





Federal Environment Agency – Austria

# SUSTAINABLE MANAGEMENT OF SOIL AND GROUNDWATER RESOURCES IN URBAN AREAS

Proceedings of the 2<sup>nd</sup> IMAGE-TRAIN Cluster Meeting Krakow, October 2–4, 2002

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#### **Projektleitung/Project Management**

Gundula Prokop

#### **Scientific Committee and Editors**

Gundula Prokop, Federal Environment Agency – Austria, Spittelauer Lände 5, 1090 Vienna, Austria, Email: prokop@ubavie.gv.at

Martin Bittens, Tuebingen University, Sigwartstrasse 10, 72076 Tübingen, Germany Email: martin.bittens@uni-tuebingen.de

Piotr Cofalka, Institute for Ecology of Industrial Areas, Kossutha 6, 40833 Katowice, Poland, Email: piter@ietu.katowice.pl

Karl Ernst Roehl, Karlsruhe University, Kaiserstrasse 12, 76128 Karlsruhe, Germany Email: ke.roehl@agk.uni-karlsruhe.de

Martin Schamann, Federal Environment Agency – Austria, Spittelauer Lände 5, 1090 Vienna, Austria, Email: schamann@ubavie.gv.at

Paul Younger, University of Newcastle upon TyneNE1 7RU Newcastle upon Tyne, UK Email: p.l.younger@ncl.ac.uk

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## FOREWORD

Innovative Management of Groundwater Resources in Europe – Training and RTD Coordination (IMAGE-TRAIN) is an initiative funded by the European Union's Research Directorate – General and has the ambition to improve cooperation and interaction between ongoing research projects in the field of soil and groundwater contamination and to communicate new technology achievements to young scientists by means of training courses.

The 2<sup>nd</sup> IMAGE-TRAIN Cluster Meeting "Sustainable Management of Soil and Groundwater in Urban Areas" was held in Krakow (Poland) at the University of Mining and Metallurgy, from October 2 to 4, 2002. The meeting was jointly organised by the Austrian Federal Environment Agency and the Polish Institute for Ecology of Industrial Areas.

The Cluster Meeting was targeted at project partners of the "Key Action Water" of the European Union's 5<sup>th</sup> Framework Programme for Research and Technology Development (FP5) and functioned also as project review meeting of the European Commission. In total 20 projects of FP5 – Key Action Water were presented.

The Cluster Meeting focused on sustainable use of water resources in urban areas, in particular on the practical application of integrated water management systems at large scales, the development of appropriate guidelines, technologies and tools, regarding water availability and water quality status, spatial planning, and land use changes (rural/urban interactions). The meeting included

- #an **overview of relevant European policy** and new visions towards soil an groundwater protection (session 1),
- #a special session on "Integrated Solutions" (session 2), referring to comprehensive measures and responses for soil and groundwater contamination,
- ∉#a focus on the particular "Challenges in Urban Areas" (session 3) addressing the specific problems in urban areas; i.e. pressures on drinking water resources, leaky sewer systems, urban sprawl, reuse of brownfields, surface sealing, groundwater level containment, documentation of polluting sources,
- #a focus on technical solutions, namely "**Risk Assessment**" (session 4a), referring to human health risk assessment or groundwater risk assessment (session 4b) "**Monitoring**" of environmental and remediation processes, and "**Remediation**" (session 4c) of contaminated soil and/or groundwater, and
- #finally a Brainstorming Workshop (session 5) on "Sustainable Management of Land and Groundwater in Urban Areas in the European Research Area" aiming at defining the problem and state of the art and at coming up with problem solutions and research needs along front table discussions. Specific attention was given to the new objectives and tools of the European Commission's New Framework Programme for Research and Technology Development (FP6).

With the organisation of the 2<sup>nd</sup> IMAGE-TRAIN Cluster Meeting we intended to improve the communication among scientists working in thematically related fields and to inspire their future work, to openly present existing conflicts among different stakeholder groups involved in urban land management, to explain new and emerging European policy, and to open the forum for new visions and solutions.

Gundula Prokop, IMAGE-TRAIN Co-ordinator On behalf of the IMAGE-TRAIN Scientific Co-ordination Team

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<sup>1</sup> Laboratoire de Biotechnologie Environnementale, Ecole Polytechnique Fédérale de Lausanne, CH, <sup>2</sup> Bergische Universität - Gesamthochschule Wuppertal, Department of Chemical Microbiology, DE, <sup>3</sup> Biodegradation Research Group, Division of Microbiology, GBF, DE, <sup>4</sup> University of Groningen, Department of Biochemistry, The Netherlands, <sup>5</sup> Bioclear bv, Groningen, The Netherlands, <sup>6</sup> Bergakademie Freiberg, Interdisciplinary Ecological Center, DE..... 120

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### EXECUTIVE SUMMARY

Gundula Prokop, Federal Environment Agency – Austria

#### Background

Groundwater and soil in urban areas are under enormous pressures: according to the European Environment Agency about 70 % of the European population lives in urban areas, which cover in total about 25 % of the total territory<sup>1</sup>. Sustainable use of the resources soil and groundwater and protection and conservation of their quality are hence a key issue of European environment policy and an enormous challenge for European research.

The 2<sup>nd</sup> IMAGE-TRAIN Cluster Meeting with the title "Sustainable Management of Soil and Groundwater in Urban Areas" had the ambition to review European research in this field and to bring together experts working in the field and to initiate a solution finding process.

#### About the meeting

The 2<sup>nd</sup> IMAGE-TRAIN Cluster Meeting "Sustainable Management of Soil and Groundwater in Urban Areas" was held in Krakow (Poland) at the University of Mining and Metallurgy, Cracow – Poland from October 2 to 4, 2002. The meeting was jointly organised by the Austrian Federal Environment Agency and the Polish Institute for Ecology of Industrial Areas. The meeting

- #was targeted at project partners of the "Key Action Water" of the European Union's 5<sup>th</sup> Framework Programme for Research and Technology Development (FP5) and functioned also as project review meeting of the European Commission,
- #attracted 60 participants, mainly from research organisations from all over Europe, but also from regulatory organisations, engineering and consulting companies - a total of 16 EU RTD projects and 4 networks were presented,
- #focused on sustainable use of water resources in urban areas, in particular on the practical application of integrated water management systems at large scales, the development of appropriate guidelines, technologies and tools, regarding water availability and water quality status, spatial planning, and land use changes (rural/urban interactions), and
- #closed with a Brainstorming Workshop on "Sustainable Management of Land and Groundwater in Urban Areas in the European Research Area" aiming at defining the problem and state of the art and at coming up with problem solutions and research needs along front table discussions. Specific attention was given to the new objectives and tools of the European Commission's New Framework Programme for Research and Technology Development.

<sup>&</sup>lt;sup>1</sup> EEA (1999), *Environment in the European Union at the turn of the century*, published by the European Environment Agency, Copenhagen (DK).

#### Summary of results

**Implementation of new technologies is lagging behind.** Many innovative technologies for soil and groundwater remediation are confronted with enormous implementation barriers. Confidence in their success is often low and conventional and more expensive technologies are preferred. There are various reasons for these mechanisms; i.e. bureaucratic reasons, bad communication of results, little experience etc. In recent years this conflict has been realised as one of the key issues concerning soil and groundwater management. Hence, **communication of research results, involvement of large stakeholder groups networking between researchers** and all other involved parties has gained enormous importance. Five of the presented projects reflected this need (see also Table 1). This need was also identified as a key issue for the research working group along the soil policy development (see also page 14):

#IMAGE-TRAIN a training of researchers and clustering of research results

#CABERNET à brownfield network

#SOWA à integration of soil and groundwater policy

 ${\ensuremath{\textit{\#}EUGRIS}}\xspace a$  information provider for soil and groundwater

#SENSPOL à network for sensing technologies

Many activities focusing on networking and communication have come into being in recent years. However, streamlining and avoiding duplication will be a major issue in the future.

Innovative technologies require a lot of background knowledge for their implementation. The production of reliable guidelines and decision support tools is of utmost importance and was reflected in seven of the presented projects addressing a broad spectrum of problems (see also Table 1).

 $\notin$  APUSS à decision support for urban water management

#RESCUE à manual for sustainable brownfield regeneration

#GRACOS à guidelines for groundwater risk assessment

#NORISC à decision support for investigation methods

#WATCH à decision support for MTBE and BTEX monitoring and early warning

#PIRAMID à engineering guidelines for passive treatment of acidic mine effluents

#PHYTO-DEC à decision support for implementation of phyto-remediation

Guidelines and decision support are indispensable tools to accelerate implementation of innovative technologies. In particular communication between developers/researchers and end-users needs to be improved.

**Research is evolving towards large scale solutions.** Innovative soil and groundwater contamination needs solutions at catchment scale or at regional scale. This was reflected in three of the presented projects (see also Table 1).

#INCORE à investigation of urban groundwater at large scales

#WELCOME à multiple contamination patterns at industrial megasites

#AISUWRS à urban groundwater water management

In line with the needs of the EU water framework directive, solutions at catchment scale for multiple point sources and/or multiple areal sources of contamination will dominate future research.

Project name cation & networking IMAGE-TRAIN EUGRIS EUGRIS SOWA SOWA INCORE WELCOME AISUWRS APUSS APUSS RESCUE CABERNET CABERNET TRACE-FRAC.	Decision sup-	Integrated	wa-		Moni-	Passive	Phyto		Brownfield	Contaminant
	port tools & guidelines	concepts /MS	ት	sessment			remedia- tion	degrada- tion	redevel- opment	transport
			ment							
DIMDESMOT.										
PHYTO-DEC										

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Tab.

**Risk reduction and management of uncertainties are evolving** in particular in view of situations where soil or groundwater remediation is unaffordable or not manageable. This topic was reflected in four of the presented projects (see also Table 1).

#INCORE à human health risk assessment in urban areas

#GRACOS à groundwater risk assessment

#TRACE-FRACTURE à risk assessment of contaminants in fractured reservoirs

#NORISC à risk assessment of contaminant profiles

**Monitoring of pollutants in soil and groundwater**, in particular contaminant transport and degradation mechanisms are indispensable for any type of long term observation and were reflected in five projects (see also Table 1).

#SENSPOL à network for sensing technologies

#DIMDESMOTOM à sensing technologies for heavy metals

#WATCH à sensing technologies for MTBE and BTEX

#AISUWRS à contaminant transport in urban water systems

#TRACE-FRACTURE à contaminant transport in fractured media

**Cost effective remediation technologies, with special emphasis on low maintenance, need further development.** This topic was tackled along the following projects (see also Table 1):

#PIRAMID à passive treatment technologies

∉ #PEREBAR à permeable reactive barriers

#PHYTO-DEC à phyto remediation

∉#MAROC à biodegradation

#ORGONATE à passive treatment

According to the presented projects **major sources of contamination and their major contaminant groups** are (see also Table 2).

Fuel spills à hydrocarbons and MTBE

Effluents from mines à heavy metals

Industrial spills

- Degreasing agents à chlorinated hydrocarbons
- Solvents à benzene, toluene, xylene, ethylene (BTEX)
- Polymerisation starters à phenols

Gas works à polycyclic aromatic hydrocarbons (PAHs)

Residues from military activities à explosives

Agro-chemicals à POPs

Project	POPs	BTEX	Phen- ols	CHCs	MTBE	HC	PAH	heavy metals	explosi- ves	
SOWA										contaminant behaviour
INCORE										investigation, plume modelling
TRACE- FRACTURE										monitoring, distribution in fractured media
GRACOS										contaminant behaviour
WATCH										monitoring & warning
DIMDES MOTOM										monitoring, sensor development
PIRAMID										remediation: passive in- situ rem.
PEREBAR										remediation: passive in- situ rem
MAROC										remediation: biodegradation
ORGONATE										remediation: adsorption
PHYTO-DEC										remediation: phytoremediation

Tab. 2:Pollutant groups tackled in presented projects

#### Emerging EU policy influences research strategies and vice virsa

At EU policy level soil and groundwater protection are emerging issues, new regimes are currently under development, integrating in-put from the research community. In particular historical point sources of contamination have received recognition, regular reporting and implementation measures will be key issues of future regimes.

#### Groundwater

In the beginning of the year the European Commission drafted a proposal for a groundwater directive "Establishing strategies to prevent and control pollution of groundwater"<sup>2</sup> – enforcement of the final version of the directive is envisaged for 2004. Key content of the current version is the assessment of groundwater chemical status (as required in the Water Framework Directive<sup>3</sup>) and prevention of groundwater contamination.

<sup>&</sup>lt;sup>2</sup> COM (2003) Proposal for a Directive of the European Parliament and of the Council establishing strategies to prevent and control pollution of groundwater. Draft 1.0

<sup>&</sup>lt;sup>3</sup> Article 17 "Strategies to prevent and control pollution of groundwater Directive" 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy

**Expected impacts on EU research:** Inventorisation of historic pollution and remediation measures will gain importance along with the enforcement of the new groundwater regime. First measures are expected to be implemented in 2009. Remediation measures at low costs, reduction of contaminant mass fluxes and limitation of contaminant plumes will continue to challenge EU research.

#### Soil

In the 6<sup>th</sup> Community Environment Action Programme<sup>4</sup> ambitious targets for sustainable use of soil resources are defined, requiring

#regular monitoring of national data; i.e. groundwater quality, soil impacts, and hence the definition of sustainability indicators,

#the development and implementation of new regulatory frameworks, in particular in view of the emerging groundwater directive with regard to soil protection, and

∉#concerted research efforts of the research community to meet the future needs.

As a first step in the development of an encompassing EU policy to protect soils against degradation, erosion and pollution, the Commission has published a Communication *"Towards a Thematic Strategy for Soil Protection"*<sup>5</sup>. As consequence five working groups have been formed this year and are currently busy to draft a successful strategy for soil protection. Three thematic working groups, being "soil contamination", "soil organic matter" and "soil erosion". And two horizontal working groups being "soil monitoring" and "research". In the beginning of 2004 results of the working groups are expected in form of final reports. These documents will form the basis for the future EU regime on soil policy.



*Fig.1:* Thematic and horizontal working groups to guide the soil policy development process.

**Expected impacts on EU research:** The research working group contributes to basic definitions and cross-cutting issues. This includes, among others, the following issues<sup>6</sup>:

- #Harmonisation of soil information at EU level, including typology and characterisation of soils.
- #Vulnerability of soils and exposure to damage and soil degradation associated to the typologies; development of a generic conceptual framework for soil risk assessment and management.
- #Risk management in the context of an ecosystem approach; functioning and structure of ecosystems and how land use affects them; definition and improvement of management measures to implement an ecosystem approach.

#### #Interface between soil, groundwater and surface waters.

<sup>&</sup>lt;sup>4</sup> EC (2002) Decision No. 1600/2002/EC of the European Parliament and the Council of July 2002 *laying down the Sixth Community Environment Action Programme*. in Official Journal, Sept. 10 2002, L242/1.

<sup>&</sup>lt;sup>5</sup> COM (2002)179final Communication of the European Commission "Towards a Thematic Strategy for Soil Protection", 16 April 2002.

<sup>&</sup>lt;sup>6</sup> from: First meeting of the Advisory Forum on the Soil Thematic Strategy 23 April 2003 – Brussels Document N°3 – Version N°1, Description of Specific Mandates

#Integrating of social, economic and ecological considerations into decision-making.

- #Identification of barriers for a successful application in Europe for new technologies and techniques; recommendations to overcome those barriers.
- #Innovative methods in monitoring and evaluation incorporating the potential of new technologies. Efficient spatial sampling methods to obtain representative data; frequencies and densities taking into account the complexity and variability of soils.
- #Development of a network for timely diagnosis and warning based on quality indicators and degradation indicators.
- #Interaction between detailed process studies (for example on erosion, sedimentation, organic matter) and databases at different area and time scales, and how to make best use of combined information of diverse origin.
- #Diffuse soil pollution and atmospheric deposition due to industry, agriculture, energy production, traffic; faith of pollutants, natural barriers and ecological processes in the soil.

#### Conclusions

To a great extent do current EU research projects of the key action water "pollution prevention" meet the enormous challenges of urban pressures on soil and groundwater and furthermore meet the research needs as lately defined along the development of EU groundwater protection and soil protection policy. However, a variety of gaps exist and cross-cutting issues need to be further developed, in particular to overcome application barriers of new, innovative technologies and the integration of research on soil, groundwater and surface waters.

# Full names of quoted project acronyms, contact details and websites (if existent)

- AISUWRS, Assessing and Improving Sustainability of Urban Water Resources and Systems, Matthias Eiswirth (eiwirth@-agk.uka.de)
- APUSS, Assessing Infiltration and Exfiltration on the Performance of Urban Sewer Systems, Jean-Luc Bertrand-Krajew-ski (jlbk@urgc-hu.insa-lyon.fr), http://www.insalyon.fr/Laboratoires/URGC-HU/apuss/
- CABERNET, Concerted Action on Brownfield and Economic Regeneration Network, Paul Nathanail (paul.nathanail@nottingham.ac.uk), http://www.cabernet.org.uk/index.php
- DIMDESMOTOM, Development of Improved Detection Systems for Monitoring of Toxic Heavy Metals in Groundwaters and Soils, Manuel Valiente (Manuel.Valiente@uab.es)
- EUGRIS, European Sustainable Land and Groundwater Management Information System, Jörg Frauenstein (joerg.frau-enstein@uba.de), http://www.eugris.org
- GRACOS, Groundwater Risk Assessment at Contaminated Sites, Dietrich Halm (dietrich.halm@uni-tuebingen.de), http://www.uni-tuebingen.de/gracos/
- IMAGE-TRAIN, Innovative Management of Groundwater Resources in Europe Training and RTD Co-ordination Project, Gun-dula Prokop (gundula prokop@uabvie.gv.at), http://image-train.net

- INCORE, Integrated Concept for Groundwater Remediation, Thomas Ertel (thomas.ertel@uw-d.de), http://www.uw-d.de/incore/
- MAROC, Molecular Tools for Assessing Bioremediation Potential in Organohalogen Contaminated Sites, Günter Maass (maa@gbf.de)
- NORISC, Network Oriented Risk-Assessment by In-situ Screening of Contaminated Sites, Barbara Möhlendick (Babara.-Moehlendick@stadt-koeln.de), http://www.norisc.com
- ORGONATE, On Site Remediation of Groundwater Contaminated by Polar Organic Compounds Using New Adsorption Technology, Karsten Levsen (levsen@ita.fraunhofer.de), http://www.orgonate.com/
- PEREBAR, Long-term Performance of Permeable Reactive Barriers used for the Remediation of Contaminated Groundwa-ter, Karl Ernst Roehl (ke.roehl@agk.uni-karlsruhe.de), http://www.perebar.bam.de/
- PHYTODEC, A Decision Support System to Quantify Cost/Benefit Relationships of the Use of Vegetation in the Management of Heavy Metal Polluted Soils and Dredged Sediments, Jan Japenga (j.japenga@alterra.wag-ur.nl), http://www.phytodec.nl/
- PIRAMID, Passive In situ Remediation of Acid Mine and Indus-trial Drainage, Paul Younger (p.l.younger@ncl.ac.uk), http://www.piramid.org/
- RESCUE, Regeneration of Sites in Cities and Urban Environments, Gernot Pahlen (rescue@gpembh.de), http://www.rescue-europe.com/index\_mf.html
- SENSPOL, European Network on Sensors for Monitoring Water Pollution, Susan Alcock (S.Alcock@Cranfield.ac.uk), http://www.cranfield.ac.uk/biotech/senspol.htm
- SOWA, Integrated Soil and Water Protection from Diffuse Pollution, Peter Grathwohl (grathwohl@uni-tuebingen.de)
- TRACE-FRACT, Toward an Improved Risk Assessment of the Contaminant Spreading in Fractured Underground Reservoirs, Christos Tsakiroglou (ctsakir@iceht.forth.gr), http://www.iceht.forth.gr/projects/trace\_fracture/description.htm
- WATCH, Water Catchment Areas: Tools for Management and Control of Hazardous Compounds, Thomas Track (track-@dechema.de), http://www.watch-eu.org
- WELCOME, Water Environment, Landscape Management at Contaminated Megasites, Huub Rijnaarts (h.h.m.rijnaarts-@mep.tno.nl)

### **SESSION 1: WELCOME & INTRODUCTION**

Chairman: Martin Bittens, Tuebingen University (DE)

### SUMMARY

The meeting was officially opened by the Dean of the Faculty of Geology, Geophysics and Environmental Protection of the University of Mining and Metallurgy, Prof. **Tadeusz Slomka**, and the Deputy Director of IETU, **Stefan Godzik**. **Juergen Buesing** from DG Research continued with his expectations to the meeting in particular in view of the ambitious expectation set by the 6<sup>th</sup> EU Framework Programme for Research and Technology Development to be launched a view weeks after the meeting.

