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Theme E:

SPECIAL PROBLEM ORIENTED APPROACHES

E.1 Lecture Session:

Brownfields

Use of a Brownfield Trust for Revitalising a Petrochemical Industry and a Large Contaminated Site in the City of Montreal

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Introduction

Due to the easy access provided by the Saint-Lawrence River and to the convenient proximity of the targeted market, the eastern part of the Montreal Island has been developed during the 20th century into a huge industrial area. With six refineries operating in the seventies, some of them already functional in the 20's, the petrochemical sector was for a long time a leading activity in this area, generating at time hundreds of jobs. This «Golden Age» has been followed by a large scale industrial rationalisation and resulted in the decommissioning and dismantling of four of those refineries. It is no surprise that this intense petrochemical activity, sustained for almost 80 years without, for most of the time, much concern about the environment, was responsible for the extensive contamination of the island's soils, sediments and groundwater.

One of the refinery operating in Montreal-East has been known as the Gulf Canada petroleum refinery (Gulf). The first petrochemical facility, build by the British American Oil Company, started to operate at this site in 1931. It became later the property of Gulf Canada which operated the site till 1986. It was then divided into parts. One part, a 210 000 m^2 property including the former refinery, was sold to Kemtech Petrochemical Corporation Inc. (Kemtech). Instead of resuming Gulf activities, refining petroleum hydrocarbons, Kemtech modified the plant to produce para-xylene, using naphtha as a raw material. To accomplish that, Kemtech was financially backed by diverse banks and by the Quebec Government.

Looking for partners to restart a bankrupt plant

By 1991, Kemtech financial situation had seriously deteriorated. The company finally went out of business, leaving behind the property, the plant and the workers. A group of local industrialists showed interest in acquiring the property and resuming industrial activities. But things had drastically changed since 1988 regarding the revitalisation of abandoned industrial sites, with the publication by the Quebec Ministry of the Environment of the Contaminated Site Rehabilitation Policy. Even if not backed by any legislation, this Policy had raised among all stakeholders a concern on contaminated soils, the clean up costs and the potential associated liability. Thus, before engaging themselves further, the prospective Kemtech property buyers asked for a site assessment. This has not been done by any of the previous owners. A preliminary assessment pictured a site in a poor condition, with not only a lot of abandoned surface waste and equipment waiting to be managed but also heavily contaminated soil and groundwater. The limited data suggested that it could cost as much as 100 millions $ Can. to restore the site.

When this became known, the potential buyers vanished, as well as all the Kemtech preferential creditors which preferred to renounce any claim on this piece of property (and the recovery of their loans) instead of facing the risk to have to cleanup the site The government, as one of the lender, was left alone to face the problem. Wishing to preserve the jobs and economic activity this industry had created but having no expertise to run such a plant, Quebec advertised internationally to find a third party willing to come and get involved. Some showed interest, but they withdrew when they learned about the poor site condition. For a while, it seemed as if the government would be unable to get anyone involved. If the property could not be sold, Quebec would end up not only burying a once profitable economic activity but also having the responsibility to secure the site and address its contamination. Facing losses on all side, Quebec looked for original solutions.

Restarting the plant

At one point, the Coastal Petrochemical Company, an American company showed interest to purchase the plant, refurbish it and produce para-xylene. But Coastal makes clear that it did not want any past contamination liability. Discussions pointed at a possible solution. Coastal would buy the equipment but not the land. The government, for diverse reasons, was not enthusiastic in becoming the site owner and manager of the contaminated site. Somebody else had to do it. A recent change in the Quebec Civil Law provided a solution. It has now become possible to transfer the ownership of the land and the associated liability to an independent entity, a Trust. Government and Coastal representatives explored that possibility and worked out a legal agreement which was signed in 1994. Following that agreement the Quebec Government sold, for a nominal price, the title for the buildings and equipment directly to Coastal and transferred the property's title to the «Fiducie des Installations pétrochimiques de Montréal-Est» (Montreal-East Petrochemical Installations Trust).

The agreement stated that:

- Coastal was indemnified from any environmental contamination present at the time of the transaction, but was liable for any new contamination resulting of its own activity;
- The Trust had become the owner and manager of the site and waste found in and on the site and, as such, the Trust would be responsible to manage the past contamination and the liability associated to it.

Following the ratification of this agreement, Coastal modified the abandoned Kemtech plant to produce para-xylene from more refined raw products then the naphtha used by their predecessor. The plant revival created approximately 250 new jobs.

A plan to tackle the environmental problems

But to resume industrial activity was only one part of what the government was aiming to achieve at the site. Therefore, the agreement also had sections on the environmental obligations of each stakeholders, the Trust being responsible to put forward the following action in the given order:

1. Realise in the shortest possible delay a soil and groundwater assessment ;
2. Clean up all surface waste in the following order:
    - Complete all work needed to restart the industrial complex;
    - Complete all work needed for the site to be in compliance with the environmental regulation;
    - Complete all work needed for attending potential environmental problems.

    Surface waste meant all solid, liquid or semi-liquid found in the production, storage and used water treatment equipment, as well as in the pipes, oil pipelines and gas pipelines located on the site of the industrial complex, except if those residual were used in the Coastal operation. All equipment which should be cleaned up for restarting the plant and complying to the environmental regulation were described in a Surface Waste Protocol annexed to the agreement. A priority order was also laid down.
3. Elaborate and apply a program allowing the recovery of contaminated groundwater, as soon as possible after the completion of the soil and groundwater assessment.
4. Clean up the contaminated soils

Providing the financial means to assess and cleanup the site

Having a cleanup plan does not improve much the site condition if there is no financial means to materialize it. The agreement signed by Coastal and the government answered that need in creating an Environmental Fund. This Fund, dedicated to solve the environmental problems at the Kemtech site, would be manage by the Trust and supplied by Coastal and the government. The Fund is replenished according to the following rules:

Coastal contribution

1. For the surface waste and soil clean up
   - At the start, Coastal pays an anticipated sum of 1 000 000$ U.S. to the Trust
   - Afterwards, Coastal must contribute yearly «Environmental Rights» to the Trust, The Rights are fixed like this.
     - (i) 2,50 $U.S. for each metric ton of petrochemical product manufactured and sold and;
     - (ii) 0,75$U.S. for each metric ton of other admissible products manufactured and sold.

   The maximum contribution is 1 000 000$ U.S. a year. This rate will be revised each five years following a pre agreed formula. This yearly environmental rights will be paid by Coastal to the Trust as long as the company operates on this site.
   - Coastal can anticipate voluntarily payment on its Environmental Rights if the company estimates and demonstrates that it is necessary for operating its plant to proceed at the elimination of the surface waste quicker or on a different order then what was planned in the Surface Waste Protocol

2. For the Groundwater Recovery Program
   - Besides its Environmental Rights, Coastal must contribute to the Funds:
     (a) The cost to set up a Groundwater Recovery Program not exceeding the total cost of 200 000 U.S. $ (based on 20 recovery wells dig at a maximum depth of 30 feet each) and;
     (b) The cost to maintain that program. Meanwhile, Coastal is not entitled to pay for the functioning when the recovered material cannot be treated in the normal operation of its used water treatment facilities or in other of its plant treatment installations.

Governmental contribution

The government contribution to the Fund will consist in loans allowing the Trust to realise the first site assessment, the clean up the surface waste and the put in place and execute the groundwater recovery in a timely manner. The Trust will have to start paying back the loan the day the surface waste management will be completed. It is foreseen that the cleanup should take 5 years.

Coastal contributed its environmental rights as planned till 1998. Then, unfortunately, the price of para-xylene (the product manufactured by Coastal) went seriously down and the plant had to momentarily cease production, putting an halt to the Kemtech contribution.

New plants

Soon after, interesting development, related to the existence of the Coastal plant, occurred in Montreal-East. The company Interquisa Canada Sec. (Interquisa), a spanish plastic producer, was searching for a site to build up a new teriphtaltic acid plant, a production needing paraxylene as one of its raw material. After having evaluated some sites in different countries, Interquisa Canada opted for Montreal-East, one of the main reason being the existence near buy of a paraxylene producer, the Coastal plant. The plant construction, next to Coastal on a former Esso refinery site (the plant has been dismantled and the site fully cleaned up to the generic clean up criteria by Esso), started in 2001 and the plant should be operating in fall 2003. When it will be running, the 600 millions $ Can. Interquisa plant will use the whole Kemtech paraxylene production. Following the Interquisa arrival, Coastal announced that it will resume its operation (and payment of environmental rights to the Trust) in 2003.

Soon after, the PTT Poly Canada Sec. Company (PTT), a purified terephtalate polythrimethylene producer, a fibre similar to nylon, announced that it would join this industrial production chain and locate itself next to Interquisa, as it needs Interquisa product to manufacture its own material. PTT opted to build its 150 millions $ Can plant on the former Kemtech site, next to Coastal, under similar condition as the one convened with Coastal.

The 1994 agreement had to be reopened to include PTT. It was decided that the initial 1 million $/year Coastal contribution would be split between the two companies, PTT having from then on to pay 300 000$ U.S. a year and Coastal 700 000$ U.S.. But, unlike Coastal, PTT will have to pay minimum environmental rights of 180 000 $ U.S. a year, even if it does not produce anything. PTT had also to contribute an anticipated 500 000 $ U.S to the Environmental Funds the first year.

The arrival of PTT induced the first soil clean up operation on the Kemtech site. Unlike Coastal, which reused existing facilities, PTT had to build a new plant and excavate contaminated soils. For doing so. 25 000 to 30 000 cubic meters of PAH's heavily contaminated soils had to be excavated and stored on the site. The Trust is managing all the clean up work, as well as the construction of a concrete slab at the bottom of the excavation and membrane of the side to isolate the clean fill brought on the site.

The Environmental Accomplishment from 1994 to 2002

Since 1994, the following things have been realised on the Kemtech site

Site assessment

A full environmental assessment was commissioned by the Trust and performed in 1994-1995. It concluded that:

- The soils were contaminated by mineral oil and grease, monocyclic aromatic hydrocarbons (MAH), polycyclic aromatics hydrocarbons (PAH), and at a lesser extent phenolic compounds and Polychlorinated Hydrocarbons (PCB's). Contamination could be as deep as 3.15 metres;
- The groundwater was contaminated by mineral oil and grease, monocyclic aromatic hydrocarbons (MAH), polycyclic aromatics hydrocarbons (PAH), and at a lesser extent phenolic compounds, sometimes at concentration more then hundred times the recommended criteria;
- Some sediment as well as surface water samples taken in canals boarding the sites. appeared also at places contaminated;
- A free hydrocarbon phase was located on the site

It was estimated that 40 millions $CAN would be necessary to restore the site to the industrial generic criteria now appearing in the Policy. Moreover, 5 to 8 millions $CAN would be needed to manage the surface waste.

Surface Waste Clean up

- The Trust has used the Environmental Rights paid by Coastal and the governmental loans to complete phase one and two of the Protocol on Surface Waste lean up the surface waste, following the indication of the Surface Waste Protocol. This means that all equipment needed to restart the plant as well as all equipment which did not conform to regulation have been cleaned up, repaired or replaced. All the contained waste, including hazardous waste, has been treated. The Trust just started to work at the third part of the protocol, attending to the equipment which could create potential environmental problems and plan to be through it in five years (quicker if more money become available).

Groundwater Recovery

The Groundwater recovery program has been devised and agreed on by the ministry of the Environment. It is operating since January 1998

Contaminated Soils

25 000 to 30 000 cubic meters of PAH's heavily contaminated soils have been excavated prior to the construction of the PTT plant. It is stored on site and treatment options are actually evaluated. Treatment should start in a year.

Conclusion

From the socio-economic point of view, the Kemtech Trust can be described as a real success. By relying to this unique solution, the Quebec government was not only able to restart the Kemtech plant but also to attract two other massive industrial investments in the area. Instead of ending up managing an abandoned industrial plant on a derelict contaminated site, Quebec is contemplating the build-up of a modern industrial chain revitalising the whole sector.

It will take many more years before it can established if the environmental results were as good the economic one. Clearly, the Trust should not be used as a replacing tool for the application of the polluter pays principle, when this principle can be applied. Kemtech, Gulf Canada and the former polluters should have cleaned up the site before leaving it behind. If this would have been done, the same economical results could have been achieved, at a quicker and more trouble free pace.

But, for diverse reasons, the polluters could walk away. As a fall back solution, the Kemtech site Trust gave to date interesting environmental results. The clean up is underway and a substantial environmental work have been done to date. With the arrival of Interquisa (restarting Coastal activities) and PTT, the financing for future work will resume. It may take 50 years, but, at the end, the site should be cleaned up.

Some terms of the agreement could have been written differently to reduce the risks of having a «bankrupt» trust. If relating the payment of the Environmental Rights to the production makes sense, there is a problem not having a minimum compulsory fee to pay even if there is no production. When Coastal momentarily ceased to operate, the Trust had to burrow governmental money not only to keep on cleaning the site but even to pay the recurrent expenses (staff, administration, etc.) necessary to maintain itself. The Trust could not have survived such a situation over many years. This was solved with the arrival of PTT, as the agreement signed with this company specified that minimal Environmental Rights must be paid by the company, even if there is no production .

Could the government have kept the site and managed it the same way as the Trust? Theoretically yes. But government are less manoeuvrable entity and it may have been difficult to achieve the same result as the Trust did. More over, the government was not so keen to give the signal that he was willing to collect abandoned contaminated site, even again it's own will, and manage them. Finally; and this is perhaps the best argument, if there would have been no Trust, the government would have end up divided between its regulator and owner roles when dealing with the contamination. The way it is now, the ministry of the Environment was able to play fully its role, imposing strict measures to the Trust for the surface waste cleanup, groundwater recovery program or soil cleanup.

Finally can this solution be applied to other cases? It is certainly possible. In Quebec itself, many private site owners as well as municipalities contemplated that possibility. Despite this interest and the Kemtech site example, only one other trust has been set up in Quebec with governmental financial help for an orphan site belonging to a municipality. This timid follow up can be explained by the fact that some conditions are essential for building up a potentially successful trust, conditions as: an interesting location or existing plant; a big enough site for absorbing the lawyer and paper work costs related to the setting up of the trust; investors ready to pay environmental rights; a major entity willing to lend money to start up the process, entity which may become the site owner if the trust go bankrupt. Somehow, the Kemtech site satisfied to all of these conditions.

HANSAPARK OBERHAUSEN - CORRESPONDANCE BETWEEN LIVING AND COMMERCE

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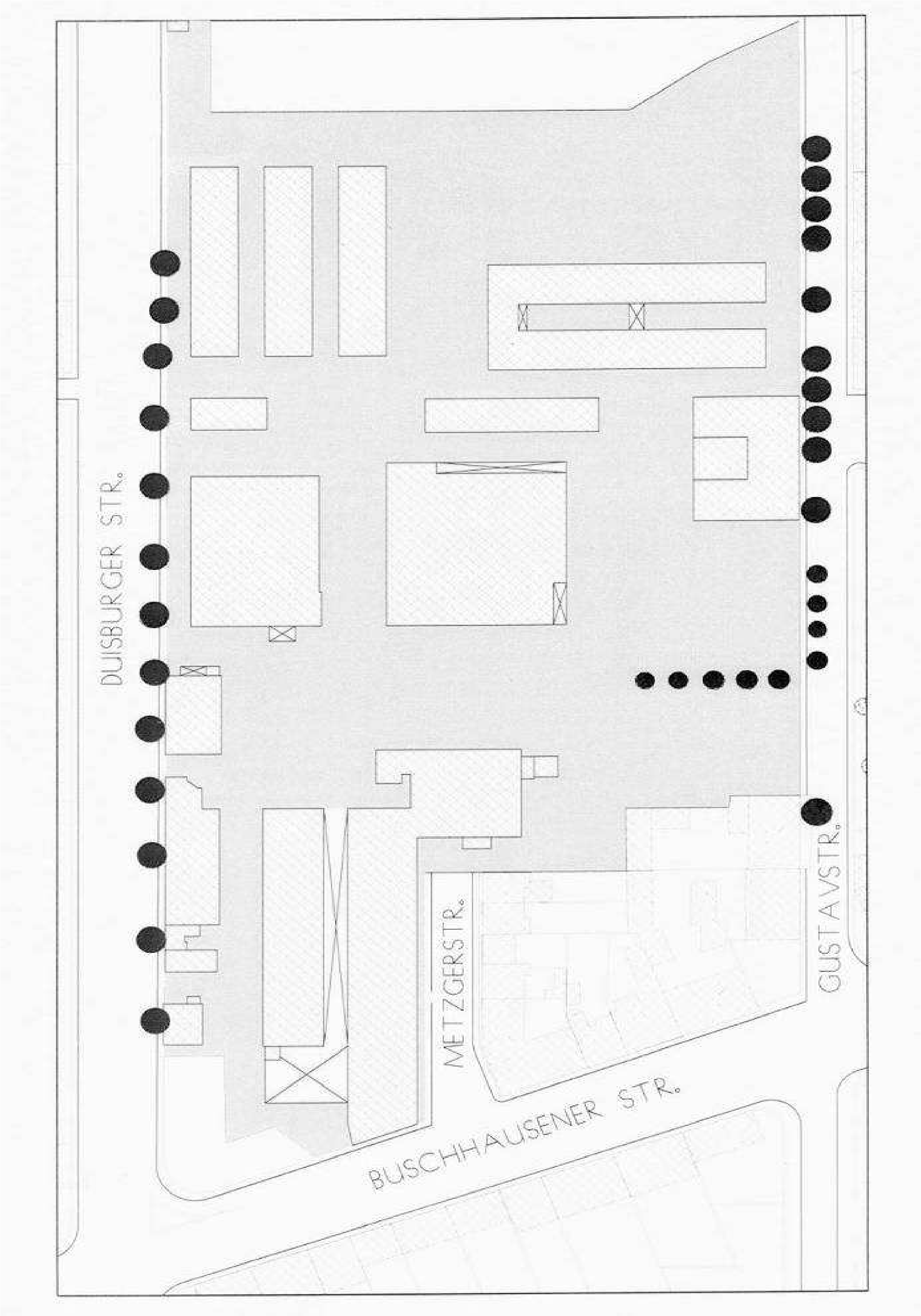
Structure:

1. The situation and history

The regional area of application of the building plan is situated in the boundary of Oberhausen, field 8.
It consists of the title numbers 21 and 167.
The regional area of application has dimensions of 35 000 m².
The history of the buildings and the use as a slaughterhouse in Oberhausen can be traced to the year 1822. In the year 1865 we found first indications of a commercial use as a cattle market without buildings.
Documents of the first buildings of the slaughterhouse were found in the year 1892.
Beginning with the area of the cattle market the buildings of the slaughterhouse were built from southwest to northeast. The last extension was finished in 1964.
In the year 1986 the slaughterhouse was closed and parts of the buildings were used for rent.

1. Site plan of the slaughterhouse



2. The idea

The owner of the area of the former slaughterhouse was the city of Oberhausen.
The idea of our companies was to realize a new use on this area.
The reason for this idea had different aspects.
In the urban area of Oberhausen existed a lack of owner-occupied flats and sites for terraced-houses. Furthermore there were no sites in the urban area for commercial-objects.
In contribution to reduce those deficits real estate potentials should be realized in the scope of urban development.
The area had good conditions because of the integration into the urban area and because of the good possibilities of development.

The main targets of the development project were:

-The creation of a commercial area
-The creation of accomodation with good location qualities
-The creation of public improvement
-The prove of sufficient subsistute planting

3. The planning

3.1. The regional development plan

The targets of the regional development plan corresponded with the idea of our companies.
There was allowed to develop accomodation and commercial objects without noise emission.

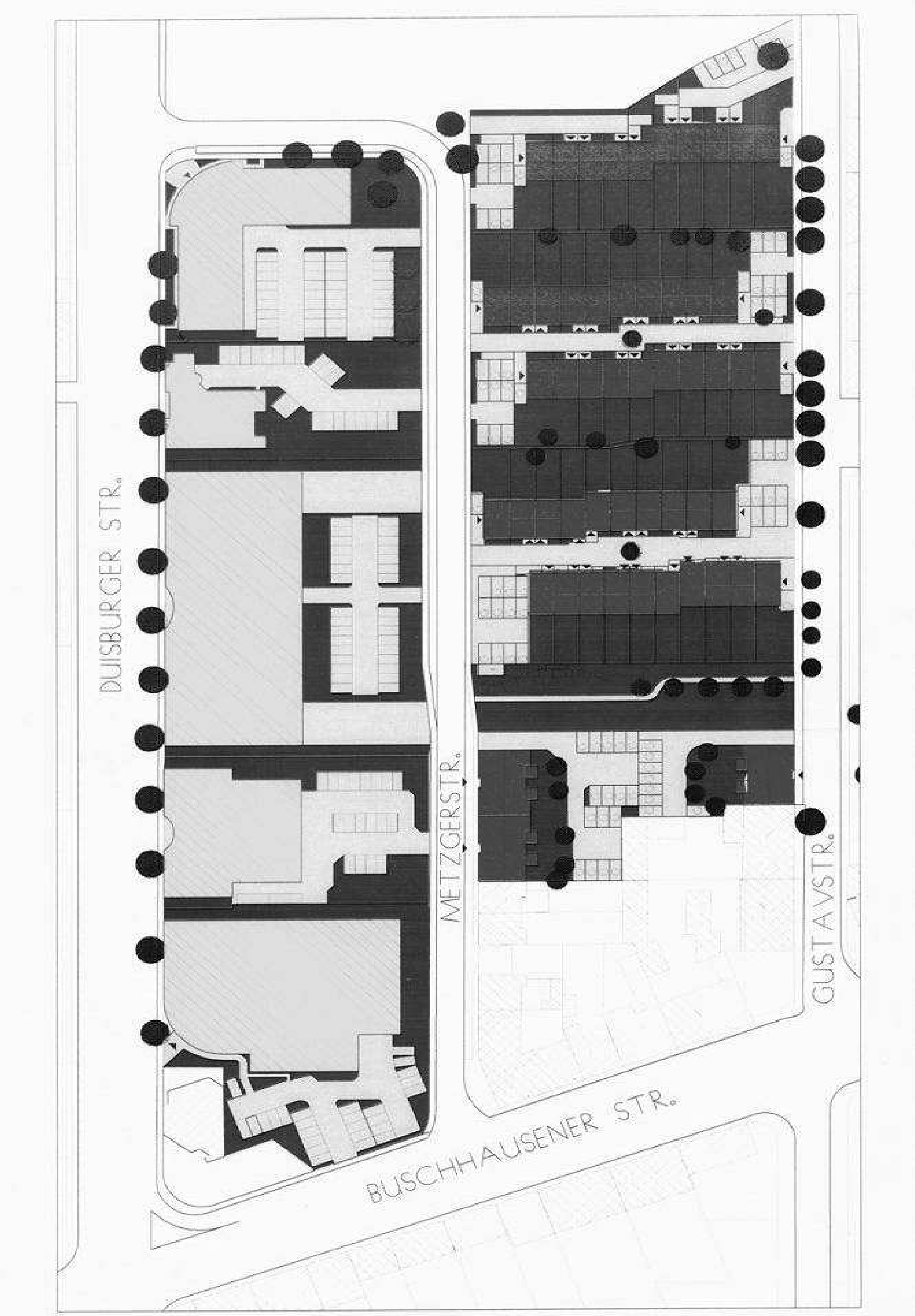
3.2. The urban development plan

The urban development plan forced accomodation development.There was a demand of 4000 units of residential buildings till the year 2000 in the urban area.

3.3. The urban building plan

The installation of the urban development plan contains the following targets:
The completion of the residential construction
The creation of a commercial area for noiseless activities.
The idea for the new use of the slaughterhouse area corresponded with all legal aspects of the different plans.

2. Site Plan Today



3.4. The environmental conditions

In the area of the building plan is situated the suspect area with hazardous wastes Nr. F 12.002, who is the area of the former slaughterhouse.

The city of Oberhausen appointed in 1993 the consultant company HPC to make a risk assessment of contaminated sites for this area.
During the investigations was found an 2 m thick dumped fill .Some chemical analysis showed that the the contaminants of the dumped fill are too high with regard to the precautionary values.
From the statements of the health authority and the veterinary control board of the city could be excluded hygienic consequentiel damage from the slaughtery house.
Additional investigations in groundwater and investigations because of the future desealing in 1998 did not indicate further actions.
The following actions were planned:
Controlled reconversion of the slaughter-house accompanied by an environmental expert persuant to a concept of legal disposal including soil-management and the removal of all underground installations as buildings, tubes, transmission facilities and disposal of all waste material.
To take precaution against injurious impact of soil contaminations in this area the developer was forced to make a cover and to preserve it for ever:
Non-contaminated soil above the existing old dump fill:
In the zone of ornamental gardens and vegetable gardens with minimum dimension of 0.6 m in connection with a digging barrier.
In the zone of playgrounds accordant to legal conditions with a minimum dimension of 0.35 m in connection with a digging barrier.
In the zone of parks and other sealed zones with a minimum dimension of 0.35 m.
These requirements were written down in the implementing contract and were protected as building regulations.

3.5 Other conditions

3.5.1 Immissions

The following aspects of pollution control had to be taken into consideration: They had to be analysed by an expert.
The possible noise pollution of the traffic.
The possible noise pollution of tram ways.
The possible noise pollution of existing and future commercial activities.

3.5.2 Infrastructure facilities

Different aspects of infrastructure facilities had to be considered
Private transport, Public local traffic, Footpaths, Cycle tracks,
Supply and Waste Disposal, Public utilities

3.5.3 Civil involvement

During the civil involvement diffferent aspects were discussed:
The problem of the side by side of commercial and living.
The objection because of the loss of public parking areas.
The installation of a public playground.
The flow of traffic in general and specially the stress of one inner road due to the quick through road.

All problems were discussed and all hints were taken into consideration.

4. The organisation

The owner of the area of the former slaughterhouse was the city of Oberhausen.The city of Oberhausen occurred as the seller of the area.
For the project Hansapark were founded the project development company “Hansapark”.
Partners having equal rights in this company were the Stadtsparkasse Oberhausen-a regional bank- and the Bangel Ltd.& Industrial Building Company .
This company bought the area from the city of Oberhausen.
The purpose to found this company was to share the risks and the tasks.
The task of the Sparkasse was to arrange all financial tasks and the marketing of the project whereas the Bangel Ltd. was responsible for all technical aspects.

4.1. The realisation contract

Besides the special building plan existed a realization contract signed by the “Hansapark” company and the city of Oberhausen.
The realization contract regulates the rights and the duties of both partners in connection with the realization of the building project.

Content: Matter of contract, description of the project, realization commitment, manufacture and completion of the public improvements, type and volume of the public improvements, invitations to bid, placing and civil construction supervision, construction work, liability and traffic safety, guarantee and inspection, assumption of the public improvements, contamination, noise protection, cost sharing, sewage connections, protection of soil, bank surety, exclusion of guarantee, final comments, legal successor, coming into force.

4.2. The engineering contract

Between the “Hansapark” company and a consulting company were made a contract about the technical advice for the reconversion of the complete slaughterhouse. There were determined the service of the consultant, the general duties of the consultant, the service of the client, the schedule and the time limits, the remuneration, payment, the representation of the client by the consultant, third party insurance of the consultant.

4.3. The project control contract

Between the “Hansapark” company and the Bangel Engineering Ltd. was made a contract for the project control .The matters of this contact were total project coordination,the setting up and control of all organisation plans ,the schedule and terms of payment ,the coordination and control of all project members, the update of the targets and clearing of target conflicts, permanent information about the project run and preparation of decisions,coordination and control of the working on finance-funding and permission acts.

5. The realization

5.1. The demolition

The basis for the demolition was the stock-taking in 1998 of all installations, where was decided how to manage the waste-disposal of the demolition-material: waste without monitoring, waste with monitoring and waste with special monitoring .All those documents were gathered by the consultant.
Before beginning the demolition of the buildings and the technical facilities the following articles were gathered, sorted and disposed or made use of :plastics, metals, transformer parts, furniture, oil-radiators, refrigerators, batteries, fire exstinguishers, spray-tins and so on.
After finishing those works the gutting of all buildings was the next step.
The permission for demolition of the buildings was given by the local construction supervisor and the the environmental consultant.
Special problems during the demolition were caused by the different isolation materials in the buildings like tinfoil, polystrene sheets, cork sheets, tar paintings.
After demolition a final report was written and given to all competent authorities.

3. Old Bulidings

4. Demolition

5.2. The rehabilitation of the ground

During the rehabiltation of the ground were excavated in total 12 000 tons of different soil qualities and disposed. These works were finished in March 2002.
During the phase of demolition the marketing of the ground started.

6. The marketing

In the year 2000 the marketing of the area started.
This work was mainly done by the Stadtsparkasse Oberhausen. Till May 2002 the five commercial buildings were finished, the owner-occupied flats and 40 from 50 of the terracced houses were sold and in construction.

7. The result

In co-operation between the Stadtparkasse Oberhausen and the Bangel Ltd.& Industrial Building Company was realised a new use on the former slaughter-house area of Oberhausen.
After three years of work were created on the slaughter-house area with a dimension of 35000 m² the following buildings:

total area:	35000 m²
Commercial buildings:	16500 m²
Residential buildings:	12200 m²
50 Terraced houses:	7500 m²
24 Owner-occupied flats:	2300 m²
5 Commercial objects:	6900 m²

total investment:	34.500.000 Euro

8. The assessment of the project

This project can be assessed as a good example of land recycling.
Some facts:

There was a comprehensive approach on every side
There was no overaccentuation of remediation
There was a sufficient coordination of land recycling concept and projected reutilization
The project teams worked interdisciplinary
There was a political guideline for this project
The concentrating effect of a public contract was put to use

With the experience of the “Hansapark” Project, we would start the next project and would be sure to have economic success.

5. Terraced houses

6. Commercial buildings

PROMOTING BROWNFIELD DEVELOPMENT IN THE UK. A CLIENT'S GUIDE TO LEGAL, FINANCIAL AND TECHNICAL ISSUES

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INTRODUCTION

The Construction Industry Research and Information Association (CIRIA), one of the UK's leading research associations, has recently published a key guidance report in its portfolio of research publications.

Brownfields: managing the development of previously-developed land - a clients guide(1) has been published by CIRIA on behalf of a wide range of funding organisations. It brings together in one guidance document the range of financial, legal planning and technical issues that may arise with projects on previously developed land which can often influence the decisions of clients who may be considering potential development opportunities. These issues may not only affect the actual viability of projects but may also influence the perceptions of decision-makers which may alter their strategies in planning to embark on such schemes within the U.K.'s regulatory and business environment

This paper describes CIRIA's guide and how its structure seeks to provide members of the U.K.'s development community, particularly those new to projects on previously developed land, with both a framework and source of information to help understand the various key issues that affect project viability. The guide also aims to assist in the logical and methodical management of these issues.

With a structure that reflects the normal stages of land development in the U.K., the aim of the guide is to set what may be unfamiliar issues within a recognisable route map from the point where a project may first be considered through to the completion of development objectives. As such, whilst the guide is written for UK development situations, the basic format and content may offer a template for similar support documents for other countries.

This paper describes:

- the background and policy drivers behind the creation of the guide
- the development of the guide's structure, including the focus on setting a management framework
- how the guide acts a communication link between clients and their advisers as well as other stakeholders to assist mutual understanding
- initiatives to help enhance its impact
- the potential for the structure of the guide to act as a model for other topic areas

CONTEXT FOR THE PRODUCTION OF THE CLIENT'S GUIDE

Government Policy

In its moves to create more sustainable approaches to land resources, utilising previously developed land for new development is now a particular focus of the UK government, which can be tracked back to the government's 1990 White Paper "*This Common Inheritance*"(2). The government's policies on planning are set out in a series of published Planning Policy Guidance (PPG) Notes, PPG 3: *Housing*(3) published in March 2000 indicated a government target of 60% of new houses to be accommodated on such land and through conversions of existing buildings by 2008. PPG 3 also provides a succinct expression of government policy:

> *"The Government is committed to maximising the re-use of previously developed land and empty properties and the conversion of non-residential buildings for housing, in order both to promote regeneration and minimise the amount of greenfield land being taken for development".*

Coupled with confirmatory statements contained in other PPG guidance notes and a raft of other initiatives targeted at sustainable development that are illustrated by examples of publications(4)(5)(6)(7)(8)(9)(10)(11), this policy framework has focussed increasing attention on previously developed land. Indeed, many decision-makers involved with land development have already recognised and taken due advantage of the opportunities for commercial and industrial development schemes, as well as housing end use. Many others, however, have not as yet considered the business case afforded by such land, often discouraged by risks that are unfamiliar and which they view as being difficult to manage and ultimately unacceptable.

The growing number of successful and attractive schemes throughout the UK, however, offer compelling evidence that with the right structure, these risks can be managed successfully and at the same time opportunities can be exploited to achieve a viable scheme.

The role of CIRIA

CIRIA has a longstanding and highly regarded reputation for producing authoritative, best practice guidance to the UK construction industry across a spectrum of technical topics. A key component of its research portfolio covers a substantial contribution to best practice in the management of contaminated land. CIRIA's recent research has also sought to underpin the technical excellence of its publications with similar high quality guidance on related broader issues of business implications. One such example was a recent major project examining the impact of land contamination on the financial management of land(12).

With the U.K. government's policies for sustainable development focussing attention on previously developed land, CIRIA had identified there was a key gap in guidance that brought together the various issues of concern to the development community(13). These cover financial, legal, planning and technical matters that may occur with brownfield land that may be contaminated. Whilst there are indeed numerous examples of successful projects on brownfield sites, it was evident that many client organisations remained unwilling to be involved in development of contaminated or potentially contaminated sites. By providing client bodies with access to such information via a guidance document, the primary intention would be to improve wider confidence in tackling such sites. A key objective of the guidance, therefore, would be to encourage wider involvement in such potential development opportunities.

To ensure the guidance report was both balanced and authoritative, a project steering group drawn from a wide range of experts provided an overseeing role of progress and content. These represented regulators and planners, together with leading specialists from the U.K.'s development community covering, financial, property, legal, insurance and technical viewpoints. The project also involved extensive consultation within the development community, incorporating wide circulation of interim drafts and a related consultation workshop.

WHEN DOES THE GUIDANCE APPLY?

Brownfield and previously developed land - defining the terms

Within the U.K., the term "brownfield land" has been widely used in recent years as a general reference for land that has been previously developed. For those involved in the process, whilst the term undoubtedly assists in helping to visualise the type of land in question defining what constitutes "brownfield land" has itself been a matter of debate, involving issues such as:

- whether to be "brownfield land", a site also has to be contaminated

- whether any definition should accommodate other common terms that are also used in the U.K. and which may be used in specific and similar policy contexts. Typical examples are terms such as "derelict land" and "vacant land".

One of the earliest resolutions within the formative stages of this project, therefore, was the need to provide clarification in respect of the nature of sites that would be covered by the guide. To provide a steer that ensured interaction with the government's policy approach to sustainable development, the client's guide employs the PPG 3 definition of previously developed land(3), namely land:

> *"that which is or was occupied by permanent structure (excluding agricultural or forestry) and associated fixed surface infrastructure. The definition covers curtilage of the development. Previously developed land may occur both in built-up and rural settings. The definition includes defence buildings and land used for mineral extraction and waste disposal where provision for restoration has not been made through development control procedures.*

Importantly, the definition applied in the guide covers land that may or may not be contaminated. As will be brought out in this paper, research(13) has confirmed that the efficient management of contamination on land, either actual or perceived, is one of the major concerns to development decision-makers in the U.K. For example, in circumstances where actual contamination is to be dealt with, advice on costs of remediation ranks highly as a key concern.

As such, decision-makers experienced with previously developed land are likely to approach such projects on the basis that, if encountered, contamination is capable of being managed. Also, it is a factor that can be discounted when appropriate investigations and assessments have been carried out and it is established that contamination is not an issue.

The guide builds upon these messages by incorporating supporting background information on the government's approach to contamination coupled with summary information on the U.K.'s associated legislative and planning regimes

THE STRUCTURE OF THE GUIDE

A route map of the development cycle

The key principle behind the structure of the guide is one of providing a support document that assists decision makers to both formulate their development strategy and then to carry out the process within a scheme from initial inception to its completion.

To achieve this, chapters of the guide are set out as a route map through the development process to reflect the broad phases of the development cycle. This commences with initial site appraisal, moves to detailed investigation, design and development planning issues, through to construction phases and finally to the completion of objectives for the scheme. As this final stage may itself involve the forward sale or transfer of the developed site, other parties' interests in the site appraisal stage will be triggered and the development cycle can therefore recommence. Figure 1 illustrates the broad stages of the development cycle.

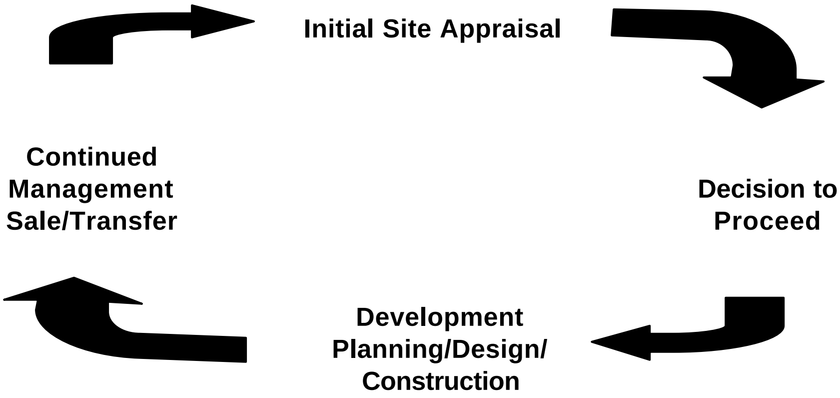

Figure 1 ***The development cycle***

Figure 2 illustrates how the stages of the development cycle have been employed as the chapters of the guide to reflect the development process. These stages are underpinned by an emphasis that reviewing factors affecting viability throughout the process will help achieve the desired final investment value for the scheme.

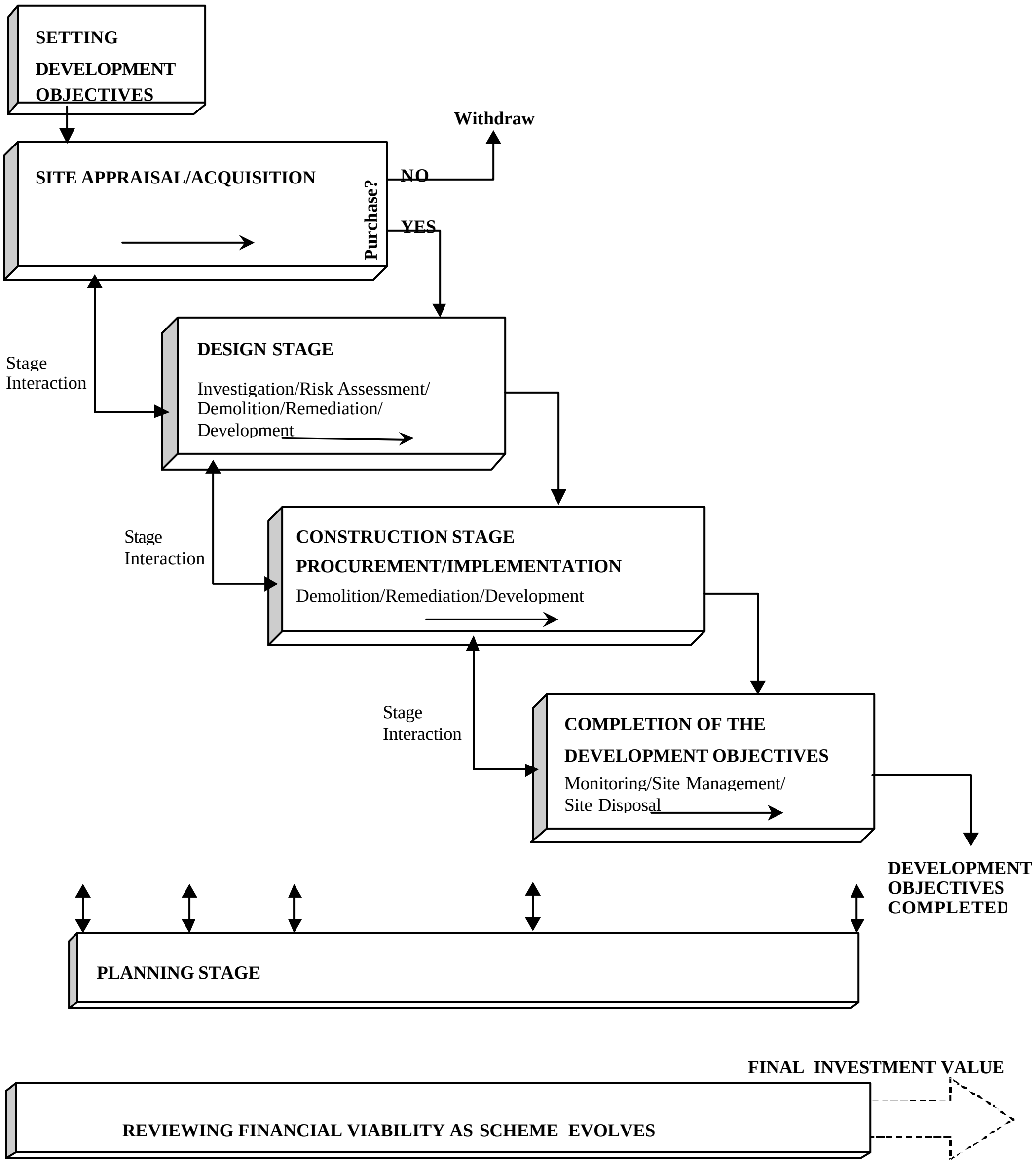

Figure 2 ***The stages of the development process - interactions and overlaps***

The key legal, financial and technical issues that may arise are not separated into separate headings. Rather they are integrated to reflect mutual interactions that can affect project viability and set under sub headings within the chapters that reflect the possible detailed components of development. For example, should the need for demolition or remediation of land contamination be both established as issues to be dealt with, then the relevant demolition and remediation subsections within the chapters covering design and construction processes will be relevant.

Inevitably, each development scheme will be unique and this may lead to varying degrees of overlap and interaction between the various issues and activities covered in the various chapters. The guide is careful, therefore, to ensure this site-specific aspect is emphasised and can be satisfactorily accommodated as part of the overall management process.

The management context - setting development objectives

In the guide's role as a support to business planning, the chapters describing the development stages are preceded by guidance on setting the process within a management context that sets development objectives and how they may be realised. Advice is offered in creating an robust management framework within which the key legal, financial and technical issues that may arise as the process unfolds, (and which may thereby impinge on business decisions), can be set out at the start of the scheme and then dealt with in a timely and logical fashion.

A key component of the guide's recommendations involves the early creation of a structured Client's Management Plan to help client bodies order their thinking to identify both opportunities to be exploited and the risks that may need to be managed. With such a management plan devised from the outset, the guide encourages it to be used as a continuing management tool throughout the process with further support provided in the chapters in the form of background information and suggested action points to take issues forward.

Table 1 below outlines key headings of the Client's Management Plan. These incorporate a number of specific principles that emerge as recurring themes within the pages of the guide and which are highlighted in the next section.

Table 1 ***Framework of the Client's Management Plan***

Headings	**Content and issues**
Development strategy	Client's objectives (including financial appraisals) for the scheme
Potential opportunities	Possible opportunities that could contribute to project viability
Screening criteria	Pre-definition of circumstances that could halt interest in the scheme
Site acquisition strategy	Planned approaches to acquiring the site
Managing risks	Objectives and options to manage financial legal and technical risks. Site exit strategies-planned measures to withdraw from the development cycle
Advisers	Gaps in client's knowledge to be addressed by advisers Identifying/engaging competent advisers
Contractors	Identifying/engaging competent contractors
Project organisation	
- Team structure	Setting effective project management and supervision provisions
- Consultations	Scheduling the range and timing of statutory and other consultees
- Implementation	Programme and administration planning
- Data management	Records required to satisfy parties who may have interest in the site e.g. regulators, planners, potential site purchasers.

KEY PROMPTS PROVIDED BY THE GUIDE

The importance of management of information

Management of information covering its quality and its ready availability has been the subject of a number of recent initiatives upon which the guide provides background information:

- the Law Society's Warning card on contamination(14) has emphasised the need for the presentation of facts when a transaction has taken place, particularly where contamination is concerned
- the Urban Task Force's report(4) identified the benefits to be gained for consistency of handling of information on land contamination. This has resulted in the development of Land Condition Records (LCR's)(15) as an initiative aimed at improving rigour and consistency in documentation.
- commercial implications and real-estate issues are considered within the Royal Institution of Chartered Surveyors (RICS) guidance notes on the development and use of Land Quality Statements (LQS)(16).

The guide places strong and recurring emphasis on the benefits of efficient and effective information management

Parties to the process

A broad array of parties will be involved in consultations, approvals, authorisations and permitting as part of the U.K. development process. Deciding on the nature and, importantly, when to engage in consultation may be a critical issue in achieving a smooth progress on a scheme. The guide provides a summary of the key parties that may be involved(17) and utilises its route map structure through the development process to provide guidance on the various issues that may arise. As a result, prompts are provided on not only where authorisations or permits may be needed, but when and to whom contact should be considered.

Table 2 shows an abstract of information provided in the guide, giving some examples of parties that may need to be consulted as the development process unfolds.

Table 2 Third party approvals in the development of previously developed land (abstract)

Party	Permit Licence Application	Development Stages												
		Initial interest / acquisition	Planning	Design ground - investigation	Design - demolition	Design - remediation	Design - development	Procurement demolition	Procurement - remediation	Procurement - development	Implementation - demolition	Implementation - remediation	Implementation - development	Completion of objectives
	Chapter in Client's Guide	4	5	6				7						8
Landowner /occupier	Entry to site	✓		✓	✓	✓	✓					✓	✓	
	Access: site/adj. land													
	Permits to work			✓										
	Private Services			✓										
	- auth. to work													
	Party Wall Act													
	- prelim stage					✓	✓							
	- application													

Establishing the appropriate project team

Identifying or selecting competent advisers to form an effective project team is a normal process for any type of development scheme. With clients who may be unfamiliar with previously developed land, the range of issues can be both unfamiliar and daunting and the guide therefore provides supporting guidance to clients on the selection of advisers. This covers two areas in particular:

- *guidance on selecting and reviewing advisers' capabilities*. The guide outlines the range of skills needed across the spectrum of legal, commercial and technical disciplines as well as providing recommendations on criteria for selection of advisers

- *communication between client and adviser*. To promote dialogue, the guide recommends that clients should seek Action Plans from their advisers to act as working counterparts to the Clients' Management Plans. In a similar format to the Client's Management Plan, recommendations are provided within the guide on the topic headings to be considered.

THE GUIDE AS A LINK BETWEEN CLIENT AND ADVISER

By employing the guide, it is hoped that clients should be better briefed to take a view on the extent of advisory support that is needed to supplement their own skills to create a robust project team. At the same time, the guide aims to assist clients to understand the range of activities with which their advisers will be involved.

Where external professional support is to be sought, the guide offers an additional role to clients and advisers by providing each party with a perspective of respective viewpoints around a common base:

The client's viewpoint		**The professional adviser's viewpoint**
Clients may derive comfort that their advisers should be aware of the guide as a client support tool and as a result advisers are aware the client has access to:		As the counterpart to clients' viewpoint, advisers may be prompted that with clients having access to such a support facility they may be encouraged to:
• an overview of the issues that advisers may need to address	⬌	• demonstrate their credentials match the scheme
• good practice approaches and forward actions that may be appropriate for advisers to apply		• demonstrate that relevant good practice has been employed
		• create and maintain communication links.

The importance of dialogue between clients and advisers in exchanging their respective action plans and approaches provides an important element of the guide. Advisers with quality management systems in place may already be suitably organised to deal with dialogues and reporting. Others, however, may now find that more proactive and formal communications are expected.

With this emphasis on intercommunication and effective data management, the guide can also act as a complementary management tool that supports value engineering and value management principles that may be employed on particular projects.

THE CLIENT'S GUIDE AS A MODEL TEMPLATE

In its completed form, the eight chapters and supporting appendices of the client's guide represent a simple, straightforward template comprising four main components:

1 Scene setting (Chapters 1-2)

- The scope and use of the guide
- Describing key terms
- Opportunities that may be presented

2 Management context - setting objectives (Chapter 3)

- Establishing the project business case
- Factors that could govern project viability
- Pre preparation - setting a management framework
- Communication - who may be involved and when?
- Role of information management

3 The route map - inception to completion (Chapters 4-8)

- The range of issues to be considered - how they interrelate
- Issues set within recognizable milestones
- Examples of good practice reference texts
- Case study illustrations

4 Relevant supporting information (Appendices)

- Policy / legislation
- Supporting guidance - establishing the project team
- Contacts
- Expanded recommendations on management issues

In the context of transmitting the benefits of experience in the form of guidance, particularly to those who may be new to a particular area, the format of the client's guide should be readily applicable to a wide range of topics.

By adjusting the detailed content within the template, the format should provide the basis for the production of a family of guidance documents. This may be particularly applicable for circumstances where a subject of the guidance unfolds over a period, as is the case with brownfield development, and where there is demand for dissemination of knowledge into what may be relevant at given stages in the process.

The layout of the guide could also lend itself as a template for guidance that would be applicable to other countries where there may be a need to broaden awareness of similar issues and how they may be managed.

For example, as outlined earlier, the client's guide considers in some depth the various terms employed in the UK relating to brownfield sites. The same may well be the case in other countries, where there may be a similar need for supporting and explanatory guidance. The template offers a format, therefore, for relevant guidance to be specifically tailored to other jurisdictions and, as with U.K. experience, addressing how particular terms and concepts are understood and how they may be applied as the process under consideration unfolds.

CONCLUSION

The publication of the client's guide affords a new departure for CIRIA covering guidance aimed at many organisations outside the regular readership of CIRIA's publications. Publication of the guide was formally launched in October 2002, complete with an associated wall chart as a component of a marketing campaign of leaflets, articles, presentations and briefing workshops.
Recent studies have estimated that some 200,000hA of previously developed land remains undeveloped in the U.K. This affords the prospect of many opportunities for the U.K. development community and it is hoped CIRIA's client's guide will provide a significant and longstanding contribution to facilitating brownfield development.

ACKNOWLEDGEMENTS

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COLLOID ASSISTED TRANSPORT IN ADVANCED FILTRATION FACILITIES USED FOR THE CLEAN-UP OF URBAN RUN-OFF

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Introduction

Urban Run-off

Rain water run-off that is collected from large sealed surfaces, roofs, and roads in urban areas is contaminated with a broad range of organic and inorganic pollutants. On its way through the atmosphere, meteoric water takes up gaseous chemicals like nitric and sulfuric acid aerosols ("acid rain") and dust emitted by industrial processes. In case of roof run-off heavy metals, and in particular zinc and copper, are likely to be mobilized in large quantities as well as small particles due to abrasion, weathering or originating from airborne dust deposits [Förster 1999]. For road run-off, a greater variety of pollutants has been identified. The lead exhaustion and its accumulation in roadside soils, however, has been stopped to a large extent by banning lead-based fuel additives in the industrialized countries. Nevertheless, the historic pollution can still be detected in the soil along many roads. These days research focuses primarily on (1) heavy metals emitted by corrosion of car bodies, (2) soot produced by incomplete combustion, (3) automotive catalyst particles containing platinum-group-elements (PGE) that are blown out with the exhaust fumes, and (4) organic compounds like unburned fuel components (e.g. benzene), oil and tire wear.

Special to road run-off is also the seasonal fluctuating ionic strength and composition of run-off due to the use of de-icing salts in winter.

Current practice

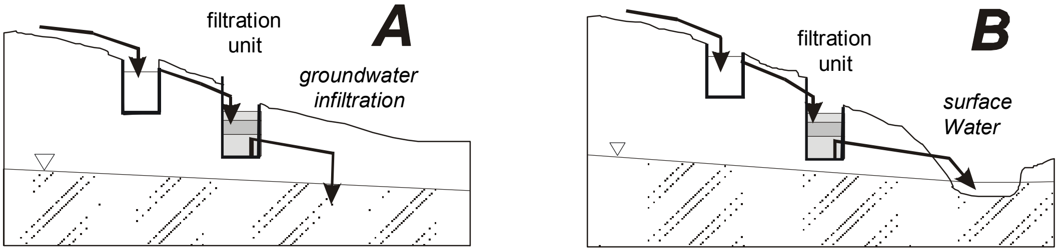
Currently, most of the run-off is either collected in urban sewage systems and passed on to surface waters without further treatment or is partly passed through purification plants where it is cleaned up with comparably expensive treatment methods. Agencies therefore seek for new ways to deal with these large and fluctuating amounts of contaminated run-off. For buildings a propagated way is to directly ooze away the run-off into the ground nearby by means of drainage systems. Argument for this is also the regeneration of groundwater resources, though recent studies have shown that increased sealing of the surface does not affect the groundwater level negatively but in most environments leads to increased recharge of groundwater due to intensive water use and leakages from sewer systems. [Lerner 2002, Foster 1990].

As to road run-off, straightforward methods like overflow basins, which remove coarse sludge, or slow horizontal sand filtration facilities with or without plantation, which are to some degree effective but consume a lot of space, are in use although not yet in many places. Mostly, however, the collected run-off is discharged directly into receiving waters or nearby ground from where it is infiltrated into the groundwater.

Future needs

To safeguard natural resources and human health, control and treatment of the contaminated run-off represent a prominent task in urban areas. As depicted in Fig. 1, treatment may be applied both (A) prior to a controlled infiltration of run-off water into the aquifer or (B) prior to discharge into a surface water body.

Fig.1 :



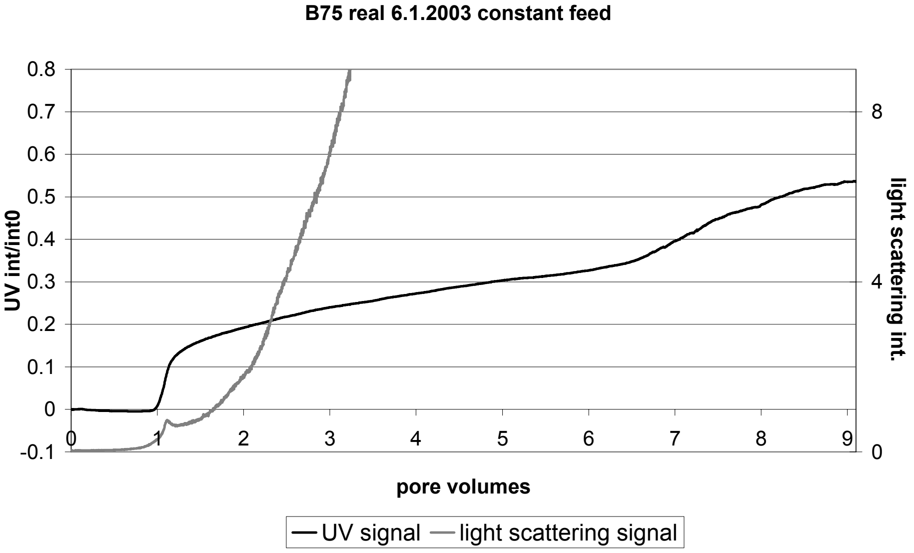
Technical requirements for filtration facilities
Specific problems for the clean-up of surface run-off are the large reception areas, and their varying amount and composition. This in case of treatment requires small-scale facilities with small “footprint”, that can handle peaks of high discharge due to thunderstorms or prolonged rainfall with sufficient retention capacity for pollutants.

Colloidal transport of pollutants

1. Subsurface transport through in-situ mobilized particles
In case of a missing effective treatment prior to infiltration to the groundwater, subsurface transport of pollutants may not only occur in solution. Contaminants can partly or totally be adsorbed onto colloidal particles which are sized in the range from 1 nm to a few microns and are themselves mobile in the flowpaths and pores of the soil. Due to size exclusion effects, mobile particles are often transported faster than dissolved conservative components. Hydraulic or geochemical gradients in the soil like shifts of pH, ionic strength, and composition and flow velocity, or changes in the redox potential can induce the mobilization or the retardation of colloidal particles and, by that, affect colloidal contaminant transport [Kretzschmar et al 1999].
The subsurface transport velocity of these pollutants towards the groundwater table may depend to a considerable extent on their association with highly mobile humic acids or colloidal mineral phases.

2. Transport bound to particles in the run-off
Already before reaching the soil, heavy metals and other pollutants are possibly sorbed on colloidal phases abundant in the run-off, like inorganic particles (clay minerals, oxides) and organic particles (humic substances, tire wear) [Grout et al. 1999]
An example of the retention capacities of pure quartz sand with grain size of 1-2 mm, is shown in Fig.2. A freshly collected run-off sample was taken as a feed solution for a filtration/breakthrough experiment on a laboratory scale sand-filled column. The sample was taken directly from the sand trap of the test site described below in a period with two weeks of permanent frost. Consequently the water in the sand trap consisted of run-off produced by the use of de-icing salts. Regardless the elevated ionic strength caused by de-icing salts a suspended colloidal fraction of 60,8 mg/L (20 nm-filtered) remained stable and was insensitive to the destabilising high Na-concentrations (4 g/L). The test-column was preconditioned with a solution of the same Na-content that was found in the sample to avoid ionic strength gradients along the flowpath. From the first to the third pore volume, the particle concentration detected with light scattering remains very low. The UV-intensity shows a steep rise which can be explained by the partial breakthrough of humic substances. With subsequent feeding, available deposition sites become occupied and small pores are blocked by particles resulting in an higher throughput in the remaining preferential flow channels. This enhances the breakthrough in the later pore volumes.

Fig. 2: Breakthrough curve of a winter sample at constant feed in a column filled with coarse quartz sand. The UV intensity is normalized to the undiluted, directly injected sample.



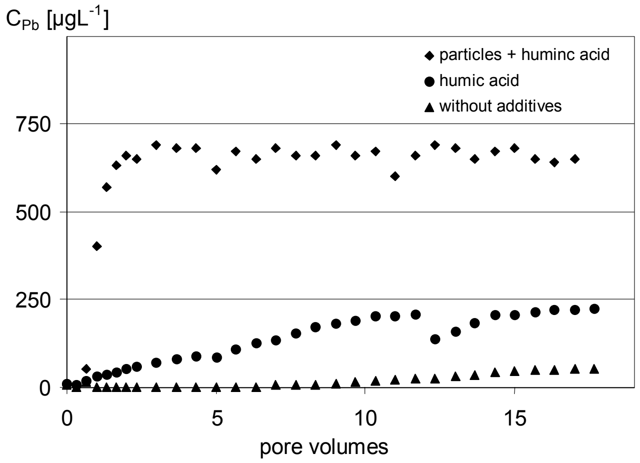
The pollutant loaded particles may travel even through advanced filtration facilities where dissolved heavy metals are usually retarded by ion exchange on e.g. natural zeolite. This could be shown in an experiment in a pre-pilot scale plant (filter columns 38 cm ∅ to 70 cm) performed at the "Hamburg-Halenreihe" retention pond test site applying a "reactive" filtration unit consisting of a 50/50 sand-zeolite fixed bed [Jacobs et al. 2000]

The results of a three month sampling campaign (35 m³ effluent treated per column) revealed the importance of colloidal or colloid bound fractions in the transport of heavy metals. Despite the presence of a natural cation exchanger (zeolite) with sufficient capacity, which showed optimal retetion for dissolved heavy metal species, the retention of several heavy metals, e.g. lead, was almost identically low in the zeolite column compared to a reference column with the same dimensions filled only with filter sand.

The cation exchange properties of the zeolite are only effective on available free or labile bound cations. Since filter grain size was about 1 mm and the water feed was at about one bed volume per hour colloidal and particulate phases could easily be transported through the short columns. The results could only be explained by a close to 100% association of the respective heavy metal with mobile colloids and particles. Subsequently, numerical equilibrium calculations using the computer program PHREEQC (Parkhurst and Appelo 1999) were carried out on the inflow and outflow solution composition. The results of these simulations revealed that a number of iron and manganese phases were thermodynamically oversaturated under the conditions given. In contrast, no oversaturation was found with respect to the trace metals within the system and these are hence unlikely to form any particulate phases by precipitation from the solution. Accordingly, it can be assumed, that trace metals were largely transported with iron and manganese phases. The field results have later been underpinned by extensive laboratory experiments [Förstner et al. 2001].

Fig. 3 shows the breakthrough curves of a lead solution fed to columns filled with sand that contained 1% natural clinoptilolithe. While the pure lead solution is completely depleted as expected, a conservative breaktrough of colloids and lead is observed if the solution is mixed with 280 mg/L stabilized natural colloids extracted from soil and 40 mg/L humic acid. The lead solution mixed only with humic acid shows a more complex behaviour which can not be explained completely at the moment.

Fig 3: Retention of free available cationic lead and breakthrough of particle bound lead in a sand column with natural ion exchanger.



The presence of colloidal matter may completely prevent the retention of pollutants. This sets new demands on advanced filtration plants applying reactive materials for retention enhancement. If retention/filtration of colloidal pollutant carriers was only determined by grain size and hydraulic conditions, predictions could be made according to the classical filter theory [Yao 1971]. The stability of colloidal suspensions and therefore the deposition in filters is predominantly related to in the ionic strength and the ionic composition (mono- or polyvalent cations, Na^+/Ca^{2+}) which changes heavily in road run-off. Also the adsorption on surfaces depends largely on the surface characteristics of particles and filter matrix.

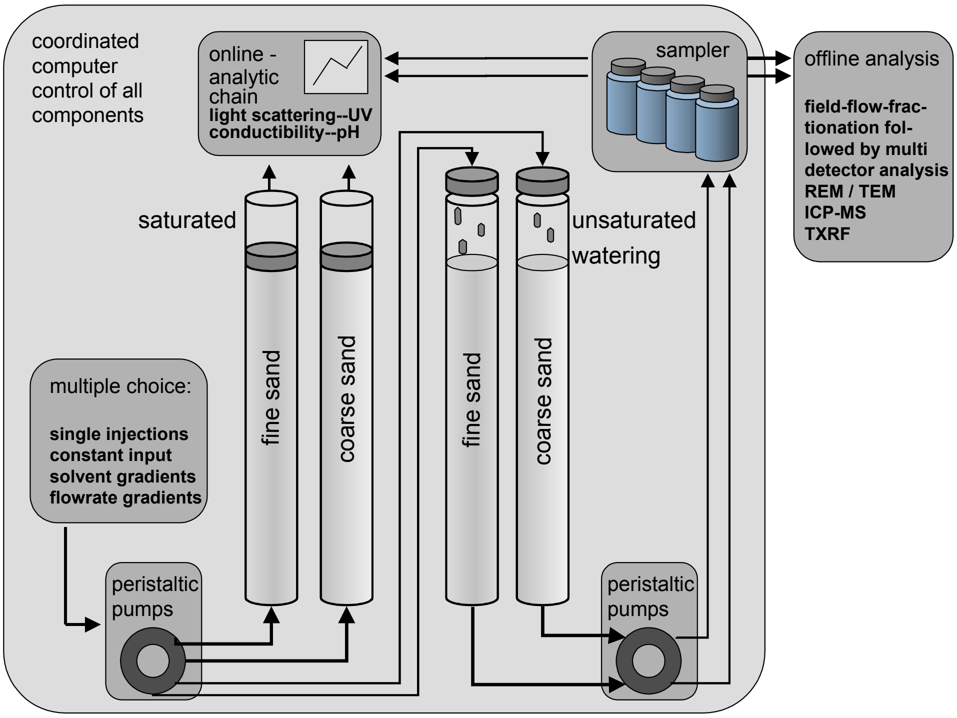
These facts are considered in the design of a new pilot-scale filtration plat presented below.

Experimental Setups

Laboratory-scale facility for fundamental experiments on colloidal transport

To investigate the numerous factors determining retardation and transport of colloidal phases, such as ionic strength, ionic values, presence of humic substances or surface properties of particles and filter grains, varying sheer forces from fluctuating run-off amounts, pore size and unsaturated conditions, quartz sand filled columns of 25 mm ∅ to 30 cm bed length were used as a small scale simplified soil model. Transport experiments were performed with real samples of run-off and stable suspensions of natural colloids extracted from soils and aquifer matrices. The installation design in Fig. 4 was optimized for computerized control of all important parameters as well as to collect important parameters online. Fig. 3 shows a filtration/breakthrough experiment on a coarse sand laboratory column fed with original winter run-off after 2 weeks of temperatures constantly below 0°C at high ionic strength due to the use of de-icing salts.

Fig.4 :



Test site for real run-off
The test site where the pilot plant was built is an amphibian dwelled pond which is fed by six gully-pots which drain an area of approx. 2500 m^2 of an highly frequented federal road (average 20.000 vehicles/day), the "Bundesstraße 75" in Harburg and a bus terminal loop, near the motorway A7.. Prior to installation of the treatment facility the collected run-off was cleaned by a biological cleaning route consisting of a meandering flowpath of approx. 100 m length which opens to a flat gravel bed armed with a steel mat followed by the small amphibian spawning pond.

The average annual rainfall at the location is 770 mm (Fuhlsbüttel meteorological station), so with an effective discharge of 90 % the pond is fed with approx. 1700 m^3 of run-off per year. Assuming an average fraction of 125 mg/L suspended solids, the pond is charged with approx 220 kg of contaminated fine particles per year. This constellation existed for 4 years. Analyzed samples from pond sediment, the meander, and the surrounding surface soil are shown in Fig. 5 and 6 These results prove an accumulation of heavy metals and a deposition of Na from the use of deicing salts in the sediments.

Fig. 5: Concentration of heavy metals in the fraction < 125 µm plotted in mg/kg. The pool sediment is compared to the fine material on the flowpath (meander) and to the "common" anthropogenic impact on the soil surface.
Additionally an uncontaminated soil sample from 1m depth was analyzed..

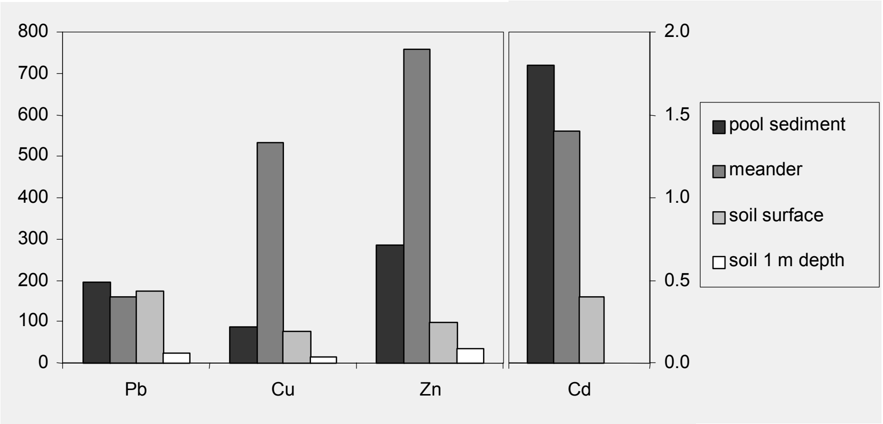
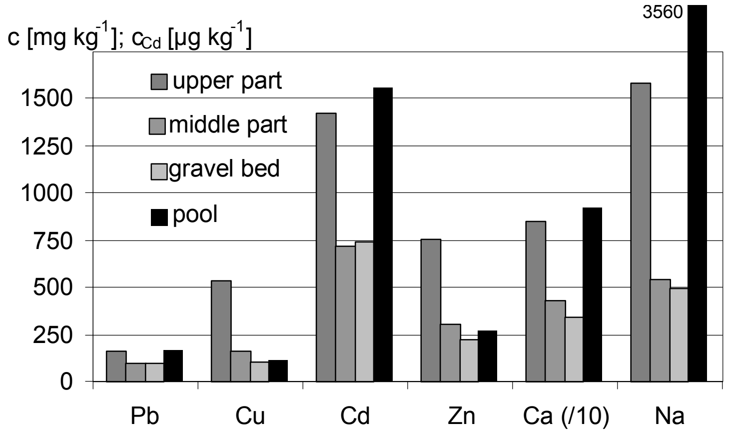


Fig. 6: Heavy metal concentrations in the < 125 µm fraction. The load of the sediment is compared to different parts of the flow meander.



Results from run-off samples taken on the test site

As an example for the analysis of a run-off sample from the test site the contents of main and trace elements are shown in Fig. 7. The sample was taken in a period with two weeks of permanent frost directly from the sand trap. The remaining suspended colloidal fraction (60 mg/L) was insensitive to the destabilizing high Na-concentrations (4 g/L) present.

Fig. 7: Table of element contents measured with ICP-MS in the raw and filtered sample taken on 6.1.2003

	B75 raw sample	B75 (<0,2 µm-filtered)	% "solved"	
Cd	1.21	1.07	88%	µgL^{-1}
Sn	2.41	0.08	3%	µgL^{-1}
Hg	4.70	3.80	81%	µgL^{-1}
Li	7.32	7.93	108%	mgL^{-1}
Ni	10.98	8.25	75%	mgL^{-1}
Cr	11.02	1.56	14%	µgL^{-1}
Pb	15.79	0.79	5%	µgL^{-1}
K	20.56	22.33	109%	mgL^{-1}
Ti	72.16	3.60	5%	µgL^{-1}
Mg	141.80	160.56	113%	mgL^{-1}
Ca	144.87	156.22	108%	mgL^{-1}
Cu	153.05	22.85	15%	µgL^{-1}
Zn	295.05	230.55	78%	µgL^{-1}
P	336.05	55.56	17%	µgL^{-1}
Mn	874.00	866.90	99%	µgL^{-1}
Al	1726.50	73.92	4%	µgL^{-1}
Fe	5224.00	1801.00	34%	µgL^{-1}

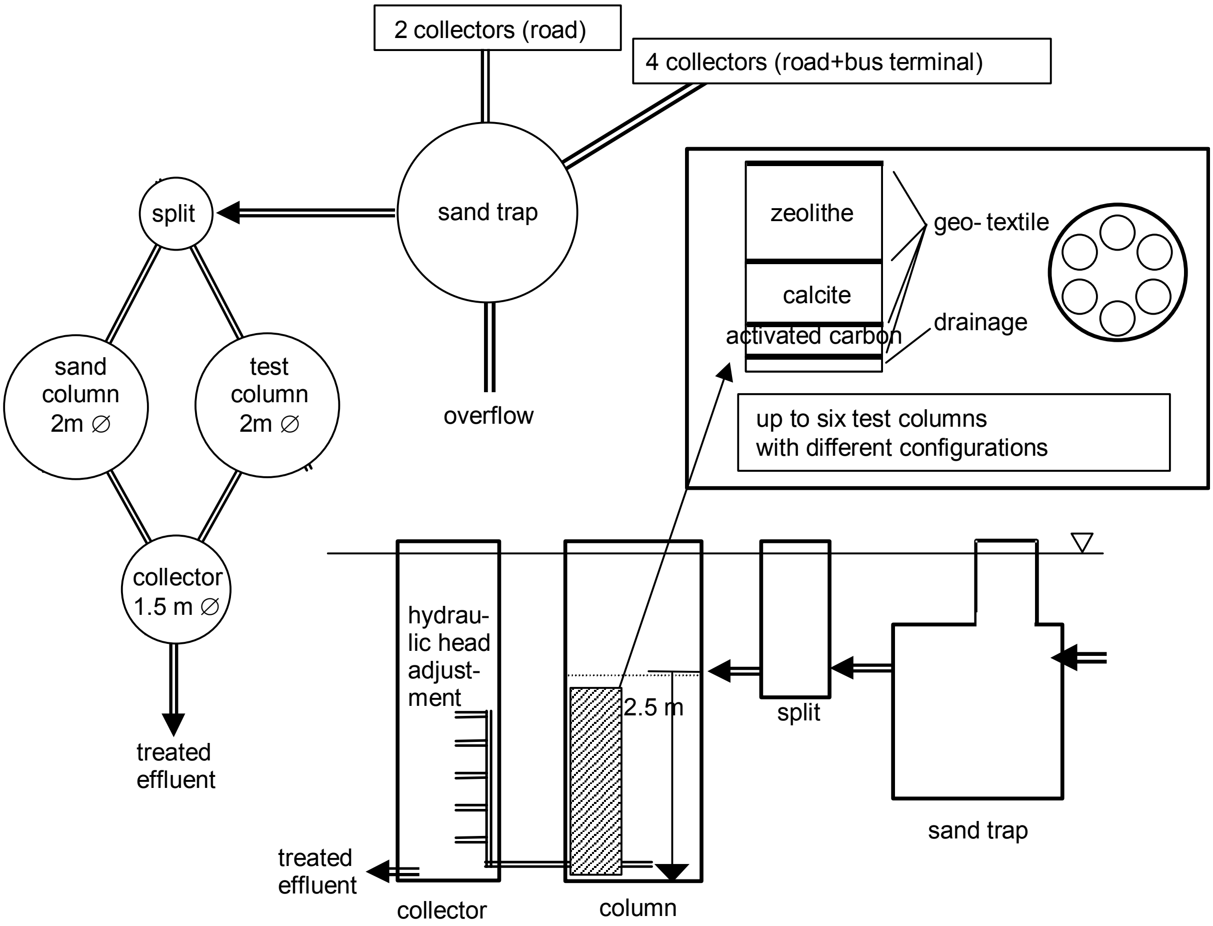
Pilot-scale treatment facility

As mentioned above, due to space restrictions a vertical filtration unit had to be constructed.
For calculation of the filter size needed, a maximum continuous throughput of 60 % of a 10-year rain event producing 30 L/s run.off is assumed. The buffer volume of the facility should guarantee the complete treatment of the highest contaminated "first flush". Due to the given topography a maximum hydraulic gradient of 2.5 m could be achieved. To ensure a constant throughput of 20 L/s with

sufficient retention of colloids and according small medium grain size of filter materials a top-to-bottom flow scheme was chosen.

This lead to the dimensions of the construction shown in Fig. 8. It includes a 6 m³ sand trap to reduce the suspension load consisting of soil particles, tire wear, and other materials as well as potential lubricant or fuel contamination. From the sand trap the water then flows into a splitting well (∅ 1 m) where automated sampling and equipment for measuring/ logging flow rate and total volume is installed. Samples can be collected here or at the overflow and in the sand trap depending on different weather and season conditions.
Automated sampling can be triggered by the flow rate or alternatively by an additionally installed rain gauge. From the splitting well the run-off is parted 50/50 to the filtration units. Two parallel filtration units have been installed to be run simultaneously; one containing several different modular multi-layer columns during a material test phase and later on the optimized multi-layer reactive filter, the other containing a simple quartz sand bed yielding a reference effluent to evaluate the efficiency of the reactive filter compared to the sand filter unit. To prevent filter clogging caused by fines leaving the sand trap, replaceable geo-textile layers are placed on top of each filling. The effluent from the plant is collected in a collection well (∅ 1.5 m) where an automated sampler is installed and the hydraulic head can be adjusted. The latter controls the fraction of the column that works under constantly saturated conditions.

Fig. 8: Top and side view of the treatment facility



Suitable reactive filter materials

As stated above single layer filtration units,as sand filters or even filters employing reative material as e.g. natural zeolite, may often prove insufficient for treating surface run-off where the contamination is complex and where suspended particulate/ colloidal matter is present. Accordingly, the sequence of reactive layers presented here was designed to enhance and to optimise the retention capacity and efficiency for a complex pool of contaminants from the surface run-off water, without reducing the hydraulic conductivity of the filter.
Reactive in terms of increased sorption or exchange capacity, selective increased retention of specific compounds or altering hydrochemical conditions to optimize cleaning, these materials can be added to technical sand resulting in the following advantages:

- Increased retention of pollutants
- Decreased consumption of space & material
- Possibility of regenerating the materials for repeated use

Suitable materials can be found as compounds in the restoration of contaminated sediments [capping, see Jacobs et al] or groundwater. Emphasis should be put to low-cost materials, technical ion exchangers or activated carbon seldom will be used.

The following materials are selected according to their retention capacity even at short contact times:

- natural zeolithe (clinoptilolithe from Herbst company) (in part washed with Ca^{2+})
- hydro-Calcite
- polypropylene-flakes
- activated carbon
- modified wood shavings (Carbion H®, EISU company)
- surface-treated natural zeoithe (clinoptilolithe, Herbst company)
- surface-treated polypropylene-flakes

The first retention experiments in the pilot plant are performed with well-defined natural zeolithe followed by other materials under current laboratory investigation.

Targets of retention and suitable materials
dissolved or weakly bound trace metal ions, for example lead, zinc, copper and cadmium, are exchanged with alkaline metal ions at the zeolithe surface.
The efficiency of this process is counteracted by the presence of particulate or colloidal phases and humic substances, which compete for the heavy metal ions.

Colloidal particulate matter has to be removed by means others than physical filtration. The physical filtration of colloids will lead to pore blocking which subsequently leads to reduced hydraulic conductivity, preferential flow in larger pores, reducing the active surface area and resulting in the enhancement of transport of colloidal/ particulate material through the filter.
Countermeasures are developed from principles of colloid chemistry: increase of the concentration of divalent ions and deposition on filter grain surfaces by means of electrostatic attraction. The first is achieved by using a Calcium-modified zeolite and an extra layer of calcite in the filter. The zeolite willl exchange other cations (as free ionic Cu^{2+}, Pb^{2+}, Zn^{2+}, Na^+ and NH_4^+) and respond with a release of Ca^{2+}. As a result colloid deposition in the column is enhanced. Since colloids are removed by deposition on surfaces rather than by filtration in small pores, the hydraulic properties are preserved.
Fig. 9 shows a comparison of the precipitation of a natural stable mineral and humic colloidal suspension which was extracted from an aquifer soil due to the increase of monovalent Na^+ and bivalent Ca^{2+} concentrations. The precipitation efficiency of even at the very low Ca-concentrations of less than 1 mmol/L can be clearly seen.

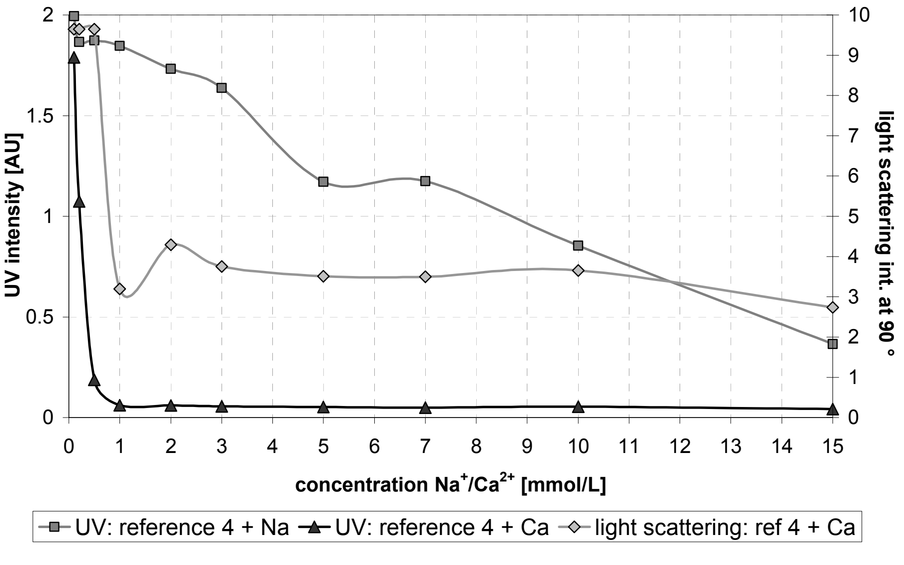


Fig. 9: UV-Absorption of the supernatant of a stable natural soil suspension (laboratory reference sample No. 4) which was mixed 1:1 with NaCl- and $CaCl_2$-solutions of increasing ionic strengths and then kept over-night. The light grey curve plotted on the second axis is from a highly sensitive laser light scattering detec-tor.

Finally natural organic matter, potentially carrying complexed heavy metals and organic pollutants as well as remaining negatively charged colloids can be retarded using activated carbon. Activated carbon will show a certain positive surface charge under the pH conditions observed.

Acknowledgements

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E.2 Lecture Session:

Harbours

A PILOT-SCALE FIELD DEMONSTRATION ON SUBAQUEOUS DEPOTS WITH ACTIVE BARRIERSAYSTEMS (SUBAD-ABS) FOR THE STORAGE OF CONTAMINATED DREDGED MATERIAL (CDM)

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Background

On a worldwide scale rivers transport eroded material as suspended solids to the coastal areas. Deltas, estuaries and their associated wetlands are natural sinks for this material. In the 1980's, the International Association of Ports and Harbors estimated about 350 million tons of maintenance dredging and 230 million tons average annual dredging. In the harbors around the North Sea, approx. 100 million m³ of sediment has to be dredged annually – about 10 time the average annual sediment discharge of Rhine River.

Due to the economic implications, there is increasing world-wide interest in the development of dredging and disposal technologies. Among the authorities particularly dealing with the subject of contaminants in dredged materials the U.S. Army Corps of Engineer Waterways Experiment Station at Vicksburg, Mississippi, has played a leading role. Further intensification of coordinated research was performed by the ARCS („Assessment and Remediation of Contaminated Sediments“) group of U.S. Environmental Protection Agency, which was charged with assessing and demonstrating remedial options for contaminated sediment problems in the Great Lakes; laboratory tests were conducted utilizing 13 processes, and a pilot-scale (field-based) demonstration of bioremediation. Particle size separation, solvent extraction and low temperature thermal desorption were conducted (Anonymous 1994).

In Europe, the Dutch Development Program for Treatment Processes for Contaminated Sediments (POSW), starting up in 1989 and running until 1996, was aimed at the development of ecologically sound dredging and processing techniques, to be used in the remediation and reuse of polluted sediments (Anonymous 1997). Technical applicability had to be demonstrated in practice, as part of an integrated remediation chain. Attention was also paid to the economic and environmental consequences of the several types of techniques..

Table 1: Technology types for sediment remediation (Anonymous 1994)

	In Place	**Excavated**
Containment	in situ-capping	confined aquatic disposal/ capping
	contain/fill	land disposal
		beneficial use
Treatment	bioremediation	physical separation
	immobilization	chemical extraction
	chemical treatment	biological treatment
		immobilization
		thermal treatment

It becomes increasingly clear, that remediation techniques on contaminated sediments are much more limited than for most other solid waste materials, except for mine wastes. The widely diverse contamination sources in larger catchment areas usually produce a mixture of pollutants, which is more difficult to treat than an industrial waste. Often, traditional remediation techniques are economically unacceptable, because of the large volume of contaminated materials to be treated. In such cases the concept of "geochemical engineering" (Salomons and Förstner 1988) can provide both cost-effective and durable solutions. Geochemical engineering applies geochemical principles (such as concentration, stabilization, solidification, and other forms of long term, self-containing barriers) to control the mobilization and biological availability of critical pollutants. This concept predominantly relates to in-situ aquatic sediment remediation and for the most relevant options, a provisional feasibility judgement has been presented by a recent investigation in the Netherlands (Joziasse and Van der Gun 2000).

Sediment remediation methods can be subdivided according to the mode of handling (e.g. in-place or excavation), or to the technologies used (containment or treatment) (Table 1). Excavated sediments can be chemically extracted or biologically treated to reduce concentrations of pollutants, or treated by additives to immobilize toxic metals. Mechanical separation of less strongly contaminated fractions may be an useful step prior to final storage of the residues. For most sediments from maintenance dredging, there are more arguments in favor of „disposal“ rather than „treatment“. Important containment techniques include capping in situ and confined disposal

In-Situ Remediation

Similar to conventional waste management, handling of contaminated sediments follows the priority sequence of prevention – reuse – safe disposal. Measures at the source are particularly important and may include improvement of traditional wastewater purification, but also more approaches for in-situ treatment of highly contaminated effluents such as introducing active barriers (fly ash, red mud, tree bark, etc.) into ore mines to prevent heavy metal dispersion during flooding (Zoumis et al. 2000). Other techniques can be applied for mechanical and chemical stabilization of interim depots of sediment in floodplains, polders and stormwater retention basins (Förstner et al. 2001).

As shown from the examples of large-mass wastes dredged material, mining residues and municipal solid waste, long-term immobilization of critical pollutants can be achieved by promoting less soluble chemical phases, i.e. by thermal and chemical treatment, or by providing respective milieu conditions. Selection of appropriate environmental conditions predominantly influences the geochemical gradients, whereas chemical additives are aimed to enhance capacity controlling properties in order to bind (or degrade!) micropollutants. In general, micro-scale methods, e.g., formation of mineral precipitates in the pore space of a sediment waste body, will be employed rather than using large-scale enclosure systems such as clay covers or wall constructions. A common feature of geochemically designed

Table 2: Selected options for in-situ sediment remediation (after Joziasse and van der Gun 2000)

Remediation type	**Scope (type of contaminants)**	**Technological concept**	**Technological implementation**
Stimulation of aerobic microbiological degradation	Organics (PAH, mineral oil, etc.)	Increase degradation rates by changing environmental conditions	Use enhanced degradation of contaminants in soil near plant
Fixation of contaminants (sorption or immobilization)	Metals	Precipitation of metals as hydroxides or insoluble complexes	Precipitation or adsorption near or at plant roots (phytostabilization)
Reduction of advective dispersion towards surface waters	All contaminants	Reduction of bank erosion/ wash out	Introduction of plants
Reduction of advective dispersion towards ground water	All contaminants	Increased hydrological resistance	Application of a clay screen

deposits, therefore, is their tendency to increase overall stability in time, due to the formation of more stable minerals and closure of pores, thereby reducing water permeation.

