these substances to toxicity of the native water samples is less than 2%.

Different water samples taken from rivers, reservoirs and cleaned wastewaters were tested for mutagenic activity both by the offered short-term cytogenetic method as described above and by the Ames' test.

Between mutagenic activity measured with Ames test, on the one hand, and genotoxicity the same native samples of natural and waste waters measured with the offered method, on the another hand, only poor correlation is observed. There are examples when no genotoxicity observed for the water sample possessing rather high mutagenic activity (Table 6).

Table 6. Comparative results of evaluation of mutagenic activity of natural and waste water under the Ames' test and by the frequency of chromosome aberrations in Chinese hamster cells

Sample type	Ames' test	Cytogenetic test

	??97		??98		??100			
	?[a] (-S9)	?[a] (+S9)	?[a] (-S9)	?[a] (+S9)	?[a] (-S9)	?[a] (+S9)	MA[b]	K_{MA}[c]
Protva (sample 1)			+	-	+	-	5.0±1.6	2
Protva (sample 2)			-	++	+	-	34±5.8	16
Cymliansk reservoir			++	++	+	-	2±1.4	1
NNP reservoir-cooler			+	++	+	-	6±2.4	2.5
Zhizdra	Acute tox.	0.88	5.69	1.06	1.0	0.98	7.0±1.9	4.1
Resseta	7.69	1.17	10.8	1.85	1.0	1.34	7.3±2.2	4.3
Wastewater-2			-	+	+	+	30±5.5	20

[a] coefficient of multiplicity of excess over the control level under the Ames' test [b] number of chromosome aberrations per 100 cells

[c] coefficients of multiplicity of excess over the control level under the cytogenetic cells.

Table 7. Data of biotesting of hexane - etherl extracts of drinking waters from underground sources of a water-supply of the settlements of Ulyanovsk and Zhizdra districts of the Kaluga region

Sampling place	Content of pollutants, ng/l		Genotoxicity (CH line 237)		Genotoxicity (CH line 237+ S9)		Ames test (salmonella/microsomes) in presence of S9-fraction* (analyzed sample/control)		
	BP	ΣPCB	Aberrant cells, %	Chromatid aberrations per 100 cells	Aberrant cells, %	Chromatid aberrations per 100 cells	?? 97	?? 98	?? 100
Control			2	2	1	1			
Zikeevo	0,3	***23,3***	***4,5***	***8,0***	***22,5***	***38,5***	1,00	1,21	***2,79***
Soudimir	***9,4***	8,0	***5,0***	***8,0***	Acute toxicity	Acute toxicity	0,92	1,26	***3,40***
Kollektivi-zator	-	-	***7,5***	***9,0***	***19,0***	***26,0***	0,90	1,13	0,89
Mouzhitino	1,0	***17,9***	***4,0***	***7,0***	***16,0***	***23,0***	1,00	1,14	1,02

* All 4 extracts in Ames test without methabolic activation (S9-fraction) possessed acute toxicity with relation to *Salmonella Typhimurium.*

Comparative bioassessment of the hexane-ether extracts from drinking underground waters and surface fresh waters in the districts of the Kaluga region of Russia, subjected to a radioactive contamination after accident on Chernobyl APS also reveal only poor quality correlation between biotesting results with Ames test and new procedure offered by us. There were examples when no mutagenic activity was observed by Ames test, but high level of genotoxicity of the same sample was registrated by offered method (Table 7). Interesting to note that rather high concentration of BP and PCB was observed in samples possessing by genotoxicity.

4 Conclusions

A new approach to nature waters genotoxicity assessment is suggested based on analysis of chromosome aberrations of cultural mammalian cells.

Sensitive of this method allows to regist effects of hydrophobic toxicants at the concentration less than 1 µg/l.

Offered high-sensitive short-term method can be used for analysis of genotoxicity of native samples of natural, waste and drinking waters.

Native samples of nature and waste waters demonstrate much more genotoxicity than organic solvent extracts from the same samples. The main part of toxicity is contributed by water-soluble unstable compounds. The contribution of these substances reaches up to 75%.

The development of the highly sensitive technique for evaluation of the mutagenic activity of environmental objects allows to begin the creation of specific industrial device for ecotoxicological monitoring of the polluted territories .

In the result of realization of ISTC project # 2397 the following main results will be obtained:

- an experimental model of the automated apparatus for estimation of mutagenic activity (genotoxicity) of environmental objects will be developed, manufactured and tested first in the world experience of ecological monitoring;
- the unique technique for the initial check-up and standardization of various cell test-cultures that are used for evaluation of mutagenic activity of environmental samples, separate chemical compounds , new medical preparations, food additives, preservatives, genetically modified food products, etc. will be developed;

- on the basis of realization of complex natural researches the objective data on toxicological situation in territories suffered from the ChNPP accident will be obtained that has fundamental significance for predicting the consequences of large-scale nuclear failures;
- the necessary procedures on practical verification and metrological tests of "Method of measurements of genotoxicity of aqueous media" for its representation as a quide document (Methodical instructions) for estimation of the genotoxicity of drinking, natural and sewage waters.

Performance of ISTC project # 2397 will provide ecological monitoring services with a highly sensitive tool for unbiased integral evaluation of the environmental quality, food chain, pharmaceutical preparations, etc. The use of this tool will permit to decrease tens and hundreds times expenses for ecological examinations of contaminated territories, reduce the groundless social tension among population living constantly in zone of influence of potentially dangerous objects, and professionally connected with its fonctioning.

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ABSORBTION AND TRANSFORMATION OF BENZENE DERIVATIVES IN PLANTS

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Benzene derivatives are ubiquitous environmental pollutants. Their fate in the environment - and their sensitivity to degradation systems in plants - are determined by the nature of the substituents carried by their aromatic ring.

Absorbtion andmain pathways of benzene derivatives - [1-6^{14}C]nitrobenzene, [1-6^{14}C]aniline, [1-^{14}C]- and [7-^{14}C]benzoic acid absorption and transformation in maize (*Zea mays* L), kidney bean (*Phaseolus vulgaris* L), pea (*Pisum sativum* L) and pumpkin (*Cucurbita pepo* L) seedlings have been studied.

After penetration in plants, benzene derivatives are transformed mainly by oxidative or by reductive reactions, conjugation with cell endogenous compounds, and binding to biopolymers. The initial stage of oxidative degradation consists in hydroxylation reactions. Then the aromatic ring can be cleaved and degraded into Krebs cycle organic acids. Ring cleavage is accompanied by $^{14}CO_2$ evolution. Aromatic ring cleavage in plants has been demonstrated for different xenobiotics carrying different substitutions in benzene ring.

Conjugation with low molecular peptides is the most important pathway of aromatic xenobiotics detoxification. Peptide conjugates are formed both by the initial xenobiotics (except nitrobenzene) and by intermediates of transformation products. The chemical nature of the radioactive fragment and the amino acid composition of peptides participating in conjugation are identified. A certain proportion of metabolites are bound to biopolymers, mainly proteins.

Approximately 10-15% of benzene derivatives undergo to the deep oxidation.

According to the results of condacted experiments and some of our previous publications it becomes obvious that plants could be effectively used for phytoremediation of soils contaminated by hydrocarbons.

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THE PLANT ASSOCIATED RHIZOSPHERE BACTERIA FOR PHYTOREMEDIATION OF PAHs-POLLUTED SOIL

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Protection of the environment from technogenic pollution is a major aspect of modern biotechnology. Intensive use of oil, gas, and coal in the last decade has led to considerable pollution of natural ecosystems by polycyclic aromatic hydrocarbons (PAHs). PAHs are pollutants which are widely disseminated in the biosphere. PAHs are known to exhibit carcinogenic and/or mutagenic properties and listed by the US Environmental Protection Agency and the European Community as priority pollutants. The use of plants to reduce contaminant level in soil is cost-effective and aesthetically pleasing method for remediation of soils polluted by PAHs [1-3]. The combination of plants and microorganisms enhances the efficiency of the remediation process. The plant rhizosphere is zone around roots exhibiting increased microbial activity. Rhizosphere provides a complex and dynamic microenvironment where microorganisms, in association with roots, form unique communities that have significant potential for bioremediation of organic pollutants. The objective of this study was to improve remediation of PAHs in the rhizosphere through enhancing microbial degradation activity.

The ability of chemotactically active PAHs-degrading bacteria to improve PAH degradation in rhizosphere was studied in greenhouse and field experiments.

Bacterial PAH-degrading strains *Pseudomonas sp*. 8A, *Pseudomonas sp.* 9A were isolated from a site polluted by coal tar and petroleum products accordingly. Bacterial strains were inoculated onto seeds of a plant. In experiments the the PAHs-polluted soils were planted with: *Medicago sativa* (lucerne*), Avena sativa* (oat cultivated)*, Hordeum vulgare* (barley common)*, Triticum aestivum* (wheat common). Chemical analysis of PAHs components was conducted using a gas chromatograph «Crystal-5000» with a flame–ionization detector and capillary column «Supelco» (Capillary GC Column PTE-5). Quantitative data were obtained by the method of absolute graduation of a detector with standard PAHs solutions (Sigma Environmental Standards). A battery of toxicity tests were used to monitor ecotoxicological effects of PAH-contaminated soil during bioremediation. The test battery included leachate (Daphnia magna, SOS-chromotest) as well as solid phase tests (earthworm Eisenia fetida, Soil respiration, lettuce seed germination).

On the basis experiments plant-microbial associations (alfalfa + *Pseudomonas sp.*9A strain and oats + the *Pseudomonas sp.*8A strain) possessing high phytoremediation potential have been selected.

The results of the greenhouse and field experiments indicated that all plants under study have germinated in PAH contaminated podzolic soil (1200 mg/kg). The ability of plants to degrade PAHs was dependent on initial level contamination.

Pseudomonas sp. 8A and *Pseudomonas sp*. 9A strains were screened for their ability to promote the germinate rate of the plant seeds in PAH-contaminated soils. The results obtained show that *Pseudomonas sp*. 8A increased seed germination of *Medicago sativa* by 60%, *Avena sativa* (80%)*, Hordeum vulgare* (36%) and *Triticum aestivum* (28%). *Pseudomonas* 9A significantly increased the germination of *Medicago sativa* by 70%, *Avena sativa* (47%) only.

Inoculation of *Medicago sativa* by *Pseudomonas sp*. 9A increased PAHs degradation at 500, 750, 1000 mg/kg contamination levels by 160, 280, 340 mg/kg accordingly within 4 weeks. Inoculation of *Avena sativa* by *Pseudomonas sp.* 8A increased the PAHs degradation at 500, 750, 1000 mg/kg contamination levels by 18%, 29%, 44% accordingly. PAHs dissipation was higher in planted soil than in the bulk one.

After 20 weeks of field experiment on rhizosphere remediation oil polluted soil with *Medicago sativa* inoculated by strain 9A the concentration of PAHs soil decreased by 64.9%. In experiment on rhozoremediation of diesel oil polluted podzolic soil with *Avena sativa* inoculated by bacterial strain 8A the PAHs concentration decreased by 95,6% at the same time.

The results of bioassay have shown reliable reduction of soil toxicity during the experiments on PAH rhizosphere biodegradation in experiment with *Medicago sativa* and *Avena sativa* inoculated by bacteria.

The work described here shows that inoculation of plants with specific bacteria increases PAH degradation in soil. Thus, plant-enhanced bioremediation of PAHs is potentially effective remediation method.

The proposed technology for rhizoremediation of soils to clean-up pollution of polycyclic aromatic hydrocarbons is ecologically and toxicologically safe. The used strains of chemotactically active microorganisms-degraders have been isolated from rhizosphere of plants grown on soil polluted with PAHs.

Harmlessness (absence of pathogenicity) of the microorganisms used for rhizoremediation have been determined by the following indicators:

- level of averaged lethal doses of microorganisms under different routes of administration to experimental animals (LD_{50});
- toxicity (availability of endotoxins, lethal for experimental animals at certain dose level);
- toxigenicity (availability of exotoxins discharged into the environment);
- dissemination (ability of microorganisms to persist in the body of warm-blooded animals for a long time).

Rigid criteria of selection regulated by existing methodic regulations, have allowed to character the *Pseudomonas 8A* and *Pseudomonas 9A* strains as harmless for rhizosphere remediation.

Taking into consideration that the plant rhizosphere is the natural environment for these microorganisms, inoculation of plants with the *Pseudomonas sp. 8A* and *Pseudomonas sp.9A* does not effect on aboriginal soil microflora and viability of sanitary-controlled microorganisms, application of the indicated microorganisms may be considered to be harmless during measures on rhizoremediation of PAH polluted soils.

During remediation of podzolic soil with the use of plant-microbial association in parallel with the reduction of PAH concentrations, there also is noted lowering their toxicity.

The rhizoremediation technology is adapted to existing agricultural techniques of soil cultivation. Expenditures on soil cleanup with the use of plant-microbial association *in situ* is ten times lower than remediation techniques conducted with excavation and removing polluted soil or heat treatment.

So, the proposed technique for soil recultivation with the use of plant-microbial association is ecologically and toxicologically safe and economically attractive. The technology has significant potential for cost saving, conservatively estimated to be one-tenth the cost of competing technologies (dig and haul, incineration, soil washing, composting).

The technology is promising for remediation of soils polluted with oil, oil products, coal-tar, and aged manufactured gas plant pollutions.

The investigations have been performed under financial support of the ISTC, the Project # 1429.

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SOIL CONTAMINATION IN THE URAL INDUSTRIAL REGION AS A HEALTH RISK FACTOR

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The objective of this work is to assess the significance of soil contamination as a health risk factor for population of Sverdlovsk and Chelyabinsk Oblasts of the Ural industrial region. This study was carried out in the framework of the ISTC 500 Project funded by the European Community.

Sverdlovsk Oblast is situated in the Middle and North Urals and on the adjacent territory of the Western-Siberian Lowland within the following geographical coordinates: latitude 56°00' - 62°00' North and longitude 57°10' - 66°10' East. Area of Sverdlovsk Oblast is 194.8 thousand square km (i.e. 1.1% of the territory of Russian federation). In the north Sverdlovsk Oblast borders on Komi Republic, in the east on Tumen Oblast, in the south on Kurgan Oblast, Chelyabinsk Oblast and Bashkortostan Republic, in the west it borders on Perm Oblast.

Chelyabinsk Oblast occupies mainly the eastern side of the South Urals Mountains as well as the adjacent region of Transurals Plain. Only north-west part of Chelyabinsk Oblast is situated on the western side of South Urals. The territory of Chelyabinsk Oblast is situated within latitude 52°00' - 56°20' North and longitude 57°10' - 63°20' East. Area of Chelyabinsk Oblast is 87.9 thousand square km. (0.5% of the territory of Russian federation). In the north Chelyabinsk Oblast borders on Sverdlovsk Oblast, in the east on Kurgan Oblast and Kazakhstan, in the south on Orenburg Oblast, in the west it borders on Bashkortostan Republic, Fig.

Figure 1

The Urals is the oldest source of mineral and raw materials in Russia. Rich natural resources were the foundation for the industry and economy of the region. The industrial development of the Urals was started in the beginning of the XVIII century. The rate of growth of mining and smelting industry was unprecedented. From 1700 to 1861, there were built 205 metallurgical plants, 144 - for ferrous metallurgy, 61 - for copper metallurgy. The second stage of the industrial development of the region took place at time of Stalin's industrialization in 1930s, when the rapid growth of new heavy industrial enterprises began. This industrialization stage was accompanied by the appearance of new environmental problems. To reduce the price of construction and exploitation of enterprises, new ferrous and non-ferrous metallurgical, chemical, heavy engineering and power engineering plants were concentrated in small towns that became large industrial centers. Industrial technologies being in use at that time were very environmentally imperfect and such industrial concentration caused intolerably high contamination of air and surface water. These negative ecological tendencies of industrial development became stronger during the Second World War in 1941-1945, when a lot of enterprises were evacuated from the European part of the USSR to the Urals. All evacuated enterprises were relocated to territories of already exiting ones, which increased industrial concentration and pollutant emission in the region.

The Ural is among the most environmentally unfavorable regions of Russia. The main reason of such situation is the extremely high concentration of environmentally dangerous industries. The other reasons are that the most part of the region's vast mining and metallurgical combines are outmoded, lack of pollution control technologies, and poor exploitation of existing equipment for pollution control. Intensive emissions/discharges of pollutants and the generation of a large amount of toxic wastes have led to high levels of contamination of air, surface waters and soils in a significant part of Sverdlovsk and Chelyabinsk Oblasts. Soil contamination is one of the most severe environmental problems. On data of the Ural Regional Headquarters for Hydrometeorology and Environmental Monitoring practicing annual monitoring of the Sverdlovsk Region for soil contamination with industry-generated toxic substances, the highest levels of soil contamination are observed in the cities of Pervouralsk, Revda, Ekaterinburg, Neviansk and Verkhnaya Pyshma, Table 1. It is also known that levels of soil contamination are extremely high in such cities as Kirovgrad, Verkhnaya Salda, Krasnouralsk, but data on specific levels of soil contamination are not published for them.

To assess the significance of soil contamination as a health risk factor the city Kamensk-Uralsky in Sverdlovsk Oblast (aluminum production center) and the city Karabash in Chelyabinsk Oblast (copper production center) were selected for detailed analyses. In the framework of the ISTC #500 Project "THE ASSESSMENT OF PRIORITIES FOR MIDDLE URALS' ENVIRONMENTAL POLLUTION PREVENTION" environmental situation at the territory of these cities were studied in details. Environmental health risks for population resulting from soil and local plant food contamination were assessed. The methodology of the environmental health risk assessment of the U.S. Environmental Protection Agency was used with cancer risk values from the IRIS database. These risks were compared with cancer risks resulting from air and drinking water contamination. Calculated environmental health risks considered above were ranked in accordance with their intensity. For comparison, data about some social risks also are presented (see Table 2). It may be concluded that not environmental health problems but general welfare and other socioeconomic factors play the key role in mortality rate and economy losses.

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TABLE 1. Average soil contamination in the Sverdlovsk and Chelyabinsk Oblasts with toxic substances of industrial origin

Territory	Concentration of contaminant, million^{-1}									
	Cr	Pb	Mn	Ni	Zn	Cu	Fe	Hg	NO_3	F
Sverdlovsk Oblast										
Pervouralsk City	79,85	72,77	1126,51	53,61	311,46	267,35	19413,30	0,16	19,52	0,00
Revda City	40,37	76,31	986,71	47,84	271,95	408,97	24832,68	0,44	70,49	39,65
Ekaterinburg City	163,60	125,17	575,81	131,74	229,57	106,13	16443,53	0,15	17,73	16,42
Neviansk City	44,97	87,95	993,06	80,68	342,81	116,82	25246,25	0,43	17,28	2,98
Nizhneserginsky Region	98,80	80,32	1655,41	128,89	189,16	69,77	20687,70	0,19	14,49	2,48
Verkhnaya Pyshma City	66,39	34,06	879,35	71,59	174,57	266,36	23551,48	0,09	12,12	77,17
Asbest City	162,01	31,02	677,96	435,89	76,34	42,35	12013,22	0,06	3,34	22,97
Alapayevsk City	105,95	47,01	1448,31	145,00	121,55	46,14	24347,89	0,18	35,40	1,67
Nizhny Tagil City	48,00	67,70	1368,23	79,99	107,22	113,78	20876,53	0,17	29,74	1,31
Kushva City	28,74	62,93	1693,00	37,40	92,54	131,97	34677,72	0,78	13,81	0,44
Artyomovsky City	68,02	35,61	709,96	100,14	156,09	58,22	21841,57	0,09	4,29	13,88
Kamensk-Uralsky City	51,49	47,82	679,18	80,97	108,44	51,38	18072,56	0,14	0,00	0,00
Krasnoturiinsk City	35,05	21,82	1010,65	40,86	154,14	212,80	20167,86	0,26	18,23	7,72
Kamensky Region	12,16	22,58	1052,18	72,32	45,08	23,16	9555,93	1,12	1,90	23,36
Bogdanovich City	20,61	30,13	1042,69	37,27	45,93	22,33	9565,31	0,05	0,00	0,00
Kamyshlov City	61,30	43,18	440,34	79,30	101,87	31,99	11180,20	0,03	6,05	4,96
Chelyabinsk Oblast										
Emanzhelinsk City	29,86	41,58	457,33	44,78	56,43	32,51	12411,22	0,148	10,20	73,95
Kyshtym City	17,90	27,05	540,36	29,69	107,34	74,47	11987,47	0,207	-	-
Kasli City	30,25	17,36	467,90	29,86	62,38	54,42	14171,98	0,052	12,76	73,30

TABLE 2. Individual risks for the population of Sverdlovsk Oblast, 10^{-6} $year^{-1}$ [1-3]

Risk factor	males		females
Suicide	729		189
Murder	593		174
Death in the result of alcohol poison	435		106
Death in the result of other poisons	109		31
Death in the result of drowning	78		6
Death in the result of car accidents		39.7	
Death in the result of incidents with fire-arms	4		0.0
Death in the result of spring floods		2.9	
Death in the result of industrial explosion		1.9	
Death in the result of ejection of toxic substances in industry		0.75	
Death in the result of hazardous meteorological events		0.46	
Death in the result of air accidents		0.24	
Death in the result of railroad accidents		0.08	
Death in the result of pipe-line accidents		0.07	
Indoor radon lung cancer rural dwellings urban dwellings	(lifetime risk) 17800 10300		(lifetime risk) 3200 1800
Cancer risk from air chemical contamination (the city Kamensk-Uralskij)		6.1 (lifetime risk)	
Cancer risk from drinking water chemical contamination (the city Kamensk-Uralskij)		1.6 (lifetime risk)	
Cancer risk from soil contamination (the city Kamensk-Uralskij)		0.6 (lifetime risk)	
Cancer risk from local plant food contamination (the city Kamensk-Uralskij)		0.09 (lifetime risk)	

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BILATERAL WORKING GROUP – MISSION; WORK PROGRAMM, AND STATUS

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INTRODUCTION

The United States Environmental Protection Agency (EPA) and the German Federal Ministry of Education and Research (BMBF) have been working in an ongoing partnership to gain an understanding of each other's approach to the cleanup of chemical contamination in order to protect human health and the environment. This partnership has now entered its third phase with a new focus on providing a variety of tools, approaches, and technologies that could facilitate streamlined, cost-effective cleanup and redevelopment of industrially contaminated sites, or Brownfields.

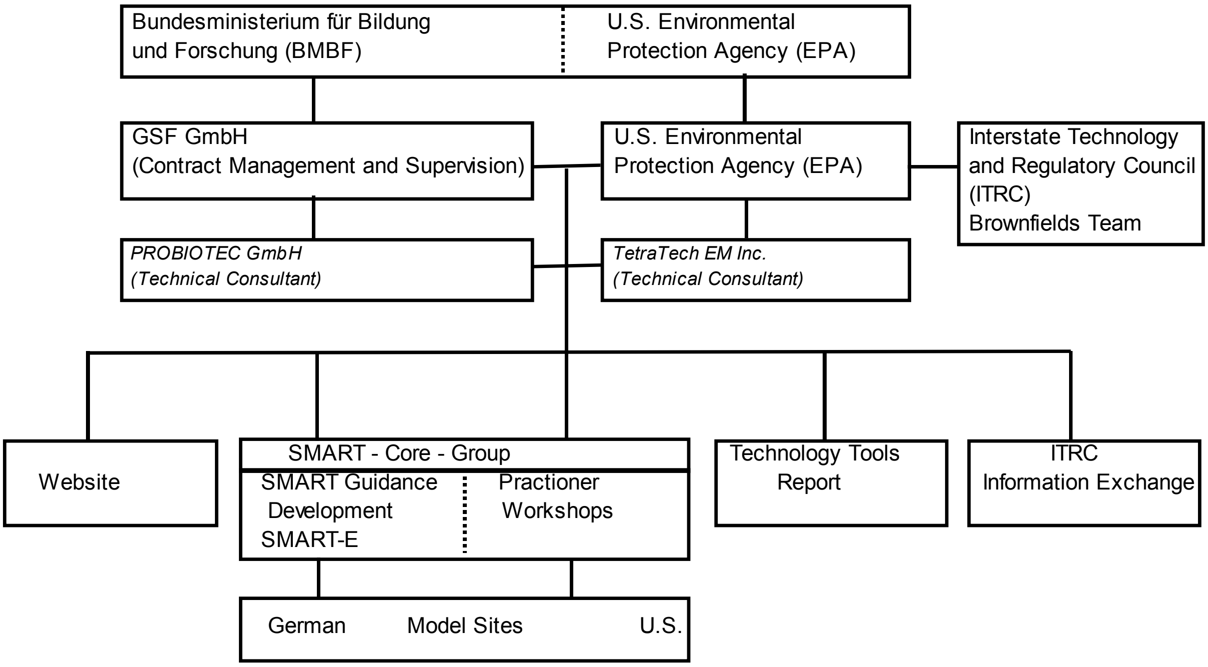
Many of the issues regarding site redevelopment can benefit from the knowledge and experience of the Bilateral Working Group. Research targeted specifically at the issues influencing redevelopment is required. Some of the proposed research can help remove real or perceived obstacles at sites where low economic value and high cleanup costs may preclude redevelopment. Sound science can provide communities with tools for decision making. This paper will present information on the workgroup structure, program goals, focus areas, work plan, schedule and benefits for the next 3 years.

WORKGROUP STRUCTURE

The Bilateral Workgroup structure goal is to develop tools and techniques to facilitate cleanup of contaminated sites. This goals has been expanded to include Brownfields Redevelopment. There are three specific objectives: (1) facilitate an understanding of each country's approach to the remediation of contaminated sites, (2) evaluate innovative remedial technologies or techniques according to the standards of both countries, and (3) facilitate international technology exchange.

The organization structure is complex and includes diverse interdisciplinary representation from each country. Since the issues related to Brownfields redevelopment are also complex and interconnected, the logical approach was to include representation from the various organizations that hold some level of responsibility for redeveloping sites. Organizational entity represented on the workgroup structure include: Local Governments, State Governments, Universities, Federal Governments, Consulting Firms and Development Companies.

The following is a pictorial view of this structure:



PROGRAM GOALS

The Program supports one common goal, to develop tools and techniques to facilitate Brownfields redevelopment. There are four basic objectives to meet this goal.

- Make Redevelopment a Sustainable Process
- Facilitate Faster Redevelopment of Sites
- Allow Greater Independence from Public Money
- Enhance Benefits to Society

Brownfields site redevelopment requires greater local government and community involvement with decision-making than other kinds of development, since there are important socio-economic and communication issues which can affect the outcome of the project. Technical projects and workshops serve as the work efforts to support these objectives and goals.

FOCUS AREAS AND WORK PLAN

The Bilateral workgroup is focused on tools, workshops and transfer of information. Specific tools will be developed for use by those redeveloping sites. Tools range from actual technology as well as internet based interactive decision tools, and models. The workshops will used to gather technical information necessary to develop some of those tools and be used as a way to exchange information between the two countries on topics of interest. Experts in both countries are participants in these workshops.

Ultimately, the intent is to disseminate the tools and information that are collected to the broader international community. This may be done through publications, training, technical conferences or at meetings. A listing of the area, projects and proposed products are as follows:

Focus Area	Project	Product
Tools	**1) SMART Guidance** **2) Technology application** **3) Strategy for Sustainable Land Management**	**1) Paper report that integrates science and business strategies.** **2) Searchable CD on technology tools applicable to Brownfields sites.** **3) Integrated strategy that links different societal groups and various scientific disciplines.**
Workshops	**1) Economic Tools** **2) Project management** **3) Risk Assessment\ Communication** **4) Sustainability Topics**	**A document will be prepared following each workshop discussing findings and areas of future need.**
Technology Transfer	**1) Feasibility Study on competence Centers** **2) Study on Financing, Tax, and Liability** **3) Communication Guidance and Education**	**Products will be determined in the future**

SCHEDULE

The proposed work under the Bilateral Workgroup is scheduled for the next 5 years. Much of the work between 2000- and 2001 was project planning and program development. During 2002, 15 model projects, 5 in Germany and 10 in the U.S. were selected to assist in the development of the SMART project. In addition, the U.S. hosted the first workshop on economic tools and finance for sustainability. In May 2003, Germany will host the second workshop on project management. The first part of the SMART guidance will be complete as well as the technologies tools interactive CD. The remaining pieces will be planning and conducted over the next 3 years.

BENEFITS

The Bilateral Working Group research provides many benefits to both countries. The initial research is designed to identify uncertainties associated with contaminated site redevelopment. This would include a broad set of topics including contamination, exposure risk, technical, cultural, social and economic issues. A long those lines the research is designed to provide information on how to reduce or manage those uncertainties. Development of a science based decision framework, like SMART, provides those responsible for redevelopment with a tool to make an informed decision. Lastly, the ultimate benefit is to provide as many individuals with the necessary information and training to support risk management decisions.

SUMMARY

The Bilateral Agreement's foundation is built on enhancing each partner country's capabilities by sharing information on tools and techniques related to cleanup and redevelopment. In addition, international partnering, such as that under the Bilateral Agreement, has and will continue to allow each country to learn about the partner's environmental regulations, policies, and guidelines. This understanding may influence the evolution of remedial regulations in each country and may help to standardize processes and procedures on an international level, which would further encourage redevelopment in other international markets.

More information on the US\German Technical Bilateral Working Group is available on www.bilateral-wg.org

US-German Bilateral Working Group

SMART GUIDANCE AS A TOOL FOR PLANNING AND DECISION MAKING

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Keywords: Brownfields, redevelopment, innovative technology and tools, social, economic, environmental, regulatory framework, cleanup

SUMMARY

The United States Environmental Protection Agency (EPA) and the German Federal Ministry of Education and Research (BMBF) created a Bilateral Working Group in 1990 to gain a better understanding of each country's efforts in developing and demonstrating remedial technologies (Phase I and Phase II). Under Phase III of the Bilateral Agreement, EPA and the BMBF are focusing on best practices for redeveloping Brownfields. As one product of Phase III of the U.S.-German Bilateral Working Group, EPA and BMBF are jointly preparing Site-specific Management Approach and Redevelopment Tools (SMART) Guidance documents. SMART Guidance documents are intended to set the framework for clearly communicating the related risks, potential opportunities, and the tools necessary to redevelop a site to all possible stakeholders in the project.

This introductory presentation on the SMART Guidance development focuses on the history of the idea, goals, focus areas, participants, model project approach, structure and content of draft SMART Guidance, future work, and schedule. The SMART guidance is an experienced-based tool that provides a framework to describe the full spectrum of the features and probable effects of a particular site redevelopment project to stakeholders. It is considered to be useful especially for practitioners who plan and develop, and covers the economical, environmental, and the social aspects of projects.

1. INTRODUCTION

In 2000, the U.S.-German Bilateral Working Group conducted a feasibility study in both countries to identify focus areas that can be addressed to overcome barriers to redevelopment of Brownfields and contaminated sites. Based on this study, the Working Group initiated several tasks including development of the SMART Guidance document and organization of a series of international workshops in both countries.

2. GOAL AND APPROACH OF THE SMART GUIDANCE

To attract investors and inform decision makers about Brownfield redevelopment projects, it is mandatory to consider the demands, interests, and requirements involved in the process of Brownfield Site remediation.

Additionally, it is necessary to specify related economic and environmental risks and opportunities, and to present them clearly and quantitatively.

The goal of the SMART Guidance is to supply site developers with ideas, formats, and best practice examples in order to aid in the creation of proper design and business plans. The SMART Guidance shall help to draw-up site-specific descriptions of redevelopment projects which reflect the project features in terms of: business, economy, environmental, and sociological issues. Key sections will focus primarily upon the many interfaces that join these features together. The guidance is a tool box covering the complete spectrum of required elements, whereas project-specific plans developed according to this guidance shall contain enough detailed information for the identified target groups of stakeholders.

In order to achieve this goal, the SMART guidance shall:

- Aid developers and site managers in the development of a business plan, financial summary, and mission for the redevelopment of Brownfield properties.
- Focus on the crucial links between social, economic, and environmental issues which are often overlooked by site developers and planners.
- Provide ideas for cost reduction, increased success rates, innovative planning techniques, project benefits, and financial planning.
- Help to streamline the gaps between municipal officials, local community, and investors.
- Include specially designed sections outlining important subjects such as assessing environmental risks, economic viability, and community relations that provide information to assist site managers in the development of strategies to make their site an environmental and financial success.

3. STRUCTURE OF THE SMART-GUIDANCE

Many failed development plans consider economical, environmental, and social aspects as individual rudiments, when in fact they are very closely related. The scheme of preserving the feature elements in a discrete manner, or 1-dimensional view, is common practice in the technical community. A successful Brownfield project will be one that is developed with a multidimensional view that considers economical, environmental, and social realms on the same plane.

One must consider the fact that Brownfields redevelopment is a process of interlinking many seemingly unrelated issues together.

Components of the document will include:

Introduction / Executive Summary

The Project Analysis: Informational Basis and Explanations on the Project

BUSINESS
Project Vision and Future Land Use
Project Mission and Goals
Site Description
Organizational Structure and Stakeholder Roles

ENVIRONMENTAL ASPECTS
Environmental Conditions
Previous Technology Applications
Regulatory Considerations

ECONOMIC ASPECTS
Economic Analysis / Cost Calculation Scheme
Financing Issues
Insurance Issues
Legal /Liability Issues

SOCIAL ASPECTS
Comprehensive Community Planning
Land Reuse Issues in Urban/Local Context
Data Gaps

Best Practices
Best Practices for Addressing Economic Considerations
Best Practices for Addressing Environmental Considerations
Best Practices for Addressing Social Considerations

Additional sections may be added by each country depending on their individual needs.

The SMART Guidance may include sections describing how to create Executive Summaries to effectively present critical data to key decision makers.

4. APPROACH

The approach to developing the SMART Guidance consists of using available literature describing the state-of-the-art on Brownfield redevelopment, collecting information from Model Brownfield Redevelopment Projects (Model Projects), and conferring with experts in Brownfield redevelopment in the forum of international workshops focussed on specific redevelopment issues. Additionally, the U.S. is involving state representatives through the Interstate Technology and Regulatory Council (ITRC) to provide a state perspective on the Brownfields issue. Model Projects are redeveloped Brownfields sites selected for this program because of the significant impact each site has had on the local economy, environment, and community.

The U.S. Model Projects were selected in spring of 2002. The projects are listed below:

- Union Station - Portland, Oregon
- Kaiser Steel Site - Fontana, California
- Barrier Industries - Port Jervis, New York
- Paper Mill Island - Village of Baldwinsville, New York
- San Diego Ballpark - San Diego, California
- Visy Paper - Staten Island, New York
- Assunpink Creek - Trenton, New Jersey
- Magic Marker- Trenton, New Jersey
- Westside Avenue - North Bergen, New Jersey
- North Marine - Portland, Oregon
- Port of Ridgefield - Ridgefield, Washington
- Ikea - Emeryville, California
- Carolinas Recycling Group Site - Spartanburg, South Carolina
- Ware Shoals – South Carolina
- Weber Block Plaza - Stockton, California
- Koppers Koke - Hudson County, New Jersey

The German Model Projects are listed below:

- AW Railyard - Saarbruecken
- Saarterrassen (Steel Mill)- Saarbruecken
- Heiterblick Russian Barracks – Leipzig
- Technology Center - Zittau
- Kienzle Watches - Villingen-Schwenningen
- OKAL Wood - Black Forest
- Schuler Scrap-Yard - Singen
- Kruse Chemicals (Commercial Area) - Lennestadt
- Stepelsche Strasse (Dump Site) - Duisburg

- Inner Harbour Service Park - Duisburg
- Duisburg North Landscape Park - Duisburg

Another informational source during the development of the SMART guidance will be a series of workshops on the interrelationships among Brownfields economic, environmental, and social phenomena. Approximately six workshops will be held over a three-year period (two workshops each year - one in each country). The objective of each workshop is to explore and share information with practitioners involved in model projects and other experts. Special emphasis will be given to the identification, analysis and sharing of best practice examples. The results of the workshops will be incorporated into the SMART Guidance.

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US-German Bilateral Working Group

THE BILATERAL WORKSHOPS – FIRST FOCUS: FINANCING

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INTRODUCTION

One goal of the bilateral working group under Phase III of the Bilateral Agreement is to exchange ideas and experiences of both countries to stimulate brownfield redevelopments. To promote this exchange and to discuss differences in the treatment of abandoned sites as well as possibilities to transfer approved tools from one to the other country. In this context a series of four workshops are planned. The first was held on November 11 and 12, 2003 in Charlotte, North Carolina, USA, with the topic "Economic Tools and Finance for Brownfield Redevelopment.

WORKSHOP PURPOSE AND OUTLINE

Sustainable redevelopment of brownfields in Germany and the United States requires harmonization between private and public sector efforts and their ability to create environments capable of luring finance and capital. Over the past ten years, brownfields redevelopment in the U.S. has been characterized by the successful application of several innovative federal, state, and local tax and financing tools. The success of these tools, such as Tax Incremental Financing (TIFs), Revolving Loan Funds, HUD's Section 108 loan guarantee programs and rehabilitation tax credits, insurance policies (such as coverage for pollution liability, remediation legal liability, or remediation stop loss coverage), reveals how well accepted they have become in urban economic development policy. Moreover, other tools and policies have emerged on the national urban development landscape, such as the Community Reinvestment Act, that warrant further analysis and discussion in an international context.

In Germany, revitalization of contaminated lands is strongly influenced by unique combinations of national and regional financial, housing, labor and economic development strategies reflect unique policies and influences on urban regeneration in Germany. Regional economic development authorities, such as Northrhine Westfalia's Landesentwicklungs Gesellschaft (LEG) and the "Grundstueckfond", as well as Nordhorn's public/private partnership, which yielded $230 million in private investment from $30 million of public investment, offer unique German lessons for U.S. cities. Other state funds as for example the "Altlastenfonds" of Baden-Wuerttemberg can be used to cover the remediation costs of public owned sites and since 2002 also partly for private owned sites. Moreover, several of Germany's national economic development policies - such as the "dual technical labor training program" for teenagers - offer lessons for national and regional urban economic development policies (the State of Wisconsin as well as several cities in New York, have already adopted the "dual system" for vocational labor training).

The purpose of this two-day workshop was to analyze and discuss innovative brownfields financing and economic development strategies in both countries. The workshop also endeavored to evaluate critical elements of successful public/private partnerships.

The agenda of the workshop included:

Topic	**Presenter**
US Land Management / Site Recycling German Land Use, Land Management, Site Recycling	Karl Alvarez, EPA Dr. Fabian Dosch, German Federal Agency of Building and Housing
Overview of U.S. Brownfield Economics	Evan Henry, Bank of America
Overview of U.S. Brownfields Financing Tools	Charlie Bartsch, Northeast-Midwest Institute
German Funding instruments applicable for brownfield redevelopment	Dr. Uwe Ferber, Projektgruppe Stadt+Entwicklung
U.S. Public Finance Tools U.S. Private Capital Tools	Doug MacCourt, Ater Wynne LLP (Moderator) Ann Sherman, Ater Wynne LLP Ken Cornell, Vice President, AIG Environmental Evan Henry, Bank of America
German Federal and State Urban Development Programs - Funding Experiences for Brownfield Redevelopment in the City of Leipzig Public-private partnership development and finance strategies The State Property Fund („Grundstücksfonds“) in North-Rhine Westphalia and the Role of State Development Agencies („Landesentwicklungsgesellschaften - LEG“)	Karsten Gerkens, Head of Redevelopment Agency, City of Leipzig Ralph Ishorst, West German Real Estate Bank
U.S. Case Studies • Trenton, New Jersey • Portland, Oregon	Leah Yasenchak, City of Trenton Doug MacCourt, Ater Wynne LLP
German Case Studies • Duisburg Innenhafen • Model project from Baden-Wuerttemberg	Martin Linne, City of Duisburg Michael Koenig, Dr. Eisele Group
Joint Panel Discussion • U.S. mechanisms and project examples of funding sustainable uses • German approaches to sustainability on Brownfields - a Current Example from German Urban Development	Colin Vance, EPA Lisa Peoples, HUD Chris Forinash, EPA Jan Eitel, GIU
Roundtable Discussion - Group Exercise Two groups were formed: one U.S. and one German group. The U.S. group worked on a German case (a pre-selected actual site) and applies its financing strategies/tools on this case parallel. The German group worked on a U.S. case (a pre-selected actual site) and applies its financing strategies/tools on this case. Groups explained their approaches and results in the plenum. The final discussion had two main functions: (1) to review the findings and most striking aspects of common interest of the previos discussions, and (2) to identify the economic and finance instruments which seem to be worth elaborating on regarding the opportunity of transferability to U.S.-German redevelopment strategies.	Ann Vega (U.S. facilitator) Stephan Tomerius (German facilitator)

RESULTS

Selected highlights of the workshop are described below:

Dr. Fabian Dosch, BBR Bonn
There is currently a land consumption rate in Germany of 47,000 hectares each year (129 per day) . This rate is 1.5 times larger than the area of Munich. The concern regarding this land consumption is the urban sprawl with an strong impact to the ecology in a densely populated county like Germany with secondary economic effects (i.e. costs of public traffic or public infrastructure). Contrary to the consumption of "green land" 127 000 hectares of usable derelicted land (from industry, commerce, military, traffic areas,...) are presently available. Land reuses are currently charted at the following: Nature - 14%, Housing - 22%, Commerce - 59%.

Best practices and the National Strategy are dictating that Germany and the European Union (EU) concentrate efforts on revitalization of the cities, reduce land consumption, and focus internal redevelopment towards existing infrastructure. Indicators to be used for this effort include tracking the increase in employment opportunities, 100% occupancy rate in dwellings in inner city locations, and the successful redevelopment of remaining derelict land.

Additional to existing economic tools new possibilities to reduce land consumption are in the discussion, which include:

- Land tax reform
- Abolition instrument fostering land consumption
- Increase urban redevelopment grants
- Regrouping housing subsidies from new housing starts to existing housing

Evan Henry, Bank of America
Possibility of unknown problems increase uncertainty and the result is to narrow the range of economic viability. The role of government in the United States is to reduce the unknowns to increase the range of economic viability through the use of technical assistance, grants and liability relief as well as subsidizing the restoration of economically less viable sites. Limitations to the role of government in the United States:

- Cannot use public funds to enrich the private sector
- Cannot use public funds to help polluter restore brownfield
- U.S. funds are set up to "find" not "fund" brownfields
- Government brownfield programs are aimed at working around the liability issue
- Arguably a change in liability scheme would stimulate private redevelopment of brownfields more than government assistance approach

Private financing includes:

- Debt
- Equity
- Insurance

Insurance is not a financing mechanism but should be considered a risk reduction mechanism.

Uwe Ferber, Projektgruppe Stadt + Entwicklung Leipzig
Contrary to the different tax reduction possibilities for redevelopment activities, which are not available in Germany, the realization of brownfield redevelopment projects can be supported by public funds on different levels:

1. European level (ERDF, KONVER, URBAN) with direct funding up to 75%
2. Federal level (Federal economic regeneration fund, Urban renewal programs, Contaminated land remediation programs,...)
3. State programs (Grundstuecksfonds NRW, Altlastenfonds Baden-Wuerttemberg,...)
4. Community based programs

All available funding instruments have the goal to minimize the public and maximize the private part of the funding.

Ann Sherman, AterWynne
Tax Exempt bonds - Income tax exempt from federal/state taxes. Interest rate is much less on these types of bonds.

- Tax exempt bonds (offered by State and Local governments):
- Taxable Bonds

Types of projects bonds are used for include: open space projects, parks, housing, golf courses, assisted living facilities, hospital, convention center, library and mixed use projects. Tax credits used in conjunction with tax exempt or taxable bonds may also be a strategy.

Ken Cornell, AIG Environmental
Brownfield reuse should take into consideration stakeholder concerns and include community support. Concerns regarding liability for newly found contamination, conditions on site, which are exacerbated or created during remediation and third party claims.

People should evaluate a risk management program. This approach will help participants:

- Minimize risks
- Assess, quantify and control costs
- Provide protection from escalating costs
- Assurance against unknown legal liability
- Thorough cleanup will be completed quickly and economically

Evan Henry, Bank of America
Bankers analyze risk. Applicant should try to reduce risk to lender. Banks assess projects using the "5 C's of Credit:

- Character - what is the reputation of the applicant
- Cash flow
- Cash - is the applicant solvent?
- Collateral
- Conditions

Leah Yasenchak, City of Trenton, New Jersey
The City of Trenton took a neighborhood by neighborhood approach by evaluating the needs of the community. These steps included site identification and the decision on reuse. The city takes steps to acquire sites through various mechanisms such as tax foreclosure, direct purchase, or condemnation. To finance the remediation of the site the city escrows the acquisition price to assist in cleanup of site. Trenton uses many state and federal mechanisms in their brownfield cleanup and reuse efforts. These tools have included:

- Federal USTFields monies
- EPA/DEP removal actions
- New Jersey Redevelopment Authority (NJRA) Brownfield Initiative
- Negotiations with the responsible party
- Property trusts
- Brownfield Cleanup Revolving Loan Fund

Redevelopment is the key to improving the quality of life for surrounding property and neighborhoods. Trenton established partnerships early on in the process. These partnerships include the use of committees, federal government, state government, county government, redeveloper and internal partnerships within the city.

Martin Linne, Duisburg

Use of International Building Exhibition to foster ways to reuse waterfront. Creative aspect of project was to implement a planning concept as a city that was initiating a process to re-create itself. Incentives for Private Investment include:

- Prepare for public environment
- Federal tax relief on the costs for preservation of buildings under monument protection (10% of total investment over 10 years)
- Business promotion discount 30% of current market value (local act of the city of Duisburg)
- Coordination with other agencies

Colin Vance, U.S. EPA

Criteria for gauging success in brownfields includes: economic benefits and costs, economic impacts, and sustainability. Where:

Net benefits = change in value of outputs - change in the cost of inputs

Outputs include more open space, reduced crime, cleaner air, etc. Inputs include resource costs to society (labor, "external" costs). Indicators include:

- Job creation
- Changes in out puts
- Changes in revenues
- Financial impacts to state and local governments
- Housing starts from existing housing stocks
- Crime statistics
- Infrastructure savings
- Neighborhood enhancements

Chris Forinash, EPA

U.S. Bill T21 is used for Transportation brownfield related activities. $16 billion is awarded each year. Various programs receive this money including the "Congestion Mitigation Air Quality" (CMAG) program. Federal Transit Act provides $1 billion for capital improvements. Some of this funding can be used for remedial activities (for example, using a roadway as a protective cap).

Smart Growth Initiative included a former 183-acre Atlantic Steel site in Atlanta, Georgia. 12 million square feet of mixed use, "pedestrian friendly". Infrastructure changes through the use of federal transportation dollars to enhance a bridge and roadway as a transportation control measure (TCM).

Lisa Peoples, Department of Housing and Urban Development

Community Planning and Development can be accomplished through the use of various financial instruments available through HUD. Such as the Brownfields Community Block Grant, Section 108-loan guarantee and the Brownfields Economic Development Initiative (BEDI) (used for larger projects). $25 million per year can be used for site acquisition, remediation, etc. BEDI funds promote partnering and are used to facilitate infrastructure development.

Renewal Communities Empowerment Zones provide $22 billion in tax incentives. The Rural Housing Economic Development Program funding can also be used for Brownfield sites.

Jan Eitel, GIU Saarbruecken

One general focus of redevelopment projects is the sustainability related to economy, ecology and energy efficiency. Economical successful projects have to be original in all parts of realization (funding, planning, technical execution, marketing,..) and contain some individuality. This can include regional prospects, historic aspects, beauty (prestige and intrinsic value instead of cost production) and functionality (privacy and flexibility).

US-German Bilateral Working Group

THE ROLE OF INTERSTATE WORKING GROUPS IN SITE REDEVELOPMENT

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ABSTRACT

This presentation focuses on the importance of site redevelopment for States in both Germany and the United States and describes the goals and procedures of some interstate working groups in both countries. Special emphasis is given to the ongoing interstate activities regarding site redevelopment and the benefits that site redevelopment may have for the States.

THE INTEREST OF THE STATES IN SITE REDEVELOPMENT

Only environmentally sound activities can be economically viable over long periods of time. This fact must be considered in the development of our urban areas. Furthermore the protection of open space is considered to be of key importance in this respect. With this guiding theme two major effects can be expected; the preservation of the natural soil functions and the improved usage of existing infrastructure. Ideas like “Smart Growth” and the reuse of abandoned areas are successful movements that promise even more benefit, as they are regarded as wholistic approaches in the sense of sustainable development. This challenge can only be solved if the States creatively define their role and promote joint efforts of stake-holders towards environmentally and thus economically sound projects.

- Responsible site redevelopment is necessary because Continued greenfield development leads to a substantial loss in quality of life and therefore can be considered to be a burden for local land values. In addition, it would be a substantial burden for urban areas, because, infrastructure like streets, powerlines, and sewers have to be built in magnitudes bigger than necessary.
- High levels of infrastructure have to be maintained in cities for both, used and abandoned areas which results in an extremely disadvantageous cost/costbearing quotient.
- The full extent of social and environmental benefits of site clean-up and redevelopment can only be expected if private investment money is leveraged and if these projects are designed in a way that achieves an optimized benefit for the investor and the surrounding community.

STRENGTHENING THE DRIVING FORCES

In many States, especially in Germany, the issues of the environment and redevelopment are connected. While this connection is obvious it is not the only one. More emphasis needs to be put on using the forces of the market with private investment money to complete site redevelopment projects in a reasonable period of time.

The major challenge in site redevelopment is the need for connecting and combining elements that were handled in a sectoral view in the past. Elements include the economic, ecological and social aspects of site redevelopment which need to be integrated in project vision, planning, permitting, execution and evaluation.

While public agencies play a critical role in environmental management, the vast majority of brownfields will not be restored without participation by the private sector. Discovering mutually beneficial ways to involve investors in redeveloping these polluted properties is crucial. A truly effective brownfields program requires a variety of tools to address three primary concerns of potential developers: legal liability, regulatory compliance and the financial burden of investigation and cleanup.

Future Goals of the States activities could be:

- Enhanced partnership with the private sector to leverage promising and beneficial projects and quicker environmental clean-ups
- Grants to support the overall goals of sustainability
- Increased ability for the matching of funds between federal, and State money.

THE ROLE OF THE STATES

State governments and their technical agencies work as the regulatory and enforcement bodies and interface between federal, regional and local levels. Federal and State laws underlie the supervision and permitting work of the States and guide their development of environmental goals and strategies.

INTERSTATE ACTIVITIES AND WORKING GROUPS

In order to collect and build the expertise to fill out their role in the context of site-cleanup and/or site redevelopment, a sharing of experiences and joint development of solutions in interstate working groups is considered to be an extremely valuable measure.

EXAMPLES FROM THE US:

In the US, the **Environmental Council of the States (ECOS)** is the national non-profit, non-partisan association of state and territorial environmental commissioners. Established in 1993, it works by connecting States with each other, with federal partners and with others, in an effort to share experiences about how to best manage environmental issues. One of ECOS' missions is to "tell the State story," that is, to describe the contributions that States make to environmental protection. During the past few years, ECOS has conducted research on many issues including the delegation of federal environmental programs to the States; State contributions to federal environmental databases; State environmental and natural resource funding and, most recently, the State contribution to enforcement and compliance. Much of that information is found on www.ECOS.org. A 28-member Executive Committee governs the organization, that has standing committees addressing Air, Water, Waste, Compliance, Planning and Cross-Media. In addition "forums" work with the federal agency partners and "working groups" focus on particular issues.

While ECOS is mainly the forum of Environmental Commissioners of the States, the **Interstate Technology and Regulatory Council (ITRC)** is a more operation-oriented forum on the State agency-level. Established in 1995 ITRC is the only organization of its kind. A State-led coalition of personnel from the regulatory and technology programs of more than 40 States; three federal agencies; and tribal, public, citizen and industry stakeholders, and academia, ITRC works to achieve regulatory acceptance of environmental technologies. ITRC targets to break down barriers and reduce compliance costs, making it easier to use new technologies and helping States maximize resources.

Core element of ITRCs activities are the technical teams built of the ITRC-members. Typical teams range in membership from 10 to 20 people who dedicate to spend 10% of their time supporting the team's activities. Teams generally meet three times each year in person and regularly by conference call and are generally active for three years. The first year is devoted to the development of a case study or technical overview document that identifies an emerging technology and any related regulatory issues. During the second year, a team develops a technical and regulatory guidance document and accompanying decision tree that focus on the specific regulatory concerns surrounding the use of the technology. In a team's last year, it develops Internet-based and sometimes classroom training to share what the team has learned and help get its overview and guidance documents into use.

The 2002 Technical Teams work on the following issues:

- Alternative Landfill Technologies
- Constructed Treatment Wetlands
- Contaminated Sediments
- Dense Nonaqueous Phase Liquids
- Diffusion Samplers
- In Situ Chemical Oxidation
- In Situ Bioremediation
- MTBE-Contaminated Groundwater
- Permeable Reactive Barriers
- Radionuclides
- Sampling, Characterization, and Monitoring
- Small Arms Firing Range
- Unexploded Ordnance
- Remedial Process Optimization
- Brownfields (see description below)

ITRC's guidance documents include technology overviews, case studies, decision trees, reference guides, and technical/regulatory guidelines. Guidelines are meant to specify a uniform set of data requirements for technology demonstrations or approvals. Once adopted by States, ITRC technical/regulatory guidance helps to make permitting processes more efficient and uniform across States. The result is helping technology vendors and consultants avoid the time and expense of meeting different sets of permitting requirements in each state where innovative technologies are proposed for use.

In addition to guidance documents, ITRC develops and delivers Internet-based training on emerging environmental technologies. Key to this success is partnering with industry and other organizations to develop classroom courses. This cost – effective training has successfully reached more than 12,000 state, federal, industry, and other stakeholders. ITRC`s value is high in that its training and documents have been determined to save time and/or money.

More information about ITRC is available at www.itrcweb.org.