**Gundula Prokop**, the co-ordinator of the project IMAGE-TRAIN presented background information in relation to sustainable management of soil and groundwater resources in urban areas. In particular developments at international level and EU level were referred to and recent and up-coming policy documents were explained. In this respect the 6<sup>th</sup> Environmental Action Programme and the definition of key thematic strategies for defined environmental issues was mentioned as basic element. New developments concerning EU groundwater protection and soil protection policy were explained. Finally achievements and perspectives of the project IMAGE-TRAIN were presented. The project has the ambition to improve cooperation and interaction between ongoing research projects in the field of soil and groundwater contamination and to communicate new technology achievements to young scientists by means of training courses.

Martin Schamann – Federal Environment Agency – Austria

#### IMAGE-TRAIN: INNOVATIVE MANAGEMENT OF GROUNDWATER RESOURCES IN EUROPE – TRAINING AND RTD CO-ORDINATION PROJECT

- Project IMAGE-TRAIN Innovative Management of Groundwater Resources in Europe Training and RTD Co-ordination Project
- Author G. Prokop, Federal Environment Agency Austria
- Keywords Groundwater, soil, management, contamination, training, knowledge transfer, Europe

#### Abstract

The EU-funded project IMAGE-TRAIN (Innovative Management of Groundwater Resources in Europe – Training and RTD Co-ordination Project) has the ambition to improve cooperation and interaction between ongoing research projects in the field of soil and groundwater contamination and to communicate new technology achievements to young scientists by means of training courses. IMAGE-TRAIN is a three year project which started in September 2001 and operates at two levels. (1) At the level of senior scientists cluster meetings for researchers of ongoing research projects are being organised with the objective to establish topic links between RTD projects dealing with contaminated land and groundwater and to promote their practical application. Furthermore, practical case studies with selected experts are being organised to perform short studies on emerging groundwater and soil issues. (2) At the level of junior scientists Advanced Study Courses are being organised with the objective to quickly transfer existing and emerging knowledge to young European academics. Last not least, IMAGE-TRAIN is maintaining a communication platform for young scientists dealing with groundwater and soil science which can be found on the project's website.

#### **Project-Structure**

IMAGE-TRAIN is an Accompanying Measure funded by the Fifth Framework Programme (FP5) on research, technological development and demonstration. Main driving forces of this project are

- #improvement of knowledge transfer (training of young scientists, better communication between established scientists),
- #better integration of EU Accession countries in the research community,
- #establishment of concerted research efforts by combining research projects and establishing research clusters, and

#practical implementation of current research activities along practical case studies.

IMAGE-TRAIN has the ambition to improve cooperation and interaction between ongoing research projects in the field of soil and groundwater contamination and communicate new technology achievements to young scientists by means of conferences and training courses. IMAGE-TRAIN is a three year project which started in September 2001 and operates at two levels.

- Senior level: At this level Cluster Meetings for researchers of ongoing research projects are being organised with the objective to establish topic links between RTD projects, dealing with contaminated land and groundwater and to promote their practical application and by organising practical case studies with selected experts to perform short feasibility studies related to current groundwater or mine water problems.
- <u>Junior level:</u> At this level Advanced Study Courses are being organised with the objective to quickly transfer existing and emerging knowledge to young European academics.

The RTD projects INCORE, PEREBAR and PIRAMID<sup>7</sup> form the basis to establish such topic-links. In the course of IMAGE-TRAIN other relevant RTD projects are being identified and considered to extend the clustering process. Major focus of IMAGE-TRAIN is to establish an efficient knowledge and information transfer towards the scientific community and potential end-users, with specific emphasis on the situation in EU Accession Countries. This is currently achieved by (see also Table 1 and 2)

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 $\notin$  clustering of ongoing RTD projects along 3 Cluster Meetings, and

#application of findings along practical case studies.

	Activity	Description	Target Group	Impact
Senior Level	3 Cluster Meetings	Scientific conferences	Researchers of ongoing research projects	Information exchange and better coherence between thematically related projects
				Input to Advanced Study Courses
	3 Case Studies	Joint expert opinions on defined topics	Selected experts	Reports and reviews on emerging topics
Junior Level	3 Advanced Study Courses	Up-to date training on innovative groundwater remediation technologies	Scientists, engineers, and consultants	Quicker understanding and application of new innovative groundwater remediation technologies

 Table 1: Overview and description of key IMAGE-TRAIN activities and their impact

All IMAGE-TRAIN products (newsletter, proceedings, summary reports and other) can be directly downloaded from the project's website: http://www.image-trian.net/.

<sup>7</sup> Acronyms for ongoing FP5 research projects:

INCORE, Integrated concept for groundwater remediation, http://www.umweltwirtschaft-uw.de/incore/; PEREBAR, Long-term Performance of Permeable Reactive Barriers used for the Remediation of Contaminated Groundwater, http://www.perebar.bam.de/

PIRAMID, Passive In-situ Remediation of Acidic Mine / Industrial Drainage, http://www.piramid.org/

#### Current Status of the project (March 2003)

#### Past Events

The 1<sup>st</sup> **IMAGE-TRAIN Cluster Meeting** was held in Karlsruhe in November 2001 and served on the one hand as Kick-off meeting for the Accompanying Measure IMAGE-TRAIN, and on the other hand as Mid-Term Review for the IMAGE-TRAIN core projects. Representatives from 30 European organisations all being involved in the EU research projects INCORE, PEREBAR, and PIRAMID reported about their scientific achievements at project mid-term. The proceedings include statements of the project co-ordinators at project mid-term, a synthesis of the meeting, and 30 papers, covering key aspects of groundwater and mine water management (IMAGE-TRAIN, 2002).

The 1<sup>st</sup> **IMAGE-TRAIN Advanced Study Course** with the title "*Innovative Groundwater Management Technologies*" was held in June 2003 in Katowice (Poland). 37 young researchers from 20 European countries participated at the course. 11 lecturers mainly from the core projects presented detailed results from their current research work. The programme focused on passive in-situ remediation technologies for contaminated groundwater and acid mine drainages, ground water and human health risk assessment and integral groundwater investigation and included an excursion to the Tarnowskie Góry site, a former chemical plant which is considered as national hot spot site in Poland. The course was evaluated by the participants by means of a questionnaire and received excellent results. Contents of the course were published in a review report (IMAGE-TRAIN, 2003a).

The 1<sup>st</sup> **IMAGE-TRAIN Case Study** was carried out under the lead of Newcastle University. Four experts on saline mine waters in Poland, Spain, and Germany provided their input and expertise concerning saline mine water management. The results of this study are summarised in a review paper *"Review of Saline Mine Water Management and Methods for Managing them"* which is available form the project's website (Gandy and Younger, 2002).

Date	Туре	Venue	Title ; Target Audience
Nov.	СМ	Karlsruhe	IMAGE-TRAIN Kick-off Meeting; Target audience: researchers of projects
01		(DE)	PEREBAR, INCORE, PIRAMID
June	ASC	Katwoice	Innovative Groundwater Management Technologies; Target audience: se-
02		(PL)	lected junior scientists and engineers from EU and EU Accession countries
Oct.	CS	Cracow	Review of Saline Mine Water Management and Methods for Managing them;
02		(PL)	Target audience: researchers dealing with mine water problems
Oct. 02	СМ	Cracow (PL)	Sustainable Management of Contaminated Land and Groundwater in Urban Areas + FP6 Workshop; Target audience: researchers from FP5 research projects
June 03	ASC	Pécs (HU)	<i>Groundwater Management in Mining Areas;</i> Target audience: selected junior scientists and engineers from EU and EU Accession countries
Nov.	СМ	Orléans	Are EU FP5 Research Results from the Key Action Water – Pollution Prevention
03		(FR)	Fit for Use?; Target audience: European researchers and stakeholder groups
Nov. 03	CS	Orléans (FR)	Application and Practice Report of EU FP5 Research Results in the Area Key Action Water – Pollution Prevention; Target audience: researches dealing with groundwater contamination
May 04	ASC	to be de- fined	<i>Title to be determined;</i> Target audience: selected junior scientists and engineers from EU and EU Accession countries
June	CS	to be de-	<i>To be defined</i> ; Target audience: researches dealing with groundwater con-
04		fined	tamination

Tab. 2: Timetable of key IMAGE-TRAIN activities (CM=Cluster Meeting, ASC= Advanced Study Course, CS=Case Study)

The 2<sup>nd</sup> IMAGE-TRAIN Cluster Meeting "Sustainable Management of Contaminated Land and Groundwater in Urban Areas" was held in Cracow from October 2–4, 2002. The purpose of this meeting was to focus on groundwater pressures in urban areas due to intensive landuse. Furthermore, this event included a specific workshop focussing on the new project tools of the European Commission's Sixth Framework Programme (FP6) on research, technological development and demonstration. The proceedings of this meeting include 20 summary papers of FP5 research projects dealing with soil and groundwater contamination and a summary of the 1<sup>st</sup> IMAGE-TRAIN Case Study (IMAGE-TRAIN, 2003a).

The 2<sup>nd</sup> **IMAGE-TRAIN Advanced Study Course** was dedicated to *"Management of Ground-water in Mining Areas"* and was held in Pécs-Hungary in June 2003. The venue is close to an abandoned uranium ore mine and processing site which was destination of a one day excursion. The course focused on cost-effective remediation of mining effluents and management of groundwater in areas affected by contamination from mining activities. Again, the contents of the course will be published in a review report and broadly disseminated.

#### **Future Events**

The **2<sup>nd</sup> IMAGE-TRAIN Case Study** is currently carried out under the lead of Tuebingen University. Key objective is to review deliverables of FP5 research projects dealing with ground-water contamination in view of their practicability for the future groundwater directive. Interim results of this study are presented along CONSOIL 2003 (Bittens and Prokop, 2003) and final results will be published in a specific review report and will also be available through the project's website.

The 3<sup>rd</sup> **IMAGE-TRAIN Cluster Meeting** will be jointly organised with three other projects. The Accompanying Measures SOWA, EUGRIS, IMAGE-TRAIN and JOINT of the EU 5<sup>th</sup> Framework Programme for RTD (FP5) are organising a workshop with the title *"Impact of European Research on Soil and Water Quality"* from Nov. 24 to 26, 2003 in Orléans (France). Between 80 and 100 attendees from selected FP5 projects, regulators, international and national networks and service providers are expected to participate. Key objective of the workshop will be (1) the definition of the current state of research concerning soil and groundwater management, (2) the definition of barriers to technology implementation, and (3) recommendations for further action. A strategy paper will precede the workshop based on a review of FP5 projects and a questionnaire to FP5 researchers concerning future research needs.

Public access to the results and information is provided through the project's website (http://www.image-train.net/). Announcements, proceedings from Cluster Meetings, review reports from Advanced Study Courses can be directly downloaded. Finally it should be mentioned that IMAGE-TRAIN is maintaining a Communication Platform for Young Scientists dealing with groundwater and soil science which can be found on the project's website. Main objective of this venture is to create a platform which allows Ph.D. students and other young scientists to present their research work and to get readily into contact with others who have similar interests or work at related fields.

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#### Contact

Gundula Prokop Umweltbundesamt/Austrian Federal Environment Agency Abteilung Altlasten/Contaminated Sites Department Spittelauerlaende 5; A - 1090 Vienna Phone: +43 1 31304 - 5923 Fax: -5911 Email: prokop@ubavie.gv.at project website: http://www.image-train.net

## SESSION 2: INTEGRATED SOLUTIONS

Chairman: Andrzej Witkowski, Silesian University (PL)

### SUMMARY

The session "Integrated Solutions" included presentations of projects with holistic approaches to urban land and groundwater management providing solutions for a broad range of stakeholders.

The project "European Sustainable Land and Groundwater Management Information System - EUGRIS" was presented by **Jörg Frauenstein** of the German Federal Environment Agency. At the point in time of the conference the project had not yet officially started. The presentation included hence an overview of planned activities. EUGRIS is a web-based information platform for all stakeholders in the field and has the ambition to structure available internet information concerning contaminated land and groundwater. The thematic scope of EUGRIS will cover local as well as diffuse contamination, in particular information on policies, site characterisation, fate and transport of pollutants, risk assessment, remediation. monitoring, risk management, socio-economic aspects and decision making. Information will be available in the form of peer reviewed digests, as database of RTD activities and research programmes at the national level and at EU level. Six countries (Denmark, Germany, Hungary, United Kingdom, France, Italy) will serve as pilot information pools to EUGIRS with information. It is the intention that EUGRIS shall outlast the funded period of 2.5 years. A final task of the project will include the definition of the market value of EUGRIS and the identification of an appropriate independent organisation to take over

The second part of this session was presented by **Peter Grathwohl** from Tuebingen University concerning the Accompanying Measure SOWA (Integrated Soil and Water Protection: Risks from Diffuse Pollution" being also in the start phase at the time of the conference. SOWA intends to bridge the gap between soil and water related research and policy making and to develop research needs and strategies along structured workshops and to identify and evaluate of rapid screening methods as developed along FP5. The project tackles local and diffuse soil contamination, in particular behaviour of pollutants in soils, sediments and adjacent environmental compartments (groundwater). Special emphasis is put on the longterm risks to water resources by diffuse pollution on top soils. Expected impact of the project's results is the early recognition of environmental damage. A key output of the project is the creation of a "soil protection think tank" through establishment of thematic working groups. SOWA is supposed to pave the way for a large integrated project proposed for the 6<sup>th</sup> EU Framework Programme for Research and Technology Development with the acronym RECONSILE (Integrated Protection of Soil and Water in Europe), which aims at harmonising European soil and water protection strategies and at supporting a future European Soil Protection Policy.

The subsequent presentation concerned the project INCORE (Integrated Concept for Groundwater Remediation) and was given by **Thomas Ptak** from Tuebingen University. INCORE aims at proposing integrated solutions for large scale groundwater contamination in urban areas, in particular for situations where sources of pollution are multiple, responsible parties unclear and land concerned of high value. Along a cyclic approach uncertainties to distinguish between clean and contaminated groundwater and soil are subsequently eliminated. In the first cycle the integral groundwater investigation method is applied: several pumping wells are applied along a control plane perpendicular to the groundwater flow and operated simultaneously or in subsequent pumping campaigns. This technology allows to efficiently identify contaminant plumes and to determine contaminant mass fluxes. As a result of this process clean areas (soil and groundwater) can be determined and excluded from further investigations. Cycle two focuses on the exact localisation of sources of contamination whereas cycle three deals with cost-effective combined solutions for source and plume remediation. The INCORE approach is implemented in four different urban areas in the cities, Stuttgart, Linz, Milano and Strassbourg. Apart from technology development INCORE includes the development of adequate administrative concepts to overcome implementation barriers.

The last presentation of the session was given by **Huub Rijnaarts** from TNO Environment, Energy, Process Innovation (The Netherlands) presenting the project WELCOME "Development of an Integrated Management System for Prevention and Reduction of Pollution of Waterbodies at Contaminated Industrial Megasites". Megasites are defined as areas of km<sup>2</sup> scale, having multiple site owners, stakeholders and endusers and which bear unacceptable remediation costs. The key objective of WELCOME is to produce an HTML based integrated management systems (IMS) for megasites. The methodology of the project is based on a "learning by doing process" being developed along the management of three megasites: the ports of Antwerpe and Rotterdam, the Bitterfeld/Wolfen area contaminated by lignite mining and the former "Tarnowskie Góry " chemical plant. All megasites are situated in river basins and generate heavy groundwater pollution. IMS development is based on the principles of risk based land management and has the overall objective to maintain the site infrastructure and commercial activities along the remediation process. The IMS structure is based on four main sections being (1) megasite definition, (2) risk reduction, (3) definition of management scenarios, and (4) long term planning. Final product of the project will be an operational IMS model for megasites by the end of 2004.

The discussion addressed mainly the data availability of the project EUGRIS, the progress at the megasites as referred to along the presentation of the project WELCOME and the ambition of the proposed integrated project RECONSILE.

Gundula Prokop; Federal Environment Agency – Austria

### EUGRIS – EUROPEAN SUSTAINABLE LAND AND GROUNDWATER MANAGEMENT INFORMATION SYSTEM

- Project EUGRIS European Sustainable Land and Groundwater Management Information System
- Author J. Frauenstein, Federal Environmental Agency, Department Contaminated Land, Germany
- Keywords Information system, groundwater, contaminated land, management

#### Abstract

EUGRIS will be a web based user-friendly information platform, a "gateway" or "one stop shop" for contaminated land information for all stakeholders in the field. It will not only offer pointers and guidance to find existing information but offer consolidation and condensation of the diverse information available from an independent perspective, and at the highest possible quality level. It will provide access to the information via a carefully structured and maintained web site. EUGRIS will be designed to address the needs of a range of users from researchers seeking advanced information on specific topics to general enquiries from those seeking a basic level of easy to digest information. EUGRIS will furnish an easy route to knowledge about contaminated land and groundwater issues for all stakeholders, and thereby improve the general efficiency of information use in a wider Europe. EUGRIS' information will be drawn from and linked to reliable sources, such as EU and governmental institutions, national and international networks, universities, leading professionals and organisations, etc. EUGRIS will bridge the apparent information divide between those who apply contaminated land and groundwater management at an operational level, and those carrying out RTD, policy and regulatory developments. It will provide a common link for the various inter-national networks. EUGRIS will provide a user-friendly and easy to use single point of ac-cess to reliable and usable information on the sustainable management of water and land for groundwater protection and restoration. EUGRIS is intended to serve the Member States of the European Union, its Accession States and in a wider Europe. This information gateway will be openly available and provide a comprehensive and overarching information resource for sustainable groundwater and land management practice. It will assist those synthesising and integrating the results of successful past and ongoing RTD projects and their implementation into policy approaches across Europe, as well as servicing future and current RTD in the field.