Recently a number of developments in remediation of terrestrial soil pollution, both with respect to policy aspects as to technical developments have led to a stimulation of in-situ remediation options: (1) remediation actions have no longer to be executed within a very short period of time, (2) the result is not necessarily a “multifunctional soil”, and (3) advantage is taken of natural processes (the self-cleaning capacity of the soil). In Table 2 (selected from a review by Joziasse and van der Gun 2000) a number of potentially relevant options are summarized: It may be conceivable that the conditions for reductive dechlorination of chlorinated hydrocarbons are optimized. Also phytoremediation (for instance degradation of contaminants near plant roots) may be beneficial in certain cases (Ferro and Kennedy 1999). As to the immobilization of contaminants by adsorption one can think of applying clay screens, or clay layers (with or without additives). The advective dispersion of contaminants toward ground water or surface water can be reduced by capping the polluted sediment with a clay layer, with organic matter (humus) or other materials as possible additives.

Joziasse and Van der Gun (2000) emphasize that for every single case the effects of the actions (either dredging, or in-situ) on the aquatic ecosystem will have to be accounted for. In concrete cases, where a conventional approach encounters serious difficulties, an investigation dedicated to the prevailing conditions will have to give a decisive judgement on the feasibility of an alternative (in-situ) approach.

Subaqueous Storage and Capping

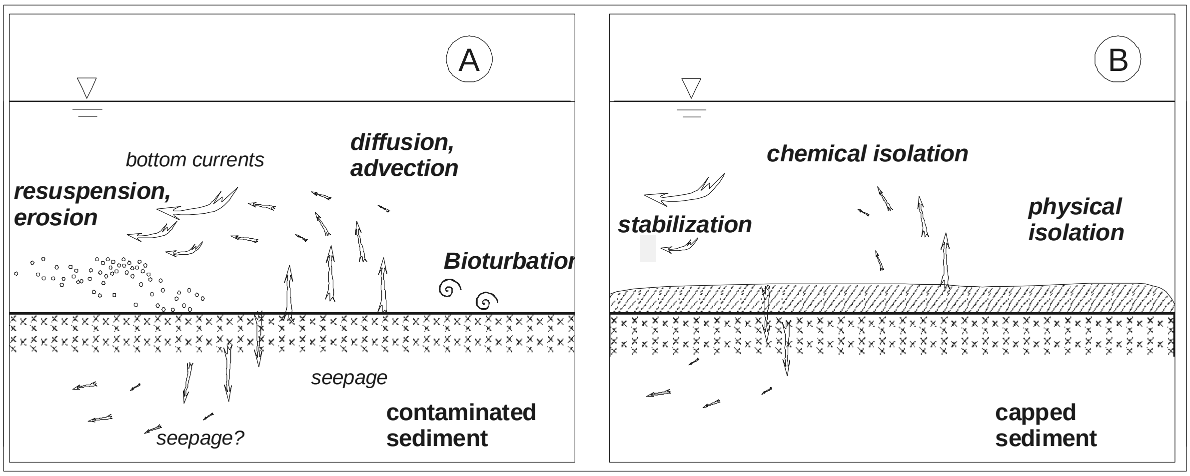

Figure 1: (A) Remobilization mechanisms of contaminants from an aquatic sediment. (B) Stabilization and Isolation of sediment by a capping layer.

Wherever economic or technical implications counteract an excavation of a contaminated sediment but remediation is required according to environmental implications, i. e. to prevent potential interference with the aquatic environment, in-situ technologies are considered. Subaqueous in-situ capping has become an attractive concept for isolating contaminated sediments. Subaqueous capping simply denotes the placement of a layer of clean material (i. e. material that is suitable for unrestricted open-water disposal) over contaminated sediments forming a permeable cap. A clear distinction should be made, however, between in situ capping of contaminated autochthonous sediments on the one hand and dredged material capping that involves sediment removal by dredging, relocation, and subsequent capping of the disposal area by a cap (Zeman 1994).

As depicted in Fig. 1, three main mechanisms inhibit the release of contaminants from the sediment through a cap into the water column (Palermo et al. 1998). Firstly, a stabilization of the sediments prevents sediment particles, that may transport solid phase bound contaminants, from being resuspended. Resuspension is considered a major path of release in waterways where strong bottom currents or ship traffic (anchoring, propeller wash) prevail. Secondly, a physical isolation of the sediment is achieved - transferring the zone of active bioturbation from the contaminated sediment into the clean cap and by this preventing the benthos from getting into contact with the contaminants.

Consequently, a direct uptake into the food chain and possible bioaccumulation can be ruled out. For an effective isolation it is thus crucial to investigate the benthic community at the particular disposal site and, on that basis, determine the required minimum cap thickness. Thirdly, a chemical isolation prevents contaminants from being transferred from the sediment to the overlying water by dissolution, desorption, or ion exchange at the sediment to water interface by sheltering the interface with a diffusion barrier.

The interaction of these three mechanisms can result in an effective prevention of contaminant release into the surface water if the cap design is adapted to the conditions at the capping site. The design of a cap requires the proper application of (1) hydraulic principles, i. e. armor and filter equations, (2) chemical principles, i. e. advection-diffusion-retention equations, and (3) geo-engineering principles, i. e. settlement and stability equations (Mohan et al. 2000). Implementation of in-situ sediment capping, thus, is a typical example for collaborative projects involving strategic research, applied research and development, and technology sharing projects (Azcue et al. 1998). Major steps are (1) characterization of sediment materials (reactivity, mobility of pollutants), (2) suitability of capping techniques (currents, steep gradients, groundwater seepage), (3) provision of capping material (sand, granular materials, geotextile, additives; logistics; soft sediment/coarse, dense cover; impermeable materials, water flow); (4) thickness of capping material, (5) reactive additives; (6) monitoring of the sediment/cap system, early warning systems.

Capping materials in projects completed to date usually have been either sand, gravel, or clean sediments. An overview over a selection of full scale capping projects is given in Table 3. The cap can either consist of a basic single layer design, e. g. a layer of sand, or a more complex multi-layer design. After Mohan et al. (2000) such a multi-layer design can consist of the following components:

– A base stabilizing layer which provides local stability to the capped sediment to support the added weight of the cap.
– A base isolation layer which provides the primary isolation of the contaminants from the environment.
– A filter layer which provides hydraulic protection to the base isolation layer
– An armor layer which provides erosion protection the cap

Table 3: Overview over selected capping projects (after Palermo et al. 1998, modified).

	Contamination	***Capped area***	***Cap design***	***Reference***
Kihama Lake, Japan	Nutrients	3.700 m²	Fine sand, 0.05 und 0.2 m	
Akanoi Bay, Japan	Nutrients	20,000 m²	Fine sand, 0.2 m	
Denny Way, USA	PAH, PCB	12,000 m²	Sediment, 0.79 m	Sumeri (1995)
Simpson-Tacoma, USA	Creosote, PAK, dioxine	69,000 m²	Sediment, 1.2-6.1 m	Sumeri (1995)
Eagle Harbor, USA	Creosote	220,000 m²	Sediment, 0.9 m	Sumeri (1995)
Sheboygan River, USA	PCB		Sand	Eleder (1992)
Manistique River, USA	PCB	1,858 m²	Geo-membrane	
Hamilton Harbor, Canada	Nutrients	10,000 m²	Sand, 0.5 m	
Eitrheim Bight, Norway	PAH, metals, nutrients	100,000 m²	Geotextile, Armoring	Instanes (1994)
St.-Lawrence River, USA	PCB	7,000m²	Sand, gravel, boulders	

The capping concept recently has been extended by the concept of active barrier systems, ABS (Jacobs and Förstner 1999). To enhance the chemical isolation component the ABS concept employs capping layers that consist at least partly of one or more reactive components. The addition of reactive matrix components aims to actively demobilize the contaminants which are transported with percolating pore water. By this a long-term retention of dissolved contaminants may be achieved even under unfavorable conditions as a notable advective transport through the barrier. Advective transport can result for example from marine groundwater discharge or squeezing of pore water while compression of the sediment due to the additional load of the cap. Under these conditions the chemical isolation potential of chiefly inert sand or gravel barriers may be exceeded. Actually ongoing research work focuses particularly on the selection and characterization of reactive materials for active barrier systems. Potential materials have to meet a number of prerequisite properties: (1) they must have a good retention potential, (2) their chemical and physical properties (e. g. specific density, grain size distribution, chemical stability) must be suited for an underwater application, (3) they must be suited for unrestricted open water disposal (i. e. uncontaminated), and (4) they must be available at relatively low cost. Generally, industrial mineral by-products and natural (rock-forming) minerals are the most promising materials but often they do not meet all requirements listed above (Table 4). Some of the listed properties may be altered by appropriate treatment of the material. For example, surfaces of clays and zeolites can be modified for an enhanced sorption of organics and anionic contaminants. Fine grained materials which would rather form a hydraulic than a reactive, permeable barrier may be granulated. However, this pre-treatment may apparently raise the capital costs. Fortunately, natural microporous materials, and in particular natural zeolites, show highly favorable chemical, physical properties with respect to their application in subaqueous capping projects along with a world-wide availability at relatively low cost (Jacobs 2000). Consequently, the actual research work focuses on these materials.

Table 4: Examples for potential reactive materials for active barrier systems (Jacobs and Förstner 2001).

	material	***target contaminants***	***physical/ chemical suitability***	***environmental acceptability***	***availability/ costs***
industrial by-products	***fly ash***	metals	+/- (very fine grained)	- (high equilibrium pH in watery suspension, potential toxicity)	+
	red mud	metals	+/- (very fine grained, not stable under reducing conditions)	(heavy metals)	+
natural minerals and rocks	***calcite***	metals, nutrients		+	+
	apatite	metals	+	+	+/-
	clays (e. g. bentonite)	metals	+/- (very fine grained)	+	+
	zeolites (e. g. clinoptilolite)	metals	+		

For the technical implementation of a cap the same conventional dredging and construction equipment can be used as for the relocation of the dredged material. This is of particular advantage from the economic point of view. However, these practices must be precisely controlled. In general, the cap material must be placed so that it accumulates as an even and homogeneous layer covering the contaminated material. It must be prevented from displacing or mixing with the material due to the use of inappropriate placement methods or equipment (Anonymus 1994). Several methods of cap placement using land based and sea based equipment are discussed by Palermo et al. (1998).

As pointed out above, subaqueous capping is considered an economic management option. The capital costs of a capping project will be determined mainly by the cap materials, the equipment used for the placement and labor costs and subsequently by the monitoring program. However, most of the equipment is generally easily available since it used for the sediment dredging and relocation prior to the cap placement. But not all costs are covered by the dredging and transportation components when specialized equipment as submerged diffusers are needed for the cap placement. Generally, the cap positioning requires a greater level of precision and control than the disposal of the dredged material. The cap materials used are favorably low-cost materials, e.g. fresh sediment, sand, or natural mineral additives as zeolites.

Disposal of dredged material

Currently, increasing efforts are made to prefer beneficial use of dredged material, i. e. the use in coastal defense and beach nourishment or habitat creation or the production of construction materials over disposal. However, beneficial use will not be compelled at unreasonable costs and, furthermore, according to national and regional stipulations as well as the above mentioned international conventions, only uncontaminated sediments are suited for beneficial use, generally. The LC provides in its annexes detailed information for the disposal of dredged materials comprising (1) a “black list” with materials prohibited from open water disposal, (2) a “grey list” with materials that require safety measures when disposed off at sea, and (3) detailed suggestions how to apply the convention in the countries having signed the convention.

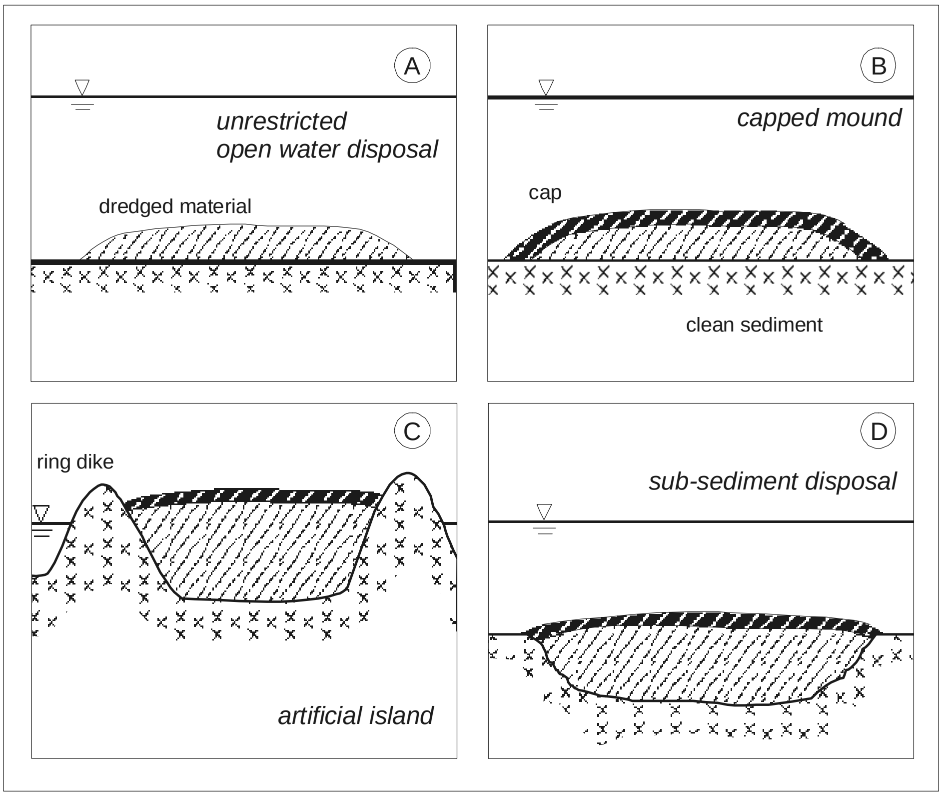

Figure 2: Types of subaqueous disposal for dredged material.

Therefore, disposal remains an important option in managing dredged material (Jacobs and Förstner 2002). The most straightforward type of subaqueous disposal is the unrestricted open water disposal

(Fig. 2 A). This denotes a disposal without any previous treatment or following technical protective measures. Unrestricted open water disposal, however, is only suited for uncontaminated sediments or more accurately for sediments that do not exceed the legal threshold values of the relevant contaminants. Sediments that exceed relevant threshold values, consequently, may not be disposed off without further protective measures. In this case there may be distinguished three main options: the material is disposed off at land, treatment steps are applied to the sediment prior to the under water disposal to meet the threshold values, or the under water disposal site is safeguarded by technical means.

In the past it was argued that - regarding the various containment strategies - upland containment (e.g., on heap-like deposits) provide a more controlled management compared to containment in marine environments. However, contaminants released either gradually from an imperfect impermeable barrier (also into the groundwater) or abruptly after a failure of the barrier could produce substantial damage (Kester et al. 1983). On the other hand, near-shore marine containment (e.g., in capped mound deposits), offers several advantages, particularly regarding the protection of groundwater resources, since the underlying water is saline and inherent chemical processes are favorable for the immobilization or degradation of priority pollutants.

Reviewing marine disposal options, Kester et al. (1983) suggested that the best strategy for disposing off contaminated sediments is to isolate them in a permanently reducing environment. Under anoxic, strongly reducing sub-sediment conditions a great part of the metal content is present as sulfides, compared to the respective carbonates, phosphates, and oxides due to microbial mediated sulfate reduction. This process is particularly important in the marine environment, whereas in anoxic freshwaters milieu a tendency for enhancing metal mobility due to the formation of stable complexes with ligands from decomposing organic matter is observed. Marine sulfidic conditions, in addition, seem to repress the formation of mono-methyl mercury, that is one of the most toxic substances in the aquatic environment, by a process of disproportionation into volatile dimethyl mercury and insoluble mercury sulfide (Craig and Moreton 1984). Furthermore, Kersten (1988) reports the degradation of highly toxic chlorinated hydrocarbons being enhanced in the sulfidic environment.

Disposal in capped mound deposits above the prevailing sea-floor, disposal in sub-aqueous depressions, and capping deposits in depressions provide procedures for contaminated sediment (Bokuniewicz 1983). In some instances it may be worthwhile to excavate a depression for the disposal site of contaminated sediment which can be capped with clean sediment. This type of waste deposition under stable anoxic conditions, where large masses of polluted materials are covered with inert sediment became known as "subsediment-deposit". Figure 2 B-D differentiates three main disposal types. The first type, the capping of the disposal site (Figure 2 B), represents a technically straightforward and economic measure to isolate the contaminated material from the environment. Due to its important role as an effective and economic passive technology, the capping concept is documented in the Dredged Material Assessment Framework (DMAF), the implementation guideline of the LC, as well as in the guidelines of the US Environmental Protection Agency (US EPA). The second type is the artificial island type, where the designated disposal area is excavated to a certain depth and the obtained sediment material is used to pile up a ring dike that encircles the disposal site. Within this ring dike the dredged material is disposed off and may be finally covered with an additional cap. The third option is to excavate an area of uncontaminated sediment, to dispose off the contaminated dredged material into the excavation and to cover the deposit with the clean excavated material. This option is of particular economic interest as no capping material has to be transported to the disposal site.

In accordance with the precautionary principle, the choice of the appropriate disposal option has to be made by means of an effects-based assessment. That means that any potential long-term impact of the planned disposal on the aquatic environment has to be evaluated. Therefore, a chemical and biological characterization of the dredged material in concert with an exact characterization of the disposal method and the disposal site is crucial. During the disposal process an short-term risk may be given due to suspension of contaminant-bearing sediment particles and desorption or dissolution of contaminants when passing through the water column. Another, possibly more serious, threat is posed to the ecosphere by the potential continuous long-term release of contaminants. In analogy to in-situ sediment caps (Fig. 1) underwater dredged material deposit without any further safeguard may be subject to (1) erosive forces resuspending contaminated sediment particles, (2) submarine groundwater discharge transporting dissolved contaminants into the water column or sea water intrusions into coastal ground water, and (3) benthic organism resuspending and feeding on the contaminated sediment. To prevent the contaminant release measures are to be taken as described in table 1.

Monitoring ABS - A Crucial Issue

Monitoring is an important part of the concept of SUBAD/ABS. Therefore, a complete monitoring concept has been developed (Jacobs 2003). A new rechargeable type of dialysis sampler (Figure 3 left, Jacobs 2002) was developed allowing an economic long term monitoring of concentration-vs.-depth profiles of pore water constituents in the sediment, the cap and the overlying surface water (Figure 3).

This concept was tested successfully under field conditions in a small scale field experiment in a lake near Leipzig, Germany. The graphs show the concentration depth profiles 3 weeks (t_1), 8 weeks (t_2), 12 weeks (t_3) and 15 weeks (t_4) after implementation.

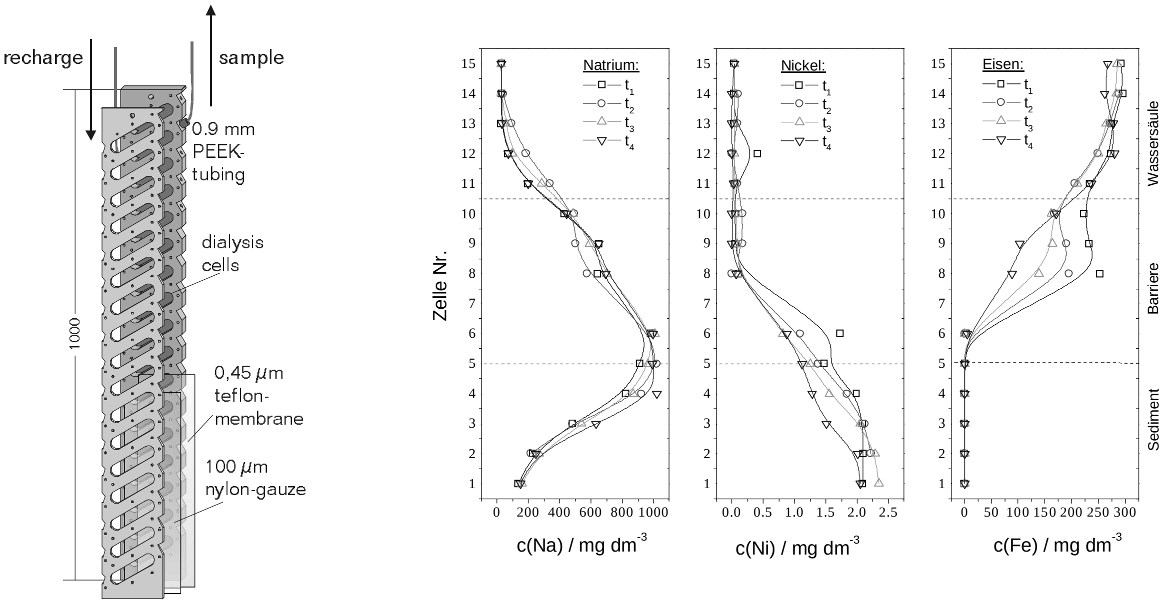

Figure 3: A rechargeable dialysis sampler design was developed to meet the particular requirements in monitoring sediment caps (left). The field testing reszlts corroborate the practicability and efficiency several months implemetation time (right) (Jacobs 2002).

Field Demonstration in the River Elbe, Germany

For the technical implementation of a cap, the same dredging and construction equipment can be used that is applied for relocation of the dredged material. This is of particular advantage from an economic point of view. These implementation, however, must be controlled precisily to prevent the cap material from being displaced or mixed with the sedimentl due to use of inappropriate placement methods or equipment (Anonymous, 1994).

As the final phase of the current research work on SUBAD/ABS, a large-scale field demonstration is planned in a canal formerly connecting a harbour with the river Elbe. Highly contaminated sediment from the harbour is to be relocated for maintenance and will be disposed of into the canal (Figure 4). A patented press and hauling system of J. Möbius Bau-Gesellschaft GmbH & Co. (Möbius Press- und Fördersystem, MPF) will be employed. This system - due to its unique technical features - is capable of largely avoiding resuspension of particles during transfer of the contaminated sediment into the confinement. The pasty material will be stored under water and will be covered on a large scale by a conventional sand cover (Mohan et al., 2000; Palermo et al., 1998; Zeman, 1994).

Within the sand-capped disposal site a test field shall be installed comprising eight cylindrical enclosures (Figures 4, 5). These enclosures shall contain the relocated sediment capped with different

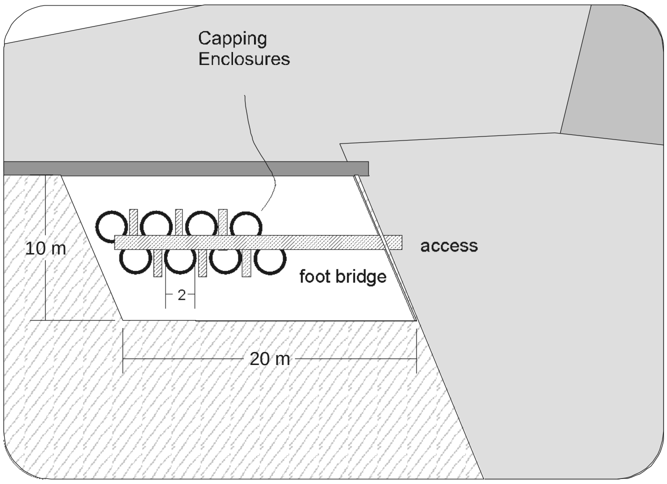

Figure 4: Top view on the SUBAD-ABS-testfield.

types of ABS-caps. The long-term behaviour of relevant contaminants as metals and organics will be monitored over two years.

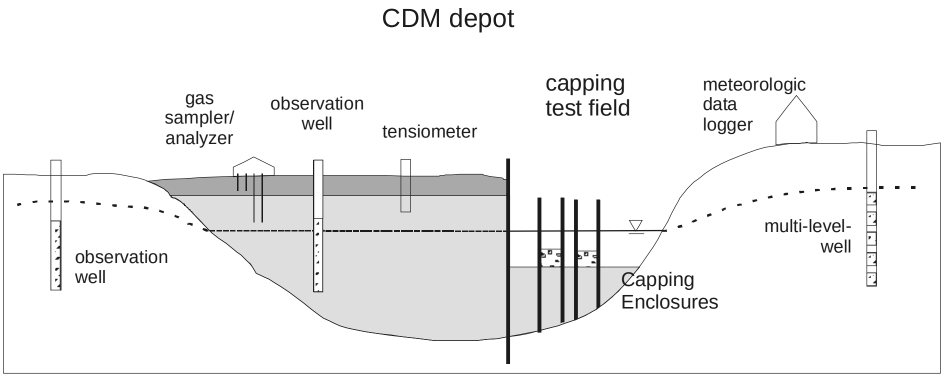

Figure 5: Cross section through the SUBAD-ABS-testfield.

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HEALTH AND ENVIRONMENT INTEGRATED FRAMEWORK: FROM A CASE STUDY EXPERIENCE TO THE ACHIEVEMENT OF A PLANNING AND DECISIONAL ASSESSMENT TOOL

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1. Background

The present study analyses the environment and health status of the population living near a municipal waste incinerator that have operated in the Pisa Southeast district for 20 years approximately. This area is located within a dense road network with heavy vehicle traffic. The local authorities are now evaluating a project for a new hazardous waste disposal plant to be located in the above district.

The study area is defined by a 0-4 km zone around the site with a population of about 12,000 residents.

2. GIS methodology and geo-referentiation

An environmental survey, linked to a territory for its own nature, is well suited to be approached by GIS. In the case presented in this work GIS is the optimal tool to manage the multilevel data, as geography acts as an implicit link for disciplinary data. Data pertaining to each field of investigation are collected into thematic layers and these can be viewed together with a cartographic representation

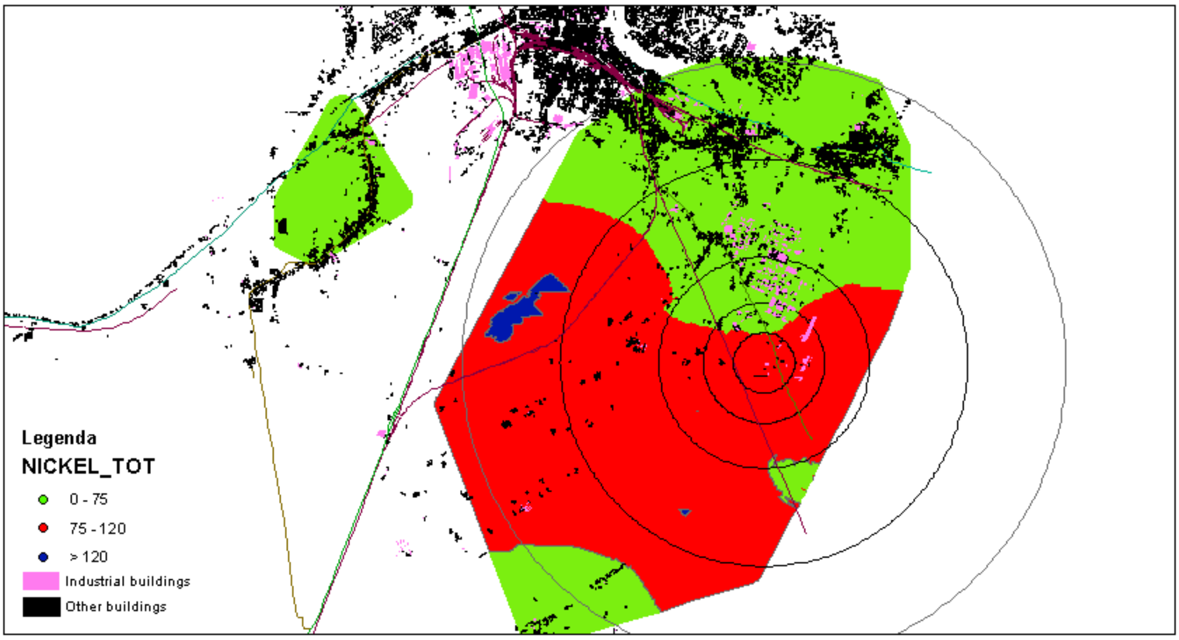
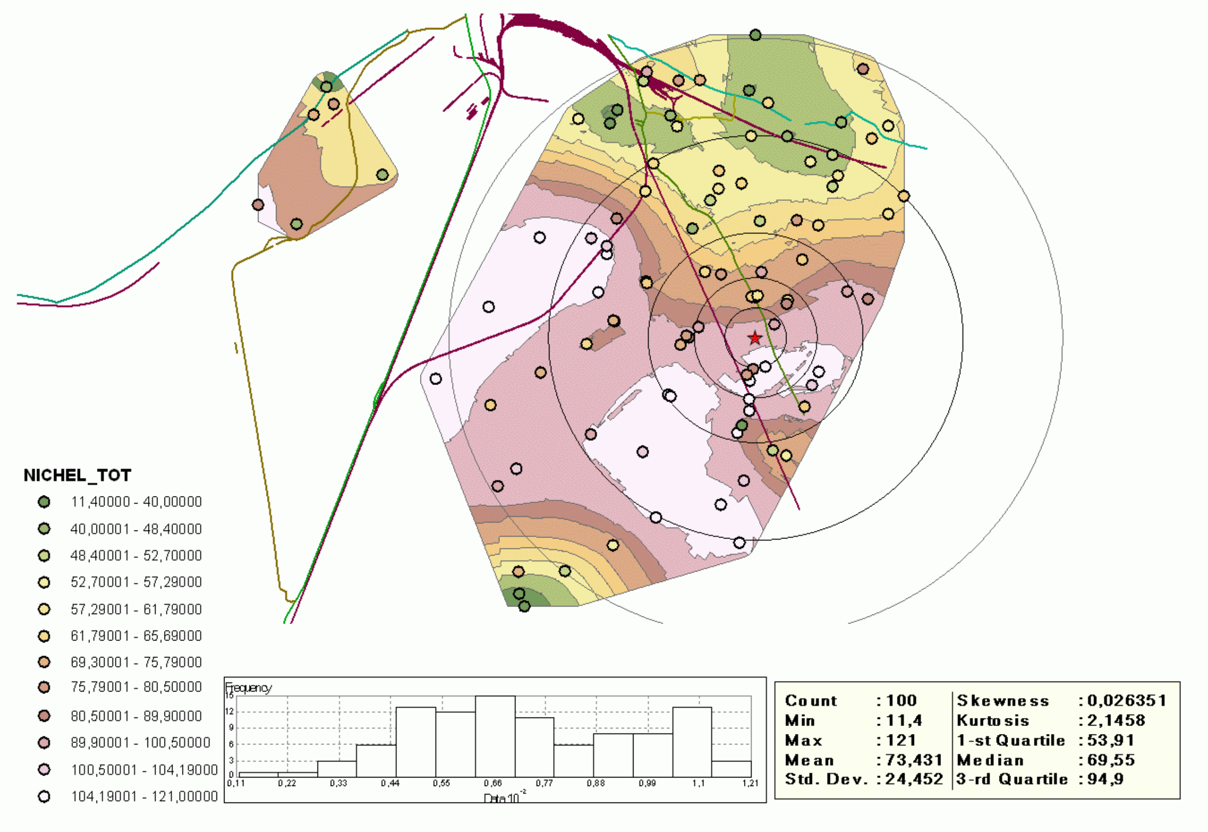


Figure 1: Risk map of nickel for administrative purpose

of the territory to assess the difference (or the similarity) among phenomena. Risk maps can be obtained for different fields and compared, resulting in the production and evaluation of different views of the same environment.

As a technical aspect, the usefulness of an underlying GIS System resides not only in the enhanced capabilities for the analysis of the results, but also in the advanced facilities available to produce Information derived from existing thematic layers or in the possibility to easily integrate information used with different technological devices. For example, we used for the project a GPS device to map the sampling sites of soil or also we integrated in the system the information from the General Register Office of Pisa Municipality to perform the sampling of subjects for the epidemiological survey on a spatial basis.



Count	: 100	Skewness	: 0,026351
Min	: 11,4	Kurtosis	: 2,1458
Max	: 121	1-st Quartile	: 53,91
Mean	: 73,431	Median	: 69,55
Std. Dev.	: 24,452	3-rd Quartile	: 94,9

Figure 2: Risk map of nickel for scientific purpose

Figures 1 and 2 are proposed as an example of the contribution to a better data exploitation carried out by a GIS integration of data: in both cases information derived from chemical analysis of soil samples (the presence of nickel) is used to produce a map. By using a GIS tool a risk map was obtained by interpolating the point-values. The map of figure 1 is prepared for the Administration Authority and it shows the classification of the area of study according to threshold values (imposed by law) of the pollutant; base cartographic data (industrial buildings –fuchsia–, civil buildings - the black ones) give a context significant to the Public Administrator. Figure 2, instead, is prepared for the scientist who wants to study the behaviour of the phenomenon on the territory: his interest is to assess the trend of the values and to know exact values in the sampling sites, so a different and richest legenda was used to represent a more detailed risk map. The locations of the points of measure were also shown, colored according to the same legenda.

3. Soil

The aims of the monitoring analytical program were to define the environmental state of the area, in order to create a reference for any future research and to verify the possible presence of pollution coming from all the local industrial activities. Besides the incinerator, many other industrial activities are based on the area and they represent possible sources of pollution, as well as the vehicular traffic.

3.1 Sampling Methodology and Criteria

In order to provide a mapping of the area, the incinerator was taken as the centre of the surface. The area was divided in 5 concentric circles, each measuring 400, 800, 1,400, 2,700, 4,000 m. A grid with a regular square mesh of 500 meters was designed on the site; the operators then used the theoretical grid as an indicator to locate the optimal sampling point. Two more areas were chosen as a blank, in the nearby countryside where the influence of the incinerator action was considered irrelevant. Each sampling point was georeferenced by using a GPS device and, also, correlated with a brief description. The criteria employed in the description were the main use (e.g. cultivated or not) and the vicinity to possible sources of pollution (e.g. roads, parking areas, canals). The GPS facilities give the possibility to come back to the point in case of the need of further sampling; the description permits a more fine identification of the place and besides it locates the point in its real context helping to interpret the analysis results. A map was drawn representing all the sampling points and their descriptive categories, grouped in three 1) agricultural, 2) urban, 3) natural. "Agricultural" was referred to soils cultivated, which included tilled and treated with chemicals (i.e. fertilisers, herbicides) soils; "urban" was referred to soils disturbed by the action of a strong anthropic context, included urban or residential and roads; "natural" was referred to undisturbed soils as evidently abandoned, non cultivated, wild.

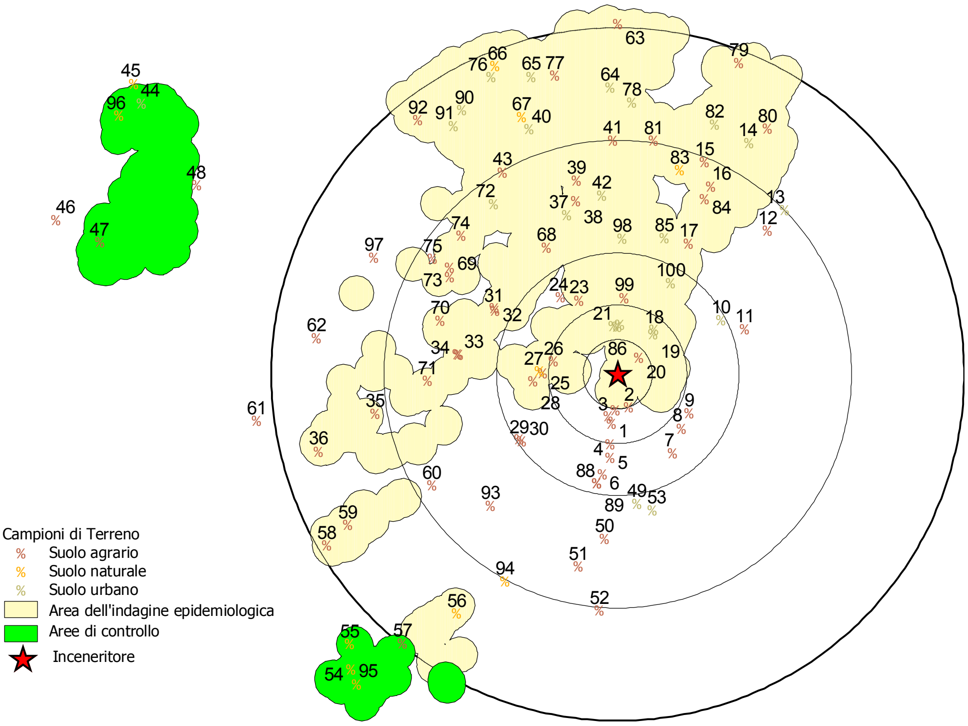


Figure 3: Classification of soil samples

3.2 Characterisation Analysis and Results

The samples were taken at 0-20 cm depth, sieved in a 2 mm mesh and analysed for pH, Organic Matter, Cation Exchangeable Capacity, Texture. The physical chemical characterisation was carried out to give a complete picture of the environmental condition of the area and to better interpret the behaviour of the pollutants. Results for the texture, ph, OM, CEC, are statistically described in table 1. Texture results demonstrate that the characteristics of the main part of the soils analysed are near to the main. It is very important for the study of bio availability of metals to know the soil texture. Because of the high surface activity and cations absorption, the fine fraction (silt and clay) can absorb the pollutant on its surface and in this way reduce the concentration of metals in the solution. These metal soluble forms are able to penetrate the roots cell membrane and though to end up in the food chain. The value of pH in the samples is constant about 8, this value reveals low metals mobility. Cation exchangeable capacity is correlated to clay and humus content and in agricultural Italian soils it ranges from 5 to 50 cmol/kg; in the present study the values are really variable, following the content of clay. Organic matter in the soils analysed ranged from 0.5 to 12.4. Organic matter is an important parameter because it interacts with metals, absorbing them on its surface and reduces the uptake by the vegetation.

Table 1. Descriptive statistics of the physical chemical characteristics observed in the 100 samples.

```
--------------------------------------------------------------------------
    variable |         N      mean        sd       min       p50       max
-------------+------------------------------------------------------------
     samples |    100.00     50.50     29.01      1.00     50.50    100.00
          OM |    100.00      3.34      2.20      0.50      2.65     12.40
         CEC |    100.00     20.90      6.03      4.90     20.80     37.40
          pH |    100.00      8.00      0.35      6.80      8.00      8.90
        clay |    100.00     24.78     12.25      6.20     21.65     60.90
        silt |    100.00     28.52      8.83      7.20     28.95     47.70
        sand |    100.00     46.80     18.79      4.30     48.00     86.60

--------------------------------------------------------------------------
```

3.3 Contaminants

The analyses of the pollutants were for:

- Metals total values: i.e. cadmium, chromium, lead, nickel, mercury, copper, arsenic, zinc;
- Metals extractable values: i.e. lead, nickel, copper and zinc;
- Organic pollutants: i.e. Dioxins (PCDD+PCDF) and PAH were investigated in 16 samples chosen in the proximity of the incinerator and in the blank area.

Because of the high number of samples it was impossible to show all the results especially to Public Administrators who are not experienced with scientific data. A descriptive statistic resumes the 100 samples in an easy to read table.

Table 2. Descriptive statistics of the characteristics observed in the 100 samples.

```
--------------------------------------------------------------------------
    variable |         N      mean        sd       min       p50       max
-------------+------------------------------------------------------------
     samples |    100.00     50.50     29.01      1.00     50.50    100.00
    total Cd |    100.00      0.46      0.32      0.02      0.44      1.30
    total Cr |    100.00     84.73     24.35     14.90     83.15    135.30
      Ext Ni |    100.00      1.47      0.52      0.70      1.35      3.00
    Total Ni |    100.00     73.43     24.45     11.40     69.55    121.00
      Ext Cu |    100.00     12.13      9.45      0.02      7.90     50.10
    Total Cu |    100.00     68.71     43.33      0.15     56.95    271.10
      Ext Pb |    100.00      8.63     11.33      1.80      3.94     76.00
    Total Pb |    100.00     39.37     34.87     14.60     27.95    207.10
      Ext Zn |    100.00      9.70     16.73      2.15      6.50    164.90
    Total Zn |    100.00    127.09    135.10     48.40     96.90   1286.00
          Hg |    100.00      0.17      0.11      0.03      0.15      0.60
          As |    100.00      5.89      1.85      2.60      5.60     12.60
         PAH |     16.00      0.09      0.07      0.02      0.06      0.24
     dioxins |     16.00      0.00      0.00      0.00      0.00      0.00
--------------------------------------------------------------------------
```

Tables 3, 4, 5, 6 show the median multiple regression analysis (MRA), that correlate the values of extractable metals to the soils components whom surfaces they are prevalently tied. Copper is positively correlated to organic matter, as well as zinc and lead, while nickel is positively correlated to clay. Results suggest limited contribution from antropogenic sources.

Table 3. Estimated coefficients, p-value and 95% confidence intervals associated with OM, CEC, clay, based on a median multiple regression model with lead as dependent variable.

```
-----------------------------------------------------------
    Ext lead |      Coef.    P>|t|     [95% Conf. Interval]
-------------+---------------------------------------------
          OM |   .7968579    0.000      .433379    1.160337
         CEC |   .1499713    0.039     .0077926      .29215
        clay |   -.088493    0.008     -.153732    -.023254
       _cons |   2.094193    0.122    -.5683919    4.756778
-----------------------------------------------------------
```

Table 4. Estimated coefficients, p-value and 95% confidence intervals associated with OM, CEC, clay, based on a median multiple regression model with zinc as dependent variable.

```
-----------------------------------------------------------
    Ext zinc |      Coef.    P>|t|     [95% Conf. Interval]
-------------+---------------------------------------------
          OM |   .2776534    0.139    -.0913143    .6466212
         CEC |    .023069    0.745    -.1174436    .1635816
        clay |   .0187691    0.577    -.0477409    .0852792
       _cons |   4.611644    0.002     1.796659    7.426629
-----------------------------------------------------------
```

Table 5. Estimated coefficients, p-value and 95% confidence intervals associated with OM, CEC, clay, based on a median multiple regression model with copper as dependent variable.

```
-----------------------------------------------------------
  Ext copper |      Coef.    P>|t|     [95% Conf. Interval]
-------------+---------------------------------------------
          OM |   1.056516    0.033     .0874005    2.025631
         CEC |   .1774433    0.356    -.2019851    .5568717
        clay |  -.1777954    0.046    -.3525184   -.0030723
       _cons |   6.928768    0.065    -.4495978    14.30713
-----------------------------------------------------------
```

Table 6. Estimated coefficients, p-value and 95% confidence intervals associated with OM, CEC, clay, based on a median multiple regression model with nickel as dependent variable.

```
-----------------------------------------------------------
  Ext nichel |      Coef.    P>|t|     [95% Conf. Interval]
-------------+---------------------------------------------
          OM |   -.034777    0.236    -.0927102    .0231563
         CEC |   .0124791    0.283    -.0104725    .0354308
        clay |   .0240262    0.000     .0131658    .0348866
       _cons |   .6170963    0.007     .1736331    1.060559
-----------------------------------------------------------
```

In order to value the results of the pollutants analysis, and the risk assessment, it is necessary to compare the data to reference guidelines. The parameters can be represented by the limits for soils, the official guidelines, the data of bibliography and the nature of soils. Another useful comparison is to the values of the soils in the blank areas. These kind of environmental studies on a large area can help to prevent risks, and have to include:

- a survey on toxic emissions by incinerators or industrial fumes, to identify which are the contaminants;
- setting up of guidelines through index pollutants and the identification of soil quality indicators;
- evaluation of critical loads of some contaminants related to Italian soils pedological characteristics.

Figure 4. Frequency distribution of Copper in the 100 soil samples

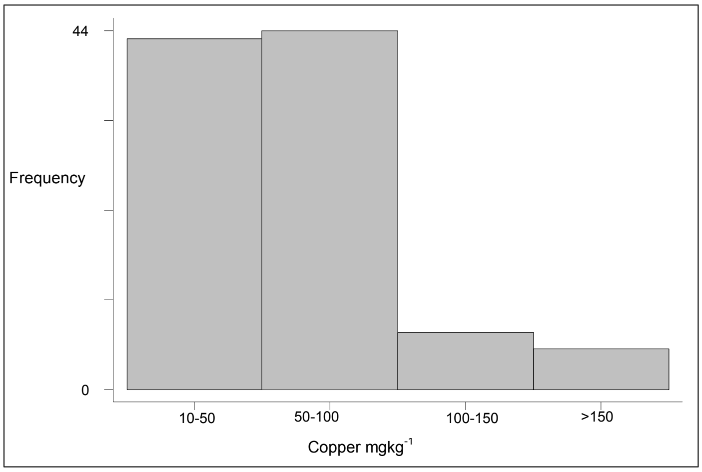
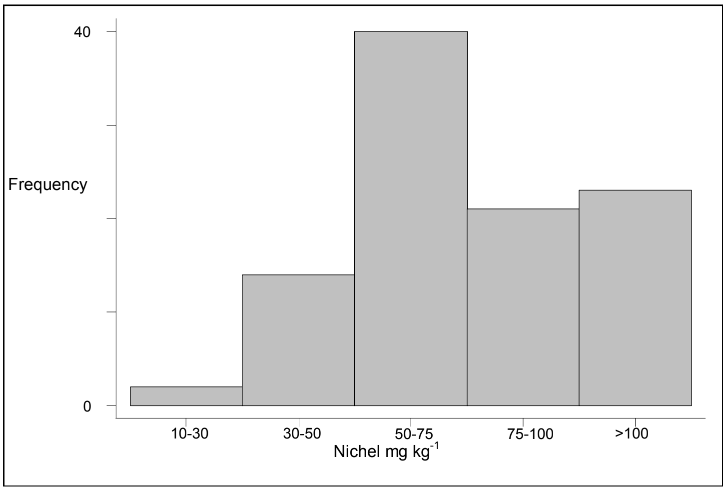


Figure 5. Frequency distribution of Nickel in the 100 soil samples



4. Epidemiological study

The epidemiological study was based on death certificates (1990-1999), hospital admission records (1996-2000), reproductive health outcomes (Certificate of Delivery Assistance 1996-1998; Birth Defects Register 1992-1999). A random sample survey to gather data on symptom reporting and risk perception was carried out concurrently by self-administered questionnaires.

All events (deaths, hospital admissions, reproductive outcomes) were geo-referenced to conduct spatial analyses of the whole area and of sub-areas defined by concentric crowns around the source. Statistical analyses to verify clustering pattern and trend in respect of the source were also performed

No significant differences emerged between the study area and the municipality of Pisa for diseases potentially associated with the environmental pollutants investigated. Only hospital admission records analysis highlighted an excess of leukaemia among women (N = 8, SMR = 262,7; CI 95%: 113,3 – 517,6).

Analysis by crowns showed an excess of mortality and morbidity for Chronic Obstructive Pulmonary Disease (COPD) in the most external crowns among men and significant excesses for non-Hodgkin’s lymphoma (2 deaths, 3 hospital admissions) concentrated in the most internal crowns.

Analysis of reproductive outcomes found some signs of excess in the district (infant death, congenital anomaly, sex ratio) to be evaluated together with an excess of hospital admissions for miscarriages and foetal problems. The random sample survey showed important results on symptoms reporting and risk perception.

Results suggest further deepening is needed in particular to enrich knowledge on individual exposure and possible confounders.

5. Conclusions

The three studies geo-referential, environmental, and epidemiological covered all the aspects requested by the local Authorities in order to take decisions on the future development of the area. The procedure can be applied to any similar environmental situation, and can be a powerful mean in making decisions about possible future industrial development of a territory.

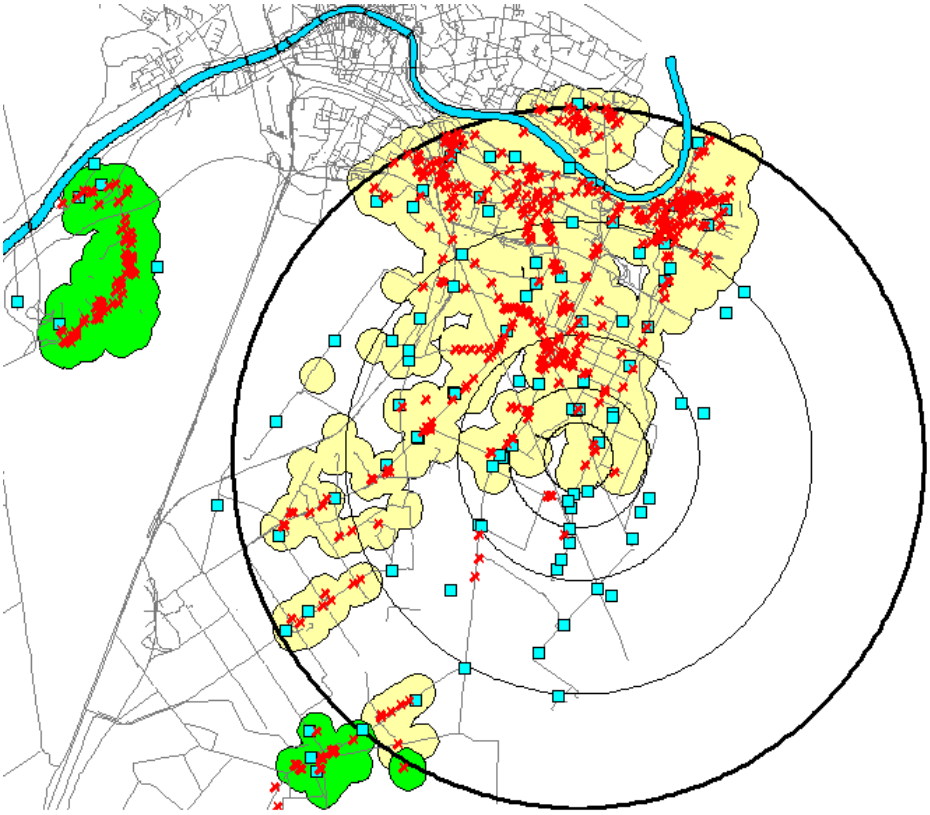


Figure 6: Spatial distributions comparison: people participating to epidemiological sample survey (red crosses) vs. soil samples (cyan dots)

IN - SITU REMEDIATION OF CONTAMINATED HARBOUR SEDIMENTS

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1 Introduction

Harbour sediments are often contaminated by a mixture of inorganic (e.g. heavy metals) and organic substances. These pollutants often cause ecological and toxicological problems in affected and surrounding areas. Considering the huge amount of dredged material, 40 Million cubic meters each year in Germany (not including large harbours like Hamburg), it is necessary to find an economic and feasible way for the minimisation of occurring problems. Despite several efforts to prevent sediments from disposals, pollutants cannot be avoided in basins. In situ techniques can be a feasible option for sediment remediation when dredging is not necessary for nautical or water management reasons, to reduce ecological risks at the harbour site, or to reduce the amount of dredged material, which has to be disposed off if dredging is necessary.

The aim of this work is to develop an in situ remediation technique for sub aquatic sediments, applying common soil remediation techniques. Aeration in combination with contribution of an oxidising agent will be employed to change anaerobic into aerobic sediment conditions to stimulate aerobic biological degradation of organic pollutants (biosparging) and to oxidise contaminants. Chemical and biological stabilisation of the sediments, reduction of pollution and prevention of pollutant mobilisation are the major issues considered. Therefore a pilot plant was installed.

The IR&D project is a co-operation between Forschungszentrum Karlsruhe (FZK) and BUTEC Umwelttechnik / C.A.U. Gesellschaft für Consulting und Analytik im Umweltbereich mbH, divided into a scientific (FZK) and a technical (BUTEC/CAU) part, which is funded by the German Federal Ministry of Education and Research (BMBF/Germany, project No 02WS0144/02WS0145).

2 Pilot plant and background features

The installation of a pilot plant was started in July 2002 at the upper Frankfurt/Main harbour and is still under construction. The plant was set up in order to get long-term information about the feasibility of in situ treatment for contaminated anaerobic sediments by continuous ventilation with air and injection of hydrogen peroxide as an oxidising agent as well as for the combination of both features. Therefore a broad analytical effort was made to illustrate the physical and chemical properties of the harbour sediment before treatment and to evaluate the success of the applied technique afterwards. Installation was based on former air sparging projects by BUTEC and developed due to experiences made in pre-tests and during the first working periods. Most of the installed equipment will still be improved step by step in the next months, till the installation is completed in February/March 2003.

2.1 *Installation status and sampling*

A mobile swimming working platform was set up and fixed at a defined position in the harbour basin limiting the demonstration area with 8 x 12 meters, as shown in Figure 1a. From this platform all sediment and interstitial water samples were taken and all technical equipment was installed, respectively and is going to be installed from there.

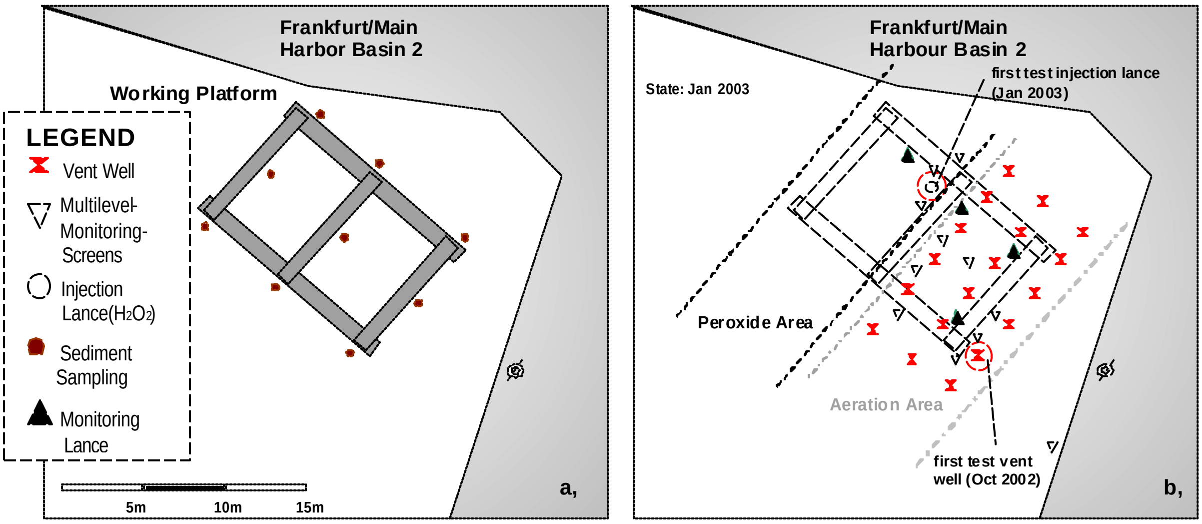


Figure 1: Frankfurt/Main harbour basin with a, working platform and b, established remediation areas

The pilot plant consists of two major parts. The first and nearly finished part, called *Aeration Area*, shown in Figure 1b, creates a consistent ventilation field comparable to air sparing projects for soil remediation. This part of the plant works partly since November 2002 with 5 (of 18 in total planed) ventilation wells, made of HDPE filter material. The ventilation wells, see double-triangles Figure 1b, are going to be fully installed till the end of January 2003 and have a size of 20 cm length x 27 mm inner radius. Air is pumped into each well through a HDPE tube with a flow of 10 L per hour. A bubble breakthrough can be observed at the water surface at a flow rate above 10 - 15 L per hour. The influence of each well can only be estimated till now and is approximately 1.5 - 5 meters from the well in all directions. Therefore the wells were installed in a distance of 2.5 meters to guarantee overlapping. The second part of the test area will be used for peroxide treatment (= *Peroxide Area*). Peroxide will be injected into the sediment only by hydrostatic pressure with lances similar to the monitoring lances, shown in Figure 2. The injection lances will have an inner radius of 27 mm and screened parts of 10 cm. First tests for the peroxide treatment will be done in January 2003 and the start of the test period is planed for February.
Sediment samples, see dots in Figure 1a, were taken from nine different spots and up to four depths per spot. The samples were taken with a steel core-sampler, 2 m length and 8 cm radius, collecting undisturbed sediment cores up to 1.6 m length. Samples were taken for laboratory analysis and batch tests. Finally a three-dimensional contamination profile could be found for various organic substances and heavy metals. Sediment sampling was done before the installation of vent wells and monitoring screens and will be done again at half time of the remediation and after finishing treatment. Interstitial water is taken in various depths in the whole monitoring area from 10 different monitoring points, see white triangles in Figure 1b. Two, respectively three monitoring screens (HDPE) are installed at each monitoring point in two respectively, three depths. Altogether there are twenty-three monitoring levels in the test area and another three levels in a distance of 10 meters from the test area as background levels. The screens have a size of 30 cm length x 32 mm inner radius and deliver approximately 250 mL sample volume each. The infiltration rate is approximately 15 mL per hour. Four monitoring lances (black triangles) are installed with 0.5 m screens to deliver up to 5 L interstitial water for the determination of hydrocarbons and other organic substances.

Monitoring lances and screens are shown in Figure 2 Interstitial water sampling was done several times before the start and in intervals of two weeks after starting the aeration for a broad analytical spectrum. Sampling will be done every three weeks in the future for the whole spectrum. Special samples will be taken after the peroxide treatment is started to get more detailed information of the influence of hydrogen peroxide on interstitial water values. Dissolved oxygen in the interstitial water was measured approximately every day after the start of the ventilation and is now measured twice a week in all screens. After starting the peroxide treatment all intervals will be shortened again to ensure a complete observation of all variables.

2.2 Background

After a number of sediments were analysed to find a harbour site, which was suitable for the application of a remediation technique and Frankfurt harbour was chosen, a broad analytical spectrum was measured to get information about the contamination status as close as possible. The sediment was analysed for organic contaminants and for heavy metals. The interstitial water was also analysed for heavy metals and further for all electrolytes and some sum parameters.

Table 1 a : Background values for Frankfurt harbour sediment compared with “Dutch List” [9]

Compounds	Range	Average amount	N.L. *
Organic	*(mg /kg dry matter)*		
AOX	170 – 550	273	-
BTX	-	< 0.01	25
Mineral Oil (TPH)	1440 – 19970	3900	5000
PAH**	12 – 50	16	40
PCB	0.03 – 0.18	0.09	1
Volatile HC	-	< 0.01	-
Inorganic	*(mg /kg dry matter)*		
Cr	50 – 100	72	380
Co	11 – 16	12	240
Ni	42 – 72	57	210
Cu	128 – 292	173	190
Zn	950 – 1330	1190	720
As	8 – 15	12	55
Cd	2 – 6	4	12
Sn	6 – 24	12	-
Pb	90 - 360	170	530

* Dutch List [9], limit values for remediation
** 8 out of 10 PAH mentioned in the N.L. were determined

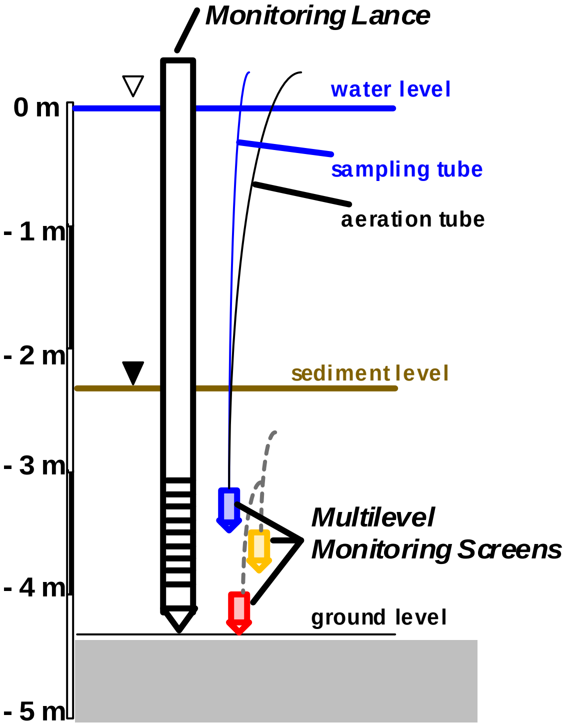


Figure 2 : Monitoring equipment

Table 1a, b show the average results and the range of values obtained from the analysis made before any treatment was started. Grain size distribution analysis determined that in average 46.5 % of the sediment belongs to the fraction below 20 µm (clay and fine silt), 40.2 % is silt (20 - 63 µm) and the residual is part of sand fraction below 1 mm particle size. The samples were analysed unfractionated to stay as close as possible to the real situation. The content of dry matter of all taken samples was in a range between 28 - 54 % and in average 42 %. Total organic carbon was between 3.1 to 8.4 %, 3.9 % in average. It was found that especially the mineral oil content (TPH) was very high. This was expected for TPH, because there was a former oil terminal at the site, which is now closed. Also PAH, Zn and Cu concentrations were above or close to the limits given by the “Dutch List” for soil and groundwater. But regarding this guideline only one organic parameter would show the necessity of remediation and PAH would be at the border for some single samples.

Other guidelines [1,6], especially for sediments, have different criteria. Considering LAGA [1], the found values of PAH and Zn are rated high and close to the values where the dredged material cannot be used anymore and has to be disposed off. According to Neumann-Hensel [6] sediments with concentrations > 10 for PAH and > 1000 mg/kg dry mass for Zn rated as high-contaminated sediments. Additionally the AOX contamination places in the class of high up to the class of extremely high-contaminated sediments. Considering these three guidelines it was chosen to investigate three compound groups, AOX, Mineral Oil and PAH closer in laboratory experiments and in the pilot plant monitoring. All other values were too low to draw sufficient conclusions concerning remediation efforts. Furthermore two samples were examined for TBT (Tribuyltin). Values from 50 – 70 µg/kg dry mass were found. The limit for TBT is between 20 - 600 µg/kg according to BLABAK [2]. Experiments shall prove if TBT would be another interesting compound, using the so far highest contaminated samples by adding hydrogen peroxide. The interstitial water samples have partly an intensive odor of ammonia and hydrogen sulfide. The values obtained in measurements on site and in the laboratory are compared in Table 1 b with the values of harbour water and with the remediation limits by "Dutch List" for some chosen compounds.

Table 1b: Measured values for interstitial and harbour water compared with "Dutch List"

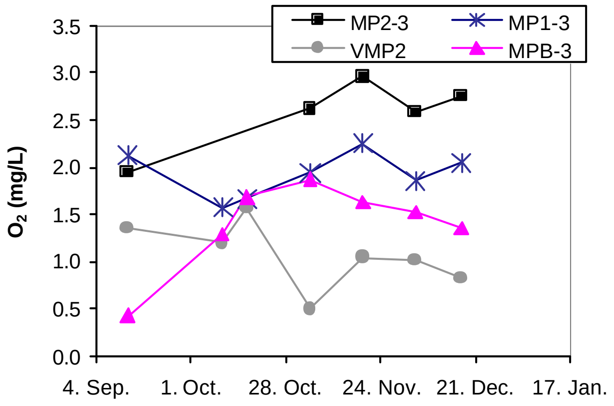
	Interstitial water		**Harbour water**	**N.L.**
	Range	**Average amount**	**Average amount**	**Limit***
pH	6.9 – 7.2	7.0	7,7	-
Conductivity (µS/cm)	1500 – 2900	2290	722	-
O_2 (mg/L)	0.4 – 3.7	1.4	8,2	-
Metals		*(mg/L)*		
Cr	-	n.d.**	n.d.	0.03
Co	-	0.01	n.d.	0.1
Ni	-	n.d.	n.d.	0.075
Cu	-	n.d.	n.d.	0.075
Zn	-	0.01	0.01	0.8
As	-	n.d.	n.d.	0.06
Cd	-	n.d.	n.d.	0.006
Sn	-	n.d.	n.d.	-
Pb	-	n.d.	0.01	0.075
Electrolytes / Nutrients		*(mg/L)*		
P	0.1 – 1.3	0.8	0.3	-
S (Sulfide)	0.2 – 3.0	1.8	n.d.	-
Ammonia as N	21 – 80	54.2	0.25	-
Nitrate	0.3 – 12.7	5.6	20.8	-
Nitrite	0.05 – 0.45	0.3	n.d.	-
Hydrogen carbonate	850 – 1770	1310	262	-
Organics				
AOX (µg/L)	110 – 340	250	39.9	-
DOC (mg/L)	9 – 69***	36.2	6,2	-
TPH (mg/L)	0.17 – 0.62	0.36	n.d.	0.6
PAH (µg/L)	-	n.d.	n.d.	0.08

* Limitation for groundwater remediation
** not detectable
*** two levels close to the surface exceed 100 mg/L, not included in the calculations

Heavy metals were not found in the harbour and interstitial water. Therefore the task for the remediation technique is to avoid any mobilisation. Data observed after the start of the aeration shows that there is no mobilisation caused by the application of oxygen only. This question will become more important when the peroxide treatment is started, as laboratory results have shown. In opposite the examined nutrients were in average over the shown limits and in case of ammonia exceeded the limit up to 25-fold. The values of the organic compounds are very interesting in case of mineral oil (TPH), which is close to the limit and DOC, which can give an idea about the total organic compounds mobilised. It will be interesting to see if there is any influence of oxygen or/and hydrogen peroxide. After two months there is insufficient data to draw any conclusions especially for the organic compounds, but some first trends can be shown in the next chapter.

2.3 Monitoring Results

Results collected by measuring oxygen at the harbour directly after samples were taken show a first tendency. In Figure 3 four monitoring levels from different monitoring points (MP) in various distances from the first installed ventilation well are compared. The deepest levels (1.10 – 1.40 m under sediment level) are shown at each MP. It illustrates that the highest oxygen values are observed in the levels closest to the vent well, MP1 and 2. The values increase after the ventilation was started at the 1. November, until a breakdown of the ventilation caused by frozen connection tubes at temperatures below minus 5 degrees Celsius. Increasing values are expected again for these MP after the restart of the ventilation and slightly monitored in the first measurements after the restart.



Monitoring points	**Distance (m) from vent well**	**Direction from vent well**
MP2-3	1,2	NE
MP1-3	2,5	NE
VMP2	6,7	NE
MPB-3	9,2	SE

Figure 3: Oxygen concentrations at monitoring points MP1, 2, B and VMP after the first vent well was started

The monitoring point in the background MPB seemed to be influenced by the ventilation as well, as the curve showed a similar shape to the other curves in the first instance and a bubble breakthrough was observed during tests at the background MP.

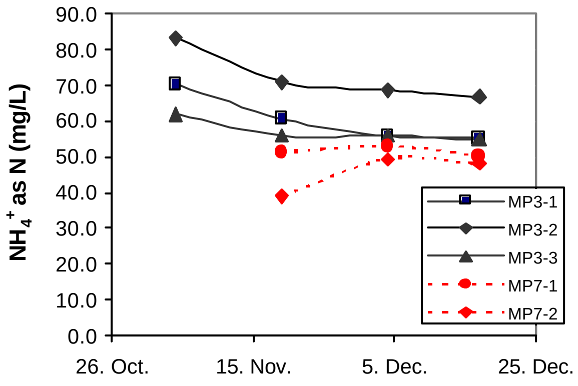


Figure 4: Ammonia in interstitial water plotted against the distance from the vent well

In opposite the monitoring lance VMP, which is in a closer distance but another direction to the ventilation well than the background MP seems not to be influenced by the ventilation. The first conclusion must be that the permeability in the sediment is inhomogeneous, because the influence radius of the oxygen is different in two different directions. Additionally the amount of oxygen decreases with distance from the ventilation well. It drops more than 0.5 mg/L in a distance of 1.3 m from MP2 to MP1. Considering the results and with the aim to provide a sufficient coverage with oxygen the distance for the ventilation wells was chosen with 2.5 m, covering an area of approximately 150 m² with18 wells.

The second trend can be demonstrated comparing the amounts of ammonia for two monitoring points. MP3 is in the same distance as MP2, but in the opposite direction, SW, and MP7 is in a distance of 12.5 meters and in NW direction. The values of ammonia in all depths of both monitoring points are shown in Figure 4. It is obvious that ammonia decreases in all levels of MP3 and is more or less constant in MP7. MP3 had an average amount of oxygen of 2.3 mg/L in all three levels after the ventilation was started and MP7 an amount of 1.5 mg/L. This difference is responsible for the decrease of ammonia. Ammonia is oxidised to nitrogen by nitrifying bacteria or the oxygen itself. According to this, a decrease in the amount of nitrite could be observed in the monitoring levels influenced by the oxygen, but not an increase of nitrate. Other compounds do not show this clear tendency till now, but further results are expected at least after the start of the peroxide treatment and the complete aeration.

3 Laboratory approaches

In the laboratory experiments work concentrates on the effects of hydrogen peroxide as an oxidising agent on degradation and mobilisation of organic and inorganic compounds as well as on biodegradation after the peroxide treatment.

3.1 Inorganic

Mobilisation of toxic amounts of heavy metals is, besides the removal of ecological dangerous organic substances, a major question if remediation is applied using oxidising agents. The mobilisation of heavy metals and other cations was studied in batch experiments depended on hydrogen peroxide addition. The used high peroxide concentrations were chosen to simulate a worst-case situation, but also a similar amount of peroxide was necessary to reduce contaminant concentrations in the sediment in the experiments described later. This fact can influence the economy of the remediation technique and has to be studied closely in the field experiment. Shown in Figure 5, the amount of released cations increases with increasing peroxide consumption. Here, the four metals are shown with the highest mobilisation rate of all investigated metals. All other metals like Cd, Pb or As showed not any noticeable mobilisation. Zn is toxic for fish. It has to be monitored closely. The high mobilisation of Zn also depends on the high background of Zn in the Frankfurt harbour sediment (Table 1a). Experiments with other sediments confirmed that Zn, Mn, Cu and Ni are the main elements mobilised. Problems may occur in the zone just above the sediments surface, therefore the metal concentrations in the harbour water will be monitored 5 cm above the sediment surface during the remediation period.

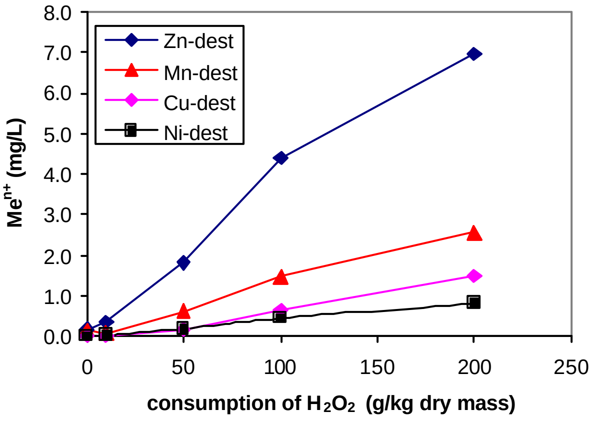


Figure 5: Mobilisation of heavy metals vs. peroxide consumption in Frankfurt harbour sediment after treatment in suspensions

Overall it can be expected that toxic effects in the surface water will not occur, because small amounts of higher concentrated interstitial water will be blended with huge amounts of harbour water.

3.2 Organics

The reaction of hydrogen peroxide as an oxidising agent for organic substances e.g. hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAH) and adsorbed organically bound halogens (AOX) is examined in laboratory studies. Hydrogen peroxide is expected to react in a Fenton like reaction with the sediment and especially with the organic compounds. In presence of ferrous salts hydrogen peroxide forms free radicals ($OH^{\bullet}$), these radicals are intermediates and non-selective oxidants for organic compounds [8]. Ferrous salts were present in the sediment and no further salt was added. Especially Watts et al. studied the efficiency of the hydrogen peroxide reaction in soil without adding additional iron salts [5, 10]. The aim is to find an economic way of adding hydrogen peroxide where the formed radicals react most effective to eliminate as much pollutants as possible. The biggest problem for an economic remediation is the total organic matter, because all organic compounds compete with the organic pollutants. With higher amount of organic matter hydrogen peroxide is decomposed faster [7]. Concentrated peroxide solution (30%) was added to the suspensions stepwise in the experiments so far. After elimination of peroxide the next dose hydrogen peroxide was added. It was found that the most promising way for an economic operation of the pilot plant is the stepwise addition of a low concentrated peroxide solution (1%).

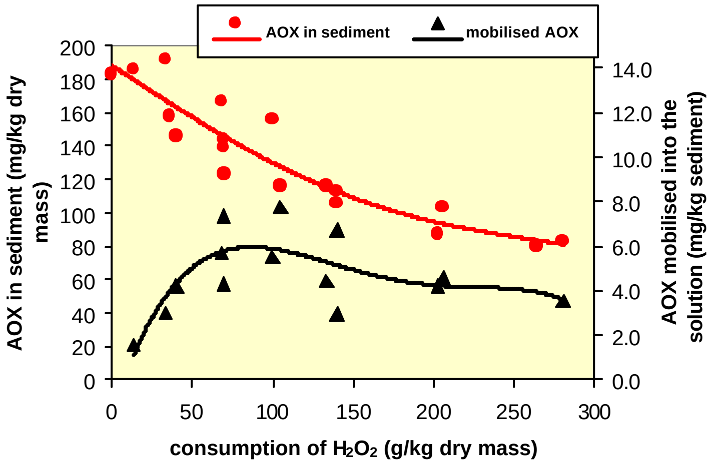


Figure 6: Elimination and mobilisation of AOX in suspensions vs. peroxide consumption

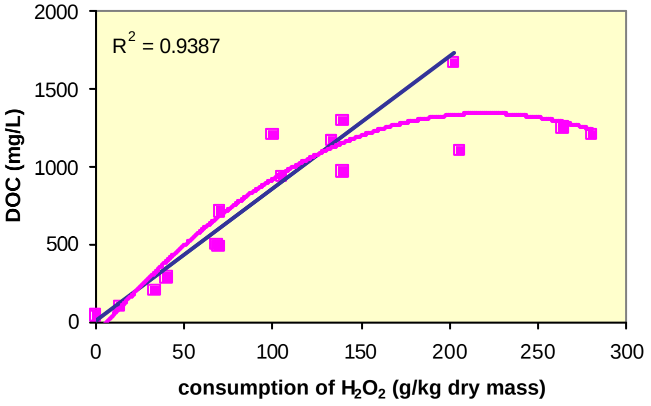


Figure 7: Release of dissolved organic carbon in sediment suspensions vs. peroxide consumption

Hydrogen peroxide decomposition leads to the in situ formation of oxygen and water as non-toxic end products. Furthermore the oxygen can support aerobic biodegradation. The curves in Figure 6 show the degradation of AOX in complex natural sediment and the simultaneous mobilisation into liquid phase by peroxide addition to a suspension of wet sediment (approx. 47 % dry mass) and Milli Q water (1:2). In this experiment AOX concentrations in the sediment decreases with increasing consumption of peroxide. The concentration of mobilised AOX in solution increases at the beginning, reaching a maximum in the course of the oxidation reaction and then decreases. AOX could be removed from the sediment of a initial concentration of about 180 mg/kg to approximately 80 mg/kg. This translates to more than 55 % removal in a sediment with a relatively high amount on total organic carbon. Despite 100 mg/kg reduction of AOX in the sediment not more than 8 mg/kg were released into the solution. This indicates that more than 90% of the eliminated AOX must be oxidized by the peroxide reaction. But the reduction required more than 250 g/kg dry mass of hydrogen peroxide. Such high needs would lead to a very inefficient treatment. The sediment contained 3,6 % of total organic carbon. The amount of organic carbon could be reduced about 42 % to 2.1 % total organic carbon. Besides the AOX compounds, the release of dissolved organic carbon

(DOC) from the sediment is approximately linear from 0 to 200 g/kg addition of peroxide (Figure 7). With higher peroxide doses a maximum is reached and then decreases again. This is similar to the curve measured for dissolved AOX. The range of the linearity depends on the total amount of organic carbon. More initial organic carbon in the sediment leads to a higher release and a wider range in linearity. Following sufficient peroxide addition, there is no further mobilisation of AOX and DOC, after 75, respectively 200 g H_2O_2 / kg, instead degradation occurs in the solution. Approximately 60 % of the released DOC is biodegradable within 30 days independent from the added amount of peroxide. Biodegradation of AOX compounds depends of the added peroxide dosage. Without adding peroxide to the suspension 60% of the released substances are eliminated after four weeks and no further degradation occurs. In the range of the increasing AOX values in the solution biodegradation decreases to approximately 45 % and takes up to 20 weeks to reach this state of decay. Furthermore the samples with more peroxide added show a better biodegradation up to 80 % in 20 weeks. This indicates that after the release maximum is reached and degradation of substances by peroxide occurs in the solution, non-biodegradable substances must be transformed into biodegradable substances.

Sediment respiration was measured for several samples taken from Frankfurt harbour regarding peroxide consumption over short and long periods. No correlation was found between the application of hydrogen peroxide and the respiration. The sediment showed approximately the same respiration before and after the peroxide treatment. An oxygen demand between 80 and 120 mg O_2 per kg dry mass was found, in average 98 mg O_2/kg dry mass. The oxygen demand of the sediment could not be reduced, but also the treatment with peroxide has no negative influence on the existing microorganisms in the sediment. The microorganisms survive the treatment and are still able to degrade pollutants in the sediment. The next step was the investigation of biodegradation of pollutants after the peroxide treatment. Hydrogen peroxide was added in portions of 10, 50, 100, 200 and 300 g/kg dry mass (samples *plus10*, etc.). AOX and PAH were measured in a fraction of the batch experiment after adding various amounts of hydrogen peroxide. After oxidation the sediment was hold in 1 L beakers under constant conditions, providing sufficient air for aerobic biodegradation. The measurement was repeated in intervals of one week in the first month and afterwards in intervals of four weeks. The sum of PAH of the three compounds chrysene, fluoranthene and pyrene was investigated which corresponds to more than 60 % of all PAH's found in the Frankfurt harbour sediments. PAH was measured in the solutions as well but could not be detected. Therefore a release of PAH caused by peroxide treatment can be excluded.

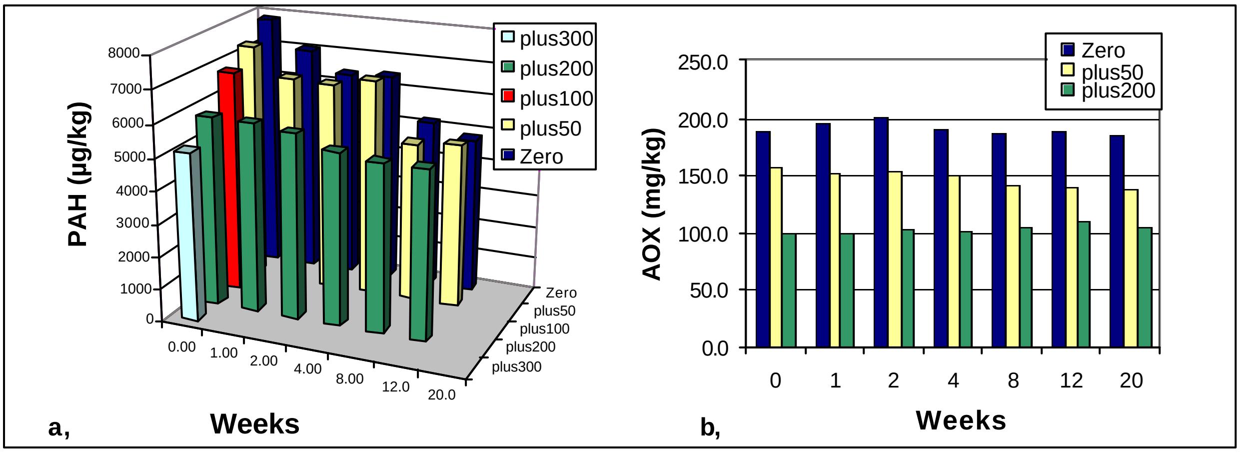


Figure 8: Elimination of a, PAH and b, AOX in sediments in dependence on peroxide dosage (e.g. *plus100* = 100 g H_2O_2 / kg dry mass) and biodegradation in untreated and treated sediments

The results in Figure 8a show that the PAH content was reduced by peroxide from 7800 µg/kg dry mass (sample *Zero*) to only 5150 µg/kg in sample *plus300* by a peroxide consumption of 300 g/kg dry mass. This translates to a reduction of approximately 35 % of the initial concentration of the three PAH's. The values show that biodegradation occurs in all samples till the end of the test period. However, comparing the results of biodegradation it could be shown that biodegradation alone leads to even better results than biodegradation after oxidation by peroxide. After 12 weeks 39 % of the three PAH's are degraded only by biological processes in sample *Zero*. In samples *plus50* and *plus200* the biological degradation was less and in total treatment lead to 37 %, respectively 35 % degradation in these samples. In opposite AOX compounds are not biodegradable in the sediments. But the elimination of AOX (in mg/kg !) by peroxide treatment is much higher compared to PAH elimination (in µg/kg). After oxidation the residual AOX do not show any biodegradation (Figure 8b).

4 Conclusion and Forecast

The first technical implementations found an easy and cheap way for the ventilation of an anaerobic sediment and in the same way sampling of enough volume for analysing interstitial water was realised. Common HDPE filter material was applied and modified to create sampling screens for interstitial water and to build the ventilation wells. The material is inert, cheap and easy to handle, so that an inexpensive installation was realised. The aeration part of pilot plant is going to be fully installed till the end of January 2003 and the peroxide treatment area will be finished soon afterwards. Therefore lances made from the same material and pumps are a promising attempt using only hydrostatic pressure to inject the peroxide solution into the sediment.

Increase of oxygen could be detected in the interstitial water close to the ventilation well. After the plant is set fully up it should be possible to turn the anaerobic into aerobic conditions for the whole remediation area and to support aerobic biodegradation. Two weeks after the start of the ventilation a decrease of ammonia concentration could be observed. Ammonia was oxidised to nitrogen. Reducing the toxic potential of ammonia could be one of the first outcomes of the project. Heavy metals were not mobilised so far, but this issue will become more important when the peroxide treatment is started, as laboratory experiments showed.

PAH's showed the ability of chemical oxidation and biodegradation, but biodegradation turned out to be more efficient than a combined treatment with peroxide plus the following biological processes. On the contrary AOX showed no biodegradation but good properties for chemical oxidation. The results demonstrate that the behaviour of pollutants to chemical and biological oxidation could be very different, also depending on the matrix of the treated sediments, especially on the amount of total organic carbon.

These preliminary results also show that the way of treatment is dependent on the specific properties of each sediment and the spectrum of pollutants. Therefore conclusions can only be drawn for the used sediment and have to be reconsidered in each other case. Here, the contribution of air to stimulate aerobic biodegradation seems feasible for the elimination of PAH's in contaminated sediments, while addition of hydrogen peroxide has benefits for AOX elimination. Economic aspects have to be considered if peroxide treatment is applied. Peroxide use can be an option for the treatment, because micro biological activity is not negatively affected.

Based on these results a final conclusions can not be drawn until now concerning the efficiency of the applied technology. In the future more parameters, like TBT and the important group of total petroleum hydrocarbons (TPH) will be measured to get a more complex view of the impact of hydrogen peroxide and the contribution of air on this sediment.

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SLUDGE TREATMENT CENTRE 'FASIVER'
SANITATION AND REDESIGN OF THE SITE 'EILANDJE' AT ZWIJNAARDE (GHENT)

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1. Introduction

In general, there's a lack of disposal sites and/or alternative treatment techniques for beneficial reuse of contaminated dredged material in the Flemish region of Belgium. On the other hand there are several sites in this region that, due to former industrial activities, are contaminated and have no longer a commercial or industrial use or even have a negative value due to the present contamination and the needed sanitation before any further use. On top of this there's an urgent shortage of industrial area in the Ghent region for the expansion of high technology oriented businesses and small to medium organizations.

In the late nineties governmental organizations in the Ghent region were urgently seeking economical solutions for the disposal of contaminated dredged material. Several maintenance dredging operations were postponed due to a lack of disposal possibilities.

Eventually several governmental organizations, including the Province of East-Flanders and the City of Ghent, and private partners, including Domo Service Gent NV and DEC NV, combined their expertise and developed the 'Fasiver-project' which includes the sanitation of a black-point (surface of about 7 ha) and the redesign of a 42 ha large site by means of a sludge treatment centre (dewatering lagoons) and a confined disposal facility for contaminated dredged material. The net capacity for dewatered dredged material of the confined disposal facility is estimated to 1.3 million cubic metres.

The final destination of the site is industrial area (approx. 30 ha) and a greenbelt (approx. 10 ha) on top of the sanitised black-point and around the industrial area. The profits that will be made by the selling of the grounds in the industrial area shall cover the costs for the sanitation of the black-point.