ITRCs Brownfields team is facing the fact that the redevelopment of Brownfields is a cross-cutting issue. While other ITRC-Teams are far more specialized, the Brownfields team addresses complex issues that may be covered by other ITRC teams. This enables the Brownfields team to serve two functions: 1. to help the other teams to determine their role and status in Brownfields projects and 2. to help the technical Brownfields community solve complex conglomerates of problems by actively identifying and creatively combining technological solutions.

Another factor is that stakeholders in brownfields projects do not necessarily speak the same language as those involved in site clean-ups. There may be different point-of-views regarding many issues in the process including tolerable strains or burdens caused by contamination and their (long-term) remediation or monitoring. Also information that might be understandable for the clean-up community is not understandable for the other groups involved in a Brownfields project.

The main benefit for the States from the Brownfields teams work is the information exchange on how Brownfields are handled in other States, which funding programs serve whom, what the key working elements of the programs are and what innovative elements are available to measure success. Furthermore, the brownfields team helps to provide information on environmental problems and solutions to an audience that is much broader than the group of clean-up specialists.

EXAMPLES FROM GERMANY:

The environmental ministers of the federal government and the state governments of the 16 German States meet twice a year in the **Umweltministerkonferenz (UMK**, Environmental Minister Conference). The chair in this conference alternates every year, with meetings prepared by lead-staff of the participating ministries ("Amtschefkonferenz", ACK). The conference serves as the political exchange forum for the heads of the environmental ministries and promotes the enforcement of environmental laws to be as similar as possible. Therefore, in the UMK, present day topics are discussed and also long-term-perspectives of environmentally relevant political solutions are initiated. More information is available at www.umweltministerkonferenz.de.

Most of the technical work is delegated to the ancillary working groups, who are founded and instructed by the UMK. These working groups are a forum for the technical staff of federal and state governmental institutions, in order to allow for a uniform administrative enforcement and to work according to the instructions of the ACK/UMK.

One of the ancillary working groups mentioned above is the **Bund/Länder-Arbeitsgemeinschaft Bodenschutz (LABO)** ("Federal/State Working Group Soil Protection"), in which the top authorities of the federal and the state government cooperate. The LABO accompanies the development of the soil protection and the relevant legal frame and supports the exchange of experience between the federal government and the state governments. One of the objectives of the LABO is uniform enforcement of the soil protection law and the preparation of suggestions for its uniform further development.

The LABO consists of the Executive Committee and five standing working committees (Staendige Ausschuesse) for: Legal Aspects, Information Sources, Soil Protection Planning, Soil Pollution, and Contaminated Sites (see description below).

In the Executive Committee, the Federal Government and each of the 16 German States are represented by the lead-executive for soil protection of the relevant top state authority or federal authority. In the standing working committees, the technically responsible staff of these authorities represents the Federal Government and each of the 16 States. Ad-hoc subcommitties can be established if technically needed and appropriate.

Recent issues, that were subject to LABOs reports and technical guidance documents included

- Quality Issues of Work on Contaminated Sites
- (Guidance on evaluation of) Filling of excavations
- Guidance for the enforcement of § 12 BBodSchV (Federal German Soil Protection Ordinance)
- Requirements for sustainable farming from the soil and groundwater protection standpoint
- Basics of Evaluation criteria for pollutants in contaminated sites

More info on LABO is available at http://www.hamburg.de/Behoerden/Umweltbehoerde/labo.

One of the five constant working committees of the LABO is the "**ALA" (Altlastenausschuss der LABO**" ["Ständiger Ausschuss 5: Altlasten"], Working Committee on Contaminated Sites).

The main tasks of the ALA is the following:

- Technical and enforcement issues regarding the registration, investigation, evaluation, remediation and long-term stewardship of potentially and known contaminated sites and harmful changes of soil quality that are related to the operation of a technical facility, if these issues need inter-state activities.
- Support for further development of the legal frame for the issues mentioned above.

The ALAs Ad-hoc-Subcommitties focus:

- Evaluation of existing results regarding harmful substances which are not yet covered by trigger, action, and precaution values as given in the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) to develop uniformly enforceable recommendations.
- Matching of result-documentation of phase 2 of the project "Quality Assurance of Work on Contaminated Sites" and preparation of final reports for a beta-test-phase in the practical enforcement.

WHAT COULD/SHOULD THE STATES DO OR EMPHASIZE IN THE FUTURE?

Various interstate activities in both countries testify to the importance of exchange of experience, matching of strategies and regulatory requirements. The information exchange in terms of joint discussions and evaluation of trigger and target criteria for environmental conditions as well as performance of technical solutions is considered to be of crucial importance in both countries. The state governments and their technical agencies are working as the regulatory and enforcement bodies at the interface between federal law and regional and local levels. The supervision and permitting work of the States as well as the development of environmental goals and strategies needs the inter-state exchange of ideas and political matching.

Interstate information exchange is especially necessary for the activities of the States regarding contamination of sites and the related clean-up that needs to be tied in into the redevelopment of sites, in order to be economically viable. The close relation with economics, land-use planning, traffic-planning and engineering aspects and furthermore the interrelation with social aspects of quality of life and environmental justice show a new dimension of complexity.

One of the main benefits of a streamlined site redevelopment approach is an increased efficiency in use of existing infrastructure and other mutual benefits for investors and communities. To leverage investment capital, sounder granting focusing sustainability of landuse and easier matching of funds, especially between different programs and departments of the States, like construction, traffic, and environment are considered to be of key importance.

Statewide strategies and development plans will be of increasing importance in the near future. Masterplans for smart and efficient landuse must supplement the States environmental plans, as it is intended e.g. for Environmental Plan of the State of Baden-Württemberg. The landuse and – development masterplan must include the special characteristics of fallow land as well as the outstanding importance of free space for the environmental quality is already described in regional planning documents. Fundamental decisions towards protection of natural soils "Bodenpolitischen Grundsatzbeschluesse" which are taken by municipal administrative bodies are considered to be a good example for a future-oriented strategy. The existing guidances for an environmentally sounder land development planning of the municipalities, e.g. issued by the Federal Ministry for Construction (2001) need an improved matching of the issues "zoning for development" and "reuse of brownfield sites" including remedial aspects.

In this respect it should be noted that in some cases, an improved grant policy would be beneficial. An example are existing remedial grants that should be converted into redevelopment grants, without being attached to a need for cleanup.

In summary, it would be helpful for the municipalities, if the States would specify basic requirements for regional and local land-use planning, help to achieve these basic requirements and emphasize the initial identification and assessment of sites to assess their redevelopment potential.

January 2003

SpS 14 Special Session

Sustainable Brownfield Regeneration: A Multi-Stakeholder Debate

SUSTAINABLE BROWNFIELD REGENERATION

Workshop to be managed and directed by the CABERNET Coordination Team:
Professor Judith Lowe, Dr Kate Millar[1], Detlef Grimski, Dr Uwe Ferber and Dr Paul Nathanail

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SUMMARY

Encouraging the re-use of formerly developed and/or industrially contaminated land raises complex issues that require multidisciplinary solutions and integrated management strategies. The EC funded 'Concerted Action on Brownfield and Economic Regeneration Network' (CABERNET)[2] was established in January 2002 to enhance the regeneration of brownfield sites by developing an intellectual framework to structure ideas and stimulate new solutions[3].

This Special Session will explore the drivers and pressures influencing brownfield rehabilitation across Europe from a multi-stakeholder perspective. Keynote presentations, based on CABERNET's first year work programme and conclusions, as well as other inputs, will highlight how different stakeholders characterise and prioritise the problems and the issues.

One of the main objectives of CABERNET is to create better awareness and shared understanding of brownfield issues across Stakeholder Groups. To do this, CABERNET has brought together a range of stakeholders involved in the brownfield regeneration process in different countries across Europe. During the first year of the project (2002) CABERNET facilitated the interaction of these Stakeholders Groups to identify common issues relating to sustainable regeneration of brownfields. Building on the discussions in Stakeholders Groups, the Members of the Network have identified a number of potential topics for the work programme for the second phase of the project. The ConSoil Special Session also gives an opportunity to explore some of these topics and identify priority issues at a European level.

The topics are considered by CABERNET under 6 broad themes identified at the outset of the project as representing key aspects of sustainable regeneration of brownfields at a European level. These are: Environmental issues; Social and cultural issues; Economic issues; Policy approaches and regulatory practices; Citizen participation and decision-making; and Professional skills. Identification of issues, best practice, case studies and research and development needs are components of all the themes.

The presentations will be followed by a debate where workshop participants can challenge the information and ideas presented. Participants will help to identify and propose priorities for future policies, research and investment in brownfield regeneration.

The ConSoil Special Session with its mix of short keynote presentations and debate will focus on how to share ideas and find new solutions. The main content will cover the following areas:

- What we mean by sustainable development of brownfields
- A conceptual model for analysing brownfields
- Drivers and pressures
- Key European challenges in environmental, social, economic, decision-making, policy approaches and professional skills aspects of the brownfield regeneration process
- Conclusions and views on priorities

As an output from the session, CABERNET will prepare a briefing paper of the workshop discussion and conclusions for access via its web site.

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[2] **CABERNET web site:** For further information please see www.cabernet.org.uk

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INTRODUCTION

1 Encouraging the re-use of formerly developed and/or industrially contaminated land raises complex issues that require multidisciplinary solutions and integrated management strategies. The EC funded 'Concerted Action on Brownfield and Economic Regeneration Network' (CABERNET) was established in January 2002 to enhance the regeneration of brownfield sites by developing an intellectual framework to structure ideas and stimulate new solutions[1].

2 This special session will explore the drivers and pressures influencing brownfield rehabilitation across Europe from a multi-stakeholder perspective. Keynote presentations, based on CABERNET's first year work programme and conclusions, as well as on other inputs, will highlight different stakeholders' characterisation of the problem and the issues they see as priorities.

3 The presentations will be followed by a debate where workshop participants can challenge the information and ideas presented. Participants will help to identify and propose priorities for future policies, research and investment in brownfield regeneration.

BACKGROUND

4 Details of CABERNET are described in "CABERNET: Enhancing European opportunities for sustainable brownfield regeneration" (Millar *et al, 2003*), also published in the Consoil 2003 Proceedings[2]. One of the main objectives of the project is to create better awareness and shared understanding of brownfield issues across Stakeholder Groups. To do this, CABERNET has

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[1] **Acknowledgements:** This research project is supported by the European Commission under the Fifth Framework Programme and is contributing to the implementation of the Key Action "The City of Tomorrow and Cultural Heritage" within the Energy, Environment and Sustainable Development Thematic Programme (http://www.cordis.lu/eesd/).

[2] See also www.cabernet.org.uk

brought together a range of stakeholders involved in the brownfield regeneration process in different countries across Europe.

5 During the first year of the project (2002) CABERNET facilitated the interaction of these Stakeholders Groups to identify common issues relating to sustainable regeneration of brownfields. At a plenum meeting in Athens in January 2003, the groups reported on some of the main areas relating to the current situation across Europe. Full details and latest thinking on these areas are available as CABERNET Baseline Information Sheets (available on the CABERNET web site - www.cabernet.org.uk), but they can be summarised as follows:

Scale and nature of the problem

6 One of CABERNET's specific tasks is to collect information on the scale and nature of the problem across Europe. To facilitate this, CABERNET circulated a questionnaire to Members of the Network to identify types and sources of information about brownfields. CABERNET had 21 responses from 16 countries, which provided signposts to further information as well as some limited detailed or local knowledge.

7 Although the information is highly subjective, the key conclusions from the work were that:

- Brownfields are categorised in several ways in different countries, for example by location (rural, sub-urban, urban), by former land use, by type (for example derelict or contaminated) or by status (in urgent need of action, undergoing redevelopment)
- The biggest brownfield challenges were presented by large complex sites with poor infrastructure (e.g. harbours and ports, railways, mining areas, chemical works and large housing areas)
- Data quality is highest at community level, but decreases with scale – with only limited data availability at regional or country level
- Different countries had different drivers for data collection which “coloured” the data

8 CABERNET would like to initiate further work to tackle knowledge gaps and improve the quality of information. This includes preparation of an accessible directory of “gatekeepers” to key sources of information, key web sites and good quality surrogate data sets; development of a model brief for brownfield monitoring and forecasting; and verification of collated time series data.

Policy and regulation

9 CABERNET includes a number of representatives from both national and municipal authorities and is linked to other networks of policy makers and regulators at different levels. As part of its work, CABERNET is developing up to date “country profiles” to include information on the main policy focus and administrative arrangements in relation to brownfields, as well as the key financial, spatial planning (or development control) and environmental instruments - or other initiatives - which affect the regeneration of brownfields in each country.

10 CABERNET sees policy and regulation as influencing the balance between economic development, social development and environmental protection. It is clear that the position of this balance – at national, regional and local levels - can determine the feasibility of individual projects. Some of the key issues also relate to improving the process – providing certainty in policy, ensuring clarity in the regulation process and using financial and other incentives.

11 The preliminary conclusions from the first year of CABERNET discussions were that the main issues for policy and regulation are:

- Seeing policy makers and regulators as potential facilitators of the process
- Exploring policy differences between countries (for example the different emphases on environmental protection versus spatial planning)
- Providing an integrated approach across disciplines, between different authorities, and involving communities
- Improving the levels of expertise in countries, both at a technical level and in understanding of funding mechanisms and how to create successful public/private partnerships
- Identifying suitable indicators to measure the effectiveness of brownfield strategies

Financial aspects

12 One of the key areas for all stakeholders was the issue of financial viability of brownfield regeneration. This covers not only the immediate cost of a particular project, but also the long term cost for countries and industries with a large number of sites. Financial aspects cover risks to investors, insurance, and valuation of land as well as wider economic issues.

13 As part of its first year collection of information, CABERNET carried out a number of questionnaire surveys of its Members to establish key information on financial issues. Information was collected on financial instruments (grants, tax incentives etc) in different countries. Opinions of the Members were sought on financial obstacles, financial solutions and information availability.

14 The main financial obstacles for brownfield sites included:

- Credit risk
- Surplus supply of land
- High clean up costs
- Lack of inward investment
- Lack of public funding
- Uncertainty

15 The analysis carried out by the financiers group, with input from other groups, considered that different phases of the brownfield process (eg close down of a site, dereliction, identification, feasibility, permitting and then remediation and redevelopment to operational new use) raised different financial issues and was subject to different financial pressures and drivers. The solutions proposed were not confined to public money at national level – they identified a wide range of possible stakeholders who could bring forward finance-related solutions and a range of possible mechanisms. These mechanisms included tax incentives, changes to the planning regime and other regimes that require use of brownfields or strategies to open up the market.

Skills

16 CABERNET identified advisors as facilitators of the overall brownfield process, contributing at a range of levels from strategic policy making to specific project feasibility, design and supervision. The range of areas where an advisor may contribute included not only technical issues and environmental assessment, but also organisational issues, economics and financing.

17 The main conclusions were that brownfield regeneration is clearly a multidisciplinary skill which also required communication and facilitation skills. There was a clear role for the development of these skills to ensure that professional brownfield project managers were available to provide leadership in the regeneration process.

Other outputs from CABERNET

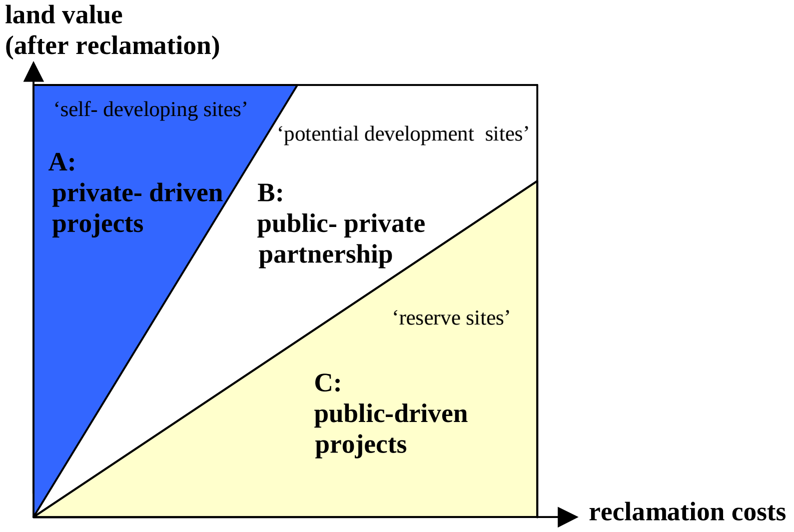
18 CABERNET is also collating and maintaining databases of research and development programmes and projects; key tools used by CABERNET Members and others; case studies and contact points for relevant organisations and projects.

The brownfield process and conceptual models

19 CABERNET has collected ideas from different stakeholders to develop a route map of the brownfield process. This starts with the original operational use of the site, showing the mechanisms by which land becomes derelict, and shows the detailed stages through to site regeneration. It enables the different tools and stakeholders involved at different stages to be highlighted.

20 At a conceptual level, CABERNET suggests that the overall generation and creation of brownfields can be represented by a "bath" – showing the inflow of sites into a brownfield condition and the outflow - controlled by a number of different parameters – to new uses. Different types of sites make up the bath – some being less capable of regeneration than others. Other models can be used to illustrate some of the different types of sites, for example the "A-B-C Model" shown below

FIGURE 1: The "A–B–C Model"



Drivers and pressures

21 More detailed analysis of the factors influencing the rate of inflow and outflow of sites is underway with work on drivers and pressures. These can be considered at both a regional (or portfolio) scale and at an individual site level, and may be differ at various stages of the process or for different types of sites.

22 What is also clear is that perceptions of drivers and pressures varies between stakeholders and between individuals. Expanding on the thinking of CLARINET working group on brownfields, which used a tetrahedron model aimed at broadening thinking from simple site preparation issues to include spatial planning, legal aspects and economics, CABERNET has developed a simple tool (please refer to the CABERNET website – www.cabernet.org.uk) to assist in identifying priority drivers – or pressures from different perspectives. This clearly shows that successful regeneration of brownfields requires understanding of a wide range of different factors, which include: Cultural

Heritage, Professional Skills, Risk and Liabilities, Financial Viability, Technical Knowledge, Spatial Planning and Community Needs.

TOPICS FOR THE FUTURE

23 Building on the discussions in Stakeholders Groups, the Members of the Network have identified a number of potential topics for the work programme for the second phase of the project. The Consoil special session gives an opportunity to explore some of these topics and identify priority issues at a European level.

24 The topics are considered by CABERNET under 6 broad themes identified at the outset of the project as representing key aspects of sustainable regeneration of brownfields at a European level, shown below. Identification of issues, best practice, case studies and research and development needs are components of all the themes:

TABLE 1: Key Themes in Brownfield and Economic Regeneration

Sustainability components	**Cross-cutting issues**
Environmental issues	Policy approaches & regulatory practices
Social and cultural issues	Citizen participation & decision-making
Economic issues	Professional skills

25 The main topics are:

Environmental issues:

Measuring effects of brownfield regeneration on overall sustainable development; urban health (people and environment); managing environmental impact of regeneration; interface between environment and other issues.

Social and cultural issues:

Social equity; intergenerational justice, characterising regional social needs and opportunities; mobilising local skills and employment opportunities; role of industrial heritage; enhancing small scale and interim uses.

Economic issues:

Understanding of how to attract money to a brownfield site; managing the rate of creation and regeneration of brownfields; financial risk management; tools for valuing brownfields and their regeneration.

Policy approaches and regulatory practices:

Indicators for brownfield redevelopment; best practice in policymaking at national and local level; influence of European policy; brownfield prevention policies.

Citizen participation and decision-making:

Communication and stakeholder engagement tools; identifying stakeholders and encouraging participation; consensus building; long term stewardship and social cohesion.

Professional skills:

Translation of science to brownfields practice; training to fit the skills matrix; stimulation of professional development.

26 These topics – and how to share ideas and find new solutions - will provide the basis for discussion in the workshop.

WORKSHOP PROGRAMME

27 The workshop at Consoil will be a mix of short keynote presentations and debate. The main content will cover:

- What we mean by sustainable development of brownfields
- A conceptual model for analysing brownfields
- Drivers and pressures
- Key European challenges in environmental, social, economic, decision-making, policy approaches and professional skills aspects of the brownfield regeneration process
- Conclusions and views on priorities

28 After the session, CABERNET will prepare a note of the workshop discussions and conclusions for access via its web site.

SpS 15 Special Session

Risks, Media and the Social Amplification of Soil Contamination

RISKS, MEDIA AND THE SOCIAL AMPLIFICATION OF SOIL CONTAMINATION

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Risks of contaminated soil in a social context

Contaminated soils and risk assessment are closely related. The European Clarinet network developed a concept or framework for contaminated soil using the name of 'Risk based land management'. The constituent term 'risk' is used as follows:

> "Risk describes the combination of the probability and the effects of contamination, for example adverse environmental effects on human health, on ecosystems, or on water resources. If an adverse effect has occurred, the consequences are often described as ***damage.*** Poor soil and water quality may in turn lead to adverse social economic effects."[1]

With this definition the 'risk' is considered as an attribute of the contamination or the contaminated site. It opens a wide range of possibilities to determine the type of adverse effects and to make some calculations about the amount of risk as a result of information from that contamination or contaminated site. It is an objective approach in the sense that the risk is considered as an aspect of an object. The implicit assumption is that anyone could experience and measure the same 'risk' from a defined perceptual position. Because 'risk' is a complex aspect risk models have been developed. There is also a subjective connotation of 'risk'. My suggestion for a definition is as follows:

> "Risk is the difference between a mental construction of a situation with expected adverse effects of contamination (or a contaminated site) and a mental construction of the desired situation."

In this definition the word 'risk' is a result of a mental process. You also need a model to deal with this kind of risks, but this is rather a mental model than a calculation model. As with the objective connotation, you need a specification to know what exactly is meant by the word 'risk'. You need to know more about the *expected adverse effects*, and you need to know more about the two situations that are compared. The only way to learn more about subjective risks is to communicate with the people that experience the risks and ask them what kind of adverse effects or situations they think of.

The introduction of the subject of the *perception of risks* opens the possibility to blend the objective and the subjective connotations of *risks.* It implies that there is something like a more or less objective chain of causal relations between contamination and adverse effects. And at the same time it takes into account that any human being has his or her own mental construction of this objective reality. The term *risk* develops within this blend a complete new connotation. It could be thought of as the result of a social process in which the objective meaning of *risks of contaminated land* is defined by a group of people, e.g. as the outcome of a certain type of modelling the chain of causal effects. The word *perception* takes into account that any person can make his or her own picture of the situation. What is vanished is the idea of a *real risk*. With the omission of the *real risk* we also lost the idea that one risk assessment is better than the other because it is closer to the *real risk*.

A group of four Risk experts (Jaeger, Renn, Rosa & Webler)[2] also noticed the many different connotations of *risks* in common language. However, *risk* always implies the possibility to some outcome. *Possibility* is, in their point of view, the first indispensable element of the idea or risk. Following the definition of the US National Research Council in 1983, they define risk as follows:

> "Risk: A situation or event in which something of human value (including humans themselves) has been put at stake and where the outcome is uncertain."

In their explanation[3], they mention four key features of this definition. First, it expresses an ontological state of the world. Risk captures the duality that humans are embedded in uncertain environments – natural and human made. Second, it explicates states (uncertain but involving human stakes) that are properly conceptualised as risk. Third, it embeds the conventional definition of risk (as the probability of an occurrence or event multiplied by the value of the outcome of that event). Fourth, it is robust, in that it subsumes both undesirable risks (the dominant concern of the field) and desirable risks, such as adventurous undertakings or investments in which risks are engaged in for thrills or similar satisfactions.

It has many advantages to see *risk* as an idiom that belongs into both the social domain and in the domain of the technical and natural sciences rather than in either one of them. One of advantages is that risk experts are more focussed on risk communication and the social effects of that communication and less on the technical calculations. Another advantage is that well known phenomena like the social amplification of risks, could be understood more easily than when risks are defined within the context of natural sciences only.

Some examples

Three cases were studied in a NICOLE project (the Network for Industrially contaminated land in Europe)[4]. The aim was to do some practical observations and present some guidelines for the risk communication on contaminated land.

The first case was a historical soil industrial contamination in a small village. Some 30 years ago the soil and the phreatic aquifer had been contaminated with heavy organochlorine products. The contamination itself was discovered in 1987. The authorities had been informed as soon as the contamination was discovered. An administrative order regulated the monitoring of the pollution, its confinement and the economically feasible remedial actions to be taken. There were no drinking water wells downstream of the plant, which could have been contaminated. The staff members of the plant were yearly informed about the state of the art. Villagers had been informed not to use the ground- and surface water for whatever use, whether irrigation, swimming, etc. In case they did want to use the water -however small the amount- they had to ask for an analysis by the environmental service of the plant. In balancing the benefits of the plant for the village and the risk of industrial activities in general and more specifically soil pollution, the people seemed to have accepted these facts. Experts were very much aware of the fact that this situation could alter quickly when the circumstances would change. Their main question was how they could prevent the situation to develop beyond their control.

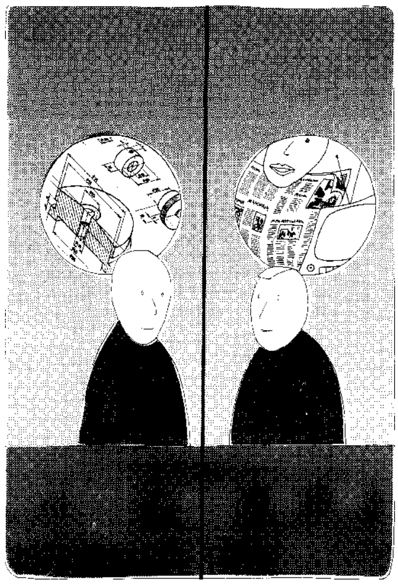
The second case was an incident that caused soil contamination. Due to a leak in the Naphtha Pipeline, 200 m^3 Naphtha was spilled on farmland, surrounding surface water ditches and open surface water. The farmland, grass, was contaminated to a depth of approx. 1 ~ 1.5m due to the fact that the land had a drainage system with a runoff to the ditches. The Naphtha in the ditches back flushed into the drains causing contamination at the depth of the drainage system. The incident had been reported immediately to the local authorities. The authorities, the plant and the media informed neighbouring villagers. The incident happened in the early morning. The local people were informed by a letter from the municipal authorities informed the local people. Those who were at home could smell a weak naphta odour. Because the wind blew the vapours in the other direction, away from the village, the situation was never dangerous. During the day the incident was on local television. The area was fenced in, but many people tried to have a look. The company reacted immediately, took all responsibilities and took care that there waas a communication expert on site a few hours after the incident was reported. The main interest of the local people was their safety. Once the message ‘everything under control’ was received, the representatives of the village wanted to know what exactly had happened. They were disappointed about the little and sometimes inadequate, information they received, but were happy with the immediate actions of the industrial company. It was interesting to see that the village representatives regarded the industrial company as more trustworthy than the local authorities, The (positive) image the people had of the company, the good skills of the communication manager and some bad experiences with local authorities were the background of their perception. The television broadcasting had hardly any influence on their opinion. The television medium was regarded as a very untrustworthy medium, compared to live communication with the responsible people.

The third case was the introduction of a new technique for soil and groundwater contamination on an industrial site. The contamination was caused by inappropriate disposal of solvents over a thirty-year period. When a new company acquired the site, they decided to clean up the site and discussed their plans with the authorities. A novel remediation technique – a reactive barrier containing iron fillings – had been used as remedial action. It entailed an environmentally friendly process, which was visually discrete and required little or no (sustainable) energy use and low maintenance. Local communities, environmental consultants and staff were informed through communication of all forms: meetings, presentations, direct mail, newsletters, articles in the media. Overall, the company’s approach to communicate with regulators, employees and the local community was a proactive one and it was keen to be as open and honest as possible. Where feasible and appropriate, information was provided as soon as it was available, regardless of the fact whether or not it had been specifically requested. A flexible approach to communication which used a combination of formats – letters, site visits, displays and presentations – enabled the company to provide current, accessible information for a range of audiences. Given the scale of the project, people living in an adjoining housing estate would not have failed to notice that excavation work was taking place. The company was pleased to receive telephone calls from curious or anxious residents and to offer them the opportunity to visit the site for further information. On the whole, the local community exhibited little concern or anxiety towards the developments which took place on the site while the reactive barrier was under construction. This reaction was – according to the project experts – almost certainly a result of the company's proactive communication policy and reputation as a company attentive to its environmental impact and performance.

It was concluded[5] that an adequate communication strategy is an essential element of Risk Based Land Management. As the remediation itself requires soil expertise and technical skills, the communication process requires psychological and social expertise and communication skills. Some new insights in this psychological and social know how were reported the last two years.

How do we think about risks?

The last few years cognitive scientists have developed new concepts of the way we think. Rational thinking is more and more believed to be a specific specialisation of the human brain. But most of our time we function because we do not think rational. Subconscious processes in our brain control our walking, driving, talking, almost everything in a way that we don't have to think about it. What seems to be very simple, like recognizing a person, is the result of very complex brain processes. Sensory information is processed in our brains, triggering all kind of physical reactions in our body that we know as feelings, actions or pleasure and pain. When we want to study risk perception we cannot just compare the rationality of an expert with the rationality of a layman and conclude that the latter just misses education and professional skills. With the study of the perception of risks we pass the border of the cognition sciences. An interesting introduction to the work of the cognitive science is a book of Gilles Fauconnier & Mark Turner with the title 'The way we think'[6]. They presume that the fundamental processes of our thinking are based upon three essential abilities, the three 'I's:



- *Identity*. The recognition of identity, sameness, equivalence, A = A, which is taken for granted in form approaches, is in fact a spectacular product of complex, imaginative, unconscious work. They are not primitive stating points, cognitively, neurobiologically, or evolutionarily;
- *Integration*. Finding identities and oppositions is part of a much more complicated process of conceptual integration, which as elaborate structural and dynamic properties and operation constraints, but which typically goes entirely unnoticed since it works fast in the backstage of cognition.
- *Imagination*. Identity and integration cannot account for meaning and its development without the third I of the human mind – imagination. Even in the absence of external stimulus, the brain can run imaginative simulations. Some of these are obvious: fictional stories, what-if scenarios, dreams, erotic fantasies. But the imaginative processes we detect in these seemingly exceptional cases are in fact always at work in even the simplest construction of meaning. The products of conceptual blending are always imaginative and creative.

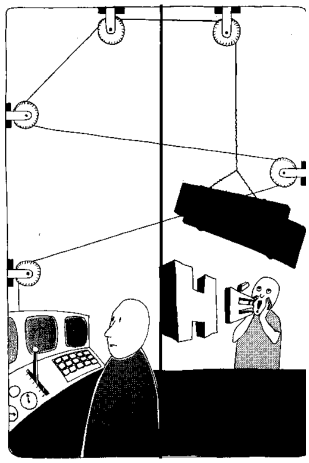
Fauconnier & Turner present a model that lifts a bit of the curtain in a scientific field that is developing rapidly. They presuppose that there are 'mental spaces' in our thinking. Mental spaces are a cluster of objects and actions that are related. 'Living on a contaminated site' is a mental space. Your brain will fill that space with information from other mental spaces. That could be anything like 'a book about contaminated sites' or your own experience with another contaminated site. But you could also fill it with mental spaces about London. Fauconnier & Turner call these mental spaces input spaces and the process that combines information from several mental spaces they call blending. A mental space could be open or it could be framed. It is framed when there is a set of beliefs, rules and logical relations that determines the relationships between the several elements. It could be that someone has framed any mental space with contaminated soils with the belief that contamination is bad for your health. When someone states that 'it is very healthy to live on a contaminated site in London' this person would immediately object. The thinking process can be considered as a dynamic netwerk of connected mental spaces. An external sensory stimulus (hearing, seeing, smelling, feeling, etc.) will start brain processes that activate one or more mental spaces at the same time. Through processes like compressing, blending, comparing, etc mental spaces we attribute 'meaning' to this external stimulus.

With this theory of our mental processes, it is very understandable that different individuals have different 'thoughts' about risks of contaminated soils. It is even comprehensible that one person has different thoughts about risks of contaminated soils at the same time. This ambiguity is one of the essences of our way of thinking. On the other hand you could ask the question: 'how on earth is it possible that several people understand each other when they are talking about risks?'. The answer is that we develop our own network of mental spaces only in communication with others.

The three cases make clear that when a risk communicator is willing to listen to his audience and provides the information that people need to fill their own mental spaces, rapport and mutual trust is built up. The result is that many complex matters can be solved. On the other hand, when a risk communicator sends information that fits within his own mental space, the audience will immediate create, on a subconscious level, new mental spaces. Those new mental spaces need new information to fill them?

How do we communicate about risks?

For many people risk communication is the one-way information from the risk experts towards the layman. Baruch Fischhoff explained risk communication as an evolutionary process in which communicators gradually reach higher levels of understanding about the nature and complexity of the (subjective) risk experience of their audience. He describes 7 stages in this process[7]:



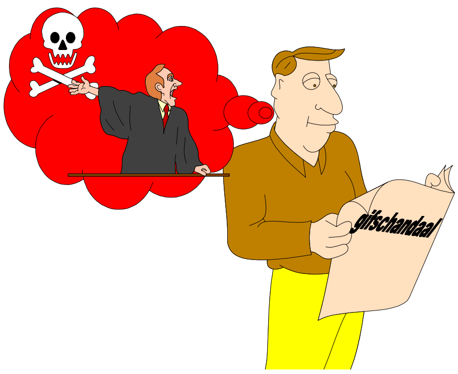
1. *All we have to do is get the numbers right*. Many risk managers (or soil remediators) hope that by doing their job well, nobody is interested in information. If this strategy fails, then people may ask awkward questions about the long silence. Was something being hidden? Or did the experts just not care?
2. *All we have to do is tell them the numbers*. The quickest response to the demand for information is to share one's work. As a result, when risk experts discover that they have a public risk perception problem, they may be tempted to present the research that convinced them that the risk was acceptable – in something close to the form in which it was produced. Although there can be something touching and forthright in such a straightforward delivery, it is unlikelyto be very effective. Moreover, not understanding the public's perspective may be interpreted as not caring about it.
3. *All we have to do is explain what we mean by the numbers*. When risk estimates do not speak for themselves, an obvious step is to explain them. That can be a difficult tas with an audience that shares no common volabulary or conceptual background with the risk experts. Often, the explanation draws the attention of the audience to the complexity and uncertainties of the models and does not fulfil the need of the audience to understand the risky process.
4. *All we have to do is show them that they've accepted similar risks in other situations*. The hidden message in this strategy is that the perception of the audience about the risk is not correct. From Fauconnier & Turner we learned that we fill our mental spaces with information from our own input spaces. Some people might fill their mental space with information from an external source when this source is as reliable as their own internal source. But many people will mistrust the expert.
5. *All we have to do is show them that it's a good deal for them*. Considering both risks and benefits in communication draws the attention to a rational choice between several alternative actions. In the model of Fauconnier & Turner people are invited to communicate within a framed mental space. When people accept this, it is possible to start some kind of negotiation process trying to balance risks and benefits. When people reject this framed mental space, the invitation could easily be interpreted as lack of care.
6. *All we have to do is treat them nicely*. People judge communications by their form and their substance. If the substance is complex and hard to understand, form becomes more important.

When there is a good rapport, there is a better chance that misunderstandings in the the substance can be dealt with.

7. *All we have to do is make them partners*. This means that the recipients are seen as individuals with their own concerns. It means providing them a seat at the table and allowing them to communicate their own concerns. In effect, it means opening a communication channel in the opposite direction.

Morgan, Fischhoff and colleagues see risk communication as a bi-directional process. Experts share their knowledge on the subject with their audience and the audience shares its perception with the experts. Their approach is known as the mental model approach. Implicitly it acknowledges the fact that experts have their own mental model based on expert knowledge and are not the interpreters of of the 'real risk'.

The role of the media

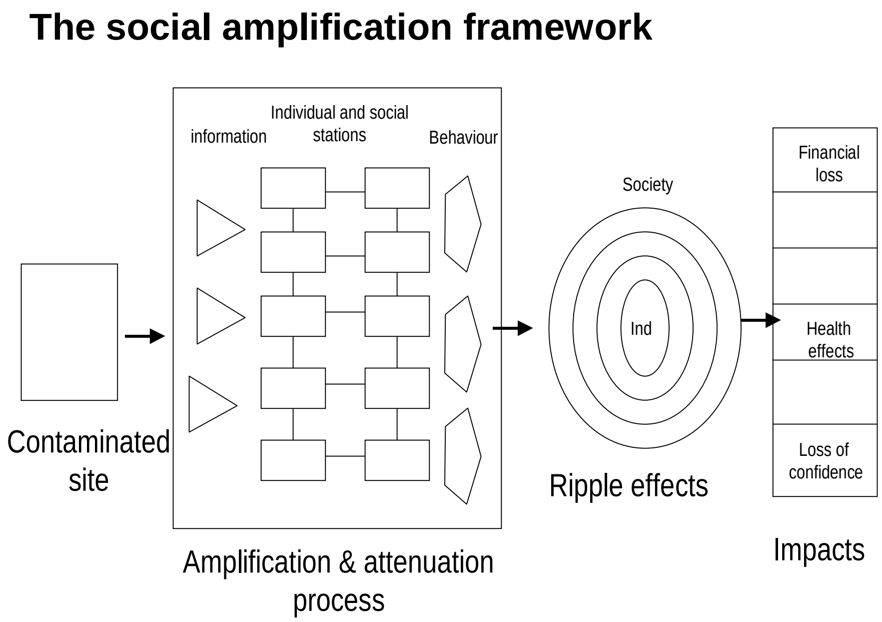


The modern media provide its audience with information that fits in their general perception. A good journalist knows his or her audience and asks the questions he or she believes that the audience is interested in. A well-managed soil remediation program with a perfect communication trajectory is as boring as a happy marriage. However, risks and uncertainties, miscommunication and lack of trust, bad management with a scent of fraud or corruption are big news. We know about Love Canal, Seveso or Lekkerkerk because mistakes were made and not because the risk models show that those sites are the most dangerous sites. Modern media can be considered as the microphones in a public meeting: you cannot communicate without them. If the meeting is not chaired well, people use the microphone to show their frustration. But if the meeting has an excellent chairman, the microphone sustains the structure in the meeting.

The social amplification framework

The social amplification of risks is the introduced by Kasperson, Renn and colleagues in the late '80ies, early '90ies[8]. The notion is based on the thesis that the social and economic impacts of an adverse event are determined by a combination of the direct physical consequences of the event and the interaction of psychological, social, institutional, and cultural processes. Social interactions can heighten or attenuate perceptions of risk. By thus shaping perceptions of risk, risk behaviours are also shaped. Behavioural patterns, in turn, generate secondary consequences that extend far beyond direct harm to humans or the environment. Liability, insurance costs, loss of trust in institutions, and alienation from community affairs are a few such examples. Secondary effects such as these are important because they can trigger demands for additional institutional responses and protective actions. The can also – in the case of risk attenuation – impede the installation of protective actions.

To understand the social amplification framework the metaphor of an acoustic amplifier is used. The framework is based on 'signals'. Amplification or attenuation occurs as individuals, groups, or institutions select characteristics of the event or observation and interpret them according to their perceptions, mental models, or goal-oriented motives. These interpretations are organized into a message, which is passed on to other individuals and groups. As individuals or groups collect and respond to information about risks, they act as 'amplification stations'. Whether signals and messages are amplified or attenuated depends on a wide range of influences. On the individual level the cognitive processes Fauconnier & Turner described, determine the outcome. On the social level individuals act as a member or employee of a social group and they will think and act according to the social rules of that group. Individuals play their role within a framed social space and other people tend to react from their role within the frame of that social space.



Figuur 1: The social amplification framework[9]

Behavioural and communicative responses are likely to evoke secondary effects that extend beyond the individuals directly affected by the original hazard event. According to Renn, secondary impact include:

- enduring mental perceptions, images, and attitudes (e.g. technology attitudes, alienation from physical environment, social apathy, or distrust in risk management agency);
- impacts on the economy (e.g., drop in business sales, residential property values, etc.)
- political and social pressure (e.g., political demands, changes in political climate and culture; social disorder);
- repercussions on other technologies and activities (e.g., higher or lower level of acceptance).

Secondary impacts are perceived by social groups and individuals so that the amplification process continues. Within the amplification process any change of signals and messages that can be imagined in the sound amplification can be recognized, like:

- volume effects
- filtering effects
- muting and adding effect
- mixing effect
- equalizing effect
- stereo effect

The framework is very helpful in understanding what is happening. If you want some more information about the way you can put risk communication in action, I would advise you to read the book 'Risk communication' a handbook for communicating Environmental Safety, and Health Risks.[10]

The workshop

We expect that most Consoil delegates have a technical-scientific background and are more familiar with the technical risk assessment models than the social and psychological risk models. This article shows the top of the iceberg of a large field of knowledge. The aim of the workshop is to let people that are not specialized in this field, taste some of its fruits.The social amplification metaphor can be a bridge between the technical world and the social theories used by social scientists. In this interactive workshop we want to take you along specific situations where you have to decide in different roles about the social aspects of the risks of contaminated sites. The role of information management, proactive communication strategies, alliances with the media, new insurance products, psychological patterns, etc. will be discussed, using a case study. Discussions will take place in small groups in a social arena, where you will be invited to associate with some of the social groups that play a role in the case study.

During the session some theoretical background information will be available for those that are interested, but the main focus of this workshop is on the practical applicability of the social amplification metaphor.

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SpS 16 Special Session

Groundwater Risk Assessment: Science and Policy

GROUNDWATER RISK ASSESSMENT AT CONTAMINATED SITES (GRACOS): DIFFUSIVE GAS TRACER TESTS FOR PARAMETER DETERMINATION IN THE UNSATURATED ZONE

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Abstract

New gas tracer methods for parameter determination in the unsaturated zone at contaminated sites were developed in the framework of the European research project GRACOS. The tracer methods rely on the diffusion of gaseous tracers from a soil gas probe into the surrounding porous medium. Initially, a gas tracer test using non-degradable tracers was developed to quantify the saturation of nonaqueous phase liquids (NAPLs) in a soil volume adjacent to the probe tip. NAPL-partitioning and conservative chlorofluorocarbons as gaseous tracers are injected into the vadose zone to form a point source at the injection point. The quantitative determination of the NAPL saturation is based on a comparison of the concentration decline of the tracers at the probe tip. Applications of this test are source delineation and repeated NAPL quantification in situ during remediation. A second similar diffusive test allows furthermore the quantification of effective and sorption-affected diffusion coefficients of volatile organic pollutants in situ. These diffusion coefficients are required for the prediction of vapor-phase pollutant migration at contaminated sites. Using biodegradable organic pollutants as gaseous tracers, it is furthermore possible to quantify in situ biodegradation rates. Because the new tests require similar equipment than that used in traditional soil gas monitoring, they are of value for risk assessment at contaminated sites.

Introduction

Groundwater risk assessment at contaminated sites (GRACOS). The research project GRACOS was initiated in 2000 with the objectives to develop and to improve methodologies and techniques for rapid, low-cost risk assessment of subsoil and groundwater pollution at contaminated sites (e.g. for polluted top soils, waste disposal sites, industrial sites, etc.). The project included 7 partners from 6 European countries and was funded from 2000 to 2003 within the 5th EU framework programme. The project dealt with different pollution scenarios for volatile and non-volatile organic and inorganic compounds. Here, only one specific part of GRACOS which aimed at understanding the fate of volatile organic contaminants such as petroleum hydrocarbons, chlorinated solvent or chlorofluorocarbons in the unsaturated zone of contaminated sites will be presented. In the case of volatile contaminants, an important and until now often neglected pathway of a potential groundwater pollution is given by diffusive/convective vapour phase transport in the unsaturated zone followed by the diffusive/dispersive transport of the pollutants across the capillary fringe into the aquifer (Pasteris et al., 2002). The method of groundwater risk assessment for the volatile compounds developed in GRACOS is based on the measurement and modelling of the in-situ vapour phase concentrations. The volatile contaminants are participating in phase transfer processes (dissolution into soil moisture and sorption to soil components). Since the unsaturated zone is also a zone of very high bioactivity, the impact of biodegradation (especially of petroleum hydrocarbons, BTEX) on contaminant spreading is also considered to be important. All processes discussed above were studied in the GRACOS project in experimental systems of varying complexity: in laboratory microcosm (Brederode et al., 2001) and column studies (Höhener et al., 2003; Wang et al., 2003), in lysimeter studies (Dakhel et al., 2003; Pasteris et al., 2002), and in a field experiment (Christophersen et al., 2002; Christophersen et al., 2003). The field experiment involved the controlled burial of 12 L of kerosene into a sandy unsaturated zone overlying a gravel aquifer on a previously uncontaminated Air Force base in Denmark. The fate of 13 typical petroleum hydrocarbons was studied during more than 12 months (Christophersen et al., 2002; Christophersen et al., 2003).

Modelling of reactive vapor-phase transport. Within the GRACOS project, numerical models capable of predicting the reactive vapor-phase transport of volatile pollutants in soils were evaluated and further developed. The codes R-UNSAT and MOFAT were found to be suited to handle scenarios of vapor-phase transport of up to 7 different volatile pollutants (Gaganis et al., 2002; Karapanagioti et al., 2003a). A grouping procedure has been developed to reduce the complexity of problems that involve larger number of VOCs (Gaganis et al., 2002). Both codes were shown to generate predictions that compared satisfactorily to experimental data of 14 VOCs studied in a lysimeter (Gaganis et al., 2002; Karapanagioti et al., 2003b). A third code (MIN3D) was further developed at the University of Tübingen for reactive vapor-phase modelling in the unsaturated zone and the transfer of contaminants through the capillary fringe (Maier et al., 2003). The capability of forward predicting the fate of VOCs in the field experiment in Denmark will be investigated for all three codes. This represents the scientific base for scenario-specific modelling of the fate of multicomponent VOC mixtures at other sites under other geologic and climatic conditions.

How to obtain model input parameters? In order to use numercial models at any other contaminated site, the relevant model parameters must be known. Laboratory experiments for e.g. the determination of effective diffusion coefficients, sorption coefficients or biodegradation rates are time-consuming, costly and often biased by sample disturbance. Empirical relationships or literature data can be quite inaccurate. Therefore, rapid in situ field methods for parameter determination are of great value. As an example, the modeling of the volatilization and biodegradation of a mass of fuel in the unsaturated zone requires the knowledge of the position and quantity of nonaqueous phase of the pollutant spilled to the unsaturated zone, the effective and sorption-affected vapor-phase diffusivities, and the knowledge of biodegradation rates. The molecular diffusion coefficients in free air can be measured or estimated from empirical relationships. However, the vapor-phase diffusion in the unsaturated zone differs from the diffusion through free air. Solid and liquid obstacles reduce the cross-sectional area and increase the mean path length in soils, and therefore diffusion coefficients are lower, with proportionality factors accounting for the effects of the physical reduction and/or partitioning. It was therefore the aim of one subproject in GRACOS to develop fast in situ methods to determine NAPL saturation, effective and sorption-affected gas-phase diffusion coefficients and biodegradation rates in the unsaturated zone. The new methods (Werner and Höhener, 2002; 2003) rely on gaseous tracers injected into the ground and are described shortly below.

Gas tracer tests for parameter determination

Soil gas probes and tracer application. Soil gas probes with low dead gas volumes (Figure 1) were constructed from stainless steel tubes with an inner diameter of 4 mm, into which three 1/16'' stainless steel capillaries were inserted (Figure 1). One capillary is used to inject the gaseous compound mixture into the soil, the remaining ones to withdraw samples. Soil gas probes are installed at field sites by pre-drilling holes of 3 cm diameter. The probes are inserted into the pre-drilled hole and then hammered an additional 35 cm into the ground, and the pre-drilled hole is backfilled with sand. This procedure reduces the risk of clogging the opening in the probe with topsoil. Gas tracers are taken from glass bottles with gastight sample lock syringes, and usually 5 mL gas tracer mixture is injected into the soil through the injection capillary, followed by 1 mL of clean air. The total mass of gas tracers or vapors of pollutants injected to the soil for one test is always lower than 1 mg and represents no harm for the environment. Samples (100 µL) are taken both before the injection (background) and at regular time intervals during 7 to 8 hours thereafter through the sampling capillary and are stocked in gastight sample lock syringes until analysis on conventional stationary laboratory gas-chromatographs equipped with FID and ECD detectors.

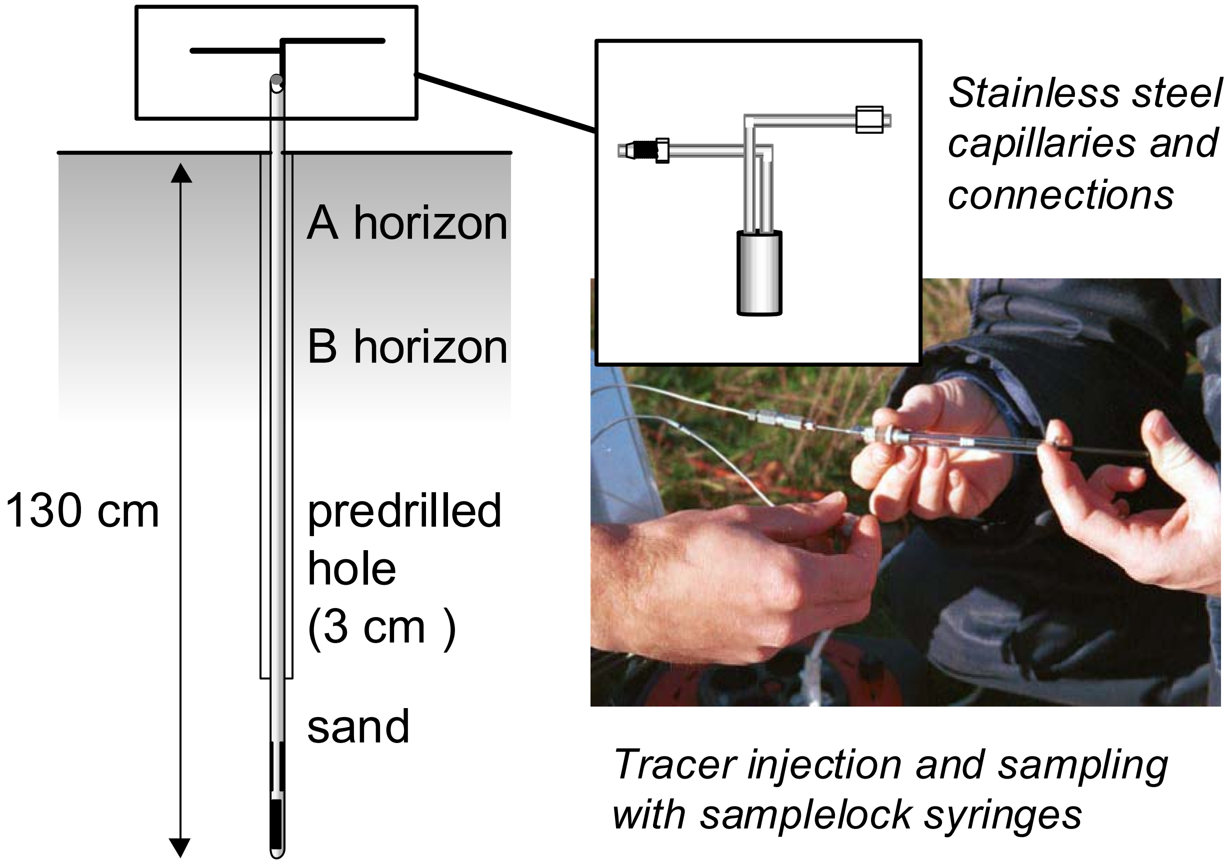

Figure 1: Soil gas probes and details of operation at the field site.

Theory and relevant assumptions. The theory used for data interpretation relies on the following assumptions: The soil can be described as a homogeneous porous medium with uniform and constant properties consisting of soil air, soil water and the solid matrix, where all solid surfaces are wetted. The partitioning of the gaseous compounds between those phases can be described by an instantaneous, reversible linear equilibrium. Gas-phase diffusion is the only relevant transport mechanism; degradation occurs in the water phase and can be described by a single first-order rate constant. The partitioning of a gaseous compound is described using the air-water partitioning coefficient or Henry's law constant H, the air-NAPL partitioning coefficient K_n, and the air-solid partitioning coefficient K_s. The latter is defined as the ratio between the Henry's law constant and the solid-water partitioning coefficient K_d. The mass fraction of the compound in the soil air f_a is calculated as (Werner and Höhener, 2002):

$$f_a = \frac{1}{1 + \frac{\rho_s(1-\theta_t)}{K_s\theta_a} + \frac{\theta_w}{H\theta_a} + \frac{\theta_n}{K_n\theta_a}} \qquad (1)$$

where θ_a, θ_w, θ_n and θ_t denote the air-filled, water-filled, NAPL-filled and total porosity respectively, and ρ_s denotes the density of the solids. The inverse value of f_a can be interpreted as the retardation coefficient R, a quantity used for the interpretation of advective partitioning tracer tests in the unsaturated zone.

For a point source of mass m_o released at r=0 in an infinite porous medium with uniform and constant properties, the concentration at distance r=0 and time t is (Werner, 2002):

$$C_r(0,t) = \frac{V_{in} f_a}{8\theta_a (f_a \tau D_m \pi)^{1.5}} \cdot \frac{1}{t^{1.5}} \cdot \exp[-k_{app} \cdot t] \ . \qquad (2)$$

where:

C_r	Relative concentration of the compound C_a/C_{in} (-)
D_m	Molecular diffusion coefficient ($cm^2 \ s^{-1}$)
f_a	Fraction of the total mass of compound found in the soil air (-)
k_{app}	Apparent first-order degradation rate constant in gas phase (s^{-1} or d^{-1})
t	Time (s)
V_{in}	Volume injected (cm^3)
θ_a	Air-filled porosity ($cm^3 \ cm^{-3}$ soil)
τ	Tortuosity factor (-)

Some of the unknown parameters in equation 2 can be eliminated by using a conservative tracer (non-biodegradable, k_{app} = 0; non-partitioning, f_a =1). The air-filled porosity θ_a needs to be estimated or determined independently and the molecular diffusion coefficient D_m is estimated from empirical formulas. The tortuosity factor τ can then be determined from the relative gas concentrations of the conservative tracer. The mass fraction in the gas phase $f_{a,1}$ can be quantified from concentration ratios $C_{r,1}(0,t)/C_{r,2}(0,t)$ of simultaneously released compounds, where compound 2 is the conservative tracer. The determination of the effective and sorption-affected diffusion coefficients, the apparent first-order degradation rate and the NAPL-saturation is based on this concept and described in detail in (Werner, 2002).