#### Objectives

EUGRIS will be a web based user-friendly information platform, a "gateway" or "one stop shop" for contaminated land and groundwater information for all stakeholders in the field. It will provide access to the information via a carefully structured and maintained web site with contextual guidance on the information on offer. EUGRIS' information will be drawn from and linked to reliable sources, such as EU and governmental institutions, national and international networks, universities, leading professionals and organisations, etc. EUGRIS seeks to:

- #provide a high-quality platform for dissemination and extraction of existing knowledge across Europe (e.g. guidelines, case studies, methods, reviews, regulations, conferences, workshops, courses, curricula etc.)
- #provide access to innovative research findings, products, technologies (e.g. on-going RTD projects and their objectives, new tools, demo sites, first findings, technology transfer etc.)
- #enhance the transfer of information between stakeholders and their networks (e.g. regulators, researchers and industry but also end-users, NGOs etc.)
- #support co-ordination of RTD funding across Europe (e.g. access to information about former, on-going and future research plans and their outcomes)
- #improve efficiency of policy and regulatory development (e.g. regulating agencies can obtain information and results on research work and strategies of neighbour countries)
- #contribute to the harmonisation of environmental standards across Europe (e.g. experiences with water and soil directives, existing and new ISO standards, etc.)
- #Develop a management or business plan to support the longterm sustainability of EUGRIS following the end of the Accompanying Measure.

EUGRIS will be delivered as a web site with linked databases. The objective is to develop a "pilot" version, based on information provided by "Pilot Countries" (incl. an Accession State), pilot projects (like SOWA), EC RTD projects, Concerted Actions and the other international initiatives. These information providers also take part in the design of the gateway and comment on its implementation. As far as possible original source material will not be replicated in this database. EUGRIS establish and provide a communication platform between the various existing and planned research centres of excellence and other stakeholders. The project includes development of a management or business plan for EUGRIS' continued existence. A package of promotional measures targeted at: information users, information providers, encouraging further countries to join, stakeholders for the future management of EUGRIS after EU funding.

#### State of the art

The Internet has become one of the most important sources of information A tremendous amount of information is collected and stored on the Internet about contaminated groundwater and land management. The available information on the Internet simply does not exist in a way that can be easily harvested by the full groundwater and contaminated land community. It is scattered over many web sites and sources, whose provenance and reliability may be unclear. Coverage for a particular information requirement may not be complete. The information offered is often not placed in a context, in particular, it may not be well explained for those who are either new to contaminated land management, nor for key stakeholders who are not technical experts on contaminated land, for instance many site owners, the financial community and insurers.

As a labour saving device for both basic and applied research, as well as technology, policy and regulatory development in general. This one stop shop for European information will be a big step forward. Such a structured comprehensive European gateway does not yet exist for contaminated land, groundwater, nor for waste management nor many other environmental sectors. EUGRIS can be an example to Europe's wider environmental research and business communities.

#### Advancing the State of the Art

EUGRIS' will allow all stakeholders equal access to reliable and quality contaminated land and groundwater information from a single point of access: a one stop shop. Its key advances are listed below.

Networks like NICOLE and CLARINET have begun the process of collating information sources on the Internet, and providing general information and support, this has been a welcome development. Yet the volume of information generated by regulators, academe, companies, research institutions and others in Europe is rapidly growing. Unfortunately, this European information is less visible.

#EUGRIS will provide a guided, scaleable and holistic approach to providing information

#EUGRIS will provide a linkage of networks and national initiatives to a central European "hub"

#EUGRIS will provide a research management tool

One of the major activities of EUGRIS will be the collation of data on national as well as EU research programmes. EUGRIS will

#provide a means for researchers to deliver and obtain information on research findings

#provide a base for funding institutions to decide about future research programmes at European level

#offer end users high-quality links to new developments and a quick feed-back to the research community.

offer a balanced overview on distance education, workshops etc. offered by leading research institutions which today are part of the dissemination strategy for any major national or international research project.

#### **Project Work Plan**

The work of EUGRIS consists of three broad components, the design of the information system, the development of its software implementation, and the population of the system with information. The information system design can be divided into two main packages of work: the design of templates, which are distinct web pages structuring specific information and providing further guidance through to the ultimately sought information by clear route navigators, quick search facilities, and the design of the digests. These digests will be carefully compiled and drafted summaries of specific information prepared by EUGRIS experts en-rolled for the purpose. Templates will be proposed by the EUGRIS project team, but will be offered for debate at workshops. Stakeholder networks will be invited to contribute digests, and will be offered digest drafts for peer review.

The data interface of the system to its users is of course the Internet, i.e. the EUGRIS-WWW site.

Information management will be based on two features: gateway structure and templates. EUGRIS will be the EU portal for national gateways, i.e. the central entry point – the hub of the system. All national gateways will have identical structure based on well-defined templates (e.g. site structure, descriptors, etc.; see below). Therefore, EUGRIS can grow to an EU portal as a flexible and open system.

Information	Gateway Tool Box	Information Exchange
Issues	Customisation	Data handling
Contaminated Land Groundwater Protection Landfills/ waste dumps	Registration Logbook Set level of detail	link maintenance update routines for new informa- tion and data PO box for new incoming data and information
Scope	Help	News / mail lists
Site Characterisation Investigation Behaviours and Fate of Contaminants Risk Management and Communication Remedial Technologies & -strategies Monitoring & Efficiency Control Decision Making Sustainability aspects Socio-economic aspects	Context Sensitive Help Add Information Glossary Contact Us	E Research projects – latest info
Resources	Internal Search Functions	Brokerage
Guidance & Regulations Technical books & reports Standards EU and National projects Research & Case Studies Decision support tools Networks & Events Discussion groups Education & training	Site Map and Library	Interactive web boards Partner finding Conference notices Researcher posts offered New programme opportunities
Country	Communication Tools	
EU overall Pilot countries Pilot Accession country	(See next column)	Country, Networks and Concerted Actions Zone,

Tab. 1: Initial Starting Point for Information System and Template Organisation

EUGRIS will be able to support education and training functions. These will in fact be integrated with the series of digests already discussed, but will also be accessible via specific training and education templates or windows. Table 1 illustrates a possible information system structure that might be used as a starting point for EUGRIS.

The software implementation of EUGRIS is managed as a single work package encompassing both the design of web pages and linkages, based on the information system and its templates, and the associated databases, going on throughout the project. Two broad classes of data will need to be stored: data which identifies where source material is located elsewhere on the web (meta-data), and data stored within EUGRIS itself.

The population of the database with information will be managed as a two workpackages, but with component parts. It includes two broad areas of activity: the collation and review of information sources and the preparation of information digests written from national, stakeholder and technical perspectives, as described previously. The component parts have been organised as activities by country. A further work package relates to the collection of information from EU and stakeholder network sources.

A specific work package includes the promotion of EUGRIS, the collation of peer review comments and other inputs from national agencies, DG Research and stakeholder networks and the encouragement of further countries to join EUGRIS, once a working system has been established. A key function of this workpackage will be dedicated to an External Advisory Group (EAG). This group will support defining and fine tuning the approach:

#Does EUGRIS provide proper, far-reaching and reasonable information ?

#Does EUGRIS provide valid data?

#Is EUGRIS usable and is the interface user friendly?

The EAG will be formed in the first three months of the project and consist of relevant stakeholder groups, such as regulators, industry and researchers.

The development of a detailed management/business plan for the future maintenance and expansion of EUGRIS is a critical part of this project that underpins the development of a fully operational implementation of EUGRIS. This activity has therefore been proposed as a discrete Work Package. This includes mainly the Identification of independent organisations willing to manage and maintain EUGRIS and its national nodes after the funding period. A further balance that needs to be struck is to find a management plan that demonstrates the value of EUGRIS to the groundwater and contaminated land community, and the value of the original EC investment. Revenue generation from EUGRIS services is a very visible means of providing this reassurance. However, this also has to be set against the amount of time that a EUGRUS service needs to exist to gain critical mass and credibility. Hence EUGRIS is very much a pre-commercial stage.

#### Contact

Jörg Frauenstein Dep. Contaminated Land Federal Environmental Agency Bismarckplatz 1 D- 14193 Berlin, Germany Tel.: +49 30 8903 2005, Fax.: +49 30 8903 2103 joerg.frauenstein@uba.de

# INTEGRATED SOIL AND WATER PROTECTION: RISKS FROM DIFFUSE POLLUTION

Project SOWA Integrated Soil and Water Protection from Diffuse Pollution

Authors P. Grathwohl and D. Halm, University of Tübingen, Center for Applied Geoscience, Germany

Keywords Sustainable developmen, soil and water protection, management

#### Abstract

This Accompanying Measure aims to integrate soil and water protection issues in Europe by bringing together all disciplines involved in environmental research and policy making, which deal with diffuse pollution and behaviour of pollutants in soils, sediments, and adjacent environmental compartments such as groundwater. SOWA provides a multidisciplinary forum for the identification of research needs and 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 developed in the 5th Framework Program such as sensors and magnetic proxies for soils and sediments are identified and evaluated.

#### 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. Facts available so far show that 1) many manmade compounds are persistent, bioactive and accumulative in the environment, 2) some already exceed environmental standards in soils and water bodies at a regional scale and 3) many accumulate continuously in soils and sediments, which finally become secondary contaminant source affecting future generations. Experience shows that large scale remediation of land is economically not feasible and that soil contamination is not reversible at a reasonably time scale. The motivation of the SOWA consortium is therefore 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. If soil is not protected and if pollutants continuously accumulate, then thresholds for storage and buffering finally will be exceeded bearing not only the risk of groundwater pollution but also of sudden contaminant release into the environment ("chemical time bombs").



Fig. 1: The water cycle: Soils can act as source (if accumulation of pollutants exceeds the "critical load") and a sink for pollutants (because of the filter, retention and transformation functions of good quality soils).

#### **Scientific Objectives and Approach**

SOWA's objective is to pull together the critical mass needed in order to integrate available and emerging scientific knowledge from various disciplines such as soil sciences, soil chemistry, soil physics, hydrogeology, water resources, agriculture, atmospheric deposition of pollutants, environmental analysis and engineering, management and remediation of contaminated soil and groundwater. SOWA addresses the lack in awareness of the risks of diffuse soil pollution, the need for the development of monitoring tools and intends to bridge the wide gaps by integrating soil and water related research, regulation and policy making throughout the EU.

#### Methodology

The work is divided into two sequences. A first sequence includes the work to be carried out by 5 thematic working groups:

- (1) Inventory: Identification of priority compound classes (persistent organic pollutants (POPs) and heavy metals).
- (2) Tools: Pollutant analysis and environmental monitoring.
- (3) Processes: Leaching and contaminant transport in soils.
- (4) Scale issues: Diffuse contamination.
- (5) Management and remediation of contaminated soil and groundwater.

Each of the working groups will cover the most relevant issues, which have to be considered under the aspect of integrated soil and water protection. All partners will strongly interact one to another in the working groups. The second sequence integrates the results of all thematic groups, which will be discussed and evaluated 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 document. Sequence 2 contains the strategic (disseminative / communicative) work, which will provide the internal transfer of knowledge and information within SOWA and the external transfer to the relevant end-users and groups of interest. A structured series of workshops and technical meetings will be organised in order to bring together and to provide a platform for researchers of different disciplines as well as for regulators, policy makers and industry.

As a new, until now 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 will 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 within the water cycle probably leading to an affect or a damage of ecological and socio-economic soil functions. The motivation of the SOWA consortium 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. If soil is not protected and if pollutants continuously accumulate, then thresholds for storage and buffering finally will be exceeded bearing not only the risk of groundwater pollution but also of sudden contaminant release into the environment ("chemical time bombs").

#### **Expected Impacts**

SOWA's major task is the early recognition of the risk of 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 will impact regulations, strategies and policies concerning the implementation of monitoring programs and related protocols on soil and water quality. It will help to streamline and harmonise environmental monitoring and spatial planning tools and policies, and advance an EU-wide soil protection policy. SOWA is in full compliance with the EU goals on sustainable development and the European citizens will benefit from it by maintaining or improving the safety of natural resources, the quality of life and finally health.

#### Contact

Prof. Dr. Peter Grathwohl University of Tübingen, Center for Applied Geoscience Sigwartstrasse 10, Tübingen, Germany Phone: +49-7071-2975429, Fax: +49-7071-5059, Email: grathwohl@uni-tuebingen.de

# INVESTIGATION OF SUBSURFACE CONTAMINATION USING AN INTEGRAL APPROACH

Project INCORE (Integrated Concept for Groundwater Remediation)

Author Th. Ptak, University of Tübingen, Center for Applied Geoscience, Germany

Keywords Groundwater pollution, urban industrial areas, site investigation, integral assessment of groundwater contamination, revitalization in urban industrial areas, complex contamination patterns, remediation

#### Abstract

At most contaminated sites pollutant hot spots with positions not exactly known, as well as aquifer heterogeneity cause an irregular distribution of contaminants in groundwater. Many monitoring wells would be needed to reliably determine the concentration distribution downstream of the pollutant source zone based on point scale measurements. Therefore, a new approach to contaminated land assessment and revitalisation, focusing on groundwater quality and complex contamination patterns, which are typical for urban industrial megasites in many European cities, was developed. The new approach comprises three cycles: (a) the assessment of groundwater contamination using an innovative integral mass flow rate 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.

#### 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. The characterisation of contaminant plumes in groundwater and source zone locations is essential for decisions about future land use at such contaminated sites, and for choosing appropriate remediation measures. The basic problem of the characterisation is that at many contaminated sites 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. In such situations, standard subsurface investigation procedures based on interpolation of point-scale concentration measurements 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, new technical and administrative tools, considering uncertainties of investigation and of assessment results, are being developed, tested and implemented within the INCORE project 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.



Fig. 1: The cyclic approach to contaminated land assessment and revitalization in urban industrial areas

#### 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.

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.

#### Cycle I, integral groundwater investigation

The basic idea of the integral groundwater investigation method (Teutsch et al., 2000; Ptak et al., 2000; Ptak and Teutsch, 2000; Bockelmann et al., 2001) is to cover a whole crosssection of a contaminant plume downstream of a pollutant source, employing pumping tests with multiple contaminant concentration measurements at the pumping wells (Fig. 2). 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. As there is no need to interpolate point scale concentration measurements, a high level of certainty can be expected for the investigation results.

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.



*Fig. 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.

#### 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. 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 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.

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. 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 (e.g. Schiedek et al., 1997) 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.


Fig. 3: Predicted zones delimiting contaminant source, and zones absent of source, example of application in the Neckar Valley in Stuttgart for benzene and CHC (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.

#### 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 situated 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.



Fig. 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.

#### 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.



Fig. 5: Examples of possible remediation scenarios in the Neckar Valley in Stuttgart (Ertel, 2002)

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#### Contact

Thomas Ptak University of Tübingen, Center for Applied Geoscience Sigwartstrasse 10, D-72076 Tübingen, Germany Tel.: +49-7071-2975238, Fax: +49-7071-5059, E-mail: thomas.ptak@uni-tuebingen.de

## DEVELOPMENT OF AN INTEGRATED MANAGEMENT SYSTEM FOR PREVENTION AND REDUCTION OF POLLUTION OF WATERBODIES AT CONTAMINATED INDUSTRIAL MEGASITES

- Project WELCOME Water, Environment, Landscape Management at Contaminated Megasites
- Authors H. Rijnaarts and C. Wolfgang, TNO Environment, Energy and Process Innovation, Apeldoorn, NL
- Keywords Megasite, contamination, water quality, integrated management system

#### 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 groundwater 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.

#### 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 "learning 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<sup>2</sup> 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.

#### **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.

#### 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.

# Organochemical Industry Complex along the Middle Area of a River in Bitter-feld/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<sup>2</sup> 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.

#### 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<sup>3</sup> of wastes were deposited on the 30 ha site, such as barium, arsenic and strontium compounds.

#### 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.

#### **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 (Fig. 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.



Fig. 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

#### **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?

- #Not focused on a total cleanup of all wastes completely
- #One that promotes cost efficient and timely solutions
- #A clear and structured process but one with flexibility
- #A decision making tool which is site appropriate, positive in its response, and simple
- #Helps with effective data gathering
- $\notin$ Incorporates boundary conditions and targets
- #A process that can be applied to any megasite
- #One that helps solve the issues at the "megasite" scale
- #Helps with the site's ability to answer to the public
- #Natural attenuation feasibility incorporated
- #Helps with locational knowledge (to answer questions about specific areas when needed)
- #Easily embedded into the management system in place already
- ∉#Helps to increase human health
- #Offers a comparison of remediation measures that show risk reduction, are cost efficient and have environmental merit.

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.

#### **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.



Fig. 2: The Four Sections of the IMS

These 4 sections can be seen in Fig. 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 Fig. 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 (Fig. 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.

#### **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 trialed 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

#### Contact

Huub Rijnaarts TNO-MEP, Dept. of Environmental Biotechnology PO Box 342, Apeldoorn 7300 AH - The Netherlands Phone: +31 55 549 34 93, Fax: +31 55 549 34 93 Email: h.h.m.rijnaarts@mep.tno.nl

# SESSION 3: CHALLENGES IN URBAN AREAS

Chairman: Thomas Ertel, Umweltwirtschaft (DE)

# SUMMARY

The session "Challenges in Urban Areas" included presentations of projects referring to specific urban problems of contaminated land and groundwater management. Two major topics were addressed, namely urban groundwater management and redevelopment of urban derelict sites (brownfields).

The first two presented projects are members of a research cluster called "City Net" – The network of European research projects on integrated urban water management and were both presented by **Matthias Eiswirth** of Karlsruhe University. In his first presentation "Assessing and Improving Sustainability of Urban Water Resources and Systems – AISUWRS" the key pathways of urban water were illustrated, key pollutants in urban waters, the frequency of their occurrence and major objectives to quality and quantity or urban waters according to their different purposes. Key part of the project is to understand sources of contamination, their flowpaths, sinks and quantification of contaminant loads. The overall objective of the project is to develop a system to quantify and manage unsustainable urban water systems and assess the impact of pollution on the underlying groundwater resources. Furthermore, AISUWRS aims to develop a GIS supported urban groundwater vulnerability assessment systems. The achievements of system development are currently tested in four urban areas three of which in EU countries and one in Australia.

The second project "Assessing Infiltration and Exfiltration on the performance of Urban Sewer Systems – APUSS" focuses on urban sewing systems, in particular infiltration of groundwater to sewing systems which reduces the efficiency of treatment plants and exfiltration of sewing systems to groundwater which impairs groundwater quality. On a long term basis both effects are critical for sustainable urban water management and bear considerable economic consequences for cities and sewer system operators. Based on tracers new methods and techniques to assess and quantify infiltration and exfiltration in sewer systems are being developed and are being tested at different scales (i.e. from the single pipe to the whole catchment) and under different conditions. The final part of the project includes the development of decision support tools to help end users to assess their performance of their sewer systems and to choose the right investment strategies.

The next two presentations focused on brownfield redevelopment and were both given by **Paul Nathanail**. In his first presentation the project RESCUE (Regeneration of European Sites in Cities and Urban Environments) was presented. Overall objective of the project is to raise the standard in brownfield regeneration projects by reducing costs of land rehabilitation on the one hand and reducing Greenfield development on the other hand. Among others major components are the development of an analytical sustainability framework and the analysis of current practice in brownfield redevelopment. Furthermore, the project includes practical implementations of derived achievements in four countries. The second presentation concerned the project CABERNET (Concerted Action on Brownfield and Economic Regeneration Project). The project aims to integrate a broad stakeholder spectrum and to integrate their perspectives in finding common agreements. The network is focusing on four key objectives: (i) improving awareness and enhancing understanding across the professional disciplines; (ii) developing a conceptual model for brownfield issues; (iii) identifying research

gaps and proposing coordinated research activities; and (iv) identifying best practice approaches and tools for practitioners. Expected impacts of this initiative are better awareness, a conceptual model for brownfield issues, Coordinated research activities, and identification of best practice approaches.