2. Situation

The site in question is located in the Ghent region, on the crossing of highways E17 – E40 and the waterways Upper-Scheldt and the ring canal around Ghent.

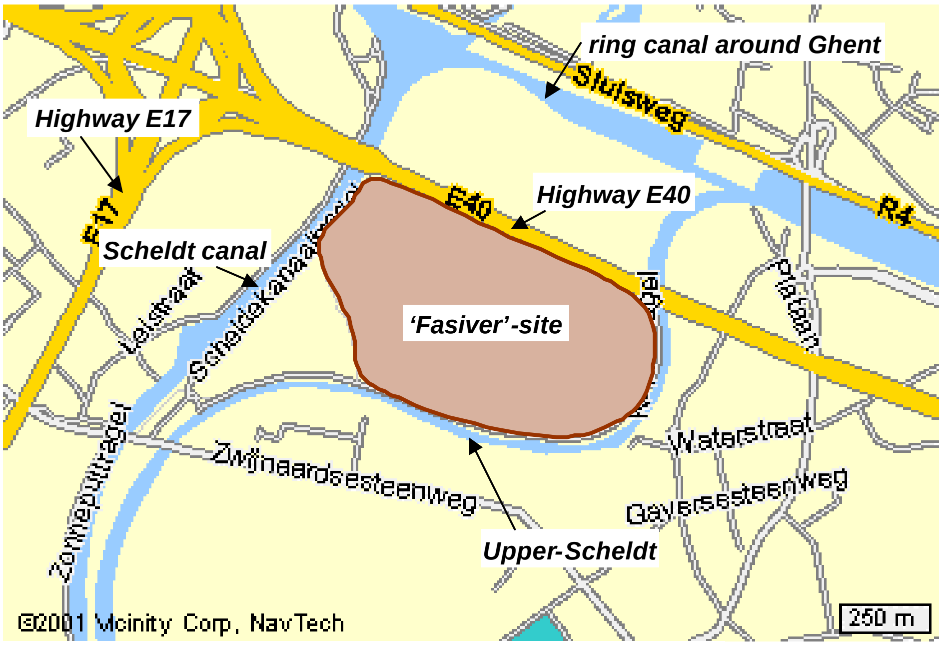

Figure 1: detailed location of 'Fasiver'-site

Figure 2: Air view of 'Fasiver'-site

3. Public Private Partnership

At first sight, public and private partners have contradictory interests. The private partner wants to reduce risks (insecurity of public policy and changing regulations) and increase financial return related to the investment, whereas the public partner wants to diminish financial risks and the financing volume and increase efficiency in execution. Through a public private partnership these opposing interests can be shared in common cooperation.

This common cooperation can be illustrated taking the redevelopment of a Brownfield site as an example.

1. Know-how
   The private partner has to take the technical risks (e.g. using new techniques, applying existing methodologies on a larger scale or under different conditions). The public partner is responsible for the planning and permit risks (e.g. delays in planning procedure, negative environmental impact assessment, failure to obtain construction permits).

2. Efficiency
   While the private partner takes responsibility for the schedule risks (delays in execution, flexibility), the public partner is responsible for the regulatory risks (changing rules, political risks, expropriation).

3. Finance
   Here, the private partner takes care of the commercial risks (cost calculation, budget control) and can pre-finance the project. The public partner has to take the final budget risk based on revenues from the Brownfield site: the contamination cost has to be lower than the revenues.

During the study period of the ‘Fasiver’-project the following public and private partners combined their interests:

1. Domo Service Gent as main owner of the site, including the black point;
2. DEC as environmental contractor for the sanitation of the black point and the exploitation of a sludge treatment centre and disposal facility;
3. Vlaamse Milieuholding (VMH) as initiator of the project, in execution of the Flemish Government policy to prevent and recycle waste;
4. The city of Ghent and the province of East Flanders as partners interested in the potential value of the site.

Through the use of a pull-out option, the public partners (VMH, city of Ghent and province of East Flanders) left the public private partnership after the study period, so that the private partners (owner and contractor) have to take the exploitation risks on their own. By giving a pre-purchase option (to the city of Ghent and the province of East Flanders) the public partners nevertheless remain involved with the project.

4. Principle of sanitation

4.1. Formulation of the problem

A part of the site in question was formerly used as a disposal site for waste products coming from the production of viscose fibres on the other side of the Scheldt canal. In that time there was practically no legislation, knowledge or concern about the environmental impact of such activities. This way about 175,000 m³ of organic viscose sludge was dumped in five basins without any lining or control measures.

For over 50 years no measures were taken to minimise the thread to the environment of the present sludge basins. Due to the lixiviation of heavy metals and other contaminants present in the sludge the groundwater in the surrounding area is contaminated and forms a possible risk to the adjacent residential area on the southeast of the site.

Because of the historical character of the problem the present owner of the site is a so-called 'innocent owner' and has no obligation what so ever in order to sanitise this black-point. On the other hand due to the presence of the black-point the site has a negative value and cannot be sold or used. Only a global project – a so-called Brownfield development – including a risk-based sanitation of the black-point and an economical revalorisation of the site, can supply a solution.

The following picture shows an overview of the black-point.

Figure 3: Overview of the black-point

4.2. Proposed solution

Because of the large volume of contaminated viscose sludge, excavation and ex-situ treatment and disposal of the treated sludge was no economically valuable solution. Therefore was chosen for an in-situ stabilisation and isolation of the sludge basins, combined with an in-situ groundwater remediation of the contaminated hot spots around the sludge basins.

For the stabilisation and immobilisation of the contaminated viscose sludge a series of laboratory tests was undertaken in order to define the best-suited recipe. Several binding agents and granulated materials were tested.

As the viscose sludge is a fluid like, fibrous, organic material with practical no mechanical structure, a granulated additive is necessary in order to improve the structure and the ground mechanical characteristics of this material. Based on the laboratory tests the use of steel slag as granulated material showed the best results. As the steel slag is a secondary by-product it is also an economically and environmentally good alternative for the use of raw materials instead. A second advantage of the use of steel slag is the presence of approximately 10% lime in this material, which ameliorates the immobilisation of the contaminants present in the viscose sludge.

As binding agent a purpose made additive mainly consisting of cement showed the best results, economically and mechanically.
The final tests showed that with our recipe a shear strength of 10 kPa was easily attainable, already after seven days. Control measurements on site affirm these results.

The following picture shows an overview of the stabilisation of the different basins on site.

Figure 4: Overview of the stabilisation of the different basins

On site the different additives (steel slag and binding agents) are first mixed in predefined quantities in a semi-mobile mixing plant. Then this mixture is transported to the different sludge basins where a long reach excavator equipped with a specially designed mixing bucket spreads and mixes the additives and the viscose sludge.
Because of the presence of large parts of wood, bricks, concrete, steel, etc. in the sludge basins there was deliberately chosen for a mixing technique without any rotating parts.

The actual isolation of the contaminated sludge volume will be performed by means of an impermeable cement-bentonite wall around the different basins. This cement-bentonite wall will be 30 metres deep below ground level and will reach a natural underlying impermeable clay layer. On top of the stabilised viscose sludge comes first a gas-drainage and second an impermeable HDPE-liner of 2.5 mm thick.

Finally the isolated area will be covered with over 2 metres of mould and arranged as a green area as buffer near the industrial zone.

5. Health and Safety

Because of the organic character of the viscose sludge and the presence and continuous production of H_2S-gas in the sludge a lot of problems were expected during the handling of this type of sludge. An extensive safety plan was made, including personal H_2S-gas detectors for all personnel working near the sludge basins. All the material that was used in the stabilisation operations was equipped with positive pressure cabins. An emergency plan was set up in order to evacuate the site in case of calamities.

During the laboratory tests – for the determination of the right recipe for stabilisation – also the H_2S-gas concentration above the sludge surface was measured. There was even a pilot study on site where the H_2S-gas concentration and odour production was measured during a simulation of the proposed stabilisation technique.
During these tests we measured in a few cases near the sludge surface (within a few centimetres) concentrations of up to 500 ppm. The MAC-value for H_2S-gas is 10 ppm. Nevertheless because of the distribution in open air and the chemical reaction in the sludge (increase of pH) due to the addition of cement it seemed that concentrations within a few metres of the surface were limited below 10 ppm. Continuous measuring on site during the stabilisation operations confirms these results.

Also the odour production because of the stabilisation operations stayed within the 'normal' concentrations observed before the beginning of the project. Depending on the weather conditions the typical odour of the viscose sludge could be observed in a perimeter of about 500 metres around the basins. During the stabilisation operations this perimeter isn't significantly wider. A specialised panel of 'noses' (a research group of the University of Ghent) is responsible for the follow up of the odour concentration around the sludge basins.

Once the viscose sludge is stabilised – and thus the pH increased – the H_2S-gas in the sludge is actually immobilised and all the risks or inconveniences that go with the presence of H_2S-gas disappear.

6. Sludge Treatment Centre

Next to the sanitation of the black-point a large treatment centre for contaminated dredged material is installed on the site. About ten hectares of dewatering fields are installed around and up the sanitised black-point.

Figure 5: Sludge Treatment Centre 'Fasiver'

Finally the whole area will be arranged as a disposal site for contaminated dredged material and this way the level of the area is brought from between +6 and +8 m TAW to a level of +13 m TAW, which is the level of the highway E40 along the site.

6.1. Quay wall

Figure 6: Quay wall at 'Fasiver'-site

In order to maximise the supply by water we first installed a quay wall along the Scheldt canal. The installed quay wall is 120 m long and consists of sheet piles and anchors.

All the drainage sand, gravel and about half of the construction sand needed for the installation of the dewatering fields and disposal site is brought over water.

Naturally all the contaminated dredged material that will be treated on site is also brought over water.

6.2. Installation of dewatering fields and disposal site

The following figure shows the structure of the dewatering fields and disposal site.

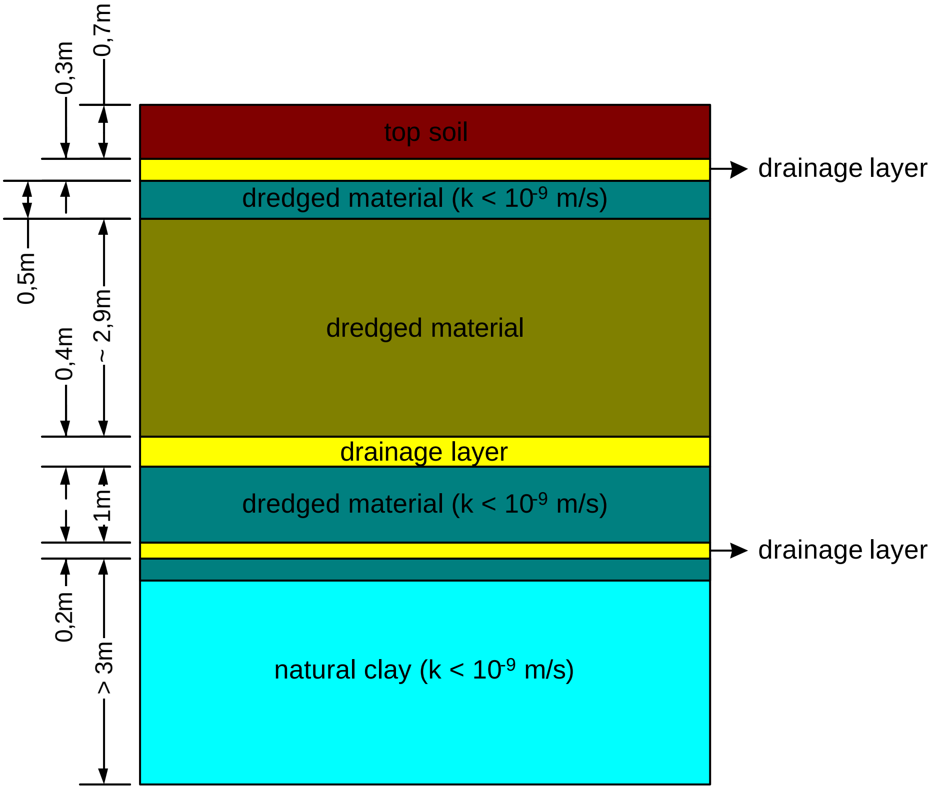

Figure 7: Structure of the dewatering fields and disposal site

The natural top layer at the site is a clay layer of about 3 metres thick. The presence of this layer and the permeability are examined in detail before the installation of the dewatering fields or disposal site is started. On these locations where the permeability is greater than 10^{-9} m/s or the natural clay layer is less than 3 metres thick an additional mineral liner is added. This additional mineral liner consists of a layer of non-contaminated dredged material of about 30 cm thick and a permeability of maximum 10^{-10} m/s or a 'sand-bentonite-polymer liner' (Trisoplast®) of 7 cm thick with a permeability of maximum 10^{-11} m/s.

On top of the mineral liner comes a drainage layer of about 20 cm thick. This drainage layer will function as a control drainage layer in order to evaluate the isolating capacities of the upper impermeable liner.

The impermeable liner on top of the control drainage is a layer of compacted, dewatered, non-contaminated dredged material with a permeability of maximum 10^{-9} m/s. Upon that comes then the percolate drainage layer. This drainage layer consists of several types of drainage sand, gravel and a network of drainage pipes. The layer functions first as a collector during the dewatering phase and evolves to the percolate drainage layer for the disposed contaminated dredged material.

At the top of the disposed dredged material again a mineral liner is installed in order to isolate the whole site. This mineral liner will consist of a layer of non-contaminated dredged material of about 50 cm thick and a permeability of maximum 10^{-9} m/s.

Finally the site is completed with a draining layer of about 30 cm and a soil layer of about 70 cm.

The capacity of the disposal site is estimated to 1.3 million cubic metres. Within the first three years (2001-2003) of exploitation 450,000 m³ of dewatered dredged material will be disposed of.

6.3. Exploitation of dewatering fields

Once the dewatering fields are installed the supply of dredged material can start. Prior to the dredging operations the physical and chemical quality of the dredged material is tested in situ. Depending on the results the dredged material is divided in several categories: material that can be used as mineral liner, contaminated material, material that can be used as top soil, … Depending on the category the dredged material is simply dewatered or treated to minimise the concentrations of contaminating substances.

First the dredged material is loaded in dumper trucks specially designed for the transportation of liquid material. This way the dredged material is transported to the proper dewatering field.

Figure 8: Accelerated natural dewatering of dredged material

In the dewatering field a continuous turning of the dredged material stimulates the evaporation and maximises the draining capacity of the bottom layer. The material is placed in rigs. This way the surface exposed to sun and wind is maximised and rainfall can flow directly in the drainage layer. In a period of three to six months the dry matter content of the dredged material is brought from less than 40% (g/100 g) to over 65% (g/100 g).

Depending on the chemical quality of the dredged material after the dewatering comes a bioremediation and/or physical-chemical treatment of the material. In order to minimise organic contaminants biodegradation is stimulated by adding proper nutrients and compost and a continuous aeration by turning the dredged material with special turning machines.
Altering the pH in the dredged material (by adding compost for example) can eliminate heavy metals and other inorganic contaminants.

All the water (process water and rainfall) collected in the drainage layer of the dewatering fields is directed to a large buffer basin. The water runs then through a water purification plant, consisting of a sand filtration and an active carbon filter. Finally the water is discharged to the Scheldt canal.

7. Final destination

The final destination of the site is an industrial area for high technology oriented businesses or small to medium organizations. On top of the sanitised black-point and within a strip of about 100 metres along the Upper-Scheldt a green belt will function as a buffer between the industrial area and the adjacent residential area on the other side of the Upper-Scheldt.

According to the planning the first 10 hectares of industrial area will be sold in 2004.

8. Conclusion

The combined expertise of the Province of East-Flanders, the City of Ghent, Domo Service Gent NV and DEC NV offers the solution to the several problems of the different partners. A historical black-point with a great risk for the environment and human health is sanitised and controlled in an economical and environmentally safe way. Maintenance dredging operations in the Ghent region are restarted and can continue for over 10 years. An industrial area is created on a very favourable location near two major highways and waterways, so the needed expansion of the industry in the Ghent region can continue without developing new sites in residential parts of the city.

E.3 Lecture Session:

Future topics

Development of an Integrated Management System for Prevention and Reduction of Pollution of Waterbodies at Contaminated Industrial Megasites

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Abstract

Problems of scale, multiplicity of site ownership and stakeholders along with an unacceptable cost for contamination clean up are the main characteristics of European megasites. This paper recommends that megasites need a new management and planning tool to protect their surface and ground- water resources from contamination. The EU project, WELCOME 's aim is to produce such a tool for the megasite manager. This tool is an HTML-based integrated management system (IMS). The IMS is currently under development and is structured with risk based decision making as a foundation. It is being tested at three main project megasites in 4 different countries: Rotterdam (NL) and Antwerp (B) Harbours; Bitterfeld (D); and Katowice (PL). The philosophy of the WELCOME approach, including the definition of a megasite, and the basic framework of the IMS are described in this report.

Key words: megasite, contamination, water quality, integrated management system

1.0 Introduction - The WELCOME project

The WELCOME project (Water, Environment, and Landscape Management at Contaminated Megasites) is a EU EESD/RTD contract that began in January 2002 and continues through December 2004. The project uses three megasites around Europe in an effort of “earning by doing” to construct an IMS. The IMS is a software guidance system to help manage megasites, directed for the protection of ground and surface waters. The IMS includes several modelling tools and methodologies developed within the WELCOME project. The system is also open to accommodate other tools developed outside of the project. The IMS can be used by organizations or land owners responsible for the management of a megasite.

A megasite is described for this project as: A contaminated area which has no simple solution, for which planning and management is made complex due to having one or more of the following characteristics:

- Large (km^2 scale) contaminated area or impact area (current or potential)
- multiple site owners
- multiple stakeholders
- multiple end users
- unacceptable cost for complete cleanup (due to political, economical, social, or technical constraints) within currently used regulatory timeframes.

2.0 Description of the WELCOME megasites

The IMS is being trialed at the three sites described below. These sites were chosen as to their location within a river basin and different countries and industrial activities.

1. Industrialised harbour area at a river delta: Rotterdam and Antwerp Harbours

Rotterdam Sea Port is situated at the river delta of the rivers Rhine and Meuse in an area of 10,000 hectares, extending from Rotterdam to the North Sea. Industry has developed into one of the main aspects of the Port economy. Approximately 60% of the 4,800 hectares of available port sites are leased to the (petro)chemical industry. The following industrial sectors are represented in the port complex: Agri-products, oil and chemical, maritime industry and recycling. Although not the only one, the (petro)chemical industry is the most important industrial cluster in the port.

Antwerp Sea Port stretches for twenty kilometres along the banks of the Scheldt River. It benefits from a strategic geographic location in the delta of Scheldt, Rhine and Meuse. With an international maritime traffic of over 110 million tonnes per year, Antwerp is in the top five of the world's biggest ports. Industries, which are situated in this area comprise (petro)chemical plants, metallurgic industry, insurance industry and services such as inspection and surveys, packaging, further processing, protection, etc. of goods.

Due to the nature of the past and ongoing maritime and industrial activities, the environmental quality of both the Rotterdam and Antwerp regions is at risk. At the old industrial areas, soil contamination with chlorinated hydrocarbons, oil spillages, polycyclic aromatic hydro-carbons and heavy metals are no exception.

2. Organochemical Industry Complex along the Middle Area of a River in Bitterfeld/Wolfen

In the Bitterfeld/Wolfen region, in the former GDR, lignite mining has been performed for over more than a century. The centre of the chemical industry was also built in old mining areas with an artificially low groundwater table. These industrial activities caused major subsurface pollutions, i.e. with chemicals like HCH, DDT, PCBs, Chlorinated Dioxines and Furanes, chlorobenzenes, chlorinated aliphatics, etc. At present an area of about 25 km^2 subsurface and groundwater is polluted to a depth of several tenths of meters and forms a large scale contaminant source threatening surrounding aquifers, lakes and the rivers Mulde and Elbe. In addition to the groundwater problems, sediments of small streams close to the industrial area are heavily polluted with strongly sorbing chlorinated organic hydrocarbons, creating a source of contamination for the downstream areas of the rivers Mulde en Elbe.

3. Metal mining Region at Spring Area of River System in Katowice, PL

The site of the former chemical plant is located in Tarnowskie Góry, Poland, 30 km northwest of Katowice. The site has been under anthropogenic pressure already since the 16th century, as in that period extraction of silver and lead ores was carried out at the site. In the early 19th century, a paper mill had operated at the site. The paper mill was rebuilt into an iron-works factory and in 1922 into a chemical plant. From 1922-1990, as much as 0.8-1.2 million m^3 of wastes were deposited on the 30 ha site, such as barium, arsenic and strontium compounds.

3.0 Problems of Megasites – The need for an IMS

This overall approach is used because the characteristics of a megasite (including the sites mentioned above) include the following problems which are not solved by the standard contamination clean up procedures:

- The size of problem requires an areal or regional approach*
- Inability to clean up due to excessive cost constraints
- Technical know how unavailable for the types/amount of contamination
- Difficulty in medium to long term planning with multiple stakeholders, site owners, liability issues and end users
- For various reasons cannot fit into normal legislative requirements with either timeframe or clean up standards

*Please note that the logics and systematics of the IMS may also be useful and offer help for smaller scale problems, although it is for larger scale cases preferred.

4.0 Overall Strategy of the IMS

Previously in Europe there has been described the concepts and case for risk based land management (Clarinet 2002; NICOLE 1997 and 2002; and others). This is an approach based on site specific risk characteristics, focused on reducing the risk for the site receptors. This is different than a standard clean up approach, focused on the regulatory clean up levels applicable generically across the board for all sites. Such risk based approaches are more complicated to initiate and maintain, in the sense that they must be negotiated by stakeholders and authorities within the acceptable legal constraints.

The WELCOME IMS builds on these risk-based remediation concepts and takes them one step further. It organizes a structured procedure for assessing risk based management and it adds the regional concepts of a megasite approach (Figure 1).

The boundary definition of a megasite may include off site property as it is affected from the contamination. It also may include a number of separate management units or contaminated sites in a region, or a receptor may be shared with more than one river basin. The idea behind the IMS is to view the contaminated sites as a whole (system approach) and to find an integrated and long term environmental management approach for the remediation.

Megasite elements are a way to disaggregate the site according to risk, to find a risk based solution for the whole that still deals with the real but different types of risks. The management unit is also part of the planning of stakeholders. The boundary conditions are important in order to consider the solution with stakeholders, including the social and economic aspects. Stakeholders include the authorities, the spatial planning and other national and regional land management institutions. Stakeholders are also the site users and owners.

The risk based approach focuses on the receptor health. Regional sustainability criteria must also be addressed to complete the megasite approach. This means that the ecosystem of the site (including components which are not a receptor) must also be taken into account in the overall wellbeing of the megasite and its management planning.

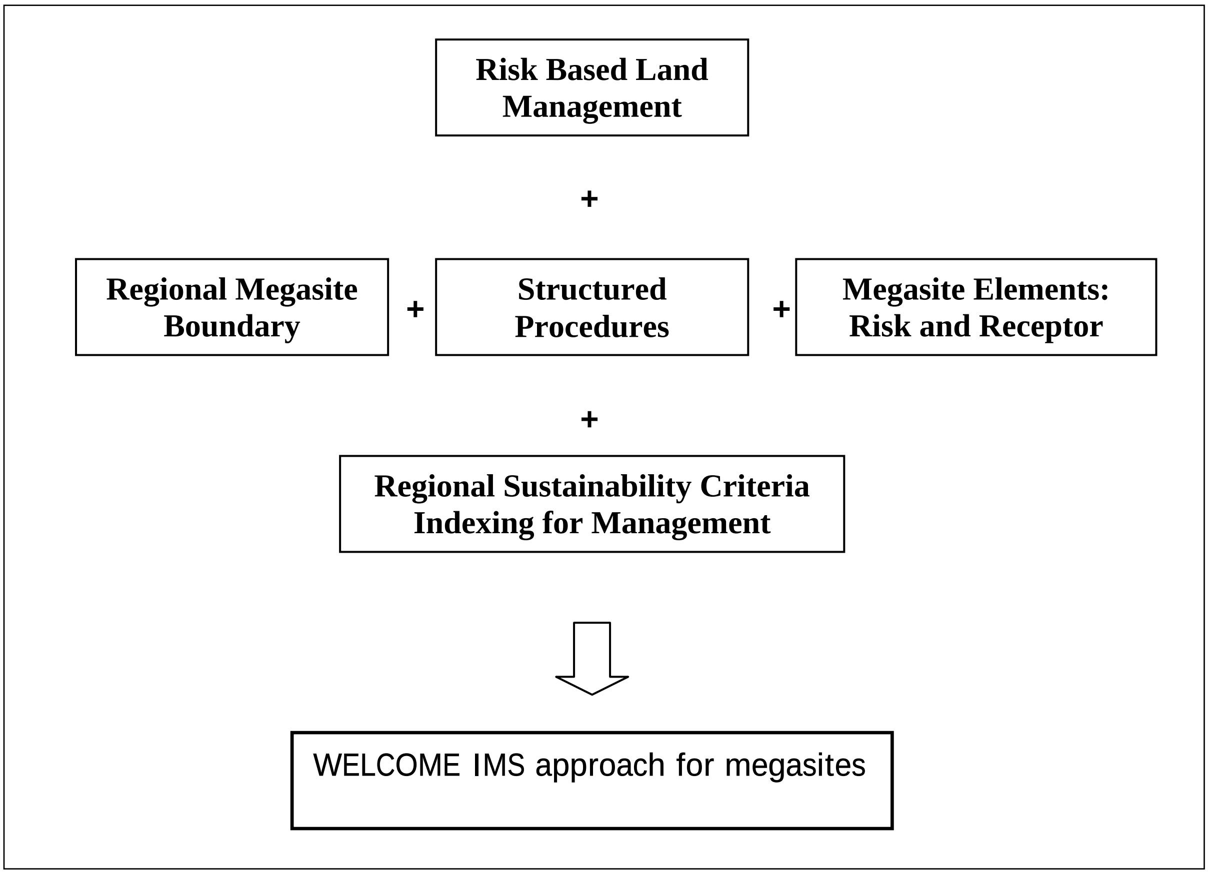

Figure 1: WELCOME approach for megasites

The overall IMS goals therefore are to:

- remediate and manage environmental aspects of the site cost efficiently while maintaining the site infrastructure and operations
- provide long term vision for management
- promote community/local/regional stewardship
- provide a tool with which a site can centralise their data and use it effectively
- offer flexibility to accept creative technical/alternative solutions for remediation and management

- offer methods to deal with integrating the megasite outcomes with other parallel regional and national and transnational issues (river basins) included in site boundary conditions

5.0 Conceptualising an Integrated Management System

In the WELCOME project a conceptual model was first made of the IMS. This involved asking the end users of the WELCOME megasites what type of megasite management system they would like to have. In most cases they had never been asked this question before, and so were enthusiastic to participate and voice their needs. Their answers are revealing and can be expected to occur at any example megasite in Europe, whether the site has been managed for many years or where management activities have just begun.

What kind of management system do megasite managers want?

- A system focused on risk-reduction and management (with respect to water quality, human health and ecosystems), not on total cleanup
- One that helps to define cost efficient and timely solutions at the megasite scale
- A clear, simple and structured process with flexibility to site specific conditions, leading to a set of potential risk-reduction and management scenarios, and the final selection of an optimal scenario (with respect to risk reduction, costs, and sustainability)
- A decision making tool which incorporates site specific boundary conditions including public perception
- Helps with effective data gathering
- Natural attenuation and immobilisation feasibility testing incorporated
- Easily embedded into the management system in place already

In addition to this ‘megasite wish list’ developed, a European wide INTEND team (International team of endusers) is established as part of the WELCOME project. It comprises regulators, megasite managers, researchers, industry and other stakeholders. This team of experts meets once/year throughout the project to advise on the progression of the IMS and to help keep it as a practically oriented tool. The first meeting of INTEND met in November 2002.

Besides this the project partners of WELCOME met many times to discuss the concept and revise the structure. The overall conceptualisation process has resulted in the basic IMS structure, as described in the next section.

6.0 Basic Framework of the IMS

The IMS structure has 4 main sections. These are given as:

1. **Megasite Acceptability:** Defining your site as a megasite and using the IMS approach within the regulatory frameworks. It is advised to install a responsible megasite coordination committee (MCC) in order to cover all stakeholder interests.

2. **Risks and Risk Reduction:** Building a megasite risk approach based on aggregations called risk clusters.

3. **Management Scenarios:** Defining risk reduction and sustainable management scenarios for clusters and the megasite.

4. **Long Term Planning and Management:** Long term sustainable planning and management of the megasite.

These 4 sections can be seen in Figure 2. Each Section has a few main steps that can be followed by the user to complete the section. For example there are three main steps in Section 1 (see Figure 2).

After going through the section, the user is directed to a checkpoint. There checkpoints are shown as: ⬢ . Checkpoints make up the quality control areas of the IMS. Within the checkpoint the user is directed to check three items:

- ✔ Data and database
- ✔ Data interpretation
- ✔ Megasite management and boundary conditions

It is only after identifying the checks and satisfied that these are completed, that you are recommended to continue forward to the next section. The arrows denote that you may have to go back from the checkpoint to the section you just finished or to a previous section. If the checks listed in the checkpoint are not completed as judged by the user, the user is recommended to go back through the section if possible at that point to make further adjustments.

At the bottom of the figure is the database (Figure 2). This is denoted as growing bigger from Section 1 to Section 4. As you progress through the IMS, the user's data and databases should be growing as more and more data are added to the process. The database is shown in this way, as it is not held within the IMS, rather the IMS is a guidance document, which can access different databases.

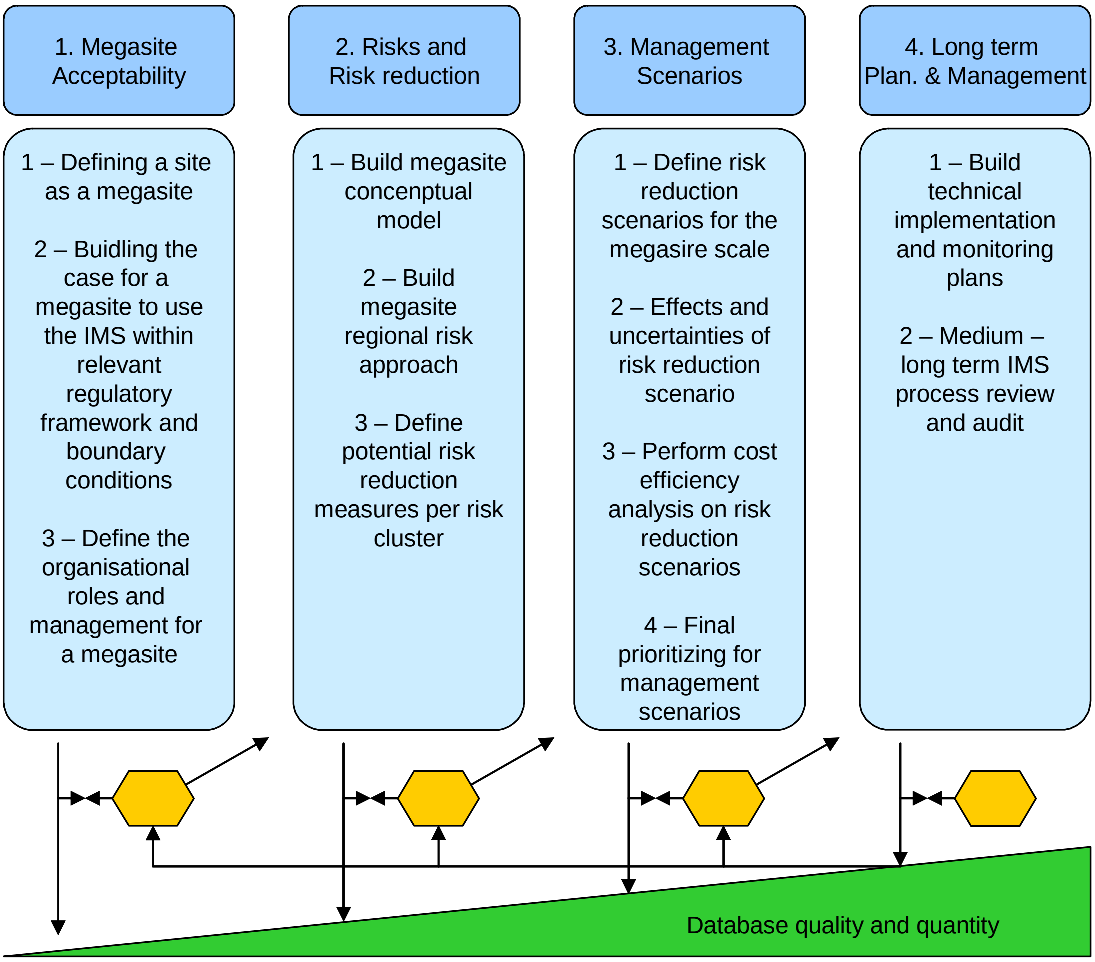

Figure 2: The Four Sections of the IMS

7.0 Conclusion and Future Work

The WELCOME project deals with European megasites. The characteristic problem of the contaminated megasite is complexity in some socio-economic, political, or technical aspect. To protect the water resources from megasite contamination it is suggested to use a new tool, since standard clean up methods are unacceptable in these situations. The WELCOME IMS is one tool which could be used to help the managers of megasites. It is a software guidance document that leads the user through a system based on risk based decision making.
Currently this IMS is being tried out at the WELCOME megasites. This is the WELCOME process of ‘learning by doing’.

The basic IMS framework contains a process which begins with accepting your site to be a megasite (by all the stakeholders). The process continues with a risk reduction approach, and builds management scenarios for long range planning of megasites.

Because development and testing of the IMS are running parallel, the structure is likely to change in the future as the continuous input from the megasites is included. Tools will be developed as part of the IMS to define a megasite risk assessment and management scenarios, as well as others. Research with MNA and immobilisation will continue to be part of the project and considered important aspects of any long term megasite management programme.

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NL	TNO Institute of Energy, Environment and Process Innovation (coordinator)
D	Grossmann Ingenieur Consult (GICON)
PL	Institute for Ecology of Industrial Areas (IETU)
D	Centre for Environmental Research Leipzig-Halle (UFZ)
B	Flemish Organisation for Technology Research (VITO)
D	University of Tübingen
NL	Wageningen University
D	Regional Agency for Site Decontamination of Sachsen-Anhalt (LAF)
D	Mid-Germany Remediation company (MDSE)
D	Quadriga
NL	Network Organisation for Quality of Environment (NOK)
PL	Technical University of Czestochowa
NL	Rotterdam Municipal Port Management

NATURAL ATTENUATION PROCESSES AT THE BITTERFELD MEGASITE (GERMANY)

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INTRODUCTION

The Bitterfeld region, one of the oldest industrial centers in Germany, is highly contaminated with a mixture of mainly chlorinated aliphatic and aromatic compounds found in soils, sediments, surface water and groundwater (Gotz et al., 1998, Walkow et al., 2000, Brack et al., 2003). Due to the regional extension of the contamination and the existence of densely populated areas, the contaminated area of Bitterfeld constitutes a difficult problem for groundwater remediation. Since complete removal of the contaminated water and soils is not possible at this scale, an effective remediation strategy must focus on risk minimization. Such a strategy should be composed of a combination of remediation technologies including 'pump-and-treat' measures, in situ-technologies such as reactive walls and monitored natural attenuation (MNA). The latter uses natural attenuation (NA) processes such as degradation or sorption to contain the spatial extension of the contaminant plume (e.g. Azadpour-Keeley et al., 2001). The concept of establishing natural attenuation as a viable remediation measure on a specific site is often based on the 'three lines of evidence' approach. These lines of evidence include several key footprints of NA processes from geochemical data, the reduction of contaminant concentrations and/or mass along the flow path as well as microbiological data giving evidence of biodegradation processes (e.g. RTDF, 1997, U.S.EPA, 1998, Wiedemeier et al., 1999). A particular problem in the case of Bitterfeld are the existing mixtures of contaminants, which may form overlapping plumes and may behave very differently from single contaminants because of possible interactions. This complicates an evaluation of the suitability of NA processes as a supportive remediation measure at the Bitterfeld site. However, certain areas within the large contaminated region may well turn out to be a promising place for the implementation of MNA, due to the type of contamination and geochemical conditions encountered there.

In the current paper, site characterization data for the Tertiary aquifer of a selected research area in Bitterfeld, considered to be a possible site for implementation of MNA, are presented. The objective of this research was to determine the contaminant composition and extension, the geochemical conditions as well as the relevant biodegradation processes with a primary focus on chlorinated aliphatic hydrocarbons, the most important contaminants in addition to chlorobenzenes and BTEX. In the future, these findings will be used for the assessment and quantification of the NA potential of this area as well as to evaluate the feasibility of NA processes as a complimentary remediation option at selected areas in Bitterfeld.

SITE HISTORY

The Bitterfeld/Wolfen industrial district is located in the chemical triangle Bitterfeld, Halle/Saale and Leipzig at a distance of 130 km South of Berlin, in Eastern Germany. The high soil and groundwater contamination of the Bitterfeld/Wolfen industrial district is mainly related to the chloro-organic chemical industry, which started to develop over 100 years ago (Walkow et al., 2000). Lignite mining and processing created favorable conditions for the growth of the chemical industry at the end of the 19th century. The continual increase of the chemical production, the extension of the product range and the increasing introduction of ecologically or toxicologically problematic substances such as chlorinated hydrocarbons and pesticides caused a huge waste problem. At the beginning, the chemical production comprised the manufacturing of basic chemicals such as chlorine, sodium hydroxide, aluminum and magnesium (Walkow et al., 2000). Later, the spectrum was extended to nearly all areas of organic chemistry, comprising the production of about 5000 different substances (Lücke, 2002).

The contamination currently present at the Bitterfeld/Wolfen district covers an area of about 25 km². The estimated volume of affected groundwater amounts to 200 million m³ and includes the Quaternary as well as the Tertiary aquifer (Weiß & Merkel, 2001). Contaminants entered the soil environment from multiple sources at the area of chemical production at different points in time. The most important input of contaminants was due to the uncontrolled dumping of chemical wastes, which was deposited into discontinued lignite-mining pits in the immediate vicinity of the chemical industry (Walkow, 1996, Weiß et al., 2001). Other important inputs of contaminants involve accidental spills, war damage and leaking pipelines at the site (Walkow et al., 2000). The vertical extension of the contamination covers the entire depth of the Quaternary and Tertiary aquifer down to a depth of 60m. The spreading of pollutant plumes in the Tertiary has progressed further as compared to the Quaternary aquifer, due to the continuous pumping measures to stop the flow of contaminated water to high risk areas in the shallow aquifer (Lücke, 2002). The contaminant situation in the whole area is very complex and heterogeneous, dominated by very high concentrations of organic compounds, in particular halogenated hydrocarbons (chlorinated aliphatics and aromatics), appropriate to the main production sectors of the chlorinated chemistry together with manufacturing of pesticides and colors. In addition, a variety of other contaminants such as BTEX, HCH, and DDT/D/E isomers are distributed on a regional scale in the Bitterfeld/Wolfen area, while chlorophenols, chloroanilines, nitrophenols, nitrochlorophenols and nitrochlorobenzenes can be found locally (Thieken, 2002). Beside the parent compounds, their metabolites are also found distributed in the groundwater. Furthermore, the groundwater pumping to lower the groundwater table in the mining areas resulted in a considerable alteration of the groundwater level in the past. Today, the flooding of mining pits causes a rising groundwater table and brings contaminants back to the surface.

MATERIALS AND METHODS

At two sites within the contaminated area in the Bitterfeld/Wolfen region, NA processes are to be examined and quantified. The first comprises the Southeastern outflow from the contaminated area towards the residual open-pit mining lake Goitsche and the other the Northern outflow area towards the river Fuhne (Fig.1). The Goitsche research area was investigated focusing on the highly contaminated Tertiary aquifer. For the second research area Fuhne, both aquifers, the Quaternary and the Tertiary aquifer will be studied. However, because of the lower data density in the Fuhne area, additional groundwater monitoring wells are currently being installed so as to study the contaminant distribution and the geochemical composition of the groundwater in more detail.

Groundwater has been collected and analyzed at the experimental site starting in 1992 by the ÖGP (Ökologisches Großprojekt – Ecological Mega Project) Bitterfeld-Wolfen, but only from 1999 onwards have data been collected continuously in six month intervals. In the Southeastern research area (‘Goitsche’), groundwater is collected from 23 monitoring wells in the Tertiary aquifer and 14 wells at the base of this aquifer. Groundwater samples were analyzed for various field as well as sum parameters, relevant anions/cations and organic constituents (chlorinated aliphatic hydrocarbons, BTEX, chlorobenzenes, chlorophenols, chloronitrophenols, nitrophenols). The distribution of various groundwater constituents was approximated using contour maps generated by Surfer (Golden Software, Version 7.02). Linear kriging as gridding method was used with an anisotropy factor 2.0. The GIS-based geological model for the Southern Bitterfeld subsurface developed by (Wycisk et al., 2002) was used to produce a geological cross section of the research area.

A quantitative method similar to the one described by (Sinke & le Hecho, 1999) was used to determine the extent of dechlorination, and is assumed to be direct evidence of natural attenuation. Based on the abiotic and biotic breakdown reactions of chlorinated solvents, the degree of dechlorination for the Southeast aquifer was calculated. The anaerobic degradation patterns of chlorinated solvents have been summarized by (Azadpour-Keeley et al., 2001). Based on these breakdown patterns and the prevalent chlorinated solvents actually encountered in Bitterfeld, the degree of dechlorination for the Bitterfeld Tertiary aquifer was calculated as follows:

degree of dechlorination [%] =

$$\frac{\left([TCE]+[1{,}1{,}2-TCA]+2\left([c-DCE]+[t-DCE]+[1{,}1-DCE]+[1{,}2-DCA]\right)+3[VC]\right)}{3\left([PCE]+[PCA]+[1{,}1{,}2-TCA]+[TCE]+[c-DCE]+[t-DCE]+[1{,}1-DCE]+[1{,}2-DCA]+[VC]\right)}\cdot 100\%$$

PCE: tetrachloroethene, PCA: tetrachloroethane, TCE: trichloroethene, TCA: trichloroethane, DCE: dichloroethene, DCA: dichloroethane, VC: vinylchloride

Depending upon the Cl atoms remaining on its molecule, a substance is weighted higher in this calculation. The more the amount of less chlorinated compounds (degradation products/intermediates) increases along the flowpath, the higher the degree of dechlorination and the intensity of degradation reactions. Possible end products such as ethene, ethane and chloroethane were not measured and are therefore emitted in the formula. Hence, a value in the above formula for the degree of dechlorination of 100% would indicate the disappearance of all substances but VC, while a value of 0% would indicate the sole presence of the parent compounds PCE and PCA. Since TCE was also found in large concentrations in the source area, it is most likely another parent compound. Hence the degree of dechlorination in the source area calculated with the above formula is expected to be > 0%.

For the chlorobenzes, only MCB and various dichlorobenzenes (DCBs) were found in relevant concentrations in the research area. To collect evidence for degradation reactions of DCBs, the concentration of MCB was related to the total amount of chlorobenzenes (sum of MCB and DCBs). A relative increase of MCB indicates breakdown of DCBs.

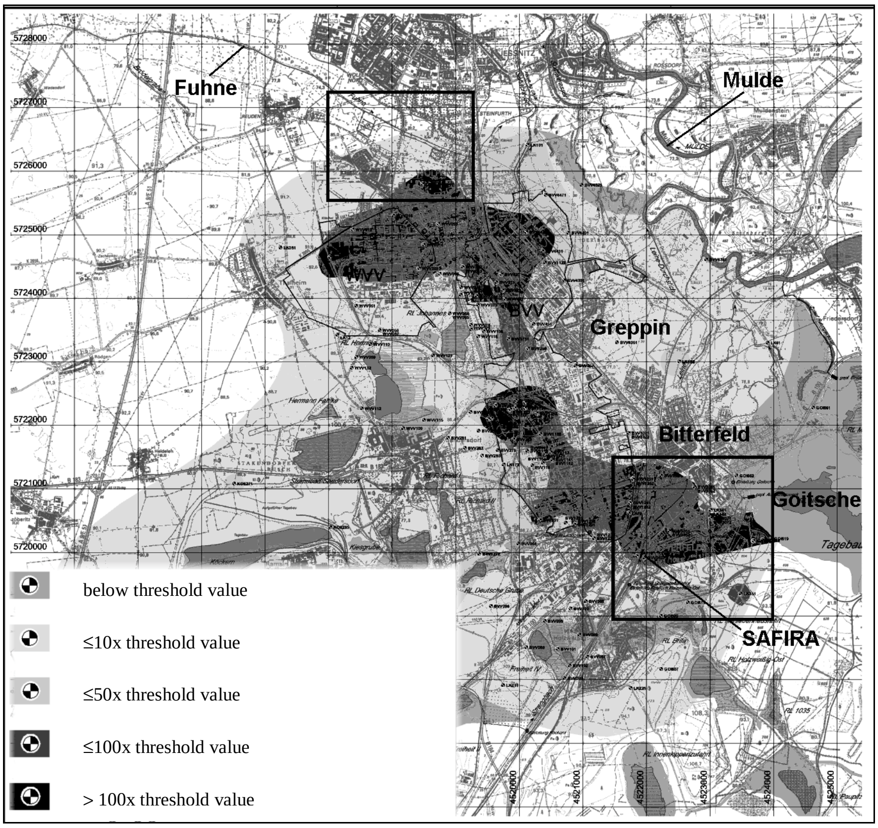


Figure 1: *NA research areas (rectangular frames) and contamination levels (May 1999) in the Tertiary aquifer at the Bitterfeld megasite (Source: Ökologisches Großprojekt Bitterfeld/Wolfen, 2001)*

GEOLOGY AND HYDROGEOLOGIC CONDITIONS AT SE OUTFLOW (GOITSCHE)

The Southeastern research area in Bitterfeld covers an area of about 6 km² (transect: N-S: HW 5721875-5719000; W-O: RW 4521500-4524000) (Fig.2). This site is underlain by Cenozoic sediments overlying an undisturbed clay layer at a depth of 50-70m, which forms the natural hydrogeological barrier to the underlying Pretertiary rocks (Fabritius, 2002). The subsurface can be divided into two main aquifers, the Quaternary (braidews rivel alluvium of Wechselian age) and the Tertiary aquifer (micaceous marine sands). The Tertiary aquifer is characterized by a ten times lower hydraulic conductivity (10^{-5} to 10^{-4} m s^{-1}) compared to the Quaternary (10^{-4} to 10^{-3} m s^{-1}) (Fabritius, 2002, Ruske et al., 1997, Dermietzel & Christoph, 2001). The two aquifers had originally been separated hydraulically by a lignite seam, which was to a large extent disturbed by opencast lignite mining (Ruske et al., 1997). As a result, contaminants at some locations freely entered the Tertiary from the Quaternary aquifer. The general flow regime is characterized by a groundwater flow direction towards the mining lake Goitzsche, which resulted from the former surface mining-related pumping of water to lower the groundwater table. The facilitated flooding of some mining pits including the Goitzsche in addition to the catastrophic floods in Eastern Germany in August 2002, is resulting in increasing groundwater levels and extensive changes in the groundwater flow direction and velocity. In the future, a main groundwater flow direction towards the river Mulde in the Northeast is anticipated.

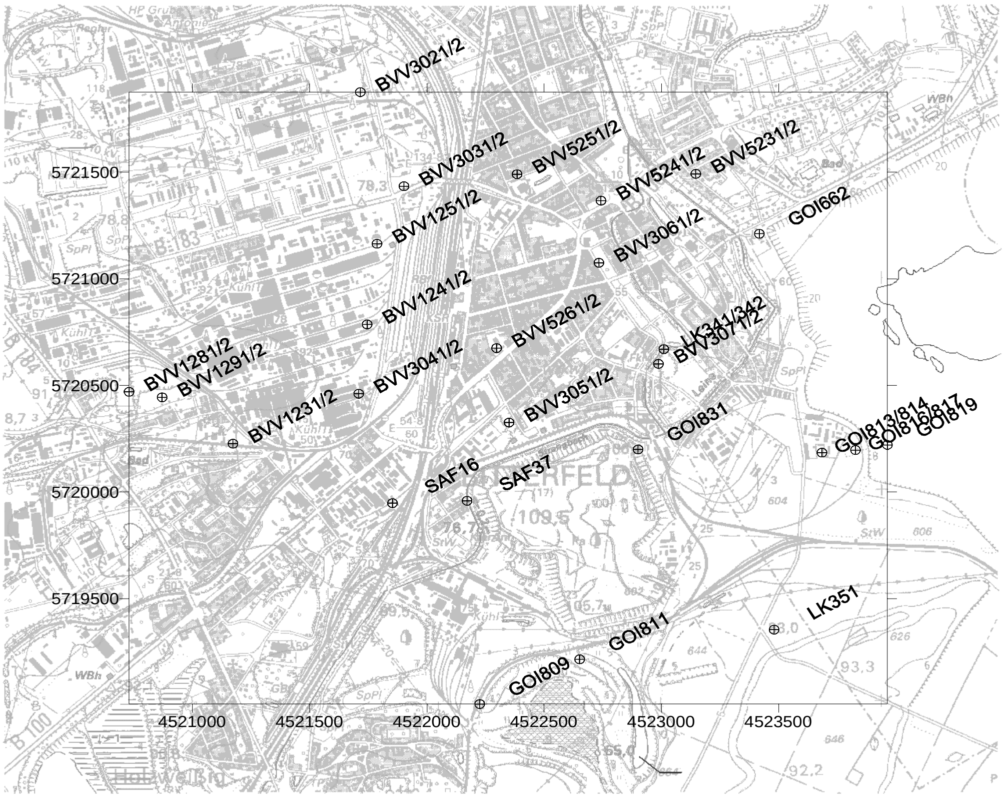


__Figure 2:__ Southeastern research area Bitterfeld and on-site monitoring wells in the Tertiary and at the base of the Tertiary aquifer (the latter indicated by backslash)

CONTAMINANT SITUATION (SE OUTFLOW)

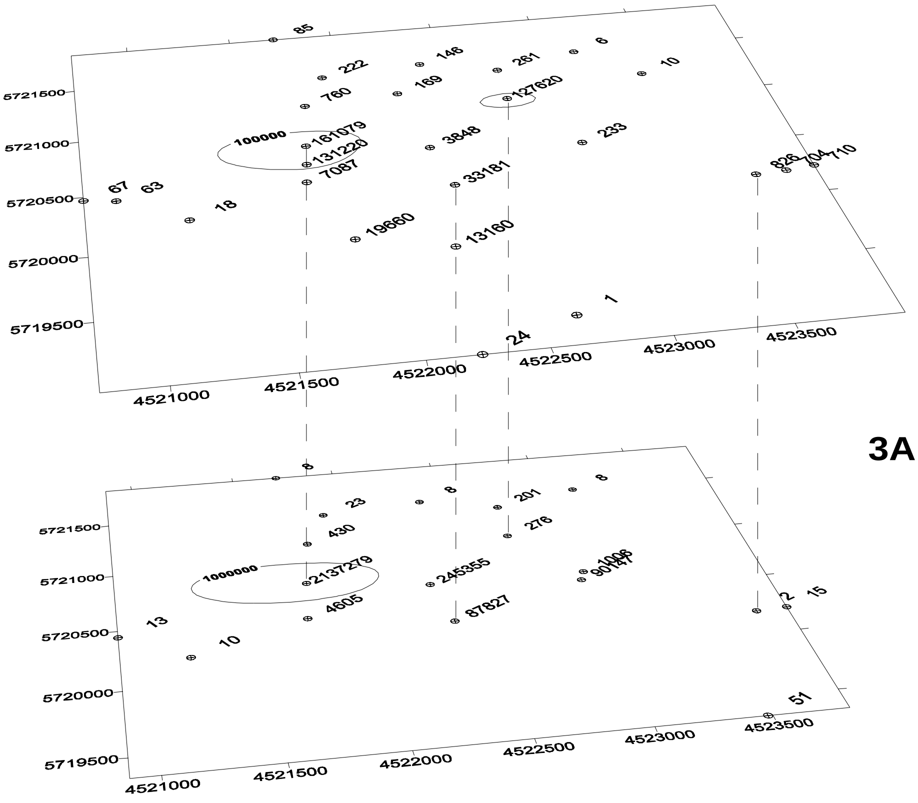
The Southeastern research area Bitterfeld is characterized by three main groups of contaminants, found in the Tertiary aquifer: chlorinated aliphatics, chlorinated aromatics and BTEX. Sum concentrations of these main contaminant groups were all far above threshold levels, which are 50 µg L^{-1} for chlorinated aliphatics (threshold level for the sum of halogenated C_1- and C_2-hydrocarbons), 5 µg L^{-1} for chlorobenzenes and 80 µg L^{-1} for BTEX (Brack et al., 2002).

The chlorinated aliphatic hydrocarbons may be regarded as the most important contaminants in the research area: especially tetrachloroethene (PCE), trichloroethene (TCE), c-dichloroethene (c-DCE), trans-dichloroethene (t-DCE), 1,1-dichloroethene (1,1-DCE), vinyl chloride (VC), 1,1,2,2-tetrachloroethane (PCA), 1,1,2-trichloroethane (TCA), 1,2-dichloroethane (DCA), trichloromethane (TCM) and dichloromethane (DCM) were found. The sum concentration of these substances reached 160 mg L^{-1} in the Tertiary aquifer in monitoring well BVV1241 (Fig.3A). Much higher concentration levels were detected at the base of the Tertiary aquifer with up to 2000 mg L^{-1} in the source zone (BVV1242). The plume of the aliphatics in the Tertiary extended far to the East and Southeast

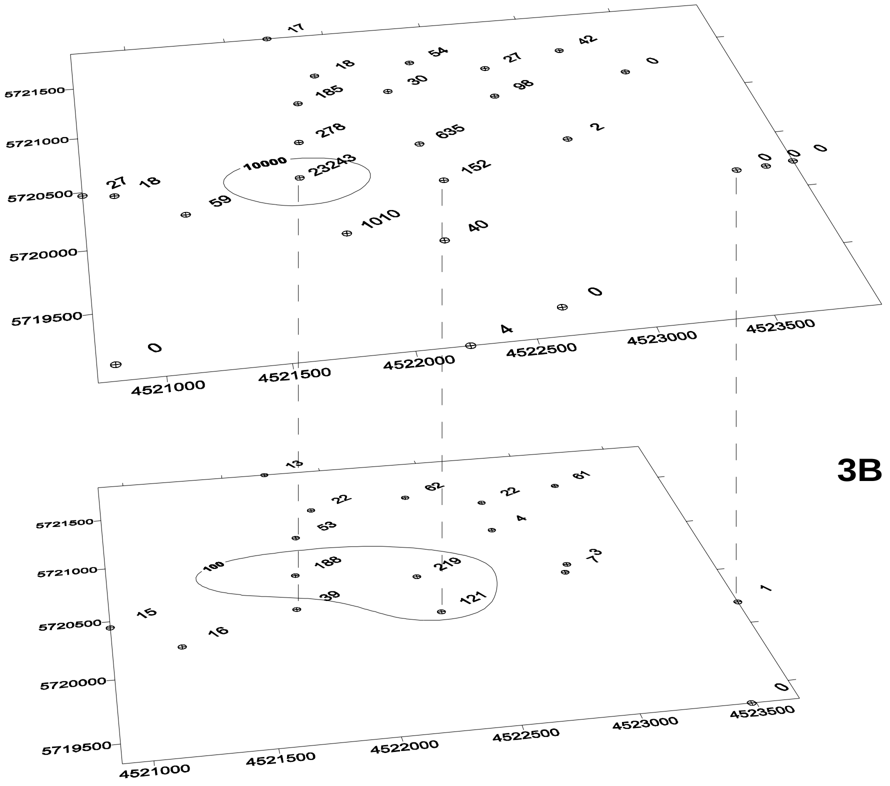
(GOI809, 811, 819). Near the surface water of the Goitzsche to the East of the research area, the time-series data since 1998 suggested an increase of concentrations in two of three monitoring wells and should be reason for concern.

Among the chlorobenzenes, the most important substance in the Bitterfeld research area is MCB with concentrations as high as 23 mg L^{-1}. The chlorobenzene plume had a lesser spatial extension than the contaminated zone of the chlorinated aliphatics (Fig.3B). The contaminated zone comprised all monitoring wells to the North and extended to the East as far downgradient as monitoring wells BVV3051 and 3071, but did not reach the Goitsche (GOI813, 816, 819). The distribution of chlorobenzenes is characterized by an opposite vertical stratification as compared to the aliphatic compounds, with lower concentrations at the base of the Tertiary (<1 mg L^{-1}).

BTEX was the third main group of contaminants in the research area. The most important compound within this group was benzene. Benzene concentrations of about 8 mg L^{-1} were detected in the source zone (BVV3041, 3051). Concentrations of toluene (700 µg L^{-1}) and xylenes (130 µg L^{-1}) were observed in BVV3041, and decreased to non-detectable levels along the flowpath. This is probably a result of better degradation under anaerobic conditions compared to benzene (Lovley, 2000, Franzmann et al., 2002). The contaminated zone of BTEX was characterized by a large extension toward the lake Goitsche and to the North (Fig.3C), with a decrease in benzene concentrations along the flowpath. On the other hand, time-series data of the three Goitsche monitoring wells (GOI813, 816, 819) showed an increase in benzene concentrations. On the Tertiary base the contamination extended not as far North as in the shallower zone, but further to the South, with the highest concentration detected in BVV3052 (12 mg L^{-1}). A similar vertical stratification as for the chlorinated aliphatic compounds were observed. Intermediates and end products of biodegradation of these contaminant groups such as ethene, ethane, carbon dioxide, methane, phenol and benzoate are to be measured in future.



3A



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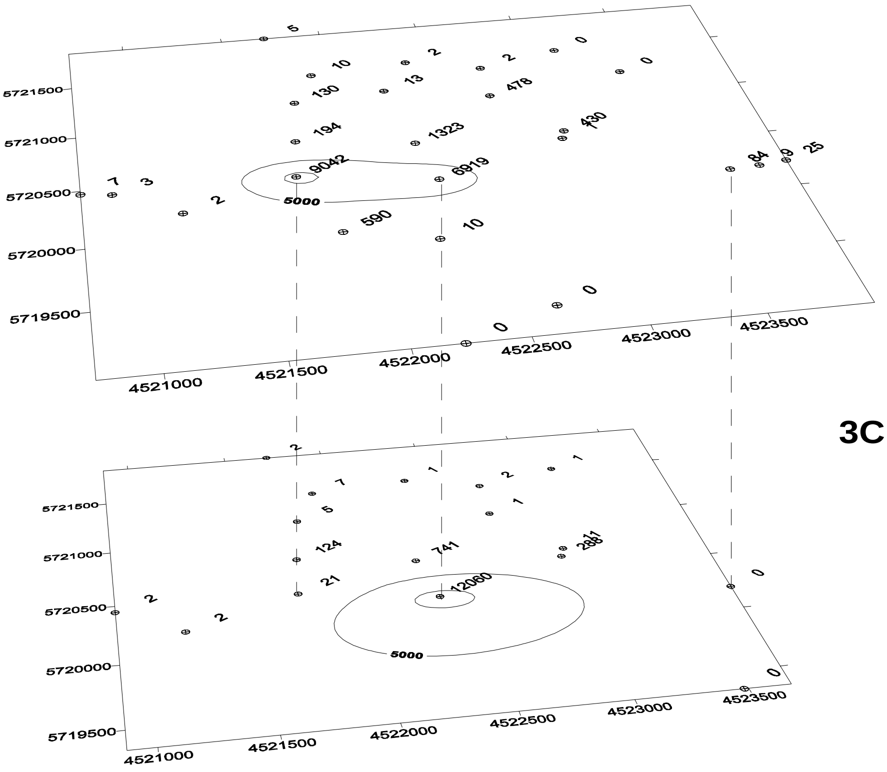

3C

Figure 3: *Two-dimensional plot of contaminant concentrations (µg L^{-1}) in the Tertiary aquifer and at the base of the Tertiary at the Southeastern Bitterfeld research site (November 2001). A: Sum of chlorinated aliphatic hydrocarbons, B: Sum of chlorobenzenes, C: Sum of BTEX.*

GEOCHEMICAL CONDITIONS

The geochemical conditions at the site may enable the anaerobic biodegradation of the contaminants present. The pH levels in most of the wells ranged from pH<6 (near source zone) to pH>6.5 (close to Goitsche), while temperatures decreased along the flowpath from 16 °C in the source path to 11.5 (Goitsche). The groundwater in the Tertiary was characterized by a strictly anaerobic milieu, low nitrate and ferrous concentrations and high sulfate concentrations. Due to the high sulfate concentrations and the anaerobic conditions, sulfate reduction appears to be the most likely biogeochemical process in the Tertiary aquifer of the research area for the oxidation of contaminants like BTEX. Background concentrations of sulfate are relatively high in the aquifer (>1000 mg L^{-1}), while the distribution of sulfate in the contaminated area is characterized by an additional anthropogenic source of sulfate in well BVV1251 (>4000 mg L^{-1}) and a decrease to levels below 400 mg L^{-1} in the flowpath (especially BVV1241, 3061, 5241). On the other hand, sulfide concentrations were not in the same order of magnitude, characterized by low background levels (0.01-1 mg L^{-1}) and a slight increase (>1 mg L^{-1}) in the contaminated zone. It is likely that sulfide produced from a possible reduction of sulfate had coprecipitated with Fe, since dissolved Fe (Fe(II)) concentrations similarly decreased in the flowpath of the contaminated zone. Geochemical conditions on the base of the Tertiary aquifer were similar to that at shallower depths.

MICROBIAL DEGRADATION CAPACITY

Microbiological studies at the SAFIRA pilot plant located within the Bitterfeld research area have shown that groundwater and aquifer sediments of the Tertiary were populated by relatively high numbers of microorganisms (groundwater: up to 10^5 cells mL^{-1}, sediments: up to 10^6 cfu g^{-1}), comprising sulfate reducing, denitrifying, iron and manganese reducing as well as aerobic autochthonous microorganisms (Wünsche et al., 1997). Alfreider et al., 2002 studied the microbiological population of the Quaternary aquifer at the same site with similar geochemical conditions as in the Tertiary and found the groundwater dominated by various members of the class of Proteobacteria among others. While the microbial colonization of the Tertiary aquifer was found to be slightly lower than in the Quaternary aquifer, a continuous decrease over depth could not be identified (Wünsche et al., 2000a).

Reductive dechlorination constitutes the most important degradation process for the chlorinated hydrocarbons under these anaerobic conditions, requiring an electron donor substance. Batch experiments and studies in the *in situ* reactors at the SAFIRA site in Bitterfeld have shown the degradation of highly chlorinated hydrocarbons to less chlorinated compounds. Werner & Stieber (1997) studied the degradation of TCE and PCE to c-DCE in batch experiments, using an additional organic cosubstrate. Similarly, Middeldorp et al. (2002) presented results showing a complete reduction of chlorinated ethenes to ethene by mixed cultures in Bitterfeld groundwater (under anaerobic conditions), when sufficient electron donor and a nitrogen source is present. In the Tertiary aquifer the content of DOC is relatively low (source areas: 20 to 100 mg L^{-1}; Goitsche: <2 mg L^{-1}) and may limit the reductive dechlorination of chlorinated solvents. Therefore BTEX as a co-pollutant might be important as an energy source for the indigenous microbial population. The plumes of BTEX and chlorinated solvents overlap to a large degree in both the shallow Tertiary and the base of the Tertiary and may therefore both be accessible to microorganisms. On the other hand, sulfate reduction seems to be the most important biogeochemical process for the oxidation of contaminants like BTEX due to the abundance of sulfate and the anaerobic milieu in the Tertiary aquifer as well as the presence of sulfate reducing microorganisms. Extended studies regarding the biodegradation of chlorobenzenes at the test site have shown that the groundwater contains MCB-degrading bacteria, which are capable of degrading the pollutants MCB and 1,4-DCB (Wünsche et al., 2000c). However, the limiting factor in the Bitterfeld aquifer is the absence of oxygen, therefore degradation of chlorobenzenes is believed to stop at the level of MCB (Wünsche et al., 2000b, Dermietzel & Vieth, 2002).

DEGREE OF DECHLORINATION AS DIRECT EVIDENCE OF BIODEGRADATION

The higher chlorinated aliphatic compounds (PCE, TCE, 1,1,2,2-PCA, 1,1,2-TCA) were detected at very high levels near the source areas, the less chlorinated aliphatic hydrocarbons (cis-DCE, trans-DCE, 1,1-DCE, VC) increased relatively along the flowpath towards the Goitsche lake. This is demonstrated by the degree of dechlorination, which shows an increase of the less chlorinated daughter compounds towards the Goitsche. The mother compounds PCE, PCA and TCE are sequentially dechlorinated by microorganisms and abiotic reactions forming less chlorinated metabolites like c-DCE, which in turn may, under adequate geochemical conditions, be further degraded to VC and Ethene. The degree of dechlorination increased along the flowpath from nearly 20% in the source area of the chlorinated aliphatics to about 80% near the Goitsche. This is an indication of a breakdown of the parent compounds, with an eventual accumulation of VC in the aquifer as the least reactive substance under anaerobic conditions.

As for the chlorobenzenes, MCB is not further degradable under anaerobic conditions. Only in three wells in the source area (BVV3041, 5261, 1241) were other chlorobenzene compounds (besides MCB) measured in relevant quantities (especially 1,4-DCB). Especially in BVV1241/42 the time series since 1998 indicated the relative disappearance of the dechlorinated compounds relative to MCB. Therefore, the eventual endproduct of microbial reactions for the chlorinated aromatic hydrocarbons appears to be MCB.

SUMMARY

The contamination of the groundwater in Bitterfeld is characterized by a variety of contaminants with a predominance of chlorinated hydrocarbons. This contaminant situation presents a complex challenge for risk assessment and remediation. Appropriate remediation techniques have to combine specifically designed remediation technologies for hotspots and plume management in addition to monitored natural attenuation (MNA) in fringe areas and left-over plumes.

Currently, two areas in Bitterfeld are under investigation regarding their suitability for the application of MNA. The first comprises the Northern outflow area of the industrial zone towards the river Fuhne, and the second the Tertiary aquifer of the Southeastern outflow towards the residual open-pit mining lake Goitsche. Due to the more detailed investigation of the latter research area, first results are presented concerning ongoing NA processes at this study site. Field data from monitoring wells going back to 1998 were analyzed regarding evidence for the prevalent biodegradation reactions. The groundwater flow direction in the Southeasterly Tertiary Aquifer has in the past been mainly directed towards the open pit Goitsche in the East. Due to a direct hydraulic contact to the Quaternary aquifer, the Tertiary aquifer is contaminated with large quantities of chlorinated aliphatic compounds, in addition to chlorobenzenes and BTEX. Few changes of contaminant concentrations are perceptible from the time-series data of individual wells. However, the plume of chlorinated aliphatic compounds and BTEX may already have reached the lake Goitsche, indicated by low, but rising contaminant concentrations in the Tertiary monitoring wells in the immediate vicinity of the Goitsche. Extensive changes in the hydrologic conditions are expected in the future, which will result in a redirection of the groundwater flow towards the Northeast. For this reason, most contaminants can be expected to bypass the reclaimed mining lake in the future.

The results of the groundwater geochemistry suggested the predominance of sulfate reducing conditions in the Tertiary aquifer: a strictly anaerobic milieu, low nitrate and high sulfate concentrations, which decline in the contaminant flowpath relative to background conditions. Feasible degradation reactions in this environment are the oxidation of BTEX compounds with sulfate as the terminal electron acceptor, and reductive dechlorination of the aliphatic and aromatic hydrocarbons. The Tertiary aquifer was shown to be populated with relatively large numbers of bacteria including specialists for the degradation of chlorinated aliphatic and aromatic compounds. Direct evidence of reductive dechlorination was observed along the flowpath due to the appearance of intermediates and a decrease in the degree of dechlorination of the chlorinated aliphatic hydrocarbons. From these results it appears that vinyl chloride (VC) will ultimately accumulate as the endproduct of the anaerobic pathway. Similarly, indications were found that higher chlorinated chlorobenzenes were degraded in the aquifer leading to an accumulation of monochlorobenzene (MCB). Both of these substances are toxic and require aerobic conditions to be effectively attacked by microbes.

Further research efforts in the Tertiary aquifer should focus on a quantification of the attenuation reactions taking place in the aquifer. Concerning the remediation strategy for this site, making use of the existing biodegradation reactions should be assisted by technology that is able to create an aerobic environment, in order to take care of the recalcitrant end products.

ACKNOWLEDGEMENTS

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INTEGRATED SOIL AND WATER PROTECTION AGAINST DIFFUSE POLLUTION (SOWA)

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Abstract

SOWA aims to integrate soil and water protection issues in Europe by bringing together all disciplines involved in environmental research, which deal with diffuse pollution and behaviour of persistent pollutants in soils, sediments, and adjacent environmental compartments such as groundwater. SOWA provides a multidisciplinary forum for the identification of future research strategies by organising a structured series of workshops for researchers and regulators. In addition, innovative, rapid and low cost screening methods for the detection of contaminants in soil and water such as sensors and magnetic proxies for soils and sediments are addressed. SOWA's major objective is the early identification of trends towards environmental damage. With that it will potentially save significant economic resources otherwise being spent e.g. for restoration of soils and eventually health care. The need for soil protection against diffuse pollution is not at all or only partially recognised in most of the European countries. SOWA intends to contribute to soil protection strategies, policies and regulation concerning the implementation of monitoring programs and related protocols on soil and water quality.

Introduction

Diffuse pollution is an imminent and progressing threat for soil and water quality. Many pollutants have already entered the water cycle either by direct emission of pollutants into surface water, groundwater, and the atmosphere or by pollution of soils by disposal of contaminated materials on land (Fig. 1). Many persistent pollutants occur globally which is an often overlooked, but relevant facet of global change (Lee and Jones, 1999). Facts available so far show that

- many manmade compounds are persistent, bioactive and accumulative in the environment
- some already exceed environmental standards in soils and water bodies at a regional scale
- many accumulate continuously in soils and sediments, which finally become secondary and long term contaminant sources.

In the hydrological cycle, water sooner or later interacts with soil and / or sediments, and this interaction determines the quality of groundwater, surface waters and finally drinking water (Fig. 1). Polluted soils, sediments, and waste materials can release contaminants into the water cycle. Clean, good quality soils, however, can remove pollutants from the water because of their filter, buffer and transformation capacity. Soil is the largest and most active compartment that governs groundwater and surface water quality and has therefore to be recognised as key zone between land surface and groundwater. Experience shows that large scale remediation of diffuse pollution is economically not feasible and that soil contamination is not reversible at a reasonably time scale. The motivation of SOWA is the protection of soil as the most active resource in the hydro- and biosphere and as the essential environmental compartment for food production and finally human health.

Fig. 2 shows the different compartments (pedosphere / lithosphere and hydrosphere) as well as media (air / water / solids) and processes, which are important for pollutant fate and transport. The complex nature of pollutant fate and transport in the subsurface environment requires to integrate soil and water protection issues. SOWA will support the integration and it will provide a platform to:

- evaluate especially diffuse soil pollution which will damage important soil functions (such as the buffering, filtering, transformation capacity) and the soil ecology.
- increase the awareness of the risks of diffuse soil pollution, which pose a risk of long-term contamination of the water cycle.
- bridge the wide gaps by integrating soil and water related research, regulation and policy making throughout the EU.
- identify tools and procedures for contaminant analysis, soil characterisation methods, and management of soil/water contamination in Europe.
- contribute to a harmonisation in standardisation of innovative, rapid, and low cost screening methods for the detection of contaminants in soils and water such as time integrative passive samplers (Martin et al. 2002).

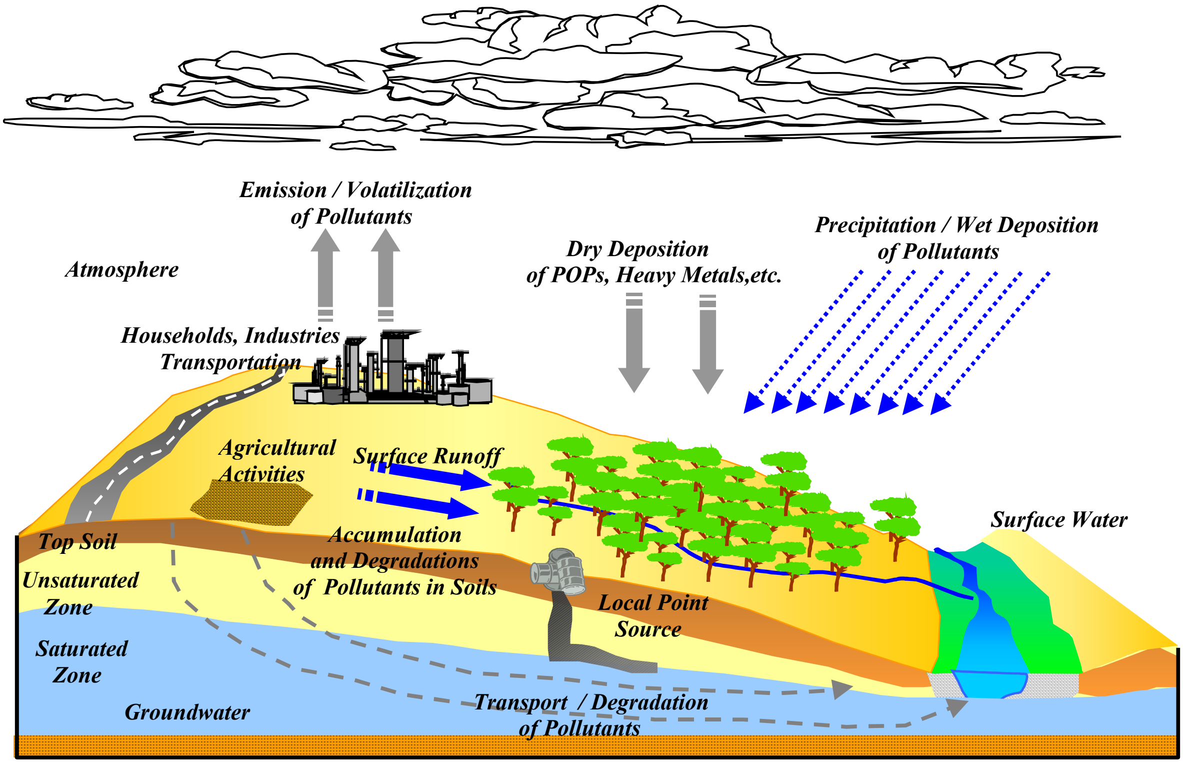

Fig. 1: *Pollutants in the water cycle: Soils can act as source (if accumulations or contaminants exceed the "critical load") and a sink (because of their retention, filter, and transformation capacity)*

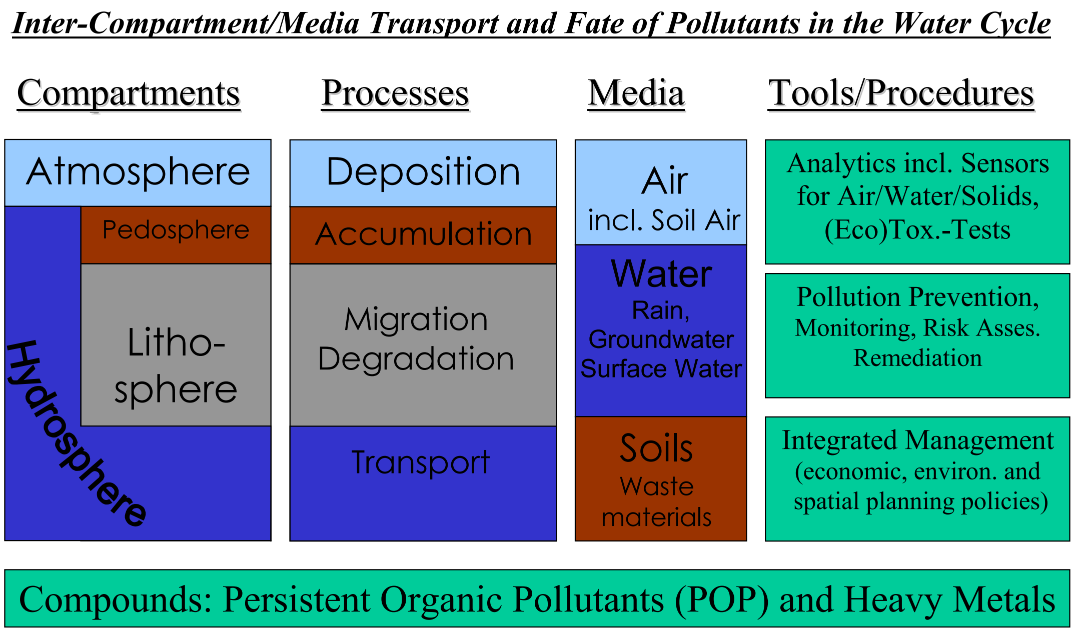

Fig. 2: *Scheme listing relevant compartments, processes and media addressed by SOWA*

Specific Goals

SOWA will organise a structured series of workshops and technical meetings in order to provide a platform for researchers of different disciplines (soil science, soil chemistry, soil physics, hydrogeology, water resources, agriculture, atmospheric deposition of pollutants, environmental analysis and engineering, management and remediation of contaminated soil and groundwater) as well as for regulators, policy makers and industry for future joint activities in environmental research. Specific topics are to:

- pull together the critical mass of scientists needed for early recognition of the risks associated with diffuse pollution in soils and the water cycle.
- establish 5 thematic working groups who provide reports on key topics in soil and water protection:
  - *Inventory:* Identification of priority compound classes such as persistent organic pollutants (i.e. in addition to the “Stockholm POP list”) and heavy metals
  - *Tools:* Pollutant analysis and environmental monitoring
  - *Processes:* Fate and transport of pollutants in soil and groundwater
  - *Scale issues:* Processes and contamination at different scales - diffuse contamination, long-term accumulation, catchment scenarios
  - *Management* and remediation of contaminated soil and water
- provide proceedings/executive summaries of the workshops/technical meetings and recommendations / statements.
- install of a web-page, which will serve as communication, dissemination and exploitation platform of the state of the art and specific knowledge in soil and water pollution.
- provide a platform for integrated soil and water research and regulation activities in the future and to support future European Soil Protection Policies.

The results of all thematic groups will be presented and discussed in the workshops and technical meetings and be disseminated and communicated to the end users. Finally, the condensed results will be disseminated in a joint consensus paper.

SOWA will not only serve as a communication forum but will furthermore create a necessary and suitable platform for soil related future research activities. In the long-term, the activities of the forum could finally contribute potentially to a future European Soil Protection Directive and / or Regulation.

Conclusions

As a new, until now largely neglected target, SOWA emphasises long-term risks to water resources due to diffuse pollution of top soils. This issue is not at all or only partially implemented in regular monitoring programs of many of the European countries. SOWA therefore can help decision makers to develop or optimise monitoring programs and related protocols concerning the deposition and accumulation of contaminants in soils. Hereby, the new innovative focus is set on the investigation of a cross contamination of varoius compartments within the water cycle likely leading to trends in deterioration of ecological and socio-economic soil functions. In addition SOWA focuses on innovative, rapid and low cost screening methods for the detection of contaminants in soils and water such as sensors and magnetic proxies for soils and sediments. It can help to prepare standardisation of such innovative technologies in Europe and therefore contribute to a better harmonisation of methodologies in the EU.

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ASSESSING RISKS POSED BY LAND CONTAMINATION AND ITS REMEDIATION ON ARCHAEOLOGICAL RESOURCE MANAGEMENT

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Key words: archaeology, land contamination, risk assessment, remediation

Summary

There is potential conflict between protection of the UK's cultural heritage and the cost effective remediation of land affected by contamination. Two of England's leading governmental bodies responsible for land contamination (the Environment Agency) and archaeology (English Heritage) respectively have jointly commissioned a project to develop guidance to assist regulators and others in the UK to evaluate the risk posed to archaeological resources by land contamination and its remediation.

The project is currently ongoing and the final output in the form of technical guidance report is due for release in Spring 2003.

This paper provides an overview of the content of the forthcoming guidance document.

1 Introduction

The UK has a legacy of land contamination resulting from its industrial history and the lack of adequate provisions in the past to protect the environment. Our cultural heritage is frequently associated with this legacy, and is sometimes the cause of it. Current UK Government policy promotes the redevelopment of previously used, and potentially contaminated, land. Thus it is possible that the assessment and remediation of contamination may have an impact on cultural heritage, especially vulnerable archaeological evidence. It is important to the preservation of the UK's cultural heritage that the presence of contamination or the activities undertaken to investigate, assess or remediate the contamination do not impact unnecessarily on these resources. Equally, it is important that the investigation and management of archaeological resources do not in themselves cause contamination of land or wider environment.

The UK has adopted a risk based approach to the assessment of environmental issues including land contamination. This approach is based on the source-pathway-receptor framework and for a risk to exist all three elements of the framework must be present. The two main legislative provisions for dealing with land contamination are the Contaminated Land regime (Part IIA of the Environmental

Protection Act 1990) and the planning and redevelopment provisions. The Part IIA regime which introduced a statutory definition of ‘contaminated land’ (DETR 2000) deals with land in its current use whereas the planning and redevelopment provisions relate to the proposed use of the land. It is envisaged that the guidance may also be of use in other legislative contexts including for example the Pollution Prevention and Control (PPC) regime (DETR 1999).

England’s archaeological resource is one of the largest and best documented in Europe and includes material from more than half a million years ago to the modern era (Darvill and Fulton, 1998). The archaeological resource includes tangible surface remains such as buildings and earthworks, distinctive features of the landscape such as ancient hedgerows and characteristic landscape types such as those typical of a past industry or agricultural regime. Buried archaeological remains, often with no tangible surface indicator are also a valuable resource for providing evidence of our cultural heritage, including that of environmental change.

Some parts of our widespread and varied archaeological heritage are obvious or well-documented and afforded protection either by statutory means such as scheduling or listing or by inclusion on non-statutory Historic Environment Records such as the Sites and Monuments Records maintained by County, District or Unitary authorities. Knowledge of the known archaeological resource informs development and structure plans devised by the local planning authorities. In some instances these may identify areas with particular archaeological constraints on development.

However, many facets of the total archaeological resource of England remain undiscovered and undocumented. Often such remains come to light for the first time during the archaeological assessment and evaluation of a development site or during the archaeological component of an environmental impact assessment for a substantial development.

The guidance developed under this project is intended to serve as a supplement to, and should be used in conjunction with, other key UK guidance documents on both archaeological and land contamination assessment, investigation and management.

Although the target audience for the guidance is principally English Heritage and Environment Agency staff involved in the assessment and management of land contamination projects the readership is expected to be much wider. Thus in the initial stages of the project a draft scoping paper was issued for external consultation to a wide range of organisations involved in land contamination and archaeological resource management. These included Government departments, the professional bodies for a range of disciplines involved with assessing and managing land contamination and archaeological resources, environmental consultants and archaeological units.

The publication of the guidance will be supplemented by a series of awareness raising seminars for the target audience.

2 Objectives of the Guidance

The forthcoming guidance document is intended to provide detailed technical guidance on the risks posed by land contamination and its remediation on archaeological resource management and how to strike a balance between archaeological protection and other technical and regulatory requirements. Within this wider perspective there are a number of specific objectives including:

- The consideration of archaeology as a potential source of contamination, as a potential receptor and as a potential pathway for the transfer of contamination.
- The potential for techniques and investigations employed by archaeologists to contribute to the investigation and management of land contamination, or vice versa.
- The identification of remedial technologies including physical, chemical and biological treatments and processes used in the UK and their potential impact on archaeological resources.
- The consideration of the health and safety of workers and the potential limitations placed on archaeological investigation activities as a result of the contamination present.

3 Legislative Context

The main UK legislative contexts for the guidance are the Part IIA and the planning and redevelopment regimes. The Part IIA regime was inserted into the Environmental Protection Act 1990 by Section 57 of the Environment Act 1995 and came into force in England in April 2000 and in Wales in July 2001. The Part IIA regime deals with the current use of the land. The provisions of the regime may only be applied to defined receptors and in terms of archaeological resource this definition is restricted to Scheduled Ancient Monuments only. The regime defines the term “contaminated land” in terms of causing significant harm or the significant possibility of such harm or the pollution or likely pollution of controlled waters (DETR 2000). Significant harm to buildings including Scheduled Ancient Monuments includes structural failure, substantial damage or substantial interference with any right of occupation. With particular reference to Scheduled Ancient Monuments substantial damage also includes damage which significantly impairs the historic, architectural, traditional, artistic or archaeological interest by reason of which the monument was scheduled. The significant possibility of such harm relates to the likelihood of significant harm resulting from the pollutant linkage in question during the economic life of the building or in the case of scheduled ancient monuments, the foreseeable future (DETR 2000).