Results and Conclusions

For the quantification of NAPLs in the unsaturated zone, non-biodegradable chlorofluorocarbons with different affinities for partitioning into NAPLs were used as gaseous tracers (Werner and Höhener, 2002). This allowed the reliable determination of NAPL saturations in sandy soils of varying water contents in either laboratory experiments (Werner and Höhener, 2002), lysimeter experiments (Werner, 2002), and at the controlled field experiment in Denmark (Werner, 2002). All tracers were selected according to low affinity for partitioning into soil water or for sorption onto soil solids. This simplified the use of equation 1 (f_a is thus only a function of θ_a, θ_n and K_n). As can be calculated by equation 2, the gas-phase diffusion is a sufficiently rapid tracer transport process to move the tracers into a sphere of about 60-80 cm radius from the injection point within 6 hours. However, experiments performed in a heterogeneous lysimeter showed that the zone of influence (the zone where the NAPL saturation is measured near the soil gas probe tip) is smaller (Werner, 2002). The saturation of the pore space with artificial Kerosene measured with the test at the field site or in the lysimeter was within a factor two or less from the NAPL saturation determined by conventional methods in soil core samples at the probe tip location. The gas tracer test was found to be especially useful for applications where the emphasis lies on the comparison of the NAPL saturation at different locations in a relatively homogenous soil, or on the observation of the evolution of the saturation at a specific location. Such applications include source delineation and the monitoring of natural attenuation processes. The test predicted correctly the endpoint of natural attenuation of a buried mass of fuel in a lysimeter (Werner and Höhener, 2002).

Using a modified setup of the tracer test, effective and sorption-affected diffusion coefficients were determined for various volatile pollutants including benzene, toluene, *n*-octane, dichloroethenes and vinylchloride (Werner and Höhener, 2003). The effective diffusion coefficient is defined as $\theta_a \tau D_m$, the sorption-affected diffusion coefficient is defined as $f_a \tau D_m$. The compounds were injected into the unsaturated zone in the field together with conservative tracer gases, either dichlorodifluoromethane (CFC-12) or sulfurhexafluoride (SF_6). The data obtained for the effective diffusion coefficients of the compounds in a sandy soil were within predictions by empirical relationships. It has to be noted that empirical relationships (e.g. those reported by Millington and Quirk or by Penman, cf. Wang et al., 2003) differ by up to 40% for certain soil water contents. In the same experiments, the first-order degradation rates of the pollutants of interest were evaluated. However, first-order biodegradation rates of all compounds were found to be smaller than 1 per day (Werner and Höhener, 2003). This was due to the relatively cold temperatures at the field site (12-15 °C), the low microbial cell numbers in the deeper vadose zone, and the lack of acclimation time for the microorganisms. In laboratory columns and in the lysimeter, apparent first-order biodegradation rates of > 3 per day have been measured for toluene and *n*-octane (Höhener et al., 2003, Pasteris et al., 2002). To accurately measure biodegradation rates < 1 per day, the in situ gas tracer test must be operated for time scales longer than 5-8 hours. This requires lower detection limits of the gas-chromatography methods, and prolonged presence of personnel on the site. Further work will include also the use of stable isotopes to measure more accurately low biodegradation rates of VOCs in the vadose zone.

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APPLICATION AND PRACTICE REPORT OF EU FP5 RESEARCH RESULTS IN THE AREA KEY ACTION WATER – POLLUTION PREVENTION: ARE RESULTS FIT FOR USE?

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Abstract

The 5th EU Framework Program for Research, Technology Development and Demonstration (FP5) started in 1998 with a duration of five years. It includes the specific program "Environment and Sustainable Development" divided in four "Key Actions". Within the Key Action "Management and Quality of Water – Pollution Prevention" more than 40 scientific projects have been funded. Most of these projects are phasing out in 2003 or are already finished. Essential project objectives have been achieved and obtained scientific research results in terms of project deliverables have been reported to DG Research and the scientific community. Consequently, a process of identification and testing needs to follow, in order to enable the transfer of results from the project level into the European-wide sustainable solutions strategy of the European Union’s 6th Environmental Action Programme “Our Future, our choice” (EC 2002).

Background

A major theme running through many EC-funded projects is the management and protection of groundwater. An increasing number of projects have addressed groundwater contamination and the rehabilitation of contaminated sites (DG Research 2000). These included the development of models to predict the risk of contamination from various sources of pollution linked to agriculture, and research into the rehabilitation of contaminated sites - with the involvement of industry. A lot of effort is also being put into investigating various pathways of soil contaminants, the related risks, and the development of monitoring and rehabilitation techniques as well as decision-support systems, which will allow appropriate prioritisation of sites and identification of most appropriate remediation techniques.

Research co-ordination: The EU funded project “Innovative Management of Groundwater Resources in Europe – Training and RTD Co-ordination (IMAGE-TRAIN)” has the ambition to improve cooperation and interaction between ongoing research projects in the field of soil and groundwater contamination and communicate new technology achievements to young scientists by means of conferences and training courses. IMAGE-TRAIN is a three year project which started in September 2001 and operates at two levels.

(1) Senior level: At this level Cluster Meetings for researchers of ongoing research projects are being organised with the objective to establish topic links between RTD projects, dealing with contaminated land and groundwater and to promote their practical application and by organising practical case studies with selected experts to perform short feasibility studies related to current groundwater or mine water problems.

So far IMAGE-TRAIN has organised two Cluster Meetings: The 1st Cluster Meeting was held in October 2001 in Karlsruhe (Germany) and focused on improving co-operation of three currently operating EU research projects: INCORE mainly dealing with urban groundwater problems, PEREBAR dealing with long-term behaviour of permeable reactive barriers, and PIRAMID focusing on the remediation of acidic mine effluents (IMAGE-TRAIN 2002). The 2nd IMAGE-TRAIN Cluster Meeting with the title *“Sustainable Management of Contaminated*

Land and Groundwater in Urban Areas" and was held in Cracow (Poland) in October 2002. The meeting was targeted at researchers from EU projects dealing with urban groundwater problems and included a specific workshop focusing on the new project tools of the European Commission's Sixth Framework Programme (FP6) on research, technology development and demonstration.

IMAGE-TRAIN includes the performance of three practical Case Studies. Selected experts are invited to perform short feasibility studies related to up-to-date groundwater or mine water problems. The 1st IMAGE-TRAIN Case Study was carried out under the lead of Newcastle University and focused on management of saline mine waters in the Silesian Region". Results of this study were summarised in a review report with the title *"A Review of Saline Mine Waters in the Silesian Region and Methods for Managing them"* which can be downloaded from the IMAGE-TRAIN website.

(2) Junior level: At this level Advanced Study Courses are organised with the objective to quickly transfer existing and emerging knowledge to young European academics.

The 1st IMAGE-TRAIN Advanced Study Course with the title *"Innovative Groundwater Management Technologies"* was held in Katowice (Poland) at the Institute for Ecology of Industrial Areas in June 2002. Lecturers for this course were mainly recruited from the 1st Cluster Meeting. The key purpose of this course was to provide young scientists and engineers with up-to date information of current research activities in the field of groundwater and contaminated land management (IMAGE-TRAIN, 2003). The 2nd IMAGE-TRAIN Advanced Study Course will be held in Pécs in Southern Hungary from June 23 to 27 2003 under the title *"Groundwater Management in Mining Areas"*. The venue is close to an abandoned uranium ore mine and processing site which will be destination of a one day excursion. The course will focus on cost-effective remediation of mining effluents and management of groundwater in areas affected by contamination from mining activities.

Last not least IMAGE-TRAIN is maintaining a Communication Platform for Young Scientists dealing with groundwater and soil science which can be found on the project's website. Main objective of this venture is to create a platform which allows Ph.D. students and other young scientists to present their research work and to get readily into contact with others who have similar interests or work at related fields.

All IMAGE-TRAIN products (newsletter, proceedings, summary reports and other) can be directly downloaded from the project's website: http://www.image-trian.net/.

Objectives

The main objective of the "Application and Practice Report", APR, is the documentation of a two-phase (identification and testing) evaluation process performed on basis of delivered research results from scientific projects running in the FP5 Key Action "Management and Quality of Water – Pollution Prevention". These deliverables include methods, concepts, and applications.

(1) The first phase consists of an identification procedure, which filters out all those project deliverables with focus on specific needs for the implementation of European water related programs and regulations (e.g. Water Framework Directive, Groundwater Directive, Landfill Directive). Identification criteria are besides scientific and technical aspects also cost-effective and eco-efficient aspects.

Approximately 40 scientific projects of the Key Action "Management and Quality of Water – Pollution Prevention" are screened. Each project produces roughly 12 deliverables, which need to be checked. Most of the identified deliverables of concern can be summarised in four topic groups:

- Site Characterisation
- Risk Assessment
- Risk Reduction/Remediation
- Monitoring

(2) The second phase includes a testing procedure In a first step the above deliverables are clustered in two categories (see figures 1 and 2). Clusters of the first category contain deliverables with similar or related topics (e.g. site characterization, monitoring) whereas clusters of the second category contain deliverables with complementing topics (e.g. site characterization and risk assessment; risk assessment, remediation options, and monitoring).

The testing procedure for first category clusters consists of a methodical comparison in order to identify advantages, limitations, and gaps of clustered deliverables with related topics. Testing of second category clusters includes the investigation of interactions and functionality between deliverables of complementing nature.

Site Characterisation	**Risk Assessment**	**Risk Reduction / Remdiation**	**Monitoring**
Project A			Project D
Project B			Project E
Project C			Project F

Figure 1: Cluster Category 1 - Deliverables of Concern with Related Topics

Site Characterisation	**Risk Assessment**	**Risk Reduction / Remdiation**	**Monitoring**
Project G	Project H		
	Project I	Project K	Project L

Figure 2: Cluster Category 2 -Deliverables of Concern with Complementing Topics

Expected Benefits

(1) As main result of the identification phase a topic-specific compilation of available scientific deliverables will be obtained. This compilation is expected to function as scientific-technical toolbox in order to support the implementation processes of European policies and regulations concerning management and quality of water.

(2) Based on the results of the testing phase the boundary conditions for the application of available deliverables shall be determined. In that way the selection of best available techniques for accompanying European implementation processes in accordance with the sustainable solutions strategy of the European Union's 6th Environmental Action Programme (EC 2002) will be enhanced.

Time Frame

Start of the identification phase:	January 2003
Presentation of first results from the identification phase:	May 2003, CONSOIL
Start of the testing phase:	March 2003
Presentation of first results from the testing phase:	May 2003, CONSOIL
Final presentation of APR:	October 2003, 3rd Cluster Meeting IMAGE-TRAIN

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IMAGE-TRAIN (in preparation) Summary Report of the 1st IMAGE-TRAIN Advnaced Study Course from June 24 to 28 2002 in Katowice (Poland).

Relevant websites:

IMAGE-TRAIN, Innovative Management of Groundwater Resources in Europe – Training and RTD Coordination Project; http:///www.image-train.net/

INCORE, Integrated concept for groundwater remediation, http://www.umweltwirtschaft-uw.de/incore/

PEREBAR, Long-term Performance of Permeable Reactive Barriers used for the Remediation of Contaminated Groundwater, http://www.perebar.bam.de/

PIRAMID, Passive In-situ Remediation of Acidic Mine / Industrial Drainage, http://www.piramid.org

"EUGRIS - EUROPEAN SUSTAINABLE LAND AND GROUND WATER MANAGEMENT INFORMATION SYSTEM "

Jörg Frauenstein, Dr. Volker Franzius, Detlef Grimski, Dr. Paul Bardos

The Internet has become one of the most important sources of information. A tremendous amount of information is collected and stored on the Internet about contaminated groundwater and land management. The available information on the Internet simply does not exist in a way that can be easily harvested by the full groundwater and contaminated land community. It is scattered over many web sites and sources, whose provenance and reliability may be unclear. Coverage for a particular information requirement may not be complete. The information offered is often not placed in a context, in particular, it may not be well explained for those who are either new to contaminated land management, nor for key stakeholders who are not technical experts on contaminated land, for instance many site owners, the financial community and insurers.
As a labour saving device for both basic and applied research, as well as technology, policy and regulatory development in general. This one stop shop for European information will be a big step forward. Such a structured comprehensive European gateway does not yet exist for contaminated land, groundwater, nor for waste management nor many other environmental sectors. EUGRIS can be an example to Europe's wider environmental research and business communities.
The presentation outlines an Accompanying Measure within the FP 5 to develop an web based **EU**ropean Sustainable Land and **GR**oundwater Management **I**nformation **S**ystem information system (EUGRIS). EUGRIS will be a web based user-friendly information platform, a "gateway" or "one stop shop" for contaminated land and groundwater information for all stakeholders in the field. It will provide access to the information via a carefully structured and maintained web site with contextual guidance on the information on offer. EUGRIS' information will be drawn from and linked to reliable sources, such as EU and governmental institutions, national and international networks, universities, leading professionals and organisations, etc.

EUGRIS seeks to:

- provide a high-quality platform for dissemination and extraction of existing knowledge across Europe (e.g. guidelines, case studies, methods, reviews, regulations, conferences, workshops, courses, curricula etc.)
- provide access to innovative research findings, products, technologies (e.g. on-going RTD projects and their objectives, new tools, demo sites, first findings, technology transfer etc.)
- enhance the transfer of information between stakeholders and their networks (e.g. regulators, researchers and industry but also end-users, NGOs etc.)
- support co-ordination of RTD funding across Europe (e.g. access to information about former, on-going and future research plans and their outcomes)
- improve efficiency of policy and regulatory development (e.g. regulating agencies can obtain information and results on research work and strategies of neighbour countries)
- contribute to the harmonisation of environmental standards across Europe (e.g. experiences with water and soil directives, existing and new ISO standards, etc.)
- Develop a management or business plan to support the long-term sustainability of EUGRIS following the end of the Accompanying Measure.

EUGRIS will be delivered as a web site with linked databases. The objective is to develop a "pilot" version, based on information provided by "Pilot Countries" (incl. an Accession State), pilot projects (like SOWA), EC RTD projects, Concerted Actions and the other international initiatives. These information providers also take part in the design of the gateway and comment on its implementation. As far as possible original source material will not be replicated in this database. EUGRIS establish and provide a communication platform between the various existing and planned research centres of excellence and other stakeholders. The project includes development of a management or business plan for EUGRIS' continued existence. A package of promotional measures targeted at: information users, information providers, encouraging further countries to join, stakeholders for the future management of EUGRIS after EU funding.
EUGRIS' will allow all stakeholders equal access to reliable and quality contaminated land and groundwater information from a single point of access: a one stop shop. Its key advances are listed below.

Networks like NICOLE and CLARINET have begun the process of collating information sources on the Internet, and providing general information and support, this has been a welcome development. Yet the volume of information generated by regulators, academe, companies, research institutions and others in Europe is rapidly growing. Unfortunately, this European information is less visible.

- EUGRIS will provide a guided, scaleable and holistic approach to providing information
- EUGRIS will provide a linkage of networks and national initiatives to a central European "hub"
- EUGRIS will provide a research management tool

One of the major activities of EUGRIS will be the collation of data on national as well as EU research programmes. EUGRIS will

- provide a means for researchers to deliver and obtain information on research findings
- provide a base for funding institutions to decide about future research programmes at European level
- offer end users high-quality links to new developments and a quick feed-back to the research community
- offer a balanced overview on distance education, workshops etc. offered by leading research institutions which today are part of the dissemination strategy for any major national or international research project.

The work of EUGRIS consists of three broad components, the design of the information system, the development of its software implementation, and the population of the system with information. The information system design can be divided into two main packages of work: the design of <u>templates</u>, which are distinct web pages structuring specific information and providing further guidance through to the ultimately sought information by clear route navigators, quick search facilities, and the design of the <u>digests</u>. These digests will be carefully compiled and drafted summaries of specific information prepared by EUGRIS experts enrolled for the purpose. Templates will be proposed by the EUGRIS project team, but will be offered for debate at workshops. Stakeholder networks will be invited to contribute digests, and will be offered digest drafts for peer review.

The data interface of the system to its users is of course the Internet, i.e. the EUGRIS - WWW site.

Information management will be based on two features: gateway structure and templates. EUGRIS will be the EU portal for national gateways, i.e. the central entry point - the hub of the system. All national gateways will have identical structure based on well-defined templates (e.g. site structure, descriptors, etc.; see below). Therefore, EUGRIS can grow to an EU portal as an flexible and open system.

EUGRIS will be able to support education and training functions. These will in fact be integrated with the series of digests already discussed, but will also be accessible via specific training and education templates or windows. Table 1 illustrates a possible information system structure that might be used as a starting point for EUGRIS.

The software implementation of EUGRIS is managed as a single work package encompassing both the design of web pages and linkages, based on the information system and its templates, and the associated databases, going on throughout the project. Two broad classes of data will need to be stored: data which identifies where source material is located elsewhere on the web (meta-data), and data stored within EUGRIS itself.

The population of the database with information will be managed as a two workpackages, but with component parts. It includes two broad areas of activity: the collation and review of information sources and the preparation of information digests written from national, stakeholder and technical perspectives, as described previously. The component parts have been organised as activities by country. A further work package relates to the collection of information from EU and stakeholder network sources.

Information	Gateway Tool Box	Information Exchange
Issues *Contaminated Land* *Groundwater Protection* *Landfills/ waste dumps*	*Customisation* *Registratio n* *Logbook* *Set level of detail*	*Data handling* *link maintenance* *update routines for new information and data* *PO box for new incoming data and information*
Scope *Site Characterisation* *Investigation* *Behaviours and Fate of Contaminants* *Risk Management and Communication* *Remedial Technologies & -strategies* *Monitoring & Efficiency Control* *Decision Making* *Sustainability aspects* *Socio-economic aspects*	*Help* *Context Sensitive Help* *Add Information* *Glossary* *Contact Us*	*News / mail lists* *EU Research projects - latest info*
Resources *Guidance & Regulations* *Technical books & reports* *Standards* *EU and National projects* *Research & Case Studies* *Decision support tools* *Networks & Events* *Discussion groups* *Education & training*	*Internal Search Functions* *Site Map and Library*	*Brokerage* *Interactive web boards* *Partner finding* *Conference notices* *Researcher posts offered* *New programme opportunities*
Country *EU overall* *Pilot countries* *Pilot Accession country*	***Communication Tools*** *(See next column)*	*Country, Networks and Concerted Actions Zone,*

***Table 1**:Initial Starting Point for Information System and Template Organisation*

A specific work package includes the promotion of EUGRIS, the collation of peer review comments and other inputs from national agencies, DG Research and stakeholder networks and the encouragement of further countries to join EUGRIS, once a working system has been established. A key function of this workpackage will be dedicated to an External Advisory Group (**EAG**). This group will support defining and fine tuning the approach:

- Does EUGRIS provide proper, far-reaching and reasonable information ?
- Does EUGRIS provide valid data?
- Is EUGRIS usable and is the interface user friendly?

The EAG will be formed in the first three months of the project and consist of relevant stakeholder groups, such as regulators, industry and researchers.
The development of a detailed management / business plan for the future maintenance and expansion of EUGRIS is a critical part of this project that underpins the development of a fully operational implementation of EUGRIS. This activity has therefore been proposed as a discrete Work Package. This includes mainly the Identification of independent organisations willing to manage and maintain EUGRIS and its national nodes after the funding period. A further balance that needs to be struck is to find a management plan that demonstrates the value of EUGRIS to the groundwater and contaminated land community, and the value of the original EC investment. Revenue generation from EUGRIS services is a very visible means of providing this reassurance. However, this also has to be set against the amount of time that a EUGRUS service needs to exist to gain critical mass and credibility. Hence EUGRIS is very much a pre-commercial stage.

The EUGRIS partnership is made up of 11 partners from 5 EU member countries and one EU candidate, namely Germany, Denmark, the United Kingdom, France, Italy and Hungary. They represent a mixture of experienced regulating and researching governmental organisations, one university and a number of SME's.

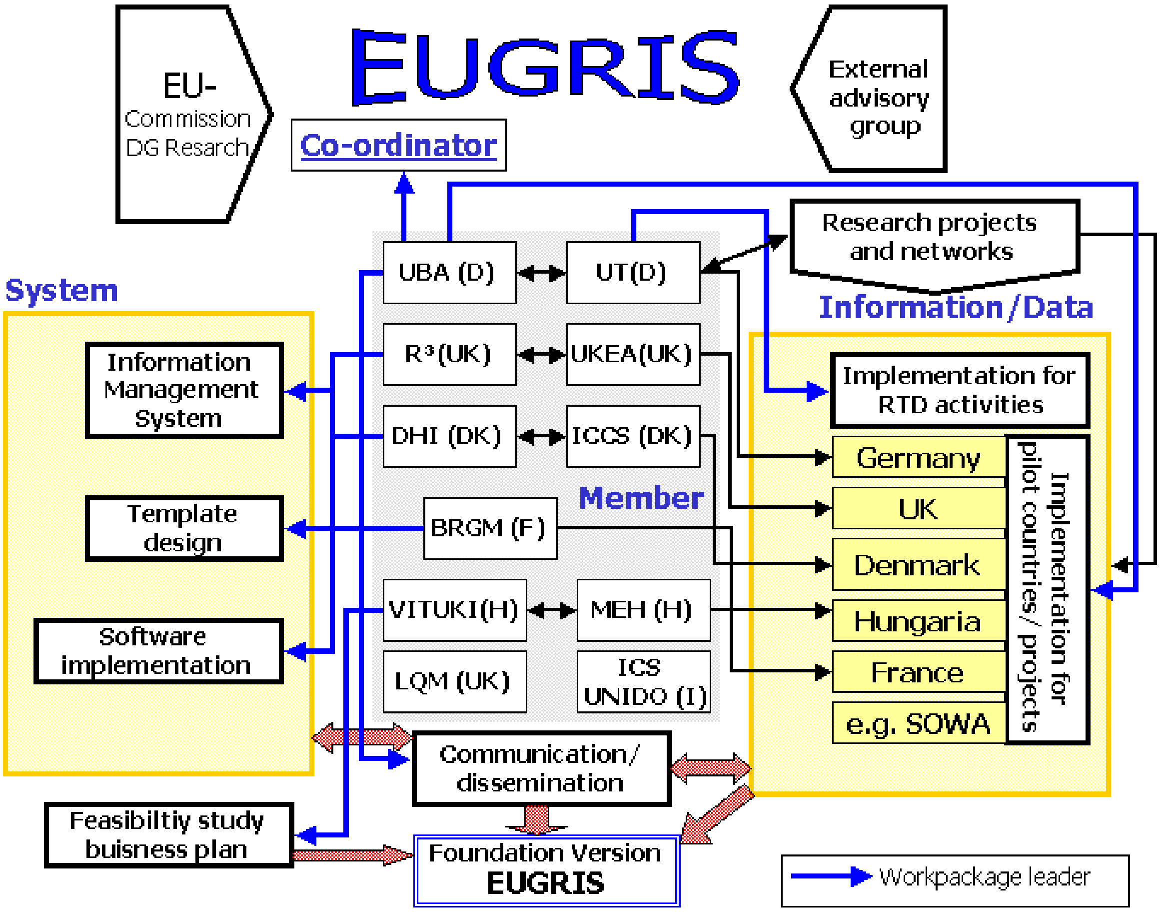

Figure 1: EUGRIS – Consortium and Management Structure

All of the partners involved have many years experience and far reaching knowledge in land and groundwater management issues and are specifically professional in the technical and IT related subject that EUGRIS is dealing with: i.e. information management and dissemination.

JOINT - JOINT TECHNICAL APPROACH FOR SOIL AND GROUNDWATER QUALITY MANAGEMENT

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Objectives

JOINT will focus on the following objectives as

- diffusion of current R&D results to a larger community than those involved in current and former networks, in particular municipalities, regions, and reclamation companies,
- updating of the sound technical approaches developed in previous networks and on national basis,
- stimulate cooperation for applied research in this field, in particular by integrating existing projects,
- support of the implementation of the Water Framework Directive and Groundwater Directive as well as mentioned upcoming soil and liability policies in the member states by formulation of technical approaches and methodologies

Within the interdisciplinary discussion JOINT will casually identify partners for the constitution of networks of excellence and different kinds of projects on contaminated land management and water resources protection.

JOINT will closely link the steps of investigation, risk assessment and remediation to one integrated process. This will help to reach a much wider acceptance of risk based decisions by stakeholder groups and the use of novel technologies at a practical level.

Motivation

In context of soil and groundwater quality management four major processes will challenge the future development of the work on these topics:

a) All European countries have specific policies and laws for the prevention and the protection of water resources. They have developed specific technical approaches for groundwater quality protection and groundwater quality remediation. In general risk assessment procedures or recommendations are used, often those that are elaborated with the scope of groundwater used as drinking water. For a practical approach to reach risk based land management in urban areas, risk assessment procedures have to integrate three main assessments: fitness for use, protection of the environment, and reduction of aftercare.

b) Investigation and remediation have to be incorporated in well established spatial planning procedures in a way which does not affect the realization of the development so that it is uneconomic. This demands new standards concerning time, costs and confidence in the results.

c) Innovative in-situ technologies and the use of natural attenuation are emerging and try hard to establish themselves against the classical technologies such as dig & dump and pump & treat. Combinations of these different approaches are already in discussion. The basic ideas of these innovative methods have to be integrated into manuals for practical work to support their application and establish the technical and legal requirements.

d) There are recent developments that urgently need a more integrated approach: the need of water resources of good quality for all the different uses (drinking supplies, irrigation, industry, leisure, …), the change in land use (more abandoned agricultural land, more industrialized and urban areas), the pressure in Europe to re-use contaminated sites instead of spoiling more greenfields, the role of soil in the global CO_2 balance and the climate change. To manage this problem, a joint effort in policy making and research may lead to a combination of resource management (water, sediment and soil protection) and risk management (addressing existing pollution, on a site-by-site approach basis) in order to better manage certain situations that are better dealt at a regional approach, taking into account the impacts of several sites on the same resource, and so the cumulative risks for both human health and natural resources.

Recent publications focus on general aspects of dealing with contamination of groundwater and soil. A number of running projects within FP 5 deal with technical approaches and technologies on this matter. Their results will obviously show the need to revise existing strategies and recommendations of action according to the demands mentioned under a) to d). National environmental agencies play a key role in developing a strategic approach and providing technical standards to support and implement the legal framework, mainly given by the Water Framework Directive and related activities as well as three additional documents published by the European Union:

- a draft **paper on Soil Protection** that takes into consideration the soil pollution aspects within others (erosion, salinization, …). The current reflection of the DG Environment consists in the definition of pollution based on concentrations of pollutants in this media and should be reviewed using the experience acquired in the different countries that have faced the problems of solving contaminated land and water resources management.
- A proposal of **European Directive on Environmental Liability** that will be stated on the application of the 'polluter pays' principle, the necessity of intervention of the states in certain cases (damage to water resources for example) and, on the technical aspects, the basis of the definition of the remediation objectives.
- The **EC Fifth Environmental Action Program "Towards Sustainability"** recognises that all players concerned should take concerted action, acting in partnership, to achieve the objective of sustainable development.

Development and revision of existing standards in this area is expected to be one of the major tasks of the national environmental agencies for the next years.

JOINT's intention is to link and cluster single RTD-projects as well as to link the single topics and successive working steps investigation, risk assessment, remediation and soil and groundwater management to one integrated process. Already existing research know-how will be brought together to reach an interdisciplinary discussion. JOINT will serve as a communication-platform between already existing networks and offer the possibility to work together on one well defined approach which will streamline the exchange of knowledge between the different expert-groups.

Besides the innovation being in the overall concept and approach, the participation of researchers representing numerous running R&D projects ensure a high degree of innovation of the single contributions on scientific and technological matters. These running R&D projects already involved are:

ANCORE, CORONA, GRACOS, IMAGE-TRAIN, INCORE, MASURIN, METALBIOREDUCTION, NORISC, PEGASE, PEREBAR, PURE, RESCUE, SENSPOL, TRACE-Fracture, WATCH, WELCOME, SOWA, EUGRIS.

Project Workplan

JOINT will finally reach its overall intention to develop a sound technical approach for industrial pollution and water management to sustainable inner development of European cities by the treatment of contamination of groundwater and soil. The technical approach will so far serve as a contribution or as a module for the implementation of the Water Framework Directive and as part of the future soil protection policy in Europe. The work will be done based on a summary of the results and especially the experiences collected in recently funded projects taking into account all innovations reached on the topic of contaminated soil and groundwater. Moreover JOINT will serve as a link between the 5th and 6th framework program as it stimulates the constitution of centers and networks of excellence, hence giving a perspective to

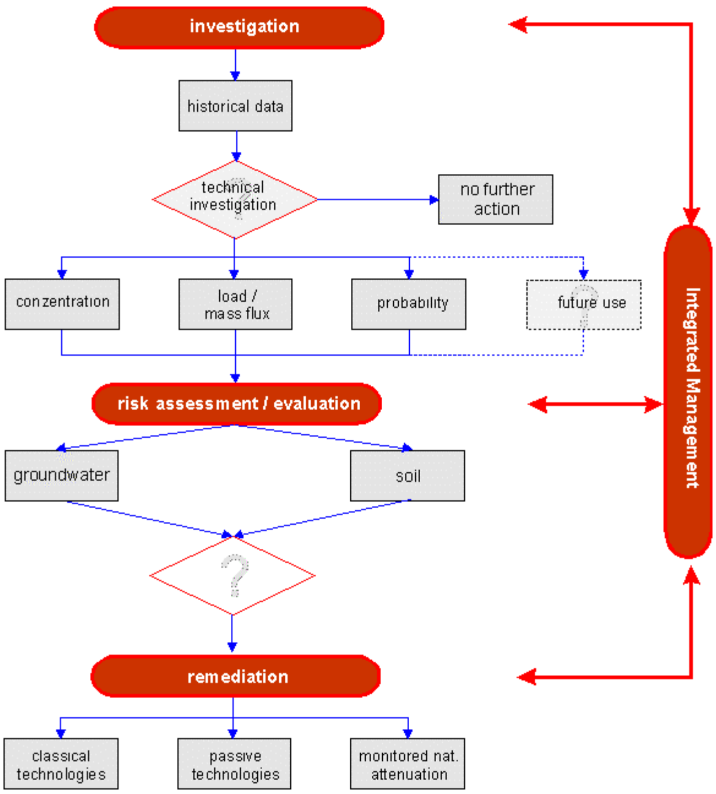


Figure 1: Generalised flow chart based on the technical assessment, as the best available approach

European research area in the field of dealing with contaminated land and groundwater. The technical approach will be presented as flow charts (see example in fig.1) for investigation, risk assessment, remediation and integrated management. These will show the main lines of evidence and interfaces to related activities and will be supported by a concise description. Basis of this work will be the results and experiences especially of the CLARINET, CARACAS and NICOLE network. The technical approach will be used by the member states of EU and can be specified according to the national legal situation. The flow charts will offer different possibilities to reach optimal and sustainable remediation and development strategies.

The necessary comprehensive evaluation and assessment of the results of projects will further give a documentation of the state of the art achieved and outline future needs for R&D activities.

Final output will be a comprehensive and well structured report of about 40 pages to be used as a guidance in the daily work of national agencies, local authorities or private enterprises.Both the sound technical approach and the state of the art will be presented in a way to be incorporated in a web available data base.

An overview of the whole JOINT work program and its integrating aspects is given in the figure below.

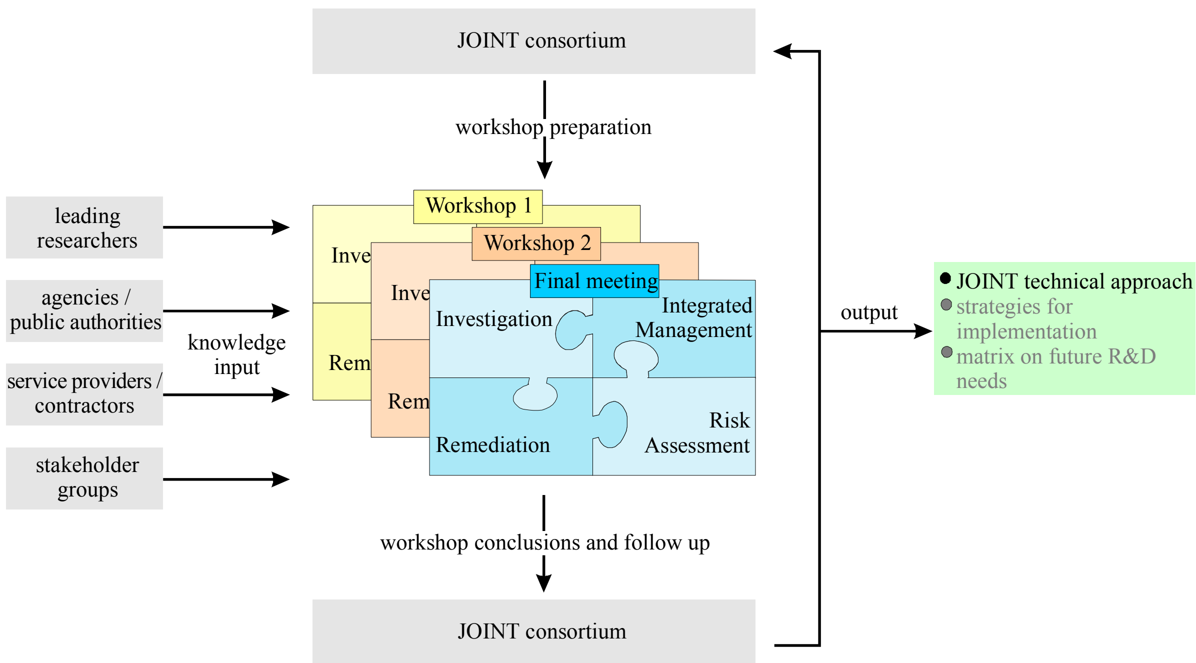
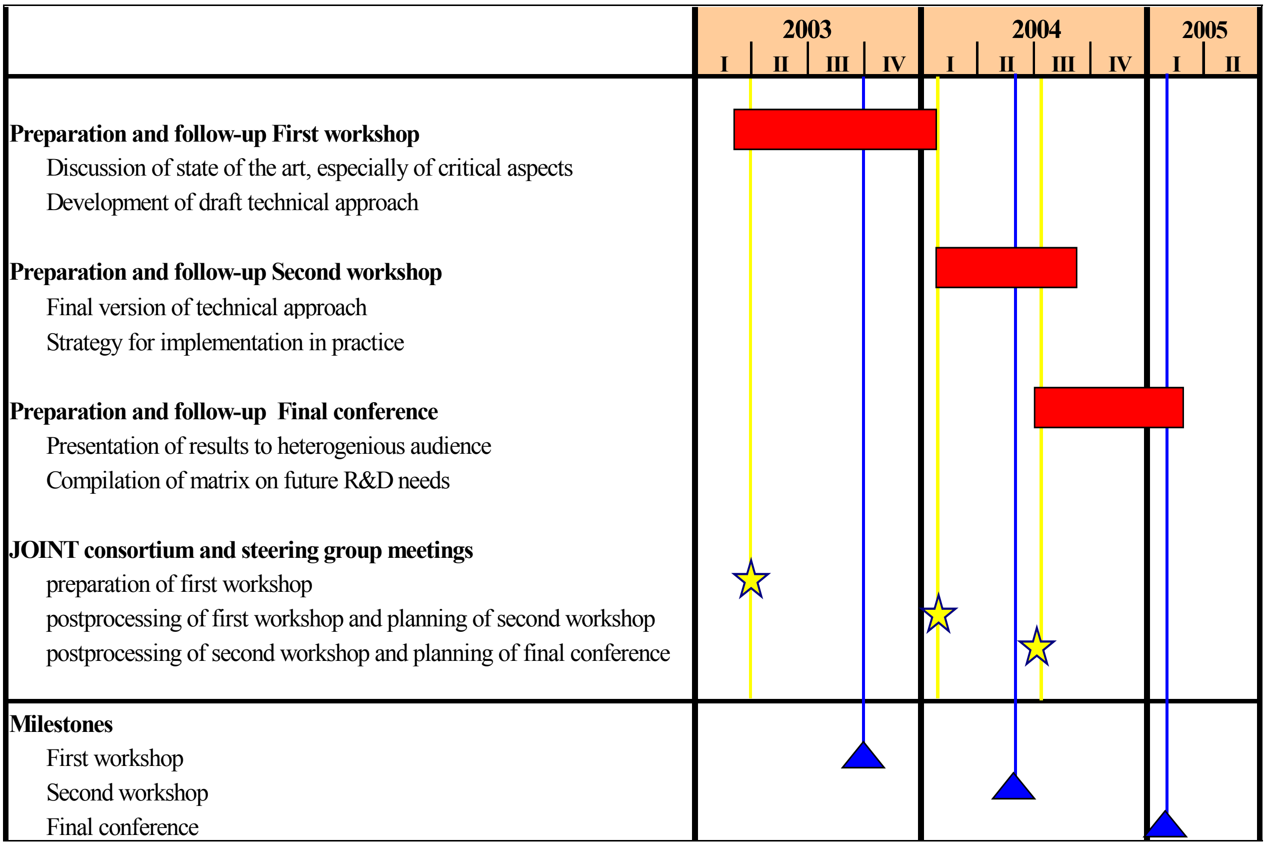


Figure 2: JOINT work program and its integrating aspects

The work will be done in a series of two workshops concluding in one final conference. The events are organised partly in parallel sessions of four teams, according to the topics: investigation, risk assessment, remediation and integrated management of polluted water and soil. Those teams are led by representatives of national or regional agencies and managed by a consultant. The leader and the manager of the teams are responsible for secretary, preparatory and evaluative work between the workshop and will co-ordinate their activities among each other in course of internal JOINT consortium meetings. Those meetings will be held before the first workshop, between the first and second and after the second workshop.

Project time table



The Consortium

The contractors forming the JOINT consortiumprovide an effective team with a broad range of highly relevant expertise from public authorities and private companies. It is made up of 8 principal contractors from Sweden, Belgium, France, Germany, Spain and Norway. All contractors are involved in various international and national research projects. The scientific and technical experience of the experts is extended by the know-how about regulatory needs of the administrators coming from agencies on municipal, regional an national level.

Besides the principal contractors forming the consortium, 4 scientific advisors and the Co-ordinators of the accompanying measures EUGRIS and SOWA join the steering group and take an active role in the developing process. The consortium will get support by researchers, planners and developers as well as national agencies representing most of the member states of EU and the NAS. Besides workshop participants recruited from projects contracted under the water key action and the above mentioned agencies the workshops will be public and open for all which are willing to participate and actively contribute to the JOINT objectives.

JOINT is organised as a series of workshops, which are prepared and followed-up by 4 topic related teams. Each team consists of a leader, coming from an authority on national , regional or municipal level, a scientific-technical expert acting as a rapporteur, recruited from well experienced consultants and a scientific adviser representing a academic institution of high reputation in the related field.

Participants of JOINT and their role in the consortium

	Investigation	Risk Assessment	Remediation	Integrated Management
European Commission, DG 11 & DG 12				
Scientific advisor	Politechnico, Milan, Italy	CSIC, Spain	VEGAS, University Stuttgart, Germany	Technical soil protection committee, Netherlands
Co-ordinator - UW Umweltwirtschaft GmbH				
Team leader	ACA, Spain	OVAM, Belgium	AfU Stuttgart, Germany	BRGM, France
Rapporteur	GEDAS, Belgium	KEMAKTA, Sweden	Aquateam, Norway	UW, Germany
related activities	Internet platform - EUGRIS Co-ordinator - UBA Berlin, Germany		Integrated strategies - SOWA Co-ordinator - Uni Tübingen, Germany	

JOINT Contractors

JOINT Steering Group

SpS 17 Special Session

Micro-emulsions:
An Efficient Solution for the
in situ-Remediation of
DNAPL-Contaminated Sites

MICROEMULSION – AN EFFICIENT SOLUTION FOR THE IN SITU–REMEDIATION OF DNAPL–CONTAMINATED SITES

THE PROJECT NETWORK: GENERAL OVERVIEW ON THE RESEARCH AND FIELD TEST ACTIVITIES

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Introduction

In many cases *in situ* and *ex situ*-remediation techniques applied provide an efficient decontamination of polluted sites. However, serious problems for the protection of groundwater arise at organic contaminants with a density higher than that of water (DNAPL; e.g. volatile chlorinated hydrocarbons) and which do not mix with water. Percolating through the pore space of the soil they can even migrate below the groundwater table until an impermeable layer stops them. If these contaminants are mobilised *in situ* by flushing processes there is a danger of dispersing the pollutants into inaccessible regions of the soil.

The results of investigation about the solubilization behaviour of microemulsions in aquifers show that in principle microemulsions are well suited for a trusty remediation of such sites. The microemulsion designed for this purpose, is able to quickly solubilize the chlorinated hydrocarbons and to transport them upward because of the lower density of the mixture compared to the density of water.

Microemulsion

Microemulsions are thermodynamically stable dispersions of two immiscible liquids (e.g. water and oil) or solutions, which are stabilised by at least one or more amphiphilic component(s) ("detergents"). In the present case the microemulsion consists of biodegradable rape oil methyl ester, biodegradable surfactants, water and $CaCl_2$.

General Characteristics

The general characteristics of a microemulsion under regard of an application at in *situ soil*-remediation are

- High solubilization capacity (up to 50 g/L uptake of contaminant)
- Low interfacial tension (solubilization)
- Good wetting of the solid phase (soil)
- Lower density in comparison with water (0.95 – 0.98).

Requirements

The requirements the microemulsion has to fulfil under regard of an application *at in situ* soil remediation are

- One-phase-stability in the temperature range of 05 °C – 35 °C (no temperature-induced splitting)
- Little influence of salinity on the phase formation
- No formation of liquid crystals (danger of clogging due to a phase with high viscosity)
- Low content of surfactant and oil (economy of the process)
- Good biodegradability of all organic components (treatment of the site following the remediation process).

The flow behaviour of the microemulsion in different types of soil has been intensively studied by two-dimensional experiments in medium-scale glass containers. In a sandy soil material with considerable content of clay the flow is mainly determined by the wetting properties of the microemulsion. Since the microemulsion is wetting the soil better than water, it can be easily infiltrated from a well. It forms a nearly spherical liquid body with a slight deformation at the upper part, which is due to the lower density. In a narrow contact zone with water the microemulsion decomposes and forms an emulsion. The microemulsion can be moved through the soil by pumping. Then the initial narrow zone of emulsion at the outside of the liquid body becomes larger and more diffuse. Since the excess oil has a density even lower than the microemulsion the upward transport is increased. Most of the microemulsion remaining in the aquifer can be removed after the extraction of the contaminant by intensive flushing with water, brine or surfactant solution. It is assumed that the residual components will be biodegraded.

Process

Based on the results of successful laboratory remediation experiments and a pilot-scale test (25 m^3, 30 kg of contaminant) with more than 90 % of contaminant removal the four partners Forschungszentrum Jülich (FZJ), DVGW-Technologiezentrum Wasser, Karlsruhe (TZW), IBL Umwelt- und Biotechnik GmbH, Heidelberg (IBL), and Universität Stuttgart (VEGAS) have the object in view to establish a technical solution for the *in situ*-remediation of DNAPL-contaminated sites applying microemulsions.

The microemulsion is introduced into the contaminated underground via wells. In a narrow contact zone with groundwater it forms an emulsion. That splitting of the microemulsion leads to an oil-in-water phase and an oil-rich phase, in the course of which the pollutant accumulates in the latter one. If the oil phase has a lower density than water it flows upwards; in the case of a higher density, it settles downwards to be then taken up by the succeeding microemulsion, which thus prevents the DNAPL from settling into deeper-seated soil layers.

Pumped from the subsurface the mixture of microemulsion, pollutant, and groundwater has to be processed. The aims of that step are the isolation of contaminants, the recovery of microemulsion constituents, and the separation of the water for release to water treatment. The oil and the surfactant(s) are reused for infiltration after adjusting the right composition of the microemulsion.

Following to the contaminant extraction the soil is flushed either with an aqueous surfactant solution or with water in order to minimize the amount of microemulsion constituents remaining adsorbed onto soil particles. The remediation process is finished by microbiological after-treatment of the site.

Flow experiments – optimisation of hydraulic systems

Different well geometries are developed, permitting the adjustment of infiltration and extraction to the conditions and the distribution of the contaminants at hot spots. The results of this working package yield a pathway for the microemulsion in order to solubilize as much contaminant as possible, and to ensure that the density of the intermediate emulsion is lower than that of water during the whole remediation process. In addition 2D laboratory and 3D pilot scale experiments are performed in order to get an understanding about the flow behaviour of microemulsions in porous media. As in sandy soil with hydraulic conductivity > 10^{-4} m s^{-1} the flow of the microemulsion is mainly governed by its low density, the spreading properties and the hydraulic forces. In a narrow contact zone with water the microemulsion decomposes and forms an emulsion. This problem has to be considered.

The aim of this working package is an optimisation of the hydraulic systems to reduce secondary effects and to bring down remediation costs. M. Stuhrmann and J. Schlüpen will report results in detail at presentation *Design of Hydraulic Systems for in-situ Remediation of DNAPLs with Microemulsion.*

Field experiments

Experiments at a test site are performed with the aim to evaluate the results from pilot scale tests under controlled field conditions. Following to an investigation of the underground in detail the main topics during the first trial are the optimisation of the hydraulic system and the adjustment of the whole process. Further to, it is to be demonstrated on the condition by natural underground structures that *in situ* remediation of DNAPL hot spots with use of microemulsions is an effective and safe process. Organic compounds remaining in the “aquifer” will be eliminated by microbial degradation.

F. Seitz and E. Kohlmeier will report this in detail at presentation *Field Studies for the Application of Microemulsions*.

Reprocessing of microemulsion

An important objective of the research activity is the recycling of the microemulsion for re-use in the remediation procedure. The extracted solution from the subsurface consists of microemulsion components, contaminants (e. g. chlorinated hydrocarbons), solids, and ground water. Due to its dilution with ground water in the subsurface, an emulsion is obtained which has to be concentrated. The treatment of this emulsion is divided up into the treatment steps sedimentation of the solids, separation of the contaminants, concentration of the emulsion to the microemulsion, and the regeneration of the microemulsion by compensating possible losses mainly from the flushing process. The separated solids and contaminants are to be disposed; the pre-processed water can be released to the local sewage system or treated with activated carbon before re-infiltration into the aquifer. The promising results of laboratory and technical scale experiments on the evaporative removal of the chlorinated hydrocarbons as well as the concentration of the microemulsion were confirmed with commercial equipment, a falling film evaporator with a throughput of 40 L/h distillate.

Different, also alternative techniques are evaluated which will be reported in detail at *Microemulsion Enhanced In-situ Remediation – Recycling Concepts for the Additive* by B. Memminger, J. Schlüpen, L. Fürst, N. Fütterer, B. Barczewski, and H. Hasse.

Microbiological degradation

In spite of intensive flushing of the remediated site after contaminant extraction a small part of the compounds of the microemulsion as well as of the contamination remains in the subsurface. Biodegradation of these components was tested under aerobic, denitrifying, Fe(III)-reducing, sulphate reducing, and methanogenic conditions applying the autochthonous microflora of the chloroethene contaminated Eppelheim site.

All the microemulsion components are biodegradable under aerobic conditions. A rapid consumption of oxygen demonstrated the high potential of the autochthonous microflora to utilize RME. Also the non-ionic surfactant Uniperol and the anionic surfactant AOT were degraded, but with slower kinetics.

In the absence of oxygen, the biodegradability of the microemulsion compounds was quite different. A. Tiehm, H. Schell, and M. Stieber will report results of this working package in detail at presentation *Biodegradation of Microemulsion Components*.

Acknowledgement

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DESIGN OF HYDRAULIC SYSTEMS FOR IN-SITU REMEDIATION OF DNAPLS WITH MICROEMULSION

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Introduction

The length of time required to dissolve a typical accumulation of DNAPLs on top of an aquitard can be many decades or longer even when pump-and-treat methodologies are used. To shorten remediation time and reduce costs for pumping and water treatment an innovative remediation technology is being developed using a new microemulsion formula. This research project is being carried out in collaboration with three research institutes and an engineering company and is funded by the German Federal Ministry of Education and Research. The experiments described below were performed at the Research Facility for Subsurface Remediation (*VEGAS*) of the University of Stuttgart and at the Research Centre Jülich.

First experiments realised at *VEGAS* in a large container (8.0 x 1.0 x 3.0 m) filled with coarse- and fine-sand structures already proved the high solubilization capacity of the microemulsion for DNAPLs (TCE) and its efficacy for in-situ remediation [1].

For the development and assessment of the technology detailed medium- and large-scale experiments are carried out under controllable and reproducible conditions. The aim is the transfer of experimental results to large scales and to field conditions. The technology will be tested in two field experiments at a contaminated site near Heidelberg.

Experiments

Small-scale 1D experiments with soil columns (length 0.5 m; diameter 0.1 m) were conducted, to investigate to which extent the microemulsion lowers the permeability of the soil. Alternate flushing of water and microemulsion showed pronounced permeability coefficients in different soil types. As is known from surfactant-enhanced aquifer remediation surfactants also reduce soil hydraulic conductivity significantly [2, 3].

Medium-scale experiments were performed in glass-windowed containers (1 x 0.7 x 0.12 m) filled with different soil types to investigate the dispersion and flow behaviour of the microemulsion in saturated aquifers. Some containers had pools of PCE which were removed during the simulated remediation procedure (Fig. 1).

As the microemulsion and the DNAPL were coloured with different dyes, the experiments could be video-controlled through the glass window. Water samples from the extraction well and soil samples taken after the experiment were analysed to determine accurate mass balances and remediation efficiencies. Injection and extraction wells as well as pumping rates were re-adjusted depending on the results of the preceding experiments.

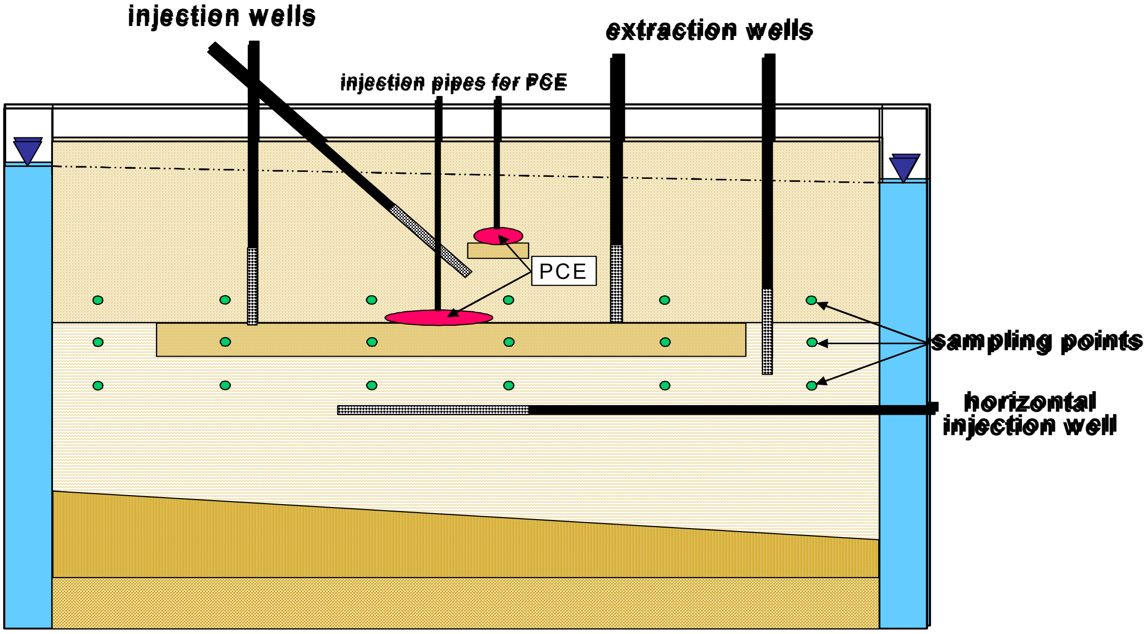

Figure 1: 2D Test container with different hydraulic systems and pools of PCE

First Results

The density and the wetting properties of the microemulsion mainly determine its flow behaviour. When the coloured microemulsion is injected as a point source into the aquifer, it spreads spherically with a slight swelling deformation at the upper part due to its low density.

Its flow behaviour can be strongly influenced by different pumping rates at the injection and the extraction wells. Experiments with different hydraulic systems showed that vertical and inclined well systems (Fig. 2 a+b) are better suited to control the microemulsion flow than horizontal systems because of subsurface anisotropy.