Martin Schamann, Federal Environment Agency – Austria

## ASSESSING AND IMPROVING SUSTAINABILITY OF URBAN WATER RESOURCES AND SYSTEMS

- Project AISUWRS, Assessing and Improving Sustainability of Urban Water Resources and Systems
- Authors M. Eiswirth<sup>1</sup>, H. Hötzl<sup>1</sup>, A. Cronin<sup>2</sup>, B. Morris<sup>3</sup>, M. Veseli<sup>4</sup>, R. Bufler<sup>5</sup>, S. Burn<sup>6</sup> & P. Dillon<sup>6</sup>
  - <sup>1</sup> Department of Applied Geology (AGK), University of Karlsruhe, Germany
  - <sup>2</sup> Robens Centre for Public and Environmental Health (RCPEH), University of Surrey, UK
  - <sup>3</sup> British Geological Survey (BGS), UK
  - <sup>4</sup> Institute for Mining, Geotechnology and Environment (IRGO), Slovenia
  - <sup>5</sup> GKW Consult (GKW), Germany
  - <sup>6</sup> Commonwealth Scientific Industrial Research Organisation (CSIRO), Australia

Keywords Urban water resources, groundwater, sustainability

#### Abstract

The overall scope of the AISUWRS project is to assess and improve the sustainability of urban water resources and systems with the help of computer tools. The project will analyse a range of existing urban water supply and disposal scenarios by demonstrating how each scenario differs in its handling of contaminants. The sources of contaminants, their flow paths and the sinks will be identified for different urban areas and a quantification of the contaminant loads undertaken. The impact of these contaminant loads on their capability to contaminate groundwater will be estimated. For the verification and validation of the model, de-tailed field studies will be carried out in 4 case study cities. In addition AISUWRS aims to develop a management and Decision Support System that will make use of innovative pipeline and urban water system assessment procedures to deliver detailed guidelines and recommendations for the safeguarding and protection of urban water resources.

#### Introduction

With over 40 % of the water supply of Western & Eastern Europe and the Mediterranean region coming from urban aquifers, efficient and cost effective management tools for this resource are essential to maintain the quality of life. Traditional water planning regularly concludes that future water demands will inexorably rise and eventually exceed water supplies available in any given location. However, the increasing concerns about the environmental impacts of water projects and their increasing economic costs mean that traditional planning concepts, which assume unlimited supplies of potable water, must be questioned. This includes the source of the water supplies and its appropriate use. With population densities increasing in urban areas and constraints on funding, it is becoming increasingly evident that the present management of urban water resources and systems will not be suitable models for service provision into the 21st century and that increased emphasis will be placed upon the use of groundwater reserves. Without an adequate knowledge base of the current status of urban water resources, and an understanding of the processes involved, the health and safety of the people who depend on urban groundwater as drinking water can not be assured. Therefore the AISUWRS initiative will provide assessment and modelling tools for planning of any alternative approaches for sustainable urban water systems and thus minimise the impact of pollution on the underlying urban groundwater resources. The AISUWRS project is member of the cluster CityNet – The network of European research projects on integrated urban water management.

#### Scientific/Technical Objectives and innovation

#### **General Concept**

In spite of strong efforts initiated by the European Union and other international organisations in the past 20 years, groundwater pollution from industry, traffic, sewers and agriculture is still very high. The complex transport processes of groundwater flow are responsible for the wide distribution of recharged water and contaminants. There is evidence that urban downstream aquifers are contaminated by inorganic, organic and microbial pollution. Special attention is therefore given in this project to urban aquifers: They are particularly vulnerable, but very important in many regions of Europe. Indeed, in many regions they are the only natural resources for drinking water supply.

Alternative approaches to the provision of urban water services do exist, but they have not been thoroughly investigated because of a reluctance to experiment with any system that could in any way compromise human health. With population densities increasing particularly in urban areas and the corresponding constraints on funding, it is becoming increasingly evident that present urban water systems will not be suitable models for service provision into the 21st century. The overall objective of the AISUWRS initiative is to develop an innovative system to quantify and manage the problems from unsustainable urban water systems and as-sess the impact of pollution on the underlying groundwater resources (Fig. 1).



Fig.1: The principal structure of the AISUWRS initiative

The overall scope of the AISUWRS initiative is to assess and improve the sustainability of selected urban water systems with the help of computer tools. Parts of these model tools have been already developed to estimate the water flows and contaminant loads within the urban water system. This model represents water and contaminant flows through the existing water, wastewater and stormwater systems, from source to discharge point and have already been applied successfully in selected areas in Australia and Germany.

#### Objectives

The European Water Framework Directive demands good water quality in aquifers and in areas with a dynamic exchange between ground- and surface water. Urban pollutants such as nitrogen-, sulphur- and VOC-compounds not only endanger the drinking water supply, they also form a hazard to the ecological integrity of surface- and groundwaters in sensitive areas. One important objective of the AISUWRS initiative is the analysis of a range of existing urban water supply and disposal scenarios by demonstrating how each scenario differs in its handling of contaminants within different urban water systems (background study and data analysis using GIS-systems). The assessment of sustainability of existing urban water systems requires that the sources of contaminants, their flow paths (and volumes e.g. UFW, recharge from leakage etc) and the sinks must be identified for different urban areas, and that quantification of the contaminant loads (e.g. sewage exfiltration, water losses etc) is undertaken (Urban water and contamination model validation and calibration). The first goal of AISUWRS is to deliver an innovative monitoring tool based on selected trace substances, which have to be measured regularly both in the urban water network (drinking water, stormwater, wastewater) and in the groundwater areas which are known to be sensitive to pollution.

The results obtained in a first investigation stage (field investigations) should allow the introduction, further development and validation of the model in three different European case study cities in the second stage, with the local partners in support. In the third stage a single decision-support system structure, possibly with minor modifications to suit local case-study conditions will be developed. With this inovative urban water and contaminant balance model different scenarios will be analysed and assessed in order to plan more sustainable urban water systems (European and global aspect). For the evaluation and interpretation of the analytical data with regard to risk assessment and resource protection strategies, the data will be referenced in relation to the vulnerability of the aquifer. The second main goal of AISUWRS is therefore to develop an advanced GIS-supported urban groundwater vulnerability assessment system. It will be based on the intrinsic components of the regional system including the climatic, hydrologic and geological conditions. It will be developed for the particularly sensitive urban areas and later on can be transferred to other aquifer systems. While some of these conditions may be specific to the selected case study cities, it is expected that the overall approach and methodologies used in AISUWRS will be directly transferable to other European urban regions. For the verification and validation of the urban water and contaminant balance model as well as of the vulnerability assessment system, detailed field studies will be carried out under natural urban conditions. The selected case study cities have been restricted to three in Europe and one well known comparison city in Australia. All case study cities offer climate and monitoring stations with good knowledge of the underlying aguifers.

In order to protect urban groundwater resources effectively the amount of transported pollutants should be identified and quantified at an early stage. For many urban pollution problems the time between recognition and relief measures are in the range of years or more. In recent years, surveillance has focused on surface water, with pollution of urban groundwater being neglected. To avoid the further degradation of urban aquifer systems, new **urban water**  **management tools and innovative DSS** are urgently needed. AISUWRS aims to develop such a management and DSS able to react on different time and space scales. In support of a much needed multi-disciplinary framework for the sustainable management of the water resources in urban areas, the ultimate goal of AISUWRS is to develop a DSS, both for slow groundwater degradation by urban contaminants as well as for catastrophic accidental impacts (pipelines bursts, tanker spills etc.). Indeed, it is the objective of this project to deduce and establish a DSS, that will make use of innovative pipeline assessment systems and an advanced, new urban water system assessment scheme. This support framework will be delivered together with detailed guidelines and recommendations for the safeguarding and protection of urban groundwater resources from urban pollution.

#### Innovation

The overall scope of the AISUWRS initiative is to assess and **improve the sustainability of urban water systems** with the help of computer tools. Parts of these model tools have been already developed to estimate the water flows and contaminant loads within the urban water system. This model represents water and contaminant flows through the existing water, wastewater and stormwater systems, from source to discharge point and has already been applied successfully in selected areas in Australia and Germany. Bulk water supply is considered an input into the urban water system. Groundwater aquifers that underlie an urban area are also included in the urban water system since they play a role in the supply and disposal of water within urban areas.



*Fig. 2: Model concept of the combined urban water model* 

In the urban water and contaminant balance model called UVQ (<u>Urban Volume and Quality</u>) the system boundaries for contaminant flows are the same with the exception of contaminant flows to groundwater. Flows of contaminants to the groundwater are not considered in the existing model but will be implemented (by integrating unsaturated flow and transport models with UVQ). The complexity of interactions between contaminants and soils require detailed descriptions of each site (field investigations). The potential loads from different urban contaminant sources (sewer leakages, stormwater overflow etc.) will then be available for further modelling with a geographic information system (GIS) and a groundwater model in order to **simulate contaminant flows to the urban groundwater** (Fig. 2).

The objective of the AISUWRS initiative is to build upon and further develop the concepts of Australia's urban water program (UWP) to identify and develop systems and technologies, integrative processes and tools of analysis, which are commercially valuable, scientifically robust and which improve the cost effectiveness of urban water services, in line with the project's vision of ecological sustainability. The existing conceptual urban water and contaminant balance model represents water and contaminant flows through the existing urban water, wastewater and stormwater systems, from source to discharge point.

The actual model includes the leakage of water mains as well as in/exfiltration from the wastewater drainage. The contaminant balance of this model has the advantage of directly representing the way in which alterations in the water delivery and disposal routes affect the movement and distribution of contaminants in the urban environment. Consequently this model will enable **analysis of alternate urban water system scenarios** and view their corresponding effects on surface, soil and groundwater contamination.

A number of procedures can be undertaken to reduce leakage in both sewers and water supply systems. Within the AISUWRS initiative analysis of alternative urban water systems and related costs will be carried out for different scenarios. For water reticulations pipelines, either rehabilitation can be undertaken or pressure management techniques instigated. Pressure management can be a very cost-effective means of reducing losses or controlling demand for many utilities, with a wide diversity of conditions.

If the state of the urban water system is known, e.g. by advanced leakage detection, decisions on how to operate asset management schemes and whether to undertake maintenance, repair or replacement can be made. Existing **decision support systems** (DSS) to evaluate replacement or preventive maintenance priorities for sewers and water mains do not necessarily address the issue of selection of the repair/replacement technology to combat the problem of pipe leakage. It is widely recognised that true asset management requires a balance between risk and planning and it is essential to develop a decision support system for rehabilitation that will support rational and objective comparisons between the engineering, cost and social benefits of each technique. Existing DSS models need to be expanded to allow operational and rehabilitation procedures to be analysed. For this reason, a decision-support system that allows selection of rehabilitation techniques incorporating wholelife-costing methodologies, to assess the viability of each selection decision, will be developed and implemented into the innovative urban water model within the AISUWRS initiative.

There is a growing interest throughout the world in studying the sustainability aspects of water management. It is clear that the social, economic and institutional dimensions of water problems are often the cause of severe deadlocks. Nevertheless, much more attention has been paid so far to the purely technological problems of water management. In fact, comparative studies on the sustainability of the whole urban water system are still not frequent, yet they can provide a good insight into the aspects that are specific for each country and common to all countries. It is clear nowadays that solving water problems requires not only adequate technologies but also a insight in the social, economic, legal and institutional dimensions of

the water problems. In the AISUWRS initiative these dimensions will be investigated and analysed comparing the different approaches in various countries.

The AISUWRS initiative will be one important step towards identifying and developing systems and technologies that could improve the cost effectiveness of urban water services whilst maintaining ecological sustainability.

#### Contact

PD Dr. habil Matthias Eiswirth Karlsruhe University (TH), Department of Applied Geology Kaiserstr. 12, 76128 Karlsruhe Phone: ++49 721 608 7368 ; Fax: ++49 721 608 7372 ; E-mail: eiswirth@agk.uka.de

# ASSESSING INFILTRATION AND EXFILTRATION ON THE PERFORMANCE OF URBAN SEWER SYSTEMS

- Project APUSS, Assessing Infiltration and Exfiltration on the Performance of Urban Sewer Systems
- Authors J.L. Bertrand-Krajewski, INSA de Lyon, URGC Urban Hydrology Laboratory, France
- Keywords Urban sewer systems, performance, infiltration, exfiltration, tracer

#### Abstract

Sewer systems constitute a very significant patrimony in European cities. Their structural quality and functional efficiency are key parameters to guarantee the transfer of domestic and trade wastewater to treatment plants without infiltration nor exfiltration. Infiltration of groundwater is particularly detrimental to treatment plant efficiency, while exfiltration of wastewater can lead to groundwater contamination. Both problems are critical on a long term basis for sustainable urban water management. The APUSS project, associating universities, SMEs and municipalities in 7 European countries, will develop new methods and techniques to assess and quantify infiltration and exfiltration in sewer systems. The methods will be tested and validated in different catchments. Associated models and tools will be proposed for scaling up and for application and enduser decision support. The APUSS project is also part of the European cluster CityNet dealing with Integrated Urban Water Management.

#### Introduction

Urban sewer systems (USS) constitute a very significant patrimony in European cities. Their structural quality and functional efficiency are key parameters to guarantee the transfer of domestic and trade wastewater to treatment plants without infiltration nor exfiltration. Infiltration of groundwater is particularly detrimental to treatment plant efficiency (hydraulic overloading due to the infiltrated volume of water which can reach up to 100 % of the wastewater volume in some cities, dilution of pollutant concentrations leads to a lower pollutant removal efficiency), while exfiltration of wastewater can lead to groundwater contamination (especially where groundwater is a water resource for drinking water production). Both problems are critical on a long term basis for sustainable urban water management and have important economic consequences for cities and sewer systems operators through the EU (Rieckermann 2000, Ellis and Revitt 2002, Neitzke 2002).

The European standard EN 7522 indicates basic performance criteria applicable to any sewer system. Among these criteria, the two following ones are especially relevant:

#receiving waters should be protected against pollution;

#the structural integrity of urban sewer systems (USS), including water tightness, should be guaranteed.

In order to evaluate the performance of USS, public and private operators need appropriate methods and techniques. The APUSS project (2001–2004), associating universities, SMEs and municipalities in 7 European countries, is developing new methods and techniques based on tracers (chemicals and/or natural radioisotopes) to assess and to quantify infiltration and exfiltration (I/E) in sewer systems, at different space scales (from the single pipe to the whole catchment) and under different conditions (steady and dynamic groundwater levels, seasonal effects, etc.). The new methods will be tested and validated in different catchments chosen in the associated cities, under various conditions, and compared to more traditional approaches based e.g. only on flow rate measurements or on large scale water mass balance. Associated models (based on conceptual approaches for both steady and dynamic groundwater conditions) and tools (GIS and data management software) will be proposed for scaling up and for application and enduser decision support.

Complementary objectives are to develop decision support to help end users to assess the performance of their sewer systems and to choose investment strategies accounting for economic value and necessary data.

The work is organised in three work areas involving ten European partners:

#INSA de Lyon (France, co-ordinator)

∉#EAWAG (Switzerland)

#Dresden University of Technology (Germany)

#Czech Technical University in Prague (Czech Republic)

∉#DHI Hydroinform a.s. (Czech Republic)

∉#Hydroprojekt a.s. (Czech Republic)

#Middlesex University (United Kingdom)

#LNEC - National Laboratory for Civil Engineering (Portugal)

∉#Emschergenossenschaft (Germany)

∉ IRSA-CNR (Italy).

#### Work Area 1: Methods

Traditionally, the assessment of I/E in sewer systems is typically based on rather inaccurate methods of flow measurement, analysis of diurnal flow and load variation and balancing of water in- and output. The APUSS project will provide methods allowing to differentiate sewer zones with infiltration and exfiltration, based on limited analytical effort and with little environmental risk. By optimising the design of the experiments and the analysis of the resulting data, it is expected that a high degree of accuracy will be achieved.

Work Area 1 includes the development, testing and validation of methods to accurately quantify:

∉#exfiltration from long sewer pipes;

∉#infiltration into sewer systems;

# the interaction of sewer sediments with chemical tracers used in the two above quantification methods;

#infiltration and exfiltration from house connections.

The methods are based on selected chemicals and natural isotopic tracers and will be validated under various operational conditions during dry weather. Field and laboratory tests together with sewer inspections will be the basis of this development which will workup innovative procedures to facilitate routine end user practice.

At the end of 2002, standard pollutants measurements and natural isotopes (18O2) have been tested to evaluate infiltration (de Benedittis 2002). Sodium chloride and fluorescent dyes (fluorescein, Rhodamines) have been tested with specifically designed experimental protocols and data processing methods to evaluate exfiltration (Ellis et al. 2002, Rieckermann and Gujer 2002). Measurements with flowmeters (de Benedittis 2003) and balloons (Roessiger et al. 2002) have also been investigated in sewer pipes. Laboratory and field tests have been undertaken in order to investigate I/E linked to house connections and to propose operational experimental protocols (Kohout 2002, Princ 2002). For all methods, a special effort is devoted to evaluate measurement uncertainties.

After preliminary tests carried out since 2001, a second phase will start in 2003 during which extended tests of these methods will be undertaken at different selected experimental sites, in collaboration with end users associated with the APUSS project.

#### Work Area 2: Models and scaling-up

By developing conceptual models related to single sewers and a scale-up procedure, the new methods and techniques to measure I/E developed in Work Area 1 will be made utilisable to estimate the rates of an entire catchment. As on the one hand the integration should be possible with only few measurements for economic reasons and on the other hand accuracy is higher with more measurements, the scale-up procedure will include recommendations on where to measure and the tool of uncertainty analysis.

Work Area 2 comprises the identification and development of conceptual models for I/E at both pipe scale and catchment scale, based on relationships to be identified between I/E rates and the structural state of the sewers (de Benedittis 2001, Rutsch and Krebs 2002). Experimental sites in some cities where end users are associated with the APUSS project will be used to establish and to validate the models. Specific software will also be developed in order to manage and to visualise data, to share information and data between partners, and to be used as basic support for model implementation. Despite the difficulty of its evaluation at catchment scale, the contribution of house connections to I/E is also studied and should be accounted for in models as much as possible.

#### Work Area 3: Application and decision support

Municipalities have to decide investment strategies to rehabilitate and upgrade efficiency and quality of their sewer systems. Frequently, such decisions are based on limited information and do not consider simultaneously the sewer pipes, the wastewater treatment plant and the environment, especially groundwater. One of the objectives of the APUSS project is to provide end users with an integrated decision support that takes into account I/E rates, impacts on wastewater treatment plant and the economic value, and facilitates the comparison of different strategies. Working with associated end users will ensure the quality and the real applicability of the proposed tools.