The planning and redevelopment provisions are concerned with the future or proposed use of the land. Land contamination and archaeology are both material planning considerations guided by planning policy guidance. In the context of land contamination and development the relevant planning guidance, Planning Policy Guidance Note (PPG) 23 (DoE 1994a) is currently under revision. A Draft Technical Advice Note was published for consultation in early 2002 (DTLR 2002) relating to development of land affected by contamination. As with the Part IIA regime the approach adopted is based on the principles of risk assessment, the source-pathway-receptor framework and the concept of unacceptable risk. The standard of remediation required through granting planning permission is the removal of unacceptable risk to the receptor and making the site suitable for its intended use.

In the context of the archaeological resource Planning Policy Guidance Note 15 (DoE 1994b) provides advice on planning issues relating to buildings and the historic environment. Planning Policy Guidance

Note 16 (DoE 1990) provides advice on the handling of archaeological remains within the planning process. It sets out Government policy on archaeological remains providing a framework to guide decisions on suitable preservation strategies. PPG 16 places the onus on the in-situ preservation of important archaeological remains, and preservation by record through excavation is seen as a last resort, where other strategies are not feasible. Unlike the Part IIA regime these planning guidance relate to important archaeological remains whether they are scheduled or not. Both PPG 15 and 16 are currently under review and, they are likely to be replaced by a single PPG setting out principles with supporting documents relating to specific issues.

4 Approaches to the Assessment of Land Contamination and Archaeological Potential

In the context of land contamination the risk based assessment and remediation of contamination is a phased, iterative approach based on the development and refinement of the conceptual model. The initial stages involve collation of information for identification of potential sources of contamination, potential receptors and any pathways that may link the two as well as the uncertainty associated with this information (Nathanail et al. 2002). As further information is collated the plausibility of these potential pollutant linkages can be assessed. The conceptual model developed in these initial stages should form the basis for all further aspects of the assessment and remediation of the contamination (BSI 2001). A site investigation is normally required to quantify the amount and distribution of contaminants across the site. The design of the site investigation is determined by the information collated and the uncertainties identified in the initial stages of the assessment. The information obtained from the site investigation allows an informed decision to be made as to plausibility of the potential pollutant linkages and whether or not a risk exists to the defined receptor. The final stage includes an evaluation of the uncertainties associated with the risk assessment process and a decision as to the acceptability of the risk from each plausible pollutant linkage. Depending on the outcome it may be decided that the risk is acceptable and no further action is required; the risk is unacceptable and risk management options need to be considered; or the risk is unacceptable and further detailed risk assessment focussing on the uncertainties identified is appropriate.

The process generally used for assessing archaeological potential on a site is quite similar to that for assessing land contamination in that it is a phased, iterative approach. Planning Policy Guidance Note 16 places a strong emphasis on a graduated approach to archaeological issues, moving from initial consultation and desk-based assessment, where appropriate to field evaluation in order to generate the level information necessary to inform the planning decision and devise a scheme of mitigation. At all stages there is a preference for the preservation *in situ* of archaeological remains or where this is not feasible for their preservation by record (i.e. excavation of those parts of the site that will be destroyed or significantly degraded by the development).

5 The Development of the Conceptual Model

The guidance draws on the similarities in the approaches used in both disciplines and focuses on the development of a conceptual model for the site incorporating land contamination and archaeological issues.

The initial information collection stages are considered vital for the identification of the potential sources of contamination, potential pathways and receptors and the possible presence of archaeological remains. If identified early in the investigation the presence of archaeological remains can be factored into the land contamination assessment and vice versa. The conceptual model may be further complicated in that the archaeological evidence may be a source of contamination or it may be a receptor or it may act as a pathway for the transfer of contamination.

In the UK our industrial history has provided much of our archaeological resource and this is a particular issue that requires careful consideration in the development of previously used land. For example a redundant gasworks may contain valuable evidence of industrial heritage including buildings and structures, industrial equipment, evidence for the development of gas generation and distribution processes over time, and residues of the raw materials and processes used. In some cases our industrial heritage including buildings and structures has been afforded statutory protection but equally many other remains have not. It is not only buildings and structures that may be of archaeological importance but also the soils, wastes and spoil and slag heaps which may contain evidence of past industrial practices or form features characteristic of past industrial landscapes. Structures of archaeological importance, for example pits and tanks may be extremely difficult to investigate as these are often significant sources of contamination. Sites where the archaeological resource is also the source of the contamination present a significant problem in devising an appropriate remediation strategy as it is necessary to balance the onus to preserve archaeological remains *in-situ,* or to extract information on past activity or technology through preservation by record, from material which may itself be a contaminant requiring appropriate remediation.

The archaeological resource present on a site as a source of contamination may also be associated with non industrial activities for example human and animal burial grounds where mercury (in teeth), lead (in coffins) and disease pathogens (anthrax in hair) may be particular contaminants of concern. Even suburban bonfires in the gardens of Victorian houses have been shown to give rise to elevated levels of heavy metals in the soils.

Archaeology may also be a potential receptor and affected by land contamination not derived from the remains. Contaminative land uses on or adjacent to the archaeological site may have a direct impact on the archaeological remains for example contaminant plumes from fuel storage areas may cause changes in the chemistry of the soils and thus directly impacting on the survival of artefacts and ecofacts. Contamination may have a direct impact on both above ground and below ground archaeologically important buildings and structures by rendering the fabric or deposit unsafe for preservation by record. The effects of the contamination are not always negative and it is possible that chemical impacts from contamination such as changes in soil pH, conductivity or redox potential may also help the survival of archaeological materials.

In some instances archaeological remains may provide pathways for the transfer of contaminants to other receptors. Buried archaeological ditches or trenches may provide pathways for contaminated groundwater. It is also possible that buried structures such as compacted floors may act as a barrier to the vertical transfer of contaminants forcing the contaminant flow horizontally into previously uncontaminated areas.

It is also necessary to recognise that land contamination and archaeological issues on the site may not be related and that activities undertaken to investigate, assess or mitigate one should not have a negative impact on the other. For example, archaeological remains, especially structures, may be a barrier to contaminant movement, and investigating them may create pathways for the transfer of contaminants to other receptors.

6 Benefits of Early Consultation

During any land contamination or archaeological assessment the benefits of early consultation between all parties involved, including among others the land owner, the consultant undertaking the contaminated land assessment, the archaeologist, the contractor(s) and the regulators, cannot be over emphasised. In the context of land contamination costly delays on development projects are often encountered due to the lack of communication between the relevant stakeholders. The Draft Technical Advice Note (DTLR 2002) explicitly highlights the benefits of early consultation between the applicant and the planning authority. PPG16 also seeks to reconcile the needs of archaeology and development by encouraging early consultation by developers with the planning authority in order to plan development around sensitive archaeological areas.

The development of a conceptual model for the site should help the consultation process and aid communication between the various stakeholders.

On any site the presence of archaeological evidence and/or contamination is costly to assess and investigate. In particular in the redevelopment context time is a key factor and delays arising due to a lack of understanding of archaeological issues among land contamination practitioners often results in unnecessary delays. Early consultation with the archaeologist can help protect the archaeological resource and reduce the likelihood of ‘accidental’ damage from site investigation or remedial techniques or the ancillary activities associated with these.

In practical terms the similarities in the approaches to assessing land contamination and to assessing archaeological resources could allow the transfer of information improving cost effectiveness and information quality. For example intrusive site investigations are costly and early consultation may help in the development of a more coherent approach to fulfill the needs of the land contamination assessment and the archaeological assessment.

Although early consultation will be beneficial it is important to recognise that the information requirements for a land contamination and an archaeological assessment are different and both need to be addressed.

7 Site Investigation Techniques

There are a wide range of site investigation techniques used in both the assessment of land contamination and the assessment of archaeological resources. The selection of appropriate investigation techniques needs to be driven by the conceptual model of the site and the potential pollutant linkages under investigation (BSI 2001; Barr et al 2002). In a land contamination assessment factors under consideration may include the type of contaminant, its spatial distribution, the presence of any structures on the site and the nature of the receptor(s). The purpose of the site investigation is to obtain information of sufficient quality and quantity to allow informed decisions to be made about the risk to the receptor.

The archaeological site investigation will seek to collect information on the spatial extent, date, character, state of preservation and significance of archaeological remains in order to prepare a mitigation strategy appropriate to the remains on the site.

On a site where both land contamination and archaeological resources are present there is the potential that the methods used to collect data for one may be appropriate for the other. For example the excavation of trial pits in a land contamination assessment permits the visual inspection of the soil profile and geology, the determination of the depth of shallow water tables and the collection of samples. In an archaeological assessment trial pit excavation allows the archaeologist to visually inspect the stratigraphy, assess the artefact density and the extent, character and state of preservation of archaeological remains, and to collect samples. The exact nature of the data requirements will be site specific and it may not always be necessary or cost effective to use the same investigation methods for both the land contamination and archaeological assessments.

It is not the purpose of the guidance document to provide detailed information on site investigation techniques which is available elsewhere (eg Environment Agency 2000a,b; Nathanail et al. 2002; McGill 1995). The guidance seeks to assist the user in identifying the potential for techniques employed by archaeologists or land contamination consultants/contractors to contribute to the investigation and management of land contamination or archaeology.

8 Remedial Options

In the risk based approach to the assessment of land contamination where an unacceptable risk is found to exist it may be considered appropriate on a site specific basis to undertake risk management measures to mitigate the risk. In some cases this may involve the use of remedial technologies and treatments. It may also be the case that the proposed development may not take place due to the prohibitive cost of addressing the risks from the contamination on the site or the risks to the archaeological resources, or indeed both.

On any site where archaeological remains are present it is important that a multidisciplinary approach is adopted as remediation measures may impact on the archaeological resources present and likewise the measures taken to protect the archaeological resource may impact on the contamination.

As with the site investigation the ancillary activities associated with the remedial measures such as the movement of people and vehicles across the site and their potential impact on the archaeological resources present need to be taken into account.

The guidance seeks to identify some of the most commonly used remedial treatments and technologies in the UK and their potential impact on archaeological resources.

Much of the importance of an archaeological site lies in the form, composition and sequence of its 'soft' deposits. Remediation techniques that involve bulk disturbance to these deposits will therefore be extremely destructive to the archaeological value of the site. Remediation techniques that involve localised disturbance to the deposits will also be destructive, but there will often be scope for designing the interventions in order to minimise this destruction. Techniques that do not involve physical disturbance to the archaeological deposits will in general be less destructive, but may involve degradation of specific aspects of the archaeological record as they may cause indirect damage to archaeological deposits due to changes in the physical or chemical environment (for example, degradation of waterlogged deposits due to lowering of the water table or oxygenation of the groundwater), and these effects may extend well beyond the target area of the treatment.

Most forms of remediation have the potential to impact adversely on archaeological remains. Soil disturbance will destroy archaeological features and context and may also destroy artefacts whereas changes in soil pH and groundwater levels may affect the corrosion of archaeological metals, organic artefacts and glass.

The guidance will also identify measures that may be taken to mitigate the impact of remedial techniques for example sealing the archaeological remains or zoning the site for a less sensitive end use thus removing the need for remediation.

9 Health and Safety

The health and safety of workers on a site is of primary importance and each site requires a site specific health and safety assessment. This guidance document seeks to complement existing good practice guidance on health and safety of workers on sites affected by land contamination and in field archaeology. It is not intended to provide detailed guidance on assessing risk to occupational health and safety but to highlight some of the issues that may need to be considered on a site where both archaeological and land contamination investigations are ongoing.

10 Discussion

In the context of land contamination, the awareness of the need to consider archaeological resources among land contamination practitioners is quite limited. Likewise archaeologists working on sites where there are potential contamination issues are not always well informed. This guidance document seeks to address these shortcomings and provide good practice guidance for regulators and others involved on sites where both archaeological deposits and land contamination are present, or suspected. The guidance will be generic and applicable across a range of statutory regimes including the Part IIA and planning and redevelopment contexts.

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Theme E:

Short Communications

Successful grassing system for mining

Egon Stalljann

Summary: Hydroseeding is a bioengineering technique which has gained a lot of importance in the grassing of extreme sites. Besides the application technique on its own, the selection and composition of suitable mixtures of seeds, fertilizers, stabilizers, mulch material and conditioners also play an important role. It is necessary to have sound knowledge of the physical, chemical and biological properties of the local soil to be grassed as well as to have some experience in the mechanical techniques. Furtheron, we are presenting our experinences with a newly developed hydroseeding method. Applied in the correct way, this new technique is a reliable tool in landscaping and bioengineering. The one who knows the possibilities and restrictions of this technique will be the one to achieve many successful grassings of extreme sites.

1 Problems

Man is permanently causing severe intrusions to the environment by, for instance, trafficway construction, by coal and ore mining, the excavation of mineral raw materials (gravel, sand, rock), the dumping of waste material (household wastes, mining wastes, ashes, slags) and by the construction of dams and buildings. These ‘wounds‘ to the natural surroundings have to be healed by suitable grassing as soon as possible.

To perform such grassings, it is required to use the instruments of landscaping and bio-engineering techniques. Besides the reintegration of such sites into the natural environment, it is also important to stabilize the site with the right measures of erosion control against wind and water, and against land slides and settlements.

Different problems arise in the recultivation of plants on damaged areas whether using the natural succession or grassing as a measure of renaturation and erosion control. Many of these problematic areas left behind show extreme conditions regarding erosion risk, micro-climate, water and nutrient balance, soil life, soil reactions, pollution by sulphurous compounds (coal mining), salts (potassium mining, ash dumps) and heavy-metal loads (mining). In the following, these severly damaged areas are called ‘extreme sites‘.

The most endangering conditions to the plants are a poor water and nutrient supply, extremely acid or extremely basic soil reactions, very high temperatures up to 70°C, large differences in daily temperatures up to 45°C, high salinity, heavy-metal loads and strong erodible forces. That is the reason why the plants often have to face hard conditions, and man has to lend a helping hand.

Besides the extreme site conditions, man is also obliged to assist in recultivation and grassing of such sites because of the need for instant stabilisation, i.e. the state-of-the-art performance of recreating measures at the requested intervals of time.

This lecture has the aim to report the possibilites of grassing extreme sites, and to describe our experiences in the fields of coal mining, potassium mining, ash dumping and rock stabilisation. This is to introduce to you hydroseeding methods combined with organic slow-release fertilizers with the addition of erosion protection systems, the support of natural succession by soil amelioration and the use of indigenous seed material in combination with soil stabilization and amelioration.

2 Approaches

2.1 Suitable seeds and support of the natural succession

One important thing to do in grassing of extreme sites is to choose the right plants, i.e. mostly seeds of grasses and herbs which are either cultivated for this special purpose or which come from indigenous plants. Indigenous seeds (authochtonus seeds) are either obtained by intended reproduction on special fields or by the mowing of meadows for hay production (hay threshing). The respective seeds to suit the special site conditions are then mixed accordingly.

One can even make use of the seeds which are carried onsite by wind or by animals moving around. However, the process of grassing extreme site can take several decades. The process of recultivation by natural succession can be accelerated in two different ways. In both cases, the extreme sites have to be prepared by fertilization and soil amelioration.

On the one hand, one can leave out the seeding and rely on natural succession alone. On the other hand, one can apply a little amount of seeds (only a few grammes per square meter). This method leads to gaps in the vegetation cover which can be closed by the seeds of the native plants (PURWIN et al., 1991). Thus, one can achieve a fast and suitable erosion control. This kind of grassing of extreme sites contributes to the conservation of numerous species (biological diversity).

2.2 Biological soil amelioration and support of the root growth

Extreme sites such as raw soils, wastes, ashes, slags which cannot be cultivated as required have to be treated by long-term soil amelioration to improve their properties. The aim is to obtain at least the minimum nutrient level of a lean grass cover in the long term. The ability of an extreme site to become cultivable is not only dependent on its physical surface structure, but also on its biological activity.

Many of the extreme sites created by man are biologically dead at the time of creation. One prerequisite to establish a successful vegetation is sufficient soil activity which cannot be achieved on its own by the developing root network. In this case, biologically degradable substances have to be added to the soil. Such substances can be, e.g. special preparations from biomass containing soil fugi and bacteria.

The efficiency of such substances is the better, the more they are like the biomass naturally contained in the soil, e.g. biomass on the basis of soil fungi and bacteria living in the soil or energy-rich sugar compounds on the basis of sugar phosphoric amides which are present in all living cells. These substances do not only activate the soil life, but are also a long-lasting slow-release nutrient source due to the microbial degradation processes taking place.

Sugar phosphoric amides applied to the soil in liquid form are more advantageous, because they are conveyed deeper into the soil and thus enhance the root growth.

Long and massively growing roots are a good soil stabilizer (erosion protection), increase the shearing strength (which is of importance on football fields), loosen up the soil (structure) and improve the water and nutrient supply to the plants.

2.3 Organic slow-release fertilization

Besides the soil amelioration, fertilization is of major importance to the solution of grassing problems. As already mentioned, most of the extreme sites have the characteristical problem of acute nutrient deficiency and low nutrient storage capacity (STALLJANN 1987, 1997). This lack of nutrients is balanced by the application of fertilizers. Fertilization can be effected in different ways, i.e. aspects like ecological compatibility, long-term effectiveness and economical efficiency have to be taken into account.

In extreme sites, it is generally recommended to use organic slow-release fertilizers; biomass of soil fungi and bacteria have turned out to be the best. Mineral fertilizers are not likely to be effective, because of their high water solubility and the risk of being washed out easily.

Organic fertilization with fungal and bacteria biomass means that the soil is provided with substances which are naturally contained therein. The nutrients are organically bound and are only released through the microbiological decomposition process. Since the micro-biological decomposition and the release of nutrients from the organic substance are also dependent on the micro-climatic conditions (heat, cold, dryness) like the nutrient absorption by the plants, the correct application of organic fertilizers protects it from being leached out.

Therefore it can be concluded that organic fertilization of extreme sites has the following advantages:

- amelioration of the soil structure
- increase of the water storage capacity
- improved aeration
- reduction of the soil consolidation
- humification
- increase of the nutrient storage capacity
- long-lasting slow-release nutrient supply
- activation of soil life
- increased mobilisation and availability of nutrients of the mineral soil components
- high ecological compatibility
- no contamination through coming-in pollutants and nitrate leaching

2.4 Bioengineering measures of slope stabilisation

If there are slopes in extreme sites, the problems to be solved in the aspect of erosion control are even greater. The seeds applied as well as the organic fertilizer and soil conditioners have to be fixed by means of soil stabilizers. These soil stabilizers are natural or artificial substances or liquids which are dissolved in water and applied together with seeds, fertilizer and soil conditioners by the hydroseeding method. After application all substances adhere to the soil surface. The effect of such stabilizers is described by STOYE (1987) and STALLJANN (1999, 2000).

The amounts to be applied are dependent on the kind of stabilizer, the erosion problem(s) to be expected, the duration of fixation and the roughness of the superficial structure. Soil stabilizers have to build a water-permeable layer, but must not cause environmental stress. They have to be biodegradable and must not delay the germination process in a significant way.

Erosion control which can be obtained by soil stabilizers is strictly limited and must not be overestimated. Generally, it has to be mentioned that surfaces treated with soil stabilizers must not be walked or driven over; the stabilization layer would be damaged by such mechanical stress. On the other hand, it has to be pointed out that the application of soil stabilizers cannot prevent soil slides or settlements.

Erosion damages cannot be avoided by soil stabilization in case of cloudbursts, coming-out water, and water running down the slope surface at individual spots. In fact, soil stabilizers tackify the seeds to a rough surface, but they cannot reinforce the soil surface itself. The soil stabilizing effect is limited by time and depends on the amount applied, the micro-climatic conditions and the superficial soil structure as well.

In certain cases it is meaningful to improve the soil stabilizing effect by adding erosion protection fibres (wood, cellulose or cotton fibres). They all have the advantage of being biodegradable, and due to their fibre structure reinforce the fixation layer. Moreover, they improve the superficial water absorption.

Regarding extreme sites which are especially endangered by erosion, so-called erosion protection mats are used to improve the effect. Such mats which can be used in combination with the hydroseeding method, are:

- Net-like mats made of jute, sisal or coir as well as plastic geogrids (mesh size: from 1 to 4 cms). These mats allow the grassing mixtures as well as the soil conditioners and fertilizers to pass through without any problems to reach the soil surface which is necessary to become effective. These mats are mainly used to neutralize the traction forces and to slow down the rain water running down the slope.

- Mulch mats made of straw, coir or other plant fibres, the mesh sizes of which have to be large enough to let the seeding mixture pass through the layed-out mats to reach the covered soil surface.

3 Examples of extreme site grassing

3.1 Coal mining

Coal mining leaves large-scale waste dumps and heaps as well as cut-out areas behind. These sites are generally dry and poor in nutrients; the partly very acid pH vlalues are based on the oxidation of sulphurous compounds. pH values in the range between 1 and 3 are quite often. Superficial soil temperatures can reach up to 70 °C; they can vary up to 45 °C during one day (STALLJANN 1984, 1985, 1999; STALLJANN & ABRAHAM, 1996).

In the following, a grassing project in the stone-coal mining area in Oberschlesien/Poland is described (table 1). The Polish mining operators used to cover the waste dumps with top soil or raw soil and to establish a vegetation cover on top. Due to the high steepness of slopes and decreasing soil masses as cover, they had to find another method by which the existing waste dump material could be grassed directly. Therefore, the FRISOL –system (STALLJANN & ABRAHAM, 1996) was chosen by which good experiences could have been made in stone-coal mines in the ' German mining territory 'Ruhrgebiet' (STALLJANN, 1984) and good grassing results in lignite open-cast mines in Middle Germany.

A closed and vital vegetation cover had developed only one year after application, and the roots were measured to exceed 35 cms in the local waste dump without top soil covering (figure. 1). A same result was observed on a landfill area covered with sandy raw soil. Here the roots were measured to exceed 45 cm in the sandy soil one year after grassing (figure. 2).

Fig. 1: Root lengths measured one year after grassing of a stone-coal waste dump (left)
Fig. 2: Root lengths measured one year after grassing of a sandy waste dump (right)

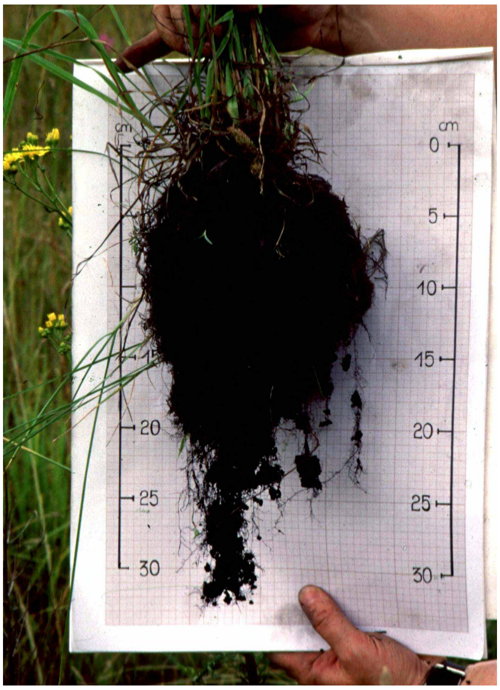

Table 1: Grassing project in the stone-coal mining district of Oberschlesien/Poland

Project:	Stone-coal mining / Poland
Period of time:	autumn 1996
Material:	stone-coal mining waste
pH value:	3.8
Inclination:	1 : 1
Method:	FRISOL method
Successful grassing since:	spring 1997
Composition:	Quantity per m²:
Biomass of soil fungi	250 g
Sugar phosphoric amide	120 g
Soil stabilizer on polybutadiene basis	20 g
Erosion protection fibres	50 g
Seeds suited to the location	25 g
Lime	5000 g

3.2 Potassium mining

German potassium mining is winning crude salts in underground mines. The residues of winning are mostly rock salts which are piled up. The heaps are pointed or flattened cones with steep slopes (angles of inclination: 34° up to 40°) of white or light red color. Due to their untypical morphology, they are a disturbing factor to the natural environment.

The dump substrates show extremely high contents of salt. The dump surface gets hard and crusty and changes permanently due to disintegration and recrystallizing processes. The slope flanks are often longer than 100 m, have no berms and are therefore not accessible. Some waste dumps create a less vegetation-incompatible surface of hardly soluble or insoluble substances. The establishment of a vegetation cover is prevented by the poor nutrient supply, insufficent water storage capacity of the substrates as well as the extreme climatic conditions on dumps (LÜCKE, 1997).

In the following, we are presenting the pilot project of the potassium waste dump ‘Bleicherode‘, Germany (table 2) in the course of which grassings with different methods should be investigated. One of the methods applied and tested was the FRISOL-system. It could be shown that, under certain site conditions, this method was able to establish a closed vegetation cover with deep-reaching roots on a potassium waste dump without soil cover.

Table 2: Grassing project on the potassium waste dump of ‘Bleicherode‘, Germany

Project:	Potassium waste dump
Period of time:	autumn 1994
Material:	potassium waste
pH value:	8.7
Inclination:	1 : 1
Method:	FRISOL method
Successful grassing since:	spring 1995
Composition:	Quantities applied per m²:
Biomass of soil fungi	400 g
Sugar phosphoric amide	200 g
Soil stabilizers on polybutatiene basis	25 g
Erosion protection fibres	100 g
Seeds suited to the location	25 g
Erosion protection mats	jute mats

3.3 Ash landfills

Coal power stations produce lots of ashes which have to be dumped in dry or wet condition. In order to minimize wind erosion and as a suitable measure of dust binding, it is desirable to soon establish a closed vegetation cover on the created landfills. Due to their physico-chemical properties, recultivation of such sites may cause considerable problems.

Due to the missing organic substances, no stable aggregates can be formed and, especially in case of wet-disposed ashes, it can cause layer-wise consolidations which make it difficult for the plant roots to penetrate. The nitrogen content is often poor, compared to high total contents of phosphorus which cannot be used by the plants in many cases. This deficiency can however be balanced by fertilization. Approximately 2 to 5 % of the ashes are soluble, resulting in high salt concentrations as well as pH values between 9 and 12 of the soil solution. Further stress factors are an unfavourable water balance and extreme micro-climatic conditions (INSAM & STALLJANN, 1989).

The following was a project located near Frankfurt/Oder in Germany (table 3). The ash landfill of Brieskow-Finkenheerd which was about 50 hectares in size, should be closed up in 1991; it should be covered with a 50 cm topsoil cover and subsequent grassing. In a pilot trial of applying FRISOL directly to the ashes without topsoil covering, it could be shown that the existing landfill could be successfully grassed for long (figure 3).

Fig. 3: Vegetation cover of a ash landfil, three years after grassing

Table 3: Grassing project of the ash landfill Brieskow-Finkenheerd, Germany

Project:	Ash landfill
Period of time:	autumn 1991
Material:	disposal ash of a power station
pH value:	11.3
Inclination:	plain area
Method:	FRISOL method
Successful grassing since:	spring 1992
Composition:	Quantity per m²
Biomass of soil fungi	350 g
Sugar phosphoric amide	150 g
Soil stabilizer on polybutadiene basis	30 g
Erosion protection fibres	20 g
Seeds suited to the location	30 g

3.4 Rock slopes

The construction of new and improved trafficways (roads and railway tracks) leads to cutouts which produce embankments, dams and earth walls alongside the tracks. These earthworks can be composed of different layers depending on the geological properties of the soil of each respective location. Necessary works in civil engineering cause the formation of unnatural compilations of soil in form of embankments. In order to keep their ground surface at a minimum, the slopes often have a ratio of inclination of 1 : 1.5. This causes problems in case of easily erodible soils such as loess and clay and the like. The stability of such slopes is considerably affected by rain and ground water. Steep slopes covered with topsoil are also subject to erosion. Erosion damages can be effectively prevented by a vital vegetation cover, the roots of which grow deep into the soil. If, such a vegetation cover does not provide enough protection against erosion, additional technical measures become inevitable to stabilise the embank-ment. Since erosion damges caused to the embankments algonside roads and railway tracks cause high recreation costs, it is recommended to apply methods of soil amelioration and grassing which are suited to the location and which require no additional soil cover.

In the following, we present the grassing project of the A7 motorway near Hannoversch-Münden/Germany (table 4), in the course of which a rocky raw soil embankment has been successfaully grassed by the FRISOL method without topsoil covering (PURWIN, WAGNER & STALLJANN, 1991). Even 12 years after grassing, a closed and massive vegetation cover can be seen with numerous other species (grasses, herbs and shrubs) which have immigrated from the surroundings (figure. 4 and 5).

Table 4: Grassing project of the A7 motorway, Hannov.-Münden/Germany

Project:	motorway, Germany
Period of time:	summer 1989
Material:	rocky raw soil
pH value:	5.6
Inclination:	1 : 1.5
Method:	FRISOL method acc. to DIN 18918
Successful grassing since:	autumn 1989
Composition:	Quantity per m²
Biomass of soil fungi	450 g
Sugar phosphoric amide	150 g
Soil stabilizer on polybutadiene basis	25 g
Erosion protection fibres	50 g
Seeds suited to the location	34 g

Fig. 4 and 5: Vegetation cover of a rocky raw soil embankment before (left) and 3 years after grassing(right).

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REDUCING THE RISK FOR TAILINGS FACILITIES

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Introduction

Tailings are fine-grained wastes of the mining industry, output as slurries, due to mixing with water during mineral processing. Tailings facilities consist of tailings ponds or lagoons, tailings dams and tailings transport systems (usually pipelines). Though separate units, the mineral processing mills have great influence on the operation and safety of tailings facilities.

Deposits of these residues in ponds, usually confined by man-made dams, can present a serious threat, especially where there is improper handling and management (ICOLD, 2001). Recent accidents at tailings facilities, such as the Baia Mare (Romania) and the Aznalcóllar (Spain) disasters, resulted in major threats to the environment and human life. Serious hazards posed by failing tailings facilities (leaks, overflow, breaking dams etc.) include

- floods and flood waves
- spills of sometimes toxic sludge and waters
- spills of sludge and rubble, burying houses or settlements and their inhabitants or destroying cropland
- contaminant spills into the environment (e.g. cyanide)
- pollution of rivers and their flood banks
- poisoning of aquatic life including massive fish kills.

Due to typically low concentrations of the useful component in mineral ores, large amounts of tailings are produced, requiring extensive tailings ponds to contain them. The most critical element of tailings facilities is usually the dam. The highest tailings dam today is as high as 230 m. Tailings dams fail ten times more often than conventional dams (73 failures occurred world-wide since 1960). The most common causes of failure are related to the forces of water, e.g. by internal erosion of the dam material or by overtopping of the dam. Dam integrity is thus particularly important under extreme weather conditions. Between 1928 and 1998 more than a thousand people lost their lives all over the world due to dam failure in tailings facilities.

Tailings dams are usually constructed using part of the material coming from the milling process. This is achieved by using hydrocyclones at the end of the pipelines transporting the slurry from the mill.

The coarser particles (sandy fraction) are used for dam construction, while the fines are deposited in the pond. A high percentage of fines in the tailings results in long settling periods, sometimes several years. In handling large amounts of inhomogeneous wet slurries, water management is a key safety factor. Deficient water management is one of the main causes of accidents and hazards emanating from tailings facilities.

The traditional construction method for tailings dams has been the 'upstream'-method (Figure 1), providing only a thin shell with instability implications. The downstream method yields better stability but requires considerably larger amounts of solids.

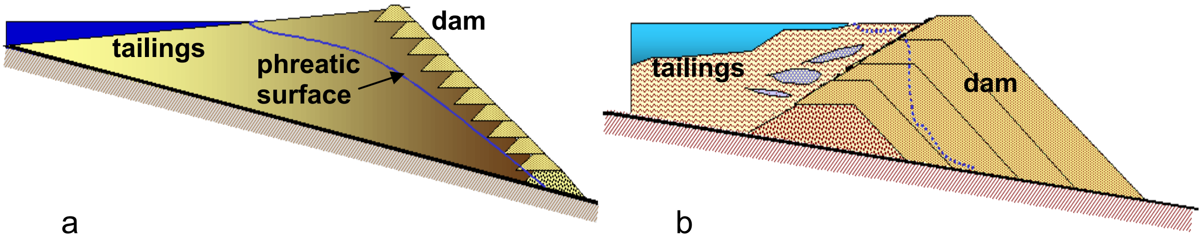

Figure 1: Tailings dam construction schemes: (a) upstream method, (b) downstream method.

Due to contact with the tailings, water seeps through the dam towards its free face (up to what is known as the 'phreatic surface'). On emerging at the downstream dam face, springs will form leading to loss of stability and, ultimately, failure of the dam. Unlike the large dams of water reservoirs, tailings dams are constructed without any impervious core, but drainage is provided to control the phreatic surface and prevent such springs occurring.

Though safety aspects and maintenance guidelines tend to be subject to regulation, they are not always as thoroughly or thoughtfully observed as they should be. Calculation methods for stability analysis are well developed, but often lack adequate input data. This lack derives from insufficient observations at operational facilities and existing dams. In most cases inspections are made only by visual or geodetic means. Sometimes boreholes, sampling and/or geotechnical tests are undertaken, but doing so can itself impair dam integrity. Non-destructive or geophysical methods have not been used as extensively as they perhaps should have been.

To reduce the risk posed by tailings facilities, within a major research project (“Sustainable Improvement in Safety of Tailings Facilities”, TAILSAFE) supported by the European Union, methods of parameter evaluation and measurement are being developed and applied for the detection, assessment and improvement of the safety state of tailings dams and ponds. Aspects of probabilistic stability analysis, water management involving paste technology, non-destructive (NDT) and minimally intrusive testing methods and monitoring methods, and intervention and practical remediation options are being considered. The results will be incorporated in a systematic risk reduction framework.

The investigations are focussed on the structural parameters of tailings dams stability, their measurement, and their evaluation as regards risk factors, with particular attention to:

- The stability of bodies of fine material and their liquefaction and mobilisation behaviour
- The special risks inherent when such materials include toxic or hazardous wastes
- Authorisation and management methods and procedures for tailings ponds and dams.

The project will advance the state of the art of tailings facilities safety in that a comprehensive parameter framework will be established to enable the systematic assembly and evaluation of parameters critical to tailings facilities safety. A wide range of parameters relating to design, materials, management, regulation and authorisation will be included in this risk reduction framework, so as to allow relevant stakeholders a better understanding and control of critical parameters for risk analysis. Special attention will be paid to pore pressure and piping, and methods for their measurement and monitoring developed further.

Site characterisation

All investigations aimed at improving the safety of tailings facilities require as reliable data as possible. For this purpose a catalogue of parameters will be established for the characterisation of tailings facilities sites, with special emphasis on geotechnical aspects. In a first approach the choice of parameters will be drawn from existing guidelines and regulations, and will be developed further based on additional experience gained in the project and geared to the needs of a practical risk reduction framework. The catalogue will consist of two or more investigation levels.

The first level will comprise the evaluation of existing data as available from literature or archives, or as supplied by site owners or authorities. Basic site characterisation and description will rely on data on location, type and size of the facilities, origin of tailings material, operating time, volumes deposited, geological, meteorological and hydrological setting, hydrogeological conditions of the site (maps and cross-sections), geotechnical key parameters, results of probes, drillings, tracer tests and sample analysis (if available), ongoing monitoring activities, legal issues and regulations, as well as foreseeable development of the site.

Further levels of detailed investigation will in general cover the same parameter catalogue as for the first investigation level, but will supplement the data base of the site by acquisition of missing or additional field and laboratory data. Field measurements could include geophysical investigations to complete information on the geological structure of the subsoil or on the internal structure of tailings dams and tailings, drilling (core drilling), in situ investigations such as probing (penetration test, field vane test), hydrogeological tests etc. Sampling of tailings ponds and dam material could be followed by laboratory analysis for mineralogical composition of those materials.

On this approach a procedure for site characterisation will be proposed, including the design of forms and a database containing all relevant basic information on a tailings facility site. The site characterisations scheme will be implemented in the TAILSAFE framework, and will also be used for the characterisation and description of the case study sites and model sites that are part of the project.

Case study sites

Findings within the project will be tested at actual tailings facilities. A number of case study sites will be selected to facilitate this practical aspect of the project. Two model sites in central eastern European countries (Hungary, Romania) are already under direct responsibility of partners from these countries. Design, management and regulation aspects will be evaluated according to the conditions on these sites. The sites will also give the chance for the refinement and testing of the suite of measurement and monitoring methods developed in other workpackages of the project.

Based on the site characterisation parameter catalogue developed for the first investigation level and on the requirements and needs of the technology developers within the project, one or two model sites will be selected as field test sites for the project. The sites will be chosen according to their suitability to support the approach and research work of the project, but also to their availability and accessibility. These sites will be investigated in detail. Additional characterisation of the two sites will be done by conventional methods to get calibration data for the new technologies. Preparation of test sites for technology testing (legal and technical issues) will be made here.

Material parameters

For the geotechnical and geoenvironmental characterisation of tailings a number of mineralogical, geomechanical and geochemical investigations will be conducted. These will in principle be a basic mineralogical analysis and a soil mechanics and contaminant survey of bodies of tailings. Sampling of dam and sludge material will be conducted on case study sites and model sites. A sampling strategy will be developed based on existing information provided by site owners and taking into account the possibly high variability of material parameters within typical bodies of tailings. Customary safety measures are to be followed throughout the sampling, due to access difficulties and the sometimes hazardous nature of the materials.

The samples will be mineralogically characterised by X-ray diffraction (XRD), thermal analysis (TA), quantitative chemical analysis, and measurement of carbon content (organic/inorganic), cation exchange capacity (CEC) and the specific surface (porosimetry).

Geotechnical key parameters to be investigated are moisture content, grain size distribution, grain and bulk density, maximum water uptake, plasticity, water permeability and shear strength. Additionally, as an important issue for the usually fine-grained tailings, the flow-deformation behaviour of fine hydraulically placed non-plastic materials will be investigated.

The chemical status of tailings bearing potentially toxic or environmentally harmful contaminants will be studied by analysis of the bulk chemical composition, contaminant content and contaminant mobility, and pH measurements. Analysis of contaminant mobility can be achieved by standard leaching tests or sequential extraction analysis.

The data measured within the project will be supplemented by collecting analogous data of other sites from reports and compiling them into a review database. The project's own data will have to be evaluated in context of this review database, and integrated into the spreadsheet/parameter framework.

Risk and Reliability

As a recognised environmental problem, two types of hazard with regard to tailings facilities are distinguished.

The first one is land contamination and groundwater pollution as a product of minerals extraction and direct emission of contaminants from the pond. The chemical pollution potential of tailings ponds is a major subject which is not dealt with in this paper. The occurring phenomena and the risk presented in terms of damage to the ecosystem can be managed by the common source-pathway-target frameworks used to quantify the harm posed by contaminated land (Petts et al., 1997). The main contaminants are radioactivity, remnant cyanide and formation of acid seepage. The problem is to define the point at which a contaminated site presents an unacceptable environmental risk. Guidelines deduced for urban areas cannot be applied to tailings facilities.

The second type of hazard is the failure of tailings dams, which are traditionally constructed of tailings using the upstream method (Figure 1a). As opposed to the first kind of risk, dam failure happens suddenly or within a short period, often with little warning. The well known effects are flood, slurry and mudflow that move downslope. The typical modes of failure are affected by different causes such as dam overtopping, seismic impacts, landslides within the valley of the basin or structural dam failure due to instability and unexpected seepage forces. To prevent such accidents the general view is that a risk assessment or reliability study must be carried out in the planning and operation phase as a part of Environmental Impact Assessment. In addition, this risk assessment can help focus on cost-effective approaches to remediation of existing tailings dams and ponds.

Depending on the available data, risk assessment can be carried out in a more or less quantitative manner, starting from a qualitative identification of possible hazards to a quantitative risk evaluation concerning the probabilities of failure and its economic consequences. Concerning geotechnical issues such as reliability and stability of existing tailings dams, considerable lack of knowledge must be faced even though structural data are available. Building up a tailings dam over a long period of times implies trends and random variation in both building technique and mechanical behaviour of the material. Therefore analysis must deal with a high degree of uncertainty and random effects. Fundamental thoughts about uncertainty and reliability in geotechnical applications are discussed in Baecher (1997).

The procedure is to create a systematically structured model of events that could lead to failure and to combine this so-called event tree or fault tree with the probability of occurrence. Therefore the formal steps are:

1) defining what failure means,
2) identifying the initiating events,
3) building up an event tree or fault tree for the system,
4) developing models for calculating the individual components,
5) checking correlations among those components,
6) deducing or determining probabilities of the events, parameters and processes and calculating system reliability.

Some examples concerning geotechnical problems are reported by Wu (1989) and Vick (1997).

The assessment of risk and reliability of a tailings facility needs disaggregation of failure sequences into component parts. One such component is failure of the tailings dam itself. However, dealing with even such a discrete component requires detailed knowledge both of the dam structure and spatial distribution of the different materials. Both fields will be studied within the TAILSAFE project. Uncertainties in the mechanical behaviour of the tailings deposited behind the shell (within the pond), as well as soil water effects, will be investigated with the help of geophysical methods under developement. Based on these results, the reliability of tailings dams and its improvement can be modelled in a probabilistic approach.

Stability analysis, one typical branch in an event tree, will be carried out in a probabilistic manner. The problem is too complex to use common methods such as first-order second-moment or Hashofer-Lind approaches. Thus other methods will be applied such as point estimate, response surface and Monte Carlo techniques. With such techniques the effect of spatial averaging will be investigated to describe the influence of spatial variation. However, the problem here is not to find an adequate method for calculation but to apply available techniques in the realistic prediction of the distribution of relevant parameters influencing the reliability of the structure.

Even if it is logically consistent and as comprehensive as practical, the analysis of risk and reliability is neither unique nor entirely replicable. The advantage is the systematic approach and transparency of uncertainty. In addition, unknown but supposedly conservative assumptions are replaced with best estimates.

Environmentally friendly tailings transport

Tailings are generally produced in slurry form. In addition to striving for an economic solution, aspects of environmental protection must be considered in choosing the method for slurry transport from the mill to the disposal area. Slurry may be transported by pipeline, which is usually both an economical and environmentally friendly technique, in which pumps or gravity head can be used, the latter if a suitable downhill route is viable. The design of slurry pipelines requires an analysis of the slurry, in order to predict friction gradients and critical deposit velocities (heterogeneous suspensions) or laminar/turbulent transition (pseudo-homogeneous slurries). If the tailings are produced in non-wet form, other methods of transport (lorry, conveyor belt etc.) or reslurrying may be considered. Reslurrying or producing slurry from originally dry materials, may sometimes require sophisticated technical solutions (e.g. for pulverised fuel ash etc.) (Debreczeni et al., 1992).

Short pipelines may be designed using empirically derived methods. Design and construction of longer pipelines with large throughputs and major influence on the overall systems reliability must be based on laboratory pipe loop testing. The diameter of the laboratory pipe must be as close as possible to the real pipeline to reduce uncertainties in scaling up the results. Effects of variation in grain size distribution and slurry concentration must be assessed in the laboratory tests. Optimisation of the transport parameters (both fluid mechanical and particle properties), selection of the pipeline transportation system, route, pipe size, pipe material and slurry pumps have major influence on transportation costs and reliability. Common failure types are excessive pipe wear, plugging and shutdown if no proper pipe diameters have been selected. The pipeline must be provided with a means of flushing, for cases of stoppage either due to breakdown or scheduled interruption. The basic data or parameters of the pipeline transportation system are (ICOLD, 1995):

- throughput or mass flow rate of solids
- particle size distribution and specific gravity
- transporting medium (usually water)
- slurry concentration and its possible variations
- pipeline length, route, pressure (head) required.

The flow can be considered homogeneous when most particles are smaller than 300 micron. They are fully then suspended in the carrier fluid, the solid particles have the same flow pattern as the fluid particles and there is no concentration distribution along the vertical axis of the pipe. In this case a pseudo-viscosity and pseudo-density can be attributed to the slurry and the type of viscosity is non-Newtonian as opposed to water which is a Newtonian liquid. Flow of homogeneous slurries can occur in both the laminar and turbulent regions.

Heterogeneous flow develops if there are larger particles in the mixture that tend to settle during transport. There is then a distinct concentration distribution along the vertical axis, the concentration is greater on the bottom than at the top. The main forms of particle motion are: suspension, saltation, sliding bed and stationary bed (when some of the particles may stay on the bottom of the pipe, still maintaining the flow for the rest). Heterogeneous flow always takes place in the turbulent region. In practice a combination of the two flow regimes takes often place: coarse particles are transported in form of a heterogeneous flow, in a homogeneous carrier fluid consisting of water and fine particles.

In most cases pumps are needed to establish a steady transport of tailings slurry from the mill to the tailings pond or lagoon. For shorter distances and greater flow rates centrifugal pumps are best suited: they can handle large amounts of solids but produce relatively low head. Positive displacement pumps can develop very high heads but the flow rate (amount of solids) is limited. Their typical applications are for long-distance transport, high elevation, high concentration and high viscosity slurries. Commonly used types of positive displacement pump are plunger, piston, diaphragm, two-cylinder piston and helical rotor type pumps. Tailings transport is also possible in open gravity flumes in cases where the terrain provides sufficient gravity head.

In addition to the aspect of pipeline transportation itself, slurry disposal also influences the desirable slurry properties. The reason for this is that not only tailings but water too has to be handled in the disposal area (tailings pond or lagoon) and increased amounts of water are accompanied with increased costs of water handling. The intention has thus been to reduce slurry concentration in order to minimise the additional costs due to water handling and disposal.

Two major ways have been followed in this effort: dense-phase flow and paste technology. In dense-phase flow, a conventional fluid mechanical approach is applied, i.e. transport of tailings particles suspended in water, but using the highest possible concentration without risking pipe plugging. Paste technology has carried on even further in this direction: the transported mixture contains up to 76 % per cent solids (Landriault et al. 2001), the particles are no more in suspended state and they do not flow, but rather slide in a form of plug flow in the pipe (like the tooth paste out of the tube). To achieve this form of transportation highly efficient dewatering is required plus high-pressure positive-displacement pumps.

The main benefits paste technology provides are (almost) no water handling problems at the disposal site and great stability for the transported tailings. Paste technology is primarily applied in mines for underground backfill and filling other cavities, but its use in surface tailings disposal and fly ash disposal in power plants is also on the increase. Consideration is being given to paste technology in the management of acid mine drainage and dredge sediments, and in dam construction for slurry impoundments. All these applications benefit from a cement-like setting behaviour of tailings, which strongly depends on material type. Additives (e. g. cement) may improve the required properties.

Field experiments

Measurement and monitoring technologies adapted for use in tailings facilities will be tested in field trials at the case study sites. Geophysical techniques as Spectral Induced Polarization (SIP, a refinement of the more common geoelectrical techniques), Radar (GPR) and seismic methods are going to be used to investigate the internal structure of the dams. They are expected to deliver results on the analysis of fluid content and fluid movement, which is important for the overall stability analysis. Other techniques (i. e. temperature measurements, self potential method, etc.) will be implemented to monitor changes of fluid movement and dam stability.

Extensive trialling and refinement of the chosen measurement equipment is planned and the measured data and interpreted results will be incorporated into the spreadsheet framework. Recommendations for stabilisation, remediation, technology changes and risk management for the test sites will be derived as practicable.

Parameter Framework

The TAILSAFE project is thus to take a strong focus on certain innovative, relevant and tractable parameter evaluation and measurement work, but within an equally strong and systematic framework which shows how that focus relates practically to wider and generally better understood parameters. Its objective is to deliver not only improvements in the way some key parameters relating to the structural stability of tailings ponds and dams are measured and monitored, but also an evaluative framework which will help sharpen the way tailings facilities are classified and assessed for risk.

For the purpose of this project, then, it is intended to distinguish between *critical parameters*, being those which tailings facility designers and operators need to watch most closely, and *contextual parameters*, being those which help determine what levels of which critical parameters are most relevant in a particular situation. It will use a structured database and user interface to enable critical and contextual parameters to change as one proceeds through design, management and regulatory procedures relating to tailings facilities. While certain parameter values are to be targeted for basic research within the project itself, others will simply be taken from literature review, industry contributions etc.

This dual approach on focus and framework is reflected not only in the structure of the workpackages, but also in the composition of the TAILSAFE team. The team involves technical measurement and evaluation expertise on both mineral processing and geotechnical structures, plus partners with special expertise on regulation and enforcement or uniquely placed to tap into the minerals industry for data and advice. Moreover the project benefits from an independent expert advisory panel to inform, critique and validate its direction, work and outputs, and guide the team in tackling issues of real innovation, practical importance and viability.

The TAILSAFE project workpackages flow from an initial phase of technology and risk review, through successively more focussed and targeted work, but always building up and testing out the parameter framework as they go:

Initial Phase

This is review and definition work, to select and clarify parameters for focussed attention:

- Existing technologies of minerals processing and slurry handling, tailings facilities design procedures and authorisation, management, monitoring and inspection practices
  - extraction of standard parameters that are relevant for the stability and safety of tailings facilities and their normal ranges
- Reliability factors for tailings facilities, as expressed by impact, risk, instability and failure mechanism parameters
  - quantification of critical parameter levels and sensitivities.

The resulting quantified parameters will be incorporated into the TAILSAFE framework, which will begin life as a database with associated spreadsheets. There the parameters will be tracked, refined and elaborated throughout the project, and additions or adjustments made as appropriate. Attention will also be given to the acquisition and organisation of metadata, both to aid proper data management within the TAILSAFE project, and to facilitate its use by others.

Core Phase

This embodies the major research and development work of the TailSafe project, covering:

- intervention actions – *parameters relevant to their choice and implementation*
- prevention and remediation – *parameter trigger levels and sampling standards*
- investigation and monitoring – *measurement methods for target parameters*
- field experiments – *refinement and testing of new measurement methods*.

While the framework will also continue to be updated with information from external sources, key data for certain target parameters will be generated by the project research itself.

The criticality of parameters is viewed as a dynamic attribute, with the critical parameters varying with problem situation and solution stage. An important feature of the core phase will thus be the refinement of this matching of procedures and parameters. We have in mind default settings derived from evidence and dialogue (including with the expert advisory panel), which can then be adapted by the user in an interactive process.

Conclusion Phase

The various threads of the project will here be brought together in an effort to consolidate and disseminate results. The central deliverable will be the TAILSAFE framework for risk reduction at tailings facilities, consisting of a Mark I version of a working tool. The framework will cover parameters and procedures of design, materials, management, and regulation. It will offer advances in methods of water management and dam structure assessment, plus guidelines on preventive measures and intervention solutions. Implications for standards and codes of practice will be addressed.

What began as a spreadsheet/database framework for defining and tracking common parameters across all workpackages, will thus be transformed into a practical risk reduction tool for tailings facilities. This will be arranged as a series of modules, through which a user can cycle, in checking out a particular problem situation or procedure. The Mark I prototype will be disseminated among relevant stakeholders, such as regulatory authorities and industrial end-users, to attract user feedback and facilitate future upgrading.

Outcome

Comprehensive although this framework should be in some respects, in others its scope is strictly delimited. In particular, while comment will be offered on costs and viability where considered helpful, no attempt will be made to incorporate cost and viability parameters into the framework itself under the present project. The framework must thus be used not to determine actions, but only to inform them alongside such other vital factors. Similarly, the main focus of the framework will be upon measures to prevent failure occurring, rather than clean-up measures following a tailings spill. Thus the downstream effects of catastrophic failure will largely be treated as externalities beyond the scope of the initial risk management framework. Users - whether industrial or regulatory - and commentators will need to take those conscious limitations into account when considering the Mark I TailSafe framework.

Risk management is ultimately a matter of controlling critical parameters. The TailSafe framework intends to offer a systematic means of organising data from this targeted research, alongside data from elsewhere, in a way which relates them not only to assessing, but also to monitoring and reducing risk. Well defined standards and criteria are specified by reference levels of critical parameters. By both clearly setting out such levels relevant to tailings facility risk reduction, and offering improved methods of their measurement and monitoring, the research will help enhance the scientific basis for regulation within Europe and elsewhere.

Outlook

It is expected that as an overall result of the TAILSAFE project knowledge and technology levels will be increased in the fields of

- materials parameters of tailings, with special reference to their heterogeneous and sometimes hazardous nature
- flow-deformation behaviour of tailings as fine hydraulically placed non-plastic materials
- probabilistic approaches for stability analysis
- structural and lithological parameters of tailings impoundments
- physical conditions and fluid content, pressures and movement inside the dams
- non-destructive/geophysical methods for dam structure assessment
- whole-process water management by further developing paste technology.

The risks associated with tailings facilities will thereby be better managed, improving health and safety, enhancing the quality of life and protecting the environment.

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DRILLING WASTES LANDFILL – THE MOST AVAILABLE METHOD OF THEIR LIQUIDATION

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1. Introduction

In spite of obvious drilling wastes utilization advantages the most available is their liquidation by the method of burial. Herewith the burial of drilling wastes is practiced in the specially set places, in deep-seated underground horizons, in earth pits directly on the territory of drilling site.

Historically the landfills were the most cost-effective and the most acceptable from standpoints of environment protection by methods of eliminating the hard wastes. Alongside with reducing an amount of wastes, recycling and technologies of disposal, the deleting of the remaining hard wastes on landfills still stays an important component of hard wastes control strategy.

Landfills are the objects used for eliminating the hard wastes in superficial layer of soil. In the past term "landfill" was used for marking a place, on which were placed wastes and covered by the soil at the end of each workday. Today term "sanitary landfill" refers to engineering objects for eliminating the wastes, developed and used to render a minimum negative influence on health of population and environment.

The burial of wastes on landfills stipulates monitoring of entering flow of wastes, allocation and pressing the wastes, as well as the installing of equipment for controlling the conditions of environment [1].

The liquid collected on the landfill floor is known as a filtrate. In the landfill depth a filtrate is conglomerated in the intermediate points. Basically a filtrate is the result of sediment infiltrations, uncontrolled effluents or irrigation water on the landfill. Filtrate can also include water, which originally was contented in wastes and infiltrating ground water. Filtrate contents a varied chemical components resulting from dissolutions of burial materials on the landfill and from products of chemical and biological reactions, occurring on the landfill.

The coating of landfill is material (natural or synthetic), intended for a bottom coating and situated under the gradient of sides of landfill. The coating usually consists of compacted clay layers or geomembrane materials enclosing for preventing migration of filtrate and gases. Controlling systems of landfills include the coating, collection system and extraction of filtrate, system of gas collection and daily and final coating.

Monitoring for the environment condition is activity, connected with the collection and analysis of water and air tests, which are used for the trailing of motion filtrate and gases. Closing of landfill describes steps, which must be undertaken to close and do a safe place of landfill after operations of filling are completed. The actions done after landfill closing, directed on permanent monitoring and maintenance in the order of closed landfill (from 30 to 50 years).

At present many different classifications of landfills exist. For example, in Canada the following classification is used[2]:

1. Sanitary landfills - landfills for home wastes, where wastes are covered with layer of soil minimum three times week.
2. Landfills for factory wastes, under development for servicing of factory enterprises. They are classified into three classes.

Class 1: Landfills for factory wastes, ensuring maximum protection of environment and enclosing for dangerous and toxic wastes. These landfills have synthetic coating, filtrate of system collection and monitoring.

Class 2: Landfills for factory wastes, having coating from the clay and monitoring of ground waters. On these landfill wastes are compacted and covered by the ground daily. Such landfills can be licensed for burial dangerous wastes on them except liquids.

Class 3: Landfills for safe dry (inert hard) factory wastes. Liquids can not be placed on landfills of this type.

In America the following types of landfill are accepted: landfills for mixed home wastes, landfills for grinding hard wastes and landfills for special wastes [1].

Applicable designs for the arrangement of landfill can be the most different: dug pits or trenches, areal and canyon design.

Dug trenches or pits are suitable to make on areas, where the level of underground waters is situated far from the surface and where there is a sufficient thickness of covering material on the place. Dug is used for daily and final covering. Pits or trenches are usually covered by coating from synthetic membranes or low-permeabilitable clay or combination of that and other for the restriction of motion filtrate and gases.

When a region is not available for digging trenches or pits the areal design of landfill is used. The ground waters situated close to surfaces of the ground the main cause of using the landfill of areal type.

Preparation of landfills includes an installing of coating and controlling system for filtrate. In this case coating material is brought from nearest quarries. As intermediate coating material a compost or temporary portable covering is successfully used.

The grinding wastes before their disposal on the landfill, as alternative method of burial on landfill in several places in USA was used. The grinding wastes can have density for 35 % greater, than density of no grinding wastes and in accordance with rules of some States it is possible not to cover these wastes daily. Disadvantages of this method are as follows installing equipment for grinding wastes and necessity to use the usual sections of landfills for wastes, which are difficult to grind. The method of grinding wastes is possible to use on areas, where disposal of wastes costs greatly by reason of big compaction and the usage of coating materials is not always available, as well as where amount of seasonal precipitation is very little or depends on a season. It is also possible to use the grinding wastes for production of compost which can be used as intermediate coating material.

These exists canyon or lowland construction of landfills using canyons, ravines and dry quarries as landfills [3]. Technology of disposal and compactions of wastes in canyon landfills is changed with the geometry of place, features of available covering materials, geology and hydrology of place, type of controlling devices for a formation filtrate and gases and access to the place of landfill location. Controlling for exposed effluent is often a deciding factor for the development of canyon landfills. Key to successful use of canyon landfills is availability of appropriate coating materials for separate layers of wastes and last covering. Coating materials for covering are taken from walls and bottom of canyon before it will be installed.

The burial of drilling wastes in specially set places provides the usage for these aims the anticipate pits, deserted soils or the stayed quarry after exploitation. Burial of drilling wastes using this method is the single possible variant of solving environment protection problems, for example, offshore drilling, drilling in resort and coastal water protecting areas, as well as in ecological vulnerable region.

At present in Kazakhstan in the most cases the burial of wastes drilling is practiced presenting itself semiliquid mass and stagnant sediment directly in cutting pits on the territory of drilling site after preliminary drying of their contents. However such burial does not eliminate a pollution of environment because polluters containing in wastes for reason of fluidity and high penetrating abilities migrate in soils, causing negative processes in them.

2. The treatment of drilling wastes in Kazakhstan sector of North Caspian

North Caspian region of Kazakhstan is an ecological forbidden zone, therefore drilling is here conducted with the zero disposals, that is, all drilling wastes (drilling cutting and waste drilling mud) are not discarded in sea, but are transported on the coast for the further refinery.

Region is subjected the most strong influences of natural ambience such, as a sea level fluctuation, a coast area flooding, carrying of bottom sediment during rundown surge phenomenon, forming an icy cover and plowing by ice furrows in bottom sediment. Flora and fauna of this area adapted to constant change.

North Caspian in spite of that rivers Volga and Ural flow into it in springtime and Emba is a shallow, particularly its eastern part, having depth 3.3 м. Besides Volga and Ural have extensive delta systems. Their coast water-logged territory are vitally important part of North Caspian ecosystem. As a whole a seabed presents itself a calm plain with some amount of small raising and valleys. The Ural furrow is the most brightly denominated form of the undersea relief and lowering with well-marked boards, situated southward from mouths of Ural and appeared under the action of erosions and tectonic power in the North Caspian. Depths in Ural furrow increases up to 10 meters.

It is generally recognized that the main contamination sources of North Caspian are polluting materials brought by waters of Volga and Ural. However it is necessary to notice that the processes of construction and drilling holes play a considerable role in negative influence upon the environment.

Drilling of North Caspian continental shelf is produced by drilling barges "Sunkar" specially built for unique natural and geological conditions of a given region (Fig. 1). This installation has no analogues in the world. The barge is adapted for working in typical conditions shoal of North Caspian. Such designs were already used in ecological sensitive conditions of shoal in other regions of the world, for example in Louisiana. A barge is installed on the small undersea base - berm, which height is 1 meter. Berm design allows it to withstand ice loads in winter and storm phenomena in the summer.

Before the transportation on the coast the drilling salt-containing cutting from holes are kept on the barge. Then they are transported on the base of provision, where it is installed a high-tech equipment for the conversion of cutting. After the conversion the drilling cutting hard material can be used for the construction or improvement. The wastes not being subjected to microbiological destroying are burned on the barge, but ashes are get out on the coast. Other wastes are processed for recurrent use in accordance with international and Kazakhstan standards.

When drilling and testing of holes exhaust and wastes, the moving transport facilities, noise, vibration and effluent discharge influence on the environment. Physical presence of berm is not significant. Discharge in atmosphere as a result working drilling equipment and from working a generator, including recovery of sulfur from is insignificant. Influence from increasing a moving transport will not be significant (though if possible it is necessary to avoid a factor of anxiety for seals, particularly in period of winter puppy). The drilling areas are situated sufficiently far off from the coast that is why noise, vibration and light will not be a problem for people living on coast. As far as berms are small, fish and other sea inhabitants will bend around this area, if they are alarmed by conducted work. Experience shows that some individuals even get accustomed to works and with a time they are attracted by fodder sources, created as sea flora and fauna develop around berm. As to unset of effluent discharge, they correspond to all state standards of Republic Kazakhstan, which are the most strict standards in the world for sea work and also corresponding to the international standards.

3. Analysis of drilling cutting, formed as a result from drilling barge exploitation.

Drilling cutting were analyzed by means of the following methods:

- total chemical analysis (including oil products and other organics compounds);
- spectrum analysis (for heavy metals);
- X-ray spectrum analysis;
- biotesting of water extract on ceriodaphnias .

Besides investigated wastes are analyzed on the contents of colour, black, rare, rare-earth, precious metals and others chemical elements.

In studied man-caused soils, in the comparison with the average contents of discovered chemical elements in the grounds of the world, is observed a significant a barium increase (approximately in 20 times); zinc is kept in the amount near 2 maximum concentration limit, MCL (against MCL for ground). The rest elements are discovered in the amount near to MCL, or in amounts on the order smaller, than MCL.

It results from analysises that studied man-caused soils are enriched by carbonates and organics (that is obliquely confirmed rather high loss when calcinations, a loss has formed up to the sixth part of tests masses). In man-caused soil are practically absent phenols. Small amount of oil products is discovered from 1.9 g/kg (test 1) up to 3.8 mg/kg (test 2), organic dirt – up to 6.4 mg/kg. Arsenic and stibium in the drilling cutting are present in highly small amount, on the limit of inaccuracy of determination literally. In the first test a drilling cutting is contained an essential amount of rolling ferric (up to 1.9 %) and general sulfur (up to 4.5 %). In the second test of drilling cutting ferric is contained in three times less, but sulfur in 1.5 times more, than in the first test. Contents of rolling copper, zinc and lead reaches accordingly 0.004 – 0.003 %, 0.002 – 0 1 % and 0.01 %.

Both tests drilling cutting do not present the radiation danger: in both tests a content of uranus forms 0.0041 % (under passport its contents in the standard sample is 0.0155 % and actual – up to 0.0159 %).

Total indexes of danger of two tests drilling cutting is greatly differently: total index of danger of the first test forms 94.11, but the second is the order more - 998.1. The most values of index of danger in the first test have sulphates of sodium and barium (68 %), as well as oxides and sulfide of sodium (about 30 %).

Calculations of danger class of the first test drilling cutting allow to refer this man-caused soil on the value of its danger total index to the material having the fourth class of danger. Calculations of danger class of the second test allow to refer this man-caused soil to the material, having the third class of danger.

Coarse polluted drilling cutting are transported by means of barges from drilling installation in the Bautino port. On Bautino base the drilling cuttings are processed on thermal desorption installation, which is named as an installation on recovering soil. Drilling cutting with the three class of danger is transmitted in the fourth category of low-danger wastes and are temporarily stored in locked warehouse for the atmospheric precipitation situated near the Bautino base. This concerns drilling cutting corresponding to the first test.

Drilling cutting of the second test are also processed on thermal desorption installation then are temporarily stored in locked for the atmospheric precipitation premises. They are assigned by III class of danger, and they carry a name of cleaned saline drilling cutting on the mineral base.

Thereby it is possible to summarize that the cleaned saline drilling cutting on the mineral base are referred to III class of danger – gently dangerous toxic factory wastes and coarse drilling wastes - to IV class of danger – low-toxic factory wastes.

Both cleaned saline drilling cutting on the mineral base (factory wastes of III class danger), and treated drilling cuttings (factory wastes IV class of danger) must be removed from the habitat, neutralized and buried so to reduce to the minimum their negative action on the environment. Exactly for these purposes are built landfill (cards) for burial cuttings both classes of danger, which are environmental construction and meant for centralized collection and burial of gently toxic wastes of factory enterprise.

4. Landfills for burial of North Caspian drilling cutting.

The landfills are designed for two types of drilling cutting – cleaned drilling cuttings [4] and cleaned saline drilling cuttings on the mineral base [5]. At present the landfills bases are in stage of construction.

On the Fig. 2 a landfill for burial of cleaned drilling cutting is presented.

The landfill is calculated on burial of 18000 m^3 of cleaned drilling cuttings or corresponds to the capacities of drilling cuttings from drilling of six holes. The landfill is divided into six independent cards, each of which is capable to contain 3 000 m^3 drilling cutting. On its design capacities the landfill is referred to low-loading categories because the height of stored drilling cuttings does not exceed 2 meters and the load on the bottom of landfill forms less than 50 000 tons on the hectare.

Cards of landfills have one and the same size and form on the bottom 61 m in the length and 22 m in the width. Sizes of cards on upper point of diking (+2 m) form: 72 m in the length and 28 m in the width. Bottom of cards is equipped with impervious clay screen and corresponds to a natural terrestrial surface level. Height of diking with respect to the natural soil level forms at the average +2 m. The diking between cards is done by the width on the 5m top. Western part of the sidebar of diking of landfill presents itself elated from the natural soil level on 2 m platform for the u-turn of motor transport by the width 20 m and length 226 m (length together with the access ramp - 276 m). Platform for the u-turn ramp is made thereby that under the most further construction of cards in western part of the area it was possible to use already built platform. Western escarpments of cards, verging to the platform for the u-turn are designed with a pawning the escarpments for convenience of moving motor transport and bulldozer. For the conservation the wholeness of cards escarpments and below lying clay screen when filling a card of drilling cutting an escarpment it is necessary to bolt with reinforced concrete demountable slabs, which after filling a card are unmounted and carried on the following card.

The method of layering (on 25 – 30 sm) compactions of soil with six passages of roller is used at making of horizontal surfaces impervious screens, horizontal surfaces of diking mound and platforms for the u-turn of motor transport. Sloping mound of landfill and layering are carefully compacted with pneumatic ramming.

On the landfill it is provided a drainage system from pipes for the collection rain and melting waters in low part of landfill and drainage tank for the collection of water. As far as all cards have a natural gradient (order O.5 – 0.8 m on the card) from the north-east on the south-west, in the south-western part of each card is assembled a drainage pipe for natural overcurrent of rain water in the nearby card, situated below. All pipes from both ends are barriered with concrete monolithic portals.

After filling a next card (cards are filled from north, because relief of terrain has a gradient from the north on the south) drainage pipe, connecting card with the nearby card, hermetically close from both sides. In the sixth, southernmost and underlying on the relief to the card for the collection of storm overflows is equipped a drainage tank. Lateral shallow tanks, contiguous with the soil are processed with hot bitumen two times.

On the upper edge of diking a drainage pallet is established. Water proofing of drainage pallet is made from the soil by the 10 sm thickness imbrued with the hot bitumen mixed with the cement up to the full saturation. For controlling the sanitary condition of ground water and influences upon ground water of landfill of cleaned drilling cutting 4 controlling-observant drilling holes are drilled around landfill with 4 sides.

When finding a contamination in controlling drilling holes a systematic controlling of stratal water not less than 2 times a month is conducted.

On the Fig. 3 it is shown a disposal scheme of cleaned saline drilling cutting on the mineral base. Landfill for these cutting is divided into two independent cards, each of which is capable to contain 1050 m^3 of cutting, or in the recalculation on the waste of drilling - one card is intended for burial toxic wastes III class of danger in comparison with drilling of three and half of drilling holes. On its design capacities the landfill cards are referred to low-loading categories because the height of stored drilling cuttings does not exceed 3.5 meters and the load on the bottom of landfill forms less than 50 000 tons on the hectare.

Sizes of cards of landfill (both one and same size) on the bottom form: 81.35 m in the length and 13 m in the width. Sizes of cards on upper spots of diking form in the length 90.15 m and in the width 17.8 m. Bottom of cards, equipped impervious clay screen on 0.3 meter of above natural terrestrial surface level. Height of diking with respect to the natural soil level forms at the average +1.9 m.

At the construction of two cards it will be taken out of ditches 2190 m^3 soil, from each ditch on 1095 m^3.

Total volume of landfill is calculated on burial of 2100 m^3 cleaned saline drilling cutting on the mineral base or corresponds to capacities of III class of danger cutting wastes from drilling of 6 drilling holes.

On the sidebar of landfill diking is done with width on the 5 m top and diking between cards is also done by the 5 m width.

Need for the soil at the making circular dam diking and separating escarpment cards will form 3815 m^3 local soils (in this amount do not include amounts impervious clay screen).

Eastern part of the sidebar of diking landfill for burial cutting presents the natural soil level on 1.9 m platform for the u-turn of motor transport by the width 12 m and length 226 m (length together with the access ramp - 276 m).

For the conservation of escarpments wholeness of cards and low-loading clay screen when filling a card with cutting the escarpment is consolidated with reinforced concrete demountable slabs, which after filling a card are unmounted and carried on the following card.

The method of layering (on 25 – 30 sm) compactions of soil at making of horizontal surfaces impervious screens, horizontal surfaces of diking mound and platforms for the u-turn of motor transport is used.

Sloping mound of landfill and layering are carefully compacted with pneumatic ramming.

In spite of deep ground water the protectability of underground waters of upper water-bearing horizons from the influence of shallow polluting in the region of building landfill is low. Exposing on the surface sediments are presented by porous shell limestones easy permeable for shallow waters.

At present in the world practice of landfill construction the most different material, ensuring total isolation from pollute materials are used. Amongst these products it is necessary to note the geosynthetic materials, produced by the German enterprise "Naue Fasertechnik". The materials produced by this enterprise, corresponds to the most strict technological requirements, regulating standards of disposal, burial, preparations and using the ecological dangerous substances, such normative acts, such as Germany Water Conservation Act (WHG) and British Environmental Protection Act (EPA). Geosynthetic materials such as CARBOFOL, BENTOFIX, SECUTEX, DEPOTEX and other are possessing greater safety, multifunctional, economical, simple using.

In 1989 CARBOFOL became the first geomembrane certified by the Federal Institute for Material Testing and Research (BAM). CARBOFOL is extremely durable, and is both chemically and UV resistant. Currently, CARBOFOL HDPE (smooth and structured) 2.5 and 3.0 mm thick are BAM certified for use in landfill engineering. For groundwater protection applications, CARBOFOL geomembranes (1.5 mm and thicker) are certified by the German Institute for Construction Technology. Further international certifications for CARBOFOL have been issued in, amongst others, most European countries.

CARBOFOL can be successfully applied for the building landfills of drilling wasters on deposits of Kazakhstan.

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Fig. 1. Drilling barge «Sunkar»

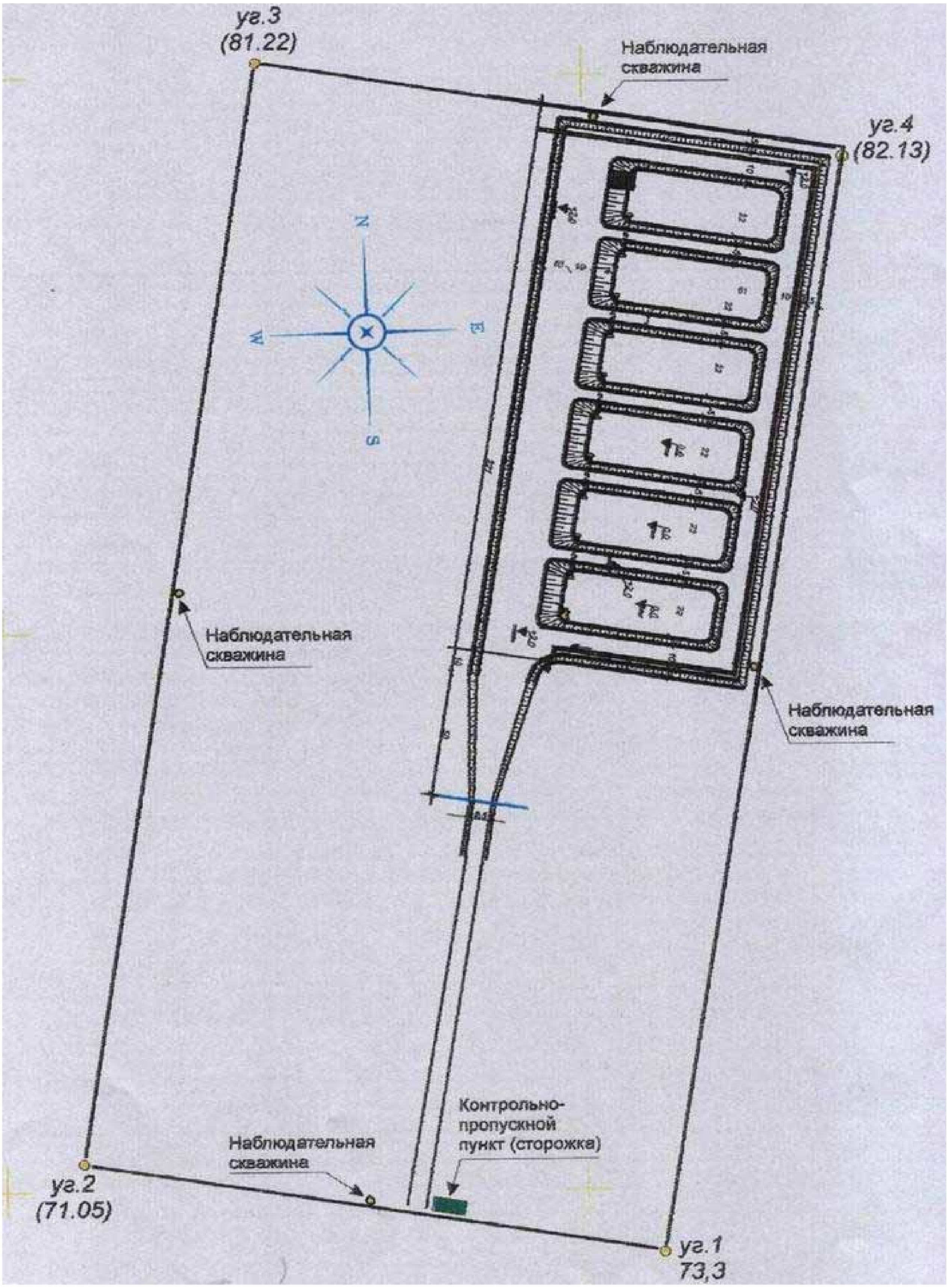

Fig. 2. Landfills for burial of cleaned drilling cutting.
Наблюдательная скважина – observation hole,
контрольно-пропускной пункт – check point.

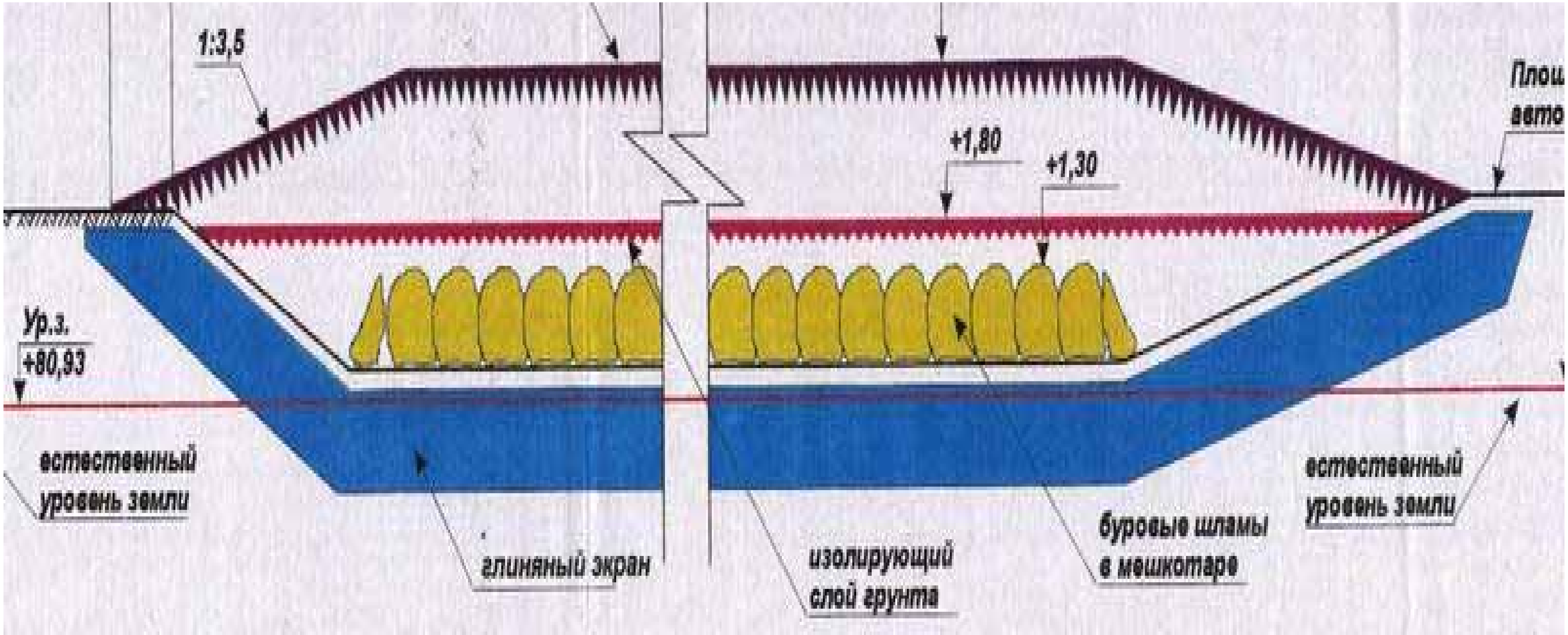

Fig. 3. Disposal scheme of cleaned saline drilling cutting on mineral base.
Естественный уровень земли – natural ground level
Глиняный экран – clay screen
Изолирующий слой грунта – seal of ground
Буровые шламы в мешкотаре – drilling cutting in sack tare
Площадка для автотранспорта – platform for motor transport

BIOLOGICAL, PHYSICO-CHEMICAL AND THERMAL TECHNOLOGIES IN COMPARISON FOR THE REMEDIATION OF A PAH CONTAMINATED SOIL

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Keywords: Polycyclic Aromatic Hydrocarbons, slurry phase bioremediation, soil, surfactant-aided soil washing, thermal desorption

SUMMARY

Lab studies were carried out to evaluate the feasibility of different ex situ technologies (slurry phase biological treatment, surfactant-aided soil washing and thermal desorption) for the remediation a benzo-polycyclic aromatic hydrocarbon contaminated soil at a former Manufacturing Gas Plant site. Results suggested that the remediation of soil could be accomplished by a thermal desorption process, with a maximum temperature of about 300°C; soil washing was technically feasible, but highly expensive; residual concentrations obtained by the biological treatment did not respect the regulatory limits.

INTRODUCTION

Restoration of Manufacturing Gas Plant (MGP) sites is a very serious problem all over the industrialised countries. In the United States, projected cleanup costs range from one million to tens of millions of dollars for many of them. Among the environmental issues related to these sites, soil pollution by Polycyclic Aromatic Hydrocarbons (PAHs) prompts to explore alternative technologies, in order to choose appropriate and cost-effective remedial options.

Many biological, physico-chemical or thermal technologies have been evaluated or full-scale applied for the remediation of polluted soils from Polycyclic Aromatic Hydrocarbons (PAHs) [Van Deuren et al., 2002]. Among these remediation systems, slurry phase bioreactors, surfactant-aided soil washing and thermal desorption processes can show high removal efficiencies [USEPA, 1993a; USEPA, 1993b; USEPA, 1997].

Since performances of the remediation technologies are always site and soil specific, treatability studies must be performed. This paper presents lab scale tests carried out to evaluate the feasibility of the above mentioned technologies in the remediation from high molecular weight PAHs of a MGP unsaturated soil at the north-west of Milan (Italy).

MATERIALS AND METHODS

Soils

Two soils (A and B) were excavated at the site at different times and dry-sieved to 2 mm. Quartering provided sub-samples with suitable weight; for each soil, homogeneity was assessed by comparing particle size distribution and PAH concentration of five sub-samples, resulting in a standard deviation lower than 5%.

Soils A and B were quite similar. They had a low content of organic carbon (2.1 % w/w for soil A and 2.4 % w/w for soil B respectively). Their mean particle size distribution are reported in Tab. 1. The mean PAH concentrations (C_{in}) are shown in Tab. 2; polyaromatic hydrocarbons above pyrene exceeded Italian regulatory soil standards for either the commercial/industrial (C_c) or green/residential (C_g) uses [DM 471/99, 1999] from 2.8 to 2070 times, depending on the compound, the soil and the limit being considered. Nearly 1000 mg/kg d.w of total benzo-PAHs were present in both soils; the total PAH concentrations were nearly 1700 and 2700 mg/kg d.w. for soils A and B respectively.

Tab. 1: Mean particle size distribution of soils (< 2 mm).

Fraction (μm)	2000-1000	1000-600	600-212	212-106	106-63	<63
Soil A - % w/w	17.1	24.7	47.6	7.0	2.3	1.3
Soil B - % w/w	21.3	20.1	49.0	7.4	1.4	0.7

Tab. 2: PAH concentration on soils A ($C_{in,A}$) and B ($C_{in,B}$), and Italian remediation limits for green/residential (C_g) and commercial/industrial (C_c) purposes (- = not established) [DM 471/99, 1999]. Data are reported in mg/kg on dry weight basis (d.w).

	N	Acl	Ace	Fluo	A	Phen	F	P	C	B(a)A	B(a)P	B(b)F	B(k)F	I	B(ghi)P	DA
$C_{in,A}$	17	28	4.0	9.3	52	71	252	191	140	126	158	129	126	139	167	60
$C_{in,B}$	21	44	5.0	26	101	199	527	393	302	282	207	196	161	108	89	44
C_g	-	-	-	-	-	-	-	5	5	0.5	0.1	0.5	0.5	0.1	0.1	0.1
C_c	-	-	-	-	-	-	-	50	50	10	10	10	10	5	10	10

N: naphthalene; **Acl**: acenaphthylene; **Ace**: acenaphthene; **Fluo**: fluorene; **A**: anthracene; **Phen**: phenanthrene; **F**: fluoranthene; **P**: pyrene; **C**: chrysene; **B(a)A**: benz(a)anthracene; **B(a)P**: benzo(a)pyrene; **B(b)F**: benzo(b)fluoranthene; **B(k)F**; benzo(k)fluoranthene; **I**: indeno(1,2,3-cd)pyrene; **B(ghi)P**: benzo(g,h,i)perylene; **DA**: dibenzo(a,h)anthracene.

Bio-slurry treatment

The slurry phase biological system used in this study and the experiment performed were described in detail in Saponaro et al. [2002b]. Soil A was mixed with water, in order to get a solid to liquid weight ratio of about 10%, and treated under aerobic conditions (dissolved oxygen > 8 mg/l) at 22±1 °C. Macronutrients were dosed at the beginning of the tests to obtain C:N:P ratios of 100:10:1 w/w. The test duration was 34 days. Approximately once a week, slurry aliquots were sampled from the reactor and centrifuged to quantify PAHs on soil as a function of the residence time in the reactor.

Surfactant-aided soil washing treatment

The surfactant-aided soil washing treatment was described in detail in Saponaro et al. [2002a]. Soil B was repeatedly extracted with washing solution containing Brij 30 at 5 g/l, with a 10% solid to liquid weight ratio. Following each extraction (4 h), the slurry was centrifuged and the supernatant was separated for quantification of PAHs extracted from soil. The PAH residual concentration on soil following each cycle was obtained by mass balance; after seven cycles, soil was analysed.

Thermal desorption treatment

A lab-scale indirectly-heated thermal desorber unit was used in this study, equipped with an indirectly heated quartz reactor placed into a cylindrical furnace. Following soil B loading into the reactor (nearly 10 g d.w.), the temperature was increased according to a linear schedule (5 °C/min) under an air flow (150 Ncm^3/min), followed by an hold (60 min) at the final temperature T_{max}, ranging from 250 to 650 °C. At the end of each test, soil was cooled down and analysed.

Chemical analyses

All chemicals were analytical grade purity (99.0 %). All glassware was silylated with $(CH_3)_2SiCl_2$.

Particle size distribution and organic carbon were determined by ISO/DIS 11277 and ISO/DIS 10694 methods [ISO, 1994] respectively. Moisture content of soil was determined by EPA 160.3 method (coefficient of variance CV: ± 0.5%) [USEPA, 1994].