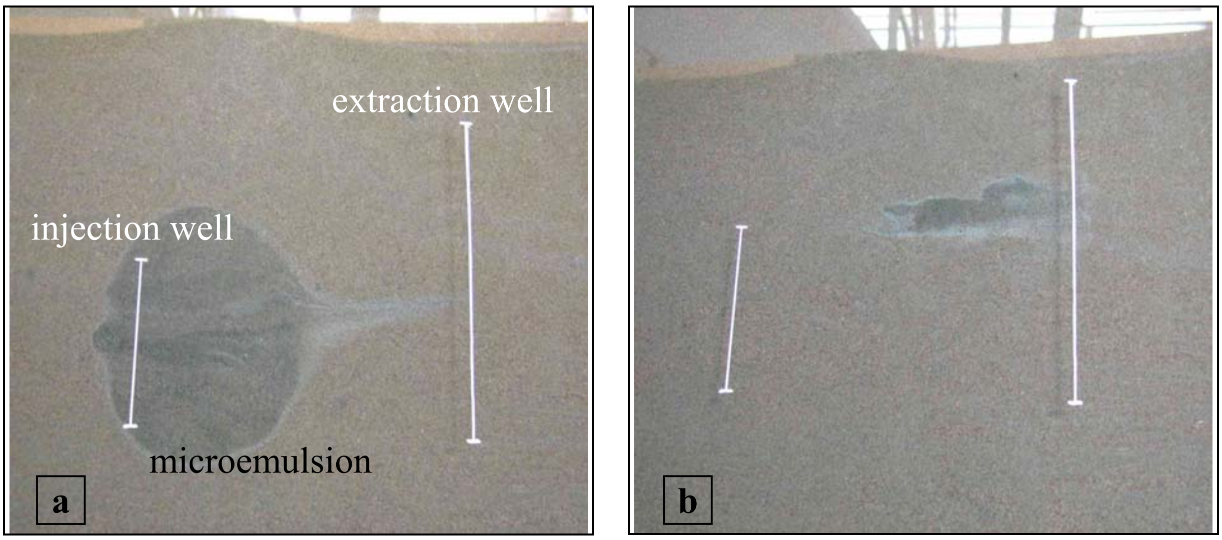

Figure 2: Vertical well systems a: 1 h after injection of blue-coloured microemulsion
b: 6 h after water flushing

As the microemulsion moves through contaminated parts of the aquifer, it even dissolves pools of phase liquids. In comparison to water, the microemulsion has a solubilization capacity for PCE, which is more than 100 times higher, corresponding to very high extraction efficiencies for DNAPLs during the extraction (Fig. 3). PCE concentrations in the extracted flushing solution reached values of more than 3.000 mg per litre.

Figure 3: Solubilization and mobilization of a PCE pool (red) with microemulsion (blue-green)

After intensive water flushing, the amounts of microemulsion components remaining in the soil were low. Methanol extraction of a soil containing clay revealed values of less than 1 g/kg of the anionic surfactant and about 2 g/kg of the rape oil methyl ester. These components are biodegradable and can be cleaned up easily with bioremediation technologies.

After the simulated remediation of the artificially contaminated test container, mass balances were calculated for microemulsion components and the contaminant. Table 1 shows the amounts recovered in the fractions “flushing solution” and “soil”.

Table 1: Mass balance for anionic surfactant (Leophen® RA), rape oil methyl ester (RME) and PCE

[%]	Leophen® RA	RME	PCE
flushing solution	71,6	80,9	53,4
soil	4,0	5,1	0,6
total recovery	**75,6**	**86,0**	**54,0**

In this experiment, total recovery of PCE was only 54 %. The high loss of PCE was due to the sampling technique of the flushing solution, which is not well engineered yet. Water samples were taken with peristaltic pumps which caused a negative pressure. It is assumed that most of the PCE evaporated during extraction and sampling of the flushing solution.

Soil concentrations of PCE after flushing were very low. More than 99 % of the originally applied PCE were removed by flushing with microemulsion.

Large-scale and field experiments are planned to prove the value of this emerging remediation technology for practical application.

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FIELD STUDIES FOR THE APPLICATION OF MICROEMULSIONS

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Introduction

Massive groundwater contaminations caused by chlorinated hydrocarbons (CHC/DNAPLs) can be removed in-situ by microemulsions within a short period of time.

Forschungszentrum Jülich (TZW), *VEGAS* (Stuttgart), *TZW* Karlsruhe and *IBL Umwelt- und Biotechnik GmbH (IBL)* in Heidelberg are working on the „Optimisation of Microemulsions for Remediation of Contaminated Aquifers“ a cooperative research project supported by the German Federal Ministry of Education and Research (BMBF). In this project IBL performs the technical realization of scientific findings within the scope of a field-study.

During the nineties different procedures were tested to remediate the existing contaminations at the test location in Eppelheim in Baden-Württemberg, Germany (Fig. 1). Therefore, five large steel columns (diameter 2.4 m, depth 10 m) were rammed into the soil in a circular pattern (Fig. 2, 3 and 4). In three columns earlier tests with different remediation techniques had been performed already. The remaining columns yet unused have been selected for the planned field-studies on microemulsions.

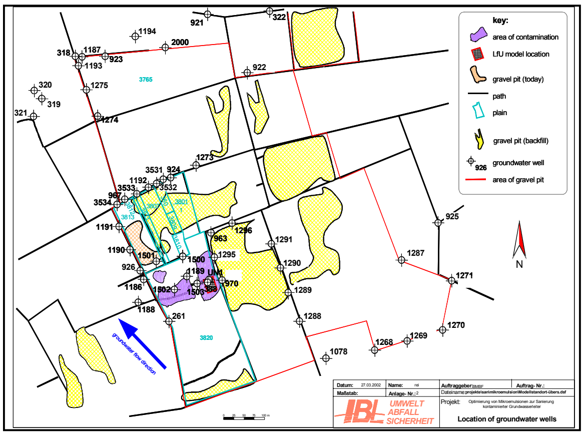

Fig. 1: Location

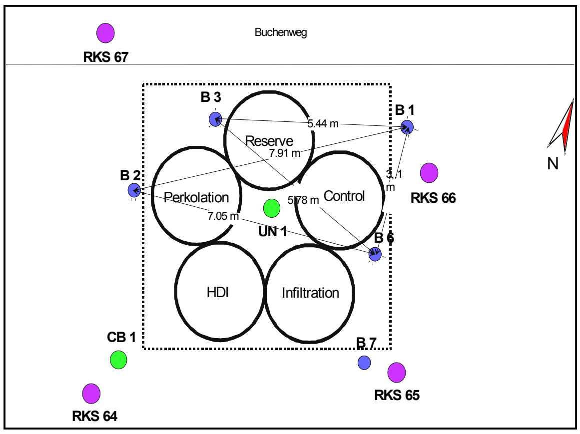

Fig. 2: Arrangement of the columns and drillings

The advantage of the existing columns in Eppelheim are the genuine conditions of the subsoil related to geology, microbiology and temperature as well as an assumed realistic design of the columns with respect to the technical application of the microemulsion. The separation of the testing area from the surrounding can easily be assured to meet the requirements of the responsible authorities for the field studies.

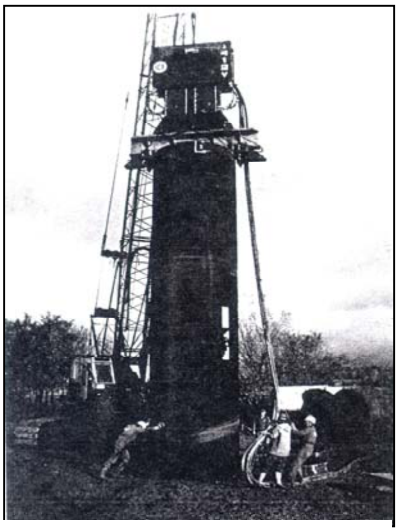

Fig. 3: Ramming of the columns

Fig. 4: Space between the columns (gap)

Preliminary Works

After the review of technical and geological information from the former experiments and studies additional testing was performed to characterize the physical properties of the soil columns with respect to the planned field studies.

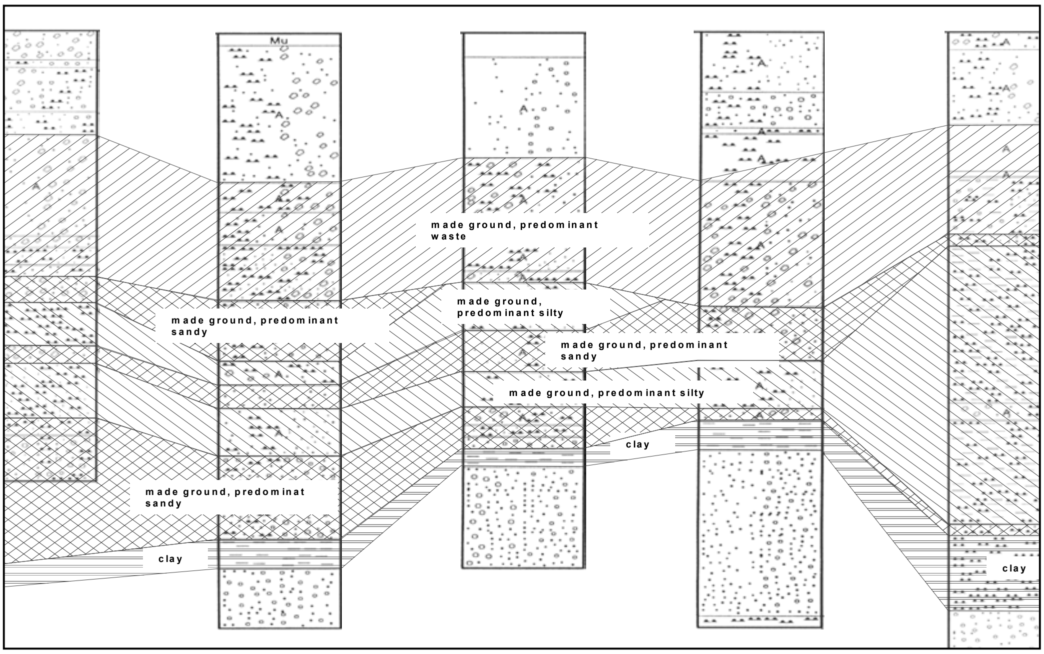

Fig. 5: Drilling profiles

The investigations of stratigraphy, concentration of contaminants, determination of the permeability of the present layers in the columns by drillings (Fig. 2), and lab experiments lead to the following conclusions. The upper part (backfilling material) of the untreated column (reserve column) is formed by impermeable layers (synthetic materials, etc.). These layers are not suited to form favourable conditions for the field studies. The underlying layer consisting of clay and silt cannot be used for field-testing due to its very low permeability and small extent (Fig. 5). With respect to the permeability the subsequent sedimentary layer, composed of sand and gravel is rather favourable for the testing with microemulsions. However, its thickness is considered to be insufficient.

Infrastructure for the field study

Taking advantage of the field-location in an effective manner - in spite of the existing soil conditions - construction work was necessary within the scope of further planning. On one hand the sealing of the soil columns towards the aquifer had to be ensured. On the other hand tests had to be performed with backfilling material similar to soil found at other contaminated sites. It was intended to excavate the backfilling material from the reserve column, to remove interfering materials, and to fill back the processed soil into the column. The excavated material was treated by separating the impermeable components and removing the layer of clay which is impermeable to microemulsion and water as shown in Fig. 6 and Fig. 7.

Fig. 6: Excavation works

Fig. 7: Sieving of the excavated material

The excavated material consisted mostly of household waste. Furthermore, permeability tests showed that the determined k_f-values were lower than 10^{-8} m/s. The material was rejected because it was not suited for the application of microemulsions. Therefore sandy material with a k_f-value between 10^{-4} m/s and 10^{-5} m/s was taken from the natural aquifer in the plume (CHC/DNAPLs) of the test location. This soil contains a flora of autochthonous microorganisms, which are adapted to the given contaminations.

To prevent a further contamination of the aquifer with DNAPL and microemulsions the base of the excavated column was sealed with a metal plate welded with the steel column before it was filled with new material. Problems caused by degassing and compactation of soil material - to simulate an original aquifer – were solved by adding local groundwater to the soil and subsequently homogenizing and filling up supported by vibration compactors.

During the filling of the soil material into the column probes for sampling and detection were installed in four different levels to monitor the first field-experiment (Fig. 8, 9 and 10). A defined amount of tetrachloroethylene (PCE) was injected into a container filled with the soil to define a centre contamination with residual DNAPLs. This container (caisson) was installed between two detection levels with a maximum amount of 14 probes to determine the flow character of the microemulsions and the eluted DNAPLs.

Fig. 8: Installation of the probes outside the pilot column

Fig. 9: Installation of the probes inside the pilot column

The described procedure facilitated the installation of the planned control system as well as the installation of infiltration and extraction wells (Fig. 10).

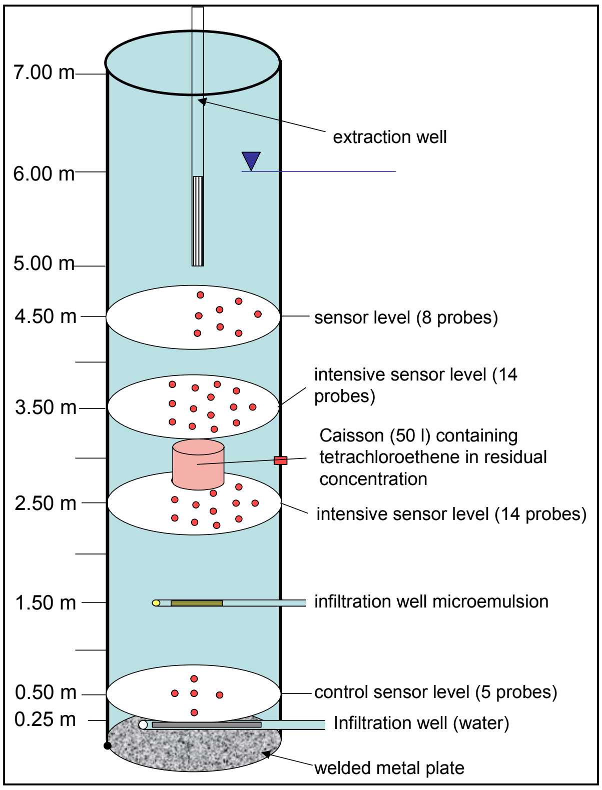

Fig. 10: Design of the pilot column

Performance of the field study

The aim of the first field experiment is to characterize the specific conditions for the use of a microemulsion for remediation purpose in practical operation. The focus was led on the flow dynamics of the infiltrated compounds, the recovery rate of contaminants, and the technical as well as biological treatment after the in-situ application of the microemulsion.

The microemulsion is infiltrated at the bottom of the column by means of an infiltration well and recovered by an extraction well placed at the top of the column. The contaminants are solubilized by the microemulsion and removed from the extraction well at the top of the artificially formed groundwater level. Within the experiment flow conditions and the effects of the soil structure are most likely be investigated following the described arrangement.

The microemulsion will be infiltrated into the soil within approx. 2 - 3 weeks and will then be extracted for a total period of 10 weeks (Fig. 11). Subsequently the soil is rinsed with the surfactant of the microemulsion. By creating a new microemulsion the eluate removes the major part of other components of the microemulsion which is still present in the ground after the first flushing with microemulsion. The rinsing with surfactants is planned to last for 1 week. Specific sensors monitor the flow dynamics of the microemulsion, of the contaminants, of the surfactant-solution, and of the rinsate.

For further removal of the microemulsion and their components the soil will be rinsed with water or brine for 2 - 3 weeks. The following biological treatment after finishing the rinsing is controlled during the remaining time of the project for approx. 1.5 years. Within this period the remaining contaminants of the components of the microemulsion are biologically degraded. The degradation rates for the components and the specific degradation conditions are tested within this time.

The presentation shows the technical set-up and the results of the field-experiment which will be discussed in detail.

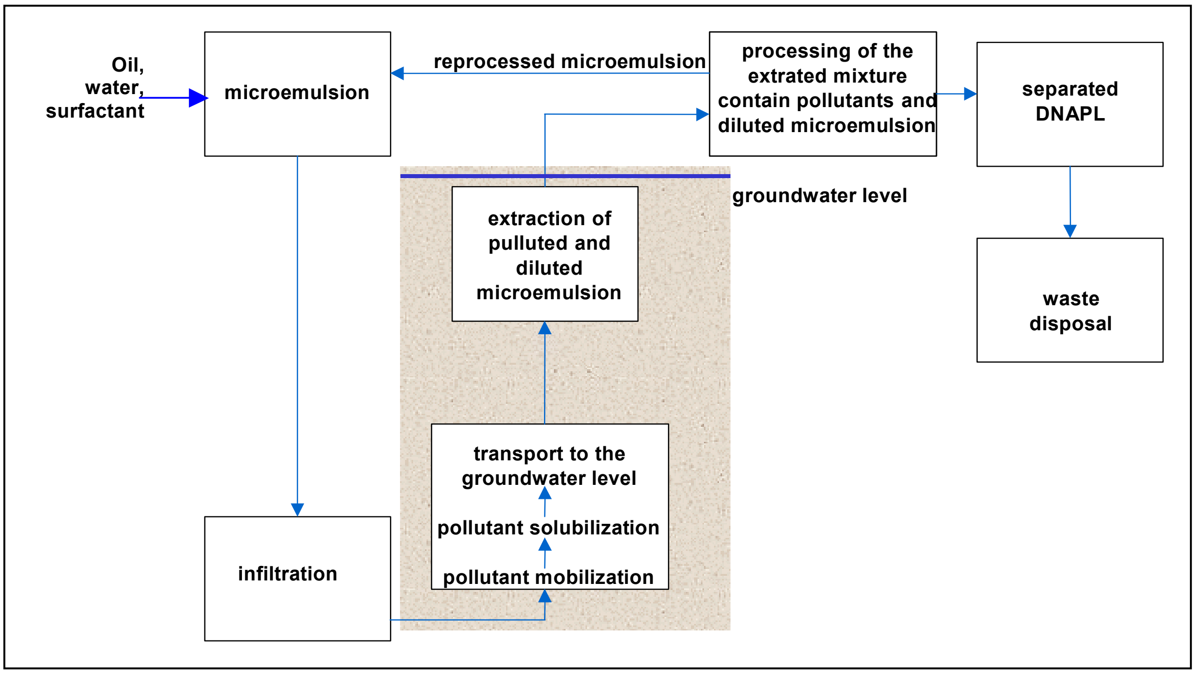

Fig. 11: Flow chart of the first field experiment

MICROEMULSION ENHANCED IN-SITU REMEDIATION – RECYCLING CONCEPTS FOR THE ADDITIVE

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Hydraulic in-situ remediation technologies have recently become increasingly important for removing underground contamination especially in urban districts. To enhance the traditional pump-and-treat, systems such as microemulsions can be used which solubilise the contaminants. For this method to be cost effective, an optimised waste water treatment is essential. On the one hand the contaminants have to be removed from the extracted ground water and on the other hand the microemulsions have to be recycled for re-use in the remediation procedure. To solve these problems is one main objective of the research project "Optimisation of Microemulsions for the Remediation of Contaminated Aquifers" which is funded by the German Federal Ministry of Education and Research (BMBF).

The microemulsion used in that project consists of the main components rape oil methyl ester (RME), anionic surfactant, nonionic surfactant, and brine. It has good solubilisation properties for organic substances. The nonpolar contaminants are solubilised in the organic phase of the microemulsion and washed out of the soil. The main advantage of the microemulsion compared to surfactant solution is, that due to its density which is lower than that of water contaminants such as chlorinated hydrocarbons, Dense Non Aqueous Phase Liquids (DNAPL), are not vertically mobilised to deeper layers but move upwards to the extraction wells.

During the remediation process an emulsion of water, microemulsion, and contaminant is extracted which has to be treated. First, solids such as soil particles have to be separated from the mixture by a sedimentation process, for example. In the next step the water-microemulsion-contaminant mixture has to be separated. Two different separating techniques have been examined: evaporation and stripping. Tetrachloroethylene (PCE) was used as model contaminant. Different degrees of dilution of the microemulsion were studied.

Experiments in a rotary evaporator and a simple bench-top distillation column showed the feasibility of a distillative separation of the contaminant PCE from the mixture and, in the following, a concentration of the emulsion until the microemulsion is regenerated. Then, several experiments in a larger scale were carried out. As evaporation had been shown to be an adequate separation as well as concentration method, experiments were made both with a thin film evaporator (Stuttgart University) and a falling film evaporator (Jülich Research Centre) as represented in **Figs. 1** and **2**.

Fig. 1: Thin film evaporator (Stuttgart)

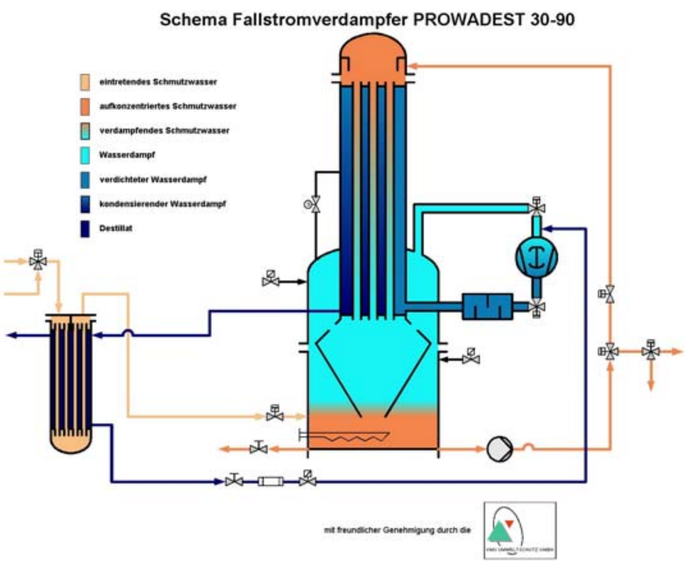

Fig. 2: Commercial falling film evaporator (Jülich)

The main results of the experiments with the thin film evaporator are:

- The contaminants can be separated from the mixture with an efficiency of more than 99 %.
- Feed and bottom product show the same mass ratios of the individual microemulsion components, whereas the condensate shows very low DOC concentrations (some mg/L). This shows that a shift in the microemulsion component ratios is more likely to happen during the soil flushing process than during the waste water treatment.
- For highly diluted samples a removal of excess water in order to obtain a microemulsion is not possible in a single pass in the film evaporator.

Future objectives here are the optimisation of the evaporation parameters like pressure and temperature, and evaporation type.

For the first field experiment in 2003, a falling film evaporator which is shown in **Fig. 2** will be used. This evaporator is a commercial product of company KMU Umweltschutz GmbH, Germany, and has been tested at Jülich. One remarkable element of the evaporator is its indifference to corrosive solutions like brine or to foaming agents like surfactants. Therefore it is commercially used to treat, e. g., waste water from car wash facilities. Moreover, the tubes in the evaporator can be cleaned: greasy dirt, residual particles or sediment can be washed off easily.

The falling film evaporator has already been tested with different dilutions of microemulsions obtained from laboratory experiments. It is capable of producing a quantity of approx. 40 L distillate per hour. After an induction period the evaporation process is driven by the dissipated heat of the vacuum pump and the condensation energy recycled into the process by carrying back the vapour on the outer face of the heating columns. That leads to a very low energy consumption of about 0.1 kWh/L distillate.

The separated distillate has an electrical conductivity of ~ 4µS/cm, is slightly turbid, and has a CSB-Value of several 100 mg/l which shows that a small amount of organic matter is present. After some evaporation cycles a very small layer of organic phase separates from the distillate which is analysed to consist of approx. 85 % RME. **Fig. 3** shows how the emulsion and the regenerated microemulsion look after different evaporation cycles.

Fig. 3:
Microemulsion, diluted (left bottle), and concentrated (right bottle) after evaporation

Another idea was to separate the PCE from the mixture by stripping which was tested with a stripping column as represented in **Fig. 4**. The height of the packing (Raschig rings) was 1 m and the diameter was 0.1 m. The experiments were conducted with feed solutions of different dilution, containing PCE and also TCE (trichloroethylene) as contaminants, and an air/water-volume ratio of 25 in countercurrent flow. The results show, that the stripping process is also suited for eliminating PCE and TCE from the flushing solutions. The contaminants can be removed from the air, e. g., by adsorption on activated carbon.

Fig. 4: Stripping column

Fig. 5 represents the decrease of the contaminants with time during the stripping process. Depending on the number of cycles, concentrations below the analytical detection limit could be achieved. For the real scale application, a multistage process with continuous flow is more suited than the pump-around operation studied here.

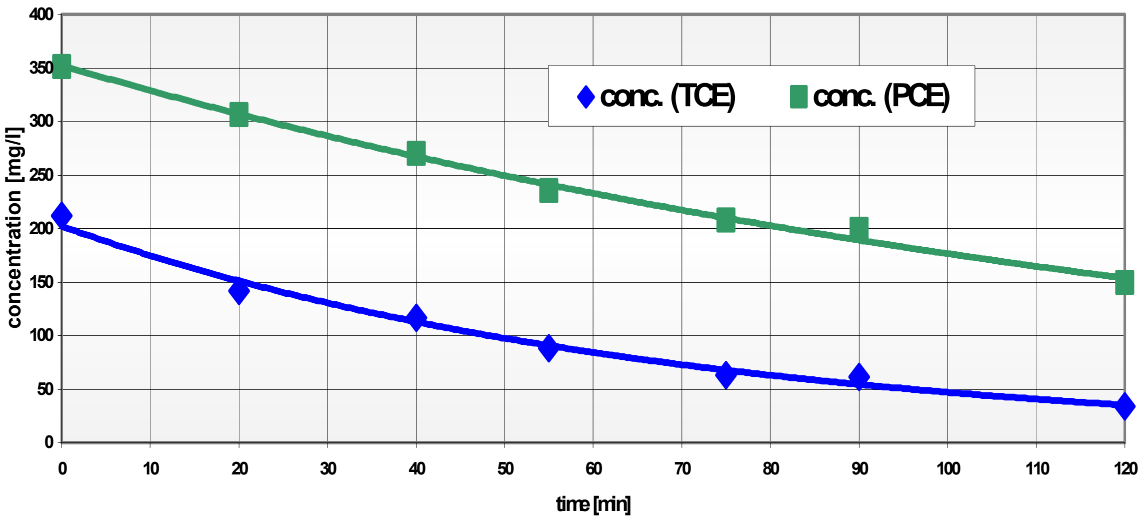

Fig. 5: Stripping of Tri- and Perchloroethylene

After stripping of the contaminants, the excess water has to be removed by evaporation. Then the microemulsion has to be regenerated before re-use in the remediation process to compensate possible losses mainly from the flushing process. This last treatment completes the regeneration of the microemulsion. A feasible overall concept of the treatment procedure is shown in **Fig. 6**.

As an alternative to the combination of stripping and evaporation, a distillation with a defined reflux ratio could also be applied in order to combine the contaminant removal and the concentration of the emulsion in one treatment step. This treatment technique will also be investigated in the course of the project. Based on all experimental results, a real scale plant will be conceptually designed and a cost estimation will be carried out. The most favourable alternative with respect to efficiency and cost will finally be applied.

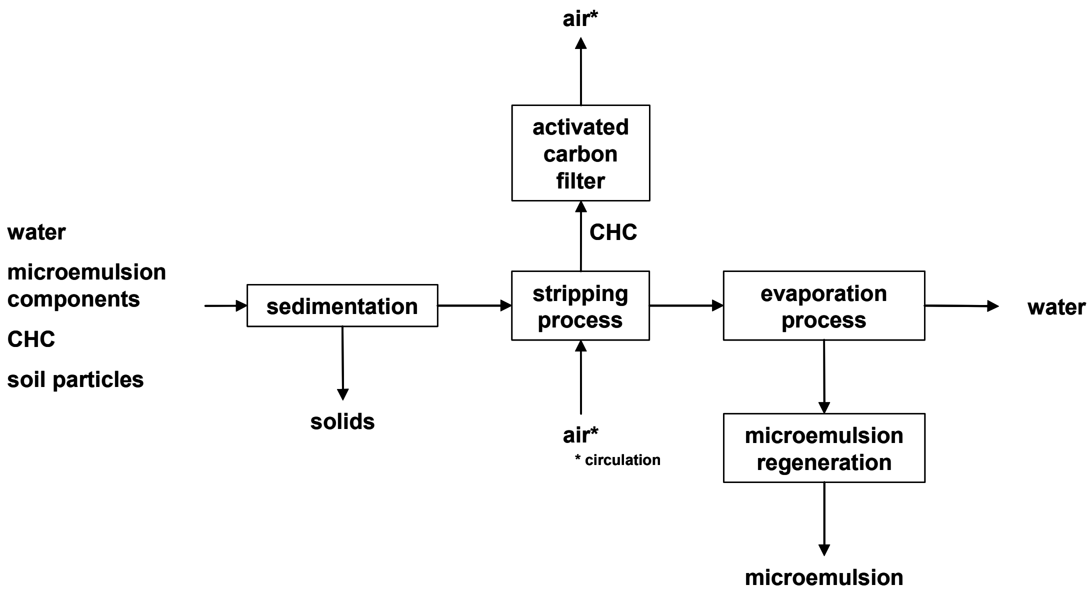

Fig. 6: Recycling concept for the microemulsion

BIODEGRADATION OF MICROEMULSION COMPONENTS

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Introduction

Soil extraction with microemulsions represents a new and promising technique to clean-up aquifers contaminated with dense non-aqueous-phase-liquids (DNAPL), e.g. tetrachloroethylene. After extracting the DNAPLs, the amount of microemulsion constituents remaining adsorbed onto soil particles is minimised by water flushing. The residual microemulsion components and DNAPL pollutants are to be eliminated by biodegradation. Engineered *in-situ* bioremediation techniques or/and intrinsic biodegradation processes are considered for this final treatment period. Therefore, understanding the biodegradability of the microemulsion components under varying redox conditions is essential to develop efficient post-extraction biotreatment strategies.

Microorganisms obtain energy for cell production and maintenance by catalysing the transfer of electrons from electron donors (e.g. microemulsion components) to terminal electron acceptors. Important electron acceptors in aquifers include dissolved oxygen, nitrate, sulphate, and Fe(III) minerals in the aquifer material. After these electron acceptors are depleted, microorganisms may ferment organic compounds through reactions that produce methane and carbon dioxide (Chapelle 2001). Due to the energy yield of the degradation processes a sequential utilisation of the terminal electron acceptors generally is observed: aerobic degradation is followed by denitrification, iron and manganese reduction, sulphate reduction and methanogenesis (Bouwer 1992). The microbial activity governs the redox regime by consumption of electron acceptors (e.g. sulphate) and formation of reduced respiration products (e.g. sulphide). On the other hand, the redox regime significantly affects the microbial utilisation of specific compounds.

In engineered *in-situ* bioremediation (e.g. bioventing, air sparging, pump and treat), biodegradation of organic compounds such as the microemulsion components usually is stimulated by the addition of electron acceptors (e.g. O_2, H_2O_2, NO_3^-). Microbial degradation of chlorinated DNAPL pollutants such as tetrachloroethene only is possible under anaerobic conditions. For dechlorination, additional auxiliary substrates serving as electron donors (e.g. ethanol, lactate) are required (Middeldorp et al. 1999, Tiehm et al. 2002).

The objective of our investigations is to develop reliable post-extraction biotreatment strategies to prevent groundwater contamination by the microemulsion and pollutant residues. In this paper, laboratory experiments are presented focussing on the biodegradability of the microemulsion components under varying redox conditions. Studies were done with the autochthonous microflora of the Eppelheim experimental field site.

Material and Methods

Microemulsions are optically isotropic dispersions of two non-miscible liquids that are stabilised by at least one amphiphilic component. The main components of the microemulsion (ME) applied in this study are: (i) rape oil methyl ester (RME), (ii) the anionic surfactant AOT [bis(2-ethylhexyl)-sulfosuccinate], and (iii) the non-ionic surfactant Uniperol EL [ethoxylated castor oil]. The chemical structures have been published previously (Dierkes et al., 1998).

Biodegradation tests were performed in mineral media. Inoculation was done with indigenous microorganisms of the chloroethene contaminated Eppelheim site. Aerobic biodegradation was examined in a respirometer in 500 mL flasks (duplicates). Biological O_2-consumption (BOC) was used as on-line parameter to assess microbial turnover and to calculate degradation degrees. The starting concentrations of RME, Uniperol, and the complete microemulsion were around 300 mg/l. AOT degradation was tested at 117 and 162 mg/L. Anaerobic degradation tests were performed in 2 L bottles with Teflon septa. O_2 was removed from the hot mineral media by purging with N_2 in a vacuum system. Nitrate, Fe(III), sulphate or carbonate was added as electron acceptors. Preparation (inoculation, addition of electron acceptors) and sampling was done in an anaerobic chamber. Microcosms inhibited by $HgCl_2$ served as controls.

Surface tension was determined according to the ring method by a mechanical tensiometer. Nitrate, and sulphate were determined by ion chromatography. Sulphide analysis was done photometrically. For the detection of methane, a gaschromatograph (GC/FID) equipped with a headspace autosampler was used.

Results and discussion

Indigenous microorganisms

The composition of the autochthonous microflora at the Eppelheim site was examined in soil samples. Growth of the microorganisms was tested in presence of the most important subsurface electron acceptors. Obviously, different types of microorganisms are present at the site. High microbial numbers were obtained under aerobic and denitrifying conditions, but also Iron(III)-reducing, sulphate-reducing, and methanogenic bacteria were detected (Table 1).

Table 1: Numbers of heterotrophic bacteria (Most-Probable-Number test) utilising different terminal electron acceptors in soil samples taken at the Eppelheim site.

[cells/ g dry sediment]	Conditions				
Sampling location & depth	Aerobic	Denitrifying	Iron(III)-reducing	Sulphate-reducing	Methanogenic
B7 8 - 9 m	2,3E+05	7,7E+04	3,6E+03	2,6E+02	1,8E+01
B7 9 -10 m	8,5E+04	2,9E+03	4,0E+03	2,6E+02	7,0E+00
B7 10 -11 m	1,2E+05	4,6E+04	8,4E+02	2,8E+02	<7,0E+00
B1 7 - 8 m	1,1E+07	1,1E+07	7,8E+05	1,1E+03	4,6E+01
B1 8 - 9 m	2,2E+07	1,1E+07	1,1E+05	7,4E+02	4,6E+01
B1 9 -10 m	2,6E+07	1,1E+06	7,8E+02	<6,6E+01	<7,0E+00

Biodegradation under aerobic conditions

Aerobic biodegradation was studied in a respirometer. The indigenous microorganisms of the Eppelheim site were capable to degrade all the tested compounds. As shown in fig. 2A, RME was utilised rapidly. Biological oxygen consumption (BOC) was most pronounced during the first 5 days of incubation. After 20 days of incubation, the BOC corresponded to 75 % of the calculated Chemical Oxygen Demand (COD) of the RME present initially (Table 2). The non-ionic surfactant Uniperol and the anionic surfactant AOT were degraded with slower kinetics (Fig. 2A+B). In the case of Uniperol, a two phased degradation kinetic was observed. The degree of degradation in terms of $BOC_{(end\ value)}$ / $COD_{(start\ value)}$ was 49 % indicating a sufficient mineralization. Whereas the degradation of RME and Uniperol started rapidly, in case of AOT an adaptation period of 25 days was observed. The degree of degradation at the end of the experiment was about 40 %. Increasing the AOT concentration from 117 mg/L to 162 mg/L resulted in an inhibition of the microbial activity. Therefore, a sufficient flushing after soil extraction is essential in order to avoid high concentrations of dissolved AOT. However, biodegradation of the microemulsion (mixture of RME, Uniperol and AOT) started rapidly and a degree of degradation of 61 % was achieved within 20 days (Fig. 2A, Table 2).

Surface tension measurements confirmed that the surface-active agents were subject to aerobic biodegradation. Before biodegradation, surface tensions between 25 and 45 mN/m were determined (Fig. 3). At the end of incubation, surface tensions had increased up to the reference value of water (about 72 mN/m) in case of RME, AOT, and the microemulsion. Only in case of Uniperol, the surface tension still was slightly reduced (Fig. 3).

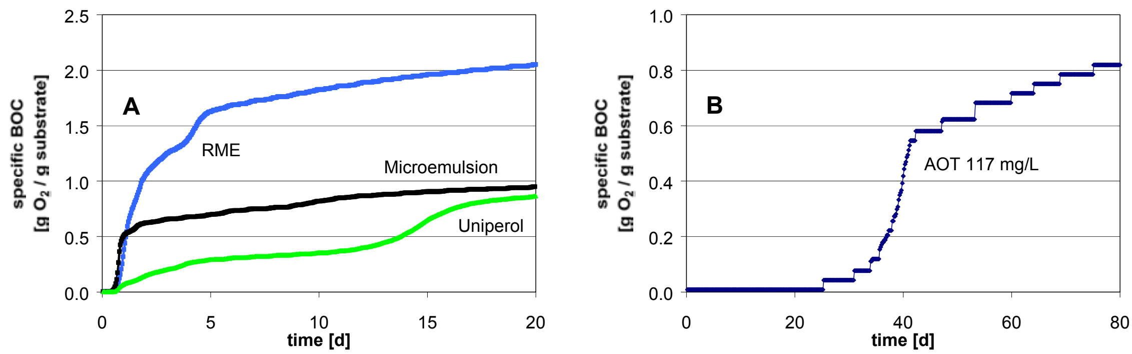

Figure 2: Biological oxygen consumption (BOC) during aerobic biodegradation. Rapid degradation was observed in case of RME, Uniperol, and the microemulsion (A). Biodegradation of AOT started after an acclimation period (B).

Table 2: Degree of degradation of the microemulsion components.

Component	$BOC_{(end\ value)}$ / $COD_{(start\ value)}$ [%]
Rape oil methyl ester	75
AOT	39
Uniperol	49
Microemulsion	61

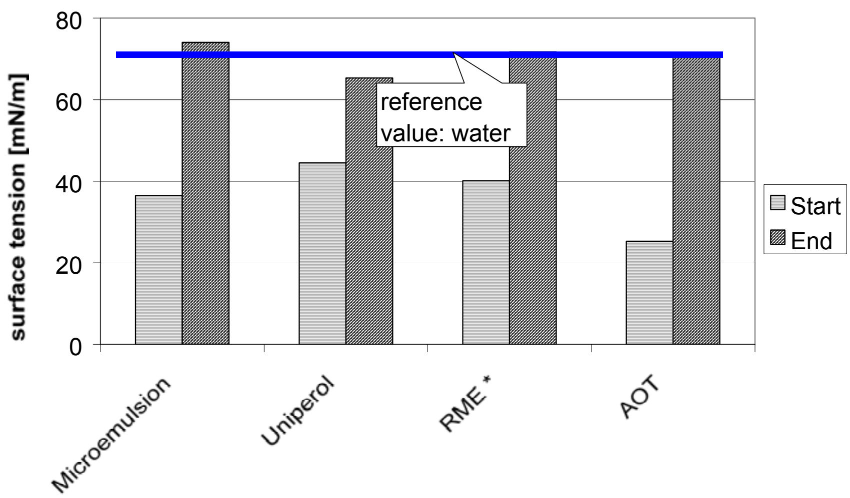

Figure 3: Surface tension before and after aerobic biodegradation (RME*: the start value corresponds to the oil phase covering the mineral medium).

Biodegradation under anaerobic conditions

RME was biodegraded rapidly in the absence of oxygen. Anaerobic biodegradation under denitrifying conditions is shown in terms of nitrate consumption (Fig. 4), and biodegradation under sulphate reducing conditions in terms of sulphate consumption and sulphide formation (Fig. 5). Visual examination indicated also a rapid biodegradation in the presence of Fe(III): The initially colourless medium changed to black (due to FeS formation), and microbial flocs developed. RME utilisation under methanogenic conditions was indicated by methane and microbial floc formation. In all anaerobic test flasks, the RME oil phase disappeared and surface tensions increased significantly (data not shown).

Also Uniperol proved to be biodegradable under nitrate-reducing (Fig. 4), sulphate-reducing (Fig. 5), and Fe(III)-reducing conditions (black colour, floc formation). Under these conditions, also the surface tension increased significantly. Under methanogenic conditions, a small methane peak was detected in the gas chromatogram at the end of the experiment, indicating microbial activity.

The anionic surfactant AOT was not degraded under anaerobic conditions. None of the parameters monitored indicated a microbial activity.

Consumption of nitrate (Fig. 4) and of sulphate (Fig. 5A) as well as sulphide formation (Fig. 5B) was observed in the flasks containing the microemulsion. As indicated by visual examination, anaerobic biodegradation also was possible in the presence of Fe(III). No activity was observed under methanogenic conditions. Surface tension did not increase in any of the microemulsion containing flasks. Most probably the microemulsion components RME and Uniperol were degraded, whereas the persistent AOT resulted in a low surface tension even at the end of incubation.

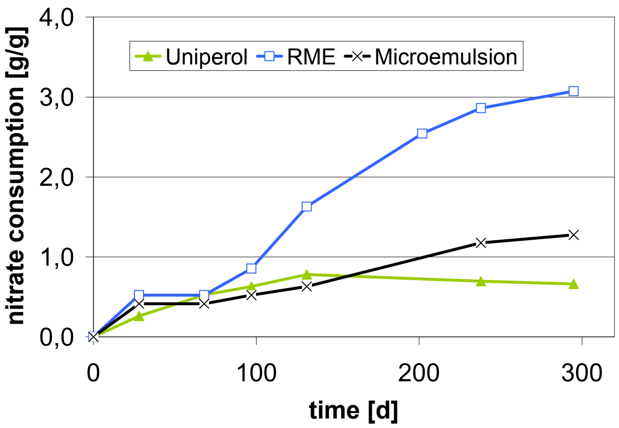

Figure 4: Consumption of nitrate in the anaerobic biodegradation tests.

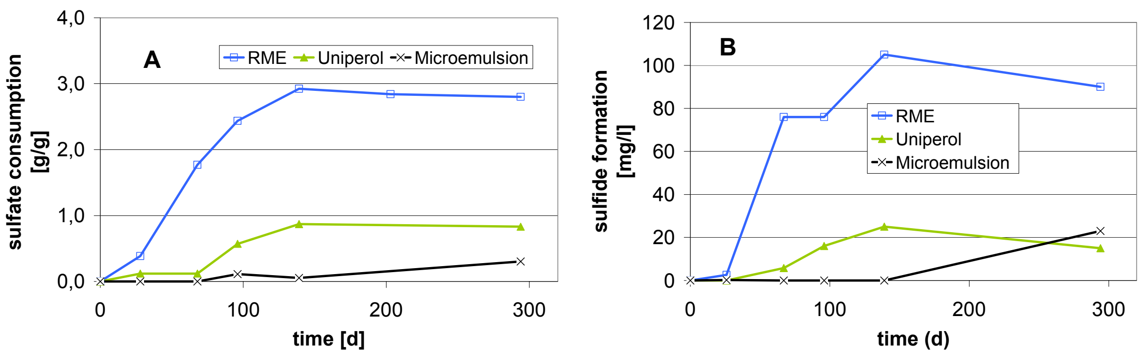

Figure 5: Consumption of sulphate (A) and formation of sulphide (B) in the anaerobic biodegradation tests.

Conclusions

The results of the biodegradation tests performed with microemulsion components and the indigenous microorganisms of the former landfill site Eppelheim are summarised in table 2. Obviously, the autochthonous microflora of the Eppelheim site has the potential to biodegrade RME over a wide range of redox conditions. Compared to the other microemulsion constituents, RME was degraded most rapidly. Also the non-ionic surfactant Uniperol and the complete microemulsion mixture were degraded under most tested conditions. Biodegradation of AOT only occurred in the presence of oxygen.

Table 2: Biodegradation of the microemulsion components in the presence of different terminal electron acceptors – summary of the experimental results

	Oxygen	Nitrate		Sulphate	Carbonate
Microemulsion	++	+	+	+	-
RME	++	++	++	++	+
Uniperol	++	+	+	+	(+)
AOT	+	-	-	-	-

- : no biodegradation
+ : significant biodegradation
++ : biodegradation with distinct turnover

According to the experiments done so far, aerobic as well as anaerobic processes can be applied to eliminate microemulsion residues after DNAPL extraction. In particular the good anaerobic biodegradability of RME is promising with respect to a stimulation of reductive dechlorination of the residual DNAPL contaminants. It has been shown recently that comparable mobilising agents (e.g. oleate, olive oil) can enhance tetrachloroethene biodegradation (Yang & McCarty 2002). On the other hand, for the elimination of AOT the addition of oxygen (e.g. provided as H_2O_2) is necessary. Our further studies will focus on the development of a biotreatment concept integrating aerobic and anaerobic periods in the most economical way.

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SpS 18 Special Session

Is One Fibre of Asbestos in Soil Too Much?

IS ONE FIBRE OF ASBESTOS IN SOIL TOO MUCH ?

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1 INTRODUCTION

Asbestos fibres are mechanically strong and highly resistant to heat and chemical attack, and due to their fibrous nature, asbestos fibres can be woven into fabrics. Due to these favourable physical and chemical properties asbestos was, in the past, used in a wide range of industrial and building applications. A large number of products made from asbestos are still found in Australian buildings. These include flat, corrugated or compressed asbestos-cement sheeting; and asbestos-cement pipes such as water, drainage (including gutter and down-pipes) service conduits and pits and flue pipes. Asbestos was also used in products such; brake and clutch linings; asbestos cloth, tapes and ropes; paints, coatings, caulking compounds and sealants; filter papers and gasket materials; as filler in gas cylinders, fireproof safes and doors and in spray-applied coating for fire protection; and as thermal or acoustic insulation.

The use of asbestos in Australia was largely phased out in the 1980, except for some asbestos gasket and friction materials applications.

In Australia the widespread use of asbestos in building materials and various industrial and household applications between the 1940's and 1980's has resulted in the potential for asbestos to be a contamination issue requiring consideration at many sites undergoing soil contamination investigations or remediation.

Experience has shown that asbestos may be present in soils both on the soil surface and within the soil profile. The forms of asbestos in soils typically encountered comprise fragments of bonded asbestos materials, fibre bundles or free fibres of asbestos.

It is difficult to accurately define the extent of potential asbestos contaminated soil in Australia. However, the relatively low cost and ease of use of asbestos-cement sheeting meant it was commonly used as a building material, particularly in the post World War II building boom on the then fringes of Australian cities and in rural areas. Asbestos-cement was commonly used in a wide range of construction applications such as cladding, roofing and guttering on low cost housing as well as in commercial and industrial buildings. Numerous underground services (including services within industrial sites as well as public utility services) such as cable conduits and junction boxes, water supply and stormwater drainpipes etc also utilised asbestos cement materials.

The redevelopment of many old housing areas and industrial sites has resulted in demolition of older housing and industrial buildings which included asbestos containing materials (ACM) located on the former city fringes. Poor building demolition practices particularly in the past, and to a lesser extent recently have resulted in asbestos contamination of soil at many of these sites. The common practice of reuse of building wastes (and excavated soils) as fill material has also resulted in many additional sites being contaminated with asbestos in soils derived from contaminated sites. Additionally, asbestos in soil contamination is also an issue at other sites where asbestos or asbestos products were manufactured and/or used. Thus, the problem is potentially widespread and recent experience has confirmed this.

Adverse health effects have been associated with asbestos in both occupational and non-occupational settings. However, current scientific knowledge suggests that a person must have sufficient exposure (non-trivial) to airborne asbestos fibres to develop asbestos related health effects, although in Australia a number of high profile court cases have incorrectly suggested that one fibre of asbestos is sufficient to cause asbestos related diseases.

Therefore, like many countries, Australia is wrestling with the problem of asbestos in soil, and in particular what are the real health risks and what is an acceptable level of asbestos in soil. The issue is complex from a social, scientific and legal perspective, and widespread, low level contamination of soil with asbestos (from building waste and other sources) has recently led to some very high and unexpected remediation costs in Australia development projects. This paper (and accompanying interactive workshop) initially outlines the Australian situation with respect to asbestos in soil contamination, presents some Australian case studies before presenting a series of starting discussion points for the interactive workshops. Participants in the workshop are asked to assist in the identification of key problem areas, drawing on experience from their own countries, as well as some possible solutions.

The reader should be aware that for reasons of brevity the information that follows assumes certain minimum background knowledge of asbestos issues and their management.

2 THE STATUS OF ASBESTOS IN AUSTRALIA

2.1 Regulatory Guidelines For Asbestos in The Occupational Environment

The recognition of occupational health risks associated with asbestos in Australia is well developed, with strong regulatory guidelines and management procedures for exposure to asbestos in the occupational environment, in place for some considerable time. These guidelines include national asbestos exposure standards for the occupational environment as detailed in **Table 2.1**.

Various States have adopted an Occupational Exposure Standard (OES) of 0.5 fibre per mL for chrysotile asbestos, and WorkSafe is recommending that the OES for chrysotile asbestos is reduced to 0.1 Fibre per mL OES in the near future.

Even though each Australian State Regulatory Authority operates differently, the New South Wales WorkCover Authority (WCA) is relatively typical, and their position is described below.

TABLE 2.1 AUSTRALIAN ASBESTOS EXPOSURE STANDARDS IN THE OCCUPATIONAL ENVIRONMENT (Worksafe Australia 1995)

Type of Asbestos	TWA Exposure Standard*
Crocidolite (blue asbestos)	0.1 fibres per mL of air
Amosite (brown asbestos)	0.1 fibres per mL of air
Chrysotile (white asbestos)	1.0 fibres per mL of air
Other forms	0.1 fibres per mL of air
Any mixture of these or unknown compositions	0.1 fibres per mL of air

* Time weighted average – 8hr day, 5 day working week

'Friable' asbestos material is defined in WCA Occupational Health and Safety Regulations as 'any material that contains asbestos and is in the form of a powder, or can be crumbled, pulverised or reduced by hand pressure when dry. The rationale behind this definition is that this material has the potential to generate airborne 'respirable' asbestos fibres. 'Respirable' fibres essentially mean any fibres that can reach the alveolar or 'air cells' of the lung. In general, respirable fibres are less than 3 micrometre in diameter. 'Bonded' asbestos material is defined as 'any material (other than friable asbestos material) that contains asbestos'.

Stringent precautions for removal and remediation are required for friable asbestos, whereas much less stringent precautions are necessary for bonded asbestos.

WCA has published a document on its web-site (www.workcover.nsw.gov.au) indicating that it regards asbestos-cement that has been 'subjected to weathering, severely damaged by hail, damaged by heat/fire or other mechanical action, or illegal water blasting *can then become* (emphasis added) a friable asbestos product, and an licensed asbestos removal contractor for friable asbestos is *required for its removal*.' The Guide is not a legal requirement, although failure to consider the guideline could be regarded as a breach of ones duty of care.

2.2 Regulatory Guidelines For Asbestos In Soils

However, while there has been recognition of the health risks associated with asbestos in the non-occupational environment, the development of guidelines for these are in their infancy, including regulatory guidelines for asbestos in soils.

The following paragraphs present a brief history of the Australian regulatory environment with respect to asbestos in soil contamination.

The recognition of soil contamination as a significant issue only really developed in Australia in the mid to late 1980's in Australia. At this stage there were no guidelines for assessing and managing contaminated sites with contaminated land regulators and practitioners calling on criteria/guidelines from other countries (principally the Netherlands).

In January 1992 the Australian and New Zealand Environment and Conservation Council and the National Health and Medical Research Council released the "Australian and New Zealand Guidelines

For The Assessment and Management of Contaminated Sites" (ANZECC/NHMRC 1992[1]). While this document included environmental soil quality guidelines, no guidance was provided for asbestos in soil, although generic risk assessment techniques are provided.

In 1993, at the 2nd National Workshop on Health Risk Assessment and Management of Contaminated Sites, Imray & Neville (1993) presented a review of the health risks posed by asbestos and outlined management options for asbestos contaminated sites. The paper included a discussion and review of laboratory analytical methods, health risks, the results of a study undertaken by Addison et al (1988) at the Institute of Occupational Medicine (IOM) Edinburgh, results of investigations undertaken at a former Australian asbestos mining town of Baryulgil (northern NSW), and the proposed classification of sites based on the amount of asbestos measured in air and soil. Their classifications as proposed in the above paper are reproduced below in **Table 2.2**.

TABLE 2.2 CLASSIFICATION OF SITES (IMRAY & NEVILLE 1993)

Asbestos Measured in Air (f/ml) Soil (%)	Ideal Fibre Count Limits	Practical Fibre Count Limits	Classification of Contaminated Site	Action Required
Air Soil	<0.0005 f/ml <0.001%	<0.001 f/ml <0.001%	Not contaminated	None
Air Soil	<0.0005f/ml ≥0.001%	<0.001f/ml ≥0.001%	Restricted	Site must not be disturbed but no remedial action needed. Management plan necessary
Air Soil	≥0.0005f/ml ≥0.001%	≥0.001f/ml ≥0.001%	Confirmed	Site requires remedial action to reduce air levels. When this is achieved manage as a "restricted" site
Air Soil	≥0.0005f/ml <0.001%	≥0.001f/ml <0.001%	Consultant's Delight	Check soil results; look for offsite source of airborne asbestos

Note: f/ml = fibres per millilitre

Thus, it was concluded that a site where asbestos concentration in soil of <0.001% (weight/weight), and concentration of asbestos in air of <0.001 fibres/ml (of air) be classified as "not contaminated".

While the Imray & Neville criteria were published they were not widely used, with most regulators and practitioners adopting a default criteria of 1% asbestos in soil (i.e. less than 1% asbestos in soil regarded as non contaminated and greater than 1% asbestos in soil regarded as contaminated requiring remediation and management). The source of the 1% asbestos level was based on the criteria used to classify asbestos as a waste in Victoria. At this stage the issue of asbestos in soil contamination was not routinely considered except for sites with a clear history of asbestos use, and this was probably attributable to the criteria.

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[1] www.ea.gov.au/cooperation/anzecc

In 1996 the National Environmental Health Forum (NEHF) issued their "Health-based Soil Investigation Levels" (Imray & Langley 1996) which included investigation levels for a range of different substances for a range of different land uses. No numeric guidelines are provided for asbestos, although reference was made to the results of the Addison et al (1988) study. Consequently practitioners tended to apply the default criteria of 1% asbestos in soil. Revised editions of the document have been issued but have not added any new information on asbestos.

In 1999, the National Environment Protection (Assessment of Site Contamination) Measure (National Environmental Protection Council – NEPC 1999[2]) (NEPM), which provides the framework for the assessment of soil contamination in Australia, was released. This document included the tables of environmental and health investigation levels, but again no guidelines were provided for asbestos.