Work Area 3 comprises:

- #application of the methods and the models in collaboration with the end users associated with the project, in order to identify data requirements and to assess their applicability and to improve the proposed tools;
- #the establishment of a global performance indicator of the whole sewer system, including wastewater treatment plants (Cardoso et al. 2002);
- #proposal of investment strategies based on infiltration and exfiltration criteria by taking into account the economic value of the sewer systems.

#### **APUSS and CityNet**

Sewer systems are only one part of urban water systems, which also include overflow structures, treatment plants and receiving surface and ground waters, in possible connection with drinking water resources. Only integrated approaches, at both research and operational levels, will allow to progress towards a sustainable urban water management and to reach the objectives of the European Water Framework Directive.

In order to contribute to such a necessary integrated approach, CityNet, a cluster of 6 European projects within the 5th Framework Programme, has been created and launched on February 2003. CityNet includes the following six projects: CARE-W (Computer aided rehabilitation of water networks), CARE-S (Computer aided rehabilitation of sewer networks), Day-Water (Adaptative decision support system for the integration of stormwater source control into sustainable urban water management strategies), AISUWRS (Assessing and improving sustainability of urban water resources and systems), CD4WC (Cost-effective development of urban wastewater systems for water framework directive compliance) and APUSS, and has also links with other research projects dealing with or contributing to an integrated management of urban water systems.

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#### Contact

Dr. Ing. Jean-Luc BERTRAND-KRAJEWSKI INSA de Lyon, URGC - Hydrologie Urbaine 34 avenue des Arts, 69621 VILLEURBANNE cedex, France Phone: +33 4 72 43 81 80, Fax: +33 4 72 43 85 21, Email: jlbk@urgc-hu.insa-lyon.fr APUSS website: http://www.insa-lyon.fr/Laboratoires/URGC-HU/apuss/ CityNet website: http://www2.unife.it/care-w/citynet1.html

### **REGENERATION OF SITES IN CITIES AND URBAN ENVIRONMENTS**

Project RESCUE, Regeneration of Sites in Cities and Urban Environments
Author P. Nathanail, University of Nottingham (UK)
Keywords Brownfield, land reclamation, contamination, sustainability, indicators

#### Abstract

The underlying principle for RESCUE is the development of a precise definition of sustainability in terms of criteria and indicators related to urban planning and brownfield regeneration. Based on the analysis and evaluation of current practice in industrial core regions in France (Nord-Pas de Calais), United Kingdom (Derbyshire, North-East of England), Poland (Silesia) and Germany (Ruhr Area, Southern District of Leipzig), RESCUE distils best practice approaches at reduced costs and integrates its results into a holistic system approach containing new methodologies, procedures and instruments for a sustainable regeneration of European industrial brownfield sites. The results will be integrated into a Manual of a European System Approach for Sustainable Brownfield Regeneration. This Manual will provide both scientifically and practically tested guidance and substantial decision making tools for stakeholders, public administration and financial funding bodies. The checklists, performance indicators, evaluation criteria, examples of best practice etc. generated in RESCUE will be disseminated throughout the European Community and the EU Accession States to scientific networks and practical end users such as real estate owners, planners, architects, engineers, public entities and public and private financiers. Moreover, the results aim at supporting the formulation of European policies in derelict land recycling programmes as well as future decisions about the public funding of brownfield projects.

#### Contact

Dr. Paul Nathanail University of Nottingham Land Quality Management Ltd, SChEME University Park, NG7 2RD Nottingham, UK Telephone: +44-115-951 41 82, Fax: +44-115-951 43 20 Email: paul.nathanail@nottingham.ac.uk

# THE INTERACTION BETWEEN SUSTAINABLE BROWNFIELD AND ECONOMIC REGENERATION ON SUSTAINABLE MANAGEMENT OF CONTAMINATED LAND AND GROUNDWATER IN URBAN AREAS

Project	CABERNET, Concerted Action on Brownfield and Economic Regeneration Network
Author	P. Nathanail, University of Nottingham (UK)
Keywords	Sustainable brownfield regeneration, CABERNET, contaminated land

#### Abstract

Brownfield sites, as defined by CLARINET Working Group1, may or may not be contaminated. However they require intervention in order to secure their return to beneficial use. For such a reuse to be considered to be sustainable, issues pertaining to environmental biodiversity and robustness, economic growth, social coherence and institutional arrangements have to be considered and balanced.

Perceptions suggest that groundwater is often the forgotten receptor and contaminated land the bête noir of project funders. The paper will report on CABERNET stakeholder group findings and review the appropriateness of European groundwater protection policies.

#### Contact

Dr. Paul Nathanail University of Nottingham Land Quality Management Ltd, SChEME University Park, NG7 2RD Nottingham, UK Telephone: +44-115-951 41 82, Fax: +44-115-951 43 20 Email: paul.nathanail@nottingham.ac.uk

# SESSION 4A TECHNICAL SOLUTIONS – RISK ASSESSMENT

Chairman: Peter Grathwohl, Tuebingen University (DE)

# SUMMARY

This session included three presentations with special focus on risk assessment of contaminated groundwater. The first presentation was given by **Christos Tsakiroglou** giving an overview of the project TRACE-FRACTUE (Toward an Improved Risk Assessment of the Contaminant Spreading in Fractured Underground Reservoirs). The quantification of contaminant spreading in highly fractured heterogeneous formations requires a comprehensive understanding of multiphase flow processes and descriptors characterizing the fate and behaviour of contaminants in the subsurface. Based on site-specific investigations the TRACE-FRACTURE project quantified and validated modelling results of 2D pore and 3D fracture networks. By updating a macroscopic simulator for the contaminant transport in homogeneous porous media with the obtained data set a tool was developed that enables the prediction of the short- and long-term spatial and temporal behaviour of liquid pollutants in fractured formations. The macroscopic numerical tool can be used for the cost effective mapping of contaminant distribution in both the unsaturated and saturated zones under varying scenarios of contaminantion. Also the tool allows the derivation of risk based and cost-effective remediation strategies.

The second presentation included the project GRACOS (Groundwater Risk Assessment of Contaminated Sites) and was given by **Peter Grathwohl**. The focus of the GRACOS project is development and improvement of a methodological approach for the rapid, low-cost risk assessment of subsurface soil and groundwater pollution at contaminated sites. The new developed tools allow the quantification of the mobile fraction of contaminants by determination of aqueous contaminant concentration to be expected in seepage water and groundwater including the forecast of long-term concentration changes. Pathways of concern are both the vapour phase transport in the subsurface and the contaminant transport into groundwater by leaching. The methodology development based on results from laboratory and field experiments as well as from numerical simulations. As a scenario dependent approach, the GRACOS risk assessment procedure can be applied to different situations in terms of classes/combinations of contaminants and site-specific conditions. Also it allows the a priori estimation of existing risks under given site conditions and contaminant properties.

The last presentation within this session was given by **Balázs Morvai** focusing on in-situ screening methods along the project NORISC (Network Oriented Risk Assessment by In-situ Screening of Contaminated Sites). The NORISC project objective is the development of a decision support software system that integrates new and existing methods for efficient risk assessment of contamination profiles in urban areas. The designed software consists of a compilation of existing and new developed databases and tools including in-situ measurement methods (geophysics, geochemistry, and hydrogeology), GIS based data processing, geostatistics, and modeling. Based on the decision support software system the site characterization and risk assessment process, as an approach for the revitalization of urban areas, can be standardized. Also the application of the system accelerates decision processes and minimizes the time and costs effort for investigation, remediation and site redevelopment.

Martin Bittens, Tuebingen University – Germany

# TOWARD AN IMPROVED RISK ASSESSMENT OF THE CONTAMINANT SPREADING IN FRACTURED UNDERGROUND RESERVOIRS

Project TRACE-FRACTURE, Toward an Improved Risk Assessment of the Contaminant Spreading in Fractured Underground Reservoirs

Authors

- C.D. Tsakiroglou<sup>1</sup>, M. Theodoropoulou<sup>1</sup>, P. LeThiez<sup>2</sup>, C. Laroche<sup>2</sup>, K.E. Klint<sup>3</sup>, P. Gravesen<sup>3</sup>, L. Molineli<sup>4</sup>, and F. Sanchez<sup>4</sup>
- <sup>1</sup> Institute of Chemical Engineering and High Temperature Chemical Processes – Foundation for Research and Technology Hellas, Greece
- <sup>2</sup> Institut Français du Petrole, Reservoir Engineering Department, France
- <sup>3</sup> Geological Survey of Denmark and Greenland
- <sup>4</sup> CH2M Hill Espana S.A / Environment Transport and Planning, Spain
- Keywords Fractured media, multiphase flow, hydrodynamic dispersion, contaminant transport, non-Newtonian NAPL, dual porosity, clay-till sediment, granite rock, numerical simulation, risk assessment, transport coefficients, groundwater pollution

#### Abstract

An integrated set of procedures was developed for the multi-scale characterization of two different and highly heterogeneous fractured formations: a granite rock situated in Spain (site 1) and a clay till sediment situated in Denmark (site 2). Discrete fracture network models, suitably adapted to the fracture systems prevailing in the various zones of granite (site 1) and clay till (site 2), were quantified and validated with respect to field-scale measurements of the hydraulic conductivity. Generalized non-Darcian models were derived for the 1-phase and 2-phase flow of non-Newtonian NAPLs in fractures and used for the numerical estimation of the capillary pressure and relative permeability curves of artificial glass-etched fractures with history matching. The quasi-static immiscible displacement of a wetting aqueous phase by a non-wetting NAPL was simulated in 2-D pore networks (single fractures) and 3-D fracture networks and the numerically calculated values of the multiphase effective transport coefficients of both investigated sites were validated with respect to data of core-scale experiments. Visualization hydrodynamic dispersion experiments performed on artificial fractures allowed the determination of the longitudinal and transverse dispersion coefficients as functions of Peclet number and fracture morphology, and enabled us to identify the steadystate pollutant dispersion regimes within fractures or homogeneous underground aguifers under or without the action of gravity. The macroscopic simulator of the contaminant transport in homogeneous porous media (SIMUSCOPP) was updated to dual porosity dual permeability media and the updated version was used to forecast the short- and long-term spatial and temporal evolution of liquid pollutants in both sites, under various scenarios of contamination. All data, theoretical tools and knowledge produced in the context of this or earlier projects are being integrated into the risk assessment of the two fractured and contaminated sites.

#### **Objectives and methodology**

The objectives of the project are: (1) to characterize highly heterogeneous fractured systems at multiple scales ranging from the pore-scale to reservoir; (2) to incorporate information concerning the morphology of fractures at different scales into the up-scaled macroscopic transport coefficients (e.g. relative permeability functions, dispersion coefficients, etc); (3) to integrate new knowledge into an improved numerical simulator of the contaminant transport in fractured media; (4) to use this simulator in order to assess the risks of groundwater contamination by organic pollutants for various types of fractured sites. The methodology used is shown in Fig.1. Fracture properties collected from field-scale and lab-scale analyses are used either for the fabrication of artificial experimental models or the computer-aided construction of fractures and fracture networks. Experiments and simulations performed on them allow the determination of the up-scaled effective transport coefficients applicable to the scale of a block of the numerical grid. The geological conceptual model of the fractured site is transformed to a dual porosity/dual permeability numerical model. The numerical model and up-scaled transport coefficients are fed as input to a properly updated simulator of the contaminant transport, which in turn, is used as predictive tool for the risk assessment of contaminated fractured sites.



Fig.1: Integrated methodology used in TRACE-FRACTURE project

#### **Description of technical progress**

#### Multiscale characterization of fractured sites (Work Package WP-1)

Two generic sites, representative of two very different types of fractured media, were selected. Site 1 is situated in Northwestern Spain, overlies well-exposed granite and has been contaminated by hydrocarbons. The site is highly heterogeneous and consists of four characteristic areas: fresh granite, fracture/fault zones, weathered granite, and sedimentary cover (Klint et al., 2001a; 2002a; 2002b; Rosenborn et al., 2001). Site 2 is situated in Funen Island, Denmark, and its subsurface consists of fractured clay till overlaying a primary sandy aquifer. The site was contaminated by leaking storage tanks of a creosote and asphalt factory (1930–1960) as well as by waste oils of automobile workshops (1960–1988). The upper zone is dominated by bio-pores, desiccation fractures and clay till matrix, the central zone is dominated by well-connected desiccation and glacio-tectonic shear fractures and the lower zone is dominated by tectonic fractures (Klint et al., 2001b; 2001c; Rosenborn & Klint, 2001). Fieldwork performed on both sites enabled us to classify fractures depending on their origin and size, to measure the statistics of the spatial distribution of their properties (e.g. density, length, orientation), to map their interconnections, and measure hydraulic conductivity (Klint et al., 2001a). Lab-scale analyses gave useful information concerning geometrical and topological properties of fracture aperture. Aerial photos were also used to establish macroscopic geological models for both fractured sites.

#### One-phase and two-phase flow in single fractures (Work Package WP-2)

Experiments performed on artificial fractures (Fig.2) aimed at quantifying the hydraulic conductivity (Theodoropouplou et al., 2001a; Tsakiroglou et al., 2001), identifying the transient two-phase flow patterns (Theodoropouplou et al., 2001b), and estimating the dynamic relative permeability and capillary pressure curves (Tsakiroglou et al., 2002a), in dependence on the NAPL rheology and fracture morphology. A two-phase flow simulator in dual pore networks (fractures embedded into porous matrix) and fracture networks representative of the different systems identified in generic sites were used to determine the up-scaled multi-phase transport coefficients (Bekri et al., 2002). The fracture network models were evaluated with respect to field hydraulic data obtained with infiltration, column and slug tests.



Fig.2: Distribution of residual NAPL (white) saturation at the end of its displacement by aqueous phase (dark) in a glass-etched dual pore network, which is regarded as a single fracture embedded into porous matrix. (a) Newtonian NAPL. (b) Non-Newtonian shear-thinning NAPL.

#### Hydrodynamic dispersion in fractured media (Work Package WP-3)

A technique was devised for the accurate measurement of the transient solute concentration distribution throughout artificial single fractures. The technique is based on the detection of colour changes occurring on a low solute concentration solution during its mixing with a high solute concentration solution because of the strong sensitivity of an indicator contained in traces in both solutions to pH. Measurements of the temporal evolution of the solute concentration profiles were performed on calibrated regions of different types of fractures, under varying scenarios of dispersion (Fig.3). Fitting of measurements to analytical models of dispersion in two-dimensions enabled us to estimate the longitudinal and transverse dispersion coefficients as functions of Peclet number (Tsakiroglou et al., 2002b; 2002c).



Fig. 3: Successive shortcuts of the solute dispersion in a single fracture (network of large pores) embedded into porous matrix (network of fine pores). The high solute concentration solution (light) is injected through a hole into the low solute concentration solution (dark). (a)-(c) Macroscale dispersion regime. (d)-(g) Microscale dispersion regime.

#### Phenomenological flow models and experimental validation (Work Package WP-4)

Analytical non-Darcian models were developed for the one- and two-phase flow of non-Newtonian shear-thinning NAPLs in fractures and fractures embedded into porous matrix (Tsakiroglou, 2002a). With the aid of critical path analysis analytical equations were described for the determination of the electrical formation factor and absolute permeability of single fractures from geometrical/topological properties of their aperture (Tsakiroglou, 2002b). The pore network two-phase flow simulator was utilized to determine the capillary pressure and relative permeability functions of fracture systems bounded within a block of the macroscopic numerical grid. Experiments performed on fractured cores were used to evaluate the predictability of analytical models, and provide data where geological information was insufficient for theoretical calculations.

#### Macroscopic numerical simulation (Work Package WP-5)

The macroscopic simulator SIMUSCOPP was updated to dual porosity/dual permeability media in order to account for porous matrix/fracture interactions. The geological conceptual models of both generic sites were translated into numerical grids, by assigning porosity and permeability values to matrix and fracture grids for Site 2 (clay till) and by establishing a highly









heterogeneous discrete fracture network model for Site 1 (granite). Various scenarios of contamination of Site 2 were investigated by ignoring and including rainfall precipitation in the simulations (Fig.4). In order to study the dissolution/dispersion of dissolved compounds at a large scale within the aquifer, a two-step procedure was adopted: (1) the macroscopic simulation of two-phase in a cross-section of the fractured (dual porosity) medium was used to determine the NAPL flux toward the aquifer; (2) the flux was used as boundary condition on the water table for the simulation of dissolution/dispersion of compounds (phenol, naphthalene) at large distances within the (simple porosity) aquifer (Fig.5).

#### Risk assessment of contaminated sites (Work Package WP-6)

The quality of groundwater in Site 1 was detected during the project lifetime by collecting samples from 20 piezometers and measuring the TPH and BTEX concentration every six months (Fig. 6).



Fig.6: Temporal variation of the spatial distribution of the total petroleum hydrocarbon (TPH) concentration in groundwater on Site 1 (North Spain).

Different hydraulic tests (pumping and slug tests) were performed on monitoring wells of site 1 in order to estimate the hydraulic conductivity for each geological formation identified on site: sand, loam, weathered granite and fresh granite. Electrical conductivity and temperature were measured on boreholes before the initiation of hydraulic tests, in order to correlate groundwater flow between different boreholes and map the hydrogeology of the area. Existing data concerning the geology and chemical status of groundwater at Site 2 (Fig.7, Tab. 1) were compiled and classified, primarily from earlier research projects on the site. Additional

monitoring wells were established on the site and new data concerning the spreading of the contamination into the groundwater aquifer facilitated the construction of a new extended hydro-geological model. New data concerning the spreading of contaminants in the groundwater aquifer showed that contamination has migrated along the floor of the aquifer and is now situated approximately 200 meters southwest of the site at a depth of 40 meter below ground-surface.



Fig.7: Spatial distribution of NAPL on Site 2

Tab. 1.	Compounds detected in groundwater on Site 2
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Concentration of different compounds in groundwater sample

compound	466664-01 9911B	466665-01 9911	466666-01 9811A	466667-01 9811	466668-01 1012
Benzen	0,19	1.800	0,39	244	0,26
Toluen	0,16	12	0,12	0,74	0,18
Xylener*	-	365	0,14	18	0,13
1,2,3-Trimethylbenzen	-	16	-	0,87	-
1,2,4-Trimethylbenzen	-	88	-	4,7	-
1,3,5-Trimethylbenzen	-	-	-	-	-
Naphtalen	-	254	-	12	-
1-Methyl-naphtalen	-	0,75	-	0,12	-
Phenol	-	34	-	7,9	-
o-Cresol	-	0,85	-	-	-
m/p-Cresol	-	1,0	-	-	-
2,6-Dimethylphenol	-	450	1,1	150	-
2,4- og 2,5-Dimethylphenol	-	39	-	0,38	-
2,3-Dimethylphenol	-	7,1	-	-	-
3,4-Dimethylphenol	-	12	-	1,4	-
3,5-Dimethylphenol	-	4,3	-	0,29	-
Carbazol	-	-	-	-	-
Quinolin	-	-	-	-	-
Thiophen	-	73	-	4,3	-
Benzothiophen	-	173	-	11	-
Benzofuran	-	3,7	-	0,56	-
Dibenzofuran	-	-	-	-	-

\*: Ethylbenzen, m-, p- og o-xylen
#### **Concluding Remarks**

Field scale studies are combined with laboratory experiments, theoretical models, and numerical simulations for obtaining reliable data concerning the geostatistics, hydraulic properties and multiphase transport coefficients of highly heterogeneous fractured formations. The information obtained is introduced into a macroscopic numerical simulator of contaminant transport in dual porosity – dual permeability media. The simulator is used as a tool to predict the short- and long-term migration of organic pollutants, and provide data for the implementation of risk assessment procedures on contaminated fractured sites. The methodologies of hydrogeological characterization as well as the improved numerical simulator are demonstrated with application to two very different fractured sites (Site 1=granite, Site 2=clay till), situated in Europe (Site 1/Spain, Site 2/Denmark), and contaminated by hydrocarbons.