PAH extraction from soil was carried out by EPA SW 3540 B, clean up by EPA SW 3630 B, GC-MS analysis by EPA SW 8270 B [USEPA, 1994]. The overall variation of PAH determination in soil was nearly 9% [Bonomo et al., 2002].

The PAH content in the surfactant-aided soil washing solutions was determined as described in detail in Saponaro et al. [2002a]. The coefficient of variance was between 5% and 12%, depending on the compound being measured.

RESULTS AND DISCUSSION

The removal efficiency obtained by the different treatments are shown in Fig. 1 a), b) and c) for some PAHs of concern.

In the slurry phase biodegradation treatment, removal efficiencies ranging from 50% to 79% were obtained for PAHs above pyrene, depending on the compound being treated, during 34 days of treatment. PAH concentrations in soil decreased very quickly in the first 10 days of treatment; a time of residence longer than 25 days did not bring a significant additional abatement of the polyaromatic compounds.

In the surfactant-aided soil washing, the PAH extraction efficiency during each cycle was constant and independent from the soil concentration at the beginning of the cycle; values between 18% and 24% were obtained, depending on the high molecular weight PAH being considered. Therefore the cumulative extraction efficiency following n cycles of treatment could be calculated as $100 \times [1 - \exp(-c \times n)]$, where c assumed a specific constant value for each compound.

Results obtained in thermal desorption tests showed that removal efficiencies above 99.7% were obtained for all benzo-PAHs, when T_{max} above 300 °C was applied. In case of T_{max} = 250 °C, the abatements decreased to values between 87.0% and 99.1%, depending on the PAH being measured.

Taking into account the remediation limits established by the Italian regulation, a removal efficiency over 90% would be required for most of the PAHs considered, even if a commercial/industrial purpose were applied. The biological treatment, therefore, do not allow to reach the residual concentrations required, even increasing the time of residence of soil in the reactor. Applying the surfactant-aided soil washing, the number of cycles necessary to remediate soil would be over ten for some compounds such as benzo(a)pyrene; even if technically feasible, costs related to a full scale counter-current leaching process should be carefully evaluated. At the moment, the thermal desorption process, performed with a maximum temperature of 300 °C, seems to be the most reliable process among those tested to reach residual concentrations below the regulatory limits at affordable costs.

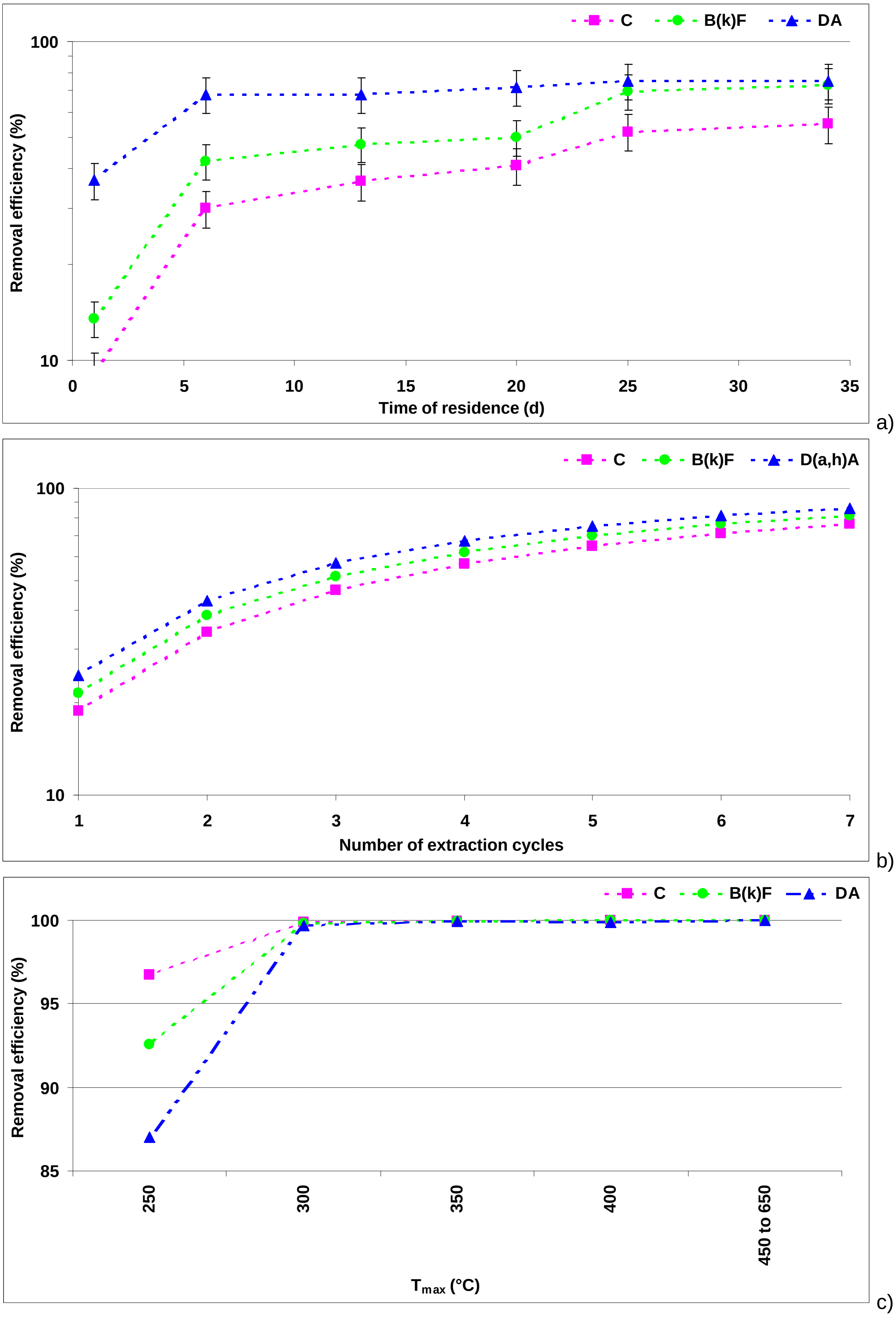

Fig. 1: Removal efficiency for some PAHs of concern (C: chrysene; B(k)F: benzo(k)fluoranthene; DA: dibenzo(a,h)anthracene) obtained during the slurry phase biological treatment (a), the surfactant-aided soil washing (b), and the thermal desorption process (c). The error bars shown in (a) represent the expanded uncertainty, calculated as reported in Bonomo et al. [2002].

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SOIL WASHING FOR TREATMENT OF SOILS CONTAMINATED BY LEAD AND ARSENIC

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Keywords: Arsenic, chemical extraction, lead, soil washing

SUMMARY

Bench scale studies were performed to assess the feasibility of a chemical extraction process of lead and arsenic from soil washing solid residues. Acid, basic and sequential processes (contact time: 5 h each step), with different liquid to solid (LS) weight ratios, were applied at 22 °C on moderately alkaline fines (<63 μm). Among the investigated processes, the sequential extraction performed by HCl 0.1 N followed by NaOH 0.1 N with 10% solid to liquid weight ratio was the most promising extraction process for a large scale application. Residual arsenic (nearly 90 mg/kg d.w.) and lead (nearly 125 mg/kg d.w.) in the fines were tightly bound to the solid matrix and a further leaching could be neglected, so that the treated residues could be reused as filling material at the site.

INTRODUCTION

Soil washing is a mineral processing technique widely used in the Northern Europe for full-scale remediation of contaminated soils. It mainly employs physical techniques to separate particles with different grain size and density in order to split contaminated waste into clean and concentrated small particle size output streams. In some cases, the process can be powered by applying a further step (chemical process), where the solid residues are mixed with water and ad-hoc chemicals, in order to promote the contaminant extraction. Following this step, also this soil fraction can be reused at the site or disposed at a lower cost [USEPA, 1993].

Metals and metalloids may be present in soils in several different physicochemical forms: as simple or complex ions, as exchangeable ions, organically bounds, adsorbed or co-precipitated with metals oxide or carbonates or phosphates or as ions in the mineral matrix [USEPA, 1992; Evanko et al., 1997; Evans, 1989; Fergusson, 1990; Tack et al., 1996]. For this type of contamination, inorganic or organic acids, bases, salts, chelating agents, oxidants or reducers can be used in the chemical step of the soil washing process [Wasay et al., 1998; Demeyer et al., 1995; Abumaizar et al., 1999; Cline et al., 1993; Peters, 1999; Peters et al., 1995; USEPA, 1997], depending on the contaminant and the matrix characteristics. Acid processes remove metallic cations (e.g. Cd^{2+}, Cr^{3+}, Pb^{2+}, etc.), and solubilize carbonates, hydroxides and oxides; basic extractions solubilize anionic metals/metalloids (e.g. AsO_4^{3-}, $Cr_2O_7^{2-}$, etc.); sequential processes (acid extraction followed by basic extraction) potentially combine contaminant removals obtained in the different steps. The addition of a reducing agent to the extracting solution generally improves the yield of metal extraction [USEPA, 1997; Kuhlman et al., 1999]. Whenever contaminants with different behaviours are present, a multi-step extractive process may be required.

Process parameters mostly affecting the extraction efficiency of metals and metalloids from soils are [Peters et al., 1995]:

a) the chemical agent applied and its concentration;
b) the contact time between soil and the washing solution;
c) the solid to liquid weight ratio;
d) the pH value;
e) the redox potential;
f) the ionic strength;
g) temperature.

This work presents bench scale studies performed to evaluate the feasibility of a chemical extraction process applied to reduce the concentration of lead and arsenic in soil washing solid residues. Tests were aimed to select suitable chemical extractive agents and their concentration and to study the influence of the liquid to solid weight ratio on the removal efficiency from fines.

MATERIALS AND METHODS

Soil

Soil (10 kg) was excavated at a contaminated former Manufacturing Gas Plant site (Italy) and wet-sieved according to the procedure described in Petruzzelli et al. [2000]. Following oven drying at 40 °C, nearly 1 kg on dry weight basis (d.w.) of soil washing solid residues with particle size below 63 μm was obtained. Quartering provided sub-samples with suitable weight (up to 2.0 g d.w.); homogeneity was assessed by comparing metal and metalloid concentrations of three sub-samples, resulting for all quantifiable elements in a standard deviation lower than the coefficient of variance of the analytical method adopted. The mean concentration of main elements in solid residues are reported in Tab. 1. High levels of arsenic and lead were measured; the other potential toxic elements analyzed had concentrations comparable to those of natural soils. The residues were moderately alkaline (pH=7.9); their cation exchange capacity and fraction of organic carbon were 8.0 meq (100 g d.w.)$^{-1}$ and 4.1% respectively.

Tab. 1: Mean (n = 3) concentration of main elements and contaminants (lead and arsenic) in the soil washing solid residues (< 63 μm). Standard deviation was below the coefficient of variance of the analytical method adopted for all elements.

Element	*Concentration (g kg^{-1} d.w.)*	*Element*	*Concentration (mg kg^{-1} d.w.)*
Si	269	S	1.9
Al	45	Ba	0.68
Fe	29	Cl	0.54
Ca	17	Mn	0.50
Na	13	As	346
Mg	9.8	Pb	273

Extractions performed

Extractions reported in Tab. 2 were tested at room temperature (22 ± 2 °C). The extraction solutions were added to soil samples (2.0 g d.w.) in 50 ml polyethylene bottles, in order to get the proper liquid to solid weight ratio; slurry samples were shaken by an agitator (300 rpm). Following each extraction step (contact time: 5 h), samples were centrifuged (2000 rpm for 15 min), the supernatants and the treated residues were separated and the solids were analysed. Preliminary tests showed that steady state conditions could be reached within 5 h; pH values were stable during this time. Triplicate runs on independent samples assessed the overall variation of the tests.

Tab. 2: Extraction processes tested (time of contact: 5 h for each step); LS is the liquid to solid weight ratio applied.

Test number	*Extractive agent*	*pH*	*LS (w/w)*
1	HCl 1 N + HNO_3 1 N	<1	10
2	HCl 0.1 N	2	2.6
3	HCl 0.1 N	1	10
4	HCl 0.1 N	<1	20
5	NaOH 0.1 N	>11	10
6	NaOH 0.1 N	>11	20
7	NaOH 0.2 N	>11	20
8	NaOH 0.1 N + $Na_2S_2O_3$ 0.03 M	>11	10
9	HCl 0.1 N followed by NaOH 0.1 N	2; >11	2.6
10	HCl 0.1 N followed by NaOH 0.1 N	1; >11	10
11	HCl 0.1 N followed by NaOH 0.1 N	<1; >11	20

Chemical analyses

All chemicals were analytical grade purity (99.0 %). Fraction of organic carbon and cation exchange capacity were determined by ISO/DIS 10694 [ISO, 1994] and EPA 9080 [USEPA, 1994] methods respectively. Moisture content of soil was determined by EPA 160.3 method [USEPA, 1994]. pH value of solid residues was determined by ISO/DIS 10390 method [ISO; 1994]. Metal/metalloid content of solid residues before and after the extractions was determined by Energy Dispersive X-Ray Fluorescence spectrometry, as described in Azzellino et al. [2001]; the coefficient of variance (CV) of the analytical method was between 5% and 15%, depending on the element being considered, except for Mg (28%).

RESULTS AND DISCUSSION

Fig. 1 shows the mean concentrations of lead and arsenic in the treated residues. Standard deviation of values from triplicate runs was below the coefficient of variance of the analytical method adopted.

The highest removal efficiency was obtained for both As (73%) and Pb (80%) by applying the acid mixture HCl 1 N + HNO_3 1 N. However, this type of extraction introduce a large amount of chlorides into the process water, and a specific treatment would be required for its disposal at the end of soil washing treatment.

Removal efficiencies obtained by the HCl 0.1 N extractions ranged from negligible values, for LS = 2.6 w/w, to nearly 40-50%, for LS = 10 and 20 w/w, for both the elements. These results suggested that 50% at least of lead was present in the solid residues as slightly soluble precipitates or sorbed on precipitates soluble in acid solutions [Fergusson, 1990]. Arsenic leaching in the acid environment was ascribed to the solubilization of precipitates whose As was sorbed on (e.g.: carbonates and oxides) and of calcium arsenate ($Ca_3(AsO_4)_2$), frequently found in moderately alkaline soils [Fergusson, 1990; USEPA, 1997].

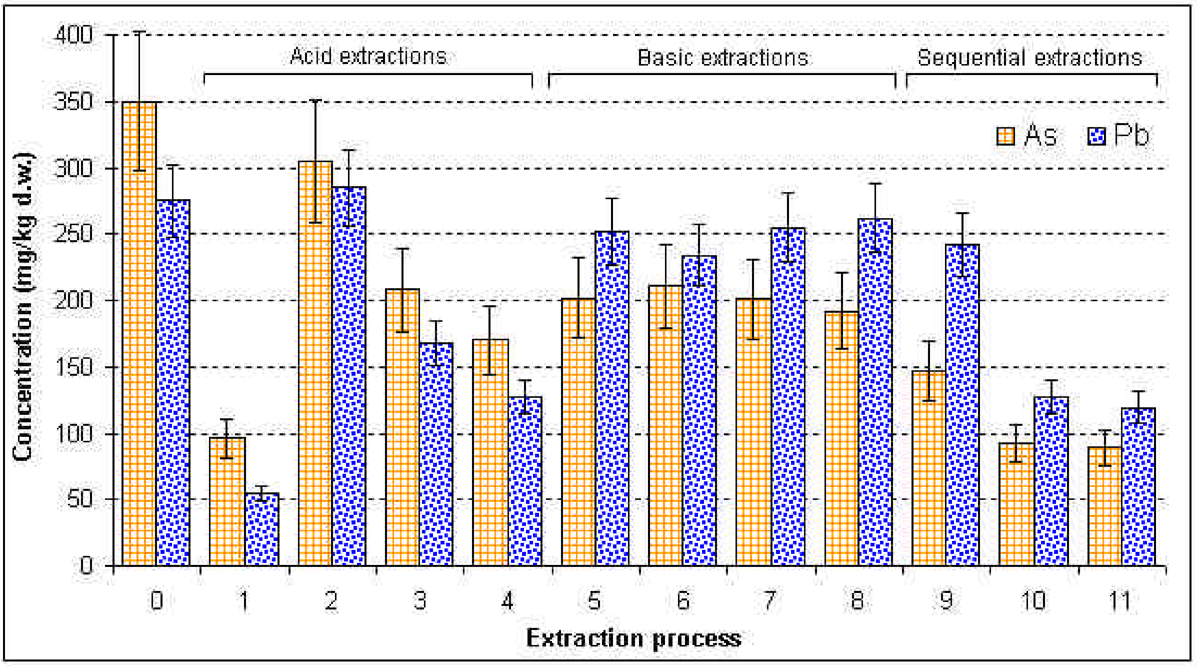

Fig. 1: Arsenic and lead concentrations on fines (< 63 µm), before and after different extraction processes. **0**: Before extraction; **1**: HCl 1 N + HNO_3 1 N (LS = 10 w/w); **2**: HCl 0.1 N (LS = 2.6 w/w); **3**: HCl 0.1 N (LS = 10 w/w); **4**: HCl 0.1 N (LS = 20 w/w); **5**: NaOH 0.1 N (LS = 10 w/w); **6**: NaOH 0.1 N (LS = 20 w/w); **7**: NaOH 0.2 N (LS = 20 w/w); **8**: NaOH 0.1 N + $Na_2S_2O_3$ 0.03 M (LS = 10 w/w); **9**: HCl 0.1 N followed by NaOH 0.1 N (LS = 2.6 w/w); **10**: HCl 0.1 N followed by NaOH 0.1 N (LS = 10 w/w); **11**: HCl 0.1 N followed by NaOH 0.1 N (LS = 20 w/w).

Basic extractions performed by using NaOH showed abatements of nearly 40-45% for As and negligible values for Pb; sodium hydroxide concentration, solid to liquid weigh ratio and the addition of moderately reducing agents ($Na_2S_2O_3$) did not play a significant effect. Arsenic extracted in the basic environment was probably bound to the soil organic matter, soluble in alkaline conditions.

The sequential processes (HCl 0.1 N followed by NaOH 0.1 N) with both 10 and 20 liquid to solid weight ratio exhibited abatements of nearly 75% for As and 55% for Pb; therefore, in these cases the liquid volume was not the limiting factor in the extraction process. Lower removal efficiencies (60% for As, a negligible value for Pb) were obtained applying the liquid to solid weight ratio 2.6.

CONCLUSIONS

Tests performed evidenced that up to nearly 75% of arsenic and 55% of lead in soil washing residues could be extracted. Among the investigated processes, the sequential extraction performed by HCl 0.1 N followed by NaOH 0.1 N with a liquid to solid weight ratio of 10 was the most interesting process for a full-scale application. The treated fines could be reused at the site as a filling material under paved areas, as a further contaminant leaching under these environmental conditions can be neglected.

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The in-situ stabilization/solidification of contaminated sediments by the 3SI technology (Surface Sediment Stabilisation by Injection)

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ABSTRACT

In most cases, the remediation of contaminated sediments is based on a complete removal by dredging, followed by treatment or disposal onshore. How effective this solution might be, it is the most expensive and cannot be regarded as sustainable because of the high volumes of contaminated sediments to be dealt with in the future.

In land based projects, immobilisation of pollutants by S/S gets more and more important and accepted as a remediation technology. In-situ application on sediments however, has not been demonstrated yet.

DEC and Dredging International joint their experience in designing equipment and recipes for the in-situ immobilization of contaminants in underwater sediments. The equipment was based on combining the SSI (Soft Soil Improvement) technology, that DEC applied for the S/S of fine contaminated soils, and the cutter suction dredger technology. The design and construction of a prototype was supported by the Flemish IWT.

The heart of the SSI system is the rotary injection system, similar to a VHP (Very High Pressure) grouting system. The SSI however can inject and mix up to three additives in the sediments. Unfortunately, by its concept, SSI works discontinuously by means of overlapping grout columns.

For the 3SI-technique, the rotary injection system was combined with the swinging arm of the cutter suction dredger, which allows a perfect three-dimensional positioning of the injection system and a continuous operation. In combination with GPS and the dredgers positioning computer a perfect controlled S/S of the contaminated sediments can be carried out.

Next to the development of the prototype various admixture recipes for the S/S of underwater sediments were determined. Two main criteria were applied to evaluate these recipes: firstly the short and long term geotechnical

requirements the stabilized sediments should have in order to avoid propeller induced erosion (and hence mechanical transport of pollutants); secondly the leaching behaviour of the stabilized sediments for the pollutants of interest.

BIODEGRADATION OF CHLORINATED ETHENES AND MONOCHLOROBENZENE IN A TWO PHASE ANAEROBIC / AEROBIC *IN-SITU* TREATMENT ZONE SYSTEM FOR THE BITTERFELD REGION: FROM BENCH SCALE TO FIELD TESTS

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Introduction

Due to former mining and other industrial activities in the Bitterfeld-Wolfen region, located near Leipzig, Germany, a 25 km^2 area has been contaminated with a variety of xenobiotic compounds. In 1999 a project has been started up to assess the possibility of a natural attenuation approach to remediate the groundwater at this location. This NOBIS/SKB project that is carried out by a consortium consisting of TNO MEP, Tebodin, HBG and Shell, is part of the Sanierungs Forschung In kontaminierten Aquiferen (SAFIRA) project in Germany, with participation of mostly German partners. In the SAFIRA project, the feasibility of physicochemical and biological technologies is tested in on site columns and *in situ* reactors. The ultimate goal of the SAFIRA project is to find (a combination of) suitable method(s) to deal with the pollution at a larger scale (Figure 1).

Monochlorobenzene is the main contaminant found in the upper aquifer in Bitterfeld. So far, literature data suggest that this compound is only biodegradable under aerobic conditions. Chlorinated aliphatic compounds, like chloroethenes are present in high concentrations in the lower aquifer. Chloroethenes are reductively dechlorinated to ethene under suitable anaerobic conditions.

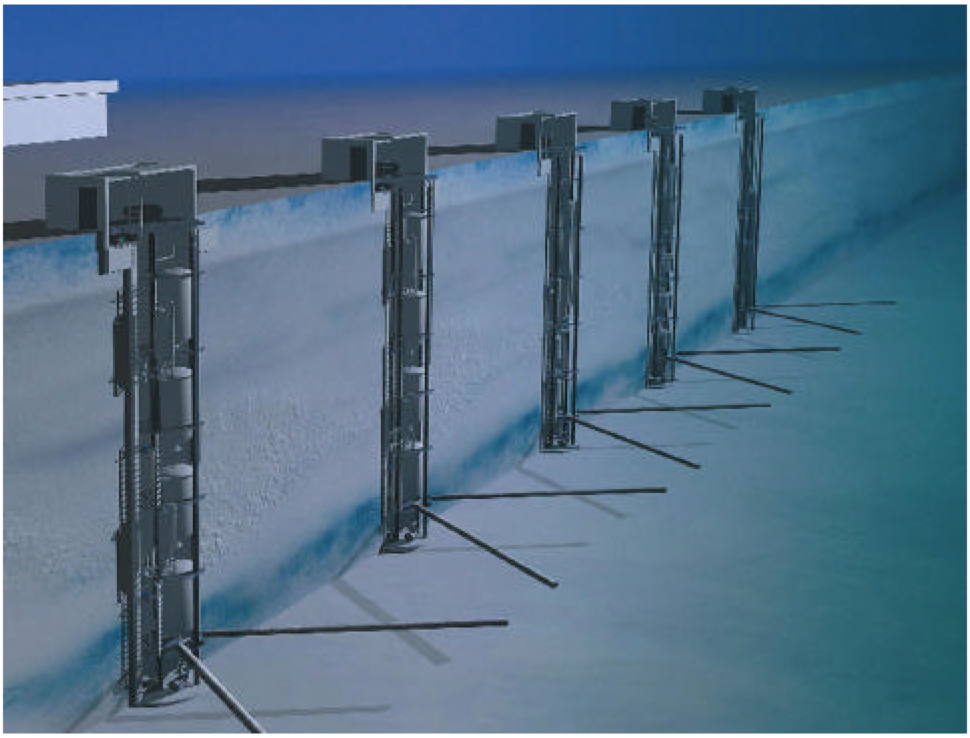

Figure 1. In situ *reactor shafts at the SAFIRA test site in Bitterfeld.*

Methods

We have investigated a sequential anaerobic – microaerobic treatment system to degrade the chloroethenes and monochlorobenzene, respectively. In the anaerobic stage, an electron donor and nitrogen source are added to stimulate the reductive dechlorination, while nitrate and oxygen are dosed as electron acceptors for the microaerobic stage. The research was carried out at several locations. On site and laboratory columns have been running both at TNO in Apeldoorn and in Bitterfeld to investigate the removal of monochlorobenzene and chloroethenes. Large-scale (4 x 4.4 m^3) reactor systems are run in Bitterfeld in a sequential anaerobic-aerobic operational mode (Figure 2).

Figure 2. Inside the in situ *reactor shaft.*

Results

The research has shown that it is possible to degrade the chlorinated ethenes to ethene provided an electron donor is dosed together with a nitrogen source. One of the difficulties in the anaerobic process lies in the high concentration of sulfate that is present in the Bitterfeld groundwater. The electron donor is largely (more than 90%) consumed for sulfate reduction, which is undesired both for financial and practical (high concentration of sulfide formed) reasons.

In laboratory experiments, the effect of low concentrations of electron donor on the dechlorination of chlorinated aliphatics was studied in a column system. With the tested low concentration, extensive trichloroethene dechlorination was observed, while only limited sulphate reduction took place (Figure 3). This indicates the possibility to achieve the simultaneous occurrence of the dechlorination and sulphate reduction processes.

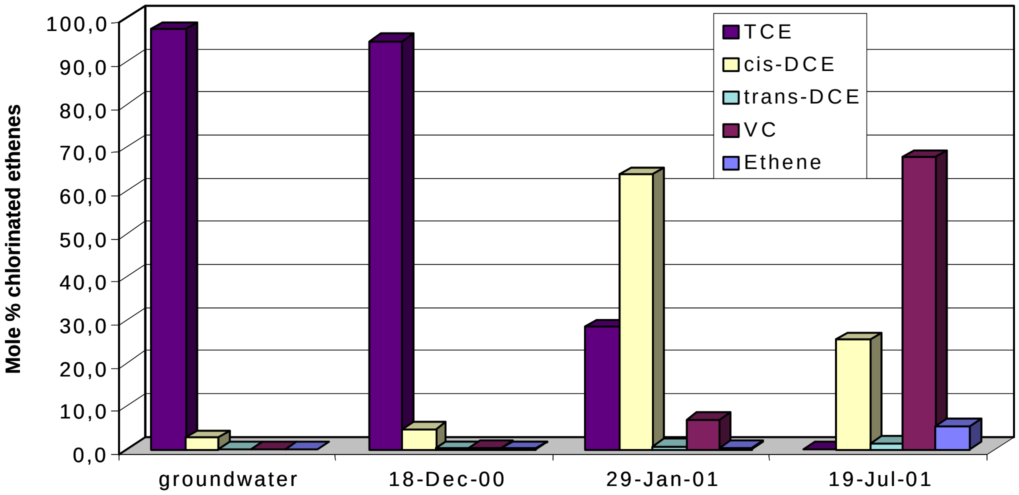

Figure 3. Progressive dechlorination of TCE in time in a laboratory column fed with TCE containing groundwater and low VFA concentrations.

Monochlorobenzene removal was found under aerobic conditions in columns fed with Bitterfeld groundwater. In batch experiments it was found that the presence of oxygen is needed for the microbiological degradation of monochlorobenzene in the Bitterfeld sediment and groundwater.

Because column research has shown that the anaerobic and aerobic stages should be separated by a buffer zone, the research in the *in situ* reactors was initially focused the anaerobic phase. Despite the high sulphate concentrations in the groundwater at the test site, the research in the *in situ* reactors has led to complete dechlorination of chloroethenes to ethene.

Discussion

The possibilities for up scaling of the two-phase system to the field situation have been investigated. The proposed two-phase system is a typical (edge of) plume treatment technology and can preferentially be applied to protect objects of risks like surface water systems from contaminated draining groundwater in the quaternary aquifer. This will mainly be the case in the north and northwest of the regional contamination, where the object of risk is the river Mulde.

For the first phase in the treatment process under field conditions, cost-efficient electron donors will be injected in the subsoil to create anaerobic conditions for the dechlorination of aliphatic compounds like trichloroethene. In the Netherlands, various types of this dechlorination system have been applied successfully on many sites. The new elements to be tested in the Bitterfeld region include the engineering and monitoring aspects of the large scale, low-maintenance, and long-term application.

Downstream of the anaerobic phase, a buffer zone will be maintained which will be followed by the second (aerobic) phase. At the SAFIRA test site, hydrogen peroxide was added to stimulate the degradation of monochlorobenzene. In the field application, natural and extensive engineered oxygen influx methods will be used to create the aerobic zone. These technologies need a large air-water interface area, and therefore space. Therefore they will be integrated into the landscape. The new research element here also considers the engineering and monitoring aspects of the large scale and extensive, long-term application. The technical design for aerating the groundwater that drains into the surface water needs to be tailor made designed to the local situation. Options that can be considered are the natural attenuation at the interface between groundwater and surface water, artificially created or natural wetlands (at some sites already present), helophytic filters or aeration cascades (figure 4).

Figure 4. Example of a helophytic filter and cascade system for the aerobic treatment zone.

The upscaled two-phase treatment zone system (Figure 5) will offer a large scale technology to manage the intermediate and long term risks, i.e. impacts on surface water quality by contamination through seepage of quaternary groundwater into the surrounding surface waters. The technology is complementary to the source zone oriented measures already planned.

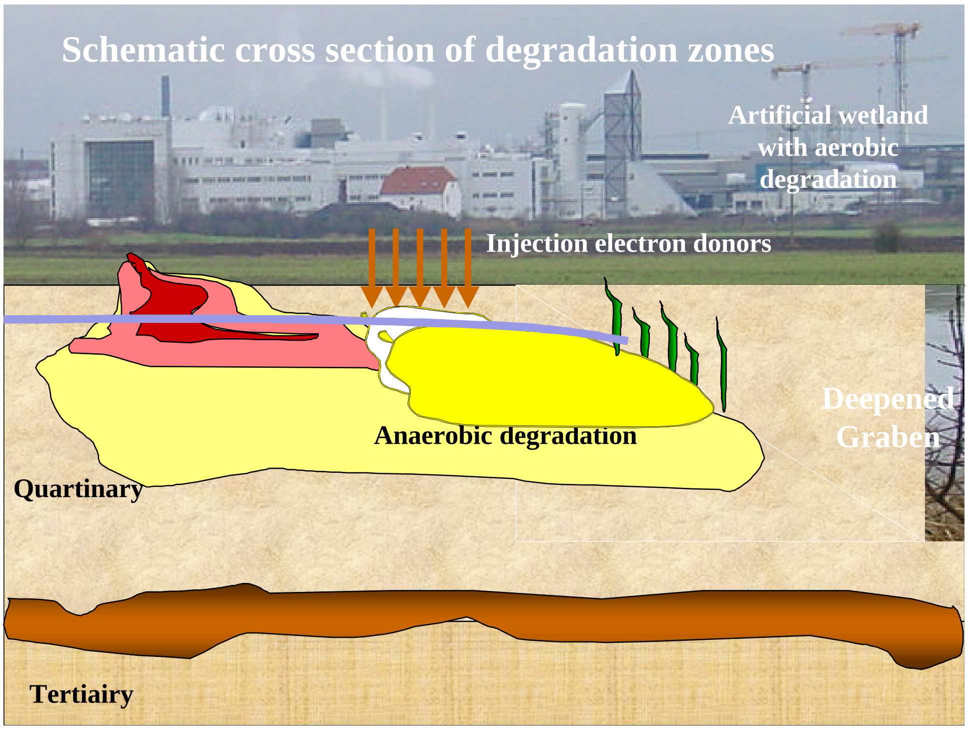

Figure 5. Schematic cross section of the anaerobic degradation zone with electron donor injection, and the landscape-integrated aerobic zone.

Outlook

Future research will focus on

- optimisation of the monochlorobenzene degradation in the on-site reactors at the test site and the up scaling of this system to one of the *in situ* reactor trains
- upscaling of the anaerobic dechlorination process with low electron donor concentrations, as has been found in the laboratory column studies.
- implementation of the anaerobic-aerobic degradation process to a large-scale field application.

Acknowledgments

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MICROBIOLOGICAL APPROACHES AND INVESTIGATIONS OF A SOIL IN STORMWATER TREATMENT BY INFILTRATION BASIN IN AN URBAN AREA

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Summary

The effect of urban stormwater on the soil of an infiltration basin was studied as part of the OTHU Research Federation (Field Observatory in Urban Hydrology of Lyon). We carried out several types of physico-chemical and bacterial measurements for three vertical profiles. We observed high heavy metals concentrations to depth 1.5m. The results differed according to the site sampled. Changes in bacterial population estimation, dehydrogenase activity and response to increased zinc concentration in medium culture were also observed according to the depth and location of the profile.

1. Introduction

The development of urban areas tends to increase the impermeable surface area, which increases the amount of run-off water. The most common techniques involve the use of drainage ditches, infiltration wells, holding basins and/or infiltration basins. Infiltration basins are particularly favoured in the eastern part of the Lyon area (France) due to the distance of this area from the local river (the Rhone) and the high permeability of the soil in this area. Numerous basins collect and infiltrate stormwater from surfaces (industrial or residential) of up to several hundred hectares in size. This type of system may concentrate dilute pollutants, resulting in a risk for the quality of soil and groundwater (Ford *et al.*, 1992; Yousef and Yu, 1992; Appleyard, 1993; Mikkelsen *et al.*, 1994). This risk is greater in urban and periurban areas due to the higher levels of pollutants in these areas (Pilgrim and Schroeder, 1997). Little is known about the bacterial characteristics and activity in such a system and their role in the non-saturated zone evolution. We studied the first four meters of the soil of an infiltration basin that collects stormwaters from an industrial watershed. Bacterial estimation were studied on three different horizontal profiles (Figures 1 and 2), and silmutaneously chemical parameters were determined (pH, organic matter, total Pb, Cu, Cd, Cr and Zn content). Moreover, we maked estimation of bacterial respiration and deshydrogenase activity on the first depth (0-30 cm), and determined the minimal concentration of inhibition (M.C.I.) on the microflora for zinc.

2. Description of the site

This system has been operational for about 20 years, and currently consists of an holding basin, an holding/infiltration basin and a disused, clogged infiltration basin. We studied only the holding/infiltration basin (Figure 1), which collects some of the water from the stormwater network and the water from the holding basin. The basin is approximately 5.5 m deep, has a bottom surface area of 7,406 m² when empty and a slope of 0.001 %. The basin can hold up to 30,856 m^3 of water and can empty at a rate of approximately 0.5 $m^3.s^{-1}$. The total surface area of the watershed drained is approximately 185 ha. The run-off coefficient is estimated to be 70 to 75%. The drained surfaces are in a stabilised industrial area. The piezometric area of groundwater is 13 metres from the bottom of the basin. The thickness of the non-saturated zone is, therefore, significant. The main pollutants involved are heavy metals, cyanides, inks, fats, hydrocarbons, and solvents.

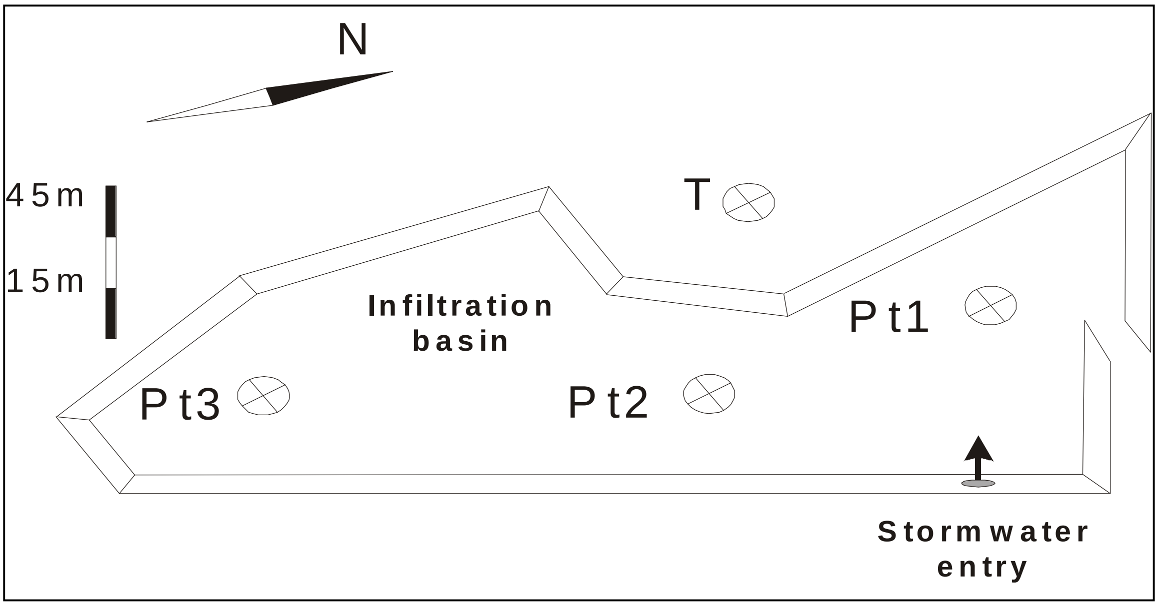

Figure 1: Plan of the infiltration basin studied with the position of three profiles (Pt1, Pt2 and Pt3) and the reference (T).

3. Materials and Methods

3.1 Sampling

Three probes were taken in the current holding/infiltration basin (Figure 1):

- Pt1: near the stormwater entry pipe,
- Pt2: in the middle of the basin,
- Pt3: at the Southern extremity of the basin.

Soil samples were collected by shovel and by hand auger every 0.05 to 0.10 m, to a depth of 0.5 m, and then by power shovel every 0.20 m, to a depth of 4 m. The soil was homogenised on site before the taking of samples for analysis.

A fourth sample was taken with power shovel from the area around the basin. This was used as a control sample not subjected to the impact of stormwater from the network. This was an averaged sample, corresponding to a homogenised mixture of the first 50 cm of the soil

3.2 Measures and methods used

The concentration of heavy metals was determined in samples dried at 60°C for 48 hours. The dried samples (0.5 g) were passed through a sieve with holes 2 mm in diameter and then mineralised by heating in a microwave oven with acid [7 ml of 65% HNO_3 (Suprapur Merck) and 3 ml of 48 % HF (Ultrapur Merck)] (Hewitt and Reynolds, 1990; Lamble and Hill, 1998). The resulting solution was analysed in detail by graphite furnace atomic absorption spectrometry (GFAAS) (Dean *et al*., 1998).

The pH in water was determined according to the standard NF X 31-103 (Afnor, 1994). The combustible (organic) matter corresponded to the decrease in mass of the sample after heating for 2 hours at 800°C. Total carbonates content was determined according to standard NF X 31-105 (Afnor, 1994).

The medium used to grow bacteria, plate count agar (PCA), was prepared according to the manufacturer's instructions (Difco) and autoclaved. An antifungal agent was added (final concentration 0.25 mg/ml), and the medium poured into 90 mm Petri dishes (Greiner). Ten grams of dry sample was placed into a sterilised Waring Blender and 50 ml of sterile 0.8% NaCl was added. The mixture was homogenised for 1mn 30s and the resulting suspension was diluted. For each dilution retained, 100 µl of suspension was spread over the agar surface in sterile conditions. The Petri dishes were incubated at 28° C in the dark for 96 hours. Bacterial colonies were counted at 48 and 96 hours. Counts were determined only for plates that contained between 30 and 300 colony-forming units (CFU). Counts were made in triplicate for each sample. Zinc ($Zn\ SO_4$) was added until 1.5 g/L in medium culture (pH veirified) for estimate the evolution of bacterial population in presence of increased concentration of zinc. The method used to measure dehydrogenase activity was described by Brohon *et al.* (2001) who used iodonitrotetrazolium (INT) as substrate and measured iodonitrotetrazolium formazan (INTF) formed. This activity was expressed by µg INTF/g of soil DW/24 h.

4. Results-Discussion

The reference soil (noted T; Figure 1) is mineral carbonated soil and has very low bacterial numbers (10^4 CFU/g DW). The bacterial population at the three sample sites was estimated to be between 10^4 and 10^7 CFU/g dry soil (Figure 2). Similar values have been reported for agricultural soils, in which the same techniques demonstrated the presence of between 10^6 and 10^8 CFU/g dry soil (Blaine Meeting, 1992). We observed that bacterial population was decreasing as a function of depth at the three sample sites. There was a two log difference in the number of bacteria on the surface and at depth. However, we noted an increase in the bacterial population (clearly visible at Pt1) between 1.40 and 1.60 m depth.

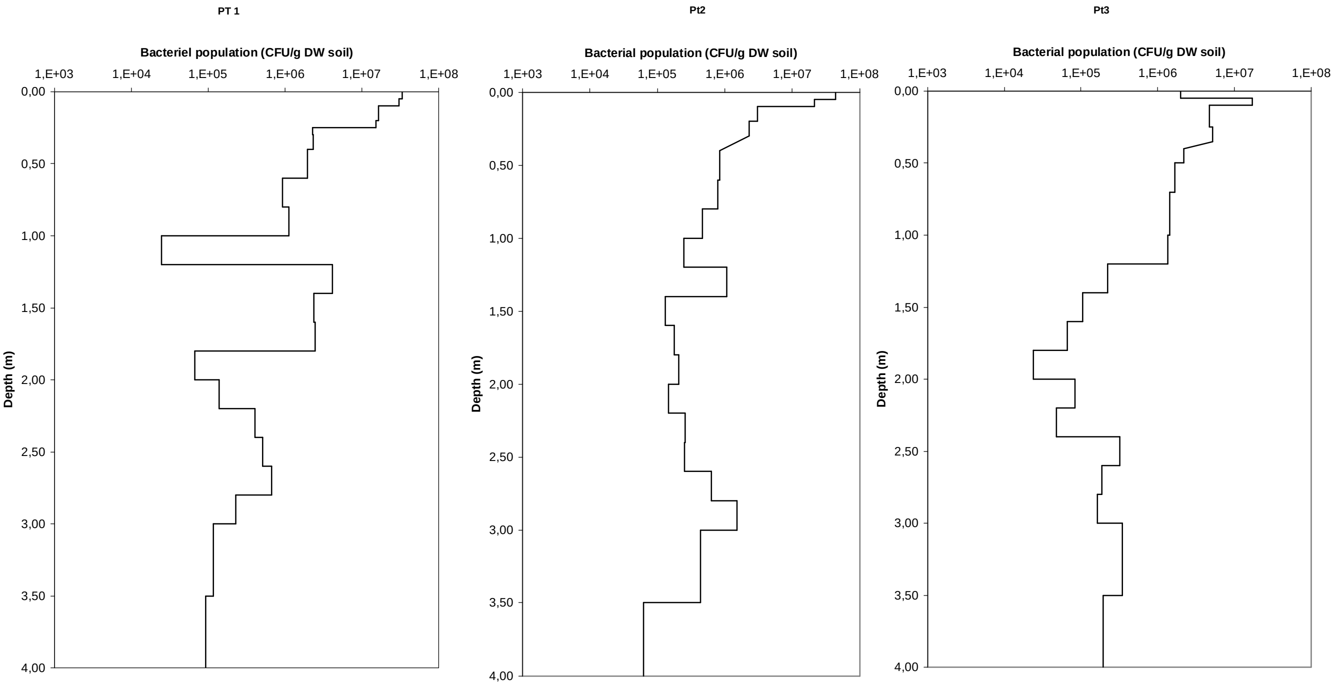

Figure 2: Horizontal profiles of bacterial population on the infiltration basin.

Table 1: Dehydrogenase activity of bacterial population.

Depth (cm)	Activity in Pt 1 (µg/g FW/24h)	Activity in Pt 2 (µg/g FW/24h)	Activity in Pt 3 (µg/g FW/24h)
0 -10	164.95 *± 9.1*	156.3 *± 11.25*	122.55 *± 6.9*
10 -20	121.26 *± 8.4*	22.04 *± 10.7*	58.51 *± 7.8*
20 -30	57.1 *± 8.5*	19.97 *± 11.2*	22.75 *± 5.2*

High dehydrogenase activities were expressed in the 10^{st} cm of the samples (Table 1). Quickly, values decreased with depth until in samples of Pt1 where measures decreased more slowly and were still twofold in comparison with samples of Pt2 and Pt3 (Table 1). Similar trend of INT activity values were obtained in soil amended with differents contaminated sludges and the first 10 cm samples of our study (Brohon, 2001).

Increased zinc concentration in medium culture showed a different evolution of bacterial population extracted of the samples (Figure 3). With high metallic concentration, values of bacterial estimation decreased from approximately 10^7 to 10^4 (Pt3) and 10^5 (Pt1) CFU/g DW excepted in samples of Pt2 where 10^6 CFU/gDW were still determined. The bacterial population showed an impact on bacterial growth with concentration upper than 0.5 g/L but not for extracts of Pt2 where not significant difference was observed in estimation with uncontaminated medium (Figure 3). High resistant bacterial population appeared to be estimate in the samples of Pt2 where the highest Zn content was measured (figure4).

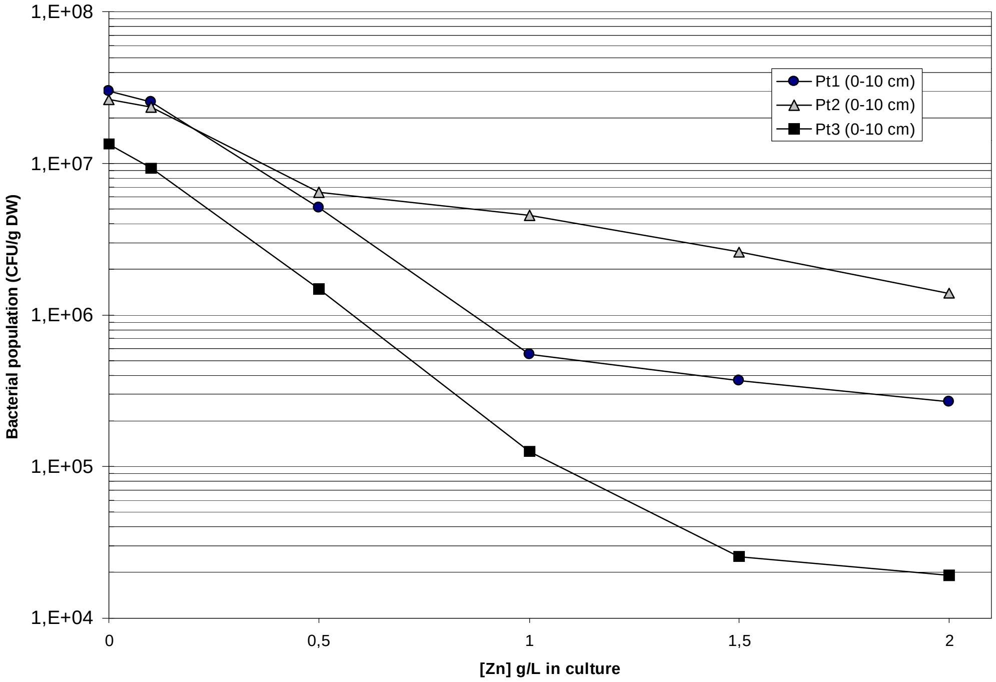

Figure 3 : Evolution of bacterial population with increased zinc concentration in medium culture.

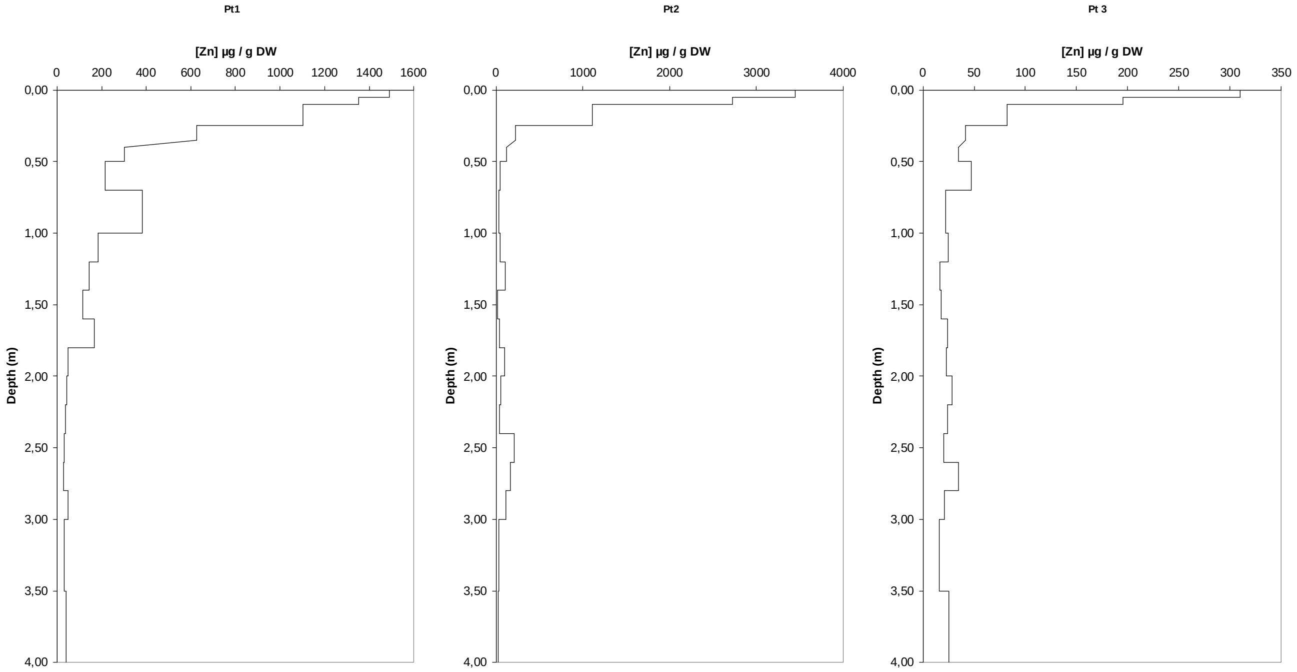

Figure 4 : Horizontal profile of Zinc contents on the infiltration basin.

We observed the similar trend as the bacterial population, physico-chemical parameters were decreasing as a function of depth at the three sample sites. At Pt1, Pb, Cd and Cu concentrations were high to a depth of 1.5 m (as Zn in Figure 4) and significantly higher than those in the control soil (date not shown). After 1.5 m, the concentrations of these elements were close to those in the control. Details of physico-chemical measurements were described before by Winiarski *et al.* (2001).

5. Conclusions

The results showed that there is high values of bacteries and pollutants at the surface, showing that micro organisms are introduced in the soil via the suspended organic solids of storm water. The influence of the infiltration is noted until 1.5 depth in the most polluted point studied. An adapted bacterial population who expressed a metallic resistance and high metabolic activity were developed in the non saturated zone of the soil and play a major role on the degradation and transfer of pollutants in the soil.

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APPLICATION OF "INTEGRAL PUMPING TESTS" FOR INTEGRATIVE GROUNDWATER INVESTIGATION IN LINZ-HEILHAM

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Keywords

ground water; integral investigation, integral pumping test (IPT), mass flow; CHC

Introduction

To investigate a CHC contaminated influx to one of the urban water works in Linz (Upper Austria), the integrative technique of "Integral Pumping Tests (IPT´s)" was applied. The objectives were to identify potential plume sources and estimate the mass fluxes. This new approach of integrative groundwater investigation allowed the monitoring of groundwater quality in within an area of approximately 45ha. Therefore long-term constant rate tests combined with concentration time series measurements (i.e. IPT´s) at 10 wells arranged within 3 cross sections were carried out. The investigations were executed as part of the **In**tegral **Co**ncept for Groundwater **Re**mediation (INCORE) project carried out under the 5th Framework Programme of the European Community for Research, Technological Development and Demonstration activities.

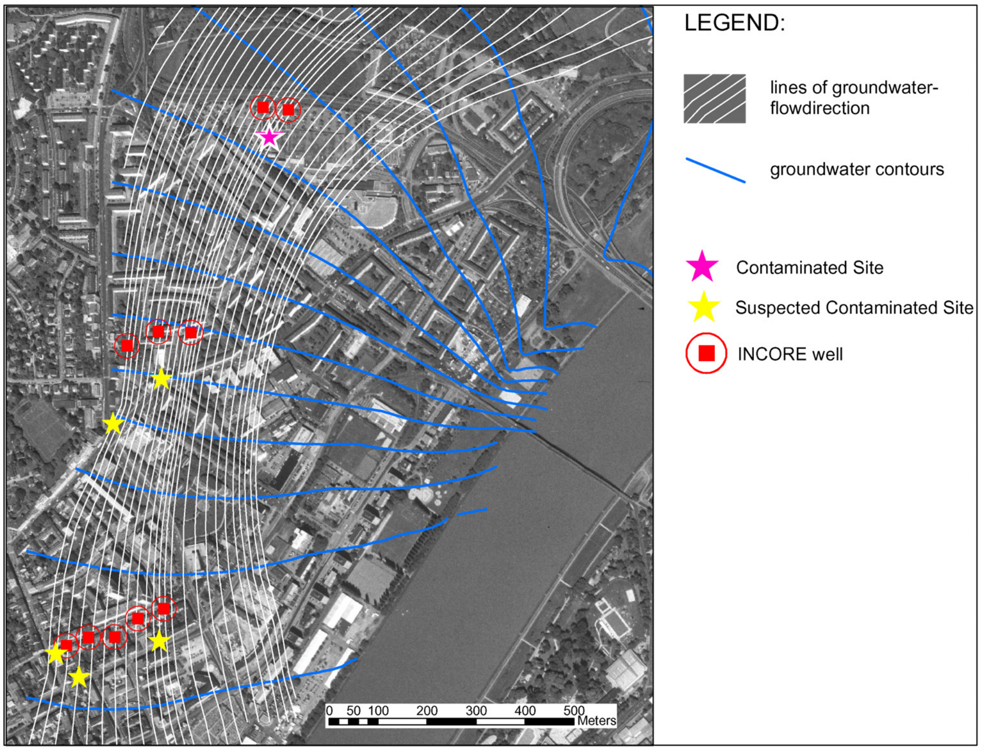

Figure 1: Project area of INCORE Linz-Heilham

Material and Methods

Up to the mid 80ies, until a CHC contamination was encountered, the high quality bank-filtered groundwater from the Heilham waterworks was used as an essential part of the municipal water supply. Since 1997 the two main wells are being used as recovering wells.

The waterworks are situated in the northwestern part of a quaternary river basin filled with well permeable sandy gravel and is framed by the banks of the Danube to the south and by the foothills of the Variszic Mountains to the north. The southern part of the catchment zone is a highly urbanized area where 6 sites, mainly dry textile cleaning operations, were suspected to cause the contaminations in Well No. 1.

With the objectives covering the potential plumes coming from these known sites and identifying the main polluters 10 new wells, arranged within 3 control planes (PL 2-4), had to be drilled. For characterization of the groundwater chemistry within each control plane, constant rate tests combined with CHC concentration time series measurements (IPT´s) at each new well were carried out. Additionally the updated groundwater model shows, that all water passing the potential source zones is captured by Well No. 1. of the water works. Hence, because the concentration of CHC is known, a complete mass balance can be calculated as Well No.1 can be understood as control plane No. 1.

To achieve diameters of influence up to 70 meters, pumping times of up to 7 days and pumping rates of up to 14 l/sec were required. As the capture zones increase during pumping, the distance of influence is a function of time. Hence, for getting a resolution of about 3 meters in radius, about 10 concentration measurements of CHC within a default time schedule at each pumping test had to be made. Furthermore the tests were accompanied by continuous measurement of water level, flow rate, pH-value, temperature, conductivity and oxygen content. To avoid disturbance by the influent groundwater they had to be performed from downstream to upstream.

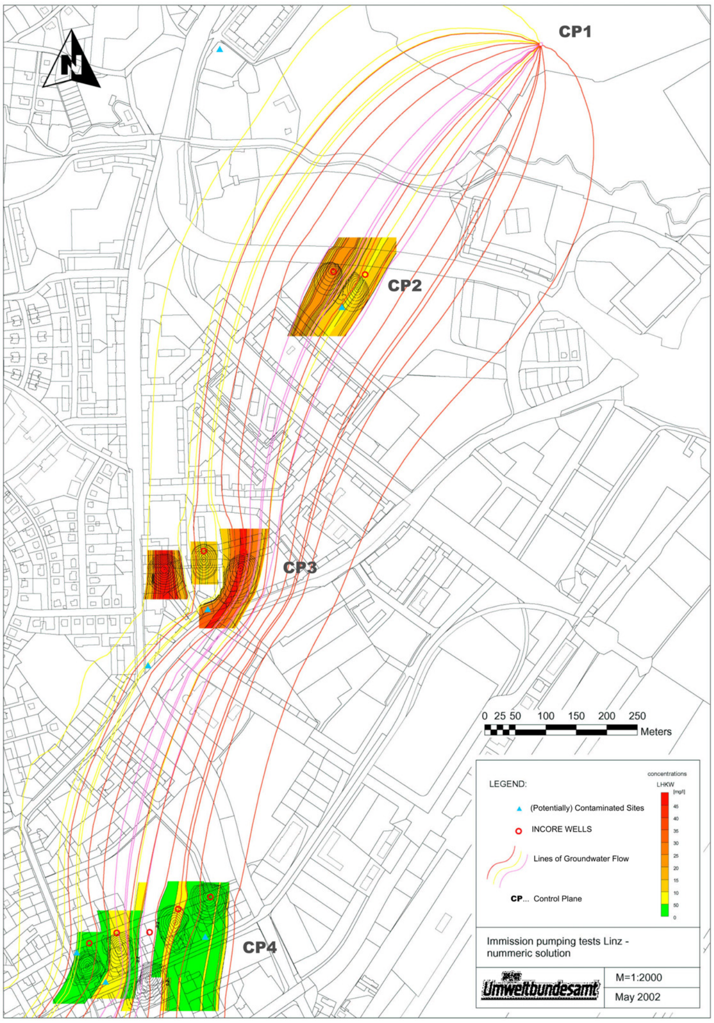

Figure 2: Interpretation of numerical processed data (INCORE Linz-Heilham)

Results

The chemical and hydraulic raw data were processed using analytical data conversion as well as a transient inversion algorithm based on a numerical flow and transport model of the field site. The results showed evidence of two distinct main plumes at control plane No. 3, where concentrations of 60 µg/l TCE were measured and mass fluxes of 5 to 7 g/day were calculated. Furthermore two or three plumes with reduced concentrations of up to 8 µg/l TCE were detected at control plane No. 2. Altogether about 22 g/day of TCE pass the 3 control planes and reach the water works.

Conclusions

In the case of Linz-Heilham "Integral Pumping Tests" proved to be a useful tool for multiple plume investigation. Compared to preliminary standard investigations this new approach offers a high level of certainty whereby the higher preliminary investigation costs could be compensated through further investigations.

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THE DISTRIBUTION OF MERCURY IN A CHARACTERIZED SOIL AFFECTED BY MINING ACTIVITIES

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1. Introduction

Mining activities enhance the mobility and dispersion of Hg in the environment and in this case the soils are a main receptor of this contaminant. These soils have evolved under Mediterranean conditions and act as a sink. Depending on the mercury form, it will be more or less available to other environmental compartments such as the vegetation as well as the leaching into hydrological systems. Mercury occurs naturally in the soil as Hg^{2+} through weathering of the lithological substrate, erosive action, atmospheric deposition (dry and wet) and to a lesser extent by the decomposition of the vegetation. Under environmental conditions, mercury can be present in any of the three oxidation states Hg^0, $Hg_2^{(2+)}$ and $Hg^{(2+)}$. The soil is considered a determinant factor in the adsorption of the contaminant and parameters such as pH, clay and organic matter influence the amount of bioavailable mercury (Yin *et al.*, 1996; Steinnes, 1990).

The Almadén district, in central Spain, contains the largest mercury concentration in the world with about a third of the known global mercury resources (Hernandez *et al.*, 1999). Mercury deposits are located within the Almadén syncline, a major tectonic structure, where mafic volcanic and subvolcanic rocks (basalt, dolerite) have been derived from a deep mantle source (Higueras *et al.*, 2000). Mercury has been exploited since the Celtic and Roman times and, apart from disasters (fire, flooding and war), has been continuous till 1999 when the mine was finally closed (Higueras *et al.*, 2001). Besides the volcanic-sedimentary origin of mercury, further deposition of this heavy metal proceeds from the airborne emissions released from an old metallurgical plant situated in the proximity of the selected study area as well as from the mining activities carried out in the area over the past milleniums.

Extensive work on the distribution of mercury in the environment of Almadén has been carried out by the Consejos de las Minas de Almadén, la Dirección General de Sanidad (Spain) and the U.S. Environmental Protection Agency (Hildebrand, 1980). More detailed studies on mercury in Mediterranean soils have included analyses of soil surface samples for bioremediation purposes (Carrasco *et al.*, 2001 and Rodríguez *et al.*, *in press*), and an environmental survey including different soil typology samples throughout the Almadén area (Higueras *et al.*, 2001). Furthermore, lysimeter experiments are within the framework of a project to restore soils affected by mercury applying phytoremediation techniques, being carried out in CIEMAT (Research Centre for Energy, Environment and Technology). Undisturbed soil monoliths of 1 m^3 were prepared and extracted from the study area (Millán *et al.*, 2002). A total of five lysimeters containing these soil monoliths were transported from Almadén and installed in the Research Centre in Madrid.

The main objective of this study is to determine the mercury content and the physicochemical properties of a soil type affected by an extensive mining history of mercury. Detailed soil analyses from two profile locations are obtained from the area where the soil monoliths have been extracted to be implemented as lysimeter experiments for monitoring the conditions of these soils applying different types of cultivation. A further aim is to obtain initial monitoring results related with the conditions found in the lysimeter soils.

2. Description of the study area

The area is located near Almadén, in the proximity of the Almadenejos village, in the province of Ciudad Real (Autonomous region of Castilla La Mancha) in the Central part of Spain. The climate is defined as Mediterranean with wet and cool winters, and dry and warm summers. According to the Almadén Minas weather station with data over 30 years (Carrasco *et al.,* 2001), the mean annual temperature is 16 ºC and the mean annual precipitation is 587 mm. The water balance for the region shows a winter surplus and a lack of water during the summer months. The mean annual potential evapotranspiration is 963 mm and peaks in the summer during less rainy months. This is significant for the soil water reserves that become depleted in summer and the soil remains dry till the autumn rains. According to the Soil Taxonomy (Soil Survey Staff, 1999), this is a xeric moisture regime.

This area, at 500 m.a.s.l., is in the Central Iberian Zone which forms part of the Iberian Hercynian Massif and is characterised by the presence of deformed and metamorphosed detritic rocks as shale, sandstone and quartzite. The Mediterranean conditions influence the flora which is represented by dominant sclerophyllous formations (Mediterranean oaks and cork trees) on siliceous bedrock. The land use of the area has been mainly pasture land where livestock could graze and a common practise in the region was to obtain charcoal by smouldering piles of wood covered by soil using the Mediterranean oak trees from the region. In the vicinity (within a radius of 1 km), the mining and roasting operations from the old metallurgical plant of Almadenejos was the source of mercury deposition from airborne emissions (Ferrara *et al*., 1998).

The specific area where the lysimeters have been extracted consists of a rectangular plot 5m by 15 m and lies on the lower slop of a depression (*Figure 1*). The two soil profiles are situated on the extreme ends of the plot at a maximum distance apart. Prior to the sampling of these soil profiles and the extraction of the soil monoliths for the lysimeters, barley was cultivated for two successive years. This included a superficial ploughing before the barley was sown with the objective of maintaining, as far as possible, the soil structure close to the surface. This enables future experimentation to be carried out in practically natural soils.

Figure 1. The study area.

3. Field and laboratory analyses

The two soil profiles have been surveyed in the field and sampled respecting the identified soil horizons at intervals from the surface to a depth of 110 cm. As the soil layers vary in thickness, the number of samples is proportional to the thickness of a soil layer. In laboratory controlled conditions, the samples have been air dried and sieved to a grain size of less than 2 mm to obtain the soil texture for the physical and chemical analyses.

The analyses include texture (Bouyoucos method), colour (Munsell chart), pH (water saturated paste), organic matter - OM (Walkey-Black wet oxidized procedure) and clay minerals (X-ray diffraction). Cation exchange capacity (CEC) was done by shaking 0,500 gram of sample with 8 ml 1M NH_4Cl for 4 hours at room temperature. The solution was analysed by ICP-AES (Ca and Mg) and FAES (Na and K). Major, minor and trace elements were determined by ICP-AES and FAES after complete dissolution of the samples using a mixture of HF and $HCl:HNO_3$ (3:1) at a PTFE closed vessel, heated overnight at 90ºC. The excess of HF was removed by addition of concentrated $HClO_4$ and the solution was evaporated to white fumes prior to final dissolution with diluted HNO_3. Total carbon, nitrogen and sulphur contents were determined by using a Leco CS-244 and a Carlo Erba EA 1108 elemental analysers. Inorganic carbon was estimated by measurement of remaining C, after ignition of the sample at 550º C. Iron (II) contents were obtained by boiling the sample with 20% HCl in a closed CO_2 atmosphere for 1 hour and final measurements were carried out with the ferrozine spectrophotometric method. Mercury content was measured using an atomic absorption spectrophotometer specifically designed for mercury determination (AMA-254), with a detection limit of 0.5 ppb. Quality control of mercury measurements was achieved by analysing two standard reference materials: CRM-281 (rye-grass, 0.0205±0.0019 ppm of Hg) and BCR-62 (olive leaves, 0.28±0.02 ppm of Hg), being the average value from ten measurements of 0.0210±0.0003 ppm and 0.290±0.002 ppm, respectively.

The instrumentation of the lysimeters includes moisture humidimeter probes with temperature sensor, electronic vacuum meters on tensiometric tubes, pH and Eh electrodes, and soil solution sampling tubes. These sensors have been set at 15, 25 and 50 cm depth in the individual lysimeters. In order to monitor the soil properties, an electronic data collector (Darwin DC100, Yokogawa) is implemented to obtain data for each sensor. The exception is the pH sensor, where the signal is too weak to be obtained by the data collector. The pH is therefore obtained with a standard pH meter. These sensors are calibrated by the makers and correction factors are supplied when purchasing them. Where possible, a calibration has been carried out for individual sensors to ensure a correct data uptake. Barley has been sown in the lysimeters as a representative crop found in the study area and one lysimeter has been left in fallow as a control.

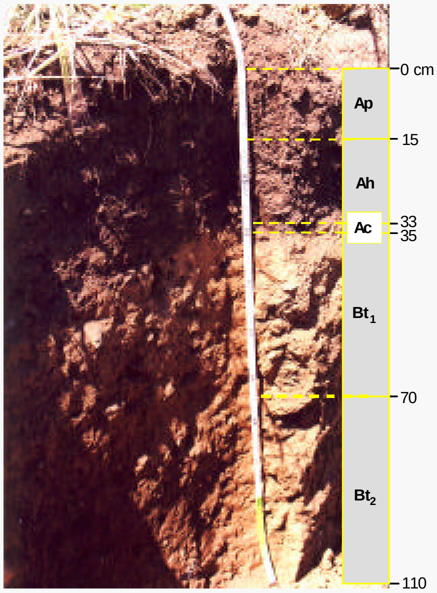
4. Results and discussion

The results are presented for the individual soil profiles with a description of the corresponding soil horizons obtained from filed observation and supported by soil analyses carried out in the laboratory. Furthermore, results of the physical and chemical analyses are represented according to the samples taken at different intervals respecting the edaphic horizons identified. Preliminary results have been obtained with the sensors monitoring the soil conditions in the lysimeters and an example is presented in association with the one of the soil profiles.

General observations for the two soil profiles show that they are located in the bottom slope of a gentle depression (0-2%). Rain fed crops like barley is a common cultivation in this area and indicates that the soil is of medium to low fertility.

Soil profile 1

The initial observations obtained in the field show that the soil profile has two master horizons, an upper A horizon and lower B horizon (*Figure 2*). As the land is cultivated, the upper horizon is under human influence and a ploughed horizon is evident. However, the ploughing is superficial and does not pass through the entire A horizon. This can be shown by the smooth lower boundary present at 33 cm. There is also a weak structure present in the Ah horizon with a slight change of colour (increase in croma).



Location: Camino de Los Santos in the Dehesa of Castilseras

Situation: Amadenedejos-Gargantiel Road (CR-4192)

UTM Coordinates: 352 180 Eastings, 428 9592 Northings

Altitude: 480 m.a.s.l.

Landuse: Rain fed cultivation

Slope: Flat or near to flat (0 – 2%)

Soil classification (USDA): Alfisol, Xeralf, Haploxeralf, Mollic Haploxeralf

0–15 cm; Colour: 5YR3/2 (dry), 5YR2.5/1 (wet); sandy loam texture; superficially ploughed horizon with no structure; high biological activity; abundant fine roots; high porosity; diffuse and wavy lower boundary.

15–33 cm; Colour: 5YR3/4 (dry), 5YR2.5/2 (wet); sandy loam texture, crumb structure, few rock fragments angular 5-10 mm; angular rock fragments (5–10 mm); high biological activity, abundant fine roots; medium to high porosity; occasional pieces of charcoal; medium faint reddish brown mottles at the lower limit; smooth lower boundary.

33–35 cm; Colour: 5YR4/2 (dry), 5YR3/2 (wet); sandy loam texture, moderately calcareous soil reaction; concretionary accumulation of calcium carbonate due to anthropogenic influence; clear and wavy lower boundary.

35–70 cm; Colour: 7.5YR5/4 (dry), 7.5YR4/4 (wet); loam texture, moderate blocky angular structure, angular rock fragments (> 3 cm); low biological activity, few medium roots, low porosity; slightly sticky and plastic; diffuse lower boundary.

70–110 cm; Colour: 7.5YR4/4 (dry), 7.5YR3/4 (wet); loam texture, blocky angular structure, few angular rock fragments (> 3 cm); very low biological activity, very few medium roots; very low porosity; sticky and plastic; lower boundary not reached.

Figure 2. Description of the soil profile Castilseras 1.

A high biological activity is present with abundant fine roots and together with the sandy loam texture results in a relatively porous soil which is important for the water infiltration. This is backed by a high OM content in the A horizon. There is presence of organic carbon in the Ah horizon as a result of the above mentioned process for making charcoal. Furthermore, there is a presence of medium faint mottles at the lower limit, indicating that there is a period of water accumulation. This could be related with the lower horizons, where infiltration is reduced as a result of an increase in the clay texture.

A fine horizon of 2 cm is clearly present which gives the unexpected calcareous reaction when a few drops of 0.1M of HCl is added. The presence of this calcium carbonate is therefore indicated as a concretion accumulation and related to the practise of elaborating carbon.

The B horizon has a clear increase of clay with depth and has been divided into two sub horizons Bt_1 and Bt_2. distinguished with a change in the value of the colour. An increase of angular rock fragments is observed together with an important reduction in biological activity and few roots. The porosity of the soil is definitely low and the touch is slightly sticky and plastic. The lower boundary of the B horizon has not been reached at a depth of 110 cm.

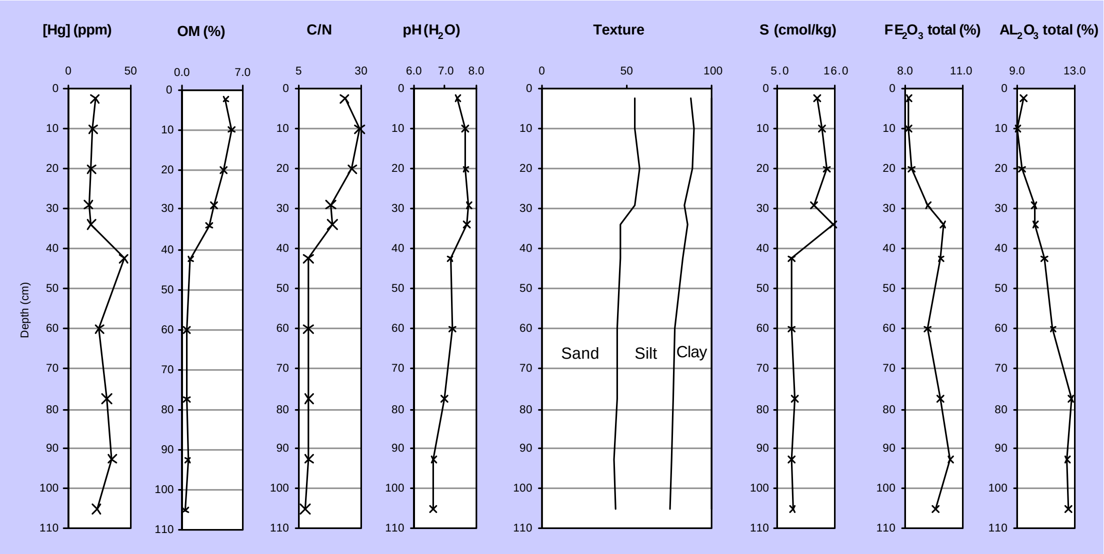


Figure 3. Soil analytical data for profile Castilseras 1.

The varying mercury content throughout the soil profile can be shown to be related with a number of soil parameters (*Figure 3.*). This is especially apparent at 35 to 50 cm, where a maximum value of mercury was 44.61 ± 3.67 ppm. This is within the upper part of the Bt_1 horizon and coincides with the increase in clay and indicates an accumulation of the contaminant. Furthermore there are sharp decreases of the OM, the C/N ratio and the CEC of the exchangeable bases (S value) once the B horizon is present. The pH value also starts to decrease with depth and reaches a minimum value of 5.8 in the Bt_2 horizon. The total iron increases in the anthropogenic influenced horizon of 33 to 35 cm and in the Bt_2 at a depth of 60 to 95 cm. This latter increase together with the total Al_2O_3 has its origin from the clay mineral layers.

The total sulphur content in the fine earth fraction (<2mm) shows values of less than 0.10% and this means that there is no significant weathering of rocks containing mercury. However, there is an important presence of cinnabar (3-20 cm) within the B horizon. The x-ray diffraction carried out for the mineral B horizon shows the presence of kaolinite and illite clay minerals.

Soil profile 2

This soil profile will have certain similarities due to its proximity with the first profile. However, substantial differences can be observed and highlighted. Again the initial observations obtained in the field show that the soil profile has an upper A horizon and lower B horizon (*Figure 4*). This time the horizon is determined as Ap and lies directly over two differentiated anthropogenic horizons. The soil has a weak structure and there are few rock fragments present. As in the previous profile, this layer has the conditions for water infiltration.

Location: Camino de Los Santos in the Dehesa of Castilseras

Situation: Amadenedejos-Gargantiel Road (CR-4192)

UTM Coordinates: 352 193 Eastings, 428 9590 Northings

Altitude: 479 m.a.s.l.

Landuse: Rain fed cultivation

Slope: Flat or near to flat (0 – 2%)

Soil classification (USDA): Alfisol, Xeralf, Haploxeralf, Mollic Haploxeralf

0–20 cm; Colour: 7.5YR3/4 (dry), 7.5YR3/2 (wet); sandy loam texture; superficially ploughed horizon with weak structure; few rock fragments (angular 2-3 mm and round approx. 1.5 cm); high biological activity; abundant fine roots; high porosity; occasional pieces of charcoal; clear and wavy lower boundary.

20–22 cm; Colour: 5YR5/6 (dry), 5YR3/4 (wet); sandy loam texture, moderately calcareous soil reaction; concretionary accumulation of calcium carbonate due to anthropogenic influence; clear and wavy lower boundary.

22–35 cm; Colour: 5YR5/8 (dry), 5YR 4/4 (wet); sandy loam texture, man-made manurial horizon due to production of charcoal; non calcareous; low biological activity; few medium roots; medium porosity; gradual wavy lower boundary.

35–110 cm; Colour: 7.5YR5/4 (dry), 7.5YR 4/4 (wet); clay loam to clay texture, blocky angular structure, few angular rock fragments (> 3 cm); sticky and plastic; very low biological activity, very few medium roots, very low porosity; sticky and plastic; lower boundary not reached.

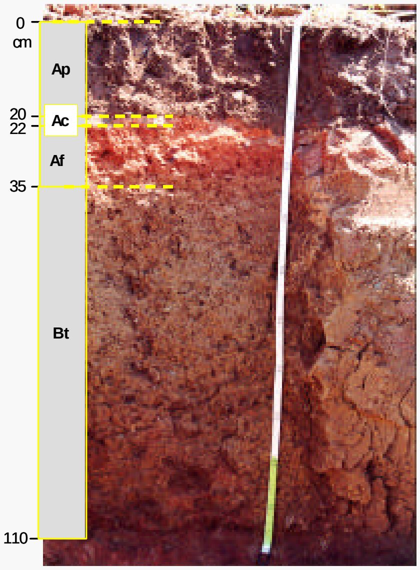


Figure 4. Description of the soil profile Castilseras 2.

The presence of calcium carbonate indicates a concretionary accumulation of anthropogenic origin. The next horizon is also anthropogenic, however there is no calcium carbonate. Instead a sharp increase in clay content is obtained from the texture analyses (*Figure 5*). A flluctuation of the total FE_2O_3 is observed with a peak of 12.9 % in the Ac and a slight reduction for the Af horizon to 12.4 %. This indicates a leaching of the iron oxides where again substantial material from anthropogenic activity has been deposited at this location.

A single Bt horizon was identified with a blocky angular structure and the touch is sticky with a plastic consistency. This is shown by the texture analysis that there is a clay content of at least 32% in the upper part of the B horizon and increases to 46 % in the lower part, and is represented with clay loam and clay, respectively. The low porosity is a further indication that this horizon is a characteristic impermeable soil layer.

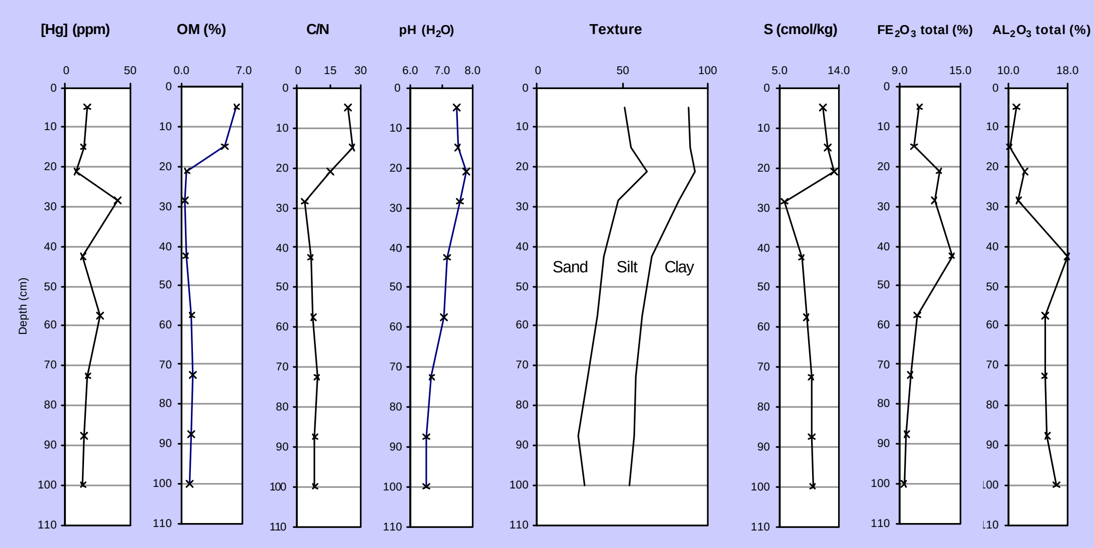


Figure 5. Soil analytical data for Castilseras profile 2.

A high mercury content of 40.23 ± 1.96 ppm is obtained at a depth of 22 to 35 cm in the anthropogenic layer identified as Af. This corresponds to similar soil characteristics, as observed in profile 1, such as an increase in the clay content, abrupt decrease of the OM, C/N ratio and the S value from the CEC of the base cations. The impermeable lower horizon impedes the movement of the mercury to a greater depth.

The classification of the soils found at these two locations is carried out according to the Soil Taxonomy (Soil Survey Staff, 1999). In both profiles, the soils have an argillic horizon and a moderate to high base saturation and fall within the order of the Alfisols. Due to the Meditterranean climate with a xeric moisture regime, the suborder is Xeralf. Within the great groups, these soils satisfy the conditions of Haploxeralfs and as these soils have an upper A horizon with a colour value, moist of 3 and more than 0.7 % of organic carbon, they are classified as Mollic Haploxeralfs.

Monitoring of soil conditions in the Lysimeters

The results presented for the monitoring of the soil conditions in the lysimeters is a sample taken over a period of two weeks at the end of the Summer, beginning of the Autumn of 2002 (*Figure 6*). The soil contained in this lysimeter was located close to soil profile 1 presented above.

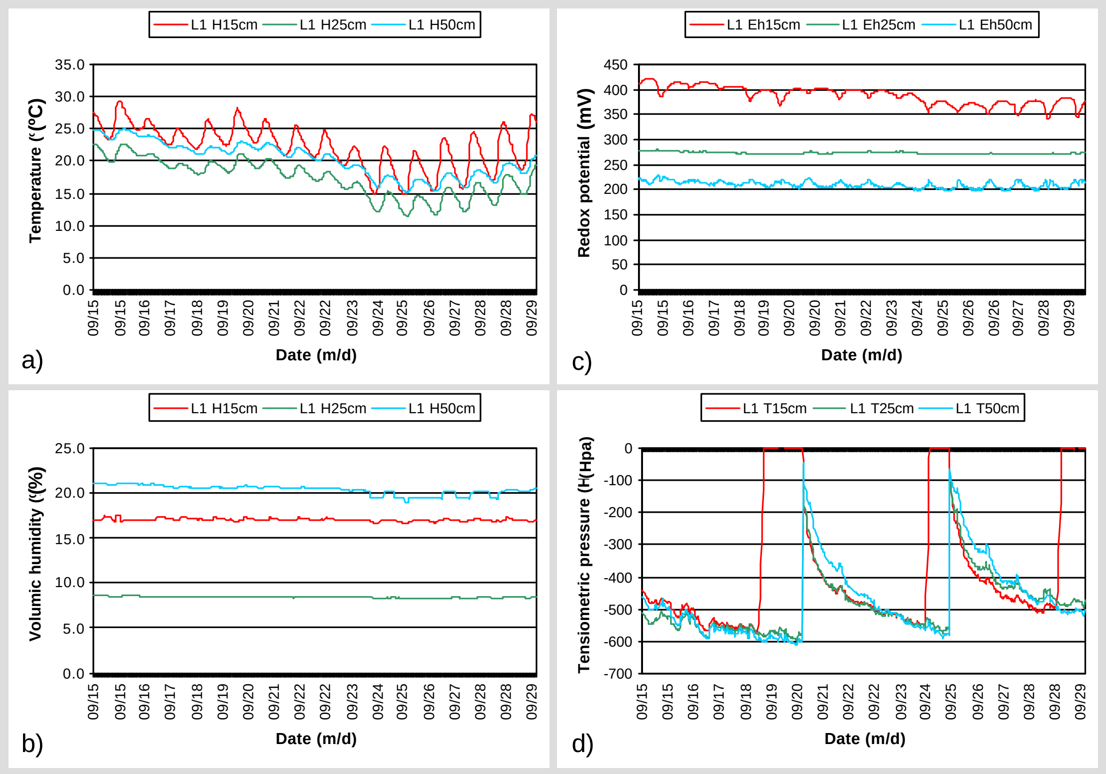


Figure 6. Monitoring data obtained from lysimeter 1 for a period of 2 weeks (15th to 29th of September) with a) soil temperature, b) volumic humidity, c) redox potential and d) tensiometric pressure.

The results are obtained at regular half hour intervals for sensors placed at the indicated depths of 15, 25 and 50 cm. The soil temperature in *Figure 6 a*) shows the diurnal cycle, where the fluctuation is in unison for the different depths. The greatest fluctuation is observed in the sensor nearest to the surface and with depth, this variation decreases. It is to note that the sensor at 50 cm registers a slightly higher temperature than at 25. Although the difference is a few degrees, the contrary is expected and a recalibration of the sensor at the end of the data campaign should account for any adjustments to be made. The volumic humidity (*Figure 6* b) for this period of the year is constant and after the Summer is expected to be low. More humidity is present in the lower part of the soil profile, which corresponds to the soil layer Bt$_1$ and therefore an increase of the clay content.