In March 2000, in response to questions regarding asbestos in soil the New South Wales Environment Protection Authority (NSW EPA) provided the following interim policy for asbestos in soil "…. *no asbestos in soil at the surface is permitted. EPA consulted the Health Department in September 1999 to seek advice regarding risk of asbestos in soil and to have the issue considered by public health authorities at national forums. The key issue of asbestos in soil is risk to human health rather than the environment."* No definition of the phrase "at the surface" was provided. As asbestos is regarded by NSW EPA as a health and not an environmental issue, their position is based on advice from the NSW Department of Health.

The NSW EPA 2000 interim policy in relation to asbestos in soils suddenly made asbestos contamination a major issue, which affected many developers and landowners wishing to redevelop residential and industrial land in the inner city and on the fringes of the city of Sydney. In response to this in early 2001 the Australian Contaminated Land Consultants Association (NSW) Inc (ACLCA[3]) began preparation of an Asbestos Code of Practice (ACLCA 2002) with the objective of developing a standardised approach for the assessment, remediation and management of potentially asbestos contaminated soils. The Code of Practice provides practitioners with guidelines for investigation, assessment, remediation/management and validation for sites with asbestos in soil contamination. The Code of Practice advocates dealing with bonded asbestos containing materials and friable asbestos in different ways. The Code of Practice, which has not been endorsed by regulators, was also prepared to assist groups involved in development of national asbestos in soil guidelines.

More recently, enHealth[4] (an Australian federal government Council which provides national leadership on environmental health issues, set priorities, coordinate national policies and programs and is also responsible for the implementation of the Australian National Environmental Health Strategy) commenced work on developing guidelines for the management of asbestos in a non-occupational environment, including asbestos in soil. They have recently finalised a consultation draft document for internal review. It is understood that the document is unlikely to provide a guideline or criteria for asbestos in soil. However, it is understood that the document is likely to advocate dealing with friable asbestos and bonded asbestos containing materials in different ways, based on the significantly different health risks posed by these different forms of asbestos.

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[2] www.nepc.gov.au

[3] www.aclca.asn.au

[4] enhealth.nphp.gov.au

At the time of writing, the NSW interim regulatory position remains, and other Australian states do not have specific guidelines for asbestos in soils. Generally in states other than NSW asbestos in soil is dealt with on a case-by-case basis, although the various states would be expected to adopt the enHealth position when finalised.

National and state regulators provide guidelines to ensure asbestos workers are protected while building unions also have a strong role in ensuring workers are protected. In recent times building unions and the local community have become involved in the management and remediation of asbestos contaminated land and protection of the surrounding community, particularly at sites with perceived or actual significant asbestos contamination issues.

2.3 Investigation and Assessment of Asbestos Contaminated Soil

If a site history review identifies asbestos as a potential contaminant then an appropriate sampling and analysis program is developed and implemented. The design of sampling programs for asbestos in soils, is generally consistent with any other potential contaminants, and is based on regulatory guidelines.

Where samples are being collected for asbestos in soils, samples are normally collected from locations and intervals within the soil profile where asbestos is likely to be present. Experience has shown that where possible it is preferable to use field investigative techniques, which provide the opportunity to observe large areas of the soil profile. For example, test pits excavated by backhoe are preferable to boreholes (as test pits provide a greater opportunity to observe soils and any evidence of asbestos fragments being present - although 'respirable' asbestos fibres disseminated through the soil will not be visible to the naked eye).

The heterogenous nature of the soil samples needs to be considered when sampling, particularly if splitting samples into smaller sub-samples. Experience has shown that significant differences (and unquantifiable errors) can occur between split samples (or duplicate samples).

Soil samples are typically placed either in clean sampling jars or securely sealed plastic bags (one bag inside another bag), while bonded asbestos fragments (cement sheeting, vinyl floor tiles etc) of potentially containing asbestos are placed in clean securely sealed plastic bags (one sealed bag inside another sealed bag). Equipment is decontaminated and sample handling and transport are consistent with normal contaminated site investigation methodologies.

Field Quality Control procedures typically include collection of duplicate and replicate (field split duplicate) samples at an overall rate equivalent to about 10% of samples collected and analysed. However, as discussed above, unless asbestos is distributed homogenously throughout the soil being sampled it is highly likely that different results may be reported for duplicates and replicate samples. Such discrepancy is not necessarily indicative of inconsistencies between the skills of sampling personnel (from the same or different laboratories) but rather is more likely simply an indication of variability between samples i.e. heterogeneity of the asbestos distribution in soils.

Personal and/or environmental monitoring for asbestos fibres in air may be undertaken during soil sampling, particularly if conditions are conducive to generating dusts or if there are expected to be large quantities of free asbestos fibres. Air monitoring during asbestos in soil contamination investigations would normally be undertaken for three main purposes: i) as a process control to check on the protection of the health of the general public, including site workers; and ii) OH&S protection for workers. iii) To place on record the fact that no detectable airborne asbestos fibres were present during site activities, to guard against unsubstantiated allegations from any source in the future.

2.4 Laboratory Analysis of Asbestos Contaminated Soil

In Australia polarised light microscopy (PLM) is the method normally used for identification of asbestos in soil media. The sample is inspected under a microscope and asbestos fibres identified by their optical properties that include refractive index and morphology. PLM is used due to its relatively low cost (>A$50-A$80/sample). Other methods of identification such as X-Ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM) are not normally used primarily due to cost (typically > A$250-A$500/sample), limited availability and user experience with these units. Although sometimes these methods may be used to confirm the results of PLM results.

Laboratories analysing for asbestos in soil should hold current, operative accreditation by the National Association of Testing Authorities (NATA[5]). All analyses for asbestos in soil must be conducted by NATA approved identifiers, and all certificates of analysis must be endorsed with the NATA logo and signed by a NATA approved signatory and identifier. Analysis of asbestos in bulk materials and especially in soils requires considerable experience, skill and judgement, and NATA accredited laboratories have a reasonable chance of correctly analysing and reporting the majority of bulk samples.

Asbestos identification by NATA accredited laboratories are conducted in accordance with the common analytical criteria described in the NATA Guidance Notes (NATA 1991), which includes a largely empirical “trace” analysis procedure to semi-quantify, the presence or absence of freely distributed asbestos fibres throughout the sample. A NATA accredited laboratory is not permitted to include any non-factual information on a NATA endorsed certificate of analysis, such as the percentage of asbestos content.

Samples received by the laboratory can be reduced if necessary if they are homogeneous samples by following a documented procedure that produces representative sub-samples. Because large errors can be created, heterogeneous samples should not be reduced, but often are.

In general, each sample is viewed by eye, a magnifying glass and/or by low power stereomicroscope to detect the presence of any fibrous material, which would be separated and treated as sub-samples.

Each sub-sample is viewed by low and high power stereomicroscope, and then mounted in one of three high-dispersion refractive index oils onto a glass microscope slide, and covered with a cover-slip. A schematic flow chart showing the basis of asbestos fibre description is shown in **Figure 1**.

The fibres from each sub-sample are viewed with a polarised light microscope (PLM) to determine a range of optical properties such as principal refractive indices, morphology, optical orientation, birefringence, optical extinction, colour and pleochroism. In summary, a certain number and type of these observed properties have to agree with those obtained from standard (reference) samples of known types of asbestos, for unequivocal identification of a specific type of asbestos is declared.

NATA permits identification by PLM only of chrysotile, amosite and crocidolite asbestos fibres. If the rarer forms of asbestos (actinolite, anthophyllite and tremolite) are present, NATA requires that these

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[5] www.nata.asn.au

be described as “mineral fibres of unknown kind”, due to significant practical difficulties in optical analysis of these fibres.

For all soil samples, a “trace” asbestos analysis has to be performed (**see Figure 1**) whereby several milligrams of the sample are placed in refractive index oil on a slide with a cover-slip. This is repeated for a second slide.

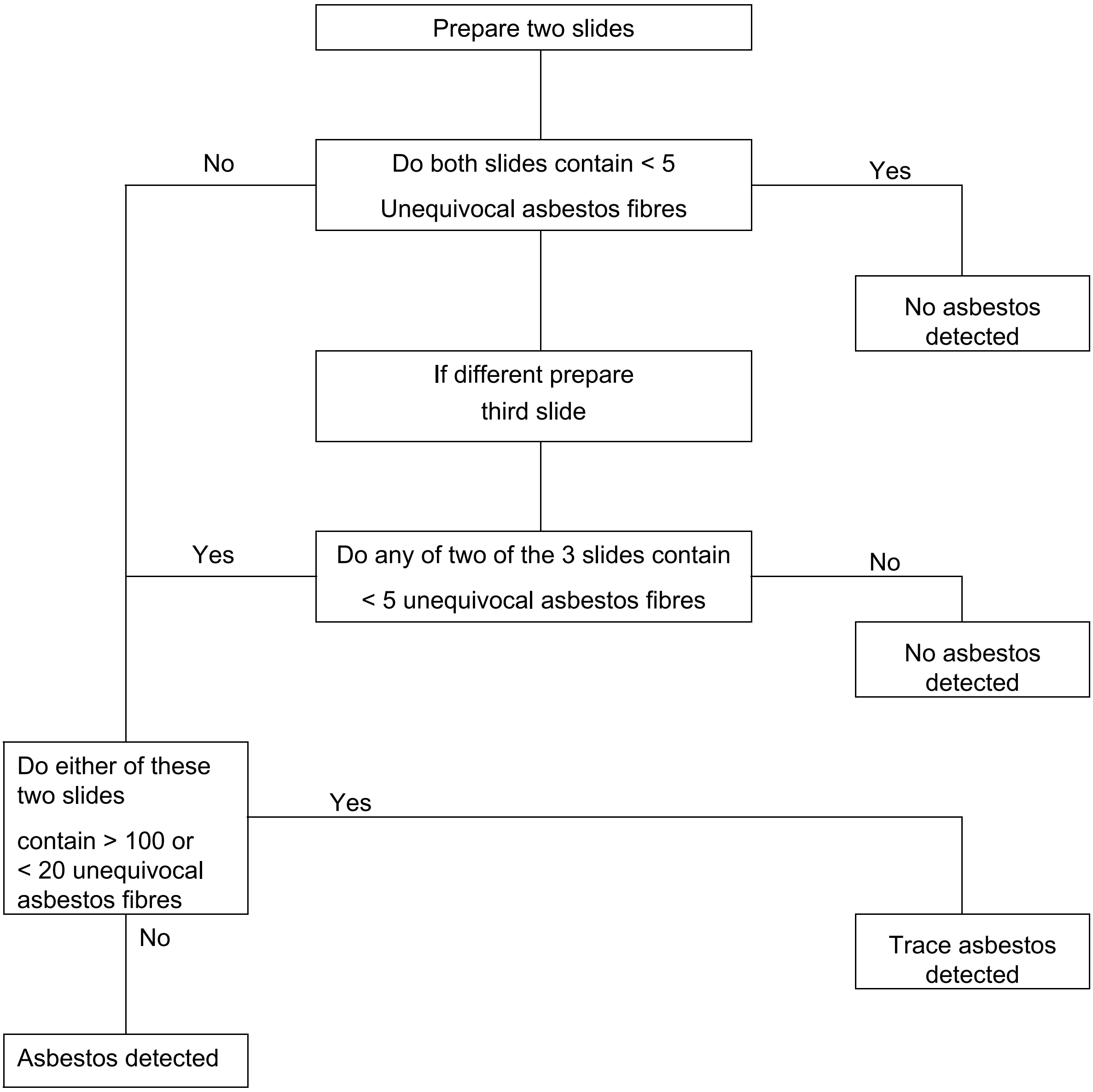

FIGURE 1 FLOW CHART SHOWING BASIS OF ASBESTOS TRACE FIBRE ANALYSIS

Asbestos identification conducted in accordance with the NATA Guidance Notes sets analytical criteria for the detection limit, below which a sample must be reported as “no asbestos detected” i.e. < 5 unequivocally identifiable fibres on each of two microscope slides. This criteria would be recommended as being utilised for defining land areas as “no asbestos detected”.

Detection limits for the asbestos identification method conducted in accordance with the NATA (1991) Guidance Notes is believed to lie between 0.1 and 1 g/kg of asbestos by sample weight, depending upon the type and condition of the fibres and the matrix, and based on an analyst with fairly basic experience. However, in ideal situations and for some samples, the detection limit can be improved by 1 to 2 orders of magnitude.

A draft Australian Standard for analysis of asbestos has just completed its public review process. The draft Australian Standard that will replace the NATA Guidance Notes, incorporates the same analytical techniques as the NATA Guidance Note (described above), and has new guidelines for sampling ores and soils, and new reporting requirements.

For asbestos-cement contaminated soil, the Draft Australian Standard AS4964 (Standards Australia 2002) analytical method permits laboratories to estimate the asbestos weight content in a sample, and then calculate the concentration of the asbestos in grams per kilogram of sample. If this concentration is less than a pre-determined 'reportable' limit, then the result can be reported as 'less than the reportable limit of xxx g/kg'. Typically the reportable limit is either 0.1 or 1 g/kg, depending upon the type of sample. More importantly, a 'trace' asbestos analysis is conducted on the sample (usually the fine dust fraction), to determine whether the sample contains 'respirable' asbestos fibres. This guards against the possibility that asbestos fibres are distributed throughout the sample – in other words, fibres that have the potential to become airborne and hence pose a risk.

When preparing the draft Australian Standard consideration was given to adopting various other international methods, which included:-

- United States Environment Protection Agency, Superfund Method for the Determination of Releasable Asbestos in Soils and Bulk Materials (USEPA).
- United Kingdom Health and Safety Research Report produced by the Institute of Occupational Medicine, 'Development and Validation of an Analytical Method to Determine the Amount of Asbestos in Soils and Loose Aggregates' (Davies et al 1966).
- United Kingdom Health and Safety Final Report produced by Thomas Schneider et al, 'Development of a Method of Low Contents of Fibres in Bulk Materials' (Schneider et al).

It was decided that all Methods were inapplicable for the majority of Australian conditions, for reasons that included:-

- Most Australian contaminated lands issues involve the presence of 'bonded' asbestos materials such as asbestos-cement, and not insulation products. The significantly lower risk associated with bonded products, and the lack of relevance does not justify the above methods.
- The cost and complexity of most of the methods would have the practical effect of reducing the number of samples analysed, thus adding significantly to the already difficult sampling problems associated with contaminated land. In other words, it was seen as more useful to analyse more samples with a 'passable' analytical technique, rather than analysing less samples with a questionably superior technique, associated with the strong possibility of faulty or incompetent execution.

2.5 Remediation and Management of Asbestos Contaminated Soil

A brief description of typical remediation / management strategies for asbestos in soils used in Australia include:

- Offsite disposal to landfill: This involves the excavation of all asbestos contaminated soils and disposal of these soils to a landfill licensed to accept asbestos contaminated soils. This is one of the most common methods of remediation of asbestos contaminated soils (particularly in NSW) due to its being cost-effective and allowing the site to be remediated to a level that will permit unrestricted use of the site, with minimal future liabilities for a site owner.
- Collection of bonded asbestos containing material fragments: This involves the removal of all visible fragments of bonded asbestos containing material fragments from soils (commonly on the surface). This typically involves collecting (picking up – emu bob) all visible asbestos containing material fragments from the surface and near surface soils. The separated bonded asbestos containing material fragments are disposed of to a licensed landfill, while the validated residual soils can be reused on site. This is only applicable for situations where there is no friable asbestos present.
- Containment: Various containment options are available for asbestos contaminated soils. The common requirement of all containment options is that the containment system effectively prevents exposure to the asbestos contaminated soils, whilst the integrity of the containment system is maintained. Containment does not involve removal of the asbestos contamination but rather provides a mechanism for managing the contamination. Adoption of such a strategy will invariably require the establishment and implementation of an ongoing management plan to ensure the integrity of the containment system is maintained. It may also require the site to be licensed in accordance with various local regulations. Containment may include:
  - Cap In-situ: this involves providing a layer of clean soil above the asbestos contaminated soils. Normally the cap would be placed directly over those areas of a site known to be contaminated with asbestos. Commonly, a marker mesh is utilised beneath the cap to indicate the presence of contaminated materials below.
  - Surface clean up and cap: this involves remediation of the asbestos contamination in surface soils and reinstating the clean soils to provide the cap as described above. This may be particularly suited to a situation where the soils are contaminated with bonded asbestos fragments, whereby removal of these from the surface soils and replacing the remediated soils to act as the cap over underlying contaminated soils. Commonly, a marker mesh is utilised beneath the cap to indicate the presence of contaminated materials below.
  - Excavation and relocation to a purpose-built containment cell onsite: this would involve the excavation of asbestos contaminated soils on the site and their transfer to a purpose-built containment cell constructed on site. Thus, the advantage of this option is that asbestos contaminated soils are consolidated to one area on site. It may be possible to reduce the volume of soil to be contained by treatment (eg removal of bonded asbestos fragments prior to transfer to the containment cell) to effectively reduce the volume of asbestos contaminated soil requiring containment.
  - Incorporating remediation within site development: this strategy is similar to capping or containment, although the capping layer or containment system is effectively provided by the

site development. For example areas of asbestos contaminated soils may be situated beneath an area of a proposed building or car park. Adoption of such a strategy results in a cost effective remediation.

- Asbestos Management Plan: In some situations, for example where asbestos contaminated soils are not situated on the surface and where there is no complete exposure pathway (or remediation involves removing the exposure pathway), an appropriate method of addressing the asbestos contamination may be through an Asbestos Management Plan. The objective of an Asbestos Management Plan is to outline management procedures, which will be implemented to ensure that the asbestos contaminated soils are managed in a fashion that poses no adverse health risks.

Other strategies, which have been used or are being trialled include:

- Separation Techniques: The authors have been involved in the application of separation strategies comprising sieving of asbestos cement fragments in soils (described above). This technique appears to shows considerable promise (the target site's soils were dry and sandy with surface contamination by asbestos fragments – probably ideal conditions). Although the success of sieving will probably depend upon the integrity of asbestos-cement and the soil types (heavy clays contaminated with asbestos-cement fragments are likely to be poorly suited to sieving). Obviously this technique may not be suitable where there are significant quantities of friable asbestos.

- Dissolution/Destruction Technologies: In-situ vitrification and acid dissolution techniques have been applied to asbestos in soil, to limited effect. Generally these techniques have not passed bench-scale testing, are very expensive, or do not meet the long-term land use requirements for the site. Attempts to dissolve asbestos fibres, such as by using strong acids, have proven monumentally unsuccessful and often the remedial techniques suggested have created a greater adverse impact.

- Risk Assessment Techniques: A number of different approaches have been used but can be grouped into either methods based on field trials to collect data for input into theoretical models or methods based on field trials with monitoring for airborne asbestos fibres to assess presence and amounts of respirable fibres. Both are based on establishing the relationship between asbestos in soil and respirable asbestos fibres in dust generated from the soil.

  Parkinson et al (2000) reported the methodology and results of a risk assessment undertaken using field trials and site and development specific theoretical modelling to determine an acceptable concentration of asbestos fibres in soils for a proposed residential development. The risk assessment included determining the relationship between asbestos concentration in soils and asbestos concentration in dust generated from the soils (on the basis of monitoring of dust trial during field trials). The relationship was then applied to an estimation of lifetime dust exposure (determined by modelling using Visual Basic, with the model incorporating the elements of the proposed development). This was then solved to an acceptable level of risk (1 in 1,000,000) to determine an allowable mass concentration of 0.05% of asbestos fibres. A court case in relation to the development of the site concluded due to uncertainty about the acceptable levels of asbestos fibres in soil, that until there is more information, which removes the doubt, the soil should be asbestos free or a relevant regulatory authority agrees the level of asbestos.

3. AUSTRALIAN CASE STUDIES

3.1 Overview

The authors have been involved in a number of projects involving asbestos contaminated materials, including monitoring for airborne asbestos fibres for occupational health and safety reasons and remediation / management of sites with asbestos contaminated soils.

Brief case studies are described in the following sections.

3.2 Monitoring for Airborne Fibres

Over the years, airborne asbestos fibre sampling has been conducted at a number of quarries, contaminated sites and concrete re-processing plants where asbestos-cement waste was present.

In all cases, the results have been less than the detection limit of the 'membrane filter method' of <0.01 fibres per millilitre, which has shown that the asbestos fibres have not been liberated from the asbestos-cement materials in detectable airborne concentrations.

In summary, extensive experience with asbestos-cement contamination in soil has shown that excavating, shovelling, screening and other earth moving activities do not liberate measurable airborne asbestos fibres. The same results occur when asbestos-cement structures are being demolished in accordance with Regulatory requirements.

Examples of these situations are included the following case studies:

Inspection, Front End Loader Handling, Sieving, Sample Splitting of Asbestos-Cement Contaminated Aggregate

This study involved personal sampling carried out on exposed workers whilst: inspecting; creating a number of sampling pads (by using a front end loader to dig), including moving, and spreading aggregate; extensive hand screening; and sample splitting of asbestos-cement contaminated aggregate.

All airborne asbestos fibre results except one were less than the detection limit. The exception sample was re-analysed by polarised light microscopy and found to contain no detectable asbestos fibres.

Mixing of Asbestos-Cement Contaminated Recycled Concrete with Dust

Airborne asbestos fibre measurements were conducted at a quarry mixing dust with asbestos-cement contaminated recycled concrete. A large articulated front-end loader was used to mix some 3,000 tonnes of contaminated recycled concrete with around 2,500 tonnes of dust.

All results – including personal samples taken on the loader operator – were less than the detection limit of the method. This also applied to samples taken down-wind of the stockpiles being mixed.

Tracked Vehicles Driving Over Asbestos-Cement Contaminated Driveways

This study involved personal and several static airborne asbestos fibre tests conducted whilst a tracked excavator was being driven on a gravel driveway known to be contaminated with small amounts of asbestos-cement, and whilst a second excavator was scooping up a stockpile known to be contaminated with asbestos-cement.

All results were less than the detection limit of the analytical method; therefore demonstrating these operations posed no measurable risk to workers or visitors.

Concrete and Building Demolition Waste Re-Processing Plant

Airborne asbestos fibre measurements were conducted at a concrete and building demolition waste re-processing plant known to contain asbestos-cement in the demolition waste.

Despite high airborne dust concentrations, airborne asbestos fibre concentrations were below the detection limit of the method. This indicates no measurable risk to health in respect to airborne asbestos fibres, during material transfer, screening or processing activities.

Cleaning and Spraying of Weathered Asbestos-Cement Roofing

Whilst not associated with contaminated land issues, this study demonstrates the low potential for asbestos-cement to release airborne asbestos fibres when handled. The Study involved static and personal samples taken on workers and under the roof whilst: cleaning a 5,000 square metre asbestos-cement roof with paint scrapers and brooms; cleaning gutters with paint scrapers and brooms; applying bitumen paint and self-adhesive aluminium gutter liners; spraying the upper surface of the asbestos-cement roof with two separate patented resin and acrylic based coatings; removing asbestos-cement roof sheets to replace with fibre-glass sky-lights; removing and replacing some asbestos-cement ridge-caps; replacing badly damaged asbestos-cement roof sheets with asbestos-free sheets.

All airborne asbestos fibre results were less than the analytical detection limit.

Manual Test Screening of Asbestos-Cement Contaminated Soil

This study involved two tests, based on unrealistically severe, 'worst case', conditions. Two ‘man-cooler’ fans were used to blow a strong wind current over a stockpile (which was heavily contaminated (ie around 3 to 6% by weight) with very old and deteriorated asbestos-cement pieces) in order to generate dusts for monitoring for airborne asbestos fibres.

The first test comprised severely disturbing the stockpile by digging into the stockpile and the asbestos-cement pieces with a shovel, and moving the material to create a second stockpile. The air was sampled downwind of the stockpile to collect any fine, respirable sized particles and fibres.

The second test comprised severely disturbing the stockpile by digging into the stockpile and the asbestos-cement pieces with a shovel, and placing it in a 1 mm screen. The screen was vigorously rotated so as to screen the material and create a second smaller stockpile. All material (including a high percentage of asbestos-cement pieces) on the screen was then dropped onto the concrete floor from a height of around 0.5 to 1 metre. The air was sampled downwind of the stockpile to collect any fine, respirable sized particles and fibres.

Even though the stockpiles contained mainly sand (which is crystalline silica, i.e. quartz), the respirable quartz concentrations were less than 0.12 milligrams per cubic metre, and most likely considerably less because of the fact that the relatively short sampling duration and the severe nature of the tests.

The amount of inspirable dust for all operations was less than the Australian Occupational Exposure Standard (Worksafe Australia 1995) for “dusts not otherwise classified”.

All airborne asbestos fibre measurements were less than the detection limit of the method.

Therefore, all of these results were satisfactory, even for very severe conditions that would not be experienced during normal site work.

Five Day Pilot Trial Power Screening of Asbestos-Cement Contaminated Soil

During a five day Pilot Trial in November 2002, around 600 tonnes of severely asbestos contaminated soil was power screened inside a large shed. The aim of this Trial was to test the effectiveness of techniques designed to remove the asbestos-cement pieces so that the remediated material can be re-used on site.

Comprehensive measurements conducted by a NATA laboratory during the Pilot Trial screening operations showed no detectable airborne asbestos fibres. These measurements included samples taken within 1 to 3 metres of the hopper accepting the contaminated soil, the vibrating screen, the waste conveyor transporting asbestos-cement into bins, and the discharge conveyor transporting the screened material onto a concrete slab.

In other words, all airborne asbestos fibre measurements conducted during the Pilot Trial were less than the detection limit of the analytical method, of less than 0.01 fibres per millilitre of air.

Degradation' Process for 'Remediated' Product

As part of the above-mentioned Pilot Trial, further analysis was conducted whereby the screened material was subjected to severe 'degradation' tests to investigate if any of the material has the potential to generate airborne asbestos fibres. These tests incorporated a high speed-blending machine that effectively grinds samples of the screened material.

A 12-litre chamber was used to elutriate the dust generated inside the blender, such that the collected particles (and fibres) were less than approximately 5 micrometres in dimension. This has the effect of 'concentrating' the 'respirable' fibres because the coarse (non-respirable) dust and fibres are not collected.

During the blending, air samples were taken and subjected to analysis by phase contrast optical microscopy (PCOM) and scanning electron microscopy (SEM). The SEM (which is a sensitive analytical tool able to detect very fine fibres down to approximately 0.1 micrometres in width) was able to differentiate between organic fibres (such as harmless plant or clothing fibres) and asbestos fibres. Except for one asbestos fibres on one sample compared to several hundred non-asbestos fibres examined, the results of the SEM studies showed an absence of asbestos fibres. This confirmed the absence of fibre bundles in the sample, or that any fibre bundles actually present were not sufficiently abundant as to produce measurable airborne asbestos fibres of 'respirable' size range.

Dust physically removed from the face of the second half of the filter used for PCOM was subjected to PLM examination, with the result that no asbestos fibres were detected.

3.3 Remediation and Management of Asbestos Contaminated Soil

The authors have been involved in various roles on investigations and remediation of a number of sites which have had various types of asbestos contaminated soils, and which have been the subject of a range of different remediation/management strategies. Details of the types of asbestos contamination and the selected remediation/management strategies are described below.

Remediation of former Air Force Stores Depot – Asbestos Cement Fragment Contamination of Soil

Asbestos fragments (but very few fibres) were identified in site characterisation. The site history confirmed the contamination was caused by some limited improper asbestos-clad building demolition practices. The Site was planned for commercial redevelopment. A comprehensive 20-metre grid-sampling program was undertaken across the 20-hectare site and "hotspots" were removed by over-excavation and validation testing. A limit of "no detectable fibres by PLM" was applied to validation samples. A specialist asbestos occupational hygienist supervised the removal and inspected the site at the end of the remedial works, providing an unconditional "signoff" that the site posed no unacceptable risk from asbestos materials". Asbestos contaminated materials removed by this remediation were classified as "asbestos-containing wastes" and they were disposed of offsite to an approved asbestos landfill.

Remediation of Former Navy Supply Centre – Asbestos Cement Fragment and Fibre Contamination of Soil

Asbestos fragments and some fibres were detected as part of the characterisation of a 50-hectare former Navy Supply centre, planned for medium density residential redevelopment. Based on the site history and initial testing, the site was divided into 10 metre by 10 metre cells, and each cell was classified as: "asbestos fibre contamination confirmed"; "asbestos fragment only contamination confirmed"; "asbestos contamination suspected"; and "no known or suspected asbestos contamination". An increasing level of assessment and remediation was performed in each cell, based on the known or suspected level of asbestos risk classification. At the completion of the remediation and validation by soil sampling and PLM analysis, all of the cells were inspected by an asbestos occupational hygienist and an unconditional "sign-off" as to the suitability of the site in relation to asbestos was provided.

Remediation of Former Military Stores Centre – AC Fragment and Fibre Contamination of Soil

Asbestos fragments and some fibres (typically non-respirable fibre bundles) were detected as part of the detailed site characterisation of this 52-hectare former military stores depot. The source of the asbestos contamination was confirmed to have been from poor building demolition (driving bulldozer through and knocking over wooden frame to allow building to collapse) of large asbestos-cement sheeting clad stores with minor burial of wastes. The degree and extent of asbestos contamination was assessed to exist between concrete building slabs of the former buildings.

Due to the extensive area of the site impacted by the asbestos (>10 hectares) the cost of offsite disposal of impacted soils to landfill was cost prohibitive (in the order of A$20M), therefore other options for remediation were explored. A sieving remediation performance pilot trial (described in detail above), using an 5 mm square screen (producing a screened product of nominally 3 mm – due to the effect of the slanting power screen) was implemented for the dry sandy soils lying in the contamination areas. The trial proved highly successful in removing asbestos fragments and no asbestos fibres were detected in the sand product, or in air monitoring carried out during the sieving. An aggressive "degradation trial" (described in detail above) was also performed on the sand product, to confirm that the soils could be reused onsite with no long-term residual risk. The degradation trial involved high-speed blending and asbestos fibre analysis of the generated airborne dust. Even under these extremely aggressive degradation conditions no detectable free fibres could be found and the soil was considered suitable for unrestricted reuse. Asbestos fragments removed during the sieving were disposed offsite to landfill as asbestos waste.

Based on the success of the pilot trial the sieving process is to be implemented for remediation of asbestos contaminated areas of the site.

Remediation of Former Agricultural Land Being Developed For A Public School – AC Fragment Contamination

Asbestos cement fragment contamination was identified to present mainly in surface soils (<150mm) with some pockets at greater depths, across former agricultural land being developed for a public school. The source of the asbestos was believed to be from uncontrolled demolition of former asbestos-cement clad buildings on the site and pockets of buried waste and surface dumped wastes containing asbestos cement fragments. Remediation involved a surface scrape of soils till encountering undisturbed residual clay soils (typically to depths of approximately 150mm) across the potentially impacted area with the exception of areas around large native trees to be retained in the development. In some areas where buried waste could not be removed by scraping (due to access limitations and ecologically sensitive environment) a 300mm cap was placed over the wastes and sown with native vegetation. The scraped soils containing asbestos cement fragments were disposed to landfill as asbestos waste. An inspection of the exposed soils was undertaken by an asbestos occupational hygienist, including collection of any visible asbestos cement fragments in the un-scraped areas. Due to the potential for additional asbestos to be present an environmental management plan was required to deal with any asbestos that may be identified, particularly in the vicinity of the retained trees. Boundary air monitoring for asbestos fibres and soil validation sampling for asbestos was also undertaken during and after remediation, respectively.

Remediation of Former Army Stores Depot – Asbestos Cement Fragment Contamination

Asbestos cement fragments (presumably sourced from demolished buildings either on or off the site) were found to be buried on the site. The burial areas were excavated and material comprising predominantly asbestos cement fragments was disposed offsite to landfill as asbestos waste. Other excavated material comprised silty clay to silty sand soils containing asbestos cement fragments. These soils were sieved onsite, resulting in the sieved soils comprising a total asbestos content of less than 0.001% (by volume) with asbestos fibres detected in no more than 5% of validation samples. The sieved soil was used to backfill the excavation but with at least 0.5m of clean soil cover over the sieved soil. Asbestos cement fragments removed during the sieving process were disposed to landfill as asbestos waste. An unconditional "sign-off" as to the suitability of the site for commercial/industrial uses in relation to asbestos was provided.

Remediation / Management of Former Power Station – Asbestos Fibre Contamination

Asbestos products were removed from the former power station and placed in a specially designed onsite containment cell, prior to demolition to slab level. The concrete building materials were crushed following demolition and used to backfill open concrete lined service trenches and canals within the former building slab. Asbestos fibres were found to be present in surface samples of crushed concrete in some areas of the backfilled trenches. The source of the asbestos is not well understood but may be related to either incomplete removal of asbestos materials prior to demolition or possibly from asbestos contained with cement used for exhaust stacks. These impacted areas were proposed to be covered with a surface seal (probably bitumen) as a short-term management strategy to allow redevelopment of the site for a new power station on the former slab. It is likely that the future development on the existing slab will effectively act as a remediation strategy (containment), although a asbestos management plan will probably be required to ensure that the asbestos contaminated crushed concrete is not disturbed or exposed in the future without appropriate precautions being implemented.

Remediation / Management of Former Power Station – Asbestos Fibre Contamination

A former power station was demolished in the late 1960s and late 1980s. Environmental investigations undertaken on the site have identified areas contaminated with asbestos fibres predominantly associated with the power station building demolition rubble. The site is proposed to be redeveloped for industrial uses. The preferred remedial strategy for the site is to cap the areas contaminated with asbestos fibres to provide a safe working platform for the proposed development. It is likely that an environmental management plan will be required to ensure that if the cap is disturbed during subsequent development appropriate management of the residual asbestos contaminated materials is implemented.

4. CONCLUSION

In Australia, the issue of health risks associated with asbestos are very emotive and has been the subject of some very sensationally stories in the media, inappropriately supporting the concept that exposure to one fibre can result in asbestos related diseases. Hence asbestos has become more of a social and political issue than a purely technical one. As a result legislators and regulators are very cautious about establishing policy and guidelines for asbestos in soil and have tended towards either delaying any clear decision making or adopting a zero tolerance guideline (as in NSW), at least as an interim position. Thus, emotion, social and political issues associated with asbestos have tended to overwhelm any technical debate based on the scientific evidence.

The impact of this conservative and non-technical approach by the regulatory community has affected many parties, including land owners and developers. Developers have probably been most affected with many expressing frustration at the policy “vacuum” and incurring, significant additional financial costs associated with remediation or delays to many projects. In many cases the easiest way out for many developers is to simply dispose of all asbestos contaminated soils from their sites to landfill, although for some others this is cost prohibitive resulting in valuable land remaining under utilised (particularly in Sydney where there is a real shortage of land). Land or house owners have been less affected but if the zero tolerance policy was rigidly applied many houses in city and country areas could find their properties devalued substantially.

Regulators are tending to deal with bonded asbestos contamination in soil in the same way as friable asbestos contamination in soil - although to be fair there appears to be a move towards recognising that bonded asbestos is less of a health hazard than friable asbestos (the impending enHealth guidelines may resolve this issue).

The authors consider that there is a large body of evidence (including that outlined above) which demonstrates that the risk of exposure and hence risks to human health from bonded asbestos is considerably lower than that posed by friable asbestos. Therefore we consider that these two forms of asbestos should be treated significantly differently.

However, it is considered that it is important to properly define friable asbestos, and in our opinion weathered or degraded bonded asbestos should not automatically be classified as friable, as is currently the case in NSW. We consider that the classification of bonded asbestos material should or be based upon a specific assessment of the risks of the particular bonded material under consideration. Further we believe in some cases it would be appropriate to carry specific degradation tests (similar to those described in Section 3 above) in order to appropriately assess the risks and enable classification i.e. basing decisions on the real risks not the perceived risks.

In the future the authors would like to see less emotion and more balance in the consideration of the risks associated with asbestos in soil contamination. In particular we believe that better communication of the real risks posed by asbestos in soil contamination (through public health awareness programs – similar to existing Australian programs for lead paint contamination) by public health authorities, would be of considerable benefit. Ongoing research in this area and publishing of peer reviewed findings by academics and practitioners should be encouraged to support the balanced communication. Ideally the outcome would have an informed community that is aware of the real risks, which would enable more pragmatic but safe policy and guidelines to be developed.

5. DISCUSSION POINTS

To help promote thought and discussion for the interactive workshop the following series of questions are posed:

- How are other countries dealing with asbestos in soil contamination ?
- Are other countries facing similar social and political issues in relation to asbestos ?
- Should we be treating bonded asbestos different to friable asbestos ?
- Should we really be worried about the asbestos content in soils or focused more on the asbestos content in dust generated from the soils ?
- If the focus should be in dust generated from soils what methods should be used for determining a relationship between asbestos levels in soils and dusts ? Should methods be field or laboratory based ?
- What analytical techniques should be used ? Can low cost low technology methods (eg PLM) be used or is there a benefit in using high cost modern technological methods (eg SEM, TEM etc)
- What are the emerging remediation / management strategies available for bonded and friable asbestos in soil contamination ?
- Are traditional sampling strategies and methods appropriate for investigating asbestos in soil contamination ?
- Should there be limitations on property title information if asbestos residues remain ?

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SpS 19 Special Session:

In situ Measurement of Contaminants in the Subsurface: Methods and Field Applications

Strategies and Technologies for In-Situ-Site Assessment

B. Barczewski, J. Flachowsky

1 Introduction

One of the most important duties of environmental protection in Germany and also in other industrialized countries is the reduction of the consumption of “green land” which has increased in Germany to 129 ha per day for settling, industrial purposes and public infrastructure. One way to reduce this consumption is the redevelopment of abandoned industrial, commercial, military or railroad sites. Those sites very often are contaminated or at least are suspected to be contaminated. Potential investors for those areas need precise information on the situation of the subsurface to minimize their financial and technical risk.

The knowledge of the type, the total mass and the spatial distribution of contaminants is essential for risk assessment and characterization of really contaminated and suspected contaminated sites. Where subsurface remediation is required, this information is additionally necessary to perform remediation successfully and cost effectively. The presently used standard procedure for site characterization is based on laboratory chemical analysis of soil or groundwater samples according to a predetermined sampling grid. This procedure is time consuming and very costly and therefore only a very limited number of samples will be analysed. The high precision of point measurements is not adequate to the problem, because the high degree of heterogeneities of both, the subsurface and the pollutant distribution. This means that the results of single point measurements are more or less random and can fluctuate significantly, resulting in a very high degree of uncertainty.

2 Objectives

Due to the strong heterogeneities with often small contaminated areas with high emissions, the optimization of site investigation methods is urgently needed. According to the German Soil Protection By-Law, the use of simple push-in penetrometer probes with integrated measuring systems is permitted. Using such easy to handle and cheap instruments, much more measurements can be done for the same price, with a slightly lower accuracy at the selected point (Fig. 1). This strategy will be considerably improve the certainty of the investigation and thus enlarge the confidence in the results. Because decisions on measures, i.e. remediation, long term monitoring ..., will be made on guide values, a precise measurement of contaminant concentrations is only necessary in the range close to those guide values (Fig. 2). If in-situ measurements yield values with a known maximum deviation, only very few measurements (close to the guide values) have to be checked by sampling and laboratory analyses.

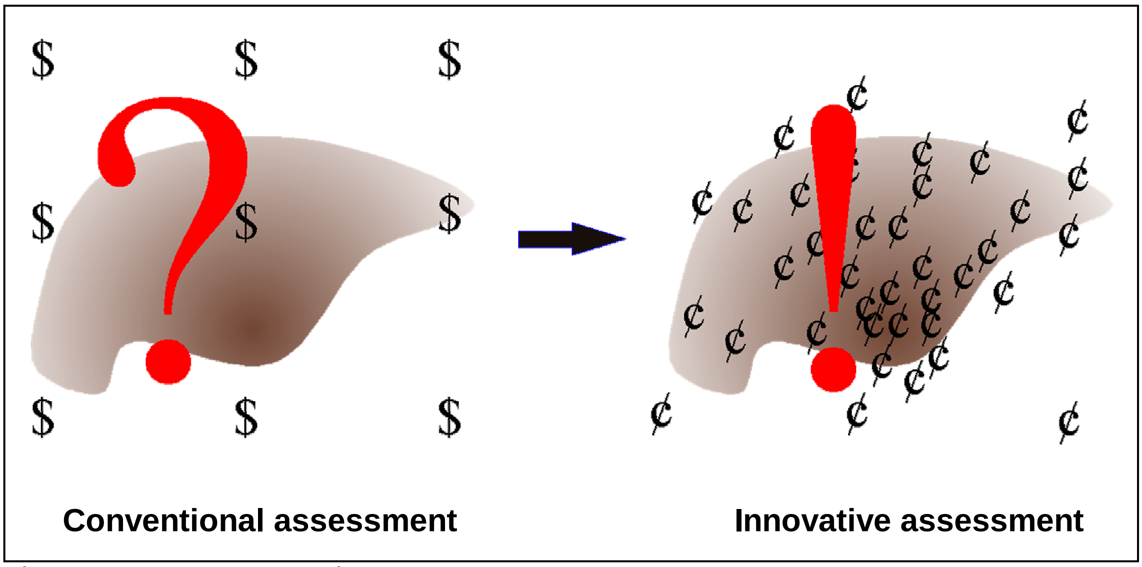
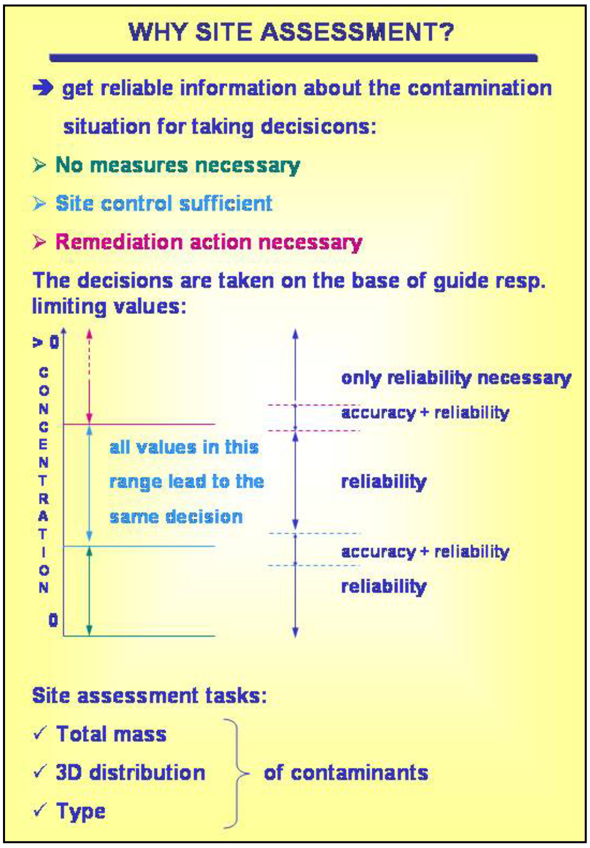


Fig: 1: Assessment Strategies

Because presently there are no suited field tested instruments, which can be used to detect contaminants in-situ in the subsurface the “Deutsche Bundesstiftung Umwelt” (DBU) has funded a research network “High Tech-Methoden der Vor-Ort-Analytik” with 6 university institutes and 5 consultant and engineering companies. To link all the know-how, the experiences and the different strategies of the research partners in optimal ways, the research network is managed by a project coordinator.

To reduce the financial risk, the funding time is divided in 3 parts, where the developers of instruments have to reach the goals defined objectives. If one project does not reach the goals the funding for this project will be stopped.



Fig, 2: Point Precision versus Certainty

3 Goals and strategies of the research network

The main goals for the instruments to be developed are:

- In-situ-measurement of concentrations of the relevant contaminants in the subsurface at the selected place (field screening)
- Use of sensors instead of expensive and complicated laboratory analysis. The sensor based measurements have to yield comparable information (for example special distribution of contaminants, mass and type of contaminants ...)
- The use of conventional and commercially available light weight motor hammers with integration of the sensors in the push in rods.
- Real time measurements must be possible.
- Modular assembly of the sensoric module, sample input, sensor, power supply and wireless or optical data transmission to the top of the rod.

All components have to fulfil important prerequisites:

- Resistant to high accelerations (robust resign).
- Small size.
- Low energy consumption.
- Easy to use, no special analytical knowledge necessary.
- Reproducible results for the used measurement principles.

Main focus of the research and development network is not the development of new analytical methods, but the adaptation of existing measurement techniques or sensors and the verification of their suitability. In addition, a multitude of different sensors should be adapted to reach a broad application spectrum for all relevant contaminations. Final goal of all the investigations and developments is the production of a prototype, which - after testing - can be transferred to a saleable commercially available product, which handheld hardware and problem adapted software and quality assurance systems.

4 Specifications for the systems

Substances:	Volatile organic compounds (VOC), mineral hydrocarbons, polycyclic aromatic hydrocarbons (PAH), heavy metals.
Measuring methods:	Sensors, gas chromatrograph, laser induced fluometry, photometry.
Detection limit:	According to the existing by.-law values in the Federal Republic of Germany.
Compartment:	Soil, sediment, aquifer.
Measuring depths:	Soil up to 5 m; groundwater monitoring wells up to 20 m.
Sensor module:	Diameter 29 mm; length < 75 cm.
Energy consumption:	12 V DC; <10 W

5 Structure of the research network and goals for the partners

The whole research and development is subdivided in 5 work packages (WP).

WP I: Project coordination
WP II: Quality assurance and certified reference material
WP III: Definition of requirements for engineering and practical applications
WP IV: Drive-in rods and field tests
WP V: Sensor developments and field tests
WP Va: Soil
WP Vb: Groundwater and leachate
WP Vc: Soil air

From the network structure of the project, the different partners have to work on different tasks:

1 Project coordination - Dr. Johannes Flachowsky
His main task is to give a adequate structure to the whole network and to represent the whole group of projects. He has to control the progress of the work and to harmonize the ideas and conceptions of the different partners. Beside this, he has to install the test set-up at the reference place and to define and to control the suitability test. Furthermore, he has to define the structure of work guides and give recommendations for the practical use in the field. His work is integrated within the research facility for subsurface remediation VEGAS.

2 Clayton - UMWELT CONSULT GmbH - Dipl.-Geologe Alexander Klug
He has to select and describe in detail the sites which are necessary for the field tests of the newly developed instruments. He has to perform the sampling for the comparison of in-situ measurements and laboratory analysis. He has to assist to derive practically useable quality assurance measures for in-situ assessment methods. Finally, he has to check European Union activities in this field to avoid parallel research and waste of resources.

3 PRODATA Gesellschaft für Qualitätsmanagement und Statistik - Dr. Stefan Ulig
His duty is to derive mathematical systems to minimize the experimental efforts to calibrate the different sensor types and additionally to recommend general quality assurance tools for all project partners and to develop validation procedures.

4 BAERMANN und PARTNER - Dr. Axel Baermann
His task is the production of contaminated reference materials (some hundred kg), the construction of the soil structures in the model site with contaminated layered profiles and the assistance during the construction of the laboratory reference sites (in the VEGAS laboratory) and during the field tests.

5 NEUMANN BAUGRUND-UNTERSUCHUNG - Dipl.-Ing. Peter Neumann
He has to lay out the construction for the type of the drive-in rods with suitable mechanical systems which allow to bring the sensors into contact to the inspected metrics (soil, soil air, groundwater...) fast, reproducible and without cross contaminations. He has to produce the systems (and prototypes), taking into consideration the different measuring systems.

6 OPTIMARE GmbH - Dipl.-Chem. Rainer Schultz

His task is to coordinate all the available experiences and all available instrumentation of laser induced fluorescence (LIF) in cooperation with the University of Potsdam and the laser laboratory of Göttingen. These joint efforts are focussed to develop a LIF measuring system which can be driven into the soil to measure mineral oil hydrocarbons like gasoline, diesel, kerosene and also polycyclic aromatic hydrocarbons as well as BTEX components. Using fibre optic systems, the instrument can be build mechanically robust and integrated in the driving rod tip.

7 VEGAS, Institute of Hydraulic Research, University of Stuttgart - Dr.-Ing. Norbert Klaas
The task of VEGAS is to build up and to manage the laboratory reference site in a container within the research facility. Exchangeable soil columns have to be installed for the tests and the instruments of all project partners and therefore offer comparable and reproducible tests and validation conditions. By this way, the performance of the sensors as well as the applied mechanical system (sensor module drive-in rod....) can be tested for their stability concerning accelerations as well as heavy contaminations (NAPL) in the soil structure.

8 VEGAS, Institute of Hydraulic Research, University of Stuttgart - Dr.-Ing. Baldur Barczewski
The main goal of this project is to apply low cost sensors which are used in industrial production sites, medicine, automotive industry or security systems, for the purpose of site assessment systems. To reach this goal, the new sensor based instruments for groundwater, soil air, leakage and additionally for the detection of NAPLS (non-aqueous-phase-liquid). Fluid contaminants have to be adapted to build the systems robust, miniaturized and applicable in the drive-in rods. The sensors have to be tested and validated for the relevant contaminants.

9 FORSCHUNGSZENTRUM KARLSRUHE - Dr. Joachim Goschnick
He will miniaturize a so called electronic KANINA and produce a vibration safe sensor which can be included in the drive-in probe system. With this type of sensor, a measurement of volatile organic compounds in the soil air can be performed and a real time software supported evaluation during the inspection will be available.

10 FORSCHUNGSZENTRUM KARLSRUHE - Dr. Michael Rapp
His task is to miniaturize an array consisting of surface acoustic wave sensors (SAW) and to produce a vibration safe sensor, which can be integrated into the drive-in rod tip. Also this system is capable to perform measurements of volatile organic contaminants in the soil air. This system is based on a special sensor system (SAGAS) which has been developed to survey chemical processes.

11 FORSCHUNGSZENTRUM KARLSRUHE - Dr. Jochen Bürck
His goal is to miniaturize an existing evanescent-field photometer system (EVAS) based on near infra red absorption technique for direct contaminant concentration measurements (for example chlorinated hydrocarbons) which are dissolved in the groundwater. The system has to be constructed very robust and applicable in standard groundwater monitoring wells.

12 TU HAMBURG-HARBURG, Arbeitsbereich Messtechnik - Prof. Gerhard Matz
The main task of the TU Hamburg-Harburg is the conception of the electronic system for the sensors including the power supply and the wireless signal transmittance by an optical system. This task will be done by cooperation with the Firma Neumann Baugrund. Additionally, Prof. Matz will develop a miniaturized gaschromatography-module for the analysis of the soil air, which also will be used a test sensor.

13 FRAUNHOFER INSTITUT FÜR PHYSIKALISCHE MESSTECHNIK - Dr. Werner Konz
His task is to miniaturize an existing IR spectrometer (BPS 100 from the EU project IMSIS) and to develop a construction which is mechanically stable, so that the complete configuration of the sensor can be integrated into the drive-in-rod. This system shall be used specially for the determination of chlorinated hydrocarbons in groundwater and leachates.

The projects were launched in January 2002. Presently, the main focus is on the miniaturizing of the measuring systems, and on the tests of their suitability. Additionally, the field reference test site is presently under construction and will be used for validating purposes of the instruments.
In the following presentations, some of the results like field measurements and development of miniaturized sensor types are presented in detail.

Field Measurements of Soil Gas

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Prototype of a field screening tool for the detection of VOC in soil gas

The relative simplicity and ease of handling has resulted in the use of metal oxide sensors (MOX) and quartz microbalance sensors (QMB) to detect contaminants which are typically found in the gas phase in the unsaturated zone on old industrial sites and brown fields. While metal oxide sensors can be tested and calibrated for the different contaminants without modification, quartz microbalance sensors have to be coated with suitable sorptive polymers for the target contaminants. A prototype with integrated MOX and QMB as well as sensors for the measurement of temperature, moisture and pressure and a sampling port are being developed and calibrated for different volatile organic compounds (VOC) under laboratory conditions. For field tests, the sensor system has been adapted to a common driving rod, as used in geotechnics, to ensure robustness and an easy handling of the instrument (FIGURE 1).

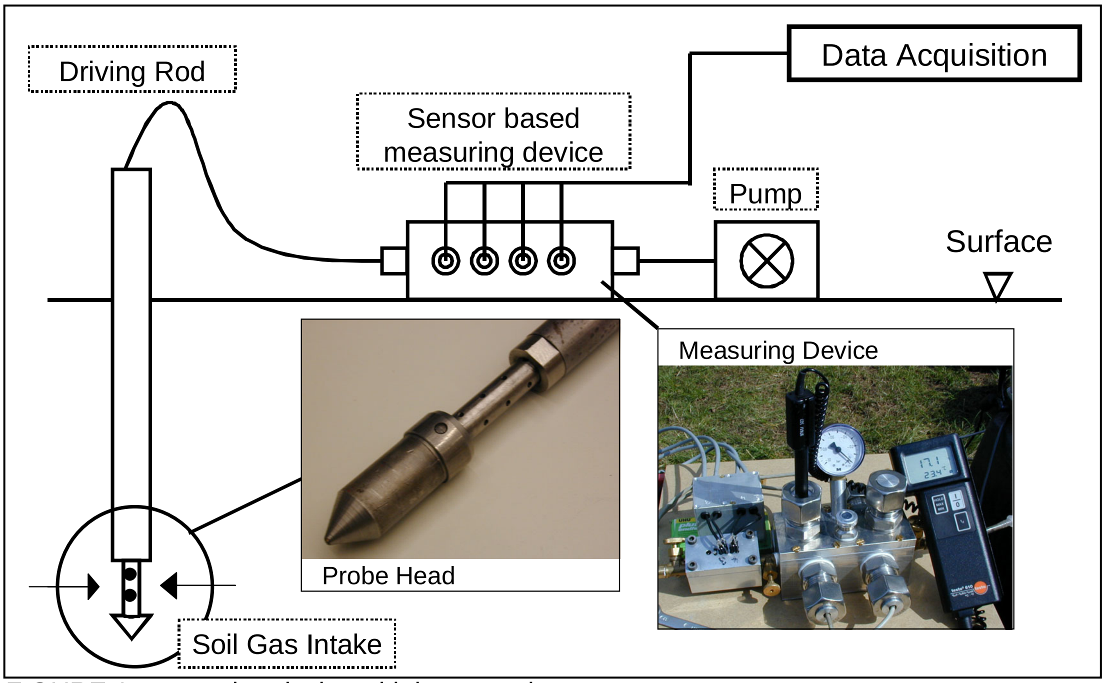


FIGURE 1: measuring device with integrated sensors

The laboratory tests show that these sensor types are particularly suitable for measuring the respective contaminants in the soil air. The sensitivity of the sensors is sufficient for the concentration range typically found for both chlorinated hydrocarbons and most mineral oil hydrocarbons thus resulting in a semi-quantitative estimation of the occurring contaminants. It can be shown, that with simple pattern detection, the distinction between chlorinated hydrocarbons and mineral oil hydrocarbons is possible (FIGURE 2).