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#### Contact

Name: Christos Tsakiroglou Organisation, Department: Foundation for Research and Technology Hellas – Institute of Chemical Engineering and High Temperature Chemical Processes Street, City: Stadiou street, Platani, P.O.Box 1414, GR-26504 Patras, GREECE Phone: 30 2610 965212 Fax: 30 2610 965223 e-mail: ctsakir@iceht.forth.gr

# GROUNDWATER RISK ASSESSMENT AT CONTAMINATED SITES (GRACOS)

Project GRACOS, Groundwater Risk Assessment at Contaminated Sites

Authors D. Halm and P. Grathwohl, Tuebingen University, Center for Applied Geoscience, Germany

Keywords Groundwater pollution, scenario approach, procedures, leaching tests, volatile organic compounds, guidelines

#### Abstract

Subsoil and groundwater pollution at contaminated sites requires new and improved methodologies and techniques for a rapid and low-cost risk assessment. The development of such new procedures and the delivering of guidelines for groundwater risk assessment and action recommendations is the general goal of the GRACOS-project. The procedures will be based on a scenario approach, which will be generally applicable to different situations in terms of classes/combination of pollutants and site-specific conditions. This scenario approach will allow a priori the determination whether, under given site conditions and contaminant properties, a minor, medium or high risk of groundwater pollution exists. To cover as many different site-specific-scenarios as possible, the project involves numerical modelling for vapour phase contaminant transport in the unsaturated zone and long-term leaching of contaminants from specific materials.

#### Introduction

Today, contaminated land poses a serious problem in Europe, leading to a decrease of soil quality and to a risk of spreading of pollutants into other compartments of the environment. A major risk at most contaminated sites is that of groundwater pollution by organic and inorganic compounds (Grathwohl and Klenk 2000). Since complete restoration of all these contaminated sites is economically and often technically not feasible, advanced procedures of groundwater risk assessment are needed as innovative tool for the ranking of sites, decision making on further use, and remediation standards.

GRACOS is a project within the Energy, Environment and Sustainable Development Programme of the European Commission implemented under the Fifth Framework Programme with seven interdisciplinary research partners.

#### Objectives

The objective of the GRACOS-project is to develop and to improve methodologies and techniques for rapid, low-cost risk assessment of subsoil and groundwater pollution at contaminated sites (e.g. for polluted top soils, waste disposal and recycling materials, etc.). In contrary to the procedures available today, these new methods focus on the quantification of the mobile fraction of the contaminants and will allow the determination of the aqueous contaminant concentrations to be expected in seepage water and groundwater incl. the prediction of long-term trends of concentration changes (Grathwohl and Susset 2001).

The procedures to be developed take the form of a scenario approach, as it is intended to be generally applicable to different situations in terms of classes/combination of pollutants and site-specific conditions, such as climatic conditions, permeability and distance between contamination and groundwater table. Such a scenario approach will allow the determination a priori whether, under given site conditions (subsurface permeability, distance to groundwater table, type of material) and contaminant properties (volatile/non-volatile/water soluble etc.), a minor, medium or high risk of groundwater pollution exists.

The most important deliverables of the project will be guidelines for groundwater risk assessment which for certain scenarios, compound classes and material types do not require or require only minor investigations. Therefore it would significantly reduce the costs for dealing with the legacy of industrial pollution. The end-users will be the governments, EPA's and regulating agencies. Finally, European Countries would benefit from a more harmonised and integrated approach to environmental regulation.

#### Methodology

The methodology for the development of new groundwater risk assessment procedures includes investigations of vapour phase transport and leaching tests according to the experimental, model and application relevant parts (see Fig. 1). The work is carried out

- #in a well controlled field experiment which comprises an emplaced source of a synthetic hydrocarbon mixture consisting of volatile to semi-volatile, (partly) biodegradable compounds (representative for i.e. gasoline or aviation gasoline).
- #in laboratory and field investigations for the quantification of contaminant transfer rates across the capillary fringe for specific scenarios. The goal is the prediction of the solute concentration in shallow groundwater from vapour phase concentrations of the contaminants in the unsaturated zone and assessment of degradation rates in unsaturated soil zone and shallow groundwater plumes.
- #in new and existing laboratory and field methods to study the aerobic biodegradation of selected volatile petroleum hydrocarbons in sandy materials of the unsaturated zone and to obtain kinetic biodegradation parameters.
- #in column leaching tests including long-term leaching for the quantification of the mobile contaminant fraction in various contaminated soils and waste materials (e.g. slag, bottom ash, construction/recycling materials).
- #in numerical scenario-specific modelling for vapour phase contaminant transport in the unsaturated zone and of contaminant release from specific materials.
- #in mobility/bioavailability tests for both inorganic and organic compounds, and in an ecotoxicological assay of the mobile/bioavailable fractions. Toxicity tests on solid are also carried out in order to assess the representativeness of the leaching protocols as a method to reproduce bioavailability of contaminants.



Fig. 1: Overview over the methodologies and objectives in GRACOS for the development of guide-lines/procedures for groundwater risk assessment at contaminated sites

#### **Results and Discussion**

A site was selected in Denmark to carry out a field experiment for the monitoring of all processes, which are relevant for groundwater risk assessment of volatile hydrocarbons such as vaporisation, transport, diffusion, sorption/desorption, and biodegradation (Fig. 2). The site has a relative thin vadose zone (3 - 4 meters), consisting of fairly homogeneous sand where the source was emplaced in the subsurface. The background characterisation of the site was performed and the design and sampling network of the experiment defined. A mixture of hydrocarbons (NAPL), which is representative for fuel spills, is used as contaminant source. Generally, the results show that the hydrocarbons migrated faster and further away from the source than expected from the preliminary modelling. Detailed results from soil gas monitoring of the hydrocarbon plume and the main gases ( $O_2$  and  $CO_2$ ) are presented by Christophersen et al. (2002). A comparison of soil air and soil water concentrations of hydrocarbons sampled with porous cups at the field site are presented in Broholm et al. (2002).

The biodegradation of volatile organic compounds and the microbial communities in the unsaturated zone during natural attenuation of petroleum hydrocarbon vapors were assessed by Höhener et al. (2002). In a large lysimeter experiment, a tracer method was successfully applied to quantify the biodegradation rates for a sandy sediment and to determine the persistence of organic chemicals (Pasteris et al. 2002).

Leaching and toxicity tests have been carried out for different materials, such as bottom ash, sludge, and organically contaminated soils. Susset & Grathwohl (2002) worked on numerical and analytical modelling of organic leaching in column tests. A new automated ASE-method for aqueous leaching of PAHs at elevated temperatures also for fine grained samples was

tested (Henzler et al. 2002). For the selection of laboratory methods for inorganic contaminant leaching from soils and waste materials, the batch pH-static test and the percolation test have been selected as the most powerful laboratory test procedures for inorganic contaminants. The source term in landfilling of waste in relation to an impact assessment based on scenario calculations and field verification was evaluated (Van der Sloot et al. 2002). To identify processes controlling "availability" of PAHs for leaching from soils and waste materials, leaching at high DOC concentrations were applied to measure the maximum amount of PAH in a soil/waste that is available for leaching. Reactive transport modelling was applied to natural and waste environments as a valuable instrument in assessing the time dependent leaching potential of waste materials as well as the fate of contaminants in the environment after leaching.



Fig. 2: Processes to be considered at the controlled hydrocarbon spill site of GRACOS

Mobility/bioavailability tests for organic and inorganic compounds the ecotoxicological assay of the mobile/bioavailable fraction provide a wide and complete information about the presence, behaviour and toxicity of pollutants in the tested materials (Cagigal et al. 2002). New methods for fast/low cost procedures of leaching and toxicity tests and for vapour phase monitoring techniques were developed, which will be able to simplify and harmonize procedures related to the applied research area.

The transport of contaminants across the capillary fringe is measured in laboratory tank experiments. Diffusion rates were determined by using small-scale column tests. Changes of the composition of organic mixtures and the impact on contaminant release rates were investigated by monitoring the equilibrium aqueous concentrations and the long-term dissolution behaviour of organic compounds from gasoline ("ageing"). The measured aqueous concentrations of gasoline constituents compared very well with the calculated concentrations from raoult's law at increasing water to gasoline mixture ratios.

In terms of modelling of both, vadose and saturated zone, relevant model systems were selected and successfully applied to the complex processes of transport modelling of contaminants at different scales in the capillary fringe and in the water saturated zone (Gaganis et al. 2002). The measured data fit well simulations, which is essential for the validation of the models and for further predictions. A first model validation with concentration profiles from the aforementioned lysimeter experiment, for use in the design of site monitoring and pollution assessment was carried out. A version of a geochemical transport model has been developed to quantify contaminant source terms from waste and contaminated soils as a function of time. A preliminary draft of guidelines for groundwater risk assessment at contaminated sites has been drawn out.

#### Conclusions and Intended Use of Results

The procedures and guidelines being developed will contribute to better soil and waste management and thereby reduce the exposure of soils and groundwater and to harmful pollutants.

At a higher level of soil and groundwater protection, GRACOS will improve the procedures to decide about preventive actions and rectification of the damage at the source. It will provide a basis for regulation focusing on the release potential and projected impact for different compound classes based on their behaviour and on local or depth-averaged concentrations in groundwater and/or overall contaminant fluxes to the groundwater. Based on the experiences to be gained in GRACOS, typical cases of subsurface contamination will require less effort in groundwater risk assessment, which would significantly reduce the costs to society for dealing with the legacy of industrial pollution. This could open opportunities for European consulting companies in an international market. The end-users will be the governments and finally the citizens of Europe who benefit from a more harmonised and integrated approach to environmental regulation. Representatives of legal authorities (State and National EPAs) are participating in meetings and workshops of the consortium. Thus, the results of GRACOS will be available for the public in terms of harmonised regulations/procedures for the groundwater risk assessment at contaminated sites and for the disposal of contaminated materials.

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#### Contact

Dietrich Halm Tuebingen University, Center for Applied Geoscience Sigwartstrasse 10, Tübingen, Germany Phone: +49-7071-2977453, Fax: +49-7071-5059 Email: dietrich.halm@uni-tuebingen.de

## INTRODUCTION TO AN ONGOING TECHNOLOGY DEVELOPMENT PROJECT ON A COMPLEX ON SITE INVESTIGATION APPROACH

Project NORISC, Network Oriented Risk-Assessment by In-situ Screening of Contaminated Sites

Author B. Morvai, Agruniver Environmental Service and Management Ltd, Hungary

Keywords Site investigation, on-site measurements and screening, risk assessment, data management, decision tool software system

#### Abstract

The aim of NORISC project is to provide a standard guideline in form of a decision tool software system for more efficient characterisation and risk assessment of contamination profiles in urban areas. The system combines and integrates new and existing site investigation methods focusing on in situ and on site techniques including geophysical screening, (hydro-) geological survey, chemical analysis, toxicological and other short tests in order to gain a faster, cheaper and more reliable site assessment. The approach is based on flexible and dynamic investigation strategy as well, supporting on site positioning and GIS based data processing that includes geo-statistics and modelling. The developed guideline is being verified against quantifiable and quality criteria, so real field tests with detailed evaluation are carried out. The NORISC system will be a valuable tool for city planners, decision-makers, landowners, investors and other stakeholders in contaminated site management, especially in brownfield redevelopment.

#### Background

The stakeholders' request, which was surveyed at the beginning of the action, has put into evidence the socio-economic relevance of brownfield revitalisation, as well as speedy and efficient characterisation of contaminated sites including secure results concerning the concentration of pollutants and their spatial distribution. Current separate use of environmental investigation techniques is not enough cost and time effective and does not provide appropriate spatial results. Site preparation is often delayed due to long lasting assessments, expensive and uncertain clean up measures, so in most cases abandoned industrial areas with certain contamination, but even with high reusage value cannot be revitalised for a significant period. Without targeted recycling of such sites, urban structures will decay, while social and cultural life will deteriorate. NORISC addresses these problems and supports a quicker, cheaper and safer site investigation, as well as offers a sound base for risk assessment and redevelopment of derelict land in urban areas.

### Objectives

NORISC is a technology development project under the 5th Framework Programme of the European Commission (Call 1.1.4-4.3.1 EESD-ENV-99-2, Key Action: City of Tomorrow and Cultural Heritage, Priority: Revitalisation of City Centres and Neighbourhoods) that provides an integrated site investigation methodology focusing on in situ and on site techniques for more accurate environmental assessment of contamination profiles in urban areas. The goals are the followings:

- #Combine and integrate new and existing investigation methods, especially innovative in situ and on site techniques
- #Provide a standard guideline for site characterisation and assessment in the form of a decision support software system prevailing on site and in situ methods for time and cost effectiveness, as well as reliability
- #Demonstrate the effectiveness of this investigation approach and the developed decision support system via field test
- #Integrate site investigation with general contaminated site management including data management, site assessment, clean up targeting and revitalisation strategy into the approach

The consortium consists of municipality bodies from some partner cities (City of Cologne, Organisation of Thessaloniki) authorities (Geological Survey of Sweden, Swedish Environment and Health Protection Administration, US EPA), research centres (Institute for Ecology of Industrial Areas, Universities of Ferrara, Florence and Uppsala, Institute of Geology and Mineral Exploration) engineering companies (Agruniver Environmental Service and Management Ltd, Clayton Umwelt-Consult GmbH) that carry out the work involving a number of scientific disciplines. The action is governed by user requirements from city planners, landowners, stakeholders, investors, insurance and engineering companies.

#### Actions and progress

#### Survey

Existing investigation standards and norms in Europe and associated countries have been analysed searching the national legislations. Case studies have been provided on total 119 of contaminated sites chosen within 3-5 urban areas from 10 European countries, and further 198 sites from the US. Then an inventory has been established containing the types of contamination and site characteristics, as well as requirements of stakeholders.

Existing and new probing, examination and evaluation techniques of the different scientific disciplines as well as data processing methods have been researched and compiled. A register of chosen site investigation methods has already been established. The individual methods are evaluated technically and economically.

	, ,					
Legislation on cont o o	taminated site management and Stakeholders request analyse Contamination guideline value	ed during the case studies				
Contaminated site	characteristics in urban enviror Case studies in European con Contamination profiles (list of General (hydro-) geological co	untries and in the US pollutants concerning different activities)				
Registers of investigation methodologies (cost and time, accuracy, applicability, obstacles) - (hydro-) geological site characterisation, chemical analysis, geophysical and biological investigation methods, sampling and probing, geostatistics						

Tab. 1: Data sets and input tables provided for the decision support software

#### Development

In the project, a guideline in form of decision support software (DSS) is established that combines the results of the catalogue of urban contaminated site characteristics and the user requirements with the register of suitable investigation methods (Tab. 1). A procedure is defined and an evaluation matrix is established for the selection of an optimal combination of methods for more appropriate, cheap and fast site assessment (Fig. 1). On site and in situ techniques are prevailed and an investigation strategy is developed according to this approach that includes also on site positioning and data processing (Tab. 2).



Fig.1: DSS working procedure flow chart.

First the input data sets were harmonised, then the software based on Access and Visual Basics was designed. At this stage the DSS is under further refinement via real field tests and an assessment procedure. Exactly, practical proof testing of the developed software and the methodology is carried out at selected sites in the partner countries.

Regular geo-technical investigation & innovative techniques					
Positioning on site with (D)GPS	Flow-meter				
	Guelph Permeameter				
	Compact Constant-Head Permeameter (Amoozemeter)				
	Slug test				
Innovative geophysical screening	Radiomagnetotelluric (RMT)				
methods	Induced polarisation technique				
	Regular sampling and probing				
On site chemical analysis including	Infrared-photometer for petroleum hydrocarbons				
specific sample preparation with	High-speed gas chromatograph with different detectors for pe- troleum hydrocarbons, aromatic hydrocarbons and halo- genated hydrocarbons				
	PID for detection of volatile organic compounds				
	X-ray-fluorescence equipment for heavy metals				
	GC/MS-system for less volatile organic pollutants (PAH, PCB)				
	Laser induced fluorescence (LIF)				
	Laser Plasma (LP)				
Various test kits	Immunoassay				
	pH, temperature measurements				
	Toxicity tests				
	Colorimetric tests				
Data management using on site available GIS in portable PC					

Tab. 2: Applicable field investigation tools with examples of innovative techniques

#### Integration

Besides the improved quality regarding site investigations, i.e. low costs, timesaving and reliability aspects, NORISC shall also be an integrated user-friendly tool for all stakeholders in contaminated site management. It requires support in proper handling and basic evaluation of investigation result. This means data standardisation and transfer into a common GIS system, further on certain risk assessment according to planned land use.

All data collected at the NORISC guided field examination are integrated in a GIS-Input-Module, in an interface to GIS that carries out the standardization of the data providing the compatibility of different data formats from different investigation methods. As the results can be entered into GIS and visualized on maps, the site assessment is meaningfully facilitated. Meanwhile a risk assessment as site specific as the investigation data allows is also included. A human health risk assessment module is developed for three typical urban land-use categories and the main exposure pathways are considered. To gain the necessary site information, on site techniques for determination of parameters required by risk characterisation and assessment are included into the list of investigation. If the results will not allow sufficient interpretation for the final risk assessment, the data management will give even the possibility of a check-up. In this way, revitalisation strategy for investigated sites can be provided. Marketing strategy for the recycling is developed on the basis of NORISC via cost-benefit or cost effectiveness analysis of different combinations of redevelopment aims and the types of necessary reclamation processes. This analysis consists of general technological and impact cost assessment, as well as of benefit assessment that concerns the change in the value of reclaimed site.

#### Conclusion

In comparison to the classical site characterisation approach for site investigation based mostly on drilling and laboratory measurements, the new NORISC methodology is a promising tool for saving time and cost, even increasing reliability of the assessment by selecting the optimal mixture of investigation methods. It also supports effectively quicker also on site decisions of how to handle the derelict land and may even lead to the faster revitalisation of the investigated area including all economic and ecological advantages. Using the guideline software system of NORISC for data processing, the existing contaminated site management systems and data-bases can be promoted to a multifunctional tool for the compilation and exchange of data among different communicators. So the NORISC system will be a valuable tool for city planners, decision-makers, landowners, investors and all other stakeholders involved in derelict land redevelopment.

#### Contact

Balázs Morvai (author) Agruniver Environmental Service and Management Ltd Ganz Abraham 2 (POBox 56), H-2100 Gödöllö Tel/fax: +36-28-417 463, bmorvai@mail.digitel2002.hu www.agruniver.hu

or

Dr. Barbara Möhlendick (project coordinator) City of Cologne, European Office Athener Ring 4, D-50765 Köln Tel.: +49 221 221 2 1594, Fax:+49 221 221 2 18 49 E-Mail: Barbara.Moehlendick@stadt-koeln.de

Project Website: www.norisc.com

## SESSION 4B TECHNICAL SOLUTIONS – MONITORING

Chairman: Thomas Track, DECHEMA (DE)

## SUMMARY

The presentations in session 4b dealt with technical solutions and monitoring. **Susan Alcock** presented the thematic network SENSPOL, which is the European Network on Sensors for Monitoring Water Pollution. The aim of the network is to enhance the development of chemical sensors, biosensors and biomimetic systems for practical applications in the abatement of water pollution from contaminated land, landfills and sediments. The introduction included description of requirements for ideal sensors and their function in sustainable land management.