The redox potential (*Figure 6 c*) remains fairly constant with the higher values in the more aerated upper horizon and expected lower values for the Bt$_1$ horizon. In this case, an increase in clay content results in poor drainage and reduced aerobic conditions. The soil water matrix potential (*Figure 6 d*) at this time of period has a high negative value. This means that water is drawn from the tensiometric tubes as there is little water registered at the different depths throughout the soil. The negative pressure is maintained till all the water has been drawn out from the tubes and once air enters through the porous capsule the pressure returns to zero. The tensiometer at 15 cm will be first to register zero due to a smaller tensiometric tube with less holding capacity The tubes have to be regularly topped up and this explains the sudden return to zero. However, the sensors register the same maximum negative value for the different depths. A diurnal cycle can be observed, where a decrease in pressure in the tensiometric tubes signifies an increase of soil moisture as a result of morning dew. the slight lag between the observed curves is also related to the permeable upper horizon and the increase in clay in the lower layer. Values of 6.8, 7.5 and 7.3 pH units at the corresponding depths of 15, 25 and 50 cm, respectively, have been obtained at regular time intervals.

5. Conclusions

The texture and chemical analyses results from the samples confirm the existence of the edaphic horizons identified in both soil profiles. This includes an upper A horizon with an important organic matter content, a high C/N ratio and CIC of the base cations as well as low inorganic contents (derived from Fe_2O_3 and Al_2O_3). The lower B horizon has a significant clay accumulation and there is a sharp decrease of OM content, C/N and CIC of the base cations. The soils are characterised as Mollic Haploxeralfs.

The soils have been under the influence of anthropogenic actions such as the on site elaboration of charcoal pasture use for grazing and recent cultivation of rain fed crops. These influences are directly reflected in the soil profiles as ploughed upper horizons and the introduction of and accumulation of materials in the form of underlying materials.

Mercury in the upper A horizon proceeds from the atmospheric deposition and in the B horizon there is the presence of cinnabar rocks which shows the tectonic origin of mercury.

The Hg contents throughout the profiles are constant, close to 20 ppm, except for the samples taken at a depth where there is an increase of the clay content and as a consequence avoids the eluviation of anthropogenic mercury to lower limits.

The monitoring of the soil conditions in the lysimeters shows the greatest changes for the soil water potential together with soil surface temperatures. Near constant values are obtained for parameters such as volumetric moisture content, Eh and pH.

Lysimeter experiments provide a continuous monitoring of the physicochemical conditions found in the soil type from the study area. This will be of importance for the future evaluation of a phytoremediation technique *in situ*.

6. Acknowledgements

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BIOLOGICAL RECOVERY OF COPPER FROM LOW-GRADE OXIDE

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Abstract

Technically and economically feasible methods are required to recover metals from low-grade oxide ores. Pyrometallurgical and hydrometallurgical techniques are expensive and can have a negative impact on the environment. Stockpiling the ores can also imperil the environment through metal release. Sustainable development of mining ores is thus required. Biological leaching to recover the metals would fall into this category. Two biological approaches are examined in this work. The first involves the employment of *Aspergillus niger* to recover metals by production of organic acids to enhance metal solubilization from a mining ore with 7,245 mg/kg of copper. Various wastes were examined as substrates for fungal growth. They included molasses, sawdust, leaves, corn kernels and potato peels. The effectiveness was further enhanced when sulfuric acid was added to the medium. Maximum copper removal of 68% was achieved with potato peels treated with sulfuric acid. This is comparable to levels obtained when sucrose was used as the substrate. With acid pretreatment, sterilization of the media was not required. The second approach is the addition of biological surface active agents called biosurfactants to the ores to enhance metal extraction. These compounds are rhamnolipids that are anionic, biologically degradable and of low toxicity. Batch tests were performed at room temperature. Using a 2% rhamnolipid concentration, 28% of the copper was extracted. Although higher concentrations extracted more copper, the rhamnolipid solution became very viscous and difficult to work with. Addition of 1% NaOH with the rhamnolipid enhanced the removal up to 42% at a concentration of 2% rhamnolipid but decreased at higher surfactant concentrations. Of the two approaches, it appears that although the amount of copper extracted is a little less, the addition of biosurfactant is more promising than growing *A.niger* as the procedure is simpler and requires less residence time (6 days compared to 15 days).

INTRODUCTION

Bacterial leaching of metals from mining ores, also called bioleaching, is a full scale process that can be performed by slurry reactors or heap leaching. Mining wastes include low grade ores, mine tailings, low grade ores, sediments from lagoons or abandoned sites. Low pH values lead to solubilization of the metals in the mining ores. Elemental sulfur or ferrous iron may be added as bacterial substrates. Reactors such as Pachuca tanks, rollings reactor or in propeller vessels have been used (Tyagi et al. 1991). Heap leaching is more common since it allows the large volume wastes to be treated in place (Boom 2000). To enhance this process, aeration can be forced through the pile or hydrophilic sulfur compounds can be added (Tichy 2000). *Thiobacilli* bacteria are responsible for the oxidation of inorganic sulfur compounds. Applications include metal dissolution in low-grade sulfide ores, generation of acidic ferric sulfate leachate for hydrometallurgical purposes, and removal of gold by oxidation of pyrite by bacterial sulfide production. The extraction of metals from low grade metals ores and refractory gold ores is a multi-billion dollar business worldwide (Rawlings 1997). Bacterial solubilization by oxidation of the sulfide minerals, pyrite and arsenopyrite, enhances gold extraction by the traditional method of cyanidation. The solubilization mechanisms have been debated extensively, however.

Biohydrometallurgical processes are efficient and cause less environmental problems then chemical methods (Torma and Bosecker 1982). For slurry processes, the oxidation rate per reactor volume, pH, temperature, particle size, bacterial strain, slurry density, ferric and ferrous iron concentrations need to be optimized. Bioleaching is very effective for recovery of gold from refractory gold pyrite and copper from chalcopyrite.

One of the most significant applications of biohydrometallurgy is in low-grade ore recovery. For instance, Hoffmann *et al*. (1989) elaborated on a process in which ferric iron was biologically reduced to ferrous iron by *Pseudomonas sp*. strain. This method has been applied in steel production. Economical recovery of gold has been the main focus of some bio-leaching processes. Kleid *et al*. (1991) illustrated the use of cyanide-producing microorganisms in refractory gold ore. Hahn (1994) described a biological method for recovering copper from solid wastes containing 5% of copper. He utilized a microbial culture fed continuously with saccharose. After 18 days 99% copper had been extracted.

Bioleaching of fly ash by the fungus *Aspergillus niger* was first reported in 1996 (Bosshard et al. 1996). The experiments were conducted in shake flasks and the leaching of different metals such as Al, Cd, Cr, Cu, Zn and Mn present in fly ash was determined. Gadd *et al*. (1998) endorsed employing *Aspergillus niger* in bioremediation of radionuclide pollution. They also mentioned that, the process commercially is not yet feasible.

Mulligan *et al*. (1999, 2000) conducted various experiments with *Aspergillus niger* in the presence of different concentrations of low-grade ore and determined that 10% pulp density was optimal. This research is, however, focused on the evaluation of different substrates and their pretreatments in order to develop an inexpensive leaching process using *Aspergillus niger* for low-grade ores, to recover metals such as copper.

Another approach was also used in this study, addition of a biosurfactant to extract copper. The biosurfactant that is used in this study, a rhamnolipid, is from the glycolipids group and is made by *Pseudomonas aeruginosa* (Tsujii 1998). There are four types of rhamnolipids (Tsujii 1998). Rhamnolipid type I and type II are suitable for soil washing and heavy metal removal while type III is for metal processing, leather processing, lubricants, pulp and paper processing. Type IV is usually used in textiles, cleaners, foods, inks, paints, adhesives, personal care products, agricultural adjuvants, and water treatment (Jeneil 2001).

In the present study, the feasibility of using various substrates for production of organic acids by *A. niger* and the addition of a biosurfactant (rhamnolipids) for the extraction of copper from a low-grade oxide mining residue were investigated. The effect of various parameters was investigated to optimize the extraction of copper by the biosurfactant.

MATERIALS AND MATERIALS

2.1 Fungal strain and growth conditions

Aspergillus niger strain ATCC 6275 was obtained from American Type Culture Collection (ATCC), in a freeze dried state. The medium utilized for growth of the culture was based on the method of Bousshard et al. (1996) in which a culture was inoculated on a Potato Dextrose Agar (3.9% w/v). In order to obtain sufficient numbers of spores, the culture was kept for 7 days at 26°C in this medium. Afterward, sodium dodecyl sulfate (0.2% w/v) was used to recover the spores. The spores were counted using a Petroff-Hausser counting chamber where 1 mL of spores (approximately 3×10^7 spores) was obtained. The spores were then added to a 500 mL flask containing 150 mL of prepared medium.

2.2 Biosurfactants

There are four types of rhamnolipids (Tsujii 1998) including, rhamnolipid type I and type II which are suitable for soil washing and heavy metal removal (Jeneil 2001). The rhamnolipids, used in this study, were biosurfactants type I and type II from the glycolipid group made by *Pseudomonas aeruginosa* with the trademark JBR215 from “Jeneil Biosurfactant Co. JBR215 is an aqueous solution of rhamnolipid at 15% concentration. It is produced from a sterilized and centrifuged fermentation broth. Two major types of rhamnolipids, RLL (R1) and RRLL (R2), are present in the solution. Several tests done by the manufacturer and independent laboratories show the degree of biodegradability and toxicity of JBR215 match the EPA requirements. The CMC was found to be 0.035 g/L through conductivity measurement at various dilutions. This value is equivalent to 0.003% rhamnolipid. Therefore, for all experiments, a concentration above the CMC was used to ensure the formation of micelles.

2.3 Characterization of the mining residues

A sample of oxidized mining residues was obtained from a mine in the Gaspe region (Canada). Because of the large size of these residues, they were crushed. The crushed ore residue (obtained by passing crushed ore through sieve no. 4 and remaining on sieve no. 8) was selected. The quantity of metals was determined after nitric acid/ hydrogen peroxide digestion of the residues as described by Environment Canada (1990). The analysis of metals was performed by PERKIN ELMER atomic absorption spectrophotometer model Aanalyst 100. The results of the analysis are: copper, 8,950 mg/kg; nickel, 27 mg/kg and zinc, 201 mg/kg.

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2.4 Preparation of substrates

ACS reagent grade sucrose was obtained from Sigma-Aldrich Canada Ltd. (Oakville, Canada) and used for medium #1 (Table 1). Molasses was obtained from a local grocery. A quantity of 20 mL of molasses was diluted with 80 mL of distilled water and then the 100 mL/L of molasses solution was added per flask for medium #2. For the experiments with sawdust, sawdust was obtained from a local workshop and passed through sieve no. 16. The fraction passed through the sieve was used in all experiments with sawdust. Leaves (maple leaf variety) were collected from a local yard and left to air dry. The leaves were then crushed by hand and passed through sieve no. 10. The sieved fraction was then used for further experiments. Locally grown potatoes were peeled to remove the skins. The skins were collected, air dried and crushed by hand. Experiments were carried out with sulfuric acid by soaking the substrate in dilute sulfuric acid (pH 2) for 24 h. The substrate was then weighed and added to the mineral salts medium and the ore.

Table 1. Substrates evaluated and type of pretreatment used .

Medium	Substrate	Pretreatment
1	100 g/L sucrose	Autoclaved
2	100 mL/L molasses	Autoclaved
3	40 g/L sawdust passing through sieve no. 16	Autoclaved
4	40 g/L leaves passing through sieve no. 10	Autoclaved
5	40 g/L potato peels	Autoclaved
6	40 g/L potato peels	Dilute H_2SO_4 , without autoclaving and yeast extract (y.e.)
7	40 g/L sawdust passing through sieve no. 16	Dilute H_2SO_4, without autoclaving and y.e.
8	40 g/L leaves passing through sieve no. 10	Dilute H_2SO_4 without autoclaving and y.e.

2.5 Leaching of the mining residue by *A. niger*

All assays were carried out in a 150 mL volume. Medium, ore samples (100g/L) and salts (1.6 g/L yeast extract, 1.5 g/L $NaNO_3$, 0.5g/L KH_2PO_4, 0.025 g/L $MgSO_4$* $7H_2O$, 0.025 g/L KCl) were sterilized by autoclaving for 20 minutes at 121°C before spores were added. Afterwards, all flasks were sealed with removable cotton. Temperature was kept at 20°C during the experiment. Each flask was shaken by a BURRELL WRIST ACTION shaker during the period of the experiment in order to keep everything in a homogeneous slurry form. Samples were collected by disposable sterilized pipettes and filtered. Metals and organic acid quantities were then measured in the supernatant after filtration through 0.45 micron filters. Each experiment was done in triplicate and was repeatable to within 5 to 10%, and a control flask, one without the microorganisms, was used maintaining the same conditions. All media compositions are summarized in Table 1.

2.6 Methodology for washing with biosurfactant

To evaluate the effect of various parameters on the extraction of copper from the low- grade mining residue as well as to optimize extraction, several tests have been performed. All tests were duplicated and the difference between tests never exceeded more than 5%. Parameters were optimized step by step.

The ore was placed in batch reactors for copper extraction. For analysis, the ore particles were allowed to settle. The supernatant solution was then decanted from the ore and digested according to the procedure of APHA (1989), Method 3030E.

2.7 Analytical Methods

2.7.1 Determination of organic acids produced by A. niger

Samples were analyzed for organic acids after centrifugation with ICE HN-S II centrifuge at 3500 rpm for 10 min. Then the samples were filtered using a 0.45 micron microfilter. The method of Bousshard et al. (1996) was employed, in which the concentration of organic acids such as citric acid, oxalic acid, gluconic acid, malic acid and tartaric acid were determined by a Beckman Coulter System GOLD Model HPLC (High Pressure Liquid Chromatography). In this method an A-312 YMC-Pack column (6.0 mm x 150 mm in length) at a flow rate of 5 mL/min (room temperature), with a mobile phase of 50 mM monoammonium phosphate adjusted to pH 2.4 with H_3PO_4 was utilized. Concentrations of organic acids were measured based on a standard solution made with 0.1% citric acid, 0.1% malic acid, 0.1% tartaric acid, 0.01% oxalic and 0.1% phytic acid. Organic acid concentrations were measured and were plotted versus time.

2.7.2 Heavy metal analysis

At the end of each set of experiments, residue samples were washed with distilled water three times. Thereafter, the residues were air-dried for 24 hours. 5g of residue from assay was digested by nitric acid/hydrogen peroxide method, illustrated by Environment Canada (1990). All samples were filtered and the metal concentrations in all samples were determined by a PERKIN ELMER atomic Absorption model AAnalyst 100. Copper concentrations over time were plotted for all media and in each graph, copper concentrations in the control media were indicated as well..

3. RESULTS AND DISCUSSION

3.1 Biological leaching of copper using sucrose and molasses as substrates

Copper concentrations in all experiments and controls were determined. The first medium as previously mentioned was a sucrose medium (#1). Up to 60% of the copper was solubilized (Figure 1). These results showed good correlation with previous experiments (Mulligan and Galvez Cloutier 2000).

Molasses (medium #2), an inexpensive byproduct of sugar production which consists of 30 to 50% sucrose, showed good potential for solubilization of copper. Approximately 48% of the copper had solubilized by day 14. High amounts of organic acids, such as tartaric, malic, citric and phytic acids were generated. Although organic acid production was higher in medium #2 (Figure 2), larger amounts of copper were removed in the sucrose medium).

3.2 Biological leaching using leaves, sawdust and potato peels as substrates

Sawdust (medium #3) and leaves (medium #4) were also evaluated as substrates (Figure 1). They, however, were not good substrates. Maximum copper removal was found to be 8% for sawdust and 3.5% for leaves.

The initial pH of the leaves was very low (approximately 2.9) and the pH of the sawdust was 5.7. Therefore, this may have had an effect on the growth of the fungus. It is also possible that the growth in both of these media was not good due to the elevated lignin and cellulose contents of these substrates and the lack of production by the fungus of the enzyme cellulase. This enzyme would enable the fungus to utilize the cellulose. This strain of fungus prefers starch or sugar substrates. Cellulase is known to be lacking in *A. niger* and therefore, various approaches are necessary to provide cellulases to the medium. One such approach was by Gutierrez-Correa et al. (1999) who co-cultured *Trichoderma reesei* with *Aspergillus niger* to provide cellulases for *A. niger* to utilize bagasse as a substrate.

Potato peels were also evaluated as a substrate (medium #5). Approximately 35% of the copper was solubilized in this medium. The pH fell from 5.0 to 2.0 in 7 days and then increased to 3.8 in the next 16 days.

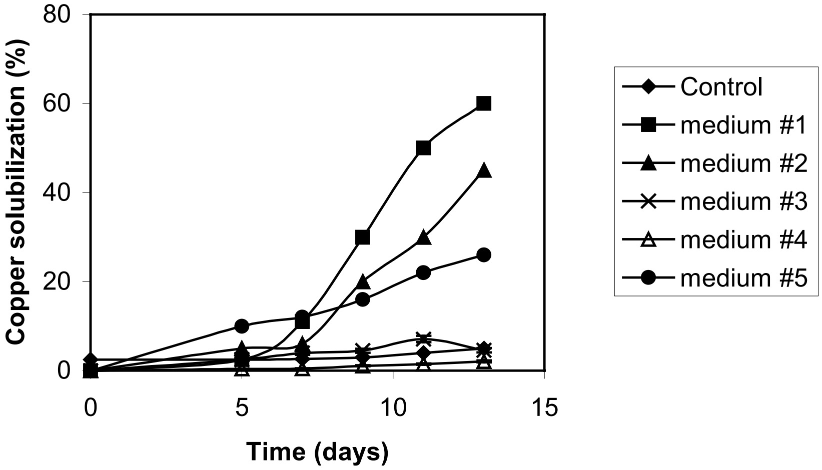

Fig 1. Copper solubilization by *A. niger* in media #1 (100 g/L sucrose), #2 (100 ml/L molasses), #3 (40 g/L sawdust), #4 (40 g/L leaves) and #5 (40 g/L potato peels).

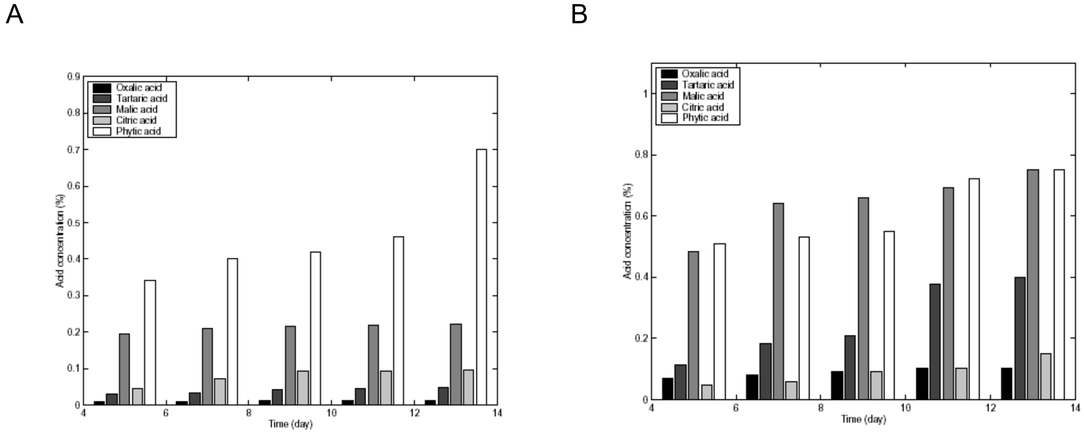

Fig. 2. Organic acid production in media (A) #1 and (B) #2.

3.3 Effect of pretreatment on biological leaching of mining ore

The effect of sulfuric acid addition was also investigated. Autoclaving was not used for these experiments. Sulfuric acid was used since it can help to sterilize the media. This effect was evaluated using leaves, sawdust and potato peels as substrates. For the leaves although only 4% of the copper was solubilized using the leaves as a substrate without sulfuric acid, 8 times more copper could be removed by adding this pretreatment step (Figure 3). The graph for the leaves indicated that the solubilization process was continuing even after 17 days. Pretreatment of the sawdust, however, was not as effective. 8% of the copper could be removed in the sawdust medium.

For the potato peels over 68% of the initial copper was removed in medium #9 after pretreatment with the sulfuric acid. The effectiveness started to diminish after 14 days, as indicated by the decrease in copper in the supernatant. It is most likely that the substrate became depleted at this time and the fungus started to use the organic acids as substrates. This was confirmed by the decrease in organic acid concentration after 15 days (Figure 4).

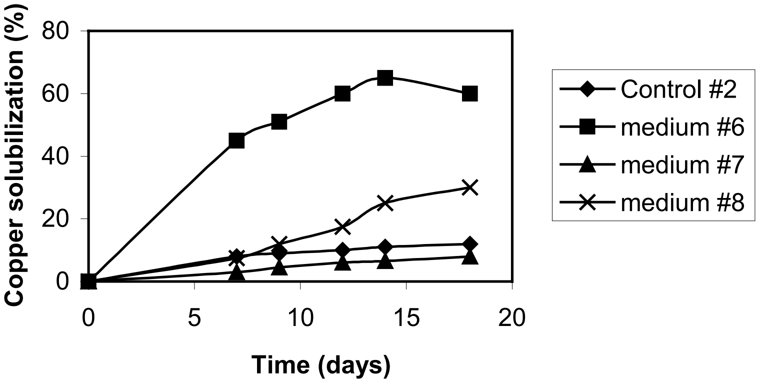

Fig.3. Effect of dilute acid pretreatment on leaves and sawdust on copper removal by *A.niger.* Control #2 is dilute acid for the experiment with medium #6 (40 g/L potato peels and dilute acid), medium #7 (40 g/L sawdust and dilute acid) and #8 (40 g/L leaves with dilute acid).

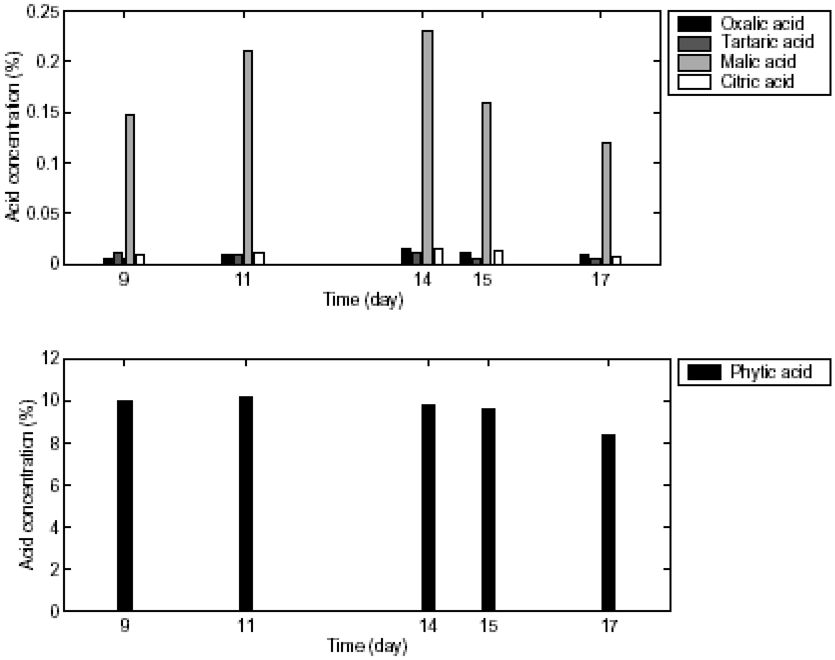

Fig. 4. Organic acid production in media number #6.

3.4 Effect of pH on copper extraction by biosurfactants

Using the data from the first test, one gram of ore with particle sizes between 0.15 mm and 0.3 mm was placed in the vials with 10 mL of 1% rhamnolipid for 5 days at various pH values. The pH was adjusted to between 6.0 and 9.5 and the removal efficiencies were found by the measurement of the copper concentration in the solutions. Figure 5 shows how the variation of pH affects extraction of copper from ore. The minimum extraction of copper occurred when the pH was around 8.8. This is similar to information in the solubility curve of Radhakrishnan (1993) which show that minimum solubility is at pH 8.7. This can explain the occurrence of minimum extraction at the same pH. The pH could not be decreased to levels similar to the citric acid tests since the rhamnolipid starts to precipitate at pH 5.

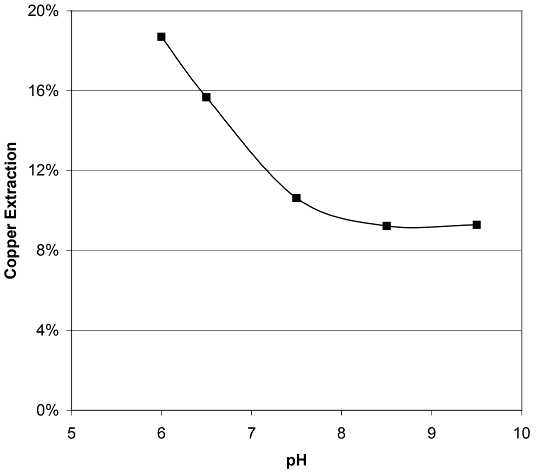

Fig. 5. Variation of copper extraction with pH. Particles were between 0.15 to 0.3 mm in diameter. Each sample contains 1 g ore in 10 mL solution of 1% rhamnolipid. The samples were kept at 25^{o}C for 5 days and left without shaking.

The effect of the concentration of rhamnolipid on copper extraction was evaluated. Concentrations of 0.05 to 5.0% rhamnolipid were prepared to extract copper from 1.0 g ore. Higher concentrations were not tested since the solution would be considerably viscous and hard to work with. According to previous studies (Mulligan et al. 1999), adding 1% NaOH to the solution will improve the copper extraction process. To verify the effect of NaOH, another test was designed in which the same concentrations were used but with co-addition of 1% NaOH.

A comparative graph is presented in Figure 6. In this figure, controls are not shown since the controls did not demonstrate significant extraction. As the figure shows, the effect of NaOH is quite remarkable on copper extraction for concentrations of 2% rhamnolipid or less while it has a negative effect on the extraction for more concentrated rhamnolipid. In the later case, the extraction of copper in the solution of 1% NaOH and 2% rhamnolipid has almost the same value as of 4% rhamnolipid without NaOH. The added NaOH increases the pH up to 13.5.The addition of NaOH makes a remarkable improvement in extraction when used with rhamnolipid concentration of 2% or less compared with rhamnolipid without any additives. At higher concentrations of rhamnolipid, adding NaOH decreases the extraction (Fig. 6).

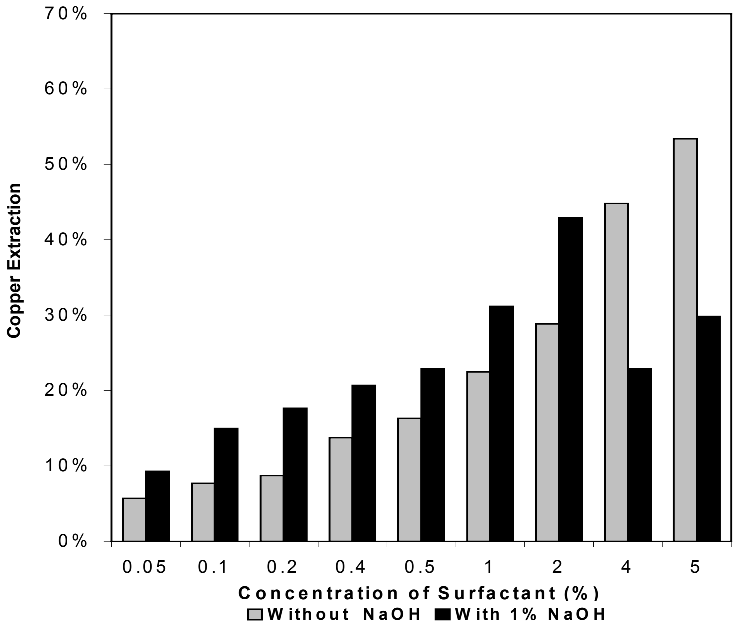

Fig. 6. Extraction of copper from mining ore (10% w/v) using various concentrations of rhamnolipid (with and without 1% NaOH) after 6 days.

4.CONCLUSIONS

Our studies show that recovery of copper from a mining ore is feasible. The residue, or ore, initially has a low concentration of copper, 8.95 g copper in 1 kg ore that cannot be economically removed. From an environmental point of view, the existing copper in the ore is a heavy metal contaminant and should be removed so that it will not impact the environment. A variety of organic acids were produced by *Aspergillus niger*. Organic acid effectiveness was enhanced when sulfuric acid was added to the medium. Various food and agricultural wastes were evaluated. Maximum copper dissolution of 68% was obtained. The addition of sulfuric acid also enabled efficient metal extraction without the need for sterilization. Highest overall removal occurred in the potato peel medium with sulfuric acid pretreatment. Further efforts will be required to increase the rate of copper removal.

This research was performed to evaluate the application of rhamnolipid on extraction of copper from mining residue.This study dealt with several chemical and physical factors involved in the extraction to find the best conditions for the extraction. These parameters were pH, and concentration of biosurfactant. Effect of NaOH addition was tested. Since the solubility of hydroxide copper is maximum at pH 6, the same pH for the extraction was found in this study, as predicted. The addition of NaOH makes a remarkable improvement in extraction when used with rhamnolipid concentration of 2% or less compared with rhamnolipid without any additives. At higher concentrations of rhamnolipid, adding NaOH decreases the extraction.

Comparison of the two methods showed that the addition of biosurfactant extracted less copper but less residence time (6 days) compared to 14 days or more was required. In addition, fungus does not have to be grown and thus the procedure is simpler. The pH optima for the two techniques were different. The rhamnolipid required a high pH by the addtion of 1% NaOH (pH 13) while the experiments with the potato peels and sulfuric acid were at a pH of 2.

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CONTROLLING (GROUNDWATER-) REMEDIATION SUCCESS VIA ON LINE BIOMONITORING OR HOW TOXIC IS REMEDIATED GROUNDWATER?

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Abstract:

Success of remediation of polluted leachates, groundwater or of other contaminated water bodies is usually controlled via physical and or chemical analysis. The reduction of the main contaminants at a certain remediation site is usually the leveling board for the estimation of remediation success. Because the main contaminants dominant in mass balances do not have to be the main toxic substances in a complex contaminated water body, control of successful remediation may also include the use of bioassays to test for the reduction of toxicity. As remediation techniques might change in their efficiency over time, this change in efficiency of a remediation technique in question is usually supervised via laborious discontinous physical, chemical or biological analysis. Here, a on line biomonitoring project is presented, which is part of the SAFIRA project aimed to develop and test high efficiency and low energy/ low cost techniques to remediate complex contaminated groundwater in Bitterfeld, Germany (SAFIRA-http://safira.pro.ufz.de/). On line biomonitor techniques are used as a tool for measuring the efficiency or change of efficiency of different techniques in a real-time mode. Advantages and limits of on line biomonitors using luminescent bacteria are discussed in consideration of remediation goals.

Background:

The quarternary aquifer in Bitterfeld, Germany (South of Berlin) is heavily contaminated, due to a hundred year old history of chlororganic chemical industry with chloralkali electrolysis as the basic process (Weiß et al. 2001). Because many different chemicals were produced until the early 90ies of the last century the contamination is composed of a complex mixture of different substances ranging from highly volatile organics (VOC) to anilines and pesticides and metabolites thereof. Possible low cost and low energy *in situ* remediation techniques are currently tested in the SAFIRA project at a test site in Bitterfeld. The test site contains a pilot plant consisting of five wells (25 m depth and 3 m in diameter) with different sized groundwater remediation reactors through which the untreated groundwater is pumped. The quality and the efficiency of decontamination of currently 14 different *in situ* remediation techniques is discontinuously tested on a two week basis with mainly headspace gas chromatography, because the VOCs are the quantitatively dominating contaminants. The efficiency of the detoxification of the groundwater is tested discontinuously by using different biotests and continuously by using novel on line biomonitors with luminescent bacteria *(Vibrio fischeri)* and green algae *(Scenedesmus vacuolatus)* as test organisms.

Here only results concerning the luminescent bacteria tests are discussed.

Materials and Methods:

Discontinuous luminescent bacteria test

The discontinuous luminescent bacteria test using the marine bacteria *Vibrio fischeri* (NRRL B-11177, German Collection of Microorganisms and Cell Cultures, Braunschweig, Germany) as test organisms was conducted as is described in DIN EN ISO 11348-1 (Anonymous 1998) with freshly prepared bacteria using the LUMISTOX© system. The only difference to the standardized test is the use of bacteria which were not stripped of the culture medium. In short, the samples are diluted with concentrated NaCl solution to a final salt concentration of 2% and a final 50 % sample concentration. The luminescence is measured at the beginning and at the end of a 15 or 30 min incubation period at 15 °C. The decrease in luminescence after incubation of the bacteria with the sample in comparison to a control (demineralized water) serves as a measure for interference with the overall energy metabolism of the luminescent bacteria and is calculated in % inhibition. Groundwater samples were stored in gas tight sampling bottles at 4°C and analysed within a day. Before the toxicity test pH, conductivity, hydrogen sulfide and temperature were analysed. The toxicity was measured in duplicates. If the standard deviation from the mean was greater than 3 % the tests were repeated. 3,5- dichlorophenol (reagent grade, Acros Organics, Belgium) served as positive control (EC_{50}: 3,2mg/L).

On line luminescent bacteria test

We adapted an on line system, the „Regensburger Leuchtbakterientest“, which was originally constructed and used for the monitoring of river water quality (Gerhardt & Putzger 1999). The continuously working on line biomonitor in general follows the methodology of the standardized DIN EN ISO test described above. Differences derive from the use of a higher test volume of 10ml. This on line biomonitor was adapted for the usage in monitoring groundwater remediation success including the parallel testing of two different samples instead of originally one, increasing of the maintainance free monitoring time and inclusion of measuring devices for the analysis of important physico-chemical parameters and data management. The sampling and testing of the groundwater were as follows (see fig. 1). The groundwater of the quarternary aquifer in Bitterfeld is pumped through several different remediation reactors located in wells directly above the groundwater table (Weiß et al. 2001). The untreated and treated groundwater is then pumped to the laboratory into a thermostated fridge (15°C) and by usage of different valves water from several remediation reactors can be selected for the analysis with the biomonitor. Different parameters (pH, conductivity, temperature and hydrogen sulfide) are continuously measured directly in the water flow prior to analysis for toxic effects.

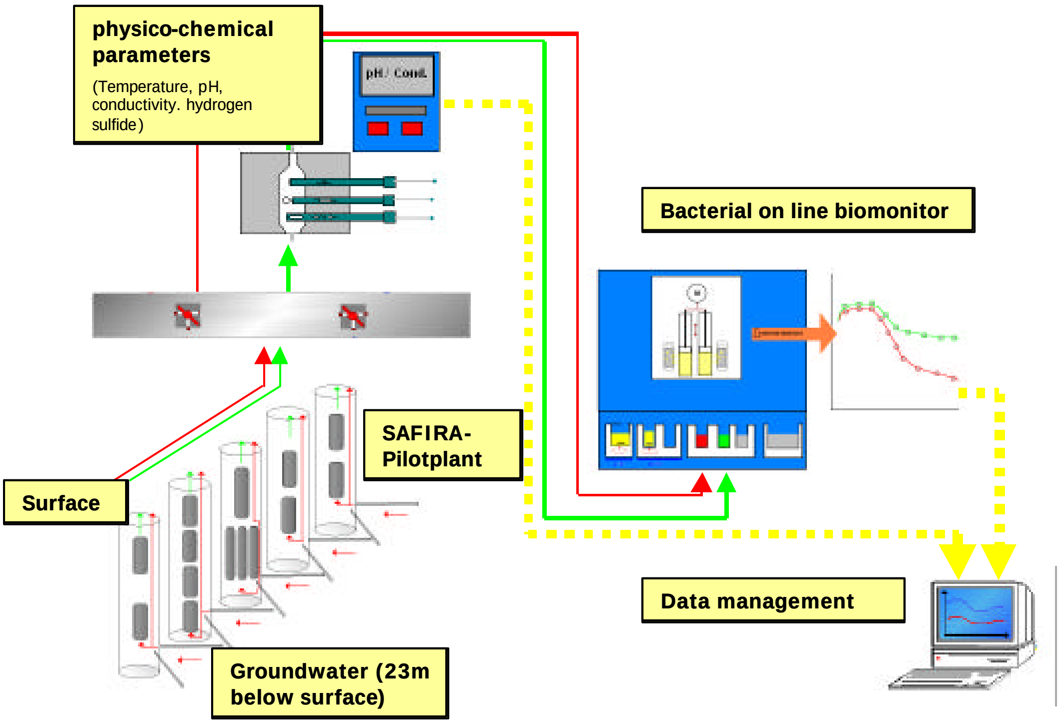

Fig. 1: Scheme of on-line biomonitors used in the SAFIRA pilot plant for monitoring different newly developed groundwater remediation techniques

Two samples (e.g. untreated and treated groundwater) are tested continuously every 30 minutes. Tap water (4.5ml) is automatically mixed with 0.5 ml NaCl (20 %) and 50µl of the bacteria. This suspension is acclimated to 15°C for 5 minutes. After acclimation 4.5 ml of sample and 0.5 ml of NaCl (20%) (e.g. groundwater) is added to the salt/bacteria suspension resulting in a 45 % dilution of the groundwater sample. Luminescence is then measured every minute during the 15 min incubation time. At the end of analysis the pipes and mixing chambers of the biomonitor which were in contact with the samples are automatically rinsed with tap water. The luminescent bacteria, were prepared freshly every week by the use of a culturing device at 20 °C in standard growth medium and are stored at 4°C in a peltier cooled container in the biomonitor. The biomonitor does require a minimum sample flow of 250ml per hour. Periodic maintenance consists of weekly change of freshly prepared bacteria and regular cleaning and rinsing of the system with 1% hydrochloric acid. A Visual Basic© based computer program automatically calculates correction factors, dilutions and toxic effects. These and the data from the measurement of pH, conductivity, temperature and hydrogen sulfide are combined in a self-programmed Microsoft Excel© data sheet for subsequent analysis and comparison of toxic effects of the different treated and untreated groundwaters.

An calculation automatism using the data of the last 11 measurements for the calculation of a variable limited slope value is used for an automated alarm system.

Process control and remediation reactor comparison

For the purpose of process control demineralized water was pumped through a remediation reactor. The progress of this tracer test was followed by measuring the conductivity and the toxic effects to the luminescent bacteria with the on line biomonitor. Stability of analysis and standing time of the biomonitor was tested with several different treated and untreated groundwaters for more than one year.

Toxicity tests

The toxicity of monochlorobenzene was analysed using the LUMISTOX© system with freshly prepared bacteria over a range of 3-100 mg/L with incubation times of 5, 15 and 30 minutes. A concentrated monochlorobenzene solution in 100% methanole was concominantly diluted to the used test concentrations. The methanol concentration in the test was 0.1% (v/v) and did not show any effect in control measurements (data not shown). Quarternary groundwater samples from different sampling wells in the Bitterfeld area were taken and analysed for the toxic effets on luminescent bacteria. Beforehand the known dose response relationship of monochlorobenzene (MCB) and the luminescent bacteria was used to calculate toxic effects expected from the quantitated MCB concentrations in the groundwater.

Results:

A short-time measurement of one untreated groundwater and groundwater of two different remediation reactors is shown in fig. 2. The first two days the difference between the toxic effects of untreated(upper line) and treated groundwater (lower line) can be clearly seen (65% to 70% and 50% respectively). At the third day the biomonitor was cleaned with diluted HCl and groundwater of another remediation reactor was tested for toxicity in parallel to the former untreated groundwater. The effect of cleaning can be seen by the increase of toxic effect to 90% due to the effect of hydrochloric acid. After about one day of continous measurement the toxic effect of the untreated groundwater is the same as before. The detoxification efficiency of the second remediation technique is lower. The analysis shows a toxic effect of about 60 % (lower line). These data did not change at periodical control measurements over the following 6 months (data not shown).

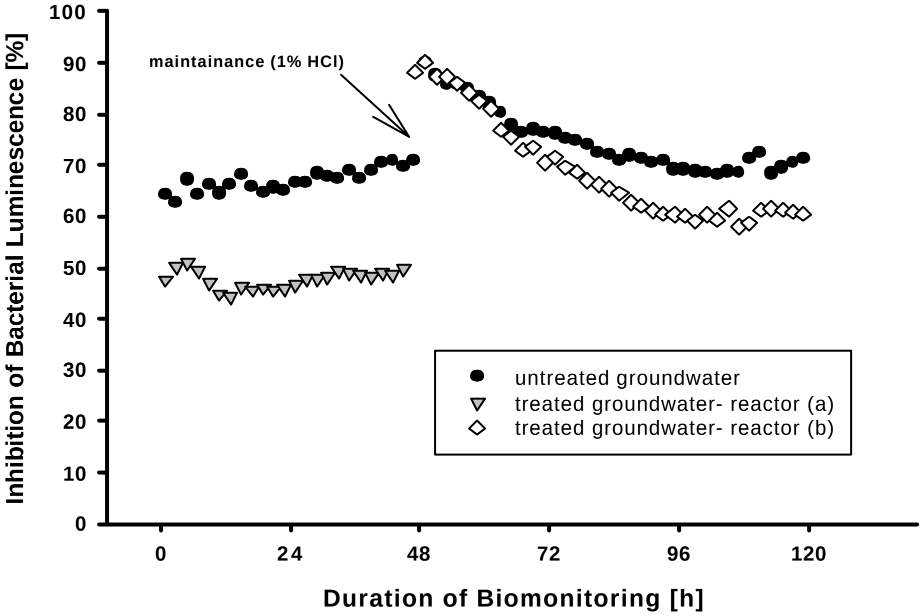

Fig. 2: Inhibition of bacterial luminescence measured on line over a period of five days of three untreated and treated groundwaters from different remediation reactors

Fig. 3 shows the results of the „tracer“ experiment with demineralized water pumped through a remediation reactor. The measurement of either the conductivity and of the toxicity to the luminescent bacteria clearly shows a decrease of both parameters before the end of the third day. The test was finished after day 6 and untreated groundwater instead of demineralized water was pumped through the same reactor again. The conductivity clearly increased to normal levels of 2.2 mS/cm^2 after another day while there is no parallel increase in toxic effects to be seen after day 8 and 9. Later the toxic effects reach the original level (data not shown). This shows that the measured toxic effects are in no correlation to the conductivity of the water.

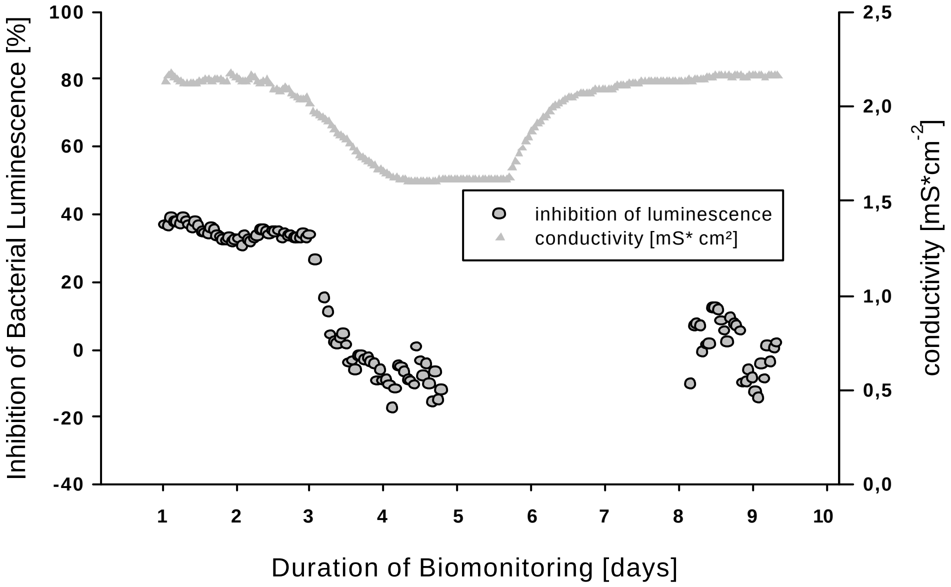

Fig.3: Results of a tracer test using demineralized water pumped through a remediation reactor over a period of six days. The progress of the experiment was followed by measurement of conductivity and bacterial toxicity.

In fig.4 the dose response curve of the quantitatively dominating contaminant monochlorobenzene at the SAFIRA test site to luminescent bacteria is shown. From the data an EC_{50} of monochlorobenzene of 55 mg/L was calculated. The concentration range of this main contaminant in the groundwater at the Bitterfeld test site lies between 2 and 15 mg/ L and thus should not be responsible for the measured effects at the SAFIRA test site which usually are above 50 % inhibition (data not shown).

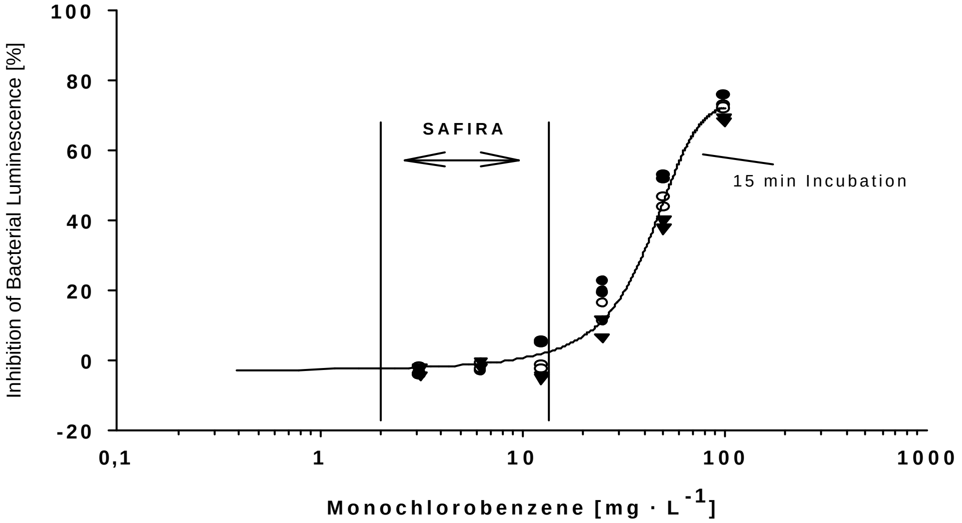

Fig. 4: Dose response relationship between concentration of monochlorobenzene (MCB) and bacterial toxicity measured with the LUMISTOX system. Arrow indicates the minimum and maximum range of MCB at the SAFIRA test site. Data represent n=2 for each concentration tested and incubation times of 5, 15 and 30 min.

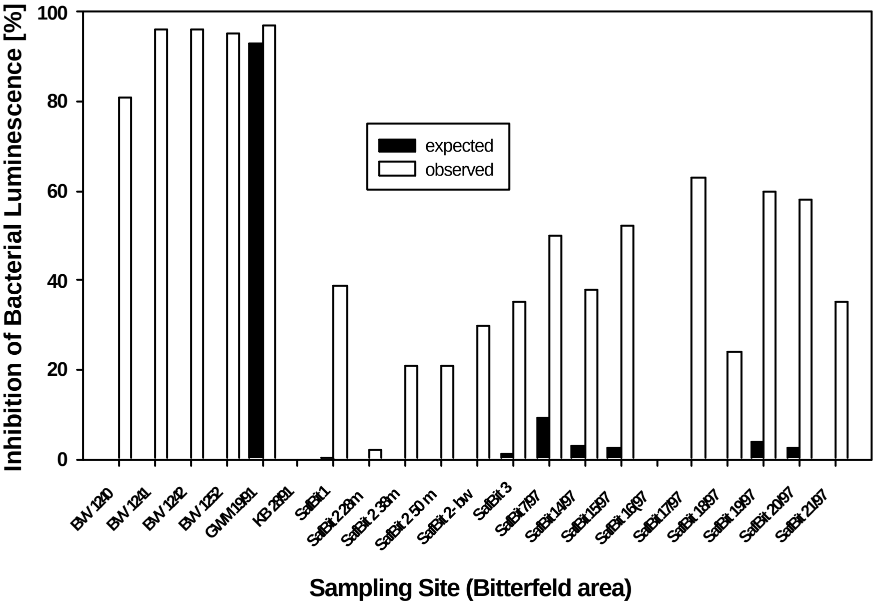

Fig. 5: Comparison of calculated expected and observed toxic effects of groundwater of different

sampling wells in the Bitterfeld area to luminescent bacteria. Calculation was based on the measured dose response relationship between monochlorobenzene and inhibition of luminescence. Data represent n=2 for every well measured with the LUMISTOX© system.

The toxic effects to luminescent bacteria of groundwater from different sampling wells in the Bitterfeld area and the results of calculations based on the known dose response relationship for the inhibition of luminescence by MCB is shown in fig. 5. The data almost uniformly show that the expected toxic effect is usually much lower than the observed i.e. measured effect.

Discussion:

The use of on line biomonitors for the evaluation of remediation success is a new field of research. The common way in ecotoxicological evaluation of hazardous waste sites, water treatment facilities, rivers water quality and landfill leachates consists of the discontinuous analysis of toxic effects to different organisms, either by taking organism samples on site or by testing water or sediment samples with different biotests of different biological levels. (la Farré et al. 2001, Liess and Schulz 1999, Ketalaars et al. 1994, Marty et al. 1991) Others combine biological and chemical testing methods for unravelling correlations (Gellert 2000, West et al. 1994). The use of toxicity identification evaluations (TIE) (US EPA 1991) and the bioassay directed identification (Brack et al. 1999) are important tools to unmask the toxic substances in a complex mixture of anthropogenic and natural contaminants. All of these testing methods have their specific advantages, however, all of them lack a real time monitoring mode. Samples always have to be taken and analysed by hand which is time consuming and expensive. The use of on line biomonitors circumvents these disadvantages. The usage of the luminescent bacteria *Vibrio fischeri* for ecotoxicity tests is well established. The combination of this organism with an automated sampling and analysing device was used for analysis of river water (Gerhardt and Putzger 1999, Levi et al. 1989) or laboratory tests (Schwedt et al. 1997) and waste water (Schwedt and Reiter 1997). Only recently so-called „biological early warning systems“ using higher organisms were used for the evaluation of landfill leachates, groundwater treatment facilities and copper effluents (van der Schalie 2001, Bloxham et al. 1999, Gerhardt et al. 1998). These on line biomonitors take advantage of the measurement of different physiological and behavioral responses of higher organisms. A real time monitoring system for evaluation of groundwater remediation success as is proposed here was not used before. The data show that the adapted biomonitor is a very suitable tool for monitoring not only the quality of groundwater but also for on line surveillance and supervision of (groundwater-) remediation techniques. The automatized sampling and analysing with the high amount of real time data allows a very sophisticated monitoring of different remediation techniques in parallel. The system is sensitive (the EC_{50} for the positive control 3,5- dichlorophenole) and has long service life time without the need for everyday maintenance. The data from fig. 1 and 2 also indicate that the biomonitor is sensitive enough to detect fast changes of water quality. This biomonitor may therefore also be used as a high quality and easy to maintain control unit for different other processes for example as sewage plant in- and outflow water quality control or any other remediation control. Besides, the results shown in fig.4 and 5 give rise to a critical view on the data. Normally remediation success is evaluated via the decontamination of known substances which are usually quantitatively dominating. The data at hand clearly show the discrepancy between the observed toxic effects in the luminescent bacteria test and the expected effects calculated from the dose response relationship of monochlorobenzene. Very likely the combined effect of several different contaminants might explain the groundwater toxicity measured in Bitterfeld (Küster et al. 2003, Altenburger et al. 2000). Research to identify the toxic substances in the quarternary aquifer of Bitterfeld will follow.

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GROUNDWATER AND SOIL CONTAMINATIONS IN SERBIA - DERIVING FROM 1999 WAR ATTACKS

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During spring 1999 NATO airplanes bombed refineries, oil tanks and chemical plants in Serbia. In the city of Novi Sad the oil refinery and their tanks on the northern banks of the river Danube were destroyed. A huge amount of mineral oil products - mostly heating oil, diesel and gasoline - burned, evaporated or infiltrated into the sandy soil. It was estimated that about 5000 cubic meters of oil seeped into the ground and contaminated the groundwater. Contaminations of this size - 5000 m^3 resp. tons - do not occur very often worldwide.

The groundwater table is only a few meters below the surface. Investigations showed that the mineral oil products spread on the groundwater table, but did not really move resp. leave the refinery plant area.

Only 200 m downstream of the refinery area - and also along the banks of the Danube - the water works of the City of Novi Sad operate their main wells for drinking water supply. To keep groundwater contaminations away from these important water wells, it was necessary to set up a gallery of special wells between the refinery area and the waterworks area. These wells will be in operation only in the case, when the contamination plume leaves the refinery plant area and moves downstream towards the water works - which fortunately did not occur until now.

The well gallery was established with technical and financial support of the city of Dortmund, Germany, which is twin city of Novi Sad. The wells were ready to operate since spring 2002.

As soon as contaminated groundwater reaches the well gallery, it is necessary to operate these wells for an undefined period of time, which is obviously the worst case. To avoid this worst case, it is urgent to improve two things:
- Permanent control of movement of the contamination plume, and
- Remediation of main groundwater and soil contamination on the refinery site.

The first requires a gallery of observation wells; the latter needs additional financial support for further investigations and for the main remediation activities.

As the size of contamination and the amount of spilled oils (5000 m^3 estimated) are not comparable with "normal" contaminated sites, normal investigation and remediation actions might fail. Pump-and-treat-techniques have to be adapted. It will also be necessary to think about usual remediation objectives. For instance: What level of contamination might remain in soil and groundwater? How clean must be treated groundwater? And in general: What is an improvement of the situation?

The poster tries to give some answers to these questions.

FATE OF TRACE METAL POLLUTANTS WITHIN A POLLUTED AQUATIC SYSTEM : CASE OF Zn, AND Pb IN THE CANALISED SCARPE RIVER (NORTH OF FRANCE)

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Introduction

Many streams across urbanised and industrial areas are greatly disturbed due to anthropogenic influence and contaminant discharge. Non-biodegradable pollutants, particularly metals, are prone to accumulate partly into the sediments (examples of Venice Lagoon, (Barbanti et al., 2001) and river Elbe (Brügman, 1995)) ; another fraction of the pollutant charge is generally transferred downstream as dissolved or particulate phases.

In the heavily industrialised region of the North of France, characterised by an extremely dense population (325 inhabitants per square kilometre for the Nord-Pas de Calais Region), a largely developed hydrographic web and a strong river sedimentation, transfer and accumulation of contaminants in the aquatic system represent an increasing struggle.

The studied area, a fraction (7km) of the Scarpe River (figure 1), located near the city of Douai (North of France) is a representative part of this dramatically polluted region. The river is currently under the influence of various industrial and urban emissions and wastes (figure 1) and its sediments could represent a stock of historical pollutants readily available to impact the whole ecosystem. The main purpose of this work is to investigate the fate of trace metal pollutants within the polluted aquatic system, from their introduction into the natural system to their release at the end of the watershed. Heavy metals concentrations in water and sediment have been determined and mass balance have been performed. We present here the results for Pb and Zn.

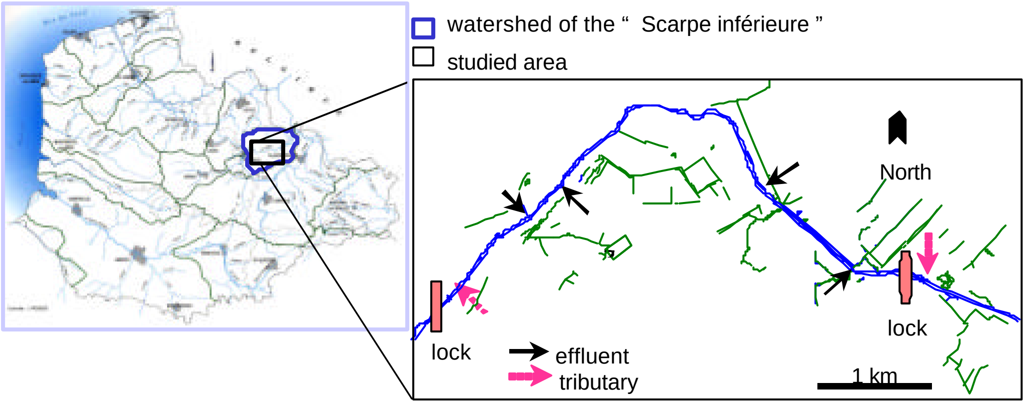

Figure 1 – The studied part of the Scarpe river in the North of France

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[*] CNRSSP is composed of following partners: ISSeP, BRGM, ENSTIMD, CdF, CEA, IPL, Solvay, TotalFinaElf, Armines, GDF

Materials and methods

Sediment characterisation :

The sediment cores (228 samples) were collected in spring 1999 in the middle and on both sides at various locations across and along the river (7 km). The choice of these sites is based on historical and topographic information in order to take into account the main industrial inputs. Metals analyses were performed, by Inductive Coupled Plasma Atomic Emission Spectrometry, after acid wet digestion (aqua regia), on surface (0-10cm) and deep (>10cm) sediment samples.

Mass balance performed in the Scarpe river system

Four campaigns have been performed on the Scarpe river system during three years (1999-2001) at different seasons : July 1999, March 2000, November 2000 and march 2001. Dissolved fraction (<0.2µm filtrate) and suspended matter have been sampled and separated using acetate cellulose filter on 9 points taking into account the localisation of incoming effluents. Samples have been analysed for metals. Pb and Cd were analysed by Graphite Furnace Atomic Absorption Spectrometry and Zn by Inductive Coupled Plasma Atomic Emission Spectrometry.
When it was possible (depending on the activity of the inputs), identified effluents (1 to 4, see figure 1) were sampled. It was achieved during three campaigns: July 1999, November 2000 and March 2001. Analyses of the metals were done on the unfiltered samples.

Pb and Zn mean fluxes (Fi) have been established for the three years study period, from the mean concentration (C_i) for all the sampled point (i) and the mean discharge (Q_i) which integrate all the identified inputs, according to the relation :

$$Fi = [C_i] x Q_i$$

Input/ouput balance has been determined taking into account all the fluxes incoming in the aquatic system (upstream flux (F_{inflow}), the effluents ($F_{effluents}$) and atmospheric ($F_{atmospheric}$) fluxes) and outflow ($F_{outflow}$) fluxes.

$$F_{outflow} = [C_{mean\ pt\ i=9}] \text{ x } Q_{mean\text{-}Lock2}$$

$[C_{mean\ pt9}]$ =mean concentration measured on the downstream sampled point.
$Q_{meanLock2}$ = mean discharge at the lock 2 calculated from daily discharges measured during the three years of the study (source : French waterway agency (VNF))

$$F_{inflow} = [C_{mean\ pt\ i=1}] \text{ x } Q_{meanLock1}$$

$[C_{mean\ pt\ 1}]$ =mean concentration measured on the upstream sampled point.
$Q_{meanLock1}$ = mean discharge at the lock 1 calculated from daily discharges measured during the three years of the study (source : French waterway agency (VNF))

$$F_{effluents} = S\, f_{input} = S([C_{input}] \text{ x } Q_{mean})$$

$[C_{input}]$ =concentration measured in an industrial or urban input.
Q_{mean} = mean annual delivery of an input (obtained from administratives sources).

$$F_{atmospheric} = S\ (D \text{ x } [C_{dry\ deposit}] \text{ x } S) + (P \text{ x } [C_{wet\ deposit}] \text{ x } S)$$

S= surface of the studied part of the canalised river
D= dry deposit
P= wet deposit (source: Méteo-France)

Results

Sediment characterisation :

The sediments of the Scarpe river present high mean concentrations of pollutants such as Zn (3575 ppm) and Pb (502 ppm) and concentrations present large variations as it is shown by minima and maxima values (table 1).

Table 1 – Metals concentrations (mg/kg dry matter), minima and maxima in the sediments (n=170) of Scarpe river

	Zn	Pb	Cd	Cu	As	Ni	Cr
Mean (mg/kg)	3575	502	113	165	40	29	60
Minima (mg/kg)	50	9	4	2	3	7	20
Maxima (mg/kg)	18000	2800	1450	1300	445	70	190

The results of all the campaigns, sampling and analytical data are integrated in a GIS (Geographic Information System). Distribution of the metals in the sediments have been performed in relation with the geographic and hydrographic context. Along the river a large heterogeneity of the metallic pollutant charge in the sediment matter is observed (see for example Zn in figure 2). High concentrations locations can be correlated with the main historical inputs (industry, urban discharges...) and specific hydrographic contexts like locks. However, relation between high accumulations of metals places and present inputs can not be clearly evidenced.

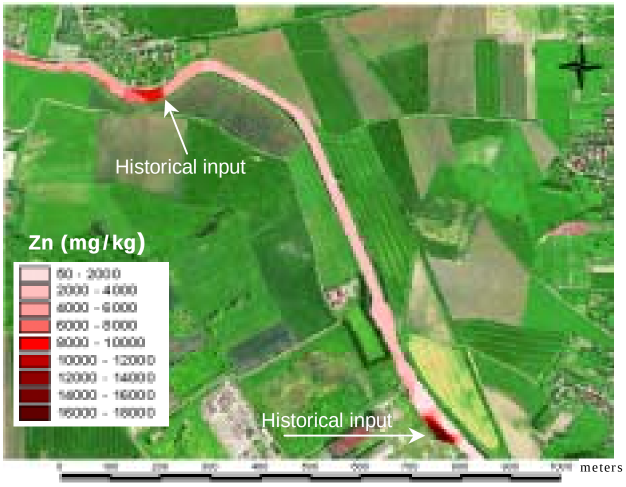

Figure 2: Zn concentrations in deep sediment of the Scarpe channel
(showing a section of the studied area)

Mass balance performed in the Scarpe river system

Zn Concentrations of about 600 mg/kg in suspended matter and of about 30 µg/L in the dissolved phase are measured at the entrance of the studied system (figure 3a).
In March 2000 and March 2001, increases from 600 mg/kg to 4000 mg/kg of Zn were observed in suspended matter sampled downstream the effluents 1 and 2. High concentrations were not observed anymore at the end of the studied portion. By the mean time, concentrations in the dissolved phase did not change significantly (figure 3c). Then, impact of inputs is observed at a local scale and does not affect the dissolved load.
However, during the campaign of November 2000 large inputs from effluents 1 and 2 bring a large pollutant plume of 7 km along the river with high concentrations in the particulate phase as well as in the dissolved phase. Indeed, Zn concentrations of 30 000 mg/kg in the suspended matter and of 1000µg/L in the dissolved phase could be measured immediately downstream effluents 1 and 2, resulting in a concentration of 5000 mg/kg and 340 µg/L respectively 7 km downstream (figure 3b and c).

Pb does not show the same behaviour as Zn. Upstream, concentrations of 1 to 2 µg/L are measured in the dissolved phase for all the campaigns. Then concentrations decrease along the downstream river. They reach a maximum of 0.8µg/L (figure 3d). Pb concentrations in suspended matter range from 80 to 240mg/kg. Their distribution along the river could not be clearly explain by any input.

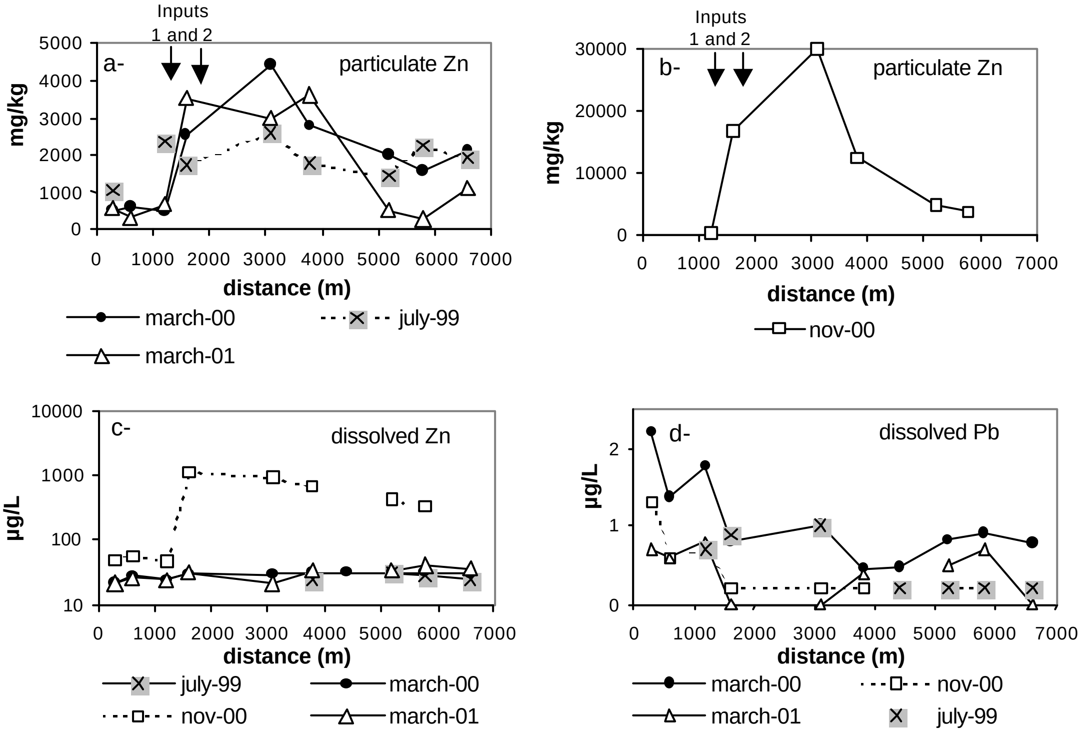

Figure 3 – Zn concentrations in particulate (a and b) and dissolved (c) phases and Pb concentrations in the dissolved phase (d) for the four sampling campaigns.

Pb and Zn concentrations in the effluents 1 to 4 are reported in table 2. For these three campaigns, high Zn concentrations are measured in effluents 1 and 2 and in a less extent for the effluent 3. These effluents present a large disparity in Zn concentrations (for example : 336 µg/L to 674 mg/L for effluent 2). Except for the effluent 2 in July 1999, Pb are not present in high concentrations in the sampled effluents inputs.

Table 2 – Zn and Pb concentrations in effluents inputs.

		july-99				**nov-00**				**march-01**			
	§	effluent 1	effluent 2	effluent 3	effluent 4	effluent 1	effluent 2	effluent 3	effluent 4	effluent 1	effluent 2	effluent 3	effluent 4
Pb µg/L	10%	-	227	<0,5	<0,5	3,8	<0,5	0,7	<0,5	2,1	0,7	-	1
Zn µg/L	2%	-	674 mg/L	608	32	8265	336	453	23	2218	573 mg/L	-	70

Dissolved and particulate fluxes have been calculated for Zn and Pb (figure 4). Pb particulate fluxes, based on four campaigns results, show an increase (from 150 to 450 kg/y) that can't be justify by any identified effluents (see above). Pb dissolved fluxes show a significant decrease (from 120 to 50 kg/y) : Adsorption of dissolved Pb on particles could be a realistic explanation. Sorption of metals could occur onto amorphous Fe-Mn oxyhydroxydes or clays minerals particles and could depend on suspended matter concentrations and pH conditions (Holmström et al., 2000; Lead et al., 1999, Sondi et al., 1994 and Zhang et al., 1994).

Dissolved and particulate Zn fluxes, established on three campaigns (March 2000; March 2001 and July 1999, show an increase (from 1700 to 3500 kg/y and 500 to 7000 kg/y respectively) downstream the river, mainly due to effluents discharge (figure 4, line [1]). For one campaign, very high Zn concentrations in the dissolved and particulate fractions are evidenced (see above): fluxes established with all four campaigns show a very large increase in the middle of the studied area which quickly decrease downstream : a rapid settling of pollutant load could be suggested (figure 4, line [2]).

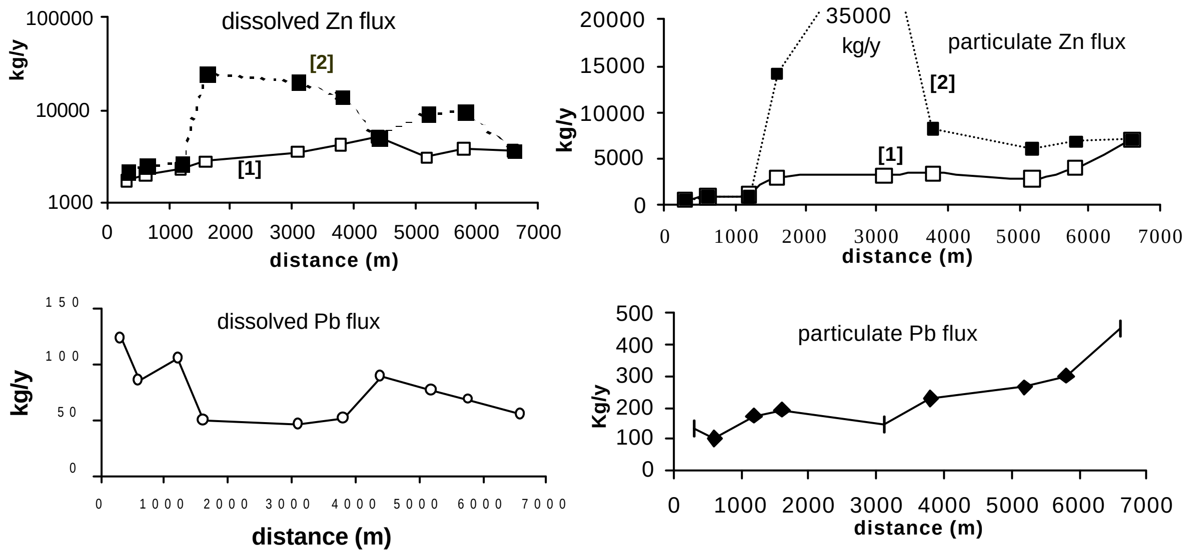

Figure 4- Dissolved and particulate fluxes for Zn and Pb in the Scarpe river (for Zn: calculated with three campaigns: line [1]; calculated with four campaigns: line [2]).

Zn and Pb mass balance has been established taking into account the dissolved and particulate load, from metal fluxes in the upstream and downstream water column and atmospheric and effluents inputs, with some difficulties to quantify accurately effluents inputs due to their alternative runnings and the high heterogeneity of their chemical composition (see above). So, we calculated effluents fluxes from minimum and maximum concentrations in order to obtain a range of fluxes values.

Zn flux at the entrance of the aquatic system is equal to 6 kg/day whereas outflux (7 km downstream) is equal to 30 kg/day. The range values for the total effluents inputs is estimated to 50-250 kg/day, atmospheric flux to 6 kg/day (figure 5). Annual balance set up for Zn shows that Zn flux at the entrance of the aquatic system represents only 2 to 10% of the total Zn input; when 80 to 95% are due to effluents incoming (figure 5). Regarding Zn output/input balance only 12 to 45% are exported. Zn deposit should occur and up to 55 to 88% could be stored in sediment.

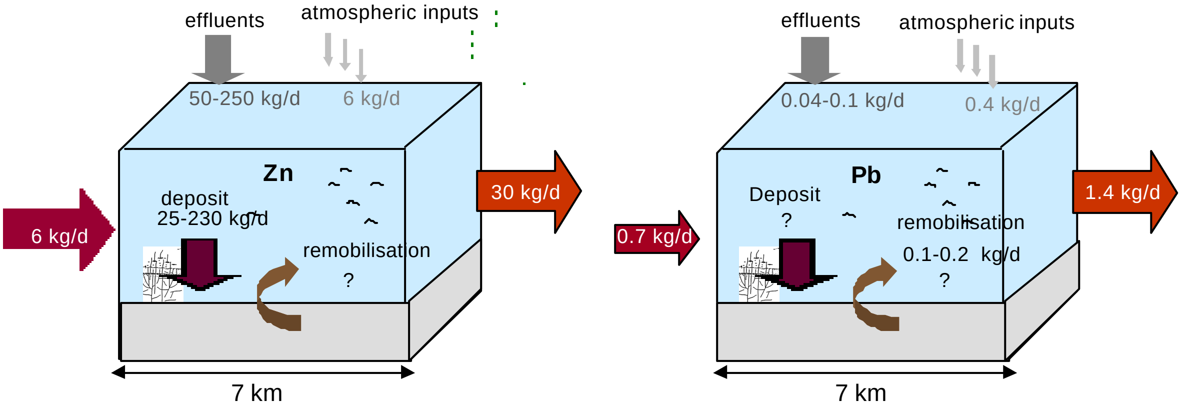

Figure 5 - Fate of Zn and Pb in the Scarpe river System.

Pb flux at the entrance of the aquatic system is equal to 0.7 kg/day and increase twofold downstream (figure 5). Total effluents inputs is estimated to 0.04 - 0.1 kg/day whereas atmospheric flux to 0.4 kg/day. Annual balance set up for Pb shows that sources taken into account can't explain the total Pb outflux. First, remobilisation of Pb coming from the sediment (esuspension) could be proposed as another source of Pb in the water column. It has been already observed that resuspension sediment processes due to flood events influence the trace-metal content of the suspended matter (Regnier and Wollast, 1993). The river bank (erosion) could be equally suggested as another source of Pb. Theses sources would represent 6 to 11% of the total Pb input.

Conclusion

Sediments of the Scarpe river represent a large reservoir of pollutant load. They are characterised by high Zn and Pb concentrations mainly explained by historical inputs. Impact of present effluents inputs is still measured for Zn, mainly associated with particulate load. Zn particulate fluxes due to alternative effluents inputs is characterised by a rapid sedimentation. The « Scarpe river » displays an important capacity for Zn particulate retention and behaves so as a present reservoir for Zn. Punctually effluents have a more significant impact on the system through a pollutant plume under 7 km along the river with high concentrations of Zn in the particulate phase as well as in the dissolved phase. However, adsorption of dissolved Zn on large and quickly deposited particles can be proposed to explain decreases of Zn fluxes along the plume.
There is no evidence for significant Pb effluent input but resuspension of the sediment or erosion of the bank can be proposed as potential sources of Pb in the aquatic system.

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AN INTEGRAL APPROACH FOR THE QUANTIFICATION OF SUBSURFACE CONTAMINATION

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Abstract: A new approach to contaminated land assessment and revitalisation in urban industrial areas, focusing on groundwater quality and complex contamination patterns at megasites which are typical for many European cities, was developed within the EU FP 5 project INCORE. The new approach comprises three cycles: (a) the assessment of groundwater contamination using an innovative integral mass flux based investigation method at the scale of entire industrial sites, (b) the delimiting of potential contamination source zones using backtracking and contaminant fingerprinting techniques, and (c) the development of emission oriented remediation strategies. The major advantage of the new approach is that the number of areas to be considered for further investigation and remediation is reduced from one cycle to the next. Consequently, a large potentially contaminated area is screened initially, but only a small area may be finally remediated, yielding a significant reduction of costs.

1. Introduction

Groundwater pollution is an important problem at many locations all over Europe. Sources for contaminants in aquifers such as chlorinated compounds, petroleum hydrocarbons etc. are for example leaking underground storage tanks and pipelines, petrol stations, gasworks sites, and all types of industries. At these locations, rapid industrial development, missing regulations and / or safety measures, changes in land use and ownership, as well as the hydraulic and hydrogeochemical aquifer heterogeneity caused complex and irregular contamination patterns with very often unknown locations of pollutant hot spots. It is generally accepted that present approaches for site investigation and assessment are either not reliable enough or not cost effective, making the development of new approaches for the quantification of subsurface contamination necessary.

The EU FP 5 project INCORE (Integrated Concept for Groundwater Remediation, EVK1-1999-00080) aims on the development and implementation of a new cyclic approach to contaminated land assessment and revitalization in urban industrial areas, focusing on groundwater quality and complex contamination patterns at megasites which are typical for many European cities.

Based on the new cyclic approach, within the INCORE project new technical and administrative tools, considering uncertainties of investigation and of assessment results, are being developed, tested and implemented under real-world conditions in the cities of Stuttgart, Linz, Milan and Strasbourg. In this way, the project results will provide an important basis for the development of future EU directives on contaminated land assessment and revitalization.

2. The cyclic approach

The new approach comprises three cycles (Fig. 1): (I) the assessment of groundwater contamination using an innovative integral investigation method to estimate contaminant concentrations and mass flow rates across control planes at the scale of entire industrial sites, (II) the delimiting of potential contamination source zones using backtracking methods, laboratory and on-site analysis as well as contaminant fingerprinting techniques, and (III) the development of emission oriented remediation strategies.

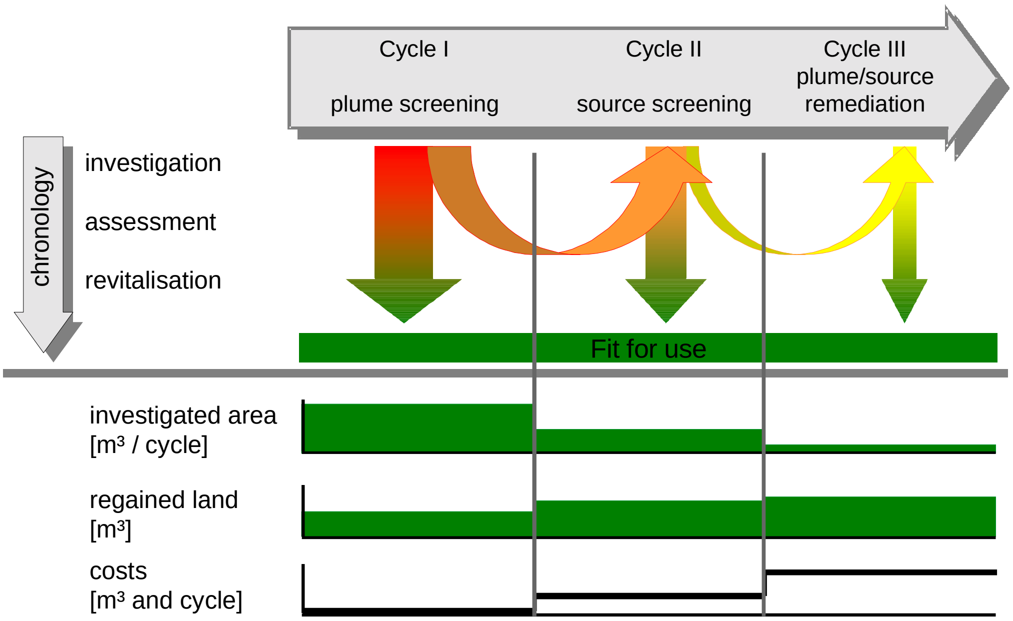


Figure 1: The cyclic approach to contaminated land assessment and revitalization in urban industrial areas

The major advantage of the new cyclic approach is that using screening procedures the number of areas to be considered for further investigation and remediation is reduced from one cycle to the next at a high level of certainty. Consequently, a large potentially contaminated area is screened initially, but only a small area may be finally remediated, yielding a significant reduction of costs needed for land revitalization.

2.1 Cycle I, integral groundwater investigation

The basic idea of the integral groundwater investigation method (Teutsch et al., 2000) is to cover a whole cross-section of a contaminant plume downstream of a pollutant source, employing pumping tests with multiple contaminant concentration measurements at the pumping wells. Due to the spatial integration of a pumping test, and due to the increasing capture zone with pumping time, both the spatial distribution of the contaminants as well as the total mass flow rate within a contaminant plume can be estimated.

To apply the integral investigation method, one or more pumping wells are placed along a control plane (control cross-section) perpendicular to the groundwater flow direction and operated simultaneously, or in subsequent pumping campaigns, downstream of a suspected pollutant source zone. The positions, pumping rates and pumping times are designed in a way to allow the well capture zones to cover the overall width of the potentially polluted area (Fig. 2). During pumping, as the capture zones increase, the concentration of groundwater contaminants is measured as a function of time at each of the pumping wells.

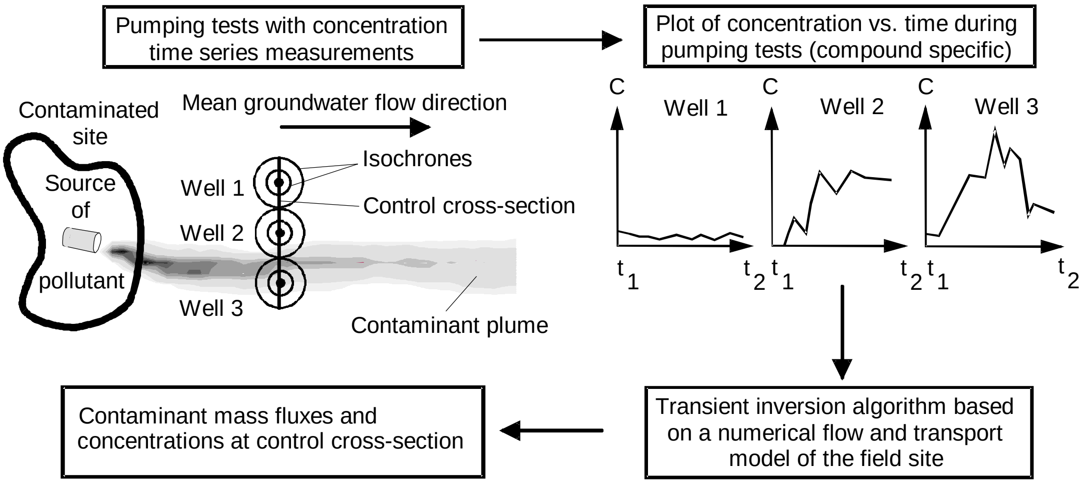


Figure 2: Integral investigation method for the quantification of groundwater contamination (Ptak and Teutsch, 2000)

Since each concentration value within the measured concentration time series is representative of a distinct aquifer zone, information on the spatial distribution of both concentrations and mass flow rates can be obtained, in addition to the mean concentration and the total mass flow rate. For the interpretation of the concentration time series, a transient inversion technique was developed (Ptak and Teutsch, 2000; Ptak et al., 2000; Schwarz, 2002; Bayer-Raich et al., 2002), which is based on a time dependent calculation of isochrones and mass balances for the increasing capture zones. The numerical implementation of this inversion approach uses backward particle tracking in a calibrated transient flow and transport model of the investigation area to determine the isochrones. The mass flow rate is obtained by multiplying the inverted concentrations in the aquifer with the according calculated groundwater fluxes.

2.2 Cycle II, delimiting of potential contamination source zones

The integral investigation method can be very effectively introduced into a general methodology for assessing the effects of aquifer parameter uncertainty on the estimates of mass flow rates and concentrations as well as on delimiting both contaminant source zones and zones absent of source (Jarsjö et al. 2002a,b).

First, the possible uncertainties related to uncertain boundary condition (BC) values are investigated. The model boundaries are given by a detailed, site-specific numerical groundwater model, and the possible variability of the BC values is estimated on the basis of either site-specific field data or data from studies on similar boundaries and / or hydrogeological settings. For each boundary, the range of variability, or lack of variability, is used to define extreme possible BC values and / or average BC values. The different possible BC values are then combined. The combinations leading to extreme values in terms of hydraulic gradients (flow) and / or flow directions are used in the subsequent uncertainty analysis.

Second, the possible uncertainties related to variability in the aquifer properties, e.g. hydraulic conductivity (K-)values, are investigated. The starting point is to estimate the statistics (e.g. the mean value and the variance) of the site-specific small scale hydraulic conductivity values, and to determine (possible) uncertainties associated with these estimates. Subsequently, the estimates are used as input for a limiting case analysis and / or for numerical stochastic simulations described below. Sources for obtaining data and statistics on the hydraulic conductivity values may be for example (i) short term pumping tests (yielding local T-values), (ii) laboratory analyses of sediments from drill-cores (sieve analyses, permeameter tests), (iii) borehole flowmeter measurements, and (iv) expert knowledge of values and variations of hydraulic parameters in characteristic sedimentological facies.

Then, a limiting case of aquifer heterogeneity is considered, namely variation of hydraulic conductivity in the vertical direction (*z*) only (layered anisotropic aquifer geometry). For this limiting case, analytical expressions for the mass flow rate estimation errors have been derived, assuming a negligible influence of the natural groundwater flow on the development of pumping well isochrones. If the uncertainty in mass flow rate estimation is shown to be relevant in the limiting case analysis, and if the numerical model indicates aquifer zonations and influence of boundary conditions that are significantly different from the assumptions of the limiting case problem solutions, the mass flow uncertainty will be addressed numerically by performing stochastic simulations.

Now, the combined influence of the uncertainty of the BCs and the uncertainty of the K values can be addressed. The total mass flow rate estimate is linearly related to both the estimated hydraulic gradient (which, in turn is determined by the BCs) and to the estimated value of the hydraulic conductivity, simply as a consequence of Darcy’s law and the advective transport assumption. Therefore, the combined uncertainty in the mass flow estimate can be fully determined on the basis of the uncertainty in the hydraulic gradient estimate (caused by the uncertain BCs) and the uncertainty of the K-distribution statistics. By considering confidence intervals of the mass flow estimates, probabilities for exceeding some regulation limits can be obtained.