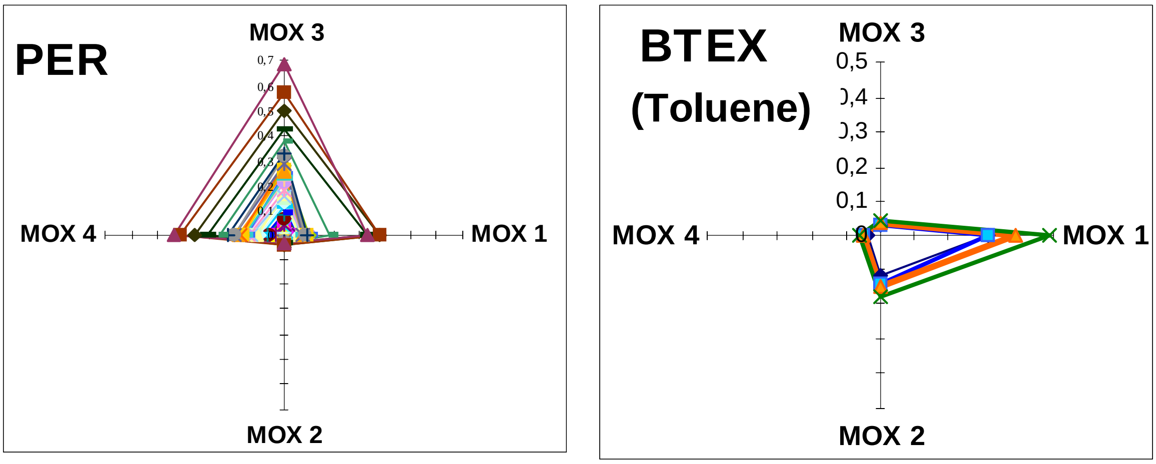


FIGURE 2: pattern for halogenated – non halogenated contaminants
(PER – Perchlorethylene, BETX – Benzene, Ethylbenzene, Toluene, Xylene)

Field application at various sites

The field applicability of this assembly (FIGURE 1) has been tested on various sites and has proven suitable for the purpose. A comparison of field data measured at contaminated and non contaminated sites demonstrates, that the sensor signals clearly result from the contamination and matrix effects are negligibly small (FIGURE 3). The prototype demonstrated sufficient sensitivity to detect volatile contaminants in the field.

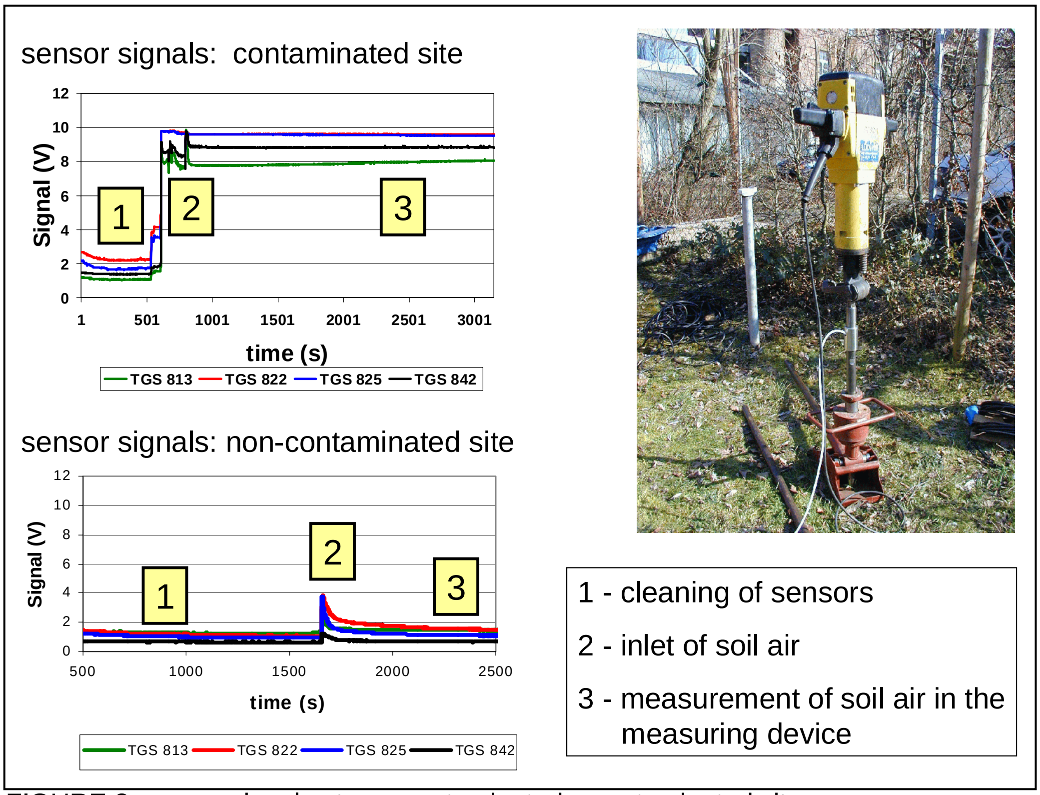
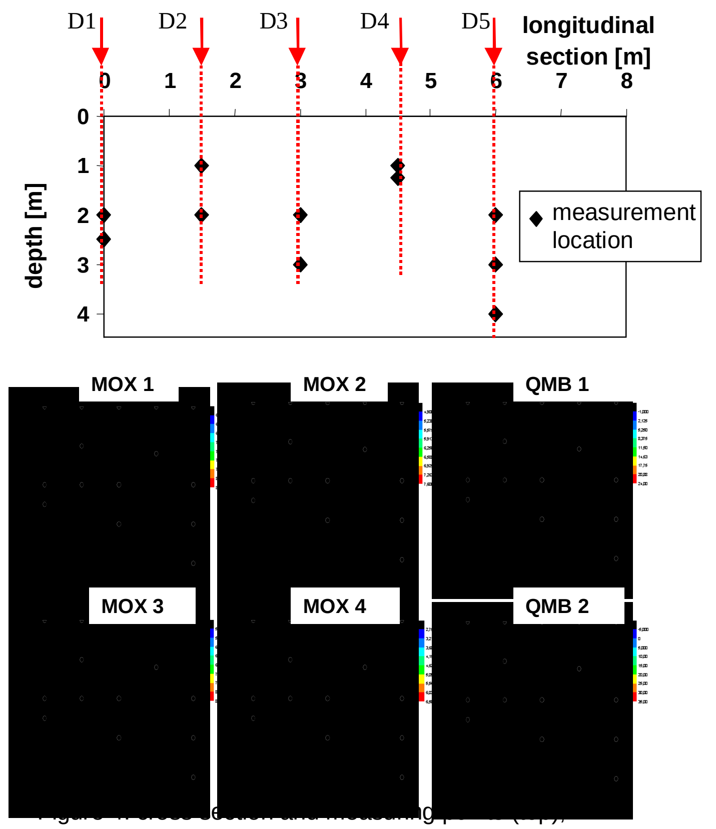


FIGURE 3: sensor signals at non contaminated – contaminated site

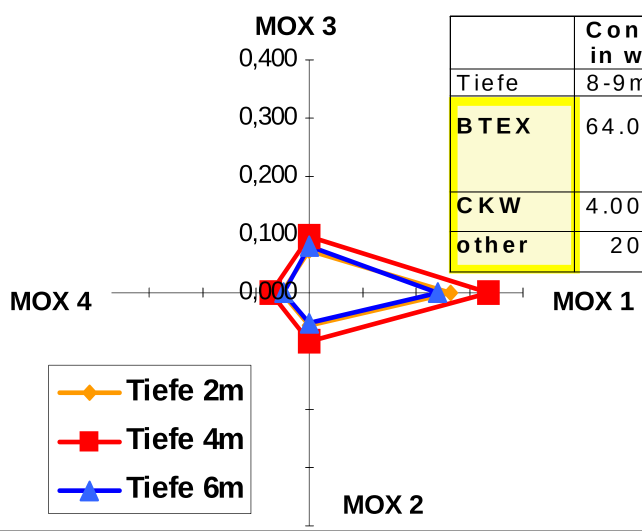
Measurements at a refinery proved that the distinction between chlorinated and mineral oil hydrocarbons can be made in the field. The increase or decrease of the signal depending on the distance of the respective measurement location from the contamination source could be shown as well.



distribution of contaminant concentration (bottom)

A systematic measurement along a cross section at a junkyard showed that many on-site point measurements of soil gas using the prototype provide detailed information about contaminants and their distribution. At each drilling (D1 to D5) several measurements of VOC have been carried out according to the schematic drawing of the cross section (FIGURE 4: top). The sensor signals have been interpolated over the cross section for the individual sensors (FIGURE 4: bottom). The blue colour indicates a low concentration while red indicates a high concentration. FIGURE 4 clearly shows that the concentration of VOC varies significantly on a small scale. As expected from the diffuse input of contaminants in the past, high concentrations can be detected in the unsaturated zone starting about 1m below ground surface and reaching depth of not more than 4m. There is no significant input of contaminants into the groundwater at 5m below ground surface. The results obtained from the conventional site assessment, i.e. taking a few samples, are: contaminants in the unsaturated zone and no significant contaminants in the groundwater. This result is similar to the findings of the on-site measurements but the information is much less detailed.

A few measurements have been conducted at an old gravel-pit which was refilled with industrial waste. The conventional site assessment shows contamination in the unsaturated zone. Chemical analyses of water samples indicate several different contaminant groups as following: 94-95% sum of BTEX, 4-6% sum of chlorinated hydrocarbons and less than 1% other compounds (FIGURE 5). Measurements of VOC with the prototype show a significant rise of the signals with decreasing distance to the contamination source. The pattern of signals is shown in FIGURE 5.



	Concentration in water [µg/l]		[%]	
Tiefe	8-9m	13-14m	8-9m	13-14m
BTEX	64.000	18.000	**94**	**95**
CKW	4.000	700	**6**	**4**
other	200	200	**0,3**	**1**

FIGURE 5: Measurement at an old gravel pit: pattern of sensor signals (left) chemical analyses of groundwater sample (top right)

From the pattern of the sensor signals it can be gathered that MOX 1 and MOX 2 are very sensitive to the detected compound which indicates BTEX in the soil air. Additionally MOX 3 responds to the measured soil gas which indicates chlorinated hydrocarbons (HCH). Compared to MOX 1 and 2 the signal of MOX 3 is small but showing the presents of CHC in a low concentration. This result compared with the chemical analyses demonstrates that the evaluation of the signal pattern results in a reliable semi-quantitative prediction. Furthermore the increase or decrease of the signal depending on the distance of the respective measurement location from the contamination source and indicates a rising concentration with increasing measurement depth.

SAW Sensor System for Integration into a Soil Probe

Another possibility to measure contaminants in the soil air is a miniaturized detection system based on existing SAW sensor technology and its integration into a standard soil probe. The system is designed to give detailed information about soil contamination in-situ and in real time while the soil probe is driven into the ground.

The detection system is using an array of eight surface acoustic wave (SAW) sensors working at operating frequencies around 433 MHz. Each sensor is covered with a different polymer to provide a characteristic chemical fingerprint. Electrical contact to the sensors is made by capacitive coupling. This approach is better suited for the design of a shock-proof system than the use of fragile bonding wires or spring contacts. Because only small amounts of soil gas may be available for in-situ analysis, the gas volume of the sensor array is minimized by mounting the sensors upside-down onto two gas channels milled into the sensor board, containing a total gas volume of 80 µl. To keep the sensor array firmly in place, a robust holder is being developed which also accommodates the electronics board performing the read-out and pre-evaluation of sensor data. The data output can be evaluated in real time using a laptop computer. For this purpose, several methods of pattern recognition are used to identify the detected analyte(s) and to produce a user-friendly visual output.

In order to create a robust and compact gas sampling stage, the design of the system does not use any valves. On the other hand, continuous gas sampling will result in signal drifts due to changes in humidity, temperature, pressure, etc. In addition, the use of a reference gas is impeded by the small dimensions of the soil probe. These problems are circumvented by using a sampling technique where the sensor array is connected in-line with a filter, and the gas flow is reversed periodically. Thus, the sensor array is alternatingly exposed to filtered and non-filtered soil gas, respectively, where the former serves as a reference gas. The soil gas is aspirated using a miniaturized rotary vane pump. Activated carbon is used for the filter. The gas flow rate is kept low in order to maximize the time to saturation of the filter and to minimize the amount of filter material needed.

Figure 6 shows as a preliminary result the response of the eight SAW sensors when exposed to 1270 ppm toluene under laboratory conditions. The gas flow is reversed periodically with a period of 130 s. A rapid rise in the frequency signal indicates exposure to non-filtered analyte. Switching to filtered analyte results in a somewhat slower frequency drop, indicating outgassing of the filter material and / or dead volume effects. Since the shape of the response curve is reproducible, the data point at the end of the latter phase can be used as a reference value. From the signal pattern of the eight frequency responses, information about the type(s) of analyte can be deduced.

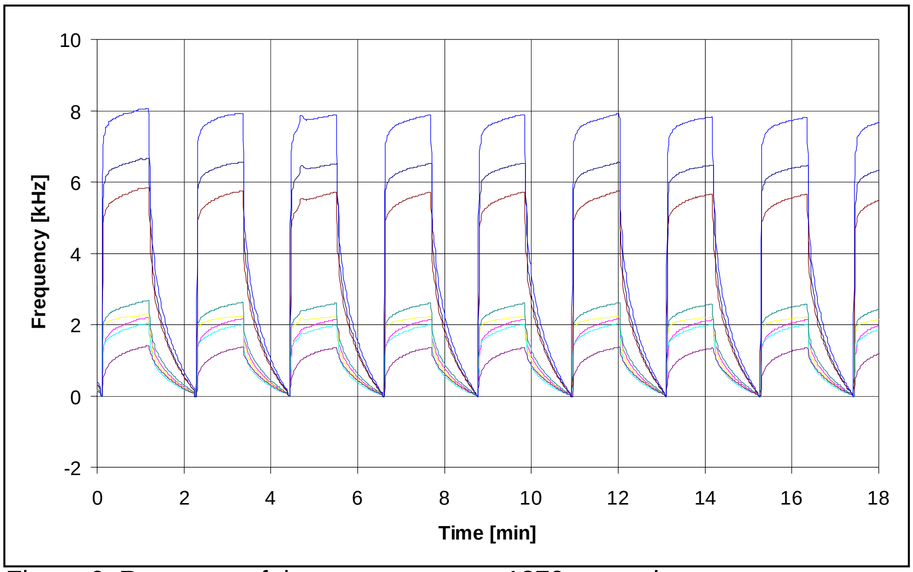


Figure 6: Response of the sensor array to 1270 ppm toluene

An amount of 1.5 g of activated carbon was chosen because it was found sufficient for continuous exposure to analyte vapor for more than one hour even at fairly high concentrations. As an example, exposure to 5700 ppm toluene resulted in breakthrough of the filter after more than 75 min (data not shown). Since the period of one cycle should not be less than about 40 s, the filter would last for well above 100 measurement cycles before it has to be replaced. Therefore, even detailed depth profiles of soil contaminations can easily be recorded.

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CONE PENETROMETER WITH WIRELESS OPERATING IN-TIP GASCHROMATOGRAPH

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Cone penetrometic detection of hazardous compounds is the fast alternative to soil sampling and laboratory analyses. Ring-analyses with several soil samples have pointed out, that the laboratory analyses of excavated soils depend heavily on the way of extraction and sample preparation. The alternative is an online detection system based on a cone penetrometer enables the characterization of a large variety of contaminants in soil on-site to avoid mistakes made between sampling and analysis in the laboratory.

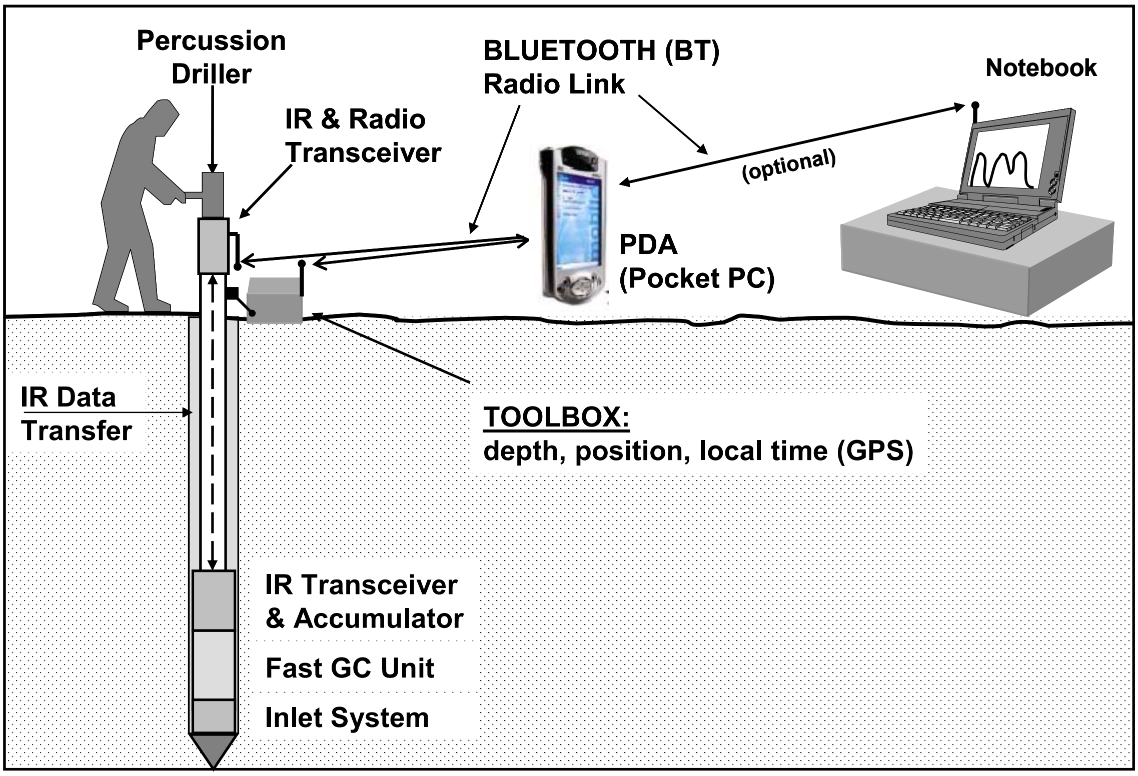

Figure 1 – Cone Penetrometer System with Fast GC Unit and Wireless Data Transfer

A new easy-to-use-system has been constructed, which avoids tedious harness handling through the penetrometer drill stem (figure 1). Gaseous samples are taken in-situ nearby the cone-tip of the penetrometer tubing. A shock proved, accumulator powered, micro controlled PID-GC unit analyses gas samples for VOCs like BTEX inside the tip of the cone penetrometer. The recorded data and the control commands are transferred digitally by IR light through the penetrometer tubing to the surface, where data is forwarded by digital radio transmission to a notebook or PDA (Personal Digital Assistant, Pocket PC) in the transportation vehicle or base camp up to a distance of 100 m.

Data exchange between subsoil GC unit and surface toolbox is achieved by IrDA modules, which control connection and report the IR link status to GC and Notebook/PDA via the radio data link. The radio data link is based on BLUETOOTH modules. The data link modules are accumulator powered and are located in a special adapter between drill rods and percussion driller. A special shock absorption system protects the module of serious harm or destruction by drill shocks.

The actual position, depth and local time of sampling are detected separately in the surface toolbox. They are transmitted wireless to PDA on request for data acquisition and quality assurance. The depth propagation of cone penetrometer is measured online by an optical navigation system onto the outer wall of the drill tubing and reaches an accuracy of 1 cm absolute. The position and local time are acquired by a GPS module. The accuracy of position is in a range of 2–5 m depending on the accuracy of the GPS module.

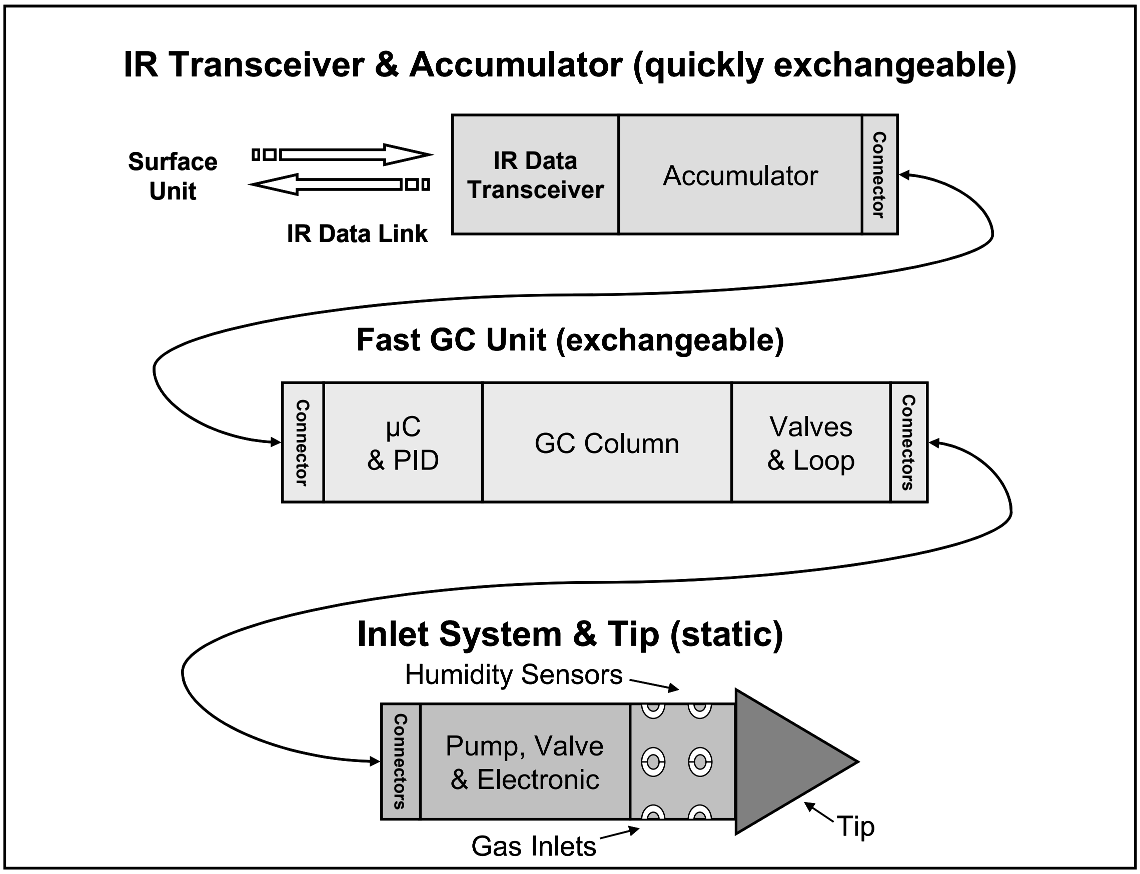

Figure 2 – Modules of the Sensing & Intake Unit

The sensor unit consist of three modules: one for IR data transfer and power, followed by the GC unit and finally an inlet system. These modules are designed for easy maintenance resp. quick exchange of accumulator module. The system is designed to fit in conventional cone penetrometer tubing (34 mm ID, 50 mm OD). A special shock absorption system protects the module of serious harm or destruction by drill shocks. The length of the sensor unit is about 1.2 m. The length of one extension rod is 1 m.

The GC consists of a filter intake with a low death volume and loop injection. The humidity of soil is sampled nearby the inlets. Humidity recording is done continuously during drilling, if the arrival at the water horizon is detected immediately the safety valve is closed and drilling is stopped to prevent the system from entering water. Compound separation takes few seconds on a multicapillary column. The column is exchangeable to a packed column, which could be used to improve the performance of the separation. After cleaning-cycles the GC switches to a stop flow mode to save energy.

The GC may generate up to 300 GC runs with fresh accumulators, respectively 3 hours of time to analyse. The sensitivity of GC unit is better than 10 mg/kg BTEX and PER in air. It enables e.g. BTEX monitoring within 10 seconds per analysis during pushing.

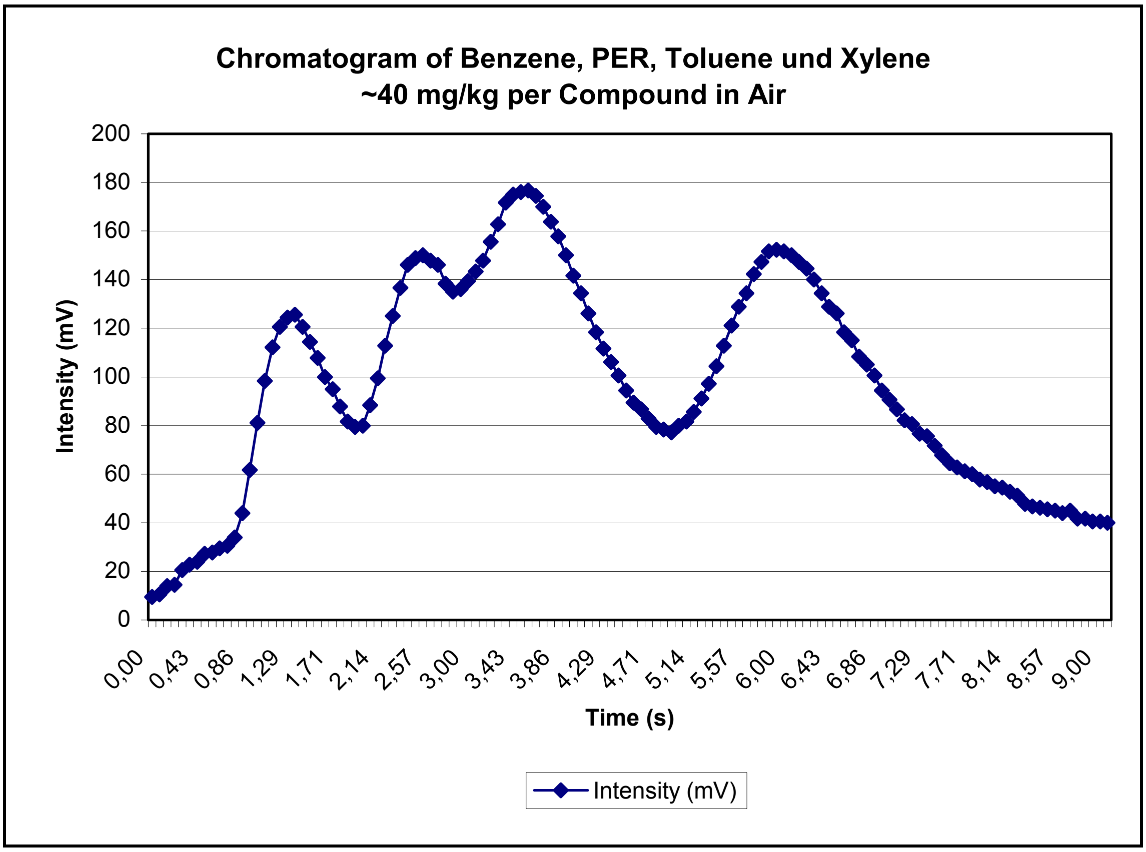

Figure 3 – Chromatogram of BTEX + PER

The PDA controls the fast GC unit via the wireless radio data link. It acquires the depth, position and local time of the surface toolbox by wireless data link too. The software displays the chromatograms and calculates the concentration of detected compounds. The data is stored on a memory card which enables data transfer to a PC. On the other hand the data could be transferred by the BLUETOOTH radio link to a PC. The PDA informs the user by an acoustical signal if the desired depth is reached and starts the analysis automatically or on user request.

The use of wireless data links on the surface and in the drilling rods on the one hand and accumulators and a PDA on the other prevents the handling with cables. Further on the modular design enables easy maintenance and exchange of the accumulators and thus is a powerful and time saving new tool for contaminated soils analyses on-site.

IN-SITU MEASUREMENT OF DISSOLVED CONTAMINANTS IN GROUNDWATER

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Introduction

In the joint project sponsored by the DBU in-situ instruments are developed which allow the detection of dissolved contaminants in the groundwater. Two main concepts are being used to detect PAH (polycyclic aromatic hydrocarbons), CHC (chlorinated hydrocarbons) and BTXE substances.

Detection of PAH

Polycyclic aromatic hydrocarbons show the effect of fluorescence in the UV-range of light. By exciting the samples with wavelengths of 200-300 nm the PAH deliver a fluorescent light in the range of 300 to 500 nm. Two assemblies are currently being developed at *VEGAS*: One system is based on optical fibers that are used to guide the light to the point of measurement (Figure 1). It can be equipped with a wide choice of light sources in order to detect different substances. By the use of special UV conducting glass fibers PAH can be detected. Different fluorescing tracers can also be measured and allow multi tracer experiments, which can be used to measure groundwater flow velocities and directions in-situ. Using fiber optic systems the whole instrument can be miniaturized and easily used in groundwater monitoring wells.
The fiber optic fluorometers for tracer tests being used for years in field measurements have proven their applicability. Therefore also the modified PAH system will be suited for field measurements. Using two photodetectors with different filters which absorb a) the excitation light and b) the emitted fluorescent light disturbances caused by particles in the sample can be eliminated.

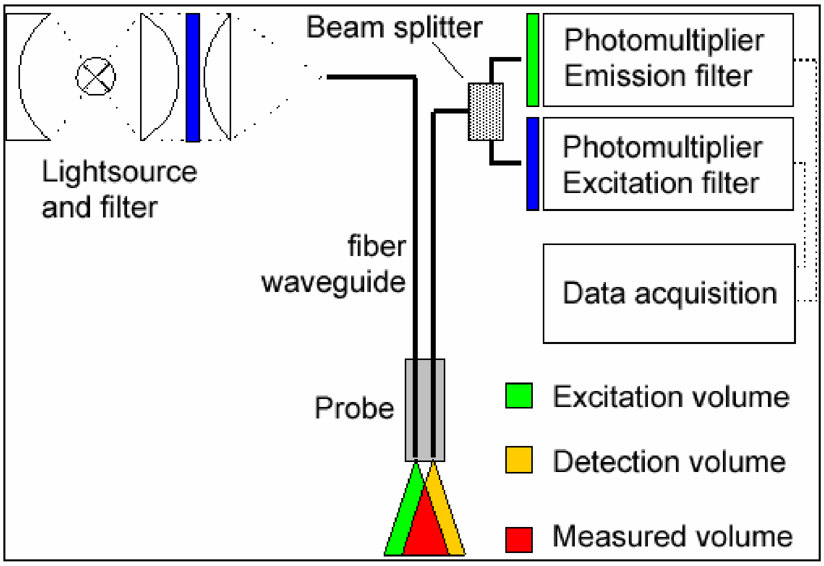

Figure 1, Fiber-based fluorometer

The other more or less classical fluorometer system is to be operated in-situ and has to fit into a driving rod with an inner diameter of approx. 30mm (Figure 2). As a very small sized UV light source a flash lamp is being used. It delivers high luminance in a wide spectral range. As detector an avalanche photo diode (APD) or a very rugged photomultiplier tube that has been tested in oil exploration drillings (PMT) can be deployed. The light source and detector are built right into a standard driving rod that is

commonly used as geotechnical equipment for site exploration. The system has to withstand the vibration and shock stress from the hammer that is used to drive the system into the ground. It has to be very small to fit into the 30mm inner diameter of the driving rod, has to run on battery and be operated remotely.
The setup inside the drilling equipment is still in an experimental stage.

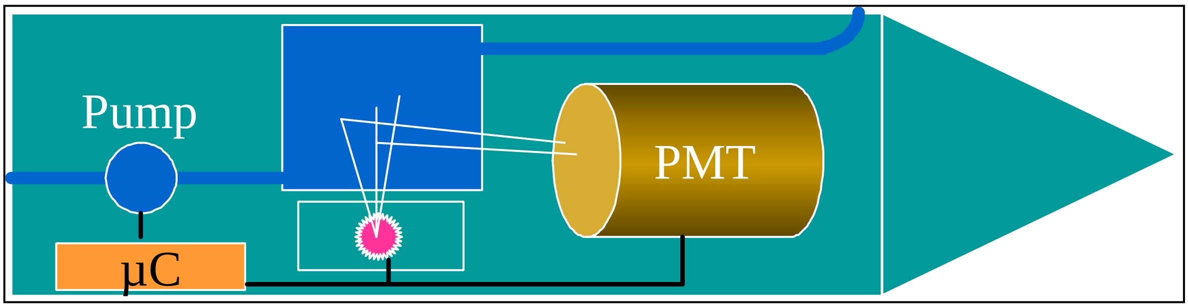

Figure 2, Fluorometer setup in drilling equipment

The fiber optic system is currently used in a couple of applications. A three level tracer experiment has successfully been carried out to detect groundwater flows. Other tracer tests have been performed as a standard method in a variety of experiments. With this setup PAH can currently be detected down to concentrations of 1 ng/m³.
As an exemplary experiment Figure 3 shows a continuous PAH measurement during a medium scale remediation experiment. Field tests at a PAH contaminated site are presently carried out.

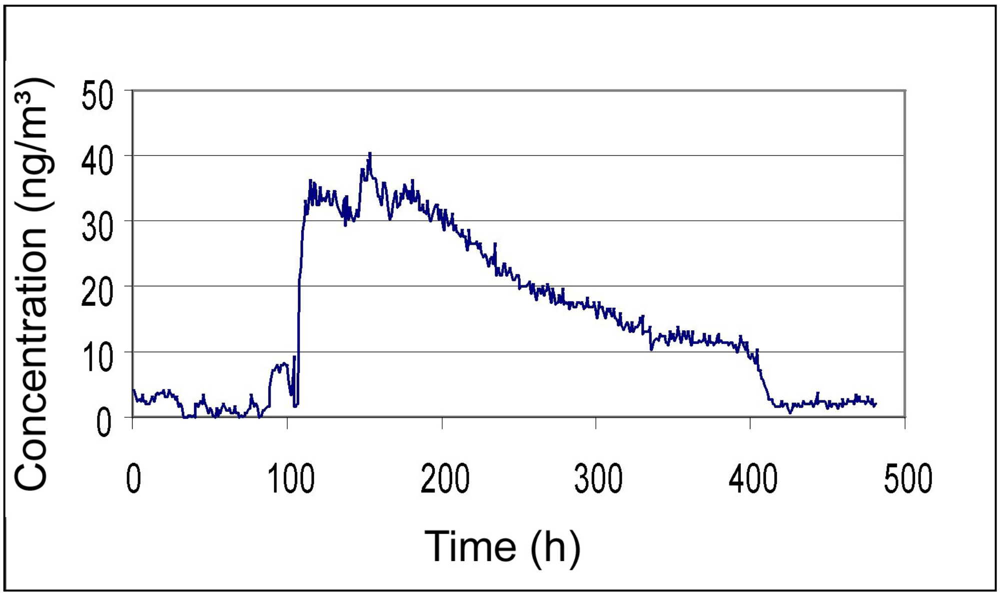

Figure 3, PAH remediation experiment

Detection of dissolved hydro carbons (HC)

Because some contaminants (CHC's, HC's) don't show fluorescence effects, other ways have to be used to detect those contaminants in-situ. One often used laboratory method is the UV absorption photometry. Because up to now no optical fibers with good transmittance in the range of 200 nm have been available other concepts are necessary. Measurements of HC's are possible by evanescent field absorption (EFA) measurements with optical fibers as sensing elements. In that case very long fibers (≈ 50 m) are used and operated in the IR-light range. Although the absorption in the IR range is very low, due to the fiber length the sensitivity is sufficient for medium concentrations (≈ 0.5 µg/m³)

The measuring light transmitted in an optical fiber by total reflection at the core/cladding interface produces a standing wave whose evanescent field penetrates into the fiber cladding over some distance, which is in the range of the wavelength of light used for the measurement. The quartz glass fiber NIR-EFA sensor developed at the Institut für Instrumentelle Analytik (IFIA) has a hydrophobic silicone cladding, which extracts nonpolar HC's from the aqueous phase. The extracted HC species can absorb energy from the portion of light in the evanescent field. Such interactions (Figure 4) lead to a specific absorption of light intensity at the corresponding C-H overtone bands of HC compounds.

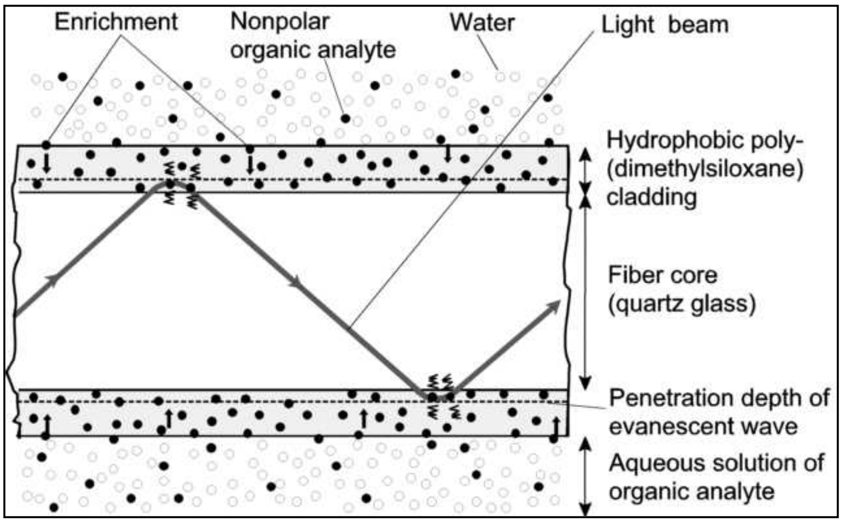

Figure 4, Evanescent field absorption (EFA) sensing principle

EFA absorption measurements of HC substances enriched in the fiber PDMS coating can be performed with any commercially available NIR spectrometer that has fiber-optic adaptation. Light from a tungsten halogen lamp first is conducted over the input fiber into the sensing fiber. The light attenuated by the HC absorption in the sensing fiber is then transferred over the output fiber into the corresponding spectral evaluation unit.

In situ determination of the HC concentration in a deep monitoring well is performed by connecting the sensor by all-silica fiber cables with a longer length (50 -100 m) to the spectral evaluation unit. After absorbance zero-setting in a beaker filled with pure water the sensor attached to the fiber cables is lowered into a pre-set water level and measurements are started.

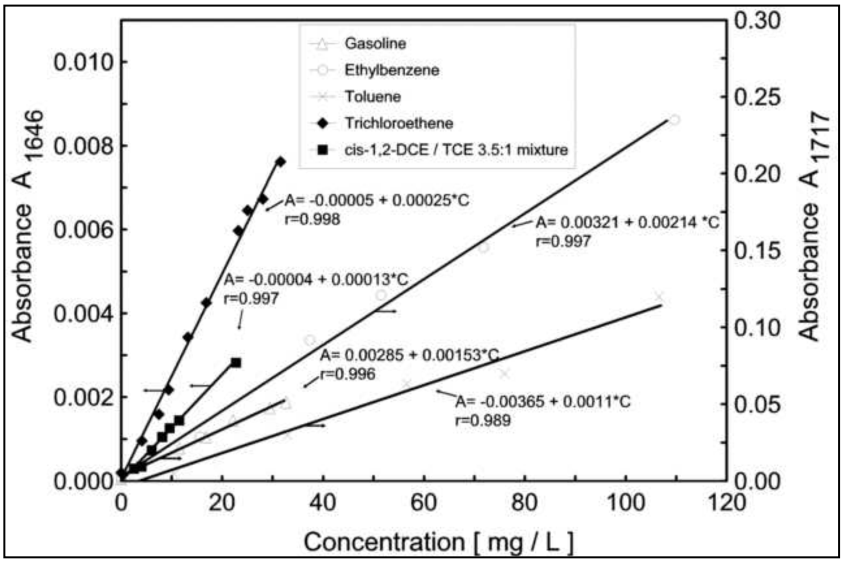

Figure 5, Calibration functions for different nonpolar hydrocarbon compounds

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ACTIVITIES OF THE SENSPOL AND THE NICOLE NETWORK CONCERNING FIELD INVESTIGATIONS AT CONTAMINATED SITES

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INTRODUCTION

It can be stated that the available equipment for contaminated land site investigations is incomplete and/or inadequate to meet the increasing data-requirements for soil environmental problems. On top of that the environmental policies in the European Community evolve (e.g. the EC Soil Strategy paper) and from this additional needs can be identified. It is also clear that the economic aspects of remediation of contaminated land and the effects on the spatial planning process lead to solutions in which land quality management and soil- and groundwater monitoring require increasing attention.

At a European level several networks can be identified aimed at developments and exchange of knowledge relevant to sustainable management of the subsurface.

The aim of the *SENSPOL* Thematic Network (as the successor to the BIOSET network) is to enhance the development of sensors for practical applications in the abatement of water pollution from contaminated land, landfills and sediments.

NICOLE is the acronym for Network on Industrially COntaminated Land in Europe. It is the principal forum that European business uses for the dissemination and exchange of scientific and technical knowledge and ideas relating to all aspects of industrially contaminated land.

NICOLE and SENSPOL have organised several workshops related to contaminated sites and groundwater and published reports to present the state of the art (e.g. E. Domínguez and S. Alcock, 2001, 2002; Bardos, 2003; van Ree and Carlon, 2003) and future developments attaining a balance between costs and uncertainties resulting from site characterisation and thus reducing the overall soil management costs. Based on the common interests of the SENSPOL and NICOLE networks links have been established resulting in coöperation in several project-activities.
In this paper two projects will be addressed:

- Seville technical meeting (Aznacollar mining site).
- Bridging gaps between sensor developers and (end) users in a pragmatic approach (GAPS-project).

SEVILLE TECHNICAL MEETING *(November 6 – 9 th 2002)*

Field technical meetings are needed to demonstrate that sensors and analytical methodologies developed in EU projects can be applied to soil samples on site. Previous field meetings in the Environment Programme took place in September 1997 and 1998 in Berlin (Hansen et al, 1999) and in April 2000 in Barcelona (Barcelo et al, 2000). The Seville Technical Meeting has been jointly organised by SENSPOL and the EU-project DIMDESMOTOM (Development of IMproved DEtection Systems for MOnitoring of TOxic heavy Metals in contaminated groundwaters and soils), in collaboration with the NICOLE network. The goal was to apply the latest sensing technologies at a site contaminated by metal mining activities, to properly evaluate the advances and limitations in the monitoring of contaminated sites for sustainable land management and to determine further steps to commercial exploitation.

Technology developers from eleven European countries were joined by representatives from industry, consultants and an environmental agency. Some 17 different instruments have been brought to the site in a cooperative effort to demonstrate the applicability of new field measurement techniques as well as to determine further steps to commercial exploitation. These included:

- Electrochemical sensors using different forms of anodic stripping voltammetry and constant current chronopotentiometry combined with several types of screen printed electrodes. A preconcentration (deposition) step is followed by a measurement (stripping) step in which free concentrations of Pb(II), Cu(II) and Cd(II) are determined simultaneously. Figures 1 and 2 show examples of a screen printed electrode and an overview of the components of the system.

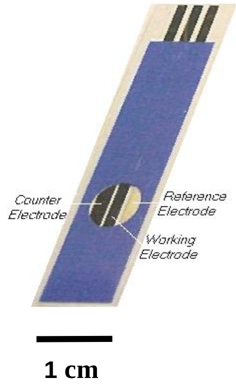

Figure 1: Typical configuration of a screen-printed electrode
(after Md-Noh, Cranfield University)

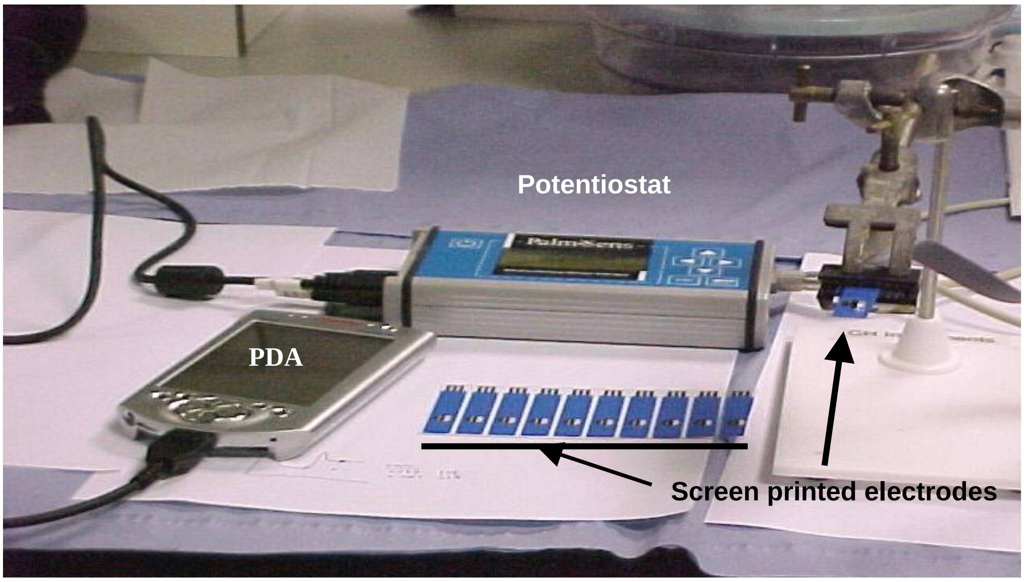

Figure 2. Electrochemical sensors (for Pb, Cu, Cd) with potentiostat and PDA for dataacquisition.
(Photo Rashid Kadara, Ibtisam Tothill, Cranfield University)

- An amperometric biosensor using screen printed electrodes, which measures toxicity by inhibition effects on urease and is sensitive to Hg(II), Ag(I), Cu(II) and to a lesser extent to Pb(II), Zn(II) and Cd(II) and a electrochemical DNA biosensor measuring overall toxicity.
- A luminescent bacterial sensors for measuring the bioavailable fraction of Cd, Pb, Zn, Cu, As, and Hg, and a bioluminescent fiber optic sensor for Hg and As.
- Toxicity testing instruments (Checklight ”ToxScreen Multi-Shot Test, ToxAlert®100 and ToxAlert®10)
- A field probe for pH, EC, TDS measurement
- A lead automatic analyser AQUAMET using a ion-selective electrode (aimed at on line monitoring).
- Pulse-neutron borehole device in which interaction of neutrons with the surrounding medium can be used to monitor changes.

In a two-day field session on the mining site participants were provided with soil samples (including aqua regia, acetic acid and aqueous extracts) as well as water samples before and after waste water treatment and groundwater. For comparison with the field data chemical analyses were performed, but these data were not available to the participants during the field session. Participants have submitted their preliminary data at the end of the meeting to evaluate the data that can be delivered on site. Reports were submitted some weeks later providing the participants also with the opportunity to check results in their own laboratories.

Below the results obtained by one of the participants (Setford et.al, 2002) using differential pulse anodic stripping voltammetry and screen-printed carbon electrodes are given as an illustration. The reference values are determined by means of ICP.

Table 1: Water samples before (693, 694) and after (695, 696) the waste water treatment plant (mg l^{-1})

Sample	693	694	695	696
Pb				
ICP	0.89	0.74	<0.05	<0.05
Asv field	1.11	1.02	0.02	0.02
Asv lab	1.09	0.84	<	<
%	123	114		
RSD	9.3	8.3		
Cu				
ICP	0.18	0.18	<0.05	<0.05
Asv field	-	1.78	0.05	0.05
Asv lab	0.18	0.12	<	<
%	100	68		
RSD	18	15		
Cd				
ICP	0.62	0.63	<0.05	<0.05
Asv field	0.65	0.99	0.02	0.02
Asv lab	0.74	0.89	<	<
%	119	141		
RSD	8	3.9		

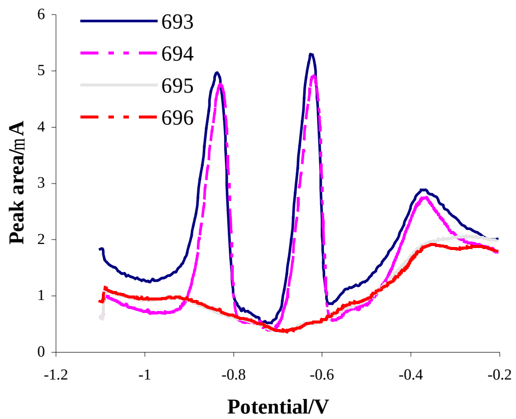

Figure 3: Cd, Pb and Cu in water samples

Although the results have not been fully elaborated yet the following observations can be made:

- The instruments provided sensible and usefull data in line with the chemical analytical results obtained. Detection limits also were within range of relevant EPA and EU standards.
- Considering that most sensors and instruments are still under development as part of researchprojects important aspects for field operated instruments like field portability, operatibility, robustness, selectivity, interpretability in the field look very promissing.
- Further development is needed in the area of rapid soil extraction procedures that can be used in the field.

The outcome of the Technical Meeting at the Aznalcollar mining area will be published in a detailed report that will be available through SENSPOL.

BRIDGING GAPS-project

Within the NICOLE network there are a number of members involved in studies applying innovative sensors to land quality management problems and with expertise regarding requirements and conditions for the application of new technologies. Identifying suitable sensors and instruments for contaminated soil and groundwater and implementing these is costly, time consuming and hampered by the lack of expertise necessary to redesign/adjust instrument to the specific needs of practioners.
On the other hand a large specialist community involved in sensor development for a wide range of environmentally relevant parameters exists. Through the networks Bioset and its successor Senspol a wide range of prototype sensors are available. From a soil- and groundwater point of view (characterisation and monitoring) the existence, availability and potential application of technologies under development is not immediately obvious for technical and economic reasons. For the Senspol community identifying enduser-needs in the development of new sensors is an important and challenging task. Also the implementation step, once a prototype sensor is ready for testing in the field, requires strenghtening of relations with end users.

A project (acronym Bridging GAPS) has been set up to share expertise and identify available sensors and instruments that have a potential to be applied in site characterisation and monitoring of contaminated land. Furthermore field applications will be performed to test the usefullness for specific categories of contaminated land problems.
The overall aims of the study are:

- to identify the needs, characteristics and requirements of innovative rapid site assessment technologies to be successfully applied in the field of soil and groundwater investigation from a practioners point of view (selection criteria)
- to create an overview of existing sensors/instruments or sensors under development which (potentially) fulfill these needs (sensor capability study)
- make an initial feasibility check to determine the fieldability of innovative technologies/sensors and make a ranking based on needs and probable success at the present state of development
- to identify a limited number of cases (3-5) which can be used to implement/demonstrate selected sensors or technologies for a significant category of contaminated land problems (proof of concept). A first demonstration for mercury and chlorinated hydrocarbon related contaminated land problems is foreseen in the first half 2003.

At present the inventory study for sensors and instruments is underway. One of the information sources will be the response to questionaires that have been sent out. This inventory should lead to the availability of a sensor catalog.

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SpS 20 Special Session

Short Rotation Coppioce and Organic Matter Recycling as Integrated Tools for Land Remediation and Helping Local Communities: Environmental, Economic and Social Aspects

THE PRACTICAL USE OF SHORT ROTATION COPPICE IN LAND RESTORATION

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Abstract

Developments of polluted sites are often hampered by presence of contaminants. Making use of Short Rotation Coppice (SRC) can return a beneficial use to these sites whilst managing their risks and stimulating *in situ* degradation and stabilisation processes. SRC is also used, in the Netherlands, to treat sediments returned to land. SRC may stimulate biodegradation of biodegradable contaminants like PAHs and mineral oil. It may reduce the bioavailability of poorly degradable or nondegradable contaminants like heavy metals through increasing organic matter in the soil.

SRC cultivation can be combined with recycling organic matter, such as green waste compost, to land, further boosting soil organic matter, and perhaps in time generating a new and uncontaminated soil horizon.

1 Introduction

SRC (Short Rotation Coppice) is a well-established technique, but is yet to realise full commercialisation in many areas Europe. It is a crop of many benefits both in terms of the energy it creates, its ability to create environmental benefit and to assist in the reclamation of “despoiled” sites. It is at its most effective when all these factors combine and the economics of this situation are highly favourable.

The level of use of renewable energy sources in Europe varies. For example, in Belgium biofuels represent only 1% of the primary energy consumption, whereas in Sweden the figure is 20%. Biomass is the most common renewable energy source, most of which is supplied by wood and wood residues from forestry. Wood is burned in wood-fired power stations as well as in domestic homes. The domestic market is strong in France, Germany, Italy, the Netherlands and Sweden. Straw contributes a significant proportion of biomass consumed overall, and is particularly important in Denmark, Portugal and Sweden. The trend in Europe is towards increasing use of renewable energy sources [Dumbleton, AEA Technology, Personal Communication]

In the Netherlands SRC is seen as an opportunity for the re-use and remediation of sediments which are a major “waste” arising by volume in that country, This paper deals with some of the practical issues involved in using SRC in the area of land reclamation and remediation of sites and sediments.

The use of SRC and compost in land remediation is a positive response to emerging markets for renewable energy resources, a legislative push to reduce the landfill of biodegradable matter and an interest in lower input risk management techniques. It also has the further advantage of bringing land back into the economic cycle and so is ideally suited for circumstances where there is at present difficulties in funding remediation. In effect it offers a system by which income is generated from contaminated land without the need for a restoration period where the land is not in use. This has a beneficial effect on the economics and in particular cash flow thus making the economics of both the restoration and the development of a commercial crop highly favourable.