The collaboration under the network, which includes over 700 members, was discussed. The coordinator of the project introduced the results of the first workshop organized by SENSPOL. The conclusions from the workshop included:

#a requirement of new monitoring tools for land remediation and for bioremediation processes,

#the need for protocols that assure European quality and for multiparametric systems that could sense priority pollutants.

Participants of the workshop have underlined that communication is a key issue for further progress, and therefore field technical meetings are valuable activities. There is number of field deployable and simple-to-use instruments that are being developed and will be available in near future. Non-selective sensing approaches, mainly based on pattern recognition, were mentioned for future development. The workshop showed that more and more instruments are developed with the portable or palm-size. Electrochemical detection of toxic heavy metals and toxicity biosensor were introduced as examples.

Further the presenter introduced sensor communication systems, which deliver data collected in situ to the server. Processed data can be available through the Web services.

Another element of SENSPOL activities is an expert meeting. The results of one, which focused on monitoring of freshwater sediments, were reported. The expert group concluded that sensor technologies can provide important information for risk assessment and also can give a useful assistance in monitoring pollutants. The need for in-situ monitoring was mentioned. The group emphasized the role of communication in bridging the technology implementation gap. The validation and implementation of prototype devices as a crucial next step was stressed.

Further the coordinator explained the rules of Collaborative Programme, which is based on co-operation, exchange of researchers, sharing of facilities and service units, industrial involvement and formulation of new projects.

In the final part of the presentation the SENSPOL coordinator described distribution of information within the network. The newsletter issued periodically includes the most important information about the network activity and future events. One of them is the next SENSPOL workshop, which will be organized in Krakow (Poland) in June 2003. The coordinator stated that the network is ready to be present within FP6 as a Network of Excellence.

The second presenter was **Thomas Track**, who reported about the results of project WATCH – Water catchment areas: Tools for management and control of hazardous compounds. The project involves 8 partners from 5 countries. Approach used in the project includes defined elements of strategy and tasks which combined together lead to protection and sustainment of drinking water resources. The project concentrated on two hazardous compounds: BTEX and MTBE/ETBE (Methyl tertiary butyl ether/Ethyl tertiary butyl ether). The main source of these substances in groundwater is leakage from underground tanks near gas stations, from refineries and chemical industry. For example in Spain 7 of 21 investigated sites were defined as "hot spots". Surveillance and monitoring techniques used in the project are based on:

∉#optical in-situ sensors,

∉#immunoassay test kits,

∉#analytical protocols and control.

Optical oil leak sensor uses a couple LED (light emitting diode)-phototransistor. Laboratory experiments showed that the sensor can fast detect leakage from underground fuel storage tanks. Further experiments were conducted in-situ with a lysimeter.

Existing BTEX immunoassays were improved to detect low concentrations (20 mg/l). For detection of MTBE/ETBE new immunoassays were developed. The achieved limit of detection (LOD) is very low (10-20 mg/l). There were presented two immunoassays: Sandwich Elisa and Competitive Elisa. The investigation of environmental behaviour of MTBE showed that it is degradable in aerobic conditions, while in anaerobic conditions no significant degradation was noticed.

Described sensors were applied in monitoring and early warning. The strategy for monitoring and early warning should integrate management tools for groundwater catchment areas. The elements which allow to build the system should include: a protocol for conceptual model system set up, development of a dynamic integrated monitoring system, integrated monitoring and management tool, for oil- and gasoline derived contaminants and finally institutional framework for early warning and pollution management at catchment area level. The final system should guarantee reliability of data series and prognoses, minimize uncertainty in decision making (monitoring strategies, protection, remediation actions).

The final part of the presentation showed the application of sensors and immunoassay kits at model sites (Germany, Austria). Duesseldorf site was investigated in 1995 and the plume of BTEX was very large. After 5 years the observed plume is much reduced. The model of the site showed that natural degradation occurred, stimulated by nitrates infiltration. Another model site is St. Leonhard (Austria), which is source of high quality groundwater. Appropriate strategy for monitoring was established as contamination was identified in this area.

The last presentation was given by **Manuel Valiente**, representing the project DIMDESMOTOM - Development of Improved Detection Systems for Monitoring of Toxic Heavy Metals In Groundwaters and Soils. 5 laboratories from 4 countries (UK, Ireland, Spain and France) are collaborating within the project. The aim of the project is to develop and validate sensing devices for real time measurements of Toxic Heavy Metals (THM) present in contaminated soils and surface waters. This aim can be achieved with the following objectives:

#development and construction of electrochemical biosensors/immunosensors for detection and analysis of toxic heavy metal ions in water and soil samples,

#development and construction of suitable screen-printed electrodes for the stripping voltammetric analysis of heavy metal contamination, also with improved electrode selectivity,

- #development and construction of a portable system for heavy metal detection in a contaminated soil and water matrices through the development of suitable instrumentation, data analysis algorithms and system software,
- #identification of THM (toxic heavy metals) pollution trends,

#validation of developed sensors under laboratory and field conditions,

- #integration of the data generated by the new instruments into a decision-taking scheme based on a GIS,
- #evaluation of the developed systems to control the efficiency of remediation processes for decontamination of polluted soils in selected contaminated areas of Europe.

These objectives should help to meet the typical monitoring needs which are: not a high accuracy for screening methods, concentration range around ppm, simplicity of the analysis, short time to get results, cost lower or similar to a conventional lab.

There were two groups of sensors presented as results of the project: optimised urease biosensors and microfabricated electrodes. The results for measurement in real samples were presented. Another deliverable of the project that was presented is HEMA 2002, which is a portable system for heavy metal analysis.

Further the speaker presented the need for speciation of heavy metals which are toxic only in the available form. To measure available content it must be extracted from the sample according to a protocol. The recommended protocol for sequential extraction was presented.

In the final part the modelling objectives and application of GIS techniques for Salsigne site were presented.

Piotr Cofalka, IETU - Institute for Ecology of Industrial Areas – Poland

## SENSORS FOR PRACTICAL APPLICATIONS IN THE ABATEMENT OF WATER POLLUTION FROM CONTAMINATED LAND, LANDFILLS AND SEDIMENT

Project SENSPOL, European Network on Sensors for Monitoring Water Pollution

Author S.J. Alcock, Cranfield Biotechnology Centre, Cranfield University, UK

Keywords Sensors, monitoring, water pollution, site characterisation, risk assessment, bioremediation

#### Abstract

Monitoring technology is required to provide information for efficient resolution of problems of multiple pollutants contaminating land and groundwater in urban areas. Sensor technologies can be used to identify trends of pollution and they will also be valuable in risk assessment approaches. They are capable of rapid assessment of toxicological risks of pollutants, including the effects of pollutant mixtures.

The overall objective of the SENSPOL EU Thematic Network is to enhance the development of sensor systems for practical applications in the abatement of water pollution. The implementation of sensors for in situ environmental monitoring would compliment the formal environmental policy of the European Union. SENSPOL clusters the sensor development activities in the EU's environmental projects and acts as a catalyst for the advancement of European technology for monitoring the environment.

SENSPOL workshops have addressed the progress and present achievements of monitoring tools for bioremediation, site characterisation, and groundwater risk assessment. Enhanced sensor devices already in existence are able to provide useful assistance in monitoring pollutants in the environment and in remediation technology. Some of the sensors are already able to monitor several analytes simultaneously and sensing systems are being developed to make simultaneous measurement of multiple parameters.

#### **Project Description**

#### Objectives

The objective of SENSPOL (Project No. EVK1- CT-1999-20001) is to enhance the development of chemical sensors, biosensors and biomimetic systems for practical applications in the abatement of water pollution from contaminated land, landfills and sediment.

#### Introduction

Sensor technologies can be used to identify trends of pollution and they will also be valuable in risk assessment approaches for contaminated soils, groundwater bodies and surface water bodies. They are capable of rapid assessment of toxicological risks of pollutants, including the effects of pollutant mixtures. The requirement for in situ monitoring of environmental pollutants places sensor devices clearly at the core of any programme to develop technology for remediation and techniques for enhancement of natural attenuation processes. The intention of SENSPOL is to provide in situ monitoring of environmental pollutants in water and contaminated soil and sediments, to facilitate optimisation of remediation technologies and natural attenuation processes. Sensor devices can be useful information and communication technologies (ICT) tools for rapid site assessment and provide information for decision making in sustainable land management. Research for on-site investigation is primarily concerned with the development of new chemical sensors and biosensors to measure chemical analytes or biological effects such as toxicity. In the most recent developments the convergence of sensors with mobile computing and telecommunications is being addressed (Alcock, 2001).

SENSPOL has established a European communication network which is facilitating the development of chemical sensors, biosensors and biomimetic systems for practical applications in the abatement of water pollution (see Alcock and Branston).

#### Results

The main theme of the first SENSPOL Workshop, held in Alcalá de Henares, Spain, May 9-11 2001, was 'Sensing Technologies for Contaminated Sites and Groundwater'. This workshop showed that the development of the field of sensing technologies for environmental monitoring has advanced considerably (Domínguez and Alcock, 2001; Dominguez and Alcock, 2002). The implementation of fundamental research (e.g. molecularly imprinting polymers, membrane technology, pattern recognition, and transducing schemes) has progressed significantly, and this provides a basis for a more integrated and collaborative approach for the management of European freshwater resources. Field deployable and simple-to-use instruments are being developed including electrochemical or optical transduction. Most of the targeted analytes are chloroorganics, BTEX, PAHs, and heavy metals. It is believed that within the next five years some of the technical research will transfer into prototype products for full assessment and evaluation.

A SENSPOL Expert Meeting on 'Monitoring Freshwater Sediments' held in Antwerp, Belgium, 12-13 Sept 2001 aimed to identify and define problems and to develop a realistic strategy to solve these problems (Alcock et al, 2002). The invited experts were agreed that in situ monitoring systems are needed to monitor freshwater sediments. New recognised tools for sediment monitoring would help industry to meet the governmental sediment quality criteria and to handle the data concerning historic river contamination and geological background data. The need to monitor by effect-related studies together with chemical monitoring was stressed. The main focus for development of new sensor tools should be for on site determination of certain priority pollutants where there would be advantage over existing methods or where no suitable method exists, and to monitor biological effects (alarm systems and effect-related on site tests). Sensing technologies would also be useful to monitor bioavailability in sediments in situ to provide information for risk assessment. They could also be of use in situ to monitor bioremediation and for screening and to guide treatment of dredging sediment.

The second SENSPOL workshop was held at King's College London, UK, 4-7 June 2002. The workshop theme was 'Response to New Pollution Challenges', with focus on sensing technologies for monitoring pollutants for sustainable ground and water management. The workshop also sought to identify clear needs for sensors to help solve new environmental problems such as those associated with emerging pollutants such as heavy metals, specific organic compounds being toxic, persistent or with a potential for bioaccumulation, endocrine disruptors, mutagens, pharmaceutical residues, antibiotic resistant bacteria. It was clear that recent technical advances in the development of sensing technologies that were reported are continuing to make steady progress towards the realisation of practical pollution monitoring systems. Sensors are already commercially available for temperature, acidity, oxygen and

redox potential. In addition, well-developed principles for sensing cover general toxicity, heavy metals, PAHs, BTEXs, nutrients, endocrine disruptors, emerging pollutants (biotoxins) and pathogens (e.g. E. coli). Bridging the technology implementation gap is a key aspect limiting sensor capabilities for on-site pollution monitoring. Validation and implementation of prototype sensing devices is a crucial next step that requires mechanisms and funding.

The foundation for responding to new pollution challenges is already provided by sensing technologies that are in development. European Union investment in the field of sensing technologies for environmental analysis continues to underpin many of these promising technical advances, and it is important for the implementation of new devices that the acquired momentum and specialised high technology skills are maintained. An Expression of Interest for EU Framework programme 6 to include a Network of Excellence on "Sensor technology for the Water Cycle" (SENSNET) has been submitted to the European Commission.

#### Conclusions

SENSPOL's work is speeding up the development of useful sensor systems to monitor multiple pollutants. Sensors are useful tools for monitoring pollution. Field deployable and simple-to-use instruments exist; automated systems are being developed for priority pollutants; biosensors are invaluable to screen for toxic chemical effects; mobile communications systems are being developed to monitor remote sensors. The technical advances in the field of sensing technologies for environmental analysis are gradually progressing towards the realisation of feasible monitoring systems.

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#### Contact

Dr Susan Alcock, Cranfield Univ., Institute of BioScience & Technology, http://www.cranfield.ac.uk/ibst Silsoe, Bedfordshire, MK45 4DT, UK. Tel: +44 (0)1525 863568 (direct) / 863539, Fax: +44 (0)1525 863540 Email: S.Alcock@Cranfield.ac.uk

# WATER CATCHMENT AREAS – TOOLS FOR MANAGEMENT AND CONTROL OF HAZARDOUS COMPOUNDS

- Project WATCH, Water Catchment Areas: Tools for Management and Control of Hazardous Compounds
- Authors
- *T.* Track<sup>1</sup>, S. Setford<sup>2</sup>, D. Barceló<sup>3</sup>, J, Wijdenes<sup>4</sup>, P. Werner<sup>5</sup>, H.P. Rohns<sup>6</sup>, E. Hitsch<sup>6</sup>, A. Brun<sup>8</sup>
- <sup>1</sup> DECHEMA e.V., Research Co-ordination, Germany
- <sup>2</sup> Cranfield Centre for Analytical Science, Institute of Bioscience and Technology, UK
- <sup>3</sup> Consejo Superior de Investigaciones Científicas
- <sup>4</sup> Diaclone, France
- <sup>5</sup> Technische Universität Dresden, Institut für Abfallwirtschaft und Altlasten, Germany
- <sup>6</sup> Stadtwerke Düsseldorf AG, Germany
- <sup>7</sup> Salzburg AG, Wasserwerke Labor, Austria
- <sup>8</sup> DHI Water & Environment, Groundwater and Solid Waste Department, Denmark

Keywords BTEX, MTBE, immunoassays, MTBE degradation pathways, analytics, IR-sensor, water supply, early warning system, groundwater monitoring, management, conceptual model

#### Abstract

The development and implementation of a co-ordinated monitoring strategy, linking general early warning pollution sensors e.g. for hydrocarbons with quantitative, sensitive and specific immunoassay test kits e.g. for BTEX and MTBE will allow environmental directives and quality standards to be applied and enforced. Beneficiaries include the general population who are provided with a safer cleaner water product and water companies who are able to monitor water quality on a frequent and routine basis. Legislators/enforcers will also have access to the technology and thus would be able to implement stringent programmes designed to safeguard the local water resource.

#### **Objectives**

Main objectives are (1) to develop and implement analytical methods and instrumentation for in-situ monitoring of BTEX (benzene, toluene, ethyl and xylenes), and MTBE (methyl tertiary butyl ether ) in groundwater and sediment (2) an integrated at-site early warning and management tool on a catchment scale (3) evaluation of both objectives on-site. Other objectives include use of oil leak sensors to indicate soil contamination, development and in-situ testing of optical reflectance sensors and rapid on site immunoassay kits, a protocol for sample handling and analysis of BTEX and MTBE, development of a BTEX and MTBE database for degradation behaviour, incl. degradation pathways and inhibition/stimulation assessment for MTBE. The sensor and management system will be tested at 3 sites owned by 2 end users to detect contaminants in soil and groundwater. Also design of an integrated management

tool for catchment areas with contaminant sources, including a risk management and reduction strategy will be addressed.

#### Sensor developments

A prototype near infra red (NIR) sensor device, previously developed by Cranfield Centre of Applied Science, has been continually refined and developed during the reporting period in order to improve its performance in soil and water matrices.

The basic sensor design is shown in Fig. 1. The sensor head incorporated an 11 mm disc of highly reflective, hydrocarbon-specific Fluorotrans membrane, which turns translucent on contact with free-phase hydrocarbon matrices.

Multi-channel sensor arrays have been constructed by linking sensors (currently to a maximum of 10 sensors) to a standard PC using via an interface board and ADC (analogue-to-digital) -11 multichannel data acquisition card.



*Fig.1:* Sensor design and exploded view of the head assembly. The sensor on the left is shown fully assembled. The sensor on the right shows an exploded view of the sensor head assembly.

The redesigned sensors were examined within a simulated in-house tank (Fig. 2). The 9sensor multi-sensor array was evaluated in a number of matrix arrangements with positive results. A full experimental evaluation using underground storage tank simulations indicate that ultimately, sensor performance is dependent upon a wide range of external variables, including soil matrix type, ground flow, soil saturation, surrounding physico-chemical conditions.



Fig. 2: Basic set-up of simulated leakage of underground storage tank. A glass tank was used to hold variable depths of sand and gravel. A 250ml volumetric flask was used to simulate an under-ground storage tank. Water inflow was controlled via a peristaltic pump (A). Excess water was extracted using another peristaltic pump at the opposite end of the tank. The flask and sensors positions were varied according to each experiment's objectives. A lid was placed on the tank to reduce any fuel evaporation.

#### Immunoassay test kits

For the development of MTBE immunoassay test kits and the refinement of BTEX immunoassay test kits concentration ranges of 10-20 µg L-1 were found to be useful for on site analytics. For the MTBE immunoassay test kits the antigens MTBE-BSA (bovine serum albumin) and MTBEn-BSA have been produced and were used for mice immunisation to produce monoclonal antibodies. After fusion with a myeloma cell line the hybridoma that are secreting antibodies which selectively react with MTBE-BSA or MTBEn-BSA are selected. Polyclonal antibodies were produced out of MTBEn-BSA. BTEX immunoassay test kits were refined to get first qualitative results at the concentration ranges of 10-20 µg/L. Commercially available BTEX immunoassays (SDI Inc., Newark, DE, USA), with a dynamic assay range of 90-3000 mg L/L did not exhibit the detection limit necessary to measure at the 10-20 mg L/L. Consequently, work has focussed on strategies to enhance assay detection limits. Preliminary approaches centred on using an alternative fluorescent assay enzyme label substrate to enhance assay sensitivity via improvements in assay signal-to-noise (S/N) with limited success. The next approach involved varying the reagent quantities in order to favour the competitive binding of analyte, which proved successful in that it was possible to consistently differentiate between samples containing no BTEX and those containing 11 mg L-1 BTEX, although absolute quantification of the analytes was not reliable. Nevertheless, as a fieldbased screening tool, the reduced reagent immunoassay approach has promise as an initial sample screening method. Current work is focussing on the use of commercially available solid-phase sorbent extraction techniques to concentrate water samples such that lower quantitative immunoassay detection limits can be obtained.