With respect to delimiting of the position of the source zone, the approach is to use backtracking in the previously defined worst-case scenarios. This yields a distribution of spatial limits for the source zone extent in the transverse direction. In addition, plume length statistics for different contaminants and aquifer conditions (alternatively first order decay rate models or sophisticated multispecies-multiprocess reactive transport models) are used in order to determine a distribution of limits for the source zone even in the longitudinal direction.

Finally, from **cycle I** and from the application of backtracking methods in **cycle II** a map of the investigation area (Fig. 3) is obtained, showing zones with different levels of contamination impact on groundwater. Using this map, the administration is able to rank these zones at a predefined level of confidence, and to set priorities for further actions. Focusing at first on the zones with high groundwater impact (Fig. 3) helps to spend main efforts and resources at sites which have the highest groundwater contamination potential. This leads to a maximum effectiveness of administrative decisions, of investigation measures as well as of remediation activities.

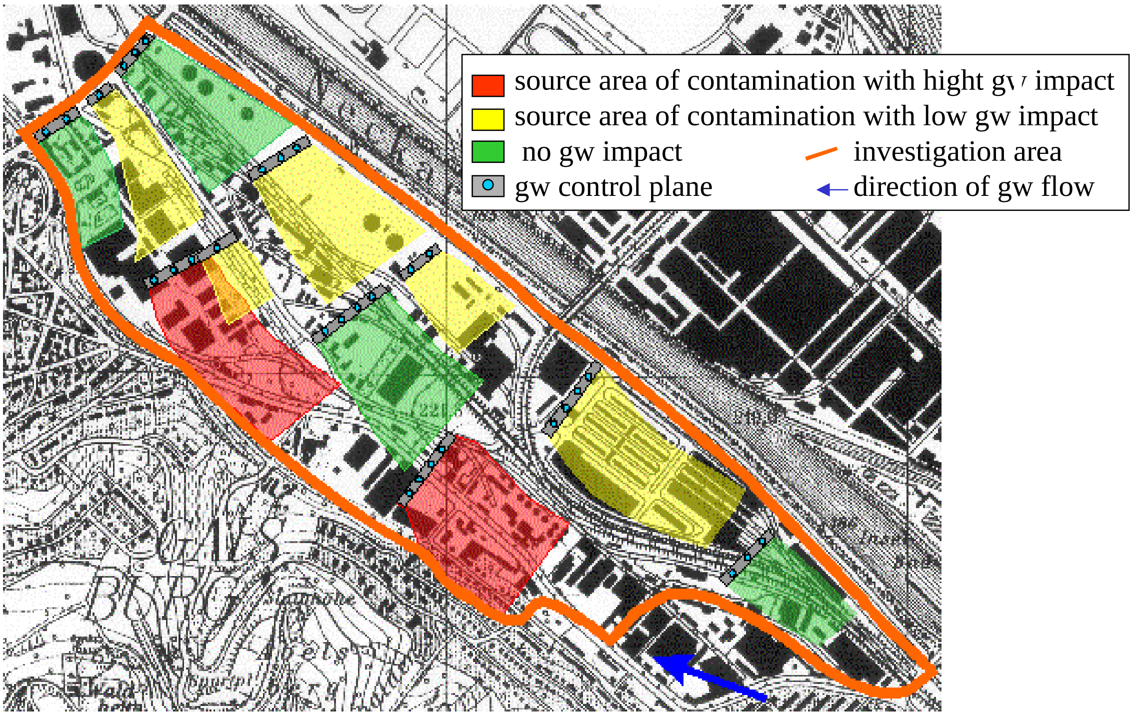


Figure 3: Predicted zones delimiting contaminant source, and zones absent of source, example of application in the Neckar Valley in Stuttgart (after Jarsjö et al., 2002b)

The different zones (Fig. 3) obtained from the integrated investigation give a localization of suspected sites at large scale. However, a local scale identification of contaminant source zones is needed in order to apply the polluter pays principle. Therefore, applying backtracking methods, starting from control planes, and using cost-effective laboratory and on-site analytical systems, direct-push methods, as well as isotopic fingerprinting techniques for source screening in **cycle II**, a precise localization of the contaminant source is possible.

2.3 Cycle III, source / plume remediation

The work in **cycle III** deals with combined solutions for source and plume remediation. Natural attenuation of contaminants is taken into account as a part of a comprehensive remediation approach, depending on the remaining / tolerable contamination levels and extents.

To asses the natural attenuation potential, the integral groundwater investigation method can be applied at multiple control planes to estimate total contaminant mass flow rates at different distances downstream from a contaminant source zone (Fig. 4). Natural attenuation processes result in a reduction of the total contaminant mass flow with increasing transport distance.

Total contaminant mass flow rates (and average concentrations) can be simultaneously estimated for a number of target compounds at each pumping well. This may include not only the original contaminants, but also potential degradation products or hydrogeochemical indicators for natural attenuation processes, e.g. pH, EH, sulfate, nitrate or dissolved iron, etc.

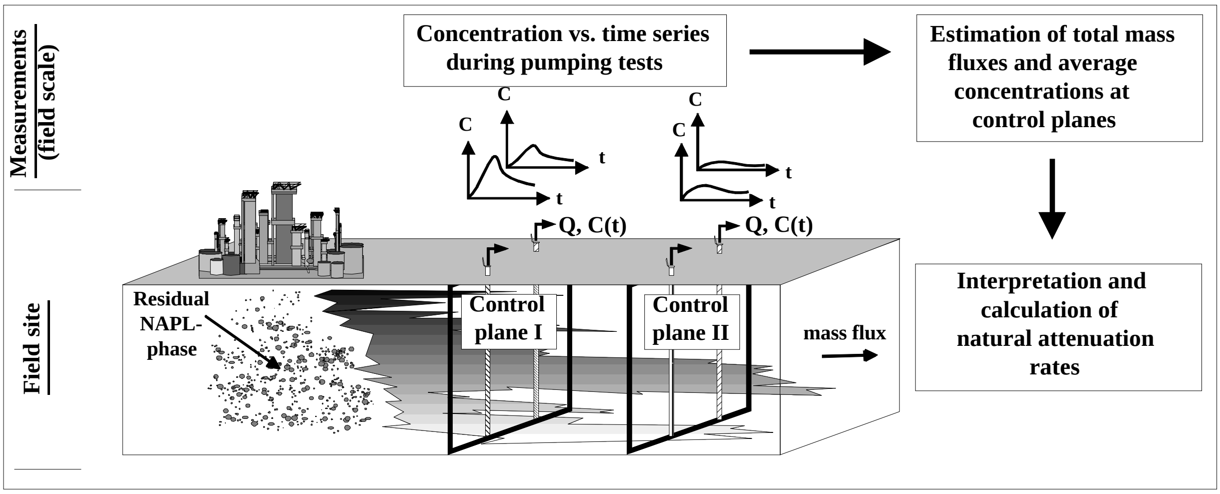
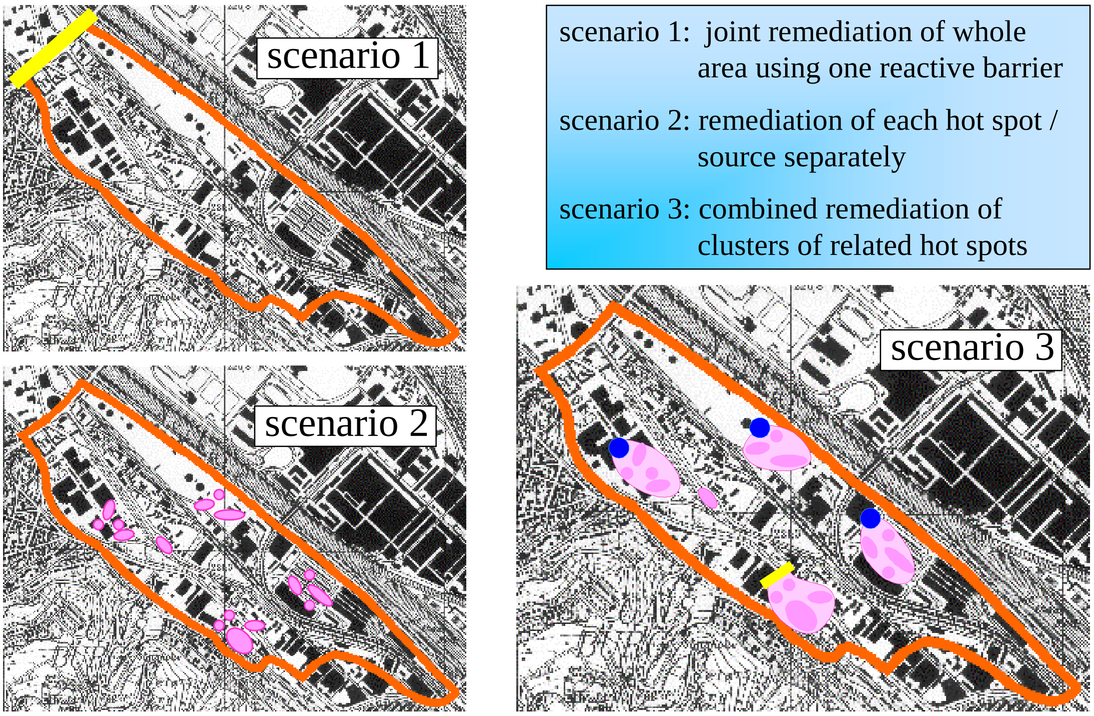


Figure 4: Concept of a multiple control plane approach for the quantification of natural attenuation rate constants at field scale (Bockelmann et al., 2001).

The aim of **cycle III** is to define and evaluate different remediation scenarios for the investigated area (Fig. 5), e.g. to find the most efficient hot spot treatment technology or combinations of technologies for a given hydrogeological and contamination situation, and to treat the remaining plumes with passive remediation methods.



scenario 1: joint remediation of whole area using one reactive barrier

scenario 2: remediation of each hot spot / source separately

scenario 3: combined remediation of clusters of related hot spots

Figure 5: Examples of possible remediation scenarios in the Neckar Valley in Stuttgart

3. CONCLUSIONS

Employing the control plane based integral investigation method, the compound specific average contaminant concentration, the spatial distribution of concentration values along a control plane, as well as the total contaminant mass flow rates downstream of an area under investigation can be estimated quickly and with a high level of certainty. The information obtained from this analysis can be considered a basis for planning of future activities and land use.

The results from the integral investigation at the scale of entire industrial areas (megasites) can be used for risk assessment purposes, for the quantification of the natural attenuation potential, as well as for the development of priorities for clean-up and / or further investigations and for the design of remediation measures. In addition, a consistent quantification of uncertainties in the results from the application of the integral groundwater investigation method is possible, considering uncertainty in the boundary conditions and uncertainty in the hydraulic property values of the aquifer. Finally, the delimiting of the source zone extent and its uncertainty allows to define priorities for further investigation measures at a smaller scale and to develop cost-optimized clean-up strategies at sites with complex contamination patterns. In this way, it is possible to obtain optimal results for the efforts spent. Therefore, the new cyclic approach may become a basis for the development of future EU directives on contaminated land assessment and revitalization in urban industrial areas.

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TRIBUTYLTIN IN SEDIMENTS: AN OVERVIEW

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1. Introduction

Tributyltin (TBT) is a biocide added to some antifouling paints, which are used to prevent growth of algae and molluscs on ships. Unfortunately TBT has severe biological effects on non-target organisms at very low concentrations. Toxic effects have already been observed at concentrations of 2 ng/l.

The use of TBT containing antifouling paints on small ships has been banned in many countries. In November 1999 the International Maritime Organisation (IMO) decided on a global ban of the use of TBT containing antifouling paints starting from January 2003. By January 2008, TBT should be removed from all ship hulls.

The problem of TBT contaminated sediments, however, will last for several decades. This paper describes the analysis of organotin components in sediments, the behaviour of TBT in sediments (adsorption, degradation) and various options to remediate TBT contaminated sediments.

2. Analysis of organotin components in sediments

Most of the analytical techniques developed for the speciation of organotin compounds are based on gas chromatography (GC). GC remains the preferred separation technique due to its high resolution and the availability of sensitive detectors. The analytical procedure for the determination and speciation of organotin compounds in sediments by GC consists of 4 steps:

1) Extraction

The extraction step determines the efficiency and the accuracy of the overall analytical procedure. The conventional method of extraction of organotin components from sediment samples is based on extraction or leaching with an acid-methanol mixture. The most commonly used acids are HCl and acetic acid. Organotin compounds can also be extracted with non-polar solvents (such as hexane). Complexing agents such as tropolone are sometimes added to non-polar solvents to increase extraction yields, especially for mono- and dibutyltin.

The accuracy of the analytical procedures is mostly evaluated through the analysis of either CRMs (Certified Reference Materials) or spiked sediments. It should be taken into account that the availability of spiked analytes in the extraction step can be higher than for the same substances present in ‘old’ environmental systems. Thus, the use of spiked samples can lead to an overestimation of the extraction efficiency.

2) Formation of volatile derivatives

GC methods generally need to include a derivatization reaction to produce volatile organotin compounds to perform their separation. Derivatization methods are based on alkylation or hydridization reactions.

Alkylation with a variety of Grignard reagents is the most widely used derivatization technique. Since the Grignard reagents are sensitive towards water, they can only by used with nonprotic apolar solvents. It is therefore necessary to complex organotin compounds with, for instance, tropolone before extracting them into such solvents. It is clear that this method is usually multi-step, tedious and time consuming. To minimise the analysis time, sodium tetraethylborate ($NaBEt_4$) derivatization has been developed. This allows one to carry out the reaction in an aqueous medium under buffered conditions. The ethylated organotin compounds can be extracted into an organic phase (hexane, isooctane) which is subsequently analysed.

In situ hydride generation with sodium tetrahydroborate ($NaBH_4$) may also reduce the analysis time, but it leads to low repeatability when applied to environmental samples (Abalos et al., 1997).

3) Separation of the volatile derivates

As stated before, in most methods, organotin speciation is based on chromatographic separation prior to the detection. GC-based speciation techniques have been widely used since they give higher resolution than LC methods. Another advantage of GC over LC is the possibility of using several internal standards, which allow the steps of the analytical procedure to be traced. The main disadvantage of GC methods is that they require production of volatile organotin derivates.

4) Detection identification and quantification

In the group of the GC detection techniques various element-specific detection methods like for example (quartz furnace) atomic absorption spectrometry (GC/QFAAS), mass spectrometry (GC/MS) and flame photometric detection (GC/FPD) can be used. MS and FPD have detection limits in the sub-to-low picogram range. The GC/QFAAS techniques have detection limits, which are circa two orders of magnitude higher than former detection systems (FPD, MS).

In general TBT concentrations as low as 50 ng/g sediment (50 ppb) can be detected by the most sensitive analytical procedures.

3. Adsorption – Desorption

In natural waters TBT is present predominantly as neutral TBT or as cationic TBT^+ species, the pKa value of TBT is 6,25 (Weidenhaupt et al., 1997).

Sorption studies of TBT on humic substances (HS) indicate that ionic interactions predominate in TBT-HS binding (Arnold et al. 1998; O'Loughlin et al., 2000). The binding of tributyltin by HS occurs primarily through complexation of the TBT^+ cation by negatively charged ligands (i.e., carboxylate and phenolate groups) of the HS, with secondary contributions from nonpolar interactions.

In a study of Weidenhaupt et al. (1997) the sorption of TBT was investigated on homoionic clay minerals (kaolinites, montmorillonites, illites) and aluminum, iron and silicon (hydr)oxides. For all minerals investigated, sorption kinetics of TBT were fast, and sorption was reversible. At clay minerals, sorption of TBT was dominated by cation exchange of the protonated TBT species (TBT^+). Adsorption of TBT onto homoionic clays increased with decreasing selectivity of the exchangeable cations ($Na^+ > K^+ \approx Rb^+ >> Cs^+ \approx Ba^{2+} \approx Ca^{2+} \approx Mg^{2+}$). The sorption of TBT^+ cations to negatively charged surface sites was the dominating interaction of TBT with all minerals. Thus, high TBT sorption to (hydr)oxide minerals occurred only if a significant fraction of negatively charged surface sites was present at pH values where TBT^+ species predominate.

Randal and Weber (1986) studied the adsorptive behaviour of butyltin compounds under simulated estuarine conditions. They found that adsorption of TBT on hydrous Fe oxide (in the presence of fulvic acid) varied from 57% to 95%, depending on the pH and the salinity of the water. Equilibrium sorption studies of TBT on selected estuarine and freshwater sediments showed high sorption coefficients indicating that significant amounts of TBT may be associated with sediments in coastal plain estuaries (Unger et al., 1988). The sorption process is reversible, so the TBT-contaminated sediments can act as sources for dissolved TBT. Wanatabe et al. (1997) could describe the desorption kinetics of TBT from a resuspended sediment by a two-site model which assumed that desorption consisted of rapid desorption and first-order kinetic desorption. Release of TBT induced by remedial dredging was assessed. Desorbed TBT may pose a high risk.

4. Persistence of TBT in sediments

The degradation of the organotins in the environment may be defined as a progressive loss of organic groups from the cation. The removal of the organic groups can be caused by various processes, which include UV-irradiation, biological cleavage and chemical cleavage.

The half-time for degradation of tributyltin in seawater at 20°C is 3-8 days in light and 7-13 days in darkness. This difference can be attributed to the removal of organic groups by UV-irradiation. The degradation rate of tributyltin in sediment is much slower than in the water column. In aerobic sediment the half-time has been measured to be 1 year and about 2 to 5 years in anaerobic sediment (Mortensen et al. 1995, Hoch, 2001).

5. Remediation techniques for TBT contaminated sediments

Wanatabe et al. (1997) found that remedial dredging of sediments would lead to the desorption of a large amount of TBT. They preferred capping, or leaving the sediment to stand prior to in situ degradation. But every year, enormous amounts of sediment have to be dredged form waterways and harbours to ensure the depth. These sediments are contaminated with organotin compounds and must be treated before relocation.

While biodegradation has been postulated in the literature as a possible treatment for the sediments, there is no strong evidence that organotins will be destroyed microbiologically in an acceptable time scale (Stichnothe, 2001). Microbial degradation is not possible when the TBT concentration is too high, because microbial organisms do not survive in these circumstances. This process is also dependent on temperature. Several reports indicate that little microbial degradation occurs in winter.

Another approach to destroy organotin compounds is a mechanical classification with a final thermal treatment of the polluted fine-grained fraction. This method is very energy consuming and expensive. Eschenbach et. al (2001) found that a newly developed steam stripping process can become an efficient way for the treatment of contaminated fine-grained particles. They realised cleaning performances of more than 95% for mineral oil, PAH and also TBT.

Preiliminary experiments, performed by Stichnothe et al. (2001) show that dibutyl and tributyltin can be decomposed by the electrochemical treatment of sediment. TBT was destroyed under oxidising as well as under reducing process conditions. A partial debutylation of tri- and dibutyltin could be achieved, although monobutyltin was not affected. This technique is promising but further investigation is necessary to improve the experimental conditions.

Since no large scale, cost-benefit remediation technologies are available for treating TBT contaminated sediments, land deposition will be one of the options. Brandsch et al. (2001) studied the land deposition of TBT containing sediments. Field studies gave a degradation rate of approximately 10%/yr in untreated sediment and 30%/yr in restocked sediments. They did not observe any interference of released TBT with groundwater or surrounding areas, and the TBT uptake in plants was low. The land deposition appears to be a sustainable solution for dealing with TBT-contaminated harbour sediments. Compared to other disposals, it is economically one of the cheapest and, from an ecological point of view, it is acceptable.

Another way to treat contaminated sediments is using them for brick production. Karius and Hamer (2001) studied the pH and grain-size variation in leaching tests with bricks made of 50% wt. harbour sediments from Bremen, Germany, which were polluted with heavy metals (e.g. Zn, Cd, Pb) and organic compounds (e.g. TBT), compared to commercial bricks. In general, leachability of heavy metals from the sediment brick was in the upper range of the commercial bricks. The organic contaminants are combusted at the high temperatures of the brick making process.

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METAL PARTITIONING IN A SULFIDIC SEDIMENT DETERMINED FROM THE INFLUENCE OF PH ON METAL SOLUBILITY IN ANOXIC CONDITIONS

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1. Introduction

In sediments, anoxic conditions often result in the microbially-mediated production of major amounts of hydrogen sulfide in marine and estuarine environments. Hydrogen sulfide reacts rapidly with iron liberated from oxides/oxyhydroxides and silicates within the sedimentary layers resulting in the formation of amorphous iron sulfide and/or crystallized iron sulfide such as mackinawite and greigite (Billon et al, 2001).

For trace metals, there is also the potential to form trace metal sulfides in anoxic conditions (Morse et al, 1987). From a thermodynamic point of view, trace metal sulfides will preferentially be formed instead of iron sulfide due to their lower solubility products (Buykx et al, 2000). However, trace metals can also adsorb onto iron sulfide minerals or coprecipitate with them. Despite the importance of sedimentary iron sulfides on the bioavailability of toxic metals in sediments, fundamental questions still remain concerning their interaction with different trace metals (Huerta-Diaz et al, 1998).

The aim of this study was to investigate the influence of pH on the solid phase partitioning of trace metals (Zn, Pb, Cu, Cd, Co and Mn) and main components (Fe and Ca) in a carbonate-rich sulfidic sediment from the Gent-Terneuzen Canal (Belgium) under the original reducing conditions of the sediment. Therefore, dissolution experiments as a function of pH were made in in a salt solution mimicking the canal water in an anoxic glove box. Anoxic conditions were obtained by continuously flushing N_2/H_2 over a catalyst inside the glove box. The use of an additional 0.1 M Na-EDTA/ 0.5 M NaAc extraction step (pH 4.65) on the centrifugates remaining after the dissolution versus pH experiments to determine eventually readsorbed and reprecipitated metal ions will be discussed.

2. Materials and Methods

All dissolution versus pH experiments were made with sediment from the Gent-Terneuzen Canal. The reducing sediment has a fine texture (70% < 50 µm) and is rich in organic carbon (5.2 %) and calcium carbonate (17.4 %). Part of the canal sediment was freeze-dried to allow a better homogenisation. Precautions were taken to avoid any oxidation during sampling, freeze-drying and storage as described in Cauwenberg and Maes (1997).

All dissolution versus pH experiments were performed inside an anoxic glove box (N_2/H_2 (%) : 95/5). The need for working under strictly anoxic conditions when studying metal speciation in anaerobic sediments was demonstrated in Cauwenberg and Maes (1997). Deoxygenated double destilled water was used to prepare all solutions inside the anoxic glove box.

In a *first series* of experiments, 3 g freeze-dried sludge was weighed into 40 ml centrifuge cups and suspended in 20 ml of a background solution of 0.035 M $NaNO_3$, 0.007 M $CaCl_2$ and 0.0053 M $MgCl_2$, mimicking the water of the Gent-Terneuzen Canal.

In the first part of these series, various batch experiments at different pH were prepared by slowly adding an appropriate volume of acid (x ml of 1 M or 5 M HCl at a rate of 0.1 ml/min, with addition times between 2 and 40 minutes) to the centrifuge cups with an automatic titrator and the total volume was made up to 35 ml with deoxygenated water. Equilibrium was assumed after overnight (18-20 hours) shaking in the glove box. The pH was measured the next morning and after a centrifugation step (10 minutes, 10000 rpm) 20 ml of the supernatant was pipetted and stored for AAS analysis (Varian, AAS-20) upon addition of one drop of concentrated acid .

The second part of these series consisted in taking EDTA/NaAc extracts from the centrifugates of the previous solubility experiments, by adding 25 ml of a 0.7 M NaAc / 0.14 M Na-EDTA solution, giving a final concentration of 0.5 M NaAc / 0.1 M Na-EDTA (pH 4.65). The tubes were then shaken overnight in the glove box. The pH was measured the next morning and the supernatant was pipetted after a centrifugation step (10 minutes, 10000 rpm) and was analysed by AAS (Varian). The concentration of 0.1 M Na-EDTA / 0.5 M NaAc used in the present study was checked to be sufficient to complex all liberated metals in presence of high amounts of calcium and iron. The standard solutions for the AAS calibration curve were prepared in the EDTA/NaAc matrix by dilution from 1000 mg/l metal standard solutions (Aldrich Chemical Company, Inc).

In a *second series* of experiments, the first series of dissolution experiments as a function of pH were repeated but the initial solution was now spiked with labelled ^{109}Cd or ^{65}Zn. No EDTA/NaAc extracts were taken from the remaining sediment samples in these series. The Cd and Zn gamma-activities were measured (Minaxi 5000 auto-γ).

In a *third series* of experiments, synthetic sediments were prepared inside an anoxic glove box. Subsequently, EDTA/NaAc (0.1 M/0.5 M) extractions at pH 4.65 were performed overnight on the synthetic sediments to evaluate its potential to extract transition metals from freshly precipitated transition metal sulfides.

The synthetic sediments were prepared with 5 g sea sand (VEL, p.a.), 5 g illite clay (Silver Hill Montana, < 200 µm), 0.050 g humic acid (Aldrich), nitrate salts of Cd, Cu, Pb, Zn and $FeCl_2$ (Merck, p.a.) in a background solution of 50 ml 0.001 M $Ca(NO_3)_2$. Sodium sulfide solution was then added to the synthetic sediments at a dose of twice the total metal concentration (mol/l) to form metal sulfides. The suspensions coloured black immediately after sodium sulfide addition indicating that metal sulfides were formed. The pH of the synthetic systems was adjusted to pH 8.5 with 1 M HNO_3. After overnight equilibration followed by centrifugation (15 minutes, 8000 rpm), the supernatant was pipetted and the pH was checked to be around pH 8.5. The metal amounts in the equilibrium solutions (pH 8.5) were measured by AAS (Varian) and were below 0.01 % of the total added concentration.

3. Results and Discussion

3.1. Metal solubility versus pH from sediment in anoxic conditions

In a former study (Cauwenberg and Maes, 1997), the partitioning of the metals Cd, Cu, Pb, Zn and Fe in the Gent-Terneuzen Canal sediment (Belgium) was determined under nitrogen atmosphere by the sequential extraction procedures of Oakley et al (1980) and Wallman et al (1993). In both extraction procedures, about 90 % of the total Cd, Cu, Pb and Zn was present in the fourth fraction and was assigned as bound to sulfides. In the case of iron, Fe was present in at least two main fractions : an iron sulfide fraction and an non-sulfidic fraction (eg. Fe incorporated in clay minerals).

In the present study, we investigated the metal solubility as a function of pH of samples taken from the same metal sulfide-rich sediment. The theoretical solubility of the studied metals under the conditions of the solubility versus pH experiment was calculated with the speciation program JCHESS (Van der Lee, 2000) and is shown by solid lines in the figures. The following essential formation constants (Log K-values) were taken from the MINTEQ database (Van der Lee, 2000) : 4.648 (mackinawite), 10.55 (iron carbonate), 8.475 (calcium carbonate), 11.618 (zinc sulfide), 15.132 (lead sulfide), 23.038 (copper sulfide), 15.930 (cadmium sulfide), 0.394 (manganese sulfide), 10.410 (manganese carbonate) and 7.374 (cobalt sulfide).

The experimental dissolution edge of Fe (Figure 1a, squares), Ca (Figure 1b , squares), Mn and Co (data not shown) had a lower slope than theoretically expected on the basis of respectively iron sulfide/iron carbonate, manganese sulfide/manganese carbonate, cobalt sulfide and calcium carbonate (JCHESS, 2000). The low slope of these experimental dissolution edges can in part be explained by the combination of the solubilities of the individual sulfide and/or carbonate minerals and by coprecipitate formation of Mn and Co with iron sulfide/iron carbonate minerals. However, metal readsorption onto clay minerals and organic matter should also be taken into account.

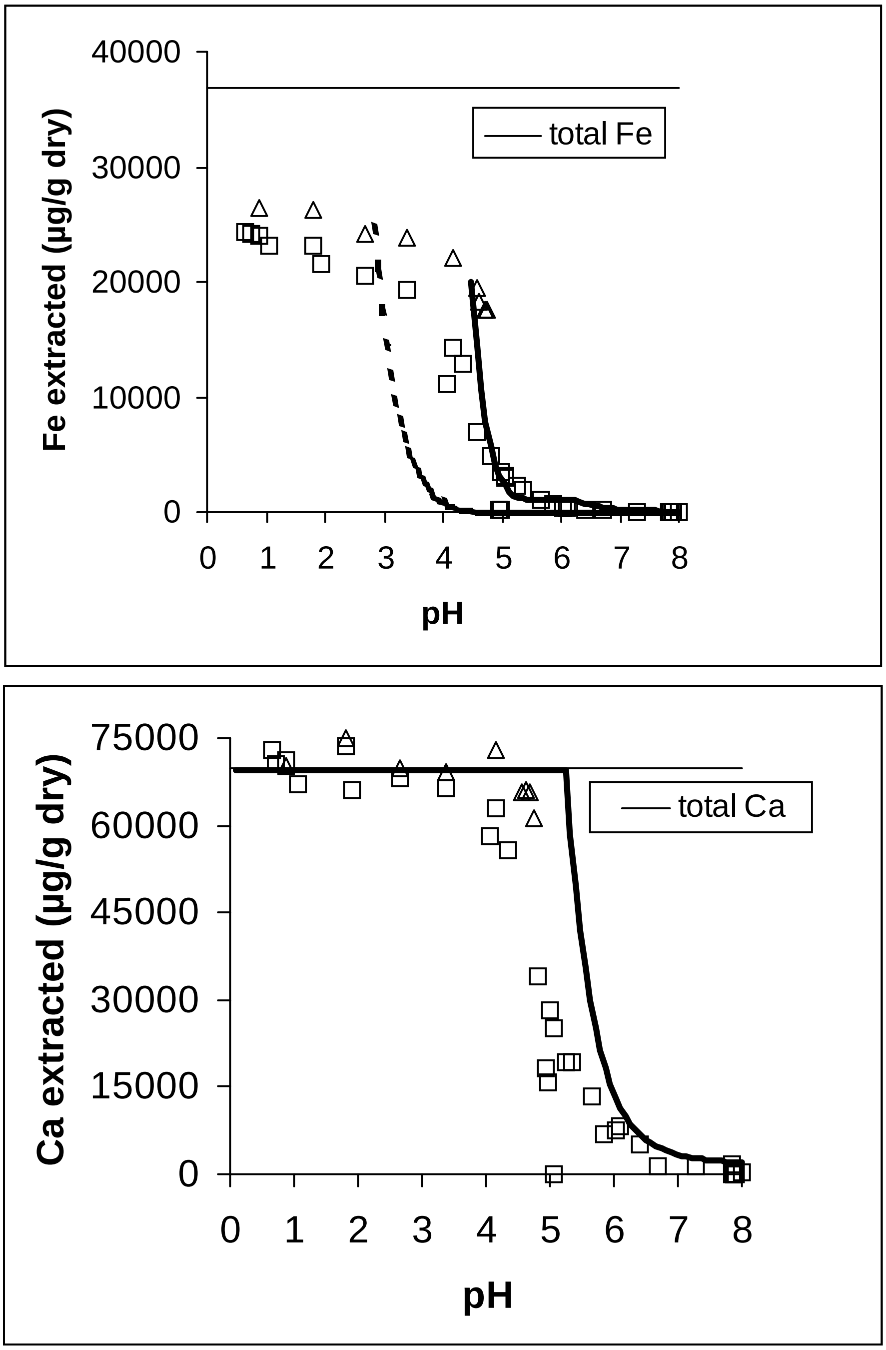
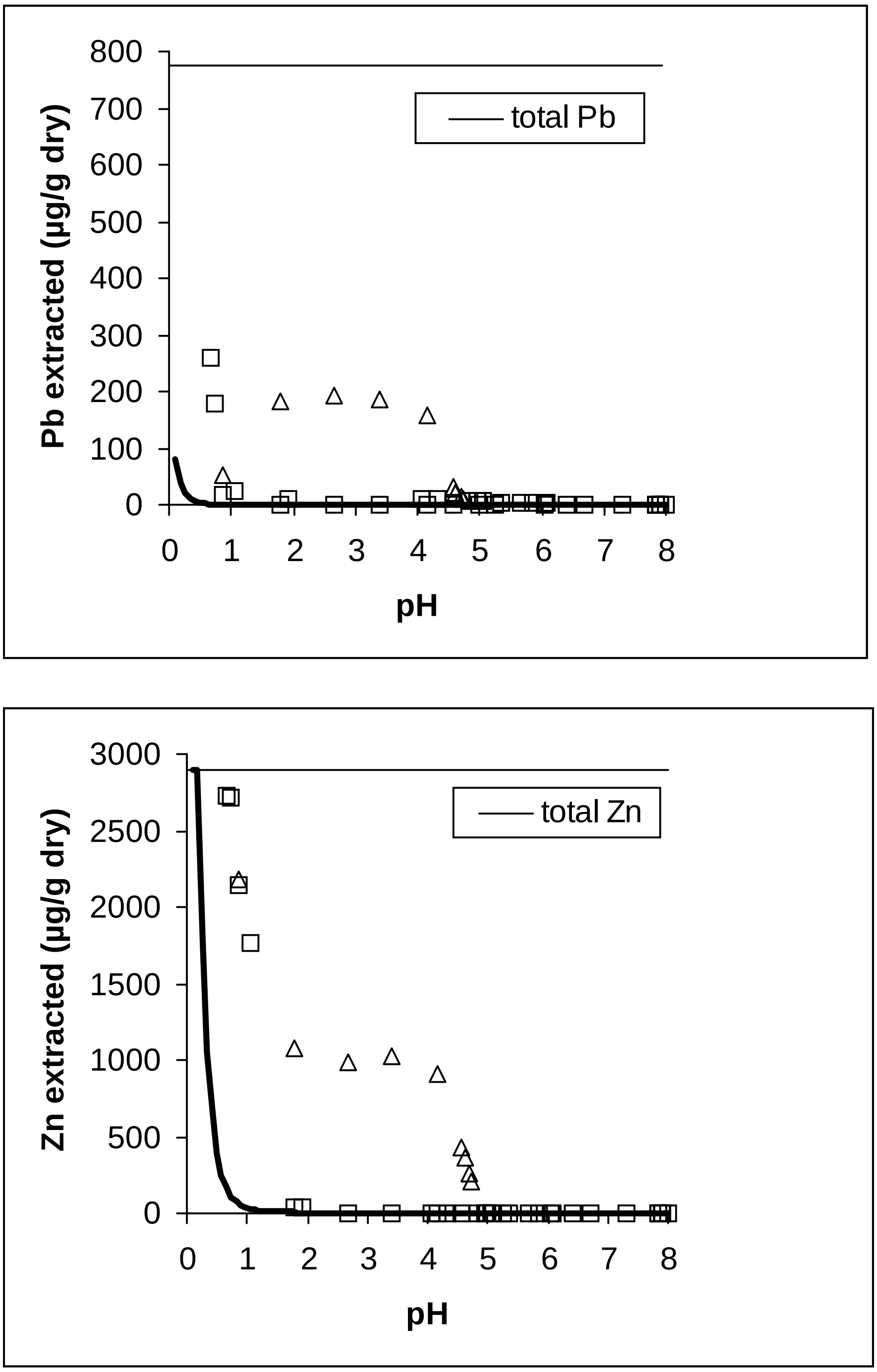
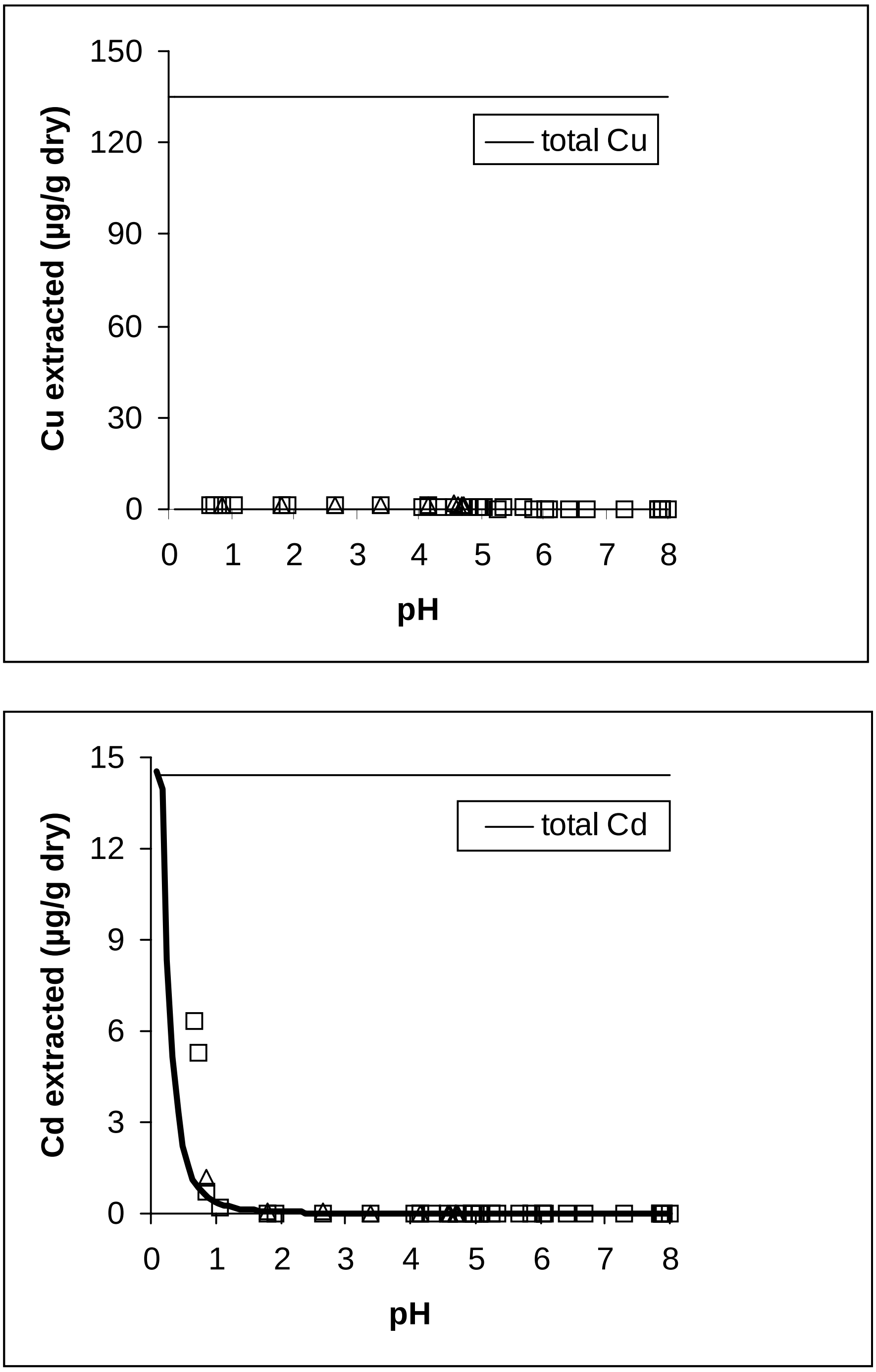


Figure 1 : (a) Iron (µg/g) and (b) Calcium solubility (µg/g) as a function of pH. Squares represent the solubility in the mimicking salt solution. Triangles represent the sum of the extractability in the mimicking salt solution and in 0.1 M EDTA/0.5 M NaAc. In the case of Fe, the solid and dashed lines represent respectively the theoretical solubility based on the presence of $FeCO_3$ and mackinawite (Van der Lee, 2000). In the case of Ca, the solid line represents the theoretical solubility based on the presence of calcium carbonate (Van der Lee, 2000).

The experimental solubility of Pb, Zn (Figure 2, a-b, squares), Cu and Cd (Figure 3, a-b, squares) is very low in the pH range 1-8. Such behaviour is in agreement with the theoretical solubility of their discrete, crystalline metal sulfides (Van der Lee, 2000). The partitioning of the overwhelming part of Pb, Zn, Cu and Cd in discrete metal sulfides is confirmed by the results of the sequential extraction procedures performed under anoxic conditions (Cauwenberg and Maes, 1997).



<u>Figure 2 :</u> (a) Lead and (b) Zinc solubility (µg/g) as a function of pH. Squares represent the solubility in the mimicking salt solution. Triangles represent the sum of the extractability in the mimicking salt solution and in 0.1 M EDTA/0.5 M NaAc. The solid lines represent the theoretical solubility (Van der Lee, 2000) based on the presence of (a) lead sulfide and (b) zinc sulfide.



<u>Figure 2 :</u> (a) Copper and (b) Cadmium solubility (µg/g) as a function of pH. Squares represent the solubility in the mimicking salt solution. Triangles represent the sum of the extractability in the mimicking salt solution and in 0.1 M EDTA/0.5 M NaAc. The theoretical solubility based on the presence of cadmium sulfide is given by the solid line (Van der Lee, 2000). The theoretical solubility based on the presence of copper sulfide is very low (even at low pH values) and is therefore not shown.

3.2. Metal solubility versus pH from ^{65}Zn and ^{109}Cd labelled sediment in anoxic conditions

The reason for doing the solubility versus pH experiment with ^{65}Zn and ^{109}Cd labelled sediment was to verify whether Cd and Zn are eventually present in coprecipitates with iron sulfide/iron carbonate minerals in the sediment and were thus not measured in 3.1 due to reprecipitation and/or readsorption phenomena.

Figure 4 shows the percentage of the added radioactively labelled ^{109}Cd present in the supernatant solutions at different pH together with the dissolved percentage of the total Cd present in the sediment. In the pH range between pH 8 and pH 2 no labelled ^{109}Cd was measured in solution, notwithstanding the fact that large quantities of spike (concentration 10^{-7} M Cd) were added. The labelled ^{109}Cd concentrations in solution only increased below pH 2 and was identical to the dissolution behaviour of the original Cd (Figure 4). In the case of ^{65}Zn labelled sediments, a similar behaviour was observed (data not shown).

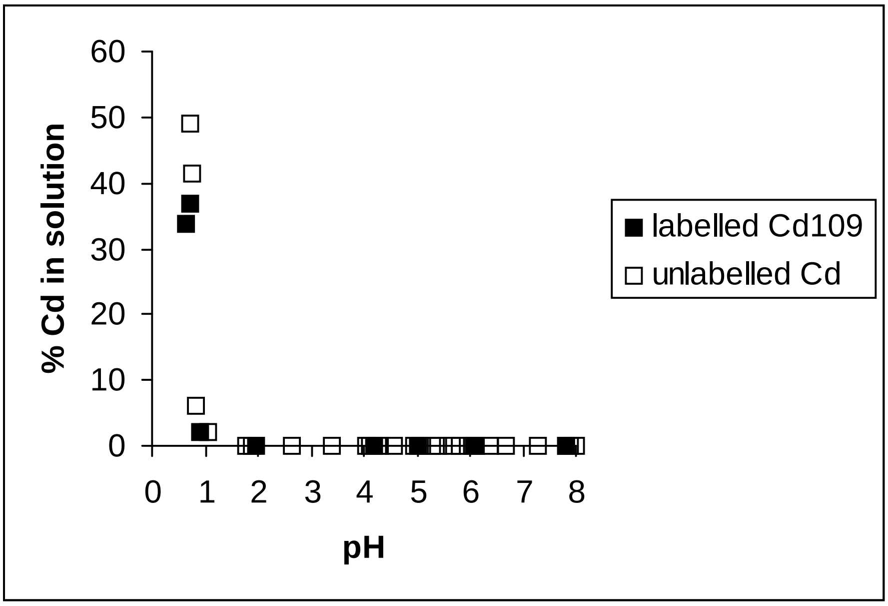


Figure 4 : Percentage of labelled and unlabelled cadmium in salt solution as a function of pH

These results demonstrate that reprecipitation of transition metals, which are (eventually) released from mixed coprecipitates with iron sulfide/iron carbonate starting from pH 6 (Figure 1a, squares), occur as amorphous, separate transition metal sulfides. Therefore, further steps need to be taken to experimentally determine the amount of Zn, Cd, Cu and Pb that are present in mixed coprecipitates with iron sulfide/iron carbonate minerals in the canal sediment.

3.3. EDTA/NaAc extraction with synthetic sediments in anoxic conditions

Extraction experiments with synthetically prepared sediments containing sea sand, illite clay, humic acid and freshly precipitated metal sulfides were performed overnight under nitrogen atmosphere to evaluate the potential of EDTA/NaAc (0.1 M/0.5 M ; pH 4.65) to extract transition metals from their freshly precipitated, amorphous metal sulfides.

The transition metal extractability obtained by overnight EDTA/NaAc extraction from freshly formed metal sulfides in anoxic conditions increases in the order : copper (0.01 %) < cadmium (0.25 %) < lead (23.03 %) < zinc (29.60 %). These observations are important for the interpretation of the EDTA/NaAc (0.1 M/0.5 M ; pH 4.65) extraction data from the canal sediment in section 3.4. in the sense that (a) copper was not extracted from freshly precipitated copper sulfide phases and (b) cadmium, lead and zinc were only partly extracted from their freshly precipitated metal sulfides.

3.4. Metal solubility as a function of pH followed by EDTA/NaAc extraction from sediment in anoxic conditions

All EDTA extractions were performed in an acetate buffer (0.5 M) of pH 4.65, irrespective of the pH history of the sediment samples. The obtained data are presented by triangles in Figure 1 (Fe, Ca), Figure 2 (Pb, Zn) and Figure 3 (Cu, Cd) and correspond to the sum of the metal amount extracted at the various equilibrium pH values (of the previous solubility versus pH experiment) and the additional metal amount extracted with EDTA/NaAc (0.1 M/0.5 M) from the centrifugates remaining after the solubility versus pH experiment.

For samples with a pH history below pH 4.65, the experimental EDTA/NaAc data are presented as a function of the pH of the salt solution in the foregoing solubility experiment. This is reasonable since at pH values below pH 4.65 higher metal dissolution occurred. However, for samples with a pH history above pH 4.65, overnight EDTA/NaAc extraction leads to an enhanced metal extraction due to the more acidic pH of the EDTA buffer solution (in comparison with the pH history of the sample). Therefore, the EDTA solubility data for samples with a pH history between pH 4.65 and pH 8 are presented at the equilibrium pH values following overnight EDTA/NaAc extraction.

Based on theoretical calculations, calcium carbonate, manganese sulfide, manganese carbonate, iron carbonate and cobalt sulfide are expected to dissolve in the EDTA/NaAc extraction step (Van der Lee, 2000). For Ca (Figure 1b, triangles) and Mn (data not shown), the theoretical calculations agree with the experimental results since almost 100 % recovery was obtained from the remaining centrifugates. However, theoretical calculations based on the presence of iron sulfide (mackinawite) showed an incomplete dissolution of mackinawite in presence of high amounts of calcium carbonate in the EDTA/NaAc mixture at pH values above pH 4.45. Indeed, the theoretical expected dissolution of iron sulfide (mackinawite) changes from 100 % at pH 4.45 to 50 % at pH 5 (Van der Lee, 2000). This is a possible explanation for the observed lower extracted amounts of iron in the EDTA/NaAc extracts with equilibrium pH values between pH 4.45 and pH 5 (Figure 1a, triangles). The enhanced dissolution of cobalt towards lower pH values in the EDTA/NaAc extracts (data not shown) can be ascribed to its association with iron sulfide (mackinawite) since cobalt sulfide should theoretically completely dissolve in EDTA/NaAc (Van der Lee, 2000).

The possible association of zinc, lead, cadmium and copper with iron sulfide/iron carbonate could not be experimentally determined in the solubility versus pH experiments in absence of EDTA/NaAc due to transition metal reprecipitation as amorphous transition metal sulfides (cfr. solubility versus pH with ^{65}Zn and ^{109}Cd labelled sediments).

By extracting the centrifugates remaining after the solubility versus pH experiment with EDTA/NaAc (0.1 M/0.5 M, pH 4.65), it was tried to investigate whether zinc, lead and cadmium were eventually partly present in iron sulfide/iron carbonate minerals in the canal sediment.The experimental EDTA/NaAc data (triangles) in Figure 2 (Pb, Zn) and Figure 3 (Cu, Cd) clearly demonstrate that differences in the extraction pattern exist among the transition metals.

In the case of copper, it was not possible to investigate whether copper is present in mixed iron sulfide/iron carbonate coprecipitates in addition to its presence in pure copper sulfide phases (which only dissolve at very low pH values) due to the fact that EDTA/NaAc extraction is not able to extract a percentage of the copper from freshly precipitated copper sulfide phases (cfr. overnight EDTA/NaAc extraction with synthetic sediments).

In the case of Cd (Figure 3b), no influence of EDTA/NaAc extraction on the cadmium solubility was observed in the experimental pH range 2-8 in spite of the fact that reprecipitated amorphous cadmium sulfide can in part (0.25 %) be dissolved by EDTA/NaAc. Thus, the solubility versus pH experiments followed by EDTA/NaAc extraction lead us to conclude that in the real sediment cadmium is present in discrete, separate cadmium sulfide phases in agreement with the theoretical solubility of cadmium sulfide in the EDTA/NaAc mixture (Van der Lee, 2000).

The observed extraction patterns for Pb and Zn in presence of EDTA/NaAc (Figure 2, a-b) are clearly similar to each other but significantly differ from the Cd pattern. For example, for a sediment sample that was brought to pH 5 in the previous solubility versus pH experiment and nothwithstanding the fact that iron sulfide/iron carbonate starts to dissolve at pH 6 (Figure 1), only small amounts of zinc (0.02 %) and lead (0.8 %) were measured in absence of EDTA/NaAc. Subsequent EDTA/NaAc extraction of the centrifugates results in the release of major amounts of Zn (15 %) and Pb (5 %) in solution. This is explained as due to their reprecipitation as amorphous transition metal sulfides. Secondly, for a sediment sample that was brought to pH 3 to 4 in the previous solubility versus pH experiment and notwithstanding the fact that the iron sulfide pool at these pH values is almost completely dissolved, again only small amounts of Zn (0.05 %) and Pb (1.35 %) were measured in absence of EDTA. In contrast, in presence of EDTA/NaAc, a plateau value is reached between pH 3 and pH 4 in the case of zinc (35 %) and lead (25 %). So, the experimental dissolution edges of zinc and lead closely follows the dissolution edge of iron in the EDTA/NaAc mixture. Therefore, we can conclude that zinc and lead are partly present in mixed coprecipitates with iron sulfide/iron carbonate in addition to their presence in discrete metal sulfides, which only dissolve below pH 2.

4. Conclusions

By performing an additional EDTA/NaAc (0.1 M/0.5 M; pH 4.65) extraction on the centrifugates remaining after the solubility versus pH experiments, it was demonstrated that in the Gent-Terneuzen Canal sediment (a) zinc and lead were partly present in mixed coprecipitates with iron sulfide/iron carbonate minerals in addition to their presence in discrete metal sulfides and (b) cadmium was solely present in pure cadmium sulfide phases.

However, no quantitative assignment of the percentage of zinc,lead and cadmium in mixed coprecipitates with iron sulfide/iron carbonate could be obtained due to the fact that in a separate experiment no full metal recovery could be obtained from their freshly reprecipitated transition metal sulfides in the 0.1 M EDTA/0.5 M NaAc (pH 4.65) mixture.

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SOME SINGULARITIES OF DESCRIPTION THE HEAVY METAL'S MOBILE FORM IN SOIL OF ORE MINING REGION UNDER VARIOUS VEGETATIVE ASSOCIATIONS

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1 Abstract

Some regularities of distribution of the mobile forms iron, manganese, zinc in soil around to Northern mining-and-processing integrated works (Krivbass) under various vegetative associations (steppe cenoses, wind forest strip, agrophytocenoses) are investigated. It was established that the wood vegetation causes accumulation in soils of all metals. The intensity of this process with depth amplifies, i.e. there is their migration for limits of a soil profile. Agrophytocenoses cause accumulation of manganese and irons and leaching of zinc.

Key words: heavy metals, accumulation, leaching, vegetative associations.

2 Introduction

The objective of this study were to: (I) characterise Fe, Mn, Zn profile distribution in a soil developed from loess in the local background sire at Kryvyi Rih Iron Ore Mining region; (ii) assess the levels of soil contaminated by these metals situated under various vegetative associations.
Materials and Methods

The study areas located on the northern part of Kryvyi Rih city (in the centre of Ukraine) around Northern Iron Ore Dressing Combine. This combine created at the north part of Kryvyi Rih city in 1396, now produces around 9 000 000 ton iron concentrate per year.

According to FAO-WRB soil classification system the soils around northern part of Kryvyi Rih is classified as a chernozem ordinary.

The number and place of the samples was selected according to the map of dust description in the air. This map was worked out by using of the program PLENER 2.15 for IBM PC. On the basis of this map, two location within the investigation areas were selected which had dust concentration in an air ranging from 0.5 mg m^{-3} to 1.0 mg m^{-3}. The first location, named as SITE-1, had lowest dust content 0.15-0.5 mg m^{-3}. The second location, named as SITE-2, had middle dust 0.5-1.0 mg m^{-3}.

Three subsites within every SITE were chosen which had different soil using and situated under various vegetative associations. The subsite-1 was located under agricultural vegetation (agrophycenoces). The subsite-2 was located under a forest vegetation (shelter belts cenoces). The subsite-3 was located under natural herbaceous vegetation (steppe cenoces). The local background site was used how control. This site selected so as to minimise the risk of direct anthropogenic contamination. The background site was distant from any industrial development, urban area or major road. But he was at boundary of Kryvyi Rih natural geochemical area.

At each sampling location the soil pits were dug up. The soil samples were collected from all soil profile (in 10 sm. increments) down to the parent material. The soil samples were air dried, crushed and sieved (<1 mm). For extracting soil samples (2g) were digest with 20 m L –1 nitric for 0.25 h at 150 o C. The digest were filtered though filter paper, made up to 25 mL. Heavy metals in the extracts (Fe, Mn, and Zn) were determined by flame atomic absorption spectrophotometer.

The soil contaminations were assessed through comparison of metals content in each horizont with the background content from same soil unite and from same kind soil horizon. In investigated areas were indicated following soil horizons: humus accumulation (A); humus transition (AB); illuvial (B); illuvial transition (BC).

3 Results and Discussion

3.1 In a soil of the background site

In a soil of local background site the Fe content can reach 824-1494 mg kg^{-1}. The highest Fe concentrations were found in AB horizon while they were lower in surface A horizon. Relatively high Fe content in AB horizon decreased rapidly with depth in soil profile. No significant difference was found between Fe content in B and BC horizons and in bedrock horizon.

In a soil at control site the Mn concentration can attain 163-318 mg kg^{-1}. Mn maximal contents were found in humus horizons (A and AB). Then Mn concentration decreased with depth in soil profile.

Among the three elements compared, Zn occurred in the soils of control at the lowest concentrations (ranging from 17 mg kg^{-1} to 35 mg kg^{-1}). Zn distribution within soil profiles showed certain similarities to Fe pattern. The highest Zn contents were found in AB horizon. Whereas the Zn concentrations were lower in surface A horizon. Similarly to Fe, Zn content decreased with depth in soil profile.

3.2 Iron

The Fe contents in soil situated under forest associations remain within the local reference range in humus A and AB horizons. While the Fe content in depth soil horizons (B and BC) can reach 1.6-1.8 time higher than control. No significant difference was found between Fe concentration1 at SITE-1 and at SITE-2.

The Fe contents a in a soil situated under agrophytocenoses and under steppe cenoces remain within the background levels in AB horizons at SITE-2, were lower than its in AB horizons at SITE-1. The accumulations of this metal in a soil under forest cenoces were found in surface A horizons and in depth B, BC horizons (at all SITEs).

3.3 Manganese

The Mn content a soil situated under steppe cenoces in A, AB, B horizons at SITE-2 and in AB horizon at SITE-1 remain within control renge. The Mn concentration in A horizon at SITE-2 were lower than its. But the Mn content in B chorizons (at SITE-1 and at SITE-1) can reach about1.5-1.6 times that of background samples. The Mn contents under shelterbelts cenoces in all soil profile and at all SITEs were in 1.3-1.8 times higher than control levels. The Mn accumulation in a soil under agrophytocenoses were found in surface A horizon (at SITE-1 and at SITE-2) and in AB horizons (at SITE-2). The MN contents in depth B, BC horizons remain within the background range.

3.4 Zinc

The Zn content in soil under steppe cenoses in all soil profile at SITE-1 and in B, BC horizons at SITE-2 can reach as much as 1.2-2.1 times than control. The Zn contents in a soil under agrophytocenoses in A, AB, B-horizons at SITE-1 and in A, AB horizon at SITE-2 were lower than reference range by 20-50%. While the Zn concentration in plots situated under forest cenoces were wound. So, Zn contents in all soil horizons and at all SITEs can attain 1.3-2.3 times that control samples.

4 Conclusions

At local background site the lowest contents of Fe, Mn, Zn were found in AB soil horizons. The levels of these metals concentration seems to decrease in the following order: Fe>Mn>Zn.

The contamination of the soils situated under tress associates is clearly apparent by Fe, Mn, and Zn. The heavy metals contents in depth soil horizons were higher than in surface horizons. It can be partially explained by mobilisation of metals by organical acid which fallen in soils with leaf.

In the soils situated under agrophytocenoses the leaching of Zn and slightly accumulation of Fe, MN were found. The ZN leach can be explained by agricultural use of these substites and uptake the Zn by plants.

In the soil situated under steppe cenoces immobilisation of Mn were fond. In can be explained by change of oxidation and redoxidation conditions in soils

The accumulation of metals seems to decrease in the following order: Zn>Mn>Fe.

The extent of influence on profile description of metals studded seems to decrease in the following order: agricultural vegetation (agrophycenoces)>forest vegetation (shelter belts cenoces)>natural herbaceous vegetation (steppe cenoces).

ANALYSIS OF BROWNFIELD REDEVELOPMENT PROJECTS UNDER ENVIRONMENTAL CRITERIA

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ABSTRACT

Since the midnineties, remediation projects have often been done only in connection with brownfield redevelopment. A remediation of contaminated sites or the preparation of construction sites on derelict land (excavation, transportation, operation of pumps and units) causes impacts on the environment (e.g. emissions, energy consumption, waste). These so-called secondary impacts on the environment are receiving more and more attention. At the moment one can find debut research in environmental balancing of subsurface remediation projects comparable to the life cycle assessment of industrial products. It seems necessary to estimate the environmental impacts on the preparation of construction sites in context with brownfield redevelopment projects – e. g. subsurface remediation, demolishing of buildings. This could be the basis for an ecological optimisation of the projects.

At the research facility for subsurface remediation (*VEGAS*) at the University of Stuttgart, a research project on the topic of environmental balancing has been started with the aim of extensively balancing brownfield redevelopment projects under ecological criteria. The main objective of the project is the estimation of the ecological impacts during the redevelopment of brownfield sites for construction purposes. This should show which steps of a redevelopment project cause the main environmental impacts. Based on the results, a quick and easy optimisation of the projects should be possible. For this purpose numerous projects are being examined and transferred into the available environmental balancing tool ‘Environmental balancing of site remediation measures’ (LFU 1999). These projects are real case studies characterized by e. g. different industrial or former military utilization and subsurface contamination.

The results of the project show that in most of the brownfield redevelopment projects the contaminated soil was excavated and transported to waste dumps. The very low prices for transportation and for dumping / reusing soil on landfills as construction material in Germany are the reasons for this behaviour. In these cases the main ecological impacts were caused by the transportation of the material to the landfills. The most commonly used means of transportation is the truck, which has a significantly higher impact on the environment than trains and ships. This is reflected in high energy consumption and the typical traffic emissions.

Contaminated soil was treated in remediation facilities on-site, or in some cases off-site. On-site treatment of contaminated material reduces transportation distances, so the main impact on environment is caused by the remediation itself.

Off-site treatment requires transportation of the contaminated material to the facility. In some balanced cases more than 75 % of the environmental effects of brownfield redevelopment projects were caused by the transports to the off-site treatment plants (biological treatment) and the transportation of the cleaned material. In many cases the transportation distances were longer than 200 km.

Under ecological criteria, in-situ and on-site remediation techniques have thus far proven to be better methods than off-site techniques. But there are some limitations: The long-time use of pumps and units e.g. for soil vapour extraction or hydraulic protection of a contaminated area, results in high cumulative energy consumption and corresponding emissions. The secondary impact on the environment can achieve an order of magnitude equalling the energy expenditures for a total excavation of the damage with a following disposal on a dump.

1 INTRODUCTION

The redevelopment of brownfields in Germany is becoming more and more important. The recycling of derelict land is one possibility to reduce our high land consumption of 129 ha per day and to prevent the negative environmental impacts of the use of agricultural land as sites for new housing, industrial areas, and traffic infrastructure. The impacts of this procedure are among others the destruction of nature, influence on the local climate and the water cycle. As a consequence, brownfield redevelopment is important to start a sustainable future.

Any action of construction work, be it recycling of an abandoned site, or use of agricultural land for housing, has a cost. The impact of each of these actions on the environment is determined by e. g. its cost in both energy and raw material. These actions cause impacts on the environment. These are the so-called secondary environmental impacts. Here is the question - what are the ecological consequences of brownfield redevelopment projects? How much energy is required to bring a brownfield back into use, and what is the ecological footprint of such projects? Are there ways to support redevelopment by ecologically improving the redevelopment procedure? In order to answer these questions, a life cycle assessment is required for brownfield redevelopment projects.

Life cycle assessment (LCA) plays an important role in connection with production processes. Numerous investigations and publications exist on the LCA of different products (plastics, packages etc.). The requirements for LCA are defined in the ISO regulations 14040 to 14043. Formally, these standards are universally applicable. However, during the elaboration of the regulations, the focus was on the LCA of technical procedures. A LCA consists of the steps ‘goal and scope definition’, ‘inventory table assessment’, ‘impact assessment’, and the ‘discussion’ of the results. The results of a LCA are to be compared and discussed with the results of other ways to solve a problem or to produce a same good (e. g. to remediate a property with a different method). In order to compare the results of a LCA of a remediation project it is important, that the level of the decontamination reached by the individual methods is the same. This is the so-called functional unit. An example for a functional unit is the rest-contamination in the soil in mg/kg.

1.1 OBJECTIVES OF THE PROJECT

Only a detailed assessment of redevelopment measures, like the demolishing of buildings or the removal of subsurface contamination, can be the basis for the evaluation of such recycling projects. Their comparison, and optimisation, can thus result in practical guidelines for decision-makers.The objective of the assessment is to determine the environmental impacts caused by site preparation of brownfield redevelopment projects (demolition, subsurface remediation) including energy consumption, emissions and quantities of waste, and land consumption. The evaluation of selected projects leads to transferable results and potential optimisation possibilities under ecological criteria, which form the basis of recommendations for action. Moreover, new remediation techniques should be balanced and compared with conventional techniques. Here, it is important to choose a reasonable system boundary for a project. In many brownfield redevelopment projects it is difficult to say when there is the beginning of the new construction and what should be considered in the balancing to make the LCA under right conditions.

The important energy and material flows from the construction site must be part of the assessment, transportation processes must be considered in the LCA, because these processes have often a significant influence on the LCA results of a project.

1.2 LEGAL CONDITIONS IN GERMANY

The consideration of the environmental impacts of the remediation of sites has been receiving increased attention. This is reflected in the German Federal Soil Protection Act (BBodSchG) and the German Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV). There are different relevant paragraphs in the act and the ordinance: In Annex 3 of the BBodSchV ‘requirements with respect to investigations for remediation and the remediation plan’, the analysis of the ‘impacts on the parties concerned within the meaning of § 12 sentence 1 of the Federal Soil Protection Act and on the environment’ is mentioned.

2 STRATEGY

2.1 DATA COLLECTION

To determine the extent of the secondary impacts on the environment, suitable brownfield redevelopment projects were examined and balanced. The sites were located in southern Germany.

Texts of invitations of tenders, reports, final accounts and records of proper waste management were investigated and analysed in cooperation with consultants and communities. Appropriate assumptions were made for values that could not be determined.

The data was then transferred into the software-tool ‘Environmental balancing of soil remediation measures’ (LFU 1999). Alternative scenarios were developed, also taking alternative remediation ideas discussed during the planning phase of the projects into consideration.

The results of the different scenarios for each site (each project) were compared and discussed from an ecological aspect to identify the process steps with the main ecological impacts and to show ways towards an environmental optimisation of the projects.

Figure 1 gives an overview of the strategy in this research project, of the data collection, and the procedure of the software-tool.

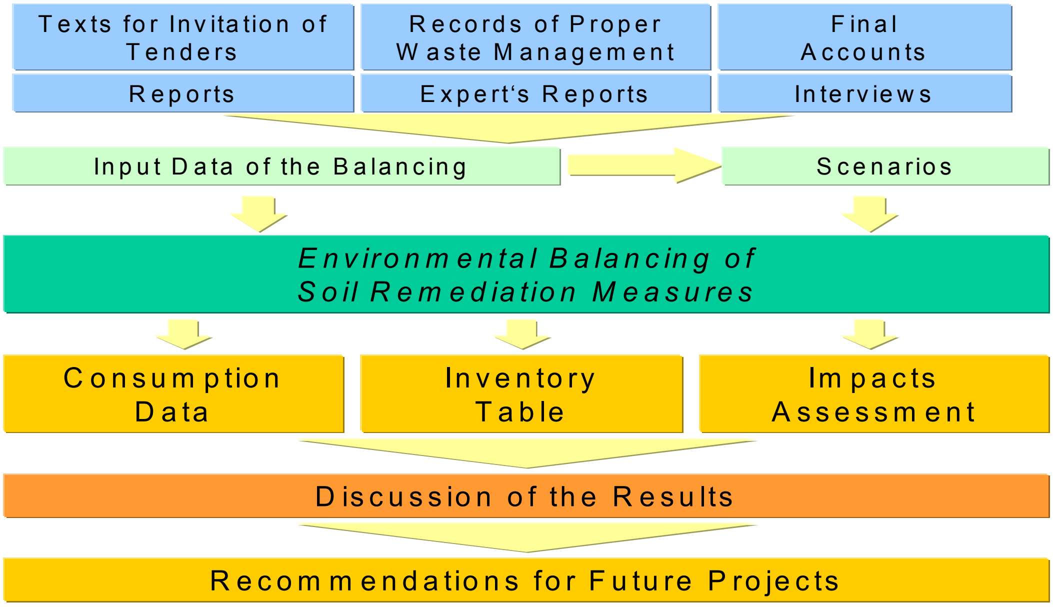

Figure 1: Strategy of the Project

2.2 THE SOFTWARE-TOOL ‘ENVIRONMENTAL BALANCING’

The tool ‘Environmental balancing of soil remediation measures’ (LFU 1999) was developed for the Environmental Protection Agency of the Federal State of Baden-Württemberg, Germany. The program makes a calculation of the secondary impacts of remediation measures on the environment possible by following the methodology of life cycle assessment according to ISO 14040. Its intended use is for remediation preplanning. It has been commercially available since 1999.

Using this tool, it is possible to balance all of the usual remediation measures and the most common construction measures through combinations of 54 so-called ‘modules’ (transportation, soil washing plant, excavation etc.). By linking the input data with a database implemented in the software, consumption data for a project, as well as the life cycle inventories and life cycle impact assessments, are calculated. In the life cycle impact assessment, the potential effects of a project on the environment are measured in different categories, i.e. cumulative energy consumption, waste, consumption of fossil resources, land consumption, greenhouse effect, acidification, summer smog and toxicity. When comparing remediation alternatives in the planning phase of a project, the results are to be compared in the specific impact categories. A description of the software tool can be found in VOLKWEIN et al. (1999).

2.3 PROJECTS

The balancing of brownfield redevelopment projects usually differs from the balancing of pure remediation projects since frequently, as in the case of contaminations with different origins, several remediation techniques are employed on the same site during site preparation.

All balanced projects are characterized e. g. by different commercial, industrial or former military utilization, subsurface contamination, and management of the preparation of the construction site. The following remediation techniques come into operation for subsurface contamination:

- Biological remediation techniques
- Soil washing (stationary/mobile)
- Air-sparging/bio-sparging
- Soil vapour extraction
- Thermal treatment of contaminated soil
- Excavation of contaminated soil, recycling or disposal of the soil
- Hydraulic protection/remediation

In addition, further necessary development activity, such as building demolition, must be taken into account. In practice, these measures are frequently coordinated to take advantage of synergetic effects.

3 RESULTS

3.1 INTRODUCTION

Every examined redevelopment project is characterized by special conditions – it has an individual setting that characterizes it (such as location and size, contamination). As a consequence individual brownfield redevelopment projects - and in particular the subsurface remediation - are only partially comparable. Nevertheless tendencies and general statements emerge from an overview of the evaluated projects.

The objective of the examination is not the ‘easy’ comparison of different remediation techniques. It would be easy to compare isolated techniques, e. g. soil washing and thermal treatment of soil by using different scenarios. In this project real cases were examined and balanced.

The decision for a certain procedure of a recycling of derelict land, e. g. the selection of a remediation technique or a disposal method, is often limited by the timeframe of the investor. He is under economic pressure due to capital charges to begin with the development of his property. As time-consuming remediation can delay the new construction of buildings, such methods are rarely used for redevelopment projects. Also, it is important for an investor to get the guarantee that contaminations are eliminated by the used remediation technique. So established techniques are mainly used.

Surveys in more than 50 communities of Baden-Württemberg indicate that the most common ‘remediation technique’ in brownfield redevelopment projects is to excavate the contaminated soil and either dispose it or use the material for the construction of landfills. This is due to favourable disposal costs, and material requirements for the filling or covering of landfills at present. The soil material rarely undergoes any treatment. In this case, the secondary environmental impacts calculated by the software-tool result from the emissions of construction and transportation measures as well as the land consumption for the landfills.

This procedure ‘dig and dump’ is not the solution of the problem of contaminated soil. It is only a displacement of the problem: You solve the problem at the brownfield site – elimination the danger for men and ground-water – by the transportation of the contaminated soil to a dump to bring the problem under controlled conditions. The ecological right way should be the decontamination.

In-situ remediation measures are rarely used in brownfield redevelopment projects as they delay site development. Another problem is the construction of new buildings during the running of in-situ remediation facilities. However, they are appropriate for cases in which a building is to be used further and an in-situ method is the only way to remediate contaminated soil under a building.

With large brownfield redevelopment projects containing substantial contaminated soil masses, on-site remediation techniques, such as biological treatment of soil, are used. Since these measures eliminate material flows due to transportation to disposal or treatment plants, the main source of environmental impact is the operation of equipment. Off-site treatment possibilities for contaminated soil include biological treatment and soil washing. Depending on the distance, transportation is frequently the largest source of environmental impact. None of the balanced cases required transportation back to the site and a refilling of the cleaned soil material.

Excavated areas on sites are either filled with material from other construction projects or are used for the construction of new buildings. In a few cases, they are refilled with gravel and sand.

At the moment, the used software can only insufficiently balance demolition measures. The use of average databases to calculate the balance of the demolition of buildings is very difficult. Reasons are the individual construction material of houses (concrete, bricks) and the indistinct energy cost of demolishing a building. For a detailed balancing a measurement of the consumption data of the machines, the amount of building debris, and the produced emissions is necessary. Here average data can only give an estimation of the environmental impacts. Often the amount of building debris is known, based on this data it is possible to estimate the fuel consumption of the machine. But with this method the error factor is very high.

Additionally, appropriate data and information, e. g. concerning the whereabouts of the demolition debris, is rarely available. In the example projects analysed, most of the rubble mass was used for landfill construction. Usually, the material is processed in a crushing and screening plant. Different processing methods are thereby used for the different material fractions (wood, scrap iron/metals). Secondary environmental impacts predominantly result from transport processes and, to a certain degree, from the use of construction machinery for demolition and debris processing. Large transport distances arise when a purposeful utilization and disposal of individual material fractions is desired. As a consequence, the transport of the building rubble is often easy to calculate. Here, there is the danger, that the transports become too important because of the available data sets.

In the following, some process steps in brownfield redevelopment projects will be discussed.

3.2 TRANSPORT PROCESSES

The largest portion of the total environmental impact in brownfield redevelopment projects is frequently caused by truck transportation of soil material and construction debris. In numerous brownfield redevelopment projects, transport distances for contaminated soil material and construction debris of greater than 200 km were considered acceptable. The environmental impact caused by transportation was, therefore, usually larger than that of the actual remediation. Figure 2 gives an example of the proportion of the transport processes in the LCA of a project: 12.000 tons of contaminated soil were excavated and transported to a biological treatment plant 450 km from the site.

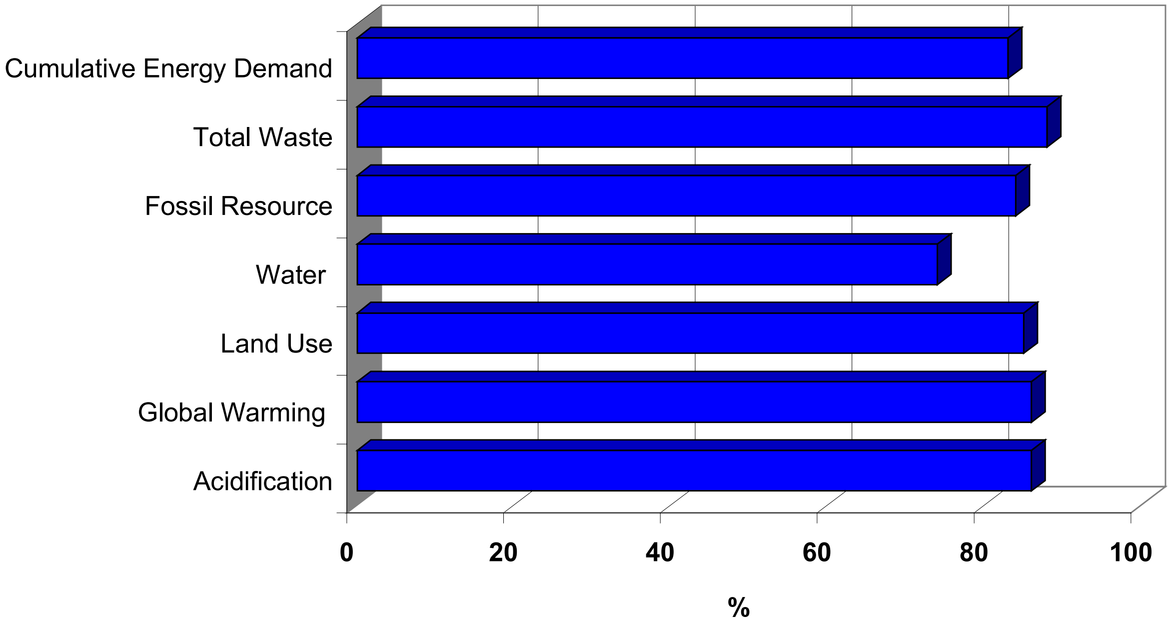

Figure 2: Proportion of the transport processes in the life cycle assessment of a project (Off-site biological treatment of contaminated soil)

One of the reasons for this handling are the available financing resources for a project. The prices for transportation are very low, so one of the main important factors to choose a remediation technique is the price e. g. for the biological treatment of the contaminated soil in an off-site treatment-facility. Sometimes it is the same with landfills that accepted contaminated material for construction works or dumping. Often the distances to the facility or landfills have only a second influence on the decision for the waste management or soil management. In the case of excavation and recycling/disposal of material, the distances to nearby dumps are usually short, so that the impact on the environment through transportation remains small here.

In the balanced projects, transportation by truck dominated, with rare cases of transport by inland ship. In Baden-Württemberg ship transportation is used to bring material to thermal treatment plants in Nordrhein-Westfalen (Herne) or to the Netherlands. The companies for disposal collect material from different remediation projects until they have enough material to charter an inland ship. The transportation procedures by truck are reflected in the result of life cycle assessment for consumption of fossil resources, the typical traffic emissions (acidification, photo oxidant formation, green house effect), by truck traffic, and the utilization of land for traffic infrastructure. These data are calculated in a quantitative way by the generic data generated by Frischknecht et al. (1995), which are in the database of the LfU software tool (LfU 1999).

3.3 ON-SITE AND OFF-SITE REMEDIATION TECHNIQUES

In the case of large brownfield redevelopment sites it is possible to use on-site remediation techniques. The most frequently used techniques are biological treatment or soil washing. These methods are only useable for some type of contaminations (mineral oil). The advantage of this method is the redundancy of long transports to a treatment facility off-site. The excavation of contaminated soil and the running of the plant cause the main environmental impacts. For the running of a biological soil treatment, tents for storage of soil and a machine for rotating the soil and mixing with organic additives are necessary. Sometimes additional equipment is needed. This is reflected in the impact categories fossil resource demand (for fuel for excavators, caterpillars, and dumpers), in some cases nutrients for the biological treatment (energy) or water for the running of a soil washing plant.

In order to compare on-site with off-site treatment facilities it is important to take the transportation of material to the off-site plants into account of the LCA. Figure 3 gives an example of a biological treatment off-site and on-site. The impacts categories are normalized of the result of the on-site treatment, so the results are disfavour-factors of the biological off-site treatment in comparison to the biological on-site treatment.

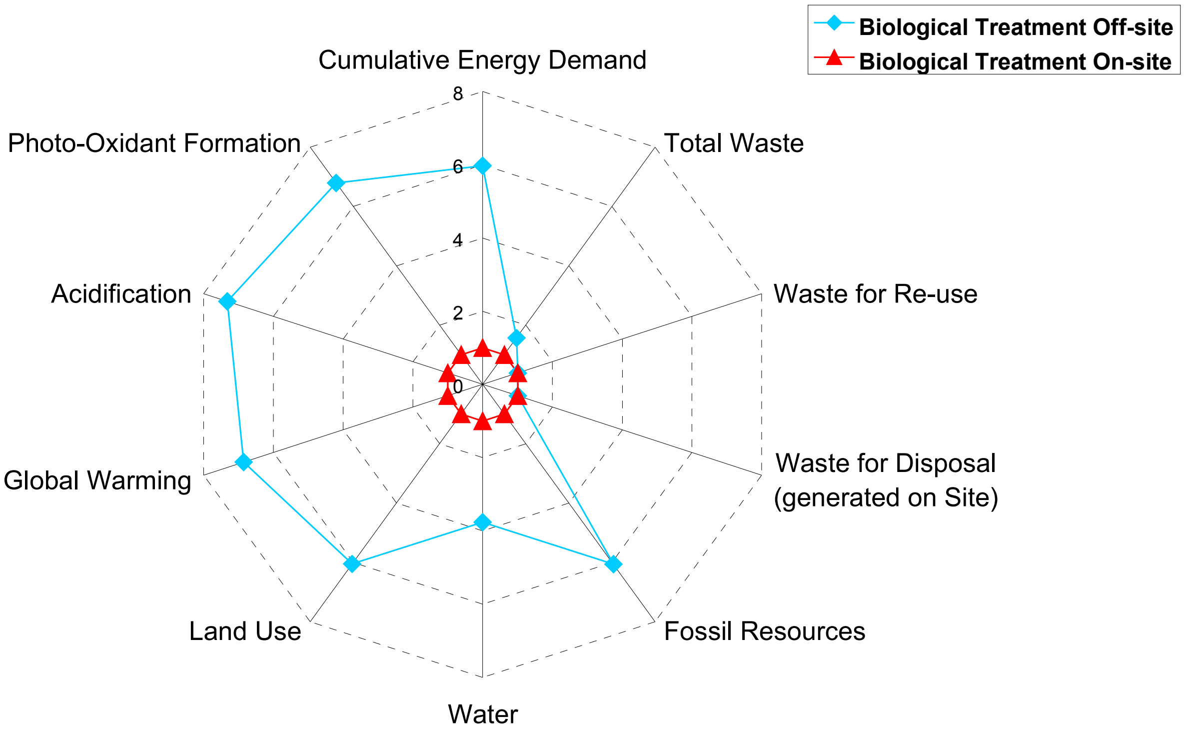

Figure 3: Comparison of on-site and off-site biological treatment of soil (including transportation and construction work) in disfavour-factors, the baseline is the biological treatment on-site (value = 1).

The disadvantage of on-site remediation techniques, in connection with brownfield redevelopment projects, is that this is a time-consuming method. This can cause the reconstruction of a site to be delayed, otherwise the excavated areas must be refilled, either with material from other site, or gravel and sand. This procedure is a source of environmental impacts – caused by transportation and land use due to the mining of sand and gravel.

3.4 OPERATION OF PUMPS AND LATERAL CHANNEL SEALERS

The environmental impact of pumps or lateral channel sealers in hydraulic remediation or soil vapour extraction depends on their running time. A long operating phase results in high cumulative energy demand and corresponding emissions. In this case, power generation is the main source of environmental impact.

With increasing running times the portion of the environmental impact caused by material consumption (pipes, filters), transportation to the plant, and maintenance steadily decreases and reaches values of less than 10 %.

In some cases the remediation targets of a soil vapour extraction for the concentration of volatile organic compounds in the soil air were not reached in the planned time frame. Here the running time for the plant had to be extended or the contaminated area had to be excavated, if possible. As a consequence for long-term remediation projects, such as inefficient soil vapour extraction, the cumulative energy demand of the soil vapour extraction can exceed that of excavation and subsequent disposal of the contaminated material. This is of particular relevance if the transport distances are relatively short.

A LCA of a soil vapour extraction and in comparison the excavation of the contaminated area and the disposal of the soil on a landfill is a possibility to show the ecological consequences of each of the alternatives. The impact categories ‘amount of waste’ and ‘land use’ of the ‘dig and dump’ procedure are significantly higher than the soil vapour extraction. The amount of used energy is a function of the running time of the plant. The result of such a LCA is an example making it possible to set priorities, what are the important categories for an engineer: in this case e. g. land use, waste or energy.

3.5 REFILLING WITH CLEAN SOIL

A consumption of clean gravel and sand as a filling material and/or as a replacement for contaminated soil material can greatly increase the utilization of land and thereby the secondary environmental impact. A land area consumption of between 0,037 m² (GWOSDZ & LORENZ 2000) and 0,18 m² (OLSCHOWY 1993) is specified per ton of sand and gravel that is mined. It is to be noted, however, that gravel pits are recultivated after the utilization phase, and the land consumption only arises for a certain period of time (FRISCHKNECHT et al. 1995).

The mining and processing of other raw materials, such as crude oil and iron ore, result in further land requirements for disposal surfaces and landfills for waste and excavated material.

It is an interesting to consider the question ‘Can brownfield redevelopment projects be considered sustainable upon comparison of the recycled area with the land consumed for its realisation?’

3.6 LIFE CYCLE ASSESSMENT OF INNOVATIVE REMEDIATION METHODS

In the context of this research project, life cycle assessments are provided for remediation methods developed at *VEGAS*, University of Stuttgart. The LCAs of new remediation techniques show the ecological consequences of using new technologies in comparison to conventional techniques.

WEISS (2002) examined the secondary environmental impact of the conventional (‘cold’) soil vapour extraction (SVE) and thermally enhanced soil vapour extraction with steam injection (TSVE) using the LfU software tool (LFU 1999).

The TSVE procedure seems very suitable for brownfield redevelopment due to its ability to remove large pollutant quantities from the subsurface in a short time. Thermally enhanced soil vapour extraction has proven to be far quicker, more effective and even more cost efficient than the cold SVE. However, critics have questioned its suitability due to its huge energy consumption for the heating of contaminated underground regions, resulting in assumedly intense environmental impact. This investigation was laid out to take a close look at the environmental effects of both thermally enhanced and conventional SVE.

The direct comparison of both procedures – the cold SVE and the TSVE - is based on an equal amount of removed contaminant (functional unit). In only 280 days, one of the examined TSVE plants had extracted 1.2 tons of a contaminant (PCE). After approximations of the SVE's based on field data, progression the 'cold' SVE would take at least 660 d for the extraction of an equal quantity of the contaminant. This scenario assumed a constant contaminant concentration in the extracted vapour and thus strongly favours the SVE. In a non-linear manner, the SVE would require 1160 days of operation to extract a similar amount of contaminant as the TSVE's. After approx. 3.8 years (1400 d) of operation, the energy consumption of the conventional system is twice as large as that of the TSVE system and thereby significantly worse. For further information and a detailed description of the methodology and the results see the paper of HIESTER et al. (2003) in this proceedings.

4 CRITICAL ANALYSIS OF THE RESULTS

When applying the software-tool 'Environmental balancing of soil remediation measures' (LFU 1999), it must be noted that the results delivered on the secondary environmental impacts contain inaccuracies caused by the application. These inaccuracies are caused by the use of averaged data, which allow a wide range of applications for the tool. Also, the quality of the generic data is unsatisfactory in those cases where processes are not yet exactly examined and calculated and where numerous assumptions must be made. Therefore, the documentation specifies that a significant difference between two remediation methods is given if the difference in the same impact category is larger than 100 %.

Within the life cycle assessment context, investigations show e.g. that it is difficult to balance the secondary environmental impacts resulting from the operation of construction machines (BUWAL 1996).