This paper sets out an overview of how SRC can be used in land remediation and sediment treatment, steps for implementing SRC, its social context and a UK and a Dutch case study.

2 SRC for Land Remediation

There is a range of tree species and clones suitable for SRC production. Extensive research has been carried out to screen species and clones for different site conditions, such as nutrient and water availability, and other environmental factors, such as disease suppression. The selection of clones to plant on a contaminated site should take account of the following factors:

- Site characteristics – a comprehensive site investigation should always be undertaken to reveal the nature of the substrate, i.e. soil chemistry, nutrient content, hydrology of the area, the type, extent and of metal loading. Clonal selection should always be based on suitability for site conditions.
- Yields – It is commercially important to plant clones that will maximise yields [Tabbush and Parfitt 1999].
- Mixing clones – The planting of monoclonal plots of SRC is considered unwise owing to the possible spread of certain species-specific diseases, such as rust. By planting a genetically diverse mix, the risk of the spread of disease in a large scale coppice is minimised [Tabbush and Parfitt 1999].
- Metal uptake – Different clones uptake different metals at different rates from the substrate. Some clones accumulate metals with considerable detriment to their yield whereas other clones are more tolerant of contamination [Riddell-Black et al. 1997]
- Harvesting – Mechanical harvesting must be possible, which gives limitations to the shape of the clone.

The yield of biomass from SRC depends on environmental and climatic conditions throughout the growing season. When biomass is grown on contaminated or restored land the situation is complex, so yield calculations can vary widely. Careful management based on a sound site appraisal can produce commercially viable yields. For example, SRC on ex-agricultural land can produce as much as 17 odt[1] per ha. Even a crop on a well reclaimed site can produce 10 odt per ha or more [Birse, British Biogen, Personal Communication] if well managed. On contaminated sites yields can be limited by contamination, such as heavy metals, pyrites or organic compounds, however treatment by the addition of organic matter, and selection of clones tolerant to the type of contamination present, may overcome problems arising from contamination.

Phytoremediation is the direct use of living green plants for *in situ* risk reduction for contaminated soil, sludge's, sediments and groundwater, through contaminant removal, degradation, or containment. An added advantage of phytoremediation is that it re-establishes a vegetative cover at sites where natural vegetation is lacking due to high metal concentrations in surface soils or physical disturbances in superficial materials. Metal-tolerant species can be used to restore vegetation to sites, thereby decreasing the potential migration of contamination through wind erosion transport of exposed surface soils and leaching of soil contamination to groundwater [US EPA 1999, 2000].

Plants may affect or effect remediation in a number of ways, including:

- Encouraging degradation activity by commensal organisms (e.g. pseudomonads) and symbiotic organisms (e.g. mycorrhizal fungi, rhizobia), encouraging activity of parasitic/pathogenic organisms (e.g. rot fungi) or by directly affecting the soil environment for micro-organisms in their immediate vicinity (e.g. changing pH, redox, pCO_2, nutrient availability).
- Maintaining a good and improving aerobic structure, necessary for biodegradation of organic contaminants

[1] odt = oven dried tonnes. This is the usual measurement of SRC yield.

- The sorption and/or possible translocation of contaminants (e.g. accumulation of metals, or, for organic compounds, their metabolism or release to the atmosphere).
- The mobilisation/immobilisation of contaminants (e.g. via production of organic ligands for heavy metals, changing pH, redox potential etc. at soil surfaces)
  - By containing contamination by breaking pathways, for example preventing the ingress of water and preventing direct contact, particularly as soil horizons develop
  - evapo-transpiration reducing or even preventing leaching of water

There are several possibilities for positive effects on *in situ* biodegradation by plants [Anderson and Coats 1994]:
- Optimising conditions for bio-degradation by indigenous soil micro-organisms.
- Providing stable habitats for introduced organisms or consortia with specific decontamination activities, where they may be preserved from competition with or predation by indigenous organisms, protected from deleterious environmental factors and supplied with nutrients, water and oxygen.

Plants may accumulate heavy metals from soils and water. The extent of this accumulation depends on the plant species and soil and contaminant type. For many plant species this accumulation process is passive. The removal of heavy metals from soils in agricultural crops will gradually reduce soil heavy metal levels in the absence of fresh inputs. However, for some plants accumulation of metals appears to be an active process possibly related to a tolerance mechanism for their survival on contaminated sites and these plants are referred to as "hyper accumulators" to distinguish the nature of their metal accumulation from the passive accumulation that is general for plants and typically does not lead to such high leaf concentrations of metals. [Baker *et al.* 1994, Baker and Brooks 1989, Japenga *et al*., 1999]. SRC species are typically NOT hyper accumulators, although some clones may have higher metal uptakes than others. There has been much recent research on the ability of SRC species to take up heavy metals, and thus decontaminate land affected by elevated concentrations of these contaminants [e.g. Riddell-Black 1994, Riddell-Black *et al*. 1997, Punshon and Dickinson 1997]. Most has focussed on various clones of *Salix* spp (willow). It is clear that there is considerable variation in the ability of these clones to take up metals, and in the metal species which exhibit most movement into the plant. For example, cadmium and zinc seem to be taken up more than lead, nickel and chromium [Labreque *et al*. 1994, Riddell-Black 1994, Östmann 1994, Riddell-Black *et al*. 1997]. In addition, different metals show different behaviour with respect to their zones of accumulation, whether in roots or shoots. In practice, while some attempts have been made to demonstrate the use of SRC for heavy metal removal from contaminated ground, the approach is in reality an emerging concept so far as technical implementation is concerned [Bardos *et al*. 2001], and the technique is open to question on sustainability and risk management grounds as well as practicability.

Risk management would need to consider both the effects of the remedial process and the long-term management of risks posed by the condition of the site, i.e.
- Preparation of the site for its conversion to SRC.
- Working on site in the SRC plantation.
- Uptake of contaminants into the wood product and their eventual destination.
- Contaminants in the ground: the fibrous and shallow rooting habit of SRC limits its ability to remediate by accumulation.
- Use of the site for amenity, considering the effects of risks upon children who are more vulnerable than adults, have a lower awareness of hazards, and are higher risk-takers.

Regulators are likely to have practical concerns, such as which contaminants are likely to be mobilised by the short rotation coppice and what would be their fate. The presence of some heavy metals in the biomass may reduce the range of its available end-uses. For example, the presence of volatile mercury or cadmium would require strict emissions control for combustion processes to avoid potential atmospheric pollution by contaminated particulate matter. In addition, the fly ash (ash collected from the flue gases) may be contaminated and would be subject to controls on its disposal. Additional controls or restrictions may be required to protect the environment from contamination by incinerator ash (ash collected in the combustion unit, also known as bottom ash) with a high non-volatile metal content (handling and disposal controls required) or dispersal of fly ash (controls on emissions to the atmosphere required). It could be argued that if the incinerator ash is recycled to the SRC site as potash, there is no net change in the site's heavy metal content so that the site is stabilised rather than remediated - under this scenario there would be no concerns over off-site disposal to licensed landfill. However, this does not comply with best practice in contaminated site management since deposition of ash containing heavy metals does not remove identified risk, nor does it have an environmental benefit. In addition, it could be viewed as a redeposition of waste by the regulatory bodies. It is unlikely that to be considered best practice by the regulator, and may cause the site to come under landfill controls.

Plants may accumulate organic compounds through the root system or via foliar uptake [Ryan *et al*. 1988, Paterson *et al*. 1990]. This accumulation varies greatly depending on plant species and contaminant and soil type. In general the more hydrophobic a contaminant, the more likely it is to remain sorbed to roots (bound to cellular lipids) or soil organic matter. More soluble compounds may be translocated to the leaves, and in some cases these compounds may be degraded by the plant or lost from the leaves by volatilisation. The ability of SRC species to stabilise land affected by organic contaminants is being researched. The greatest success has been with hybrid poplars, which demonstrate uptake and degradation of organic pollutants such as trichloroethylene (TCE) or dioxane from contaminated sites [Schnoor *et al*. 1995, Aitchison *et al*. 1997, Sytsma *et al*. 1997].

Phytostabilisation is the use of certain plant species to immobilise contaminants in the soil and groundwater through absorption and accumulation by roots, adsorption onto roots, or precipitation within the root zone. It also can describe a broader approach to using the growth of plants to break pollutant linkages, for example by plant effects on soil water management, or prevention of dust blows. These processes reduce the mobility of contamination and prevent migration to the groundwater or air, and reduce contaminant availability to the food chain. It has been known for many years that organic material in soils can complex heavy metals, reducing their availability to plants and other organisms. Additions to soil of composted organic materials have been found to produce significant decreases in amounts of bio available lead in contaminated soils [Jones and Jarvis 1981]. Soil organic matter is also a sink for many organic contaminants, in particular pesticides and PAHs [Lamar *et al.* 1990]. PAHs may bind irreversibly to soil humus [Stegmann *et al.* 1991].

The revegetation of contaminated sites, for example for biomass production, may have further beneficial effects in limiting the migration of contaminants from the contaminated area and limiting their availability through immobilisation in roots systems and added or newly generated soil organic matter. Successful revegetation may also enhance soil microbial activity, in turn enhancing processes of *in situ* biodegradation for some contaminants. The addition of organic matter, such as waste derived compost, to soils may also promote both microbial biodegradation of contaminants and the fixation of some contaminants such as PAHs, into humic materials [Kraatz *et al.* 1993, Lotter *et al.* 1993, Mahro and Kaestner 1993]. Soil organic matter also appears to be important in promoting abiotic processes of contaminant degradation for some organic compounds and in co-metabolic degradations of organic compounds [Dragun 1988, West 1994], and also strongly sorbs heavy metals [Sposito 1989].

While the fibrous and shallow rooting habit of SRC limits its ability to remediate by accumulation, it is potentially an enormous asset for remediation of contaminated land by containment and stabilisation. The *Markham Willows* project in the UK (described below) is examining an approach of combining SRC cultivation with organic matter applications to generate a new soil horizon over mine spoil. The idea is that the expanding soil horizon would gradually move the rooting zone away from the old mine spoil, and the organic matter content of the lower layers of the new soil would help stabilise pH and eH, as well as sorb any upwardly migrating contamination. In this scenario risk management is effected by interrupting pathways rather than removing the source term. The SRC would also quickly prevent direct contact on site or from dust blow, and also provide physical stabilisation for the site.

3 SRC for Treating Sediments

Large amounts of sediments are polluted with biodegradable contaminants and can be treated using bioremediation. Landfarming, were polluted soil or sediment is spread out on a special site or treated on the polluted site itself is shown to be a cost effective technology, specially for the large amounts of polluted sediments that have to be cleaned in the Netherlands. A bioremediation process can be optimised in order to increase the degradation process. It is known, however, that a recalcitrant amount of the pollutant is still present after treatment. This amount is said not to be available for the organisms responsible for the degradation i.e. the bioavailability is low. Limited bioavailability was first explained by ad- and absorption of the contaminant in the soil matrix in such a way that it could not be reached by micro-organisms. This was a theoretical approach but also a useful concept. It could be used to convince people that a long time could be necessary to decrease the residual concentration. This was another way of thinking: when a contaminant is not available for degradation it first has to become available by desorption processes, which may take a very long time. Instead of the desired treatment times of several months it could be necessary to treat a soil for several years or even decades. It was necessary to distinguish landfarming in intensive landfarming, to quickly remove the bioavailable part of the contaminant load, followed by passive landfarming for slow removal of the residual concentration [Harmsen et al., 1997]. These slow processes make an intensive and optimised treatment not the most wises choice and this is even not effective [Harmsen, 2001]. Treatments with a low labour and energy input (passive) will be cost effective then, especially if bioavailability is the determining factor [Sims and Harmsen 2001].

The long treatment time has its impact on the way sediments have to be treated. Large areas will be necessary for a long period. Leaving the sediment somewhere, applying the proper conditions, is not a real option. Not in a dense populated area, because the claim on limited area will be too large, but also not in natural areas because of the influence on the ecosystem. Treatment of sediment should be in harmony with the environment and remediation should therefore be combined with another function. As long as such a function does not interfere with bioremediation, a lot is possible, as there are growing of biomass [Breteler et al., 2001] and nature development. Growing biomass is also a solution for another social problem, the need for sustainable energy. If the other function gives a profit, for instance selling the crop, the benefits can be used to pay the costs of bioremediation. This aspect, combination with beneficial land use will be essential for the large-scale bioremediation of dredged sediments, not only in the Netherlands, but world-wide.

Unfortunately, heavy metals, which are not biodegradable are often also present in contaminated soil and sediments. Vegetation can play a role in phytoextraction or phytostabilisation. As stated before the amount that can be removed by phytoextraction is low and therefore only applicable on sites with values just above the target value for clean up. Phytostabilisation, where roots play a role in immobilisation of the heavy metals, can be an important development for heavily polluted sediment sites.

From technical point of view as described above, there are several possibilities to bio remediate polluted sediments on a large scale, which will be necessary to handle the large amount of polluted dredged sediment present in a sedimentation area as the Netherlands. With the passive methods described costs of remediation will be low. The NIMBY-effect (Not In My Back Yard), however, prevents real applications of these methods. In order not to isolate polluted sites, or creating depots and landfills far away from urban or valuable natural areas or leaving the pollution for future generations, it will be necessary to consider contaminated soil and sediments as a problem that has to be solved in conjunction with other problems. It is only one aspect in future town and country planning and should not be a hampering factor.

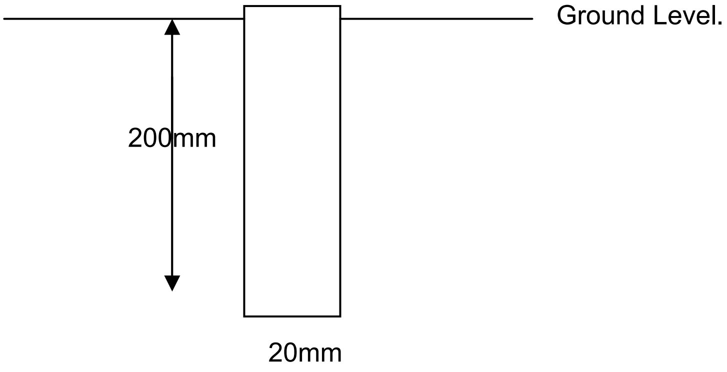
4 Implementing SRC

Prior to the physical establishment of SRC it is essential to identify the factors that will influence the establishment of it. Therefore a suitable set of soil sampling and analysis needs to take place. In essence this should cover general plant nutrients and metals as well as any specialist contaminants that the site may harbour. Site investigation information must be compared with published standards and historical knowledge of the levels of contaminants that SRC will tolerate. If levels prove to be outside of that suitable for establishing SRC then either an additional material i.e. compost/green waste as a soil improver/conditioner or a biosolids type application be made to the land may over come this. In extreme situations a resting period may be required before the soil is suitable to support any plant species growth whatsoever. Adequate planning for topography is also essential, particularly when slopes are an issue and so there exists potential for physical soil erosion. The roots of SRC can bind unstable soils together and so full advantage of this must be taken. Also site plans needs to reflect the cultivation, planting, management and harvesting requirements for the crop. In essence machinery is at its most vulnerable when turning across slopes and so wherever possible the safest operation is by travelling directly up and down the slope thus avoiding potential slippage and overturning. From a commercial harvesting point of view there need to be suitable breaks in the crop to allow full trailers to exit and empty ones to join without the need to travel along the rows for a great distance (thus creating compaction) or having to drive across harvested stools (causing splitting and potential disease/fungal insertion).

Following the suitability of the site being assessed and the design layout being prepared, then physical on site operations can begin. The objective of this phase is to create a suitable medium for the SRC to establish and then grow in by a series of soil cultivations. For the crop to reach full potential, it requires a compaction free soil structure. Thus deep tilled cultivation of the soil is desirable and it is best if this is carried out during dry conditions to maximise the shattering effect. This may however conflict in the short term with the requirement to stabilise unstable slopes. In these cases it is still preferable to carry out the operation but to do it as close as possible to planting in order to minimise the time during which the soil is unsupported and thus at risk of erosion or slippage. Seedbed preparation follows subsoiling and offers the opportunity to apply and incorporate any additional materials such as green waste/compost and biosolids. By incorporating these materials to a depth of around 200mm so a suitable growing medium can be created. This technique has been demonstrated successfully in restoring sand and gravel quarries and on colliery shale where the base soil is inherently deficient in nutrient and water holding capacity. Even with the addition of the biosolids these soils are only capable of sustaining low quality grass, conventional woodland or SRC, with economic, environmental and social returns making SRC the current crop of choice.   Planting of SRC is by done by mechanical methods, for example with a modern “step” type planter capable of planting 6-8Ha per day. This requires a weed and debris free seedbed, with at least 200 vertical millimetres of passable material in order to vertically plant the cutting. This is illustrated below:

Ongoing management practices also require access to the site to both recycle more materials and also to encourage the process of remediation. The picture below shows a system that irrigates “thick” viscous liquids onto an SRC crop. Materials it has been used to apply include treated bio-liquids and animal slurries. It is essential for both the health of the crop and the development and improvement o the soil layer and its inhabiting species that ongoing nutrient is applied to these soils. The machine shown can apply to mature coppice when the crop is some 8-9 metres tall.

A planted cutting and its dimensions.



Harvesting is the final operation in the in field crops life and again it is important to consider the practical and physical requirements involved. Slope and stability are the major factors on sites such as colliery spoil, and on sand and gravel quarries the emphasis swings more to the soils ability to carry machinery (aided by the root network) and the drainage of surface waters. Commercial machinery for harvesting is necessarily large as it has to cut and chip “trees” that are 9 metres tall with a stem base of 50mm at a rate of some 60 tonnes per hour. On wet sites the best way of ensuring that crop is harvested in conditions that do not detrimentally affect the root structure (and so future growth) is to harvest during the summer months when the sites are at their driest.

Generally there will need to be an area for crop storage on site. It is essential that this area is dry, level and of hard base material (see picture above) to allow access for vehicles to collect the fuel.

Harvested fuel can be stored for over 6 months in outdoor clamps such as these shown below. Interestingly the site shown is on top of a mound of pulverised fly ash that was piped from a coal-fired power station into and across a quarry restoration in the 1980's and with current developments the restored land may now be used to grow SRC for co firing in the same stations.

One market already mentioned is that of co firing with coal in large power stations. Other options range from small-scale heat units on individual or a district heating type scheme through industrial heat of various scales. There are also the higher technology systems of gasification and pyrolisis that may offer future opportunity for electrical and heat based energy generation. Perhaps the greatest benefit comes when the fuel produced is used in community or local authority based schemes of small-scale energy clusters or in purpose built energy parks. These will create the greatest additional benefit in social terms and can be targeted at areas that are in need of regeneration following the closure of traditional mining and heavy industrial processes that probably created the land to be remediated in the first place.

5 SRC in a social context

SRC fits conveniently into that category of subjects that can be generically termed 'environmental'. This is very useful because it provides an automatic link to the subliminal, almost visceral, relationship that people have with nature.

For a host of reasons, people find many benefits in the natural environment. This finds an expression in the way they will, for example, utilise the resource of green space near to where they live. Local communities who have found that, the landscapes on their doorsteps, can be places in which to play, take exercise or simply enjoy nature have quietly sequestrated many a tract of abandoned post-industrial land. It should be quite possible to harness this community affinity for green spaces with projects such as those involving SRC - provided that care is always taken to obtain the community's support.

Environmental projects can provide society with more than just facilities for leisure and recreation. There are many positive socio-economic benefits to be found in this area. In most modern societies, employment is cyclical. The change between phases presents different challenges. When the level of unemployment is low, environmental projects can be a useful means of targeting the disadvantaged and long-term unemployed. When unemployment is high and the 'market' is unable to deal with the redundant labour resource, then socio-environmental projects can help to take up some of the slack, providing hope and some form of income for those vulnerable members of society who are less well able to compete for scarce jobs.

For example the UK is currently in that part of the cycle when unemployment figures are low. In fact, they are the lowest for nearly thirty years. When the economic transition from an industrial to a post-industrial society commenced some two and a half decades ago the UK government concentrated huge resources on regenerating the country's economic base. This was absolutely necessary in order to mitigate the rising levels of unemployment witnessed at the time. To some extent, this driver is still present in the economy. This is why regional regeneration agencies persist in skewing efforts into building commercial premises and creating jobs and why there tends to be a paucity of funding for environmental projects. However, macro-economic policies, which were fine when the cycle demanded the creation of a huge number of jobs, are too crude now the problem has changed. In this part of the cycle, there is a need to be far more focussed. We need look no further than the law of supply and demand to recognise the fragility of a strategy that attempts to apply a blanket approach to creating ever more jobs when supply is diminishing. We do need to create jobs but these have to find a ready target. With the bulk of the employment problem resolved what we now need to concentrate on are those members of society who are lodged in circumstances that reduce their employability. The people in need of most help often live in areas suffering high rates of depravation. They are trapped in circumstances that disrupt their education, which further reduces their chance of a job. Locked in to a poverty and educational trap they become disillusioned, disaffected and form the strata commonly termed 'the long-term unemployed'. It is at this point that special assistance is required and the use of socially orientated ventures can be of use in this endeavour. The value of these schemes is that they provide controlled surroundings within which people can be helped back into long-term employment. Under the heading of the Intermediate Labour Market (ILM), Social Enterprises or

Transitional Employment, many such ventures tap in to the rich resource offered by the environment. Basing an ILM scheme on the use of SRC is particularly interesting because it offers huge amounts of additional benefit - much beyond the notion of helping people back into work.

6 The benefits of an SRC based social enterprise - Outcomes and Outputs

The first strength to recognise about a social enterprise is that it is locally based. This means that there is a high degree of ownership by local partnerships and communities. Any SRC initiative carried out on this basis therefore becomes automatically embedded in the local community. This provides an excellent base from which to open a dialogue with the local people, to highlight their concerns and aspirations and find an expression for these aspirations in work within the environment.

There is a natural symbiosis between post-industrial land and people. Simply speaking, the resources occurring at a particular location led to the development of industry and populations grew as a result of the available work. In a post-industrial era, we now have the situation that many communities have been left behind. They occur adjacent to the derelict land that once was the location for their employment. Global trends and a change in the economic uses of land have often left large amounts contaminated land in close proximity to people. In many instances, for complex related reasons [Barton 2000], these areas are also those that suffer the highest rates of social and environmental damage and depravation. This provides an excellent opportunity for an SRC based ILM to strike at many problems simultaneously.

An ILM based on SRC offers many associated benefits. Not all would be directly related to helping people into full time employment. Some would help to deliver sustainable outcomes and outputs and would be of great benefit. The recycling of green wastes as a source of nutrients, the recycling of contaminated land and the provision of renewable energy are all exciting examples of how to support the principles of delivering inter-generational equity through SRC. Although the use of 'sustainable' in this context is in accordance with the definition developed by Gro Harlem Bruntland, 'sustainable' is often also used in the context of 'having the capability to endure'. To some extent, this duality is unfortunate because it dilutes the all important concept of preserving the earth's resources for those who will come after us, but the notion of projects needing to maintain their benefits into the future is also important. This is especially true of schemes that involve producing changes to the landscape; changes that are likely to develop and mature in time-scales measured in decades.

The effort to clear away post-industrial dereliction has led to many projects where the outcome was an area of green space. All too often, these schemes have been attended by poorly structured funding for their long-term maintenance. Finding revenue funding for this aspect of stewardship can pose a substantial problem. SRC embedded in a social enterprise may offer a satisfactory means of solving this problem. Where the area of land to be reclaimed is sufficiently large, it may well be possible to develop the greater part as green space whilst at the same time incorporating a social enterprise into a part of the scheme. Clearly, the proportion of land devoted to SRC must be sufficient to make the enterprise itself economically viable in the long term. The idea would be to support and develop a scheme that employed local people and which also generated income from the SRC to support the long-term maintenance of the entire project. One advantage of this idea would be that any detrimental visual and ecological effects of the SRC could be largely mitigated by the careful landscape design of the entire scheme. The outcomes would cover a wide spectrum of social, economic and environments benefits including:

- Providing employment.
- Assisting neighbourhood renewal.
- Promoting community health.
- Providing a recreational/leisure resource.
- Assisting with the mitigation of storm water run-off.
- Dealing with post-industrial land.
- Aiding biodiversity and nature conservation.
- Promoting sustainability.
- Improving visual amenity.
- Playing a part in the reduction of air borne pollution.
- Providing an educational resource.

In short, this type of development would deliver an integrated, functional green infrastructure that transformed derelict, contaminated post-industrial land and provided a legacy for future maintenance.

7 UK Case Study: Markham Willows

In the United Kingdom, there are reputedly over one thousand redundant or abandoned coal mine sites. Most of these sites share common features. They are usually:

- Owned by the public sector
- Unsuitable in whole or in part for commercial development
- Chemically contaminated
- Physically unstable
- Subject to erosion
- Unsightly
- An economic burden on their owners, potentially for generations to come

During 1999/2000 a consortium of interested organisations was formed. This grouping consisted of Groundwork, AEA Technology Environment, r^3 environmental technology, VHE, University of Reading, Forest Research and exSite. These organisations, each with a particular and highly specialised set of skills, combined to develop an exemplar project which could prove the concept of short rotation coppicing and concomitant organic matter build up, as a means to promote phytostabilisation of soil contaminants on former colliery spoil heaps. A concurrent aim was to promote local area regeneration, community enablement and "green tourism". The ultimate aim was to establish a means of addressing the negative features of significant numbers of abandoned coal mine sites in a holistic, sustainable and reproducible way. These ideas developed from a scoping study carried out for exSite in 1998 (Bardos *et al 2001* and Nortcliff *et al* 2000). The study concluded that an integrated approach was feasible and that a large field demonstration was justified and essential.

The location chosen for the demonstration is the area occupied by the former Markham Colliery and its extensive spoil tips that span the Bolsover, Northeast Derbyshire and Chesterfield District Boundaries lying to the East of the M1 Motorway between Junctions 29 and 30. The project became known as "Markham Willows".

This site was considered to offer the required profile for the project for a number of reasons; including the existing derelict nature of much of the site, the strong local authority and regeneration agency support and the existence of partners such as Groundwork Creswell who could provide an effective and durable link into local communities. A further impetus was afforded by the ambitious regeneration proposals for the area, including the proposed commercial development initiatives to be served by the nearby M1 Motorway junction 29a and the Markham Enterprise Growth Zone (MEGZ).

The Markham Willows project now forms a vital part of the sustainable regeneration of not only the Markham area, but also will provide a new focus and new identity for a major part of the North Derbyshire / North Nottinghamshire coalfields region through its potential position as an internationally recognised exemplar of environment-led regeneration.

The project seeks to integrate organic matter reuse SRC willow growing and phytoremediation works into a coordinated and synergistic range of environmentally focussed activities that could in turn promote local community business formation, the development of training opportunities and community involvement of a truly fundamental nature.

In particular, and in support of all of the overall ideals, it is considered that the project could provide a wide range of opportunities for social enterprise formation in a range of activities, such as woodland / coppice management, green waste composting, materials recycling linked to the proposed business park (that could in turn support the development of a "Green Business Park") and woodland enterprises, possibly linked to the green tourism industry.

The "technical core" objectives of the Markham Willows project will be the regeneration of despoiled, ex-colliery land through the utilisation of biological processes associated with (SRC) and the concomitant build up of organic materials to form soils and by so doing contain and "fix" contaminants, rendering them less harmful. As part of the core objectives the coppice material is to be utilised as a feedstock fuel for a biomass-energy plant that will power / heat the proposed industrial park.

All in all, the Markham Willows project has the potential to add significant value to the regeneration process even if all it were to achieve is its technical core goals of land remediation and biomass-energy production. However, it has been recognised that the project could have an even more profound regeneration potential and could be worthy of the status of an international exemplar if it includes added value elements beyond those strictly necessary to achieve the core objectives such as:

- Engendering wider community involvement and ownership from planning through to implementation, leading to greater sustainability of the site.
- Developing local training and job creation opportunities in new “Green-collar” industries.
- The development of additional “Green” businesses on the site, which are sympathetic to the core project, such as timber and construction/demolition, waste recycling. If sensitively handled, such additional businesses could help to “sell” the green credentials of the Enterprise Zone and boost the image of the area. Such businesses could also potentially support the development of a “Green Business Park”, by recycling waste materials produced by other industries. (Green Business Parks are industrial estates where the businesses seek to operate to high environmental and social standards, in a good quality environmental setting).
- Wider academic involvement that will monitor the site and assess the success of its various elements, thus validating the results and providing wider dissemination, as well as providing an excellent learning opportunity for a wide range of students, from biochemists through to social scientists.
- Developing the site for local amenity use and “Green tourism” potential.
- Developing a programme of actions that seeks to protect any important existing site ecology and widen the biodiversity of the site by encouraging the development of habitats that are suitable for the introduction or attraction of rare flora and fauna on to the site.

It is considered by the wider partnership, that Groundwork Creswell is the organisation best placed to develop these “Added value” items and it is accepted by the partnership that these items are necessarily an intrinsic parts of the whole regeneration package rather than being “bolt-on” issues if the true international exemplar status of the project is to be realised.

7.1 The Project Partners.

Partners in the project are Derbyshire County Council, exSite, AEA Technology PLC, r^3 and Groundwork. Envirosphere has been commissioned by the project partners to work with Groundwork Creswell to support their activities in the project.

Funding partners include:

- EB Nationwide (***Shanks first fund***)
- Derbyshire County Council
- East Midlands Development Agency
- Groundwork

7.2 Research Rationale

Research and Development (R&D) projects are essential to investigate the potential of the Markham Willows approach in the long term for sustainable reclamation of derelict environments. The reasons for Markham Willows research interests are:

- Verification / proof of concept studies, e.g. of risk management, economic assumptions
- Developing a better understanding of the mechanisms involved in the incorporation of organic matter and coppicing on derelict land and the impacts and benefits of this practice
- Develop an environmental technology focus for the region and link this to the development of MEGZ as a sustainable technology business park
- Understanding the reproducibility of Markham Willows activities at other sites

As well as considering the detailed operations and construction of Markham Willows, the master-planning for Markham Willows will establish theoretical constructs for the predicted and/or desired outcomes for the site in terms of:

- Risk Management
- Waste Management
- Added-value (e.g. in terms of social benefits)
- Economic performance
- Exemplar (how well the project is promoted and serves as an example of good practice)
- Community participation

7.3 International Perspective

MEGZ, within which Markham Willows resides, has been chosen as one of the UK sites in the EU 5th Framework RESCUE project. RESCUE (Regeneration of European Sites in Cities and Urban Environments) is a partnership project aiming at establishing, measuring and promoting sustainable best-practice in brownfield development. It started in March 2002 and will be completed by March 2005.

The Markham Willows Project Managers, exSite, are RESCUE partners, together with:

- GPE Germany
- Umweltbundesamt, Germany
- Projektgruppe Stadt und Entwicklung, Germany
- Ruhr Universität Bochum, Germany
- BRGM, France
- Conseil Régional Nord Pas de Calais, France
- Université des Sciences et Technologies de Lille, France
- CNRS, France
- Municipality of Sosnowiec, Poland
- Municipality of Bytom, Poland
- Central Mining Institute, Katowice, Poland
- University of Nottingham, UK
- Geoenvironmental Research Centre, Cardiff, UK

The Markham Willows project, and the research infrastructure that it will provide, will enable national and international collaborative research to be carried out in the field in the UK. However, exSite is currently considering the possibility of setting up “mirror” projects in France, Poland and Germany that can use the models developed at Markham within their own distinct national, regional and local circumstances. Once this potential opportunity has been sufficiently explored, it may then be possible to consider wider geographic links to stakeholders in Asia, Africa and the Americas. Again, this will be developed further at the UK workshop in March 2003.

8 Dutch Case Study: Oostwaardhoeve

Oostwaardhoeve is an experimental farm in the north/west of the Netherlands. Cultivation of willows as biomass for energy production has been studied since 1993. From 1996 this cultivation has been combined with the remediation (landfarming) of polluted sediments. During this treatment the quality of the sediment improves due to biodegradation of PAHs and mineral oil. At the moment 20 ha are used for the combination cultivation of willows and bioremediation of sediments. It is the intention to increase the area used to 100 ha.

The investigation has been started as a project of the Wageningen research institutes IMAG and Altera and the contractor De Vries en van de Wiel in Schagen. First projects were successful and Oostwaardhoeve is now functioning commercially (co-operation of IMAG and De Vries en van de Wiel) and combines this with further development of the concept. The activities of Oostwaardhoeve Co. are strictly regulated by Dutch environmental legislation, which requires regular checks of soils, sediments and water, the very careful transport and application of the polluted sediments, and thorough bookkeeping.

The proper application of sediments on a hectare scale requires a thorough macro-filtration of the sediment, so that objects that may be encountered in the sediments removed from the bottom of waterways, like bicycles, safes, car wheels, *etc*. are removed before the sediment is transported to the landfarm. Application of sediment in an even layer on the land requires experience and technical skill to tune the pumping equipment to the acceptable variation of quality and quantity of the applied sediment. At this site, it appeared easier to apply sediments to an existing willow crop than to establish a new crop on a layer of fresh sediment. On the other hand, the existing crop presented a barrier towards the even distribution of sediment. On the average, approximately 1.0 m of sediment was applied on the land, eventually leaving approximately 0.5 m of matured sediment. With this concept, 10 to 20 years of landfarming are available to clean the sediments to the extent that the remaining material fulfils the requirements for reuse (Breteler et al., 2001).

Sediment settling in SRC for remediation

The crops are harvested in the winter, during periods that it is possible to drive on the land (dry or frosty conditions). The willow stems are dried completely on the field as shown below, and are not cut. Cut willow is easily composted, which reduces the benefit for energy supply (Gigler, 2000).

Whole Rod Harvesting of SRC

9 Conclusions

Developments of polluted sites are often hampered by presence of contaminants. These sites can be rapidly returned to an economic use with SRC.

The SRC farming also creates opportunities for the re-use of organic wastes and for managing the risks of derelict or contaminated land in the long term, using a process that effectively pays for itself.

Furthermore, the return of economic activity to the land can be a focus for community regeneration efforts and return a blighted environment to a more appealing environment, supporting local employment and community pride, without incurring crippling long term financial commitments for local authorities that might already be financially impoverished.

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SpS 21 Special Session

Four Successfully Completed Clean-ups Treating Different Kinds of Contaminants

4 successfully completed clean-ups treating different kinds of contaminants

Contaminated sites are places, where

- materials have been deposited, which, according to today's level of knowledge, should have been identified as hazardous waste and should have been treated accordingly. Normally such deposits represent an endangerment for humans and the environment.
- the environment is affected by chemicals released upon accidents and spills or
- former industrial and/or chemical production areas.

The following 4 papers demonstrate that there is no such thing as a "standard procedure" for a remediation of a contaminated site. The local situation (geo- and hydrogeology, history of the site, environment etc.) and the hazardous components involved (solubility, biodegradability, toxicity, etc.) are normally too different and complex to allow a "recipe" to be applied. Each case requires an individual setup.
There are however some major principles and priorities that help to achieve a positive result:

1. Compilation of an inventory of the site
2. Rating of the site
3. Supervision of the site
4. Securing of the site
5. Remediation of the site

All of the following remediation projects were run in different environments and under different constraints. The basic principles cited above were always applied however. The 4 projects / sites showed the following characteristics:

Amponville (F)

This projects represents a successful clean up of an uncontrolled dump by drums containing Chlorophenol-waste from an old agrochemical production site.
Approximately 15'000 tons of contaminated sandy soil had to be excavated and treated in a Thermal Desorption unit on site.
The whole project is well documented by means of a presentation on an interactive CD-ROM data medium.

Niederglatt (CH)

A new construction project was planned on the Refonda site, which looks back on a long industrial history leaving its traces in form of residual contaminations by organics (hydrocarbons, polyaromatics) as well as by chromium Cr(VI). The excavated soil for the basement of the new building had to be treated consequently.

30’000 m^3 of soil were excavated. The quality of the remaining underground after excavation had to be approved by the authorities. This was done field wise (fields of 10x10 m) during the weekly meetings on the site.
The following main elements of the remediation merit to be mentioned:

- the basement floor of the former building had to be left in place as a protection against rain infiltration.
- Cr(VI)-containing material was treated on-site, could only be refilled above the maximum ground water level and had to be covered by the new building.
- Cr(VI)-contaminated material was crushed and reduced to Cr(III) by iron chloride (immobilisation).
- after reduction the Cr-contaminated soil had to be mixed with chalk (conditioning and stabilisation).
- material with concentrations of polyaromatics or hydrocarbons above the limits for inert material had to be treated off site separately.
- a considerable space requirement resulted for intermediate storage of materials while they were being analysed for further treatment.
- water flowing off the site had to be thoroughly analysed before being allowed to discharge to the municipal sewage system.
- monitoring extended to groundwater control and to dust deposit measures in the near environment.

Dielsdorf (CH)

Wastes from former Lindane-production, containing HCH, Dinitro-o-Cresol and metals like As, Cu and Pb, had been buried beside a production area for years, and formed a threat for the underlying groundwater-aquifer.
The wastes and more than 30’000 tons of contaminated soil had to be excavated, analysed, partly backfilled and the rest treated in different ways.
An on-site almost on-line functioning analytical laboratory helped tremendously to limit costs of further treatment.
Residual pollutants concentration was calculated following a risk-analysis/mobility-calculation and agreed upon with the authorities before starting the remediation work.

Schweizerhalle (CH)

A huge fire destroyed a warehouse where some 1'300 tons of pesticides had been stored. The agro-chemicals and their incineration-products were partly mobilized with the water from fire fighting and entered the soil underneath the warehouse. The most harmful pollutants were mercury and phosphoric esters.
The area of the incident was isolated by trenches and covered by a tent. The groundwater level was lowered. 25’000 m^3 of gravel and sandy soil had to be excavated and sent to an on-site large-scale Soil Washing and Treating installation, the biggest remediation project of its kind. The washing water contained surfactants and other reagents to separate the pollutants.
The soil could be backfilled afterwards on-site. Less than 5 % of the soil volume containing hazardous waste had to be thermally treated separately.

The 4 papers cited can be found on the following pages.

SITE CLEANUP IN AMPONVILLE (FRANCE)

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Amponville is a little village just outside the Fontainebleau State Forest, 40 miles away from Paris.

In 1963, the QUINOLEINE Company decided to move its production facility away from Vernou, on the Seine River and 20 miles away from Amponville. In this process, several hundred drums of miscellaneous wastes had to be sent to an approved facility. Most of them contained Chlorophenols from the manufacturing of herbicides.

Unbeknown to the shipper, the transporter decided to **dump** the drums in a public landfill located in a depleted area of the Amponville sand quarry.

A number of drums were damaged while being unloaded, while others were drained on the spot and recovered by neighbours.

As a result, a memorable stench spread throughout a large area and generated an uproar from the local population who had the authorities order the removal of the drums.

In 1967, the drinking water supply of a nearby village was **contaminated**. Since the beginning of the 80's, a number of **wells** allow the monitoring of the water table around and inside the sand quarry.

In 1994, the wells **results** indicated no residual pollution. However the quarry's own pumping station still showed clearly identifiable trace amounts of Chlorophenols.

From 1995 to 1997, a number of **core samplings** were made and analysed, which allowed identifying the area of polluted soils, both in concentration and in volume. After the feasibility study was carried out, the **cleanup proposal** was submitted and approved by the **authorities**.

As a result, 15'000 tons of sand needed cleanup on a surface of 3'500 sqft, (315 m^2) 100 ft (30 m) deep. In order to limit the impact of the smell, the whole operation was conducted on site with a **Mobile Desorption Plant** under a large tent, which also protected the excavation from rain and snow.

The **soil beneath** was quite a mix: 40 ft (12m) of heterogeneous backfill, followed by layers of sand stone and sand. It was necessary to carry detailed **investigations** (tomography, georadar) to identify this underlying structure.

Between February and June 1998, during the **preparatory site works**, 150 drums were uncovered close to the surface, 25 of which were still in good condition. Further investigations, together with the previous boring information, allowed identifying an area where several more hundred drums were resting up to 40 ft (12m) deep. Altogether a total of roughly **900 drums** were to be extracted and incinerated in an approved fixed facility, almost 300 of which were still full.

The **shoring** of the future **excavation** was constructed during the fall of 1998, while the actual excavation and thermal treatment were simultaneously conducted during the 3 months of February, March and April.

On April 30th, the cleanup itself was completed as the phase of excavation and thermal treatment came to an end.

Now completed, the project shows a reclaimed area of approximately 2 acres (1 ha), partially protected by a bituminous **geomembrane** and completely **replanted**.

This project turned out to be a success, as 4 key conditions were met:

1. Stress **health, safety** and the **environment** as the true priority, by insisting on preventive measures and by monitoring the quality of the work conditions on site.
2. Maintain and **open door policy**: the public was fully and continuously informed through the local press, the various key officials and direct public hearing and visits.
3. **Partnering** with the authorities and among the contractors, as the only way to achieve an exemplary project while making the best of ways and means available.
4. Select the **best** contractors and service providers.

Finally, it is necessary to mention that the owner took two unusual steps. First, he granted the necessary amount of time and money to conduct the studies targeted at reducing the surprises, which are too common on such projects. Secondly, he involved the main contractor from the very early start of the project's conception, while accepting to take very rapid decisions at the key junctures of the operations. As a result, both the schedule and the budget were met for a project that was spread over **8 different phases.**

Every aspect of the project is well documented. To be able to present the project and its different criterions to all stakeholders, especially to the authorities and to NGOs, the project team decided on setting up a special tool for lectures. For the topics highlighted in the text above, additional data and especially graphics were installed and compiled on a CD-ROM with an interactive surface.

The CD-ROM helped both the project-team to present all aspects in an appealing way and the respective audience to better understand the complexity of the project and the solutions applied.

REMEDIATION OF THE CHROMIUM CONTAMINATION AT THE REFONDA SITE IN NIEDERGLATT (CH)

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1. The Problem

On the Refonda site in Niederglatt (CH) with a history of one hundred years of different industrial activities, the last of which was the re-melting of recycled aluminium, the existing buildings and an important volume of soil were contaminated with organics (hydrocarbons, polyaromatics) as well as with chromium Cr(VI).

The main contamination was chromium, originating from the production of synthetic camphor from 1926 to 1932. The re-melting of different metals, operated from 1939 to 1992, lead to a contamination with chlorides. The hydrocarbons and polyaromatics came from leaking of fuel, hydraulic oils and lubricants.

The investigation of the site showed a groundwater table near to the surface, with contamination mainly in the northern part of the area, menacing a pumping station of drinking water farther downstream. The remediation project included the buildings, the contents of various sub-basement basins as well as the underground. This presentation covers essentially the remediation project of the underground.

The remediation of the site was combined with the construction of a new centre for the distribution of aluminium products. The remediation works had thus to leave a surface, which was defined by the geometry of the bottom of the new building, ready to lay out the steel reinforcement for the basement concrete and fulfilling the necessary geotechnical properties beneath the foundations.

2. Remediation Goals and concept

Remediation goals

Buildings: Part of the contaminated material resulting from the demolition of the buildings hat to be eliminated to different waste-treatment facilities, according to the legal prescriptions. The main goal however was to treat and reuse a maximum of this material on site, to reduce elimination costs.

Groundwater: The remediation goals for the protection of the groundwater were fixed as follows:

- At the downstream area-limit, the groundwater had to fulfil drinking water standard, i.e. maximum concentration 0.02 mg/l Cr (VI), to be achieved 7 years after remediation.
- Cr (VI) - contaminated material is to be removed from groundwater layers or must be prevented from contact with groundwater.

- remediation has to be controlled by groundwater monitoring. Intervention-values are drinking water limits.
- The migration of chloride into the groundwater is to be reduced on a long-term basis.

Underground: Material not meeting the following standards had to be excavated:

- Below maximum groundwater table plus 1 m: Quality according to clean excavation material, i.e. 0.005 mg/l Cr (VI) in the elution-test water.
- Above maximum groundwater table plus 1 m: Quality according to inert material as defined in the Swiss directive on wastes, i.e. 0.01 mg/l Cr (VI) in the elution-test water.
- Treated material refilled in secured spaces located above maximum groundwater table plus 1 m with special protection against contact with water: 0.5 mg/l Cr (VI) in the elution-test water.

Remediation Concept

The remediation concept was to stop the source of contamination by the following means:

- Removal and external treatment/disposal of oil tanks, contents of old basins, oil-contaminated soil (hydrocarbons and PAC's).
- Removal of contaminants to a level of inert material quality above groundwater table plus 1m, clean excavation material quality below groundwater table plus 1m.
- Reducing the toxic potential by excavating Cr(VI) - contaminated material and transferring Cr (VI) to Cr (III) by immobilization.
- Reducing the emission potential by compacting the (treated) Cr- and metal-contaminated material in dry compartments separated by capillary barrier and protected by overlying new buildings.

3. The chromium immobilisation

Cr(VI), normally present as CrO_4^{-2} or $HCrO_4^{-}$, is highly soluble in water and is toxic, due to its oxidative capacities, whereas the metallic Cr^{+3} is non-soluble and non-toxic. The former may appear at pH above 6 and can be transformed to Cr^{+3} by lowering the pH. It was estimated from data of the site investigation, that about 50 metric tons of chromium were contained in the underground, 5% of it as Cr(VI).

Various treatment or remediation methods were studied. Finally it was decided on excavating the chromium contaminated underground material, passing it to on-site treatment in order to reduce Cr(VI) to Cr(III) and refilling it in controlled and watertight spaces.

In a first step, the underground material was crushed together with Cr(VI)-contaminated concrete from the demolition of the buildings. In a second step iron chloride was added in a mixing process (**immobilisation**).

As the Cr-contaminated soil was wet after immobilization and of rather fine granulometry, the geo-technical properties of the material had to be improved, mixing it in a third step with chalk or similar products (**conditioning and stabilization**).

The stabilization with chalk led to the best geotechnical properties, but had the disadvantage of partially reversing the pH-transfer reached by the iron-chloride-treatment. Part of the material was therefore treated with a bonding agent consisting of a mixture of burnt oil-slate and cement (commercial name Dorodur), an alternative treatment with argillaceous earth having resulted in insufficient geotechnical properties.

4. Remediation

The remediation was realized from March to December 1996. 30’000 m3 of material were excavated, 5000 m3 came from the demolition of existing buildings. The quality of the remaining underground after excavation had to be approved by the authorities. Excavation was executed by layers of 50 cm. The bottom surface was then probed and analysed in fields of 10x10 m. The decision, if the excavation had reached deep enough, was taken field by field during the weekly meetings with the authorities on the site.

The following main elements of the remediation merit to be mentioned:

- The demolition of the existing buildings had to leave the basement floor as a protection against infiltration of rain. The excavation works in the (previously determined) Cr-contaminated areas were executed under a tent.
- Material contaminated with Cr(VI) was excavated, treated on site and refilled at least 1 m above the maximum ground water level. The refilling zones had to be separated from the rest of the underground by a capillary barrier and were to be covered by the new building or a similar protection against infiltrating water.
- Material with concentrations of polyaromatics or hydrocarbons above the limits for inert material had to be treated off site. Most of it was washed, with reuse of coarse granulometry and incineration or underground deposit of fine material.
- A very important factor as far as cost and quality control is concerned, was the identification and separation of the materials with different contamination during the excavation work. The fact, that very big surfaces under roof could be used for intermediate deposits in the existing buildings, was a decisive logistical advantage on this site.
- The water running off the site during the remediation works was stored in tanks and only let off to the public sewage system, if the quality was sufficient. During demolition works, measures had to be taken against dust production.
- Monitoring extended to groundwater control and to dust deposit measures in the near environment.

5. Costs

The total cost were approximately 11 Mio €, distributed as follows:

Demolition of buildings	14 %
Treatment of chromium contaminated material	42 %
Treatment of sub-basement basins	12 %
Elimination of oil contaminated materials	32 %

A total of 8’000 m^3 of chromium contaminated material, 14% of which was contaminated concrete, were treated and refilled on-site, at a cost of approximately 420 € per m^3.

6. Conclusions

- Remediation of underground is far more expensive and far less predictable than remediation of buildings.
- It does not pay to invest too much in detailed quantitative examination and analysis of underground: you need to know what you'll find and how to treat or dispose of it, plus a rough estimate of quantities.
- It pays to invest in the sorting- and realisation procedure: the better you can separate contaminated materials in different classes, the more money you will save on treatment and disposal costs.
- The exact methods of analysing the different parameters are to be defined with the authority before you begin examination. Take into account the different purposes of analysis: investigation, sorting, controlling.
- You save money if you plan the remediation in combination with a new construction project: Do not remediate first and plan constructions afterwards.

REMEDIATION OF THE MAAG-SITE IN DIELSDORF (SWITZERLAND)

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Between 1935 and 1965 the Dr. R, Maag AG produced agrochemical products, like Arsenic-, Copper- and Lead-compounds and also 2,4-Dinitro-o-cresol (DNOC) and Lindane (Hexachlorcyclohexane=HCH). The residues of production and other wastes were buried near the production building.
In the late 1980's contamination of groundwater was detected downstream the site. Since 1990 ground water had to be pumped and treated. During construction work in the 80's, contaminated soil was excavated.

For the investigations in the soil we dug trenches, because we assumed on the basis of our information, that the buried waste could not be very deep below surface. We took more than 400 soil samples and analysed 130.

The goals of remediation had to be established by a risk-assessment supported by a cost-/benefit-consideration and an ecobalance. The only pathway for mobilisation of contaminants has been ground water that flows into a nearby river. For the risk-assessment we used the Swiss quality standards for rivers and calculated the acceptable groundwater concentrations of the contaminants at the border of the site. We compared these values with the soil/water equilibrium and fixed the residual concentrations in soil. With this approach the goals of remediation (in mg/kg: HCH 4, DNOC 1, As 75, Cu 200, Pb 200) had been up to 40 times higher than Swiss authorities are normally asking for, but we could show that more than 95 % of the contamination would be eliminated.

We did a feasibility-study for the clean up. Because of the different kind and the different levels of contamination, and the limited time frame for the clean up (liability of the former site owner), it was not possible to develop a special treatment technology and we had to go to different disposal and treatment facilities. When the quality of the soil was below the goals of remediation, the soil was back-filled after excavation. Soil with an intermediate level of contamination was treated in a nearby soil washing installation, higher contaminated soil had to be disposed of to a landfill for special wastes or in under-ground storage in a German potassium mine. Organic material was treated in the incinerator for special waste in Basle.

Before we started excavation, we installed tents over the contaminated areas to keep out rain from the contaminated area. We also installed a well-point system to lower the groundwater level.
We laid a grid of 5 x 5 m over the contaminated area. We started to excavate 50 cm of every square. We filled the soil in containers of 7 m^3. Every container was analysed. With the result of the analyses, we could decide if the soil could be back filled or had to be transported to the different disposal facilities. When the soil met the goals of remediation, we stopped the excavation within the squares (at the end, the site looked like an archaeological project). During excavation we had a lot of surprises, e.g. after a thunderstorm the whole site was floated or at a depth of 9 m we found an oil-layer that transported HCH into the groundwater.

Our estimation after investigations had been to excavate 5000 m3 with a back fill rate of 40 % and the work would have to go for 5 months. At the end we excavated 17'585 m3 of soil in 12 months. The back fill rate of 40 % was correct. Explanation for the difference between budget and final volume of excavated soil are the following surprises: contamination was deeper as expected (oil-layer, deeper disposal holes), 100 tons of pure HCH had been found.
Groundwater-monitoring results after the end of the remediation are very positive. In one year the contamination of the groundwater decreased by a factor of 4 and we could stop pumping and treating. Two years after finishing the clean up, the contamination of the groundwater arrived at 10 % of the original level. Monitoring could now be reduced to sampling every three months.

Costs:	Preparation of the project (1991-1995)	4.5 mio SFr.
	Clean up (1995-1996)	13.5 mio SFr.

When we started the project in 1990, we estimated total costs of 20 mio SFr.

SCHWEIZERHALLE
A RETROSPECT OF A SUCCESSFUL LARGE SCALE SOIL REMEDIATION

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On November 2. 1986, fire broke out in a warehouse storing more than 1'300 tons of pesticides at Schweizerhalle, an industrial area on the Rhine River near Basel, Switzerland. The fire destroyed most of the pesticides, but the fire-fighting water carried the pollutants into the Rhine River and into soil and groundwater at the site.

The soil cleanup, believed to be the world largest successfully completed soil washing project, was performed by the former MBT Environmental Engineering Ltd. today BMG Engineering AG, Schlieren Switzerland.
The Sandoz Ltd. warehouse contained at least 90 chemicals, but those of greatest concern were 20 pesticides, primarily mercury and phosphoric esters. Runoff from water used to fight the fire swept pesticides from the burning warehouse into soils and groundwater over an area of 30'000 m^2. In some areas the contamination reached a depth of 14 meters.

Sandoz engineers acted immediately after the fire, to isolate the problem and to protect the groundwater. They collected the debris from the fire in drums and disposed it of. They lowered the groundwater table; covered the warehouse area with a tent and sealed the site with asphalt.

Then the long process was initiated by MBT/BMG to assess the extent and distribution of the contamination and gather the data needed to plan an effective overall program for the cleanup.
Concurrently a trench was excavated around the site to prevent lateral spreading of the contaminants.

The chemicals stored in largest quantities in the warehouse were the organophosphorous insecticides, Disulfoton and Thiometon, and the mercury compounds, Ethoxyethyl-mercury-hydroxide and Phenylmercury-acetate. There were many gaps in knowledge of the behaviour of these compounds in the environment, particularly that of organic mercury. The involved specialists needed 2½ years to complete this chemical risk assessment, using chemical, biological and toxicological testing and research. The research was complicated by the fact that the compounds were transformed by the fire, and were found in other forms in the soil.

The risk assessment also required determining the extent and distribution of the soil and groundwater contamination, and the environmental behaviour of the most important pollutants. The data developed for the risk assessment included physical-chemical characteristics of the soil and of the contaminants; hydrologic and geologic site conditions and toxicological trials to establish toxicity levels.

As the risk assessment was being developed the group of process specialists conducted laboratory, bench scale and pilot testing to determine the most effective soil cleaning process. The engineers evaluated soil washing, thermal treatment and chemical immobilization. When these studies were complete, the final strategy for the soil cleanup could be developed.

The Soil Washing Decision

The volume of affected soils ruled out removal and disposal elsewhere. This option was too costly and would only move the problem to another location. Of the remaining options, soil washing was a process that would allow the return of most of the treated soil to the site and would cause no environmental harm. Engineers determined that the most practical method, from the standpoint of time required, as well as effectiveness and cost, was a wet chemical soil washing procedure with the addition of a flotation stage.

Soil washing is a water-based process to wash contaminants out of soils. There is lasting interest in soil washing, not only because of the high cost of disposal and the scarcity of landfill space, but also because of its simplicity, relatively low cost and environmental advantages. Essentially, it is a method of reducing the volume of contaminated materials by concentrating the pollutants in smaller soil particles, which can then be treated or disposed, leaving the bulk of the soil clean and reusable at the site.

Soil washing most easily removes contaminants from larger rocks and gravel with smooth surfaces and few pores. Other remediation processes can be added to clean contaminants that adhere to finer particles. The process water can be cleaned by advanced wastewater treatment processes.

Like any technology, there are site-specific conditions that dictate whether soil washing is the appropriate solution. These conditions include the nature of the contaminants, as well as the composition of the soil. At Schweizerhalle, the contaminants were feasible for flotation and the soils were predominantly gravel and sand with relatively low clay content. These conditions made soil washing the optimal choice. The specific process uses technology based on proven processes used for many years in the mining industry and the wastewater engineering.

Full-Scale Soil Washing

The soil treatment plant was installed in 1989 in a specially constructed building. In preparation for soil treatment, engineers took soil samples from various locations, obtained chemical tests and divided the site into contamination zones. For four months, engineers conducted a pilot phase to test and optimise its operation, using material of various levels of contamination. Full operation of the 15-ton-per-hour facility began in mid 1990.

The project team established a logistics program for coordination of site activities and recording data. A safety team monitors all the procedures connected with excavation work and the flotation system and regularly monitors the air and dust.

When excavation began, workers opened the asphalt cover using protective clothing and safety measures including monitoring the air for contaminants. Because of odours, the excavated soil was stored in sealed containers awaiting treatment. Workers excavating the soil took soil samples that were analysed on site to characterize the contamination and labelled each container with the date, location on site, type and quantity of contamination based on test results. This data was logged in a central computer so the whereabouts of every container could be determined at all times. The purification output of the facility and the analysis of material flow, including pollutants, were also automatically recorded.

How the Process Works

The contaminated material goes into a feeder and is carried on a conveyor belt to a sieving apparatus, where the gravel is separated from the sand and fines. The gravel falls into a rotary drum washer, where contaminants are washed off in a counter-current process with purified water. This is the only treatment needed for the gravel, which makes up about 60 to 70% of the soil at the site. After testing, the clean gravel is later reincorporated at the site.

The wash water, sand and fines are pumped into the hydrocyclone, where coarse clay mineral particles are roughly separated from the sand. The coarse clay contains the main portion of the pollutants. The water and coarse clay minerals flow into a thickener. Here water is separated from the highly contaminated fines. The remaining contaminated coarse clay particles within the sand fraction require additional remediation. The sand passes through an attrition mill where the contaminants are removed mechanically.

In the next treatment unit, the flotation cell, the removed contaminants are suspended in the surfactant-containing water. The contaminants are adsorbed onto artificially produced air bubbles; only sand remains in the water. These air bubbles build a foam on the water surface, which is skimmed off with the contaminants. The foam of concentrated contaminants flows into vats and undergoes special remediation. The water is circulated. Accumulation of contaminants that dissolve in the water is prevented with the addition of chemicals that destroy the contaminants. The soil washing plant has treated an estimated 25’000 m^3 of contaminated soil. Most of the treated sand and gravel was within the limits indicated by the risk analysis and was reincorporated at the site. Only about 1’100 m^3 of silty material, clay and contaminants had to be thermally treated or disposed of as toxic waste.

Critical Success Factors

One of the key factors for the success of this project was the consequent step-wise approach from the scientific findings to the full-scale operational plant. This required a project organization with a fully integrated team of all the involved specialists, working in close collaboration. The success of the project was also fostered by the open-minded cooperation of all involved parties as Sandoz, the executing engineering group, the insurance companies, the involved governmental agencies and the affected public stake holders.

The critical success factors for such a project can be summarized by the 4-pillar-principle of BMG, which says, that scopes and actions of a project must be:

- Technically feasible
- Sociopolitically acceptable
- Economically reasonable

And last but not least

- Beneficial to the environment

SpS 23 Special Session

Manufacturing Gas Plant Site Management

THE MANAGEMENT AND REHABILITATION OF FORMER GAS WORKS SITES LED BY GAZ DE FRANCE

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0 - ABSTRACT

Gaz de France manages 467 former gas works sites. In April 1996 the French Ministry of the Environment and Gaz de France signed an agreement laying down the general framework for coordinated management of these sites. The agreement sets out the procedures and a schedule of actions. It has since been complemented by a definition of semi-generic objectives for rehabilitating the soil of sites with development potential that have been earmarked for redevelopment or resale. These aims vary according to the uses planned for the sites and are based on a risk assessment approach. The Ministry, following consultation with Gaz de France, has also defined the procedures for monitoring the groundwater tables for the sites covered by the agreement. The rehabilitation of these sites with development potential is the subject of iterative studies based on site surveys and intended site uses, the purpose being to work out economically viable redevelopment projects in complete safety.

1 - INTRODUCTION

From 1798, the year LEBON invented the process for producing town gas, up to the end of the 1960's, several hundred gas works were in operation throughout France. In the 19th century the gas industry was a mark of real progress because the pyrogenic reaction of coal could be used to produce town gas capable of providing lighting, heating and a means of cooking food in totally new conditions of comfort and well-being.

The introduction of natural gas progressively brought about the closure of all existing gas works up to 1971. While surface installations were generally demolished, the by-products of the final production runs, which should have been recycled in the normal course of events, do not always have been removed, and varying amounts of certain by-products may still be found on the sites of former gas works, usually contained in storage buildings, in the soil or more rarely in groundwater tables.

Gaz de France manages 467 of these sites.

Among former industrial sites, gas works are a special case insofar as they are usually very old, most of them having been built in the 19th century, relatively small (in France, 80% of them are under 1 hectare in area) and often located near town centres. What is more, they contain low-mobility by-products (tar, purifying substances) that are often better left in place, from an environmental point of view, rather than being removed, thereby risking further pollution that has until now been contained.

Notwithstanding the limited environmental risk of such former gas sites, the current state of scientific and technical knowledge is such that one cannot afford to ignore the principle of precaution as set out in the 1995 "Barnier" Act.

Some of these sites are used for Gaz de France's own needs (sales branches or operational premises), but others are industrial wastelands with underemployed urban potential.

In such a context, what is at stake in rehabilitating these former gas works sites is to encourage a return to urban development in complete safety and in acceptable economic conditions, thereby adopting an approach based on sustainable development.

2 - GAZ DE FRANCE POLICY FOR MANAGING AND REHABILITATING FORMER GAS WORKS SITES

2-1 The agreement : a voluntary and contractual approach with the State

Gaz de France, with the full agreement of the Ministry of the Environment, has decided to adopt and pursue an environmental protection policy. This requires a balance to be achieved between the management of its "legacy" and its main core business.

Gaz de France's strategy is based on 3 guiding principles :

- The control and active monitoring of all former gas works sites, in particular those that have been earmarked for redevelopment or transfer,
- Research and development programmes to develop highly efficient and technically and economically viable soil analysis and pollution control processes,
- Participating in study and research programmes designed to assess health and environmental risks.

A number of factors, such as the large number of former gas works sites, findings regarding the stability of possible contaminants, the Company's financing capacity, the nationwide context of the pollution control sector and the nature of national legislation, led Gaz de France to categorize its sites according to their environmental sensitivity (with no presumptions as to the degree of site pollution), with a view to taking priority action on the most sensitive sites and scheduling environmental audits for the less sensitive ones.

And so on 25th April 1996 the Ministry of the Environment and Gaz de France signed a ten-year agreement clearly mapping out this long-term programme.

The agreement classifies all these sites into 5 classes according to their potential impact on occupants and immediate surroundings.

- *For class 1 sites (2 sites):*

Gaz de France undertakes to complete initial diagnosis as soon as possible, and embarks on the requisite rehabilitation works adapted to the local context. Such works are completed according to terms mutually agreed to with the government departments in charge of inspecting classified installations for environmental protection purposes.

- *For class 2 sites (61 sites):*

Gaz de France undertakes to complete initial diagnosis within 3 years. Depending on the results, Gaz de France undertakes to take the appropriate steps in agreement with the inspection authorities and within the same time-frame.

- *For class 3 sites (272 sites):*

Gaz de France undertakes to complete a historical survey within 8 years. Any tanks that may still contain by-products will be systematically located, drained and filled in.

- *For class 4 and class 5 sites (127 and 5 sites):*

Gaz de France undertakes to complete a historical survey within ten years. Any tanks that may still contain by-products will be systematically located, drained and filled in.

As far as class 3, 4 and 5 sites are concerned, if tank drainage operations reveal residual pollution, then further investigations will be carried out in agreement with inspection authorities.

In addition, Gaz de France undertakes to carry out initial diagnosis on the 467 sites before they are sold off, transferred or redeveloped. Rehabilitation procedures, laid down in agreement with the inspection authorities, should be geared to the site's sensitivity classification and its intended purpose.

Such are the terms and conditions of the private agreement Gaz de France has undertaken to fulfil. These undertakings meet the joint expectations of the Ministry and Gaz de France in environmental terms.

Initial diagnosis of the 63 most sensitive sites (classes 1 and 2) were completed within 3 years, as was the work that the authorities deemed necessary (rehabilitation work or the setting up of monitoring systems).

For the other sites, Gaz de France has drawn up an annual survey programme to meet the last two deadlines.

Sites in classes 3 to 5, which have redevelopment potential and currently number around 90, are subject to the same diagnosis provisions as those applicable to classes 1 and 2. They will then be rehabilitated in accordance with their future use.

The approach to rehabilitation Gaz de France adopted pursuant to the agreement, which concerns class 1 and 2 sites and sites intended for resale, transfer or redevelopment, complies with national methodological guidelines laid down by the Ministry of the Environment.

Any adjustments to the agreement required by changes in legislation are made by a joint consultative committee that meets at least once a year.

To facilitate local implementation of the agreement, the need for scheduling and coordinating plans of action became clear. In particular, two basic concerns have led to a global approach aiming to achieve consistency in how to proceed at national level:

- Setting rehabilitation objectives for development sites,
- Inspecting and monitoring the quality of underground water.

2-2 The semi-generic study laying down soil rehabilitation objectives for sites of former gas works with development potential

The Ministry of the Environment and Gaz de France have agreed to set uniform rehabilitation objectives for the entire territory to ensure standardized and consistent management of former gas plant sites.

This is when the need appeared for a decision-making tool for the redevelopment sites covered by the agreement : the semi-generic study.

As a result, Gaz de France embarked on a long drawn-out study in 1996, the aim of which was to draw up semi-generic objectives for soil rehabilitation of the former gas plant sites coming under its responsibility.

This approach was iterative in nature. At the Ministry’s request, two independent audits were completed. The Gaz de France study was conducted in compliance with French national methodology relative to polluted sites and soils.

Gaz de France conducted far-reaching studies with a view to gathering accurate knowledge of the characteristic substances in manufactured gas production that are likely to be found on the sites of former gas plants. With the resulting knowledge it was possible to determine the substances necessary to take into account for the semi-generic study.

Several criteria were taken into consideration to draw up the rehabilitation objectives : the health aspect, the olfactory aspect, and surface pollution leaching into the groundwater table. The health factor study consisted in carrying out a detailed health risk assessment in six different scenarios representing sensitive or non-sensitive site usage as appropriate.

The various parts of the study were validated by on-site tests. The study is therefore not a theoretical one.

The approved rehabilitation objectives have a margin of security.

They are economically feasible with the remediation techniques currently at our disposal.

The rehabilitation objectives set out in the Gaz de France semi-generic study were approved by the Ministry of the Environment in April 2001. They are now used in concrete terms for soil rehabilitation of the sites of former Gaz de France gas plants whenever such sites are earmarked for redevelopment or transfer.

2-3 Inspecting and monitoring the quality of underground water

There again, the Ministry of the Environment and Gaz de France have a common desire to adopt a consistent approach with regard to all the sites covered by the agreement.

As a result, Gaz de France conducted a study in 2001 and 2002 broadly based on the feedback it has acquired in the field of monitoring underground water directly underneath or near its former gas works sites, with a view to proposing decision-making criteria for setting up monitoring systems.

This study confirmed that these sites of former gas works have little impact on underground water, this often being limited to the site itself. This state of affairs can mainly be accounted for by the nature of the by-products most likely to be found on such sites and the length of time they have been there.

The detailed analysis of monitoring data from fifty or so sites reveals that class 2 sites have little impact on underground water, and sites classified in classes 3, 4 and 5 have even less impact. The results therefore bear out the classification criteria stipulated by the agreement.

In the light of this study, it appears that the criteria forming the basis for setting up monitoring systems are as follows :

- The presence of a groundwater table in use or reserved for a sensitive purpose,
- Any event that may cause pollution transfer : rehabilitation works or the existence of a runaway tar tank.

In a 19th September 2002 circular sent to inspection authorities, the Ministry of the Environment specified the implementation procedure for monitoring underground water on the sites covered by the agreement.

3 – <u>REHABILITATING FORMER GAS WORKS SITES HAVING DEVELOPMENT POTENTIAL</u>

In accordance with the provisions of the agreement regarding sites having development potential, namely those sites that are earmarked for transfer or redevelopment, Gaz de France is conducting an environmental audit, carrying out rehabilitation works adapted to the future use of such sites. Rehabilitation is an iterative approach comprising several stages, each of which depends on the results of previous stages and the site’s intended use.

<u>3-1 Initial diagnosis</u>

Gaz de France contracts out initial diagnosis surveys to a specialized firm whose job it is to :

- Assess the quality of underground water,
- Check that there is no risk of direct contact with polluted surface soil on sites.

<u>3-2 In-depth diagnosis</u>

The aim of this study, also conducted by a specialized survey firm, is to quantify the volumes of polluted soil requiring treatment according to envisaged uses for the site. Quantification is based on the conclusions of the semi-generic study. Wherever appropriate, a complementary detailed risk assessment study is also carried out.

Soil investigations therefore cover the entire plot of land on the site, not just the sensitive zones as revealed by historical surveys but also zones that are theoretically pollution-free.

3-3 The development feasibility study

This study takes into account the market, the wishes of local authorities and Gaz de France's aims. Gaz de France only decides to go ahead with development projects that are financially viable. In other words, the capital gain generated by property transactions must at the very least cover the cost of surveys and rehabilitation works.

3-4 Fine-tuning and approving projects

By fine-tuning their projects, Gaz de France is able to meet both pollution abatement requirements and urban constraints. When this stage is complete, the project is approved as soon as administrative and statutory permits are issued (ensuring that the project complies with local planning regulations, prefectoral pollution bylaws etc.).

3-5 Treating the site

As we have seen, the way the site is treated depends on the results of the applied semi-generic study and on any further conclusions arising from complementary detailed risk assessment studies in respect of the future use of sites.

Site rehabilitation may involve a variety of solutions:

- straightforward site monitoring if the site presents no risk with regard to its intended use,
- restrictions on how certain zones on the site can be used,
- reducing the mobility of pollutants by means of containment or disposal in waste reception centres,
- removing pollutants by means of soil treatment.

Generally speaking, there is no miracle solution for sites and a combination of these various options is usually decided on, taking the cost and overall efficiency of treatments from an environmental standpoint into account.

Whenever Gaz de France decides on soil treatments, the most common technique used is thermal desorption. If this technique is ill-adapted (the soil is too dirty or contains substances that do not react to thermal desorption), then the incineration technique is applied or soil is buried in technical burial centres.

3-6 Selling sites off: historical records

Notarized sale contracts for rehabilitated gas works include provisions for informing the buyer and contract restrictions binding the parties. These are kept at the mortgage registry and transferred to future buyers.

4 - ORGANIZATION, IMPLEMENTATION, RESOURCES

With a view to implementing the actions resulting from its management and rehabilitation policy relative to former gas works sites as part of the agreement, Gaz de France has set up a 3-tier organization:

- A local level located in Gaz de France's regional offices, for day-to-day site management and liaising with local authorities,

- An expert regional level preparing, supervising and coordinating on-site actions in one or more administrative regions, and permanently in contact with the inspection authorities,

- A national level comprising a team of experts based at the Property Delegation in Paris, which works out Gaz de France's general policy guidelines relating to former gas works, supervises on-site work nationwide and sees to it that the requisite resources are available; this team brings together both rehabilitation experts and real estate specialists, two types of skills required for this type of project.

In addition, Gaz de France calls on the services of many independent service providers specializing in site and soil pollution : surveyors, contract managers, building contractors, and soil treatment specialists.

It establishes and maintains the contractual relations with these various different partners in line with its national procurement policy, which is underpinned by a concern for cost control and compliance with French and European regulations and legislation.

In this context, Gaz de France draws up various types of contracts with all these partners:

- National or regional contracts : environmental audits, safety coordination on work sites, project management for tank drainage operations and rehabilitation works, thermal desorption soil treatment, and underground water quality monitoring,

- Special site-specific contracts for draining tanks and rehabilitation works.

5 - CONCLUSION

On 25th April 1996, the Ministry of the Environment and Gaz de France signed an agreement on the control and planned rehabilitation of the former gas works managed by Gaz de France at the time of signing. This contractual commitment by the State and a major industrial and landowning corporation is a unique example of pragmatic management of potentially polluted sites and soils.

The proportionality principle, which aims to prevent the risk of harming people and damaging the environment by taking effective and balanced measures, has been the driving force behind their common desire to implement the rational and coordinated policy governing this agreement.

At the outset, the agreement only made provisions for procedures and a time-frame of actions on both types of sites ; those for which no change is planned, remaining under the ownership of Gaz de France, and those earmarked for other uses. The agreement naturally evolved in two major ways. Firstly, with the definition of semi-generic rehabilitation objectives geared to the intended use of sites and based on risk assessment. And more recently, the establishment of underground water quality monitoring procedures.

Since October 2000, the general public can consult descriptions of the 467 sites in question, which are kept constantly up-to date, on the Internet site of the Ministry of the Environment (http://basol.environnement.gouv.fr).

When a plot of land is sold off, the site's history is also preserved in fully-documented and notarized records that also set out any contractual limitations of use binding both parties. The use in question is not perpetual and irreversible as far as the plot of land is concerned. The buyer still has the option of applying for an official change of use and thereby bearing the expenses and liabilities his decision entails, including the obligation to obtain the requisite official permits and authorizations.

Within this constantly evolving framework, Gaz de France has since the early 1990's successfully completed urban redevelopment programmes for around 300 hectares of land.

REDEVELOPMENT OF MANUFACTURED GAS PLANT SITES IN THE UNITED STATES

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0 - ABSTRACT

Of the many manufactured gas plant (MGP) sites throughout the United States, only a small percentage have been remediated and redeveloped. EPRI has performed extensive studies on characterization and remediation of MGP sites. This investigation focuses on analyzing the status of rehabilitation and reuse of these sites, including approaches to planning and use of remedial technologies that have been successfully used at sites throughout the United States. Many site owners are working cooperatively with state environmental officials and local communities to bring these sites back into some type of reuse. Risk-based approaches to site clean ups are used to limit active remediation to areas where risk associated with construction and future use scenarios are required. Cooperative efforts by all interested parties, including potential developers, are key to making these types of projects successful.

1 - INTRODUCTION

Before pipeline construction made natural gas and oil accessible to a large customer base in the 1950s, manufactured gas was produced locally in cities and towns by thermally cracking coal, oil, and coke at manufactured gas plants (MGPs). MGPs were located throughout the United States, typically on small parcels of a few acres in urban areas and town centers (GRI, 1990). They provided local production of gas for commercial, residential, and public street lighting from the early 1800s through the mid-20th century. Many of the sites were located adjacent to water bodies where boats were used to bring in feedstock (GRI, 1990).

Saleable byproducts associated with MGPs included coal tar, light fuels, liquors, ammonia, and coke. Typically, when the facility ceased operation, the MGP surface structures were demolished. However, byproducts and remnant process structures were often left behind at the site, sometimes in the subsurface. Current estimates indicate that there is between 1,000 (GRI, 1989) and 2,500 (American Gas Magazine, 1997) MGP sites throughout the United States, many of which still contain MGP byproducts below ground.

The market value of the property, regulatory enforcement, and internal corporate initiatives of site owners currently drive cleanup and redevelopment of MGP sites. There may be greater financial incentive to cleanup and rehabilitate a site if it is located in a highly desirable, urban area where property prices are high and available land scarce. In the spirit of recent Brownfields initiatives, reclamation of MGP sites for re-use has seen an upswing in the past few years (Larsen, 1997). A cooperative approach is being used to return these properties to beneficial reuse. Utilities, governmental agencies, and local communities have begun to jointly formulate cleanup and redevelopment plans.

A common redevelopment end use of MGP sites is as open space (i.e., greenways) for recreational areas. The locations of these sites are typically adjacent to water bodies in urban areas, making them ideal for recreational development. A relatively small percentage of MGP sites have been remediated and redeveloped with new buildings and infrastructure. The overall purpose of this investigation was to research, identify and identify a few MGP sites, and the methods used to successfully redevelop them.

A literature review was conducted to identify MGP sites that have been successfully redeveloped nationwide. An evaluation of planning, remediation and engineering approaches used to deal with environmental conditions at MGP sites were conducted. Current trends of MGP cleanups were identified. And, finally, the characterization of potential risks, limitations and incremental costs, compared with sites unaffected by coal tar residues were evaluated.

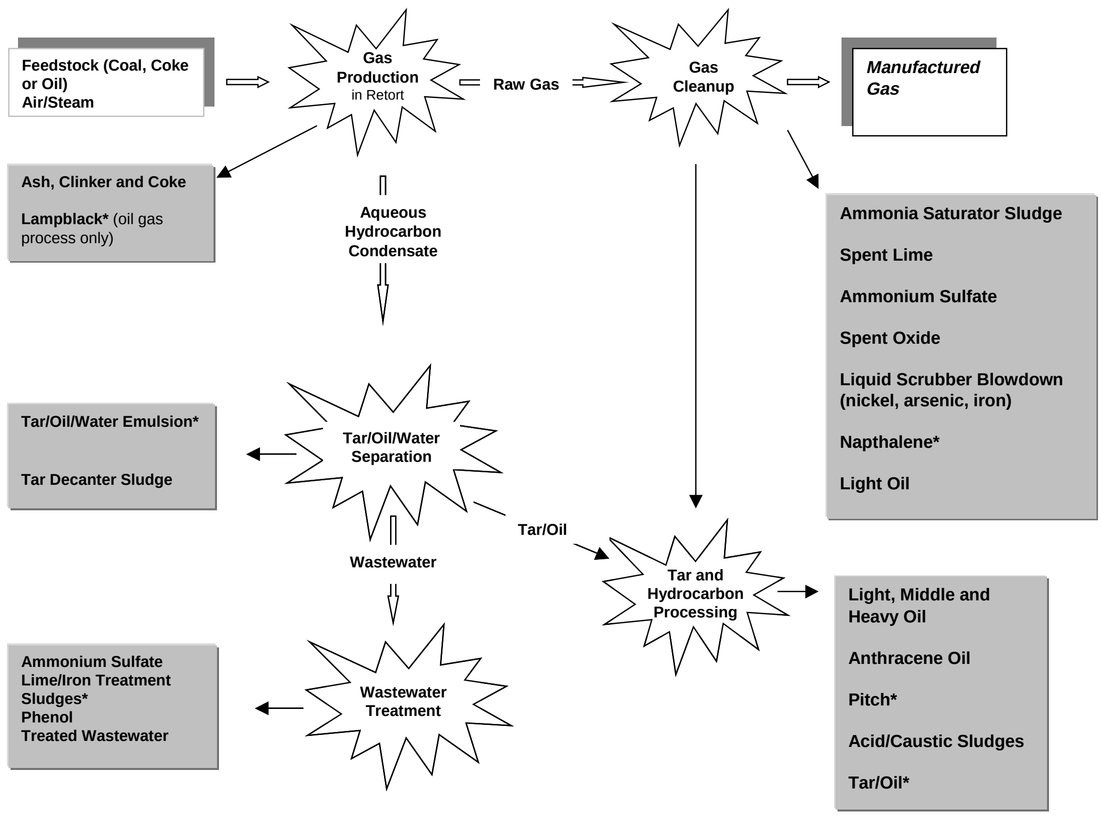
Research conducted during this study indicates that both innovative technologies and conventional, low technology types of clean up strategies are used by industry in the US. This investigation focuses on how innovative approaches are used in overall project development and management to return MGPs into productive or beneficial use. Based on the findings of this investigation, a protocol has been developed as a model for approaching project development and management for redeveloping MGP sites.

2 - GENERAL DESCRIPTION OF MGP SITES IN THE US

2-1 Operational History

The basic manufactured gas process involved heating a feedstock of coal, coke or oils with air and/or steam in retorts to produce raw gas. The raw gas was then processed by different methods to remove impurities. The byproducts generated during manufacture and purification of the gas depended on the composition of the feedstock, and varied widely (GRI, 1996; Larsen, 1997). It is estimated that there may have been 500 separate patented gas-making processes that utilized different configurations of equipment to manufacture gas using the basic process (Hatheway, 2000). Thus, various types of feedstock were used and byproducts generated. Figure 1 provides a general overview of the processes commonly used and their resulting byproducts; note that not all MGPs produced every byproduct listed.

Figure 1: Generic Manufactured Gas Plant Process



Modified from GRI, 1996. By-products shown in shaded boxes. Common environmental contaminants are starred

The three main categories of process types were: coal gas process, carbureted water gas process and oil gas process. These processes are briefly described below.

The coal gas process was used in early MGPs. Coal was loaded into a retort and heated. The raw gas generated was then sent through several process units to take out particulates and tar. The gas production process included purifier boxes of wood shavings or white lime, which cleansed the gas of inorganics, cyanides and sulfides (GRI, 1996).

The carbureted water gas process was introduced in the late 1800s and was in widespread use in the 1900s. This process could utilize the coke waste from the coal gas plants as feedstock. It was also a more efficient gas producing process. The carbureted water gas process involved injection of light oils into the manufactured gas downstream of the producer (Hatheway, 2000). In addition to coal tars, this process produced a water-rich emulsion of tar, oil and water.

The oil gas process used a range of oil feedstock such as naphtha, gas oils or heavy fuel oils. This process produced a tar byproduct, and is the only MGP process to produce lampblack as a byproduct (GRI, 1996).

2-2 Process Byproducts

The byproducts produced at various steps in a generic gas production process are shown in the shaded boxes on Figure 1. The types of byproducts are dependent on the chemical makeup of the feedstock and the type of process used. The initial gasification step produced raw gas, an aqueous/hydrocarbon condensate and solid waste (ash, clinker, and coke) (GRI, 1996). The oil gas process also generated lampblack as a byproduct.The raw gas was then subjected to cleanup to remove impurities, particulates, and tar. Gas was often purified by passing through boxes of wood shavings or white lime to remove inorganics, cyanides and sulfates. Other byproducts of the gas purification process included ammonium sludge, light oils, and naphthalene (GRI, 1996).

The coke byproduct from the first gas production step was reutilized, but there was little use for the ash and clinkers. The aqueous hydrocarbon condensate was subjected to tar/oil/water separation, which resulted in tar sludge, watery tar emulsions, and wastewater. In particular, the carbureted water gas process produced a water-rich emulsion of tar, oil and water (Hatheway, 2000). In some cases the tar could be re-used, but it was often left on site if no market existed for the byproducts. The wastewater was sometimes treated to recover ammonia or phenol, but this was rare (GRI, 1996).

2-3 Environmental Impacts

Environmental contaminants at MGP sites typically occur in three forms: coal tar residues in soils in the vadose zone above the ground water table; coal tar occurring below the water table as a dense non-aqueous phase liquid (DNAPL); and dissolved phase contamination in ground water.

A ubiquitous environmental contaminant at MGP sites, coal tar components are relatively immobile and vary in viscosity. Because coal tar is denser than water, and most components have a low solubility in water, it often migrates vertically and horizontally over time, and can end up in the saturated zone below the water table as a DNAPL. The DNAPL is sometimes found on the top of a low permeability layer, such as till, which in some cases can be relatively deep below the water table. It may also migrate horizontally along the slope of the till surface. However, since the tar is a viscous material, lateral movement is typically slow. The viscous, sticky nature of the tar and its occurrence in saturated soils deep below the water table make coal tar residues difficult to remove.

MGP byproducts contain both semi-volatile organic compounds (SVOCs) and volatile organic compounds (VOCs). VOCs typically associated with MGP coal tar include benzene, toluene, ethylbenzene, and xylene, commonly referred to as BTEX. These compounds are relatively soluble in water and are common ground water contaminants at MGPs. Benzene is considered to be carcinogenic, and has the lowest risk-based cleanup concentrations of the BTEX compounds. Because the allowable concentrations of benzene in ground water are less than or equal to 5 ppb (EPA Maximum Contaminant Level), benzene often drives ground water remediation at MGP sites. However, due to the age of these sites, the benzene plume may have moved off-site or it may have naturally attenuated through biodegradation and dilution.

The SVOCs associated with coal tar are primarily polycyclic aromatic hydrocarbons, commonly known as PAHs. PAHs have low solubility in water, tend to stick to soils, and are viewed as relatively immobile environmental contaminants. Some of the lighter PAH compounds, such as naphthalene, have some solubility in water. In particular, the PAH compound benzo(a)pyrene (B(a)P) can drive soil cleanup because it is one of the most carcinogenic of the PAH compounds, and therefore has the lowest cleanup criterion. However, B(a)P is very rarely found in ground water. Phenolic compounds and furans are also SVOCs sometimes associated with coal tar residues.

Cyanide, arsenic, and other inorganic contaminants are sometimes associated with MGP sites, but they are not considered a common occurrence. These contaminants tend to be found with purifier wastes, which include spent lime and sawdust.

Contaminant hot spots can be associated with MGP process structures, such as tar wells, gas purifiers, gas holders, and disposal areas (ash, purifier waste) (GRI, 1990). It is important to identify and account for them when planning a remedial strategy. Often, they are not identified until excavation has begun as part of remediation, when they can unexpectedly increase the scope and cost of soil treatment.

3 – CURRENT TRENDS IN MANAGEMENT OF MGP SITES

MGP site owners are often responsible for multiple sites, and develop comprehensive plans for the management and disposition of all their sites. Site owners often work closely with environmental regulators to formulate long term management plans. Management of the MGP closure includes consideration of current use, plans for redevelopment and re-use, site cleanup, and owners' relationships with local and state environmental regulatory authorities.

This section presents an overview of how MGP sites are currently being managed. It includes summaries of:

- The current uses of MGP sites
- The regulatory context of managing, cleaning up and redeveloping these sites
- Cooperative approaches to planning
- Remediation alternatives

3-1 Current Uses of MGP Sites

Many MGP sites are used by the utility for ancillary purposes such as natural gas service and distribution (GRI, 1990). Many of the sites that are redeveloped were completed before current environmental regulations were put into place. Of the sites that are currently being remediated and redeveloped, many are being used for open space and recreational purposes. Development of the parcels for open space/recreational use produces a beneficial community resource and is often a positive public relations initiative for both the current owner and government regulators.

3-2 Regulatory Context

The vast majority of MGP sites are addressed through applicable state regulatory programs or via consent orders (GRI, 1996). Only a relatively small percentage of MGP sites is cleaned up through the Superfund Program. Eight MGP sites are currently listed as final on the National Priorities List (NPL) and three sites are proposed (EPA, Personal Communication, 2002). Currently, many site owners across the country are cleaning up their sites and often are participating in official, state-run, cleanup programs. Generally, the site owners work with the state regulators and community groups to develop a comprehensive program for dealing with their MGP sites.

3-3 Cooperative Approach to Planning

The objectives of MGP owners, environmental regulators, and local communities are to clean up the sites and find a suitable end use for the properties. Risk-based approaches have been successfully applied at many of the redeveloped MGPs identified in this study. The future redevelopment and use of the site are considered, and cleanup/redevelopment plans are generally developed jointly by all interested parties.

Strategies used in redeveloping these sites are often formulated by a group of concerned parties including the landowner, the local community, environmental regulators, and potential developers. These approaches generally combine engineering, remediation, and institutional solutions. For the landowner, the main objectives are to clean the site to regulatory requirements and to relinquish long-term liability so that the property can be transferred and/or redeveloped.

3-4 Remediation Alternatives

The nature of the tarry soils located below the water table at MGP sites complicates cleanup; it is relatively difficult to deal with this type of contamination. Remediation plans usually include cleanup of at least a portion of the contaminated soils at MGPs where relatively high or unacceptable risk is indicated. There are many cleanup technologies that have potential for use at MGP sites, but the findings of this study indicate that the most commonly used approach by far is excavation of contaminated soils with off-site disposal. In most cases, the sites are small enough to make excavation practical, although alternative approaches may be appropriate for larger sites or sites with engineering controls on them. The prevailing view is that excavation is the most effective approach, and that in the long run, it is the most cost-effective.

Given the difficulty of removing and treating saturated, tarry soils at depth below the water table, sometimes contamination must be left in-place. In many cases, contaminated soils below the depth of construction and outside the footprint of on-site buildings, etc. are left in place. This is possible where deep contamination does not pose a significant risk to construction and future use scenarios. Deed restrictions are put into place that limits excavation down to the depth of contamination to avoid future exposures to the contaminants.

Alternative treatment technologies, which are discussed in Section 4, have been used less frequently, and are often not completely proven to be effective at MGPs. However, there are some instances where excavation is not feasible and an in situ (in-place) method is required. One such case is described in Section 5, where the location of the MGP site on a riverbank complicated excavation, and an in situ remedy was successfully applied.

The dissolved phase benzene plumes that often occur at MGPs must also be addressed. A risk-based approach to evaluating the need for ground water remediation is an important factor in redeveloping MGP sites. Ground water and contaminant transport modeling is used to estimate concentrations of benzene at possible ecological and human health exposure points such as surface waters and water supply wells. Since many MGP sites are located adjacent to surface water bodies, the surface water is often the main receptor. This makes evaluation of potential impacts to ecological receptors the driving force behind ground water remediation at many MGP sites. Natural attenuation has been appropriate in many cases where benzene is not impacting a receptor.

In the majority of cases identified, source removal, deed restrictions (also known as deed notices) and natural attenuation of dissolved ground water plumes form the remedial component of the redevelopment plan. These plans are developed and implemented jointly with the engineering and construction design for the new development. In a few cases, additional remedial actions are incorporated, such as containment, ground water treatment or solidification of contaminated soils.

Under the 1999 Battery Recyclers Case ruling (208 Federal Third 1047, D.C. Circuit Court), contaminated soils from MGP sites are not subject to classification as a hazardous waste based on TCLP results. However, this is a federal ruling, and states must either adopt it or make their own ruling. Some states require thermal treatment of MGP wastes to be exempt from the TCLP testing requirement. In some cases, MGP wastes could be classified as hazardous based on other criteria, including ignitability and corrosivity, or if they are mixes with a hazardous waste.

4 - REVIEW OF REMEDIAL TECHNOLOGIES APPLICABLE TO MGP SITES

There are many innovative cleanup technologies that could be successful in cleaning up MGP-related contamination, and numerous summaries and compendiums of these technologies already exist. For example, the EPA publication A Resource for Manufactured Gas Plant (MGP) Site Characterization and Remediation (EPA, 2000) provides a thorough survey of remedial technologies with detailed descriptions and case summaries.

However, based on the results of this overview, innovative cleanup technologies have not generally been used to clean up and redevelop MGP sites. Low technology, low-cost approaches to site construction has been preferentially utilized to remediate and redevelop MGP sites. Rather, it is the use of innovative approaches that has been adopted in developing holistic solutions for site cleanup and redevelopment. Innovation is employed in reaching out in new ways to regulators and local communities to jointly develop redevelopment plans for these unused sites. Using cooperative approaches, regulators are more open to creative remedial approaches and long-term management of the sites, resulting in community and regulatory acceptance of technology.

5 - CONCLUSIONS AND FURTHER READING

The majority of sites that have been remediated are re-used for recreational purposes. However, there is a growing trend that has established the value of regentrifying these parcels into commercial real estate. Many former MGPs are located on waterfront parcels, often in prime, downtown locations, making them eminently suitable for recreational/open space use and many parcels are in areas that have been reborn into commercially valuable space.

A risk-based cleanup strategy, with recreational or commercial re-use in mind, often allows immobile subsurface contaminants to be left in place or capped in place. This type of redevelopment produces favorable results for all parties. Previously unused parcels are turned into useable open spaces for the community, where warranted. A risk-based cleanup strategy often minimizes cleanup costs, which provides incentive to the property owners. Regulators achieve site cleanup with the support of the community and site owner alike. A full study of different sites that have been redeveloped has been reviewed by EPRI (Coleman et. al. 2001). This study identified and catalogued sites that have been redeveloped with new infrastructure or as open space in conjunction with remediating environmental contaminants.

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THE SUSTAINABLE MANAGEMENT OF FORMER GAS WORKS SITES UNDER THE PART IIA CONTAMINATED LAND REGIME

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0 - ABSTRACT

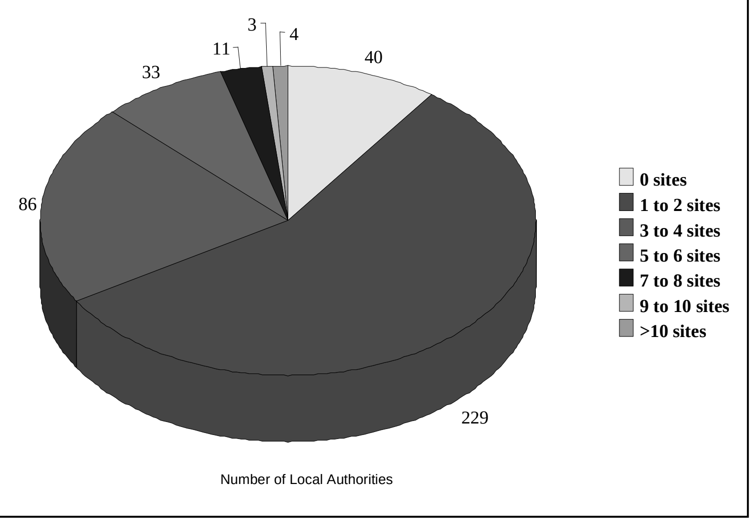
Secondsite Property Holdings (SPH), part of National Grid Transco (NGT), manages a large national portfolio of land including many former gasworks and associated sites arising from a history of gas manufacture extending back nearly 200 years. As well as managing its own land, it also manages the issues associated with historic gasworks contamination for Transco – the UK's national gas distribution company. Secondsite Property Holdings was established with the twin goals of managing the potential contaminated land liabilities associated with the portfolio and releasing value from the surplus land.

With regard to remediation, the industry will have to change significantly in response to European and national legislation and the foundations have been laid through a variety of research projects. However, many of the innovative and sustainable approaches being developed will only see wide spread application if the current conflicts between different areas of legislation can be resolved. This should be a priority for both industry and regulators alike.

1 INTRODUCTION

In April 2000 (England), July 2000 (Scotland) and July 2001 (Wales), Part IIa of the Environmental Protection Act 1990 was introduced onto the statute books, making local authorities (LA's) the front line regulators for contaminated land. This created over 400 local environmental regulators in total, most of which have a direct interest in how the portfolio is managed.

Figure 1. Distribution of Sites Across Local Authorities



The distribution of ex-gasworks sites nationally in the UK is by no means even, the original gasworks being formed to serve local communities and industry before the advent of the national gas transmission system. This resulted in a higher density of gasworks in the major urban areas, but with most small towns also possessing at least one gasworks. This is illustrated in Figure 1 which shows the distribution of National Grid Transco owned gasworks sites by local authority.

For several years Secondsite Property (and its predecessor Companies) have adopted a phased approach to the environmental management of its complex property portfolio to support its key business objectives of:

i) identifying and reducing real or major latent environmental liabilities
ii) adding value through property sales and rental income

The National Grid Transco (NGT) Group gasworks portfolio sits in 366 local authorities in England, Scotland and Wales. Each of these authorities has a duty under Part IIa to inspect the land in their area in order to identify Contaminated Land against a statutory definition and to encourage voluntary remediation or to take enforcement action where necessary. In many ways, Secondsites management objectives mirror those of the local authorities (e.g. LA's have a duty to inspect – Secondsite has a planned inspection programme; LA's must set priorities – Secondsite require priorities to manage budgets and environmental risks; both parties have an interest in encouraging brownland regeneration). To this end, Secondsite considers that the best interests of the environment and brownland redevelopment are served by a properly structured national approach to the management of the portfolio. This means that, despite the similarities in approach and objectives, there is the potential for conflicts of priority to exist between up to 366 local area based strategies and Secondsites single national strategy, without any strategy being technically in error.

The Statutory Guidance issued under Part IIa encourages voluntary action over enforcement as the best means of using limited resources. However, local authorities require comfort that voluntary action will be taken over an appropriate timescale and have a duty to demonstrate to their communities that appropriate and proportionate assessments have been carried out. Whist this is an objective that can (and should) be supported by industry, unless managed correctly by all parties, there is a danger that the proactive management of large portfolio's such as Secondsites can lead to 'blight' of land values by drawing disproportionate attention to those sites compared to landowners who have not been so active in investigating their potential liabilities and environmental impacts. This paper describes the prioritization and management process used by Secondsite that is used to support communications with local authorities and to define its annual programme of environmentally driven remediation projects.

Due to its favorable geology, the UK has a long history of managed, reactive, landfill sites and the low cost, coupled with the fact that it has often been Best Practical Environmental Option (BPEO) to dispose of contaminated land to such sites has meant that this approach has dominated the UK remediation marked. The introduction of the Landfill Directive will have major implications for the way that contaminated land is remediated in the UK with many types of waste either being banned or becoming prohibitively expensive to dispose of in this way. Adapting to these new market conditions will be a challenge for industry and regulators alike. Failure to adapt could result in a significant decrease in the amount of brown land being redeveloped and hence increase pressure on greenfield sites. Some of the issues that this raises and the steps that Secondsite, and others, are taking to address these changes are also discussed.

2 ENVIRONMENTAL MANAGEMENT MODEL

In the early 1990s an environmental risk-screening model was adapted for gasworks from a Canadian Government CCMS approach to screen potential problem sites. It addressed the key issues in the emerging legislation on contaminated land, namely the source, pathway and potential receptors around and on each site. The objective was to develop a consistent approach to ranking sites for further attention based on increasing levels of site knowledge. The ranked sites provide the basis for developing programmes and budgets for further work based on environmental need, e.g. site investigations, risk evaluations, remedial design, remediation or monitoring. Since then, the model has gone through several stages of evolution and now incorporates detailed spatial information on each site entered as well as its chemical and physical characteristics. It represents a robust and pragmatic method of comparing hazards from sites, whilst at the same time assessing their potential impact on the previously identified receptors.

The model uses a series of six generic source – pathway – receptor pollutant linkages to assess the hazard posed by each site. These six linkages are shown in Table 1 and have been selected to combine the key sources of hazards associated with former gasworks and associated sites and those targets listed under Part IIa. Only linkages 1 –4 are used directly in the prioritization process; linkages

5 and 6 are assessed to help ensure that site security and management measures are sufficiently protective of workers on the site and people living close to it. Thus, for example, an action arising from identifying such a hazard might be to ensure that the perimeter of the site is maintained in a secure condition or that surface contamination is covered, thus interrupting the potential pathway.

Table 1. Pollutant Linkages used in the EM model

Pollutant linkage group	**Source**	**Pathway**	**Receptor**
1. Leaching soils impacting surface water	Leaching soils	Run-off or Lateral Flow (through underlying strata or along conduits such as Drains or pipes)	1. Surface Water 2. Humans 3. Environment
2. Leaching soils impacting groundwater	Leaching soils	Vertical flow (through underlying strata or along conduits)	1. Groundwater 2. Surface water 3. Environment
3. Contents of tanks impacting surface water	Contents of tanks (e.g. tar)	Run-off or Lateral Flow (through underlying strata or along conduits such as Drains or pipes)	1. Surface Water 2. Humans 3. Environment
4. Contents of tanks impacting groundwater	Contents of tanks (e.g. tar)	Vertical flow (through underlying strata or along conduits)	1. Groundwater 2. Surface water 3. Environment
5. Exposed soils impacting off-site humans	Exposed soils/ waste deposits on surface	Airborne/ dermal/ingestion	1. Humans (off-site) 2. Environment
6. Exposed soils impacting on-site humans	Exposed soils/ waste deposits on surface	Air borne/ dermal/ingestion	1. Humains (on-site) 2. Environment

The model has been designed to address historical land contamination and does not priorities sites on the basis of environmental hazards associated with the current operational activities of either SPH, Transco or any of SPH's tenants. However, any historical contamination, which may not have been generated by the coal or oil gasification activities on the sites, will be identified.

The overall aim of the model is to provide a generic screening approach to prioritize the national portfolio of sites using standard, formatted datasets that are sourced and digitized from the findings of desk studies, site investigations and remediations. The model is constructed in database software and uses a bespoke program to interpret each site-specific dataset and prioritize each site with respect to the others. The model is a dynamic system which rapidly responds to new or improved data, e.g. new soil guidelines, effects of remediation, a revised water quality objective for a river. By changing one factor (e.g. removal of tar tank), the relative priority of that site is instantly revised.

It should be noted however that the EM model is not an exclusive decision making tool, but is used to aid in the processing and assimilation of large quantities of data. Final priority and programme decisions are taken using additional inputs from external environmental consultants, internal Secondsite staff with direct 'on the ground' knowledge and also from external sources such as the local authorities, the Environment Agency (EA) and Scottish Environmental Protection Agency (SEPA).

3 PORTFOLIO MANAGEMENT STRATEGY

Programming of remedial action is based on a rolling site-specific sales program coupled with environmental priorities derived from the model and other sources. A specific environmentally driven remediation programme is required because the sales driven programme does not necessarily target the sites with the highest potential environmental risks.

In order to select and track risk management decisions on sites, a risk management database has been developed from the environmental screening model, which also incorporates information from other sources such as the sales programme and 'on-the-ground' knowledge. This identifies five categories/priorities for action (High; High-Medium; Medium; Medium-Low; and Low) that are used build a rolling remediation programme as described below. It is important to recognize that the categories do not define a site as Contaminated according to the Part IIa definition but indicate where there are HAZARDS that require attention (which may simply be further assessment)

In order to meet the aim of managing priorities on a national basis this is used to drive information flow between SPH and local authorities as follows. A facility to implement 'emergency' action remains although if a specified site is introduced into the programme this will normally be at the expense of a lower priority one. The relationship between sales and environmentally driven sites is shown is Table 2

Site Name	Environmental Priority	Sale program ?	Action
GW1	High	No	Remediation. prog
GW3	High	Yes	Remediation. prog
GW2	High-Medium	No	Provisional prog.
GW4	High-Medium	Yes	Remediation. prog
GW7	Medium	No	Review date defined
GW5	Medium	Yes	Remediation. prog
GW10	Medium-low	No	Review date defined
GW6	Medium-low	Yes	Remediation. prog
GW8	Low	No	Review date defined
GW9	Low	Yes	Remediation. prog

Table 2. Relationship between Sales and Environmentally Driven Site Remediation Programming

i) For sites defined as 'high' priority or for sites in the current years program, the LA and EA/SEPA will be contacted as part of the usual build up and planning for site works. Regulators may be contacted earlier in some cases where it is anticipated that a longer lead-time is required. In the first instance, the response to a site specific Part IIa enquiry is to state the intention to remediate the site and give some indication of when it is proposed to enter detailed site specific discussions. It is felt that this satisfies the 'voluntary action' requirements under Part IIa.

ii) Sites defined as high-medium priority are placed in a provisional programme. As works commence, and high priority sites are remediated or assigned lower priorities as a result of further risk assessment, sites with a high-medium classification will be moved from the provisional to the defined programme of works. Again, environmental regulators would be contacted and supply detailed information as part of the build up to site works. In this instance detailed programme information is not be available and a response to a local authority enquiry would be to identify the provisional programme year to which the site has been allocated (although this may change as more detailed information from the rest of the portfolio is assessed and prioritized)

iii) Sites with a medium, medium-low or low rating that are not in the sales programme, are not placed in a formal remediation programme but are kept under review. The review date being determined by the hazard rating. Again, this is consistent with the recommended LA prioritization approach. A local authority will be supplied with the proposed review date in response to detailed enquiries supported by a valid inspection strategy. Detailed site investigation reports are not issued for these sites unless a LA identifies legitimate site specific issues (such as a pollutant linkage under Part IIa)

iv) In the absence of specific concerns related to individual sites, a first response to a LA would be to supply a contact point, basic ownership details and grid references in order to assist LA's in the compilation of databases

4 DELIVERY OF REMEDIATION

In the UK, remediation has been historically dominated by disposal to off-site landfill, with landfill gate prices being available at less than £10/tonne for hazardous wastes. However, the introduction of the European Landfill Directive is a significant driver for investment in remediation technology research, as it will have a major impact on the cost of traditional 'dig and dump' approaches to remediation.

Landfill Tax was also introduced several years ago to act as a further incentive to reduce waste generation from all sectors of industry, including domestic refuse collection. Following extensive lobbying by industry, contaminated land remediation was exempted from landfill tax (subject to certain conditions such as only applying to historic contamination) but this is unlikely to remain the case in the medium to long term, again driving the need for research into alternative approaches. Whilst at first appearing to be unsustainable, the industry view was in fact formed (and recognized by Government) from a recognition that most brown land regeneration projects are undertaken on a purely commercial basis where remediation is driven by the voluntary change of use rather than the possibility of enforcement under environmental law. Significantly changing the cost base of this would have driven developers towards the less sustainable use of greenfield sites. Landfill tax exemption is thus considered to be a temporary measure until the the technical and commercial basis of alternative approaches has been developed in the UK market – an objective that organizations such as CLAIRE are working towards (see www.claire,co.uk)

Where remedial action is necessary, it is useful to categorize projects into the varying degrees of intervention required to achieve the overall goal. Three categories of risk management are therefore defined;

1. site boundary control and treatment (e.g. where a source cannot be accessed due to the presence of live plant or a building);
2. in-situ source treatment;
3. ex-situ source treatment (on site and off site – including disposal)

Choice of approach is dictated by the end use of the site, cost effectiveness and durability of the solution, and constraints imposed by the existing use of the site. For example, direct access to sources of contamination is often not possible on operational Transco sites so boundary control approaches will be more suitable in many cases.

In recognition of the need to move towards site based solutions, Secondsite have invested in full scale technology demonstrations of Soil Washing, various forms of bioremediation, accelerated bioremediation in a purpose built bioreactor, permeable reactive barriers (PRB's), long term research into the performance of cement bentonite walls and a range of groundwater treatment systems including air sparging, enhanced DNAPL recovery and pump and treat.

As well as the usual range of technical factors governing selection of a suitable remediation technology, in the case of Secondsite, choice of remediation approach is also heavily dictated by the size of the site. Approximately half of the sites in the portfolio have areas of less than 1Ha and 80% of the sites in the portfolio have areas of less than 4Ha, making it not cost effective to mobilize many technologies to site. Fixed soil remediation centers have yet to be established in the UK and it is likely to be some time before such facilities are widely available at reasonable haulage distances. In order to bridge this gap, Secondsite in conjunction with the Soil and Groundwater Technology Association (SAGTA – a UK contaminated land holders industry network, see www.SAGTA.org.uk) and exSite Research (see www.exsite.org) have initiated a project, CLUSTER, to investigate the technical, economic, commercial and regulatory issues associated with the establishment of temporary hub sites for the remediation of local clusters of small sites.

Critical to the success of all ex-situ processes, whether using mobile plant, hub sites or fix treatment centers is the ability to re-use the material generated without the constraints and stigma attached to the classification of such material as ‘waste’. In common with some other European Union countries, there appears to be a conflict between the definition of waste (being hazard based) and the definition of contaminated land (being risk based). This results in circumstances where ex-situ treated contaminated soil can still be regarded as a waste and therefore subject to strict controls even though it can be shown to be fit-for-purpose and of a higher standard that soils that were deemed suitable to remain in the ground on a risk assessment basis. This situation is exacerbated when the source of recovered soil is a different site and there have been several cases where natural clays have been categorized as waste and subjected to controlled re-use simply because they were surplus to requirements on the donor site. Clearly such matters require resolution if alternatives to disposal to landfill are to be widely accepted and it should be the aim of regulators and industry to work together to achieve this on a national and Europe wide basis.

5 CONCLUSIONS

Part IIa requires that inspection strategies are rational, ordered and efficient with the most serious problems identified first. Second site’s environmental risk management process is, by necessity, operated on a national basis but in all other significant respects mirrors the requirements placed on Local Authorities under Part IIa. The approach adopted is considered to be scientifically robust and is used to target resources to where they are most needed to maximize environmental benefits through voluntary action. Although identification of Contaminated Land under the new regulations is still in its early stages, there are positive signs that Secondsites national objectives and approaches are being recognized by many local authorities.

The challenge over the next few years will be to maintain a program that represents best use of resources to attain maximum environmental improvement in the face of potentially differing, but legitimate, local priorities. This can only be achieved by continuing a positive dialogue between industry and regulators so that each are aware of, and understand, the others perspectives.

With regard to remediation, the industry will have to change significantly in response to European and national legislation and the foundations have been laid through a variety of research projects. However, many of the innovative and sustainable approaches being developed will only see wide spread application if the current conflicts between different areas of legislation can be resolved. This should be a priority for both industry and regulators alike.