5 RECOMMENDATIONS FOR THE RE-USE OF BROWNFIELD PROJECTS UNDER ECOLOGICAL CRITERIA

5.1 OVERVIEW

On the basis of the results, brownfield redevelopment projects can be categorized in four different classes under ecological criteria: Engineers should have a look at the following process steps in the planning phase of a project to minimize environmental impacts:

1, Excavation of the contaminated soil and transportation to a landfill or waste dump:

The excavation, the transportation due of the transportation distance and the land consumption of the landfill cause the main ecological impacts.

→ Important: type of transportation, transportation distance

2, Excavation of the contaminated soil and transportation to soil treatment facility:

The ecological impacts are a question of the transportation distance and the type of remediation or treatment facility.

→ Important: see 1, type of treatment facility, re-use of the cleaned material.

3, Excavation of the contaminated soil and on-site treatment:

The main influences are caused by the construction work and the treatment plant (e.g. soil washing or biological treatment)

→ Important: re-use of the cleaned material, demand for new material for refilling of excavated areas

4, In-situ remediation techniques:

The environmental consequences depend on the running time of the equipment (pumps etc.)

→ Important: Effectiveness of in-situ methods to reach the remediation targets

The following recommendations for action under ecological criteria can be derived:

5.1.1 ADJUSTMENT OF LAND DEVELOPMENT

The adjustment of land development to the conducted treatment is an efficient way of optimising brownfield redevelopment projects under environmental criteria. The excavation created by digging can be effectively used for the construction of new buildings. Another possibility to secure a contaminated area is to seal the contaminated area and use the surface as a parking lot. Excavation and transportation can thus be avoided and/or resulting synergies can be made use of. In many cases this kind of optimisation is done under economic criteria to minimize the costs of the preparation of the construction site.

A use-related remediation is also favourable under the aspect of secondary environmental impact. In Germany, there is a difference if the site is being prepared for industrial versus residential use. The critical boundary values for heavy metals, for example, are higher for an industrial site.

Coordination of future land development must occur in the planning phase of a project. For this, close co-operation between planners/architects and engineers/geologists is important. The coordination of the land development with the remediation can make refilling measures unnecessary, reduce transport distances, and eliminate issues regarding the construction of building foundations.

5.1.2 REDUCING TRANSPORT DISTANCES

Transport distances should be minimized for brownfield redevelopment measures by using close landfills or treatment facilities. Ship or rail transportation performs much better regarding the environmental impact as compared to truck transportation. In some rare cases the use of train transportation was a condition of the awarding authority (communities) – but in time of small financial resource often the cheapest method and the cheapest type of transportation win.

5.1.3 RECYCLING OF CONSTRUCTION MATERIAL

Recycling of construction debris for filling purposes opens the possibility of reducing or eliminating transportation requirements. If building debris is sufficiently free of contamination, it can be used as a filling material. In this context, it should be pointed out that controlled demolition measures could lead to a mass reduction if 'pure' material can be brought back into the material/economic cycle. This is a prerequisite to conserve landfill space and substitute natural material such as sand and gravel through a high debris-recycling rate.

5.1.4 PREFER ON-SITE REMEDIATION TECHNIQUES

In comparison with off-site treatment, on-site remediation techniques (mobile soil washing plants, biological procedures) have proven to be favourable under environmental criteria – especially because transportation can be avoided. A prerequisite for the use of such a system is that space must available at the site (for the system itself and storage of the soil). Furthermore, the factor time is of importance, since such measures can only be used for certain concentrations.

Likewise, reintegration and/or on-site re-use of cleaned soil material should be possible in order to avoid the transportation of materials from other sites.

6 CONCLUSIONS

Brownfield redevelopment can lead to the re-use of land and to the removal of negative environmental impacts (subsurface contaminations, ground-water loads). It is one of the main bases of a sustainable future. A modernization of infrastructure, industry or housing can be possible by recycling of derelict land without continuing deconstruction of agricultural land. However, a redevelopment project also needs and consumes resources, not only energy and raw materials, but land, too. A necessary requirement for brownfield redevelopment projects is that natural resources must be preserved to a large extent and that measures with environment effect as low as possible should be used.

As a consequence, a useful and new evaluation approach for brownfield redevelopment projects is to determine the consumption of land caused by the measurement and the comparison with the area of the recycled site.

As an example it is quite obvious that the direct use of gravel or sand to refill excavation pits resulting from a soil exchange causes an expansion of the gravel or sand pits. This leads to a direct consumption of land. Moreover, the consumption of energy and raw materials make a further land consumption happen. This occurs often in other countries or continents.

An additional land consumption results from landfills and dumps – but this is difficult to bring into account, because most of the material from brownfields are brought to dumps for construction work, surface design or the renaturation of the dumpsite. These forms of consumption are considered partially in the generic data records used (see FRISCHKNECHT et al. 1995). Additional investigations are necessary to develop a clever evaluation system.

A brownfield redevelopment project is only worthy of that term if it does not cause the loss of natural space through the mining of resources, infrastructure or the expansion of landfills.

The investigations so far indicate that brownfield redevelopment projects still possess substantial potential for ecological optimisation. The usual remediation practice (excavation of material/utilization or disposal) must be inspected and optimised under environmental criteria if possible.

In the context of this project, further remediation and brownfield redevelopment projects, as well as new innovative remediation methods will be balanced. This will be the basis for further general results and a simplification of methodology and application of environmental balances.

ACKNOWLEDGEMENTS

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REMEDIATION OF CONTAMINATED URBAN AREAS

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Although Finland is a sparsely populated country, a large part of the population is concentrated in big cities in southern Finland. Changing land use is one of the major challenges facing urban planners in these areas. The industrial structure has changed and the industries have moved outside the cities. New commercial activities and residential areas are planned in former industrial areas. In planning of the land use changes, suspected or actual contamination of the soil has been one of the most common problems.

The poster presents the findings of a project, the aim of which was to give recommendations on how the special qualities of densely populated urban areas and the characteristics of the activities planned for these areas should be taken into consideration in the risk management of suspected contamination. The basis for the development of remediation goals for various land use scenarios and the uncertainties of land use based risk management are discussed in the project report. Practical guidance on the use of various constructional and institutional measures for risk management has also been produced. Information is presented on technical solutions that are either already in use or feasible in the future.

Co-ordination of spatial and urban planning aspects with the contaminated land management process is also dealt with. Recommendations are given about how the investigations and risk assessment of the site should be linked with the strategic and detailed planning process to identify the most appropriate after-use for the site. The most feasible constructional and institutional control measures should be identified during this process. Community participation is an essential part of the planning process. The risk is not merely a scientific question. Especially in residential areas, the psychological aspects of land contamination influence the selection of risk management measures.

Environmental conditions and sources of contamination in urban areas

Anthropogenic influence is clearly visible in the chemical and geological quality of soil as well as surface and groundwaters in urban areas. Most of the big cities are situated on the coast, where surplus material from construction and industrial activities has been used for filling to make construction possible. Many of these filled areas were previously in harbour or industrial use. The changes of land use have raised the problem of contaminated fill materials. Such contamination may be varied and point-specific and it may extend to a depth of several metres. The retention capacity of this material is highly variable. There may also be additional contamination due to the former activities in the area. Major sources include oil, gasoline and chemical storage, shipbuilding, various mechanical engineering industries, car repair shops, service stations and former landfills (Table 1). Heavy metals, PAHs, PCB and oil/gasoline hydrocarbons are the most common contaminants found.

In addition to local pollution, background levels of lead, mercury and PCB, in particular, are also elevated in the organic surface layer of urbanised areas and may be above guideline values. They are mostly distributed from industrial, energy and traffic sources by atmospheric fallout.

Table 1. *Typical former activities and common contaminants in urban areas to be redeveloped.*

Former use of the area	***Former activities or sources of contamination***	***Additional activities***	***To be noted***	***Typical contaminants***
Ports and other shore areas	Oil, fuel and chemical storage Dock industries Shipbuilding	Other industrial activities Landfills Energy production	May be filled with waste materials	Heavy metals Oil components In places other contaminants
Industrial areas	Metal industries and machine shops Scrap-yards Car repair shops	Food industry Gasworks Chemical storage (small scale)	Usually mixed contamination, heterogeneous	Metals, oils, PAH
Filling stations	Leaking tanks, overfilling		Usually minor sites, risk of groundwater contamination	Oil and gasoline compounds (including BTEX, MTBE)
Old landfills	Disposal of industrial and municipal waste		Variable contaminants	Heavy metals, oils, solvents, cyanides, PAH, PCB
PCB-contaminated areas	Jointing mastics of prefabricated structures		Surroundings of apartment houses	PCB
Other sites	Shooting ranges Traffic depots Waste water treatment plants			Pb, As, Sb, Cu, Ni Oils, metals

Major cities are situated in close proximity to water systems, either on the seaside or in lake districts. Some of them are also in groundwater areas. This means that the risk of surface or groundwater contamination always has to be taken into consideration. In addition, the quality of soil and groundwater conditions are highly variable in Finland. Therefore, adequate site-specific investigations and assessment of the significance of soil and groundwater conditions for risk are essential. In filled seaside areas, the leaching of contaminants by water flushing, and eventual geotechnical problems, such as soil subsidence, have to be considered. Layers of perched water are common in developed areas. This water may leach contaminants and transport them to surface or groundwaters.

Urban development affects the hydrological cycle, for example by reducing water percolation and by increasing surface runoff. Especially in city centres, many areas are covered by asphalt and surface drained. The decrease of percolated water may cause a lowering of the groundwater table. On the other hand, constructions such as piping channels and roads offer new routes for water flow.

Consideration of land use and chemical properties of contaminants in remedial actions

Until recent years, the remediation goals in urban and countryside areas have been based on soil target and limit values presented by the Finnish Environment Institute and Ministry of Environment in 1994. The number of site-specific risk assessments has, however, clearly increased during the last few years. Several internationally available human risk assessment and transport models are used. There are no common guidelines or recommendations on the use of these models. This is somewhat a problem for environmental authorities in the permit consideration process, because judgment of the reliability of risk assessments requires wide experience of different models and their basic assumptions. In several cases, the final decision has been to use guide values instead of suggested risk-based remediation goals because there was no satisfactory proof about the reliability of risk assessment.

If remediation goals are strict the high amounts of soil which have to be treated or disposed of may become a problem. The utilisation of weakly contaminated soil is nowadays highly limited by its waste character. This is mostly based on the fact that there is always some uncertainty about the existence of unidentified contamination. In most cases, removed soil masses are landfilled. In urban areas this means long transport distances, increased use of fuel and increased traffic emissions. In addition, landfill space is more and more limited.

Although there are no land use based soil target values in use in Finland, it is commonly acknowledged that the future land use is one of the key determinants of exposure. The exposure routes in paved commercial and office areas clearly differ from the natural conditions that are the basis of general guide values. In densely constructed areas, most of the land surface is covered by asphalt paving and other constructions, which limit the exposure of human beings and also of most ecological subjects. In addition, habitats in these areas have adapted to urban conditions.

The potential of human and ecological subjects to be exposed to soil contaminants depends strongly on the mobility and volatility of the compounds in question. In paved areas the risk to human beings of coming into contact with immobile and non-volatile contaminants is quite low. As regards ecological impacts, the most important question is what the significance is of ecological functioning of soil in paved urban or industrial areas.

Based on mobility and volatility, the most common contaminants may be grouped into three main groups. The impacts of land use to exposure potential can most easily be predicted for immobile compounds.

Table 2. *Mobility and volatility of the most common contaminants* .

Contaminant group		***Worth noticing***
Group 1: Most immobile contaminants		
Heavy metals		Hg is volatile and mobile
Non-volatile, sparingly soluble organic compounds	PAH	Following compounds may be soluble and semi-volatile: Naphthalene (solubility 32 mg/l) Phenantrene (solubility 1 mg/l)
	PCB	Monochlorinated PCBs slightly soluble and volatile (solubility of monochlorinated biphenyl 1.2 – 5.5 mg/l) Subject to protocol on persistent organic compounds (Aarhus 1998)
	Heavy oil fractions (heavy fuel oil, lubricants)	C22-C39, Boiling point > 380 – 480 ^{0}C
Group 2 . Slightly soluble and mobile contaminants		
	Diesel and heavy oil fractions, As	Diesel and heavy oil fractions are retained by dry and humid soil, not retained by wet soil, may be long term risk Depending on the speciation As may be mobile and form a risk to ground water. Because of toxicity a special consideration is required.
Group 3. Soluble and mobile contaminants		
	Chlorinated aliphatic compounds, gasoline fractions (BTEX, MTBE), chlorinated phenols	Remediation goals based on target values or site-specific risk assessment

Human beings are not normally exposed to immobile contaminants, such as heavy metals, when the soil is covered by asphalt. However, no contaminant is totally immobile. The mobility is dependent on conditions; soil quality (pH, redox, sorption capacity), amount of water available, speciation of the compound, etc. There may be some unexpected exposure situations, which include:

- transport of soil, e.g. in connection of excavation work to locations, where people and organisms can be directly exposed to contaminants

- increased leaching and transport of contaminants by flushing of soil due to variable water table at seaside areas
- transport of contaminants to ground or surface water through the routes made by constructions or tree roots
- increased water percolation through holes and fractures in paving.

In addition to assessment of health risks and potential transport of compounds the acceptance of risk-based remediation values is an important issue. In urban areas one has also to consider the potential risks to constructions, such as:

- corrosion of concrete in presence of sulphate
- corrosion of metals when e.g. coal fly ash is present or in abnormal pH conditions
- diffusion of chlorinated and aromatic hydrocarbons through polymeric materials.

Role of constructive measures and other protective measures in risk management

In moderately contaminated areas, the least complex protective measure against non-volatile and slightly mobile contaminants is to use pure soil cover on contaminated areas. The required depth of non-contaminated soil layer must be assessed on the basis of the activities in area. It is recommended to change the contaminated soil to a depth where people, plants or ecological subjects do not commonly come into contact with contaminants. For example:

- most plant roots extend to 50 – 150 cm from the surface, lawn 20 – 30 cm from surface
- children may reach to 30 – 40 cm when playing
- pipe tunnels may reach to 200 – 250 cm.

Covering of soil using asphalt, slabs, flagstones, etc also prevents exposure of people and domestic animals to non-volatile contaminants. In addition to direct contact, the spreading of hazardous compounds by wind as well as leaching of the contaminants by percolated water are significantly prevented. If a cover is used as a protective measure, there must be a special inspection and maintenance schedule to ensure its suitable condition.

In moderately contaminated sites, vegetation, such as thick lawn or thick bushes that prevent access to the contaminated area, may be used as protective measure. Most appropriate are undemanding species which are well adapted to local conditions. Harm to the ecosystem is minimised if animals do not favour the use of the plant as nutrition.

Impermeable liners are suitable if there is no need for earth mowing or excavation. If there is a risk of soil subsidence it must be taken into consideration in constructional design. Potential liner materials include bentonite sheet, HDPE –coating, and various combinations of mineral and polymer materials.

When building on contaminated sites, the most significant issues to be considered include:

- protection of building materials from the hazards caused by contaminants either by using materials, which are not sensitive to contaminants; by substituting the most contaminated soil with pure soil or by paying attention to the drying of building ground.
- protection of residents from exposure to contaminants. The most significant risk is transport of volatile compounds inside the building. This can be minimised by using airtight constructions and by using negative ventilating pressure in the foundations.

SEDIMENT DYNAMICS AND POLLUTANT MOBILITY IN RIVERS – INTERDISCIPLINARY APPROACH

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Introduction

The disastrous flood events in summer 2002 on the rivers Elbe and Donau and several of their tributaries revealed the lack of conceptual models for prediction of sediment erosion and transport as well as the mobility and final spatial distribution of sediment associated pollutants. The reason has to be seen in the fact that understanding of coupled hydrodynamic-hydrogeochemical-biological processes is still poor. The co-ordinated research project SEDYMO (Sediment Dynamic and Pollutant Mobility in Rivers) integrates 18 sub-projects in 3 priority research areas to create substantial knowledge for an integrated sediment quality assessment.

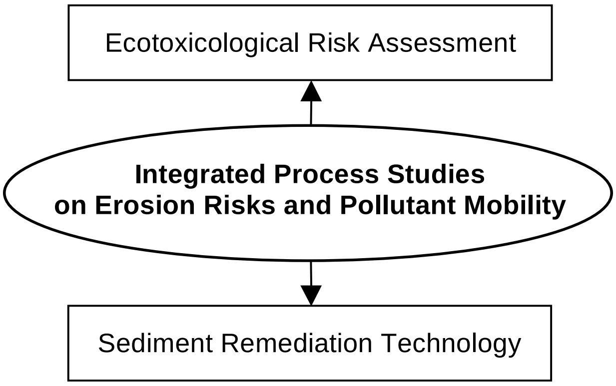

Figure 1: The position of integrated process studies between ecotoxicological risk assessment and remediation technologies in the management of aquatic sediments and dredged materials

1. Managing Contaminated Sediments – Integrated Process Studies

Both for establishing sediment-related quality objectives and for developing and implementing technical problem solutions a set of practical process knowledge is needed that uses a wide range of simulation techniques as well as models in different spatial and temporal scales. In practice, specific information on interacting hydro-mechanical, biological and geochemical processes will be required for two reasons:

1) Sediment quality assessment is considerably more complex than water quality assessment due to the many site specific parameters that need to be considered which are not a factor for water. Bio-availability of a contaminant is not only species specific, but also depends on sediment

characteristics and sediment deposition and erosion. The methodologies developed to date do not adequately deal with the complex nature of sediments.

2) Remediation techniques for contaminated sediments are generally more limited than for other solid waste materials. Considering the worldwide dredging activities only a very small percentage of these materials can undergo “treatment“ in the closer sense – solvent extraction, bio-remediation, thermal desorption, etc. Here, geochemical mechanisms such as stabilization and other forms of long-term, self-containing barriers could reduce the mobility and biological availability of critical pollutants.

2. Evaluating Erosion Risks and Pollutants Mobility in River Sediments

Due to their particular dynamics, three characteristic features of sedimentary and erosive processes in rivers should receive special attention:

- The dramatic effects of stormwater events on particle transport,
- the rapid and far-reaching effects of sulfide oxidation during resuspension, and
- the biological accumulation and potential release of toxic elements.

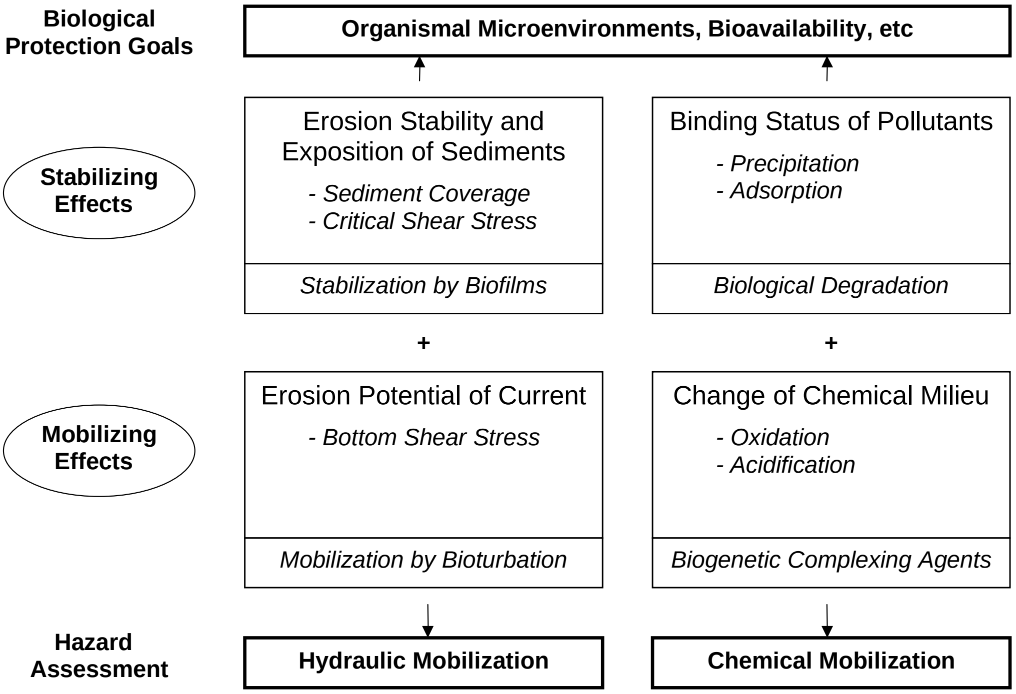

Figure 2: Stabilizing and mobilizing effects on pollutants of river sediments

Using model calculations the hazard potential arising from resuspension of contaminated sediments can be estimated from the product of hydraulic mobilization and chemical mobilization (Figure 2). Mobility is then the net result from stabilizing and mobilizing effects in both sectors. For example, hydraulic mobility can be assessed by measuring sediment coverage, critical shear stress and actual bottom shear stress. Geochemical mobility, e.g. for heavy metals, can be estimated from solubility and desorption data, but changes of the chemical milieu may strongly influence these data. For heavy metals, acidity plays a dominant role, and protons may be produced from the oxidation of metal sulfides.

Future development of process studies and models urgently requires the inclusion of biological information. Boxes with solid lines in Figure 2 indicate typical examples for biological implications both for stabilizing and mobilizing sediments and their associated pollutants. Biofilms, for example, will stabilize sediment deposits mechanically. However, some of their exo-polymers may become effective as complexing agents for mobilization of heavy metals. With regard to organic pollutants, biological degradation can be considered as a stabilizing effect, when degradation reaches its completion. However, it is possible that metabolic reactions will produce more mobile and more toxic intermediates than is the original pollutant.

3. Sediment Dynamics and Pollutant Mobility – An Interdisciplinary Approach

An interdisciplinary approach to the release of dissolved organic carbon (DOC), nutrients and pollutants into the open water has been derived from evaluation of the international state-of-the-art technology with three major themes: “experimental techniques“, “processes and properties“ and “development and validation of models“ (Figure 3). Special study targets are the formation of aggregates in turbulent water, flocs and biofilms from organic reactions, and formation of new surfaces for re-adsorption of dissolved pollutants. Of greatest importance is the degradation of organic matter, which affects both hydrodynamic processes – erosion vs. sedimentation – and geo-chemical redox cycles providing driving forces, e.g. for metal mobilization.

On the basis of this concept, a proposal for an interdisciplinary research project on sediment processes was initiated by the Senate Commission of Water Research, German Science Foundation (DFG). During discussions concerned with the new EU water directive and with sediment removal by hydraulic dredging – a highly controversial issue on a national level – the theme of interacting sediment processes included more practical aspects. The coordinated program - comprising 18 subprojects, is now funded by the Federal Ministry of Education and Research (BMBF); the first seven subprojects (Nos. 1/13, 2, 3, 5, 14, 18b in Figure 3) and the coordinating project (Prof. U. Förstner, Dept. of Environmental Science and Technology at the Technical University of Hamburg-Harburg) started in May 2002. Sampling campaigns have been conducted on water and sediments from summer 2003 and experiments are currently undertaken regarding erosion stability of sediments.

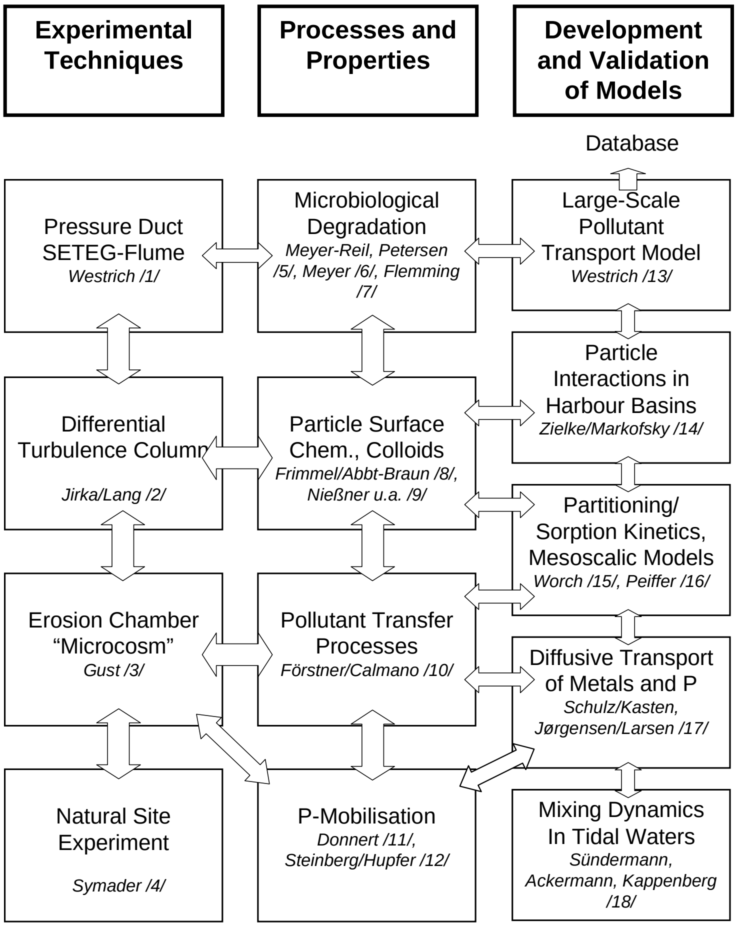

Figure 3: Structure of SEDYMO program. In total 18 sub-projects will be involved in the coordinated research project 2002-2006

<u>Project participants by project number:</u>

(1) Institute of Hydraulic Engineering, Hydraulic Laboratory, Univ. of Stuttgart
(2) Institute for Hydromechanics, University of Karlsruhe
(3) Dept. of Ocean Engineering, Technical University of Hamburg-Harburg
(4) Dept. of Hydrology, University of Trier
(5) Institute of Ecology, University of Greifswald
(6) Dept. of Limnology, University of Münster
(7) Dept. of Aquatic Microbiology, University of Duisburg
(8) Engler-Bunte-Institut, Department of Chemical and Process Engineering, Water Chemistry Section, University of Karlsruhe
(9) Dept. of Hydrogeology, Hydrochemistry and Environmental Analytical Chemistry, Technical University of München
(10) Dept. of Environmental Science and Technology, Technical University of Hamburg-Harburg and Institute for Coastal Research, GKSS-Research Centre Geesthacht
(11) Institute of Freshwater Ecology and Inland Fisheries, Berlin
(12) Institute for Technical Chemistry, Section of Water and Geotechnology, Research Centre Karlsruhe,
(13) Institute of Hydraulic Engineering, Hydraulic Laboratory, Univ. of Stuttgart
(14) Institute for Fluid Mechanics and Computer Applications in Civil Engineering, University of Hannover
(15) Institute for Water Chemistry and Chemical Water Technology, Technical University of Dresden
(16) Institute of Hydrogeology, RWTH Aachen
(17) Dept. of Geochemistry and Hydrogeology, University of Bremen and Max-Planck-Institute for Marine Mikrobiology, Bremen
(18) Institute for Oceanography, University of Hamburg and German Federal Institute of Hydrology, Koblenz and GKSS Research Centre, Geesthacht

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TUNNEL CONSTRUCTION AND SOIL QUALITY MANAGEMENT

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Introduction

Several bored tunnels are being constructed in the Netherlands as part of the development of new road and railway infrastructure.
Such tunnel projects involve important aspects with regard to soil management, especially in relation to environmental conditions.
Along the route of the Betuweroute Railway there are two bored tunnels: the Sophia tunnel near Rotterdam and the tunnel passing underneath the Pannerdensch Kanaal, near the German border. There is the tunnel being constructed underneath the Westerschelde, built to improve road transport from Rotterdam harbor to Antwerpen. This tunnel is over 6 kilometers long and reaches a maximum depth of 60 meters below the surface. The Groene Hart tunnel, part of the high speed railway from Amsterdam to Paris is worth mentioning, because it is excavated by world's largest tunnel boring machine (TBM), forming a single-tube tunnel. The TBM has a diameter from almost 15 meters and will bore its way through more than 7 kilometers of soil (sand).

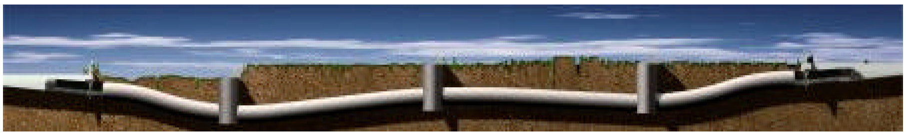

Figure 1: Cross section Groene Hart tunnel

The technique and design method used for a bored tunnel depends, amongst others, on the structure of the soil (soft ground or rocky ground), the length and depth and the requirements for the final construction (for example the speed with which a train should be able to pass through the tunnel). Two techniques are well known:

- Slurry shield
- Earth pressure balanced shield

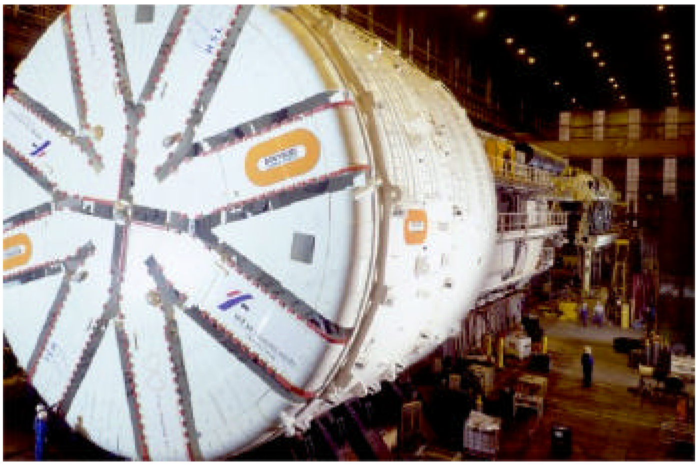

Figure 2: Tunnel boring machine Groene Hart, slurry shield method

When constructing a bored tunnel, there are several aspects regarding soil management to take into account. These concern both geophysical (such as settlement and upwards pressure of groundwater) and geochemical (such as handling contaminated soil) aspects. Other points for consideration are objects with historical value, explosives, transactions, durability and logistics.

This poster shows the environmental and logistic aspects of soil management during the process of constructing a tunnel. It is based on the experiences in the Netherlands, but also relevant for the rest of Europe, because of the ongoing development of legislation on environment. Also the pressure on free space is ongoing, resulting in more and more building activities below the ground level.

Process

From the outset, when preparing the preliminary design, until the completion of the construction of the tunnel, the project deals with soil management aspects. Both the client and the contractor have to deal with the soil related aspects from tunnel boring. Compared to other infrastructure projects and sunken tunnels, bored tunnels have some special features:

- ensuring the ground level is left intact
- lowering the groundwater level, possibly causing settlements
- additives which are applied in the process
- handling the logistic aspects of the excavated soil (like storage and removal)
- handling the waste materials

To protect the soil from becoming contaminated, the tunnel has to be constructed with materials that do not have a negative effect on the soil (or other aspects of the environment, for example water). Additives that are applied during the process such as bentonite and polymers require special attention. National and regional acts dictate the majority of relevant conditions.

Excavated soil can be reused in other construction operations. The type of soil (sand, clay, peat), the civil engineering quality, the properties of the materials and the environmental quality are important factors for this. (In the Netherlands the Building Materials Decree (1999) dictates the conditions for using and re-using stony building materials, including soil. Also the Exemption facility in respect of soil moving dictates some conditions for re-using soil. Although both regulations are national, especially the latter can cause regional differences, which makes it complex to comply with these regulations and conditions.) Prior to the start of the project, insight into the environmental quality of the excavated soil and possible contamination can be gained by soil surveys. However, the tunnel boring process can alter this original quality of the soil. Additives such as bentonite may be added to the soil before excavating. The excavated slurry therefore has to be treated to make the soil reusable. While treating the slurry, granulates, bentonite and water are separated from the soil.

Reuse

After treatment, the water can be reused in the process. The excavated soil and the bentonite can be reused in other construction operations. Therefore both the environmental and civil engineering quality have to meet the requirements of the intended use. Thus these requirements have to be clear to make sure they can be complied with. Examples are the content of water and bentonite in sand, the size of the granules and the content of pollutants. These pollutants may originate from the original soil of from additives like polymers, used in the separation process.

Logistics

Besides the quality of the excavated and treated soil, the storage of the soil can be a 'bottleneck'. In tunnel boring projects such as the Groene Hart, a volume of 1,250,000m^3 soil will be produced over two and a half years. This cannot be stored entirely before reusing.
In advance of the production of the reusable soil therefore it is necessary to know its destination (besides the required quality). The time at which the soil is produced and the time at which it is required for re-use therefore requires careful consideration and co-ordination. At the building site, where the soil is produced, storage is needed, because the soil will not be removed constantly. The volume of this storage depends on the speed of the boring process, the production of the separation plant, the volume and frequency of removal of the soil and the progress of the destination construction.

Clearly it needs a high level logistical control to prevent the formation of a stockpile of over one million cubic meters of soil.

Figure 3: Storage of excavated soil

COB

In 1994 the COB was esthablished in the Netherlands. This 'Center for Underground Constructions' is a public-private partnership that studies relevant aspects concerning the use of space underground. The main activities of the COB after formation were to decrease the lack of knowledge on this subject, especially regarding bored tunnels in soft ground, by large scaled research. Nowadays the focus is on deepening and broadening the knowledge network.
In the second half of 2002 the COB completed a study on environmental legislation and the reuse of soil arising from bored tunnels. Two handbooks were produced, called 'Environmental Policy and Legislation for Bored Tunnels' and ‘Reuse of Soil in Bored Tunnel Projects’.
Royal Haskoning is one of the participants of COB.

Figure 4: Depiction of the Groene Hart tunnel

Figure 5: Insight of the Westerscheldetunnel

PROBLEMS AND CHARACTERIZATION OF A POLLUTED SOILS IN A SUBURBAN INDUSTRIAL AREA OF SE SPAIN

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Introduction

The inhabitant's health, as well the vegetation and soil around industrial areas placed close to cities, are clearly influenced by the industrial pollution. An industrial area of chemical production near the town of Cartagena (SE Spain) has been working for last 50 years. Soil pollution and its problems have been evaluated.

These former industrial lands are now being included into urban areas. Besides, these industries are incorporating new technologies and most of them are being relocated in new industrial areas outside the city. This situation, joint to the demographic and urban growth, is generating some problems such as the transformation of these soils in urban areas. Therefore, and first of all, this soil reusing should solve great inconvenient such as the restoration and reduction of the high pollution levels.

Consequently, a lot of soils should be restored before their reusing for urban purposes. Therefore, characterization studies related with these environmental problems are actually being carried out prior to any reclamation program based on techniques such as thermal desorption (Anderson, 1993; EPA, 1994), air stripping (McDevitt *et al.*, 1986; EPA. 1991), or even bio and phytoremediation (Meagher, 2000).

Materials and Methods

Since March 2001 up to date, a systematic sampling program has been developed for characterization of these for polluted areas. So, natural soils, industrial waste ponds, industrial waste spills and a “rambla” bed through the study area have been sampled.

This industrial area is placed close to Cartagena city (SE of Spain; 20 m a.s.l.; 37° 36´52´´ N, 0° 58´07´´ W). It is a termomediterranean region with temperature averages 18 °C throughout the year and annual precipitations that ranges from 200 mm to 300 mm.

Superficial soil samples (0-30 cm) were sampled, air-dried, ground through a 2 mm sieve, homogenized and stored until analysis. A scanning electron microscope (HITACHI S-3500N Scanning Electron Microscope) equipped with energy dispersive X-ray microanalyser (SEM/EDX) has been used to obtain an overview of all elements content in polluted soils and sediments. Fine ground soil samples have been dried at 65 ^{o}C for 72 h and weighed 0.2-0.5 g per sample before its examination and analysis in the SEM. Each sample has been thoroughly compacted with a mechanical pressure press up to getting a polished sample disc. Finally, each specimen has been mounted on specimen stub with sticky tape, establishing a good electrical contact by running a track of conductive paint from the specimen to the stub and coated with a conductive paint such as colloidal graphite (Lyman *et al.*, 1990).

Extraction of representative bioavailable heavy metals (Fe, Cu, Zn and Mn) in the selected soil samples was determined by a DTPA extraction solution (Lindsay and Norvell, 1978). These extraction reagents included 0.005 M DTPA, 0.01 N Cl2Ca, 0.1 M triethanolamine -pH = 7.3- and distilled water. The extraction solutions were filtered with an Albet Nº 242 filter paper. Total concentrations of lead in soils were determined by digestion in extractant solution for 2 h. Final concentrations of heavy metals in the solution have been done by flame AAS method -atomic absorption spectrophotometer- (UNICAM 969 AA spectrometer) with a hollow cathode lamp of lead.

Besides, speciation and phase research is actually being developing, using for that X-Ray Diffraction techniques (Bruker, 8 Advance).

Results and Discussion

Prior to soil transformation, all these lands and sediments must be remediated, and their contamination level should be minimized.

Up to date there are not studies about characterization of these industrial soils and sediments. Nevertheless, preliminary studies have been undertaken previously (Faz *et al.*, 2001). Elements such as Ca, Na, Mg, Al, P, S, Cl, K, Fe, Zn, As and Ti have been found in these previous studies. Nevertheless, most of the results are being actually generated.

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Contamination and Electrokinetic Remediation of Copper Mine Tailing and Soil

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The heavy metal contamination from mining industry has become a growing problem both in Chile and worldwide. This contamination includes large areas with soil pollution, contaminated rivers and continuous generation of mining waste deposits.

In this work the problems caused by the pollution from copper mining is highlighted. Soil surrounding a copper mine in the central part of Chile, contaminated with different heavy metals, is analysed together with solid waste from mining industry either as directly produced waste or as deposited waste. The solid waste that will mainly be analysed in this project is the so-called mine tailings, which are the residual products after the flotation process in conventional copper mining. These are known to contain considerable amounts of different heavy metals (Benvenuti et al., 1997). Today the mine tailings are deposited directly on soil close to the mine itself without any controlled pretreatment or ground and surface water protection.

The first part of this work considers the sampling and analysis different waste products and soil. These samples are analysed in the laboratory for metal content, metal speciation and distribution of metals between the liquid and the solid phase. Furthermore, determination of other relevant physical/chemical parameters of the soil/solid waste are carried out – such as electrical and hydraulical conductivity of the solids, particle size distribution, content of organic matter, carbonates and oxides, and the metal desorption as a function of pH. The results will be presented. Leaching experiments with water, salt solutions, acidic solutions and solutions containing selected microorganisms that oxidize CuS or complexing agents in order to evaluate if an addition of reagents optimize the desorption of the metals.

The second part consists of series of electrochemical remediation experiments using an electric field as remediation agent (Lageman et al., 1989) in order to remove/concentrate heavy metals (specially copper) in a way that minimises the volume of contaminated matter significantly. During the experiments several parameters are monitored such as current density, voltage drop, pH in the soil/waste, metal mobility and removal rate. Adjustable parameters are current density, water content, distance between electrodes and remediation time. Furthermore, the remediation process can be optimised with the use of ion exchange membranes (Hansen et al., 1999), which also is included in the experimental part of this project. Other parameters that will be discussed in this project are: the use of pulsed direct current, addition of CuS and CuO dissolving microorganisms or other additives/complexing agents, and use of different electrolyte solutions.

It was found that electrochemical remediation of mine tailings and soil contaminated from mining industry could be an alternative to depositing the waste. To positive aspects are generated by this remediation technology: 1) an environmental friendly soild waste without elevated concentrations of metals, and 2) a profit consisting of dissolved copper that can be used directly in the copper refinery proces meaning that natural copper containing minerals can be saved.

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EFFECTS OF DIFFERENT PH AND REDOX CONDITIONS ON MOBILITY OF ARSENIC IN A TAILING MATERIAL

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Introduction

In mining areas, residues of mineral processing are deposited as waste dump or tailings. These mining site materials are often polluted with arsenic (As) and heavy metals. Due to internal dissolution and exposure to the weather microbial and abiotic oxidation processes begin and the oxidation state of arsenic, metals and sulphur change. As a result the material turns acidic and the contaminants can be easily mobilized [HIRNER ET AL. 2000]. These materials therefore act as a source of contaminants, which may pollute especially ground and surface waters.

Important factors controlling the mobility of As in the source material include the pH value, redox conditions and the characteristics of the source material [MASSCHELEYN ET AL 1991, IRGOLIC 1994, BERGFELDT 1995, HIRNER ET AL. 2000, HAURY 2001]. Although of great environmental importance, little is known about the role of pH-redox conditions in the mobility and speciation of As in mine waste materials. Moreover, there are disagreements in the literature data.

The aim of this study is to clarify the effects of different pH and redox conditions on the mobility and speciation of As by using a tailing waste from former tin-ore processing in Gottesberg (Erzgebirge, Germany). These flotation residues (approx. 400,000 t) are poor in sulphur compounds but highly polluted by As. The As concentration in the solid ranges from 500-1,500 mg/kg, and As is released into the ground and surface waters in concentrations up to 1 mg/l.

Experimental

The tailing samples used for the study contained approx. 700 mg/kg As; 2,600 mg/kg Sn; 250 mg/kg Cu; other heavy metals in lower concentrations; the total S was approx. 200 mg/kg.

To rule out any transport limitations, leaching tests were performed in suspension. For the experiments 'microcosms' were used. These are temperable stirred reactors with extensive measuring and automatic control systems, allowing the pH, redox potential and temperature to be continuously recorded. Each microcosm contained 200 g tailing material and 2,000 ml water.

The test programme comprised series at 4 different pH ranges (acidic, neutral, weakly alkaline, strongly alkaline) each under aerobic conditions (aeration) and in an anaerobic state (nitrogen atmosphere). The acidic range was regulated to pH 3 by alternating addition of sulphuric acid and sodium hydroxide solution. The tailing material was investigated under neutral conditions without additives. The weakly alkaline conditions were realized by adding 5 % $CaCO_3$ related to the solid quantity. To obtain strongly alkaline conditions 4 % $Ca(OH)_2$ related to the solid quantity was mixed into the suspension. The leaching times were 21, 28 and 35 days, respectively.

Suspension samples were taken out of the reactor at intervals of 2 or 3 days. The samples were separated by centrifugation resp. filtration, stabilized with phosphorous acid and refrigerated, or alternatively stored at 4 °C without stabilization until analysis. The concentrations of total arsenic in the aqueous phase were determined by ICP-AES with a Spectroflame (Spectro Inc.) in accordance with German DIN 38422-E22. Speciation analysis of dissolved As was performed by coupling ion chromatographic separation with inductively coupled mass spectrometry (IC-ICP-MS). Using elution by a nitric acid gradient and an anion exchange column, the arsenic species can be separated within a few minutes and sensitively detected at m/z 75. The recorded data were analysed using the ORIGIN® software package.

Results

Table 1 summarizes the solubilities of total As, As(III) and As(V) under the conditions tested. It should be noted that differences between the results of IC-ICP-MS and ICP-AES may be caused by the different sensitivities of the analysis methods; this particularly concerns the As(III) species detected with ICP-AES. The solubilization kinetics of As (calculated as solubility in mg/kg solid) during the leaching of the tailing material under aerobic and anaerobic conditions are shown in Figs. 1 and 2.

Table 1. Solubility of total As (ICP-AES), As(III) and As(V) (IC-ICP-MS) related to the solid during suspension leaching of the tailing material under different surrounding conditions

Surrounding conditions		Leaching time [d]	pH	Eh [mV]	total As [mg/kg]	As(III) [mg/kg]	As(V) [mg/kg]
Acidic	Aerobic	35	3.0	725	63	82	0.0
	Anaerobic	21	3.0	545	26	24.5	3.9
Neutral	Aerobic	21	6.9	480	6	0.2	6.3
	Anaerobic	21	7.5	100	12	0.1	8.7
Weakly alkaline	Aerobic	21	8.1	440	8	0.1	6.9
	Anaerobic	28	9.5	100	25	0.0	23.8
Strongly alkaline	Aerobic	21	13.3	200	< 0.8	0.0	0.2
	Anaerobic	28	11.6	0	< 0.8	0.0	0.2

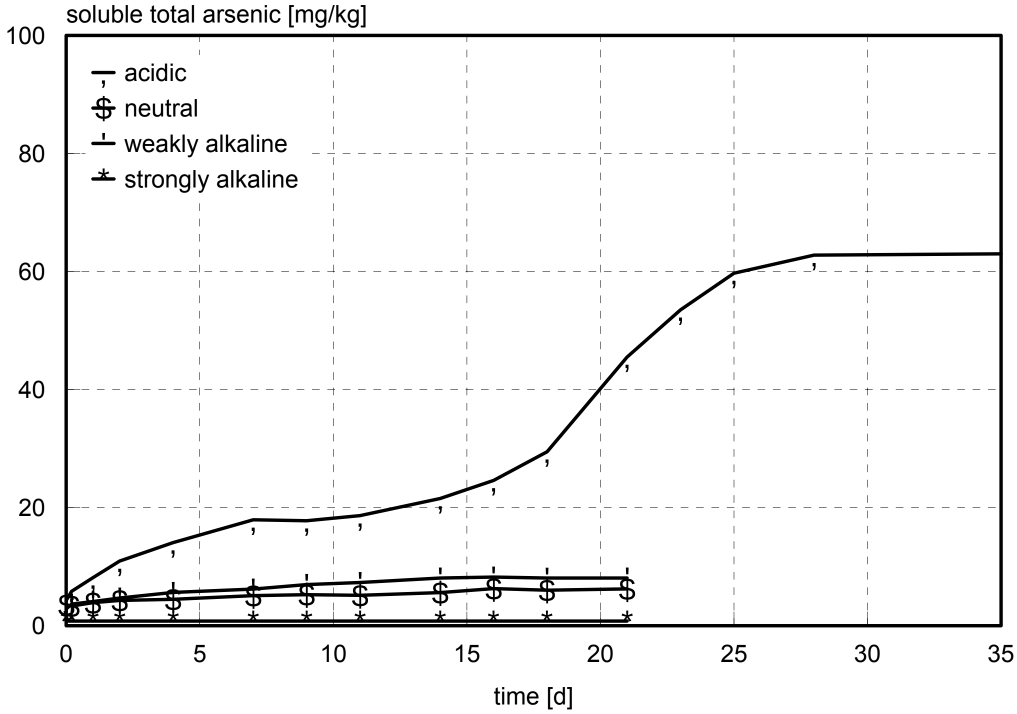

Fig. 1. Soluble total arsenic related to the solid quantity at different pH ranges under aerobic conditions (ICP-AES analysis)

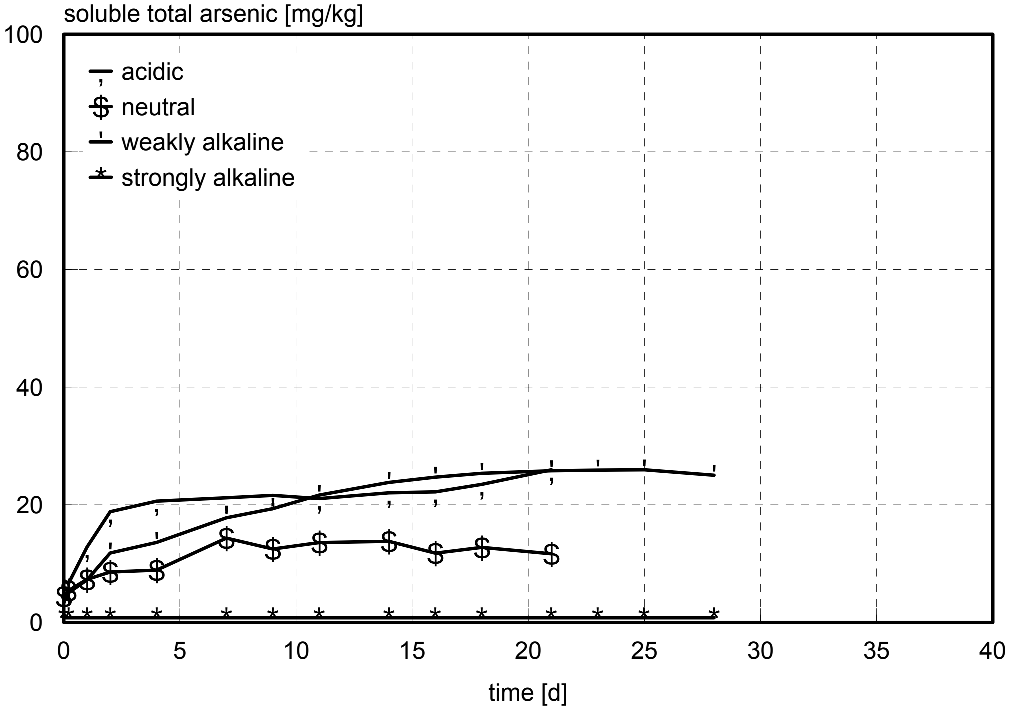

Fig. 2. Soluble total arsenic related to the solid quantity at different pH ranges under anaerobic conditions (ICP-AES analysis)

One main result was that under acidic-aerobic surrounding conditions a significantly higher As solubility occured than under all other conditions. Species analyses showed that in equilibrium the dissolved As was entirely present in the reduced form As(III) (Table 1). Changing aerobic to anaerobic conditions resulted in a decrease in As solubility but had no influence on the dominance of As(III).

At neutral range As was hardly dissolved with the predominance of the oxidized form As(V) under both aerobic and anaerobic conditions.

In a weakly alkaline range in the presence of $CaCO_3$, As solubility depended on the redox surroundings. Under aerobic conditions the total As solubility (8 mg/kg) was as low as in the neutral range. Changing to anaerobic conditions caused an increase in As solubility up to 25 mg/kg. The dissolved As was almost completely present as As(V).

In the strongly alkaline environment (aerobic and anaerobic) only trace amounts of soluble As(V) were detected. The results of ICP-AES analyses were usually below the detection limit.

Discussion

The results above contradict some of the literature data for contaminated soils. TAYLOR ET FUESSLE [1994], JONES ET AL. [1997] and SADIQ [1997] found As mobilization from the source material to be enhanced by an increasing pH value. PANTSAR-KALLIO AND MANINNEN [1997] determined the highest As solubilities in soil samples under both extremely alkaline conditions (pH 13) and strongly acidic conditions (pH 1) with As(V) as the dominant species in all cases. Sorption reactions also often depend on the oxidation state of As. Thus As(V) is preferentially adsorbed by or coprecipitated with aluminum [HALTER ET PFEIFFER 2001] or iron hydroxides [BOWELL 1994, MASSCHELEYN ET AL 1991], whereas the adsorption of As(III) on iron hydroxides is described in WHO [1996].

Our results indicate that As is mobilized particularly from the mine waste material in the acidic environment (pH 3) but immobilized under alkaline conditions (pH 11-13). The high As solubility at pH 3 may be explained by the dissolution of As sorbed on iron or aluminum hydroxides, which become soluble under acidic conditions. The immobilization of As at the alkaline range may be caused by sorption effects of calcium carbonate or calcium hydroxide, which can act as adsorbents [WHO 1996; SADIQ 1997] or as potential reactants [BOTHE ET BROWN 1999]. These factors were not considered in the tests described. In further series the effect of calcium compounds on the precipitation of As will be investigated.

Contrary to SMEDLEY ET KINNIBURGH [2002], we found that in the acidic environment the dominant species was As(III), although under the adjusted conditions only As(V) ought to be detected in solution. Within the pH range between 7 and 13 our results correspond with the authors' findings.

Our data indicate that the characteristics of the solid material play an important role in assessing the mobility of arsenic. Further attention will be paid to investigating the sorption effects of iron and aluminum hydroxides on arsenic mobility.

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ON-SITE REMEDIATION OF CHROMIUM CONTAMINATED SEDIMENTS BY COMBINATION OF SEDIMENT WASHING AND STABILIZATION WITH MAGNESIUM OXIDE

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Key words: chromium, soil pollution, soil washing, sulphuric acid leaching, caustic magnesia and limestone mixtures.

Summary

The objective of this work was the evaluation and development at laboratory scale of an on-site remediation process for soils and sediments polluted with chromium. The process integrates two steps: a) chromium leaching from soil and sediments using diluted sulphuric acid solutions and b) treatment of the acidic leaching effluents by a passive in-situ treatment with magnesium oxide/limestone mixtures. In this second step leach chromium species are retained onto limestone/magnesium oxide cells by precipitating as chromium oxide after acidity neutralisation. The paper describes results on the performance and the optimisation of both steps including leaching ratios, influence of sulphuric concentration, chromium dissolution rates and removal efficiency, ageing of the reactive mixtures as well as levels of chromium on the treated effluents.

1 Introduction

The remediation of heavy-metals-contaminated soils and sediments is of significant value to industrialised nations facing the problem that resulted from economic activities including agriculture, mining and mineral processing. Removal of metal pollution from sediments and soils could be achieved by different remedial actions: a) off-site after the excavation of the polluted soil/sediment; depending on the metal concentrations, deposition on a controlled waste dump or treated in a soil-cleaning installation, b) on-site as above with the difference that the soil/sediment-cleaning installation would be situated on location and c) in-situ, the polluted sandy soil/sediment would be cleaned by percolation with a de-sorption medium; the percolate would be pumped into a groundwater-cleaner installation and would be re-infiltrated.

Preliminary cost estimation indicates that an in-situ technique if available could be always the better solution. However, scarce commercially available in-situ techniques could be found, and many efforts are nowadays made to evaluate on-site ones, specially those based on washing approaches. Soil/sediment washing techniques are water-based process for scrubbing soils ex-situ/on-site to remove contaminants. The process removes contaminants from sediments in one of the two ways: a) dissolving or suspending them in a washing solution (which can be sustained by chemical manipulation of pH for a period of time) and b) by concentrating them into a smaller volume of sediment through particle size separation, gravity separation and attrition scrubbing (similar to those techniques used in sand and gravel operations).

Chemical extraction techniques can be effective treatment options for the remediation of heavy-metal contaminated soils, providing the permanent removal of toxic elements from the soil. The main categories of reagants used are acids and chelators (EPA 1989, 1991). Acid treatment is not appropriate for calcareous soils, due to the dissolution of soil calcite, but may be a cost effective option for soils poor in calcite (Papassiopi et al. 1998 and 1999).

The first approach based on direct washing or leaching of the metal polluted sediment is widely investigated and applied. Although chelating agents have been tested and are known to be capable of extracting heavy metals from contaminated media, the difficulty in metal recovery, as well in valuable chelating agents recovery the for reuse, rendered the technology economically less attractive. Additionally, factors that may limit the applicability and effectiveness of the process include: complex waste mixtures (e.g., metals with organics), as they make difficult the formulating of the washing fluid, and high humic contents in soil, as it may require pre-treatment.

In this work the technical feasibility of developing an on-site remediation project for chromium polluted soils and sediments is carried out. Chromium soil pollution was generated in an open channel after the spill, containing chromium wastes, from a tannery plant into a sewage urban plant system. The pollution extension has been estimated to be in the order of thousands of tonnes of soil to be treated, with chromium contents ranging from 500 to 15000 mg/Kg soil. The on-site remediation program was defined using a first treatment cell to achieve the chromium removal by a leaching process, and a second cell containing a caustic magnesia/limestone mixtures for the immobilisation in of chromium contained in the leaching solution. Mixtures of both materials showed high capacity to neutralise the residual acidity present on the effluents and to remove chromium by precipitation. The efficiency provided by both materials to remove chromium is shown in Figure 1.

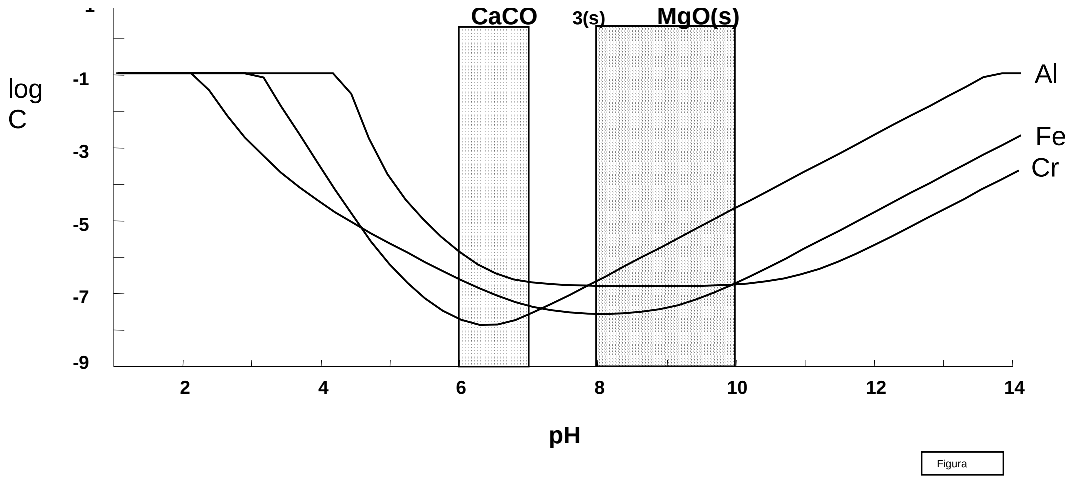


Figure 1. Variation of the metal concentration in equilibrium with the metal hydroxide. Thermodynamic data from the Wateq4f database (Ball et al., 1987). The vertical rectangular fields indicate the pH values expected after passive treatment of metal containing effluents with limestone and caustic magnesia.

2. Experimental conditions.

Materials and Reagents.

Samples of caustic magnesia (Magna L) provided by Magnesitas Navarras S.A., Spain, were used. Magna L sample was selected according to the grain size and permeability criteria. It is made up of major amount of periclase (MgO) (76%), and minor lime (CaO) (11%), quartz (SiO_2) (5%), Fe_2O_3 (2%), Al_2O_3 (1%), and magnesite ($MgCO_3$)/ calcite ($CaCO_3$) (5%). For the experiment, caustic magnesia was sieved to grain size range from 4 to 2 mm. Limestone samples were obtained from natural deposits and were milled to achieve similar grain sizes (8 to 6 mm). Apatite II®, a primarly amorphous form of carbonated hydroxyapatite was used in preliminary test of chromium removal from sulphuric solutions. Natural zeolites were used as chromium polishing adsorbent of the treated acidic leaving the caustic magnesia/limestone cell.

Methods

Batch experiments. Batch experiments were used to investigate the optimal conditions for chromium leaching with sulphuric acid solutions. Typically, experiments were conducted using open glass batch reactors, maintained at room temperature 21±1C and continuously agitated. For each run, typically between 0.2 to 0.5 kg of polluted soil and between 1000 and 2000 ml of a sulphuric acid solution were placed in the reactor. Sulphuric acid content of the initial solution was adjusted between 1 to 3 % (w/w) by using a concentrated solution of H_2SO_4 (67% (w/w)). At pre-selected time intervals 5 ml of solution was sampled and filtered through a 0.45 μm filter. Experiments were run for a maximum of two days. Solution acidity was also measured immediately after a sample was taken using a Crison® electrode connected to a pH meter and by acid base titrations when the acidity was higher than 0.5 M H_2SO_4. An aliquot of the samples was diluted when necessary with 1% H_2SO_4 and analysed for chromium with a Varian 640 Flame Atomic Absorption Spectrophotometer (FAAS). Analytical detection limits were 0.1 mg/l. Analytical errors are estimated to be on the order of 2% based on the reproducibility of the standard.

Column experiments. Column experiments were devoted to measure both the leaching efficiency of the sulphuric acid solutions under dynamic conditions and the reactivity of the reactive mixtures of caustic magnesia and limestone to remove chromium from the leaching solutions under realistic flow conditions. Bench-scale columns were designed to ensure uniform saturated flow over the cross-sectional area. The columns were filled with caustic magnesia, Apatite II and limestone gravel. Solutions were administered continuously through Teflon tubing connected to a multi-channel variable-speed Gilson Minipuls® peristaltic pump. Flow rates used ranged between 0,1 and 0,3 $ml.min^{-1}$. They were selected to match the range of flux conditions expected in the soil washing step. Influent solutions were different depending on the type of experiment. In the preliminary set of experiments dedicated to the reactive material performance on chromium removal solutions were prepared by dissolving chromium(III) sulphate reagent-grade, in tap water. For the experiments simulating the immobilisation process the influent solution was the effluent leaching solution generated on the soil washing step.

During routine monitoring column effluent samples were collected in 30-ml plastic vials, and flow rates were determined gravimetrically. An unfiltered aliquot of the sample was transferred to a separate vessel for acidity and/or pH determination. Acidity was determined by an automatic titrator using 0.1 M NaOH as titrant. The remaining sample was filtered to 0.45 µm and acidified with H_2SO_4 to pH lower than 1. The filtered-acidified were transferred to 25-mL polyethylene scintillation vials and refrigerated at 4^{O}C for target component analyses. Analyses were performed using FAAS.

Soil properties. Soil samples from the polluted area were collected and the total content on chromium was analysed by using standard methods. Values of chromium content ranged from 500 to 15000 mg/kg. Sample texture was typically sandy and with relatively high content of organic matter specially those dredged from bottom of the water channels. In XRD analysis only quartz, kaolinite, clinochlore, albite and muscovite. Due to the presence of chromium in a percentage below 5% any mineral phase to which chromium is present in the sample was not possible to identify by XRD. Taking into account that chromium pollution was due to the spill of Cr(III) effluents and taking into account the high content of organic matter on the soil the presence of chromium species on the soil samples was associated to chromium (III) species. Analysis of the leaching solutions obtained with sulphuric solutions all over the experiments performed showed that total content of Cr measured corresponded to the values determined for Cr(III) when specific analysis to differentiate between Cr(III) and Cr(VI) were carried out. Differences were always inside the analytical errors provided by the FAAS and UV-VIS measurements.

3. Experimental results and discussion.

Chromium leaching experiments.

Diluted sulphuric acid solutions were selected to leach chromium (III) from the polluted soil and sediment samples. Selection of this leaching solution was due to the low cost in comparison with alternative washing solutions commonly used in such type of applications as hydrochloric acid or complexing acids as acetic acid or ethylendiamintetraacetic acid solutions (EDTA). The suitable concentration range to achieve the total dissolution of chromium (III) were in a first step theoretically predicted by assuming the presence of Cr(III) as chromium hydroxide ($Cr(OH)_{3(s)}$) as major component (Figure 2).

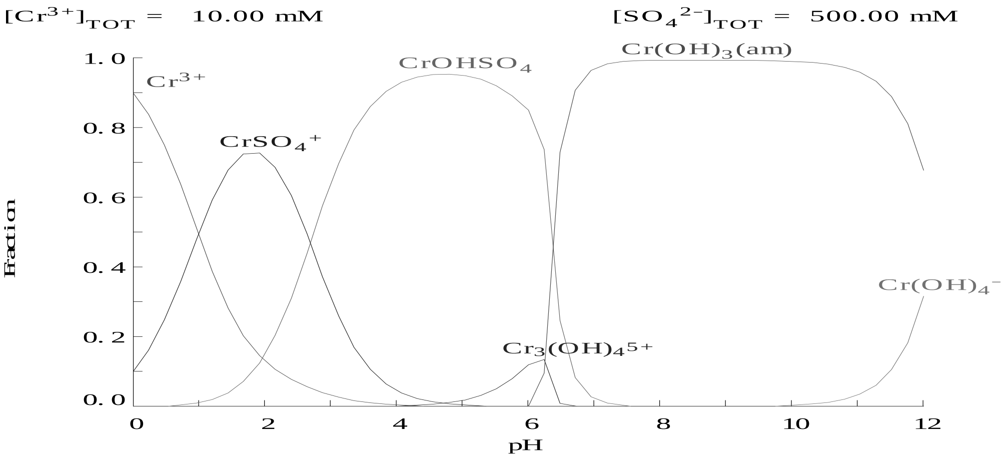


Figure 2. Species distribution diagram as a function of pH for the system Cr(III)-SO_4^{2-}–H_2O (from Medusa and Hydra equilibrium calculation codes).

Figure 2 shows that suitable pH range to obtain the hydroxide dissolution could be achieved when the pH of the aqueous solutions is below 6. Dissolution of chromium hydroxide (III) is achieved by complexation with sulphate anions to form Cr(III)-SO_4^{-2} as $CrHSO_{4(aq)}$ and $CrSO_4^+$.

Leaching experiments showed however that a high excess of sulphuric acid, in relation to the stoichiometric ratio, should be used due to the consumption of acid by basic minerals present on the soil samples as carbonates, aluminium and iron oxides. Additionally a minimum level of acidity should keep to assure the dissolution reaction, and to fight against the presence of chromium associated to organic matter whose high complexing properties makes difficult the leaching from the rich organic matter fraction.

Figure 3 shows the Cr(III) leaching values achieved over time for several sulphuric concentration and a function of time. The increase of the sulphuric concentration from 1.8 to 2.6 shows an increase of the leaching rates by a factor of 3.5; the increase of the sulphuric content to 3.1 % did not show any improvement on the leaching efficiency and then 2.6% content for the washing agent was fixed for further studies.

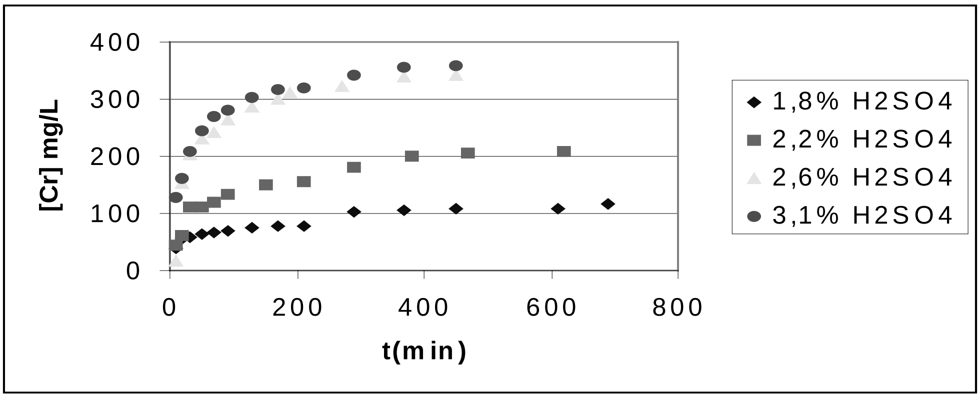
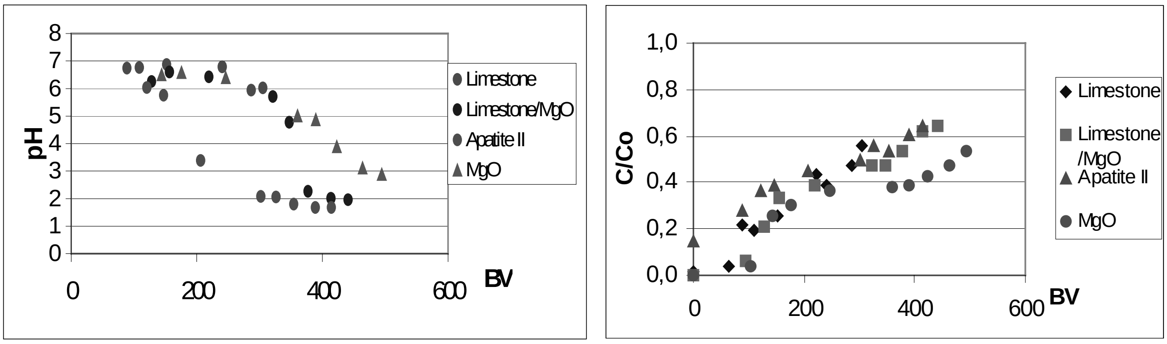


Figure 3. Sulphuric acid concentration influence on chromium leaching efficiency in batch assays. (Leaching solution 2 litters and mass of polluted soil 0.5 kg).

The leaching experiments were modelled by using classical models used on mineral processing. However, all the models tested were not able to predict the experimental data obtained on the present studies. This fact is an indication that probably chromium is present on the soil associated to different mineral phases or present as chromium hydroxide and oxides or complexed to organic matter. Leaching efficiency achieved on the leaching experiments using concentrated solutions of sulphuric 2.6%/3.1% was estimated by using the mass balance and by total analysis of the leached samples by following standard procedures. Values achieved were up to 85% for concentrated sulphuric solutions. For all the conditions evaluated excess of sulphuric provided high acidity conditions ($[H^+]$=0.5 to 1 mol/). The evolution of the acidity within the experimental runs were always very similar independently of the initial sulphuric concentration.

Chromium adsorption tests. Treatment of the solutions generated on the leaching step was evaluated using different reactive materials: calcite**,** caustic magnesia and Apatite II® (Figure 4).



a) b)

Figure 4. pH and chromium in column experiments treating a 25 mg/l Cr(III) solution of pH 2. (Column experiments contain 25 g of reactive material).

More selective systems as ion exchange were discarded due to the complexity of the leaching solutions containing chromium, specially for the high levels of acidity typically present on those effluents. The use of an adsorption step was considered as a polishing option following the removal process with those reactive materials. Performance on the chromium removal efficiency was evaluated by using column experiments. As could be seen in figure 4.b, breakthrough curves for the three reactive mixtures provided a buffering capacity of the calcite and Apatite columns around 6.5 to 7, while the buffering capacity of caustic magnesia columns shown pH control around 8. Due to the high cost of Apatite II in comparison to calcite and caustic magnesia this material was not evaluated in columns experiments

Integration of the leaching and adsorption processes. Laboratory runs simulating the future field assays in treatment cells were carried out by using double column system as described in the following scheme (Figure 5).

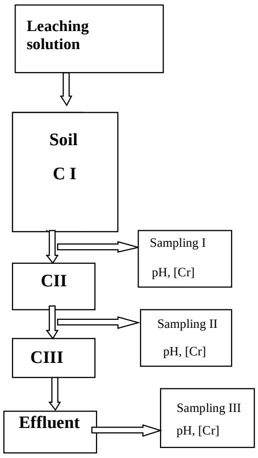


Figure 5. Scheme of the experimental set-up for integrated experiments of chromium leaching from soil samples and adsorption onto limestone/caustic magnesia mixtures. (CI: soil compartment, CII: limestone/caustic magnesia compartment and CIII: polishing compartment).

The samples of polluted soil were always placed on the head of the system (C1) to achieve natural flow (gravity based) conditions and avoid the need of pumping units. Those columns containing the polluted soil samples were washed /eluted discontinuously with known volumes of sulphuric solutions. The leachates produced on the bottom part were directed to the medium column containing the mixtures of calcite and caustic magnesia to achieve the neutralisation of the acidic solutions and to achieve the removal of chromium from those leachates. Finally a polishing column containing a natural zeolite was placed on the bottom part of the experimental set up. Samples of the effluent liquors of the three compartments were periodically collected for monitorization of total chromium content and acidity (sampling points I,II and III). Details of the composition of the different columns as well as the amounts are collected on Table 1.

Table 1. Details on the leaching assays and chromium removal using column experiments

	Run#1	**Run#2**	**Run#3**	**Run#4**
I: Soil compartment Soil Type	SA (6 gCr/Kg) 1.5kg	SA(6g Cr/kg) 1.5Kg	SB (2g/Kg) 1.5 Kg	SB (2 gCr/Kg) 1.5 Kg
II: Reactive mixture compartment	40%limestone60% MgO (70 g)	60% limestone 40% MgO (70 g)	40% limestone 60% MgO (70 g)	60% limestone 40% MgO (70 g)
II: Zeolite polishing compartment	Zeolite (30 g)	Zeolite (30 g)	Zeolite (30 g)	Zeolite (30 g)

Analysis of the effluents solutions of the leaching cells showed the decay on the chromium concentration with the increase of leaching runs (Figure 6). From the high values measured for the first runs (up to 800 mg/l) after four leaching steps content of chromium were below 200 mg/l. However close to 8 runs were necessary to achieve values on total chromium concentration below 20 mg/l.

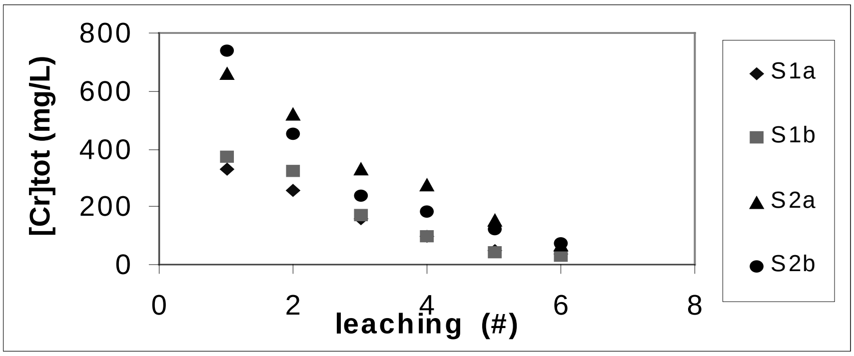


Figure 6. Chromium concentration evolution as a function of the leaching runs for two different types of polluted soil.

Effluents generated were characterised by high contents of acidity, the pH values were always close to 0.5, as is shown in Figure 7a. The different solutions generated in each of the leaching runs were treated in a second column containing mixtures of limestone and caustic magnesia as described in Table 1. Figure 7a shows the high efficiency of neutralisation of the sulphuric solutions. After more than 8 runs, pH values of the effluent on the chromium removal columns were always above 7. At this pH values the expected values of chromium on solution are below 0.5 mg/L (Figure 8b). Values of total chromium content were always below the detection limit provided by AAS technique.

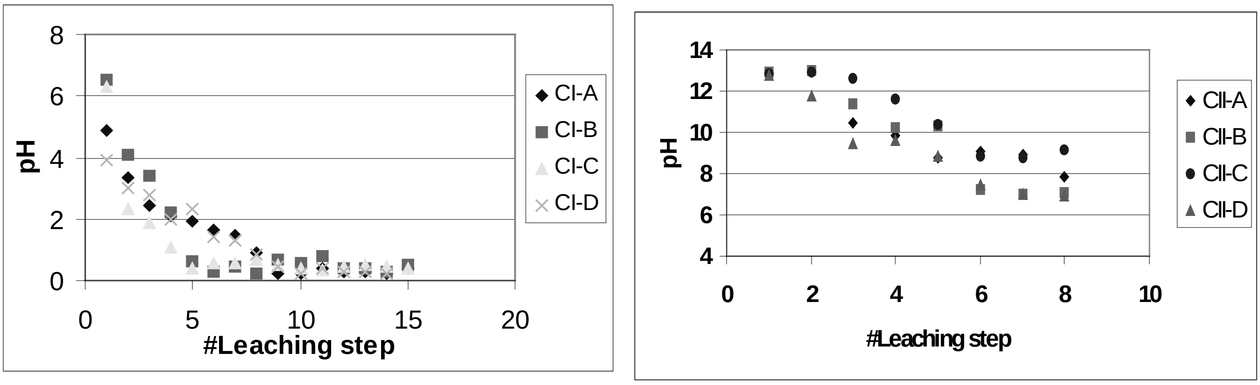


Figure 7 Variation of effluent pH of the a) leaching cell (C1) and b) reactive mixture cell (C2).

Levels of chromium concentration follow typical elution/leaching curves (Figure 8a) with values up to 1300 mg/L in the initial leaching runs. In the first leaching step, low values of chromium, due to neutralisation of sulphuric by the calcareous content present on the soil were reached.

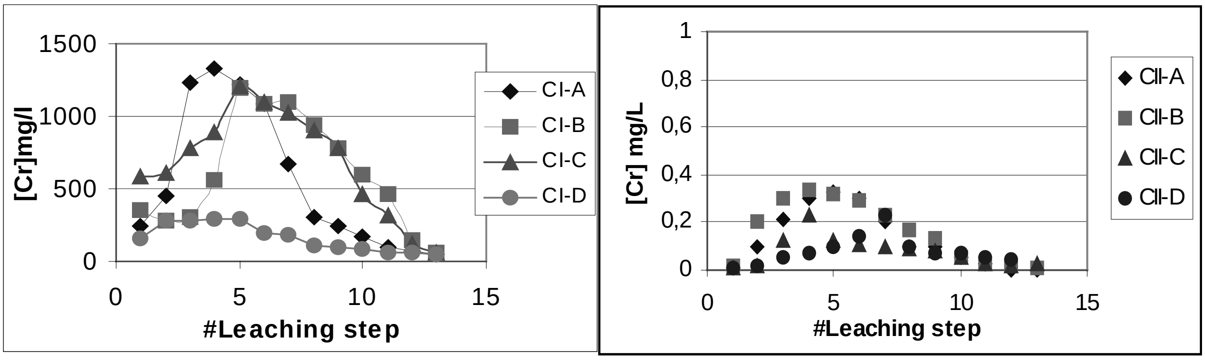

a)
b)

Figure 8. Variation of chromium content in the outlet solutions on a) leaching cell (C1) and b) reactive mixture cell C2.

4 Conclusions

From the preliminary results obtained on the chromium leaching and immobilisation with caustic magnesia at laboratory scale it could be pointed-out that:

- diluted sulphuric acid solutions (3 %) showed high efficiency on chromium removal from sandy polluted soils on leaching experiments on the kilogram scale. The increase on sulphuric concentration above this value did not provide any substantial increase that justified the increase on the amount of acid use and the decrease on the acidity of the leaching solutions generated. The acidity achieved, generally, below pH 1, is low enough to achieve the dissolution of chromium present as chromium hydroxide. The batch reactor assays showed typical patterns of mineral dissolution control by particle diffusion, where the dissolution of the chromium hydroxide takes place as far as acid is available to chromium hydroxide.

-) it is necessary to use an excess of sulphuric diluted solutions in order to achieve the removal levels needed to provide final contents of chromium on the soils acceptable for future soil uses (e.g. agriculture, industrial or non-industrial uses. This situation would be more efficiently achieved if the residence times of the leaching solution on the soil washing/leaching treatment cell is increase as much as possible. One possible solution to achieve this condition is to disperse or spray the diluted sulphuric solutions on the treatment cell.

-) the acidic effluents generated on the leaching steps at laboratory scale, using from 0.5 to 2 kg of soils with chromium contents from 500 to 15000 mg/l, could be efficiently neutralised and additionally the chromium content reduced by precipitation as chromium hydroxide, even with acidic solutions with pH between 0.5 and 1. Mixtures of limestone and caustic magnesia provided better efficiency than limestone. Between the limestone and caustic magnesia mixtures, those containing more than 60% of caustic magnesia provide the higher efficiency.

- the increase on the residence time of the effluent on the retention cell provide and improvement of the chromium removal treatment cell. Samples of caustic magnesia with particle size in the order of millimetres should provide those conditions.
- future work would be directed to the evaluation of the integrated process of leaching and chromium precipitation on column at the scale of 100 to 1000 kg.

5 Acknowledgements

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UNIVERSITÄT STUTTGART

INSTITUTE OF HYDRAULIC ENGINEERING – LABORATORY

Prof. Dr.-Ing. habil. Bernhard Westrich

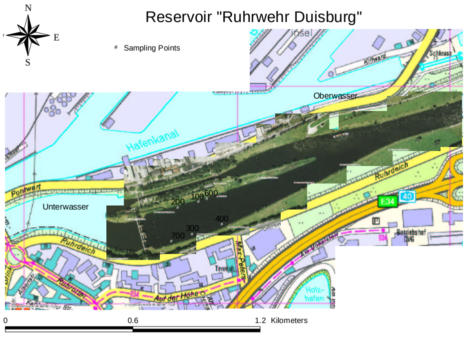
Investigation on Erosion Stability of Sediments Deposited in the Head-water of Hydropower Stations at the River Rhine and its Tributaries

Project committed by: International Commission for the Protection of the Rhine (ICPR)
Project conducted by: Dipl.-Geoecologist Oliver Witt

Introduction -

Contaminated sediments and their impact on water quality are major problems in rivers, lakes etc. A key question is whether the contaminated sediments can be exposed and eroded during floods and storms. Because of the spatial and temporal variability of the erosion process no general description can be given.

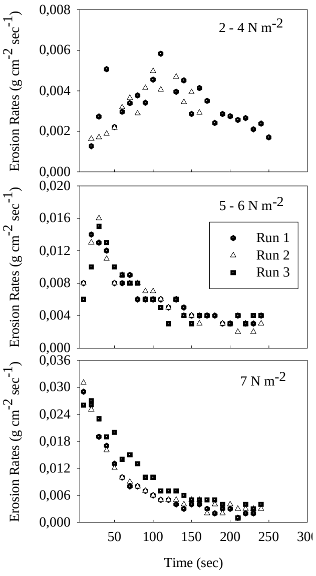
Therefore different experimental facilities have been constructed for erosion tests in the lab and field.



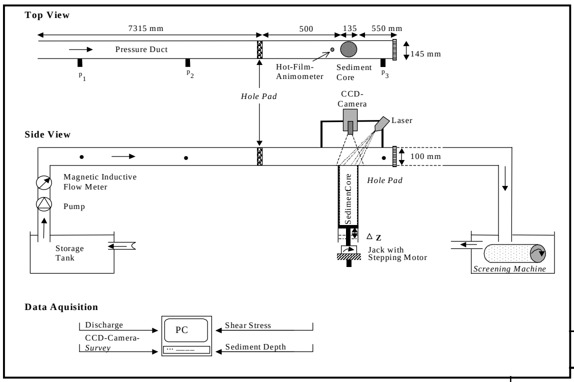
Site Description

Technical and general information:

- Weir (3 to 5 segments), lock chamber, hydro power station
- Max. $Q_{Turb.}$ = 1400 m³/s (River Rhine)
  HQ_{100} = up to > 5000 m³/s (River Rhine)
- Flow over weir and power station (depending on discharge)
- Water level fixed by weir
- Sedimentation in the headwater of the weir
- Sediment contamination by Industry, Agriculture etc.



↑ Sediment erosion rates with time

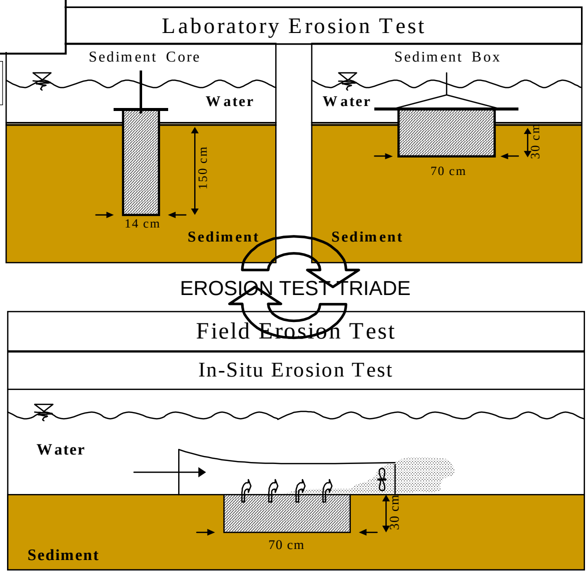


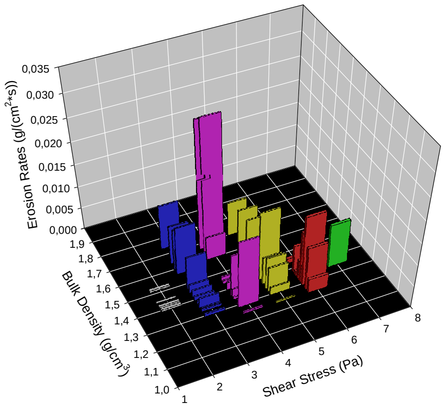
↑ Schematic setup of the extended SETEG-System

Laboratory and Field Methods

- Extended SETEG-System
  - a) Critical shear stress of erosion (sediment depth of 1.5 m; shear stresses 0.5 to 14 Pa)
  - b) Erosion rates measurements by laser optical methods
- Sediment Box, Flume Experiments
  - a) Critical shear stress of erosion (sediment depth of 0,3 m)
  - b) Scale effects of erosion
- In-Situ erosion test

⇒ EXPERIMENTAL EROSION TEST TRIADE





Sediment erosion rates of undisturbed sediment cores depending on bulk density and shear stress →

Results

Sediment parameters

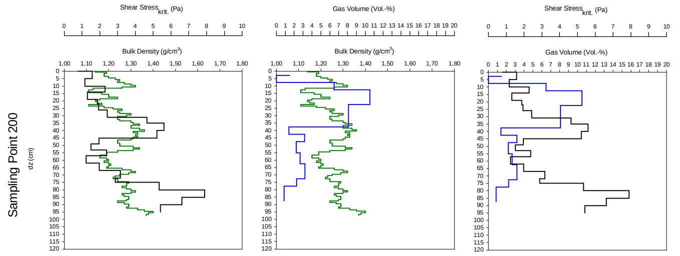
- Average sediment bulk density 1,4 g/cm³ (1,2 g/cm³ to 2 g/cm³)
- Gas volumes ranging from 1 to 15 and higher Vol.-%
- Particle sizes between clay and sand fraction

Critical shear stress of erosion

- Critical shear stresses of erosion range from 0.5 Pa to 9 Pa
- Variation in critical shear stress with depth is correlated with a variation in particle size , water content and biological factors

Erosion rates

- Erosion rates are increasing with time
- Influence of other unknown parameters on erosion stability



Critical erosion shear stress, bulk density, gas volume – Ruhrwehr Duisburg