#### **MTBE/BTEX** analysis

For laboratory analysis a final purge and trap-GC-MS (gas chromatography – mass spectrometry) protocol for the analysis of MTBE, its main degradation products, other fuel additives including ETBE (ethyl tert-butyl ether), TAME (tert-amyl methyl ether) and DIPE (diisopropyl ether) and aromatics (BTEX) at low microgram per litre levels in groundwater has been accomplished. Different sampling methods (direct measurement, previous mixing and acidifying) for analysis of MTBE and its degradation products where investigated. As expected, MTBE did not show significant differences between sampling methods, since it shows very slow biodegradation. Although the mixed and acidified samples were always highest, there was not a common behaviour for the rest. Besides, relative standard deviations were below 7 % between replicates. On the other hand, acidified ones. These differences were significant due to its relative standard deviations above 20 %, whereas TBA concentrations were very similar between separated and mixed samples. But in acid conditions the other degradation product, TBF (tertiary butyl formate), is not detected and in addition can be hydrolysed to TBA.

#### MTBE degradation studies

For MTBE degradation studies under different environmental conditions (aerobic – methanogenic) are in progress with originally contaminated soils from ten different locations. All aerobic experiments degraded MTBE over the first 5 months. Some of them show more than 50 % decrease after 3 weeks, where as parallel sterile controls showed no changes in MTBEconcentrations. In these degradation studies none of the reported intermediates (TBA, formaldehyde, etc.) where detected. Under anaerobic conditions no evident signs of MTBEdegradation were found in the first 4 months. However, in a few cases a decrease of MTBE was observed, in particular under iron- and nitrate reducing and methanogenic conditions (20 % loss of MTBE). The verification of these observations is currently under progress.

#### **Field sites**

Along sampling campaigns at field sites it could be demonstrated that the MTBE site in Duesseldorf has time dependant variations in groundwater concentrations. The BTEX site in Duesseldorf provides a wide variety of concentrations (<10  $\mu$ g/L to more than 4000  $\mu$ g/L) for the testing of the sensing devices. A switch of remediation wells will cause a controlled BTEX-contamination plume that will be used to detect a simulated contaminant spreading. At the Salzburg water facilities no contaminants were found. This emphasis the high protection demand of these groundwater resources and the need of an early warning and management system.

#### Early warning and decision support

For early warning and water management in groundwater catchment areas a framework for the integrated system has been formulated and the various components necessary to implement the system have been identified. This system is based on a conceptual model (CM) system including contaminant transport. It is the framework for mathematical model systems and the decision support systems. At the Salzburg water facilities a basic dynamic integrated monitoring system (DIMS), based on an automatic semi-on-line monitoring system is installed. A conceptual model for the catchment area is under development and refinement. First results from Salzburg show safety relevant changes in the previous hydraulic system description, discovered by CM refinement in the project.

#### Contact

Dr. Thomas Track DECHEMA e.V., Research Co-ordination Theodor-Heuss-Allee 25, 60486 Frankfurt/Main, Germany Phone: +49 (0)69 75 64 427; Fax: +49 (0)69 75 64 117 Email: track@dechema.de Project Website: http://www.watch-eu.org

## DEVELOPMENT OF IMPROVED DETECTION SYSTEMS FOR MONITORING OF TOXIC HEAVY METALS IN GROUNDWATERS AND SOILS

- Project DIMDESMOTOM, Development of Improved Detection Systems for Monitoring of Toxic Heavy Metals in Groundwaters and Soils
- Authors M. Valiente and G. Perez, Universitat Autónoma de Barcelona, Departament de Química, Spain
- Keywords Toxic heavy metals, monitoring of contaminants, chemical sensors, biosensors, field measuring instrument, pollution trends, chemical speciation, sequential extraction schemes, geographical information systems

#### Abstract

The monitoring of contaminated land and ground water bodies with heavy metals is particularly important both for identification of trends of pollution and to control the efficiency of remediation activities. Monitoring of contaminated lands and waters with toxic heavy metals (THM) requires development of novel analytical detection systems for their quantitative determination in matrices of different complexity including ground waters and soils of different types. The solution of this task requires, in turn the translation of measurements obtained by using analytical methods developed for the determination of THM in the laboratory (e.g, based on atomic absorption/emission spectroscopy, X-ray fluorescence, polarographic techniques, etc.) to simple field portable instruments. The current THM detection systems are generally limited to spectrophotometric chemical test kits. These offer the convenience of field analysis but have several important limitations:

#Speciation is not achieved, only total content is determined

#Chemical and physical interferences to measured signal can be dramatic

#Still require a high degree of user competence

Thus, data are poor to determine trends in pollution and to contribute to a proper risk assessment.

A more attractive approach should accomplish for a proper solution of the above limitations. In this concern, the present project is addressed to the development and validation of sensitive and robust sensing devices, including chemical sensors and biosensors and biomimetic systems for on-line operation and real time measurements of THM present in contaminated soils and surface waters, to identify the trends of pollution and control of the efficiency of remediation activities.

### Objectives

Within this context, the specific objectives of the present project can be summarised as follows:

- (1) Development and construction of electrochemical biosensors/immunosensors for detection and analysis of toxic heavy metal ions in water and soil samples based on two different type of biological sensing receptors such as enzymes and available antibodies. The proposed electrochemical sensors use advanced manufacturing technology and are hence amenable to scale-up. Production of a batch of sensors for field trails.
- (2) Development and construction of suitable screen-printed electrodes for the stripping voltammetric analysis of heavy metal contamination. Production of a batch of sensors for field trails.
- (3) Development and construction of screen-printed electrodes for the stripping voltammetric analysis of heavy metal contamination with improved electrode selectivity. The improvement of electrode performance will be achieved due to immobilisation of catalytic coatings and metal chelators on the electrode surface for Adsorptive Stripping Voltammetric (AdSV) analysis.
- (4) Development and construction of a portable system for heavy metal detection in a contaminated soil and water matrices through the development of suitable instrumentation, data analysis algorithms and system software, which allow for field trial assessment of the developed heavy metal sensor. The main role of the instrumentation in the system is to guide the user through the measurement steps, acquire the necessary signals for system compensation and the signal in the anodic or adsorptive stripping voltammetric detection step. The signal-processing algorithm within the instrument will calculate the required compensation functions and correlate the compensated metal signal with leached soil concentration. The system software will control data acquisition and processing and control all user input and output functions.
- (5) Identification of THM pollution trends by determination of appropriate parameters that include: a) Characterisation of THM chemical speciation in samples of contaminated soils and waters from European polluted areas under different environmental conditions such as acidic, alkaline, reductive and oxidative. b) Determination of the evolution of THM chemical species with the change in the environmental conditions. c) Identification of the THM mobilities in soil samples by both the interactions of soil-water interfaces and the evolution of chemical species under the mentioned conditions. Soil samples from two polluted sites in France and Spain will be collected. Appropriate number of samples will be collected from each site. Some of these samples will be analysed by using sequential extraction schemes followed by determination of THM species by using hyphenated techniques, i.e. ion chromatography-ICP-MS, capillary electrophoresis-ICP-MS and other related spectroscopic and electrochemical techniques as detector systems for separation methods. Other samples will be used for laboratory validation of electrochemical and biosensors developed.
- (6) Validation of developed sensors under laboratory and field conditions by detection of heavy metals content in soil, water and soil-water samples. Parallel validation trails (using alternative analytical techniques) will be carried by consortium partners to establish objective criteria of sensors performances. The main emphasis will be done to the reliability and reproducibility of the screening sensors developed for detection of Cd, Pb, Cu, Zn, Hg, and As. This objective also include systematic validation procedures by using soil sample standards and normalised tests applied to this type of samples.

- (7) Integration of the data generated by the new instruments into a decision-taking scheme based on a GIS (Geographical Information System). The data of increased quantity and improved quality obtained through the sensors development will be converted into information for the purpose of risk assessment and remediation control. This will be achieved by the development and demonstration of specific GIS modules. They will mainly provide risk assessment schemes taking into account: sampling density and data uncertainty, spatial distribution of toxics and of risk factors, and the geochemical transformation potential (linked to the binding form of heavy metals). Thus the GIS will demonstrate the practical benefit obtained by developing the new sensors.
- (8) Evaluation of the developed systems to control the efficiency of remediation processes for decontamination of polluted soils in selected contaminated areas of Europe. This will include a minimum of two remediation processes which efficiency will be characterised by the novel sensor system. The related data will be evaluated by the GIS procedure to demonstrate the potentiality and flexibility of this technique. A corresponding database will be available in the project web site.

These objectives are characterised by a multidisciplinary technical and scientific content, including chemical engineering, separation chemistry, fluid dynamics, analytical chemistry and process ecology.

#### **Objectives Achieved To-date**

- (1) Design and production of screen-printed carbon/gold sensors for target metals
- (2) Design and production of surface-modified sensors
- (3) Development and characterisation of enzymed based sensors
- (4) Characterisation of surface modified sensors
- (5) Optimisation of chelating agent selectivity
- (6) Specification of sensor operating characteristics
- (7) Prototype Analogue interface circuits
- (8) Development of hyphenated technique procedures for chemical speciation of THM in soil and water samples
- (9) Compilation of relevant database
- (10) Evaluation of real samples
- (11) Investigation of sensor array possibilities
- (12) Collection of soil and groundwater samples from contaminated sites
- (13) GIS functional specifications
- (14) GIS software description
- (15) Data input and validation module
- (16) GIS application report to one site
- (17) Marketing reports (2)

#### **Objectives Remaining**

- (1) Final Optimisation, characterisation and validation of sensors
- (2) Identification of main measurement interference's
- (3) Assessment of interference's on measurement
- (4) Robust signal processing algorithms
- (5) Prototype field instrument
- (6) Pre-production microcontroller-based field instrument
- (7) Field trials of developed sensors
- (8) Application and validation of the coupled sediment-water quality module
- (9) Specification and software structure for the cost estimated module

#### Specific Scientific/Technical Results Achieved To-date

- (1) The screen-printed electrodes were successfully fabricated. The problems encountered with the sensor sensitivity to metal ions have been overcome by changing the immobilisation of the urease layer.
- (2) Enzyme based biosensor has been tested with Cu (II). The linear range of inhibition was found to be up to 50 ppb of Cu (II).
- (3) A bovine-serum albumin (BSA)-GSH-Hg and BSA-GSH coating conjugates were prepared to develop the Hg (II) immunosensor. The ELISA test was developed, how-ever low response was achieved with the antibody. Several experiments were conducted to improve the ELISA test, but low sensitivity was achieved. Visits to Technical University of Munich, Germany taken place, where the antibody was developed to carry out further experiments. All results from the visit also showed low antibody response. It was decided to raise new antibody in order to improve the performance of the test.
- (4) Microelectrode array sensors have been fabricated and are under test. Preliminary results show that the electrodes and packaging are stable in acidic media.
- (5) The screen-printed chemical sensors have been fabricated and characterised. The sensors have been tested for a range of metal ions detection. Sensitivity to different metal ions has been established. The sensors have also been tested with real samples and the results achieved are very promising for metal ions detection.
- (6) Both screen-printed and planar gold electrodes have been investigated. The behaviour of monolayer coated gold electrodes in the BCR extraction media has been assessed. The use of polymer-modified screen-printed carbon electrodes has been assessed for metal detection. Cadmium detection at thiol-based self-assembled monolayer electrodes is possible, it appears the detection is based on underpotential deposition/stripping. This causes the linear ranges to be quite small. Competition between the surface carboxylate groups and the solution carboxylate groups will limit the applicability of these SAM sensors to BCR extracts 2 and 3.
- (7) A prototype field instrument for implementation of electrochemical sensor measurements has been developed, constructed and tested in the laboratory. This involves the analogue interface circuits and control/processing software for the micro-controller. The instrument has been shown to operate with a real electrochemical cell under laboratory conditions. The instrument was demonstrated to the consortium at the consortium meeting at end of year 2.

- (8) The development and validation of the conventional BCR-SES for the analysis of the toxic heavy metals have been accomplished. All metals are traceables for fractions F1, F2 and F3, except Cr in F3.
- (9) Preliminary results indicates MW-SES produces similar results to the conventional SES. In the analysis of the pseudo-total content (F4) by microwave oven (CM 141R as reference material), only Cu is non traceable. This achievement will reduce the sample processing from 54 hours to 50 minutes. The validation and optimisation of F1, F2 and F3 is under process.
- (10) An intensive database has been compiled from the remediation project. The former includes geographical, geological, historical and analytical information. The data collection criteria has emphasized the potential usefulness of this information for the development and application of the GIS system.
- (11) The transport and risk evaluation model has been developed at the Salsigne site (site 1). All software functions have been defined. The data input and validation functions are available. All necessary field data have been collected on site and have been put into the model. The model is now ready for being calibrated in order to perform risk assessments.
- (12) The statistical data representation has been developed for the Vallecas site (site 2). The software functions have been defined. The pollution on site has been represented statistically.

## Contact

Manuel Valiente Grup de Tècniques de Separació. Unitat de Química Analítica. Departament de Química. Edifici C. Facultat de Ciències. Universitat Autònoma de Barcelona. 08193, Bellaterra.Barcelona, Spain. Phone: 0034935812903 Fax: 0034935811985 E-mail. Manuel.Valiente@uab.es

## SESSION 4C TECHNICAL SOLUTIONS – REMEDIATION

Chairman: Martin Bittens, Tuebingen University (DE)

## SUMMARY

The session focused on scientific findings in the field of soil and groundwater remediation. Of the sessions of the cluster meeting this was the most "technical" session since all presentations addressed specific scientific and technical issues of remediation techniques. A wide range of remediation methods were addressed including passive treatment methods, biore-mediation, adsorption treatment, and phytoremediation.

The first two project presentations dealt with passive water treatment methods such as permeable reactive barriers. Representing the project "Passive In-situ Remediation of Acidic Mine/Industrial Drainage – PIRAMID", **Carlos Ayora** of the Institute of Earth Sciences 'Jaume Almera' of CSIC, Spain, gave a presentation on the use of caustic magnesia in passive remediation systems. The process targets mainly at the removal of two- and three-valent inorganic contaminants (heavy metals) from aqueous solution. The removal mechanism employed is the formation of metal hydroxides governed by the increase of solution pH by the caustic magnesia. Results of laboratory experiments proving the efficacy of the process were presented, and limitations such as the reduction of hydraulic permeability due to the formation of precipitates were discussed.

An overview of the project "Long-term Performance of Permeable Reactive Barriers used for the Remediation of Contaminated Groundwater – PEREBAR" was given by **Karl Ernst Roehl** of the Department of Applied Geology, Karlsruhe University, Germany. PEREBAR is one of the core projects of the IMAGE-TRAIN Accompanying Measure and supports IMAGE-TRAIN's ongoing activities. Similar to the PIRAMID project, the scientific focus of PEREBAR lies on the efficiency of different materials and geochemical mechanisms to remove contaminants from aqueous solution in passive treatment systems, with special emphasis on the long-term performance of such systems. An overview of the laboratory and field work was given and a summary of preliminary results presented. Following the project overview, **Mihaly Cs vári** of Mecsek Ore Environment Corp. in Pécs, Hungary, reported on the implementation of an experimental reactive barrier at the project's field test site in Pécs. The experimental barrier is located on the site of a former uranium ore processing plant and consists of a pilot-scale zero-valent iron treatment wall.

The project "Molecular Tools for Assessing Bioremediation Potential in Organohalogen Contaminated Sites – MAROC" was presented by **Christope Regeard** of the Laboratoire de Biotechnologie Environnementale, Ecole Polytechnique Fédérale de Lausanne, Switzerland. An overview of the project and its objectives was given, and results for the evaluation of degradation processes of chlorinated hydrocarbons based on genetic analysis were presented. Molecular detection methods like those developed in the MAROC project could prove useful for the assessment of the biodegradation efficacy, e.g., in natural attenuation schemes.

**Karsten Levsen** of the Fraunhofer Institute of Toxicology and Aerosol Research in Hannover, Germany, presented the project "On Site Remediation of Groundwater Contaminated by Polar Organic Compounds Using New Adsorption Technology – ORGONATE". Within this project, new polymeric sorbents for the on-site removal of polar organic contaminants from contaminated groundwater have been developed and tested. Adsorption isotherms and column breakthrough curves were presented for a variety of organic compounds, as well as first results of a newly installed pilot plant. The new sorbents appear to be regenerative (e.g., by steam) and insensitive towards fouling or pore plugging, respectively.

The last presentation in this session was given by **Meri Barbafieri** of the Italian National Research Council, Pisa, Italy, on the project "A Decision Support System to Quantify Cost/Benefit Relationships of the Use of Vegetation in the Management of Heavy Metal Polluted Soils and Dredged Sediments – PHYTODEC". A brief introduction of the project was followed by a discussion on the advantages and disadvantages of phytoremediation for inorganic contaminants. Results of greenhouse and field experiments were presented and the bioavailability of the inorganic contaminants highlighted as the most limiting factor to plant uptake. Chemical treatment was discussed to increase the metal mobility. The discussion following the presentation focused on general aspects of feasibility of phytoremediation, and on the implication and potential risk of the proposed additional chemical soil treatment, especially concerning the leaching of mobilised inorganic compounds to the groundwater. The use of phytoremediation not only to extract but also to immobilise contaminants was emphasised.

Although dealing with a variety of issues such as organic vs. inorganic contaminants or active vs. passive methods, all presentations described technical efforts to improve the contamination management of sites and make it more cost effective and sustainable.

Karl Ernst Roehl, Karlsruhe University – Germany

## PASSIVE IN SITU REMEDIATION OF METAL-POLLUTED WATER WITH CAUSTIC MAGNESIA: EVIDENCE FROM COLUMN EXPERIMENTS

Project PIRAMID; Passive In situ Remediation of Acid Mine and Industrial Drainage

C. Ayora<sup>1</sup>, J. Cama<sup>1</sup>, J.L. Cortina<sup>2</sup>, I. Holtermann<sup>2</sup> and J. de Pablo<sup>2</sup> <sup>1</sup> Institute of Earth Sciences Jaume Almera, CSIC, Spain <sup>2</sup> Dept. of Chamical Engineering, Universitat Palitàeniae de Catal

- <sup>2</sup> Dept. of Chemical Engineering, Universitat Politècnica de Catalunya, Barcelona, Spain
- Keywords Acid drainage, passive remediation, metal removal, column experiment, magnesia, brucite

#### Abstract

**Authors** 

Passive remediation is an inexpensive and ecologically friendly alternative to treating acid metal-polluted waters. It is a permeable system which enables the water to pass through whilst retaining metals by means of biogeochemical reactions. Conventional passive treatments are based on calcite dissolution, which increases pH to values between 6 and 7 which are insufficiently high to precipitate two-valence metals. Alternative treatments are based on sulfate reduction with organic matter in order to precipitate metal sulfides. However, redox reactions are usually too slow to treat large groundwater flows as currently found in gravel aquifers (>50 m/a).

Caustic magnesia obtained from calcination of magnesium carbonate was tested as an alternative material to devising passive remediation systems. Caustic magnesia reacts with water to form magnesium hydroxide, which dissolves increasing the pH to values higher than 8.5. Then, zinc and lead are mainly precipitated as hydroxides, copper as sulfate and manganese (II) is oxidized and precipitated as manganese (III) oxides. Magnesia dissolution is sufficiently fast to treat large flows.

The new precipitates may lead to a permeability drop in the porous treating system. Mixtures of caustic magnesia and an inert material such as silica sand (approx 50 % of each) have been shown to be sufficiently reactive and much more durable than pure magnesia.

#### Column experiment #1: Multi-component solution

The capacity of the caustic magnesia to precipitate metals in dynamic conditions was tested using a column experiment and an inflowing solution containing several metals. The evolution of the different solutes and of the pH of the outflowing solution are represented in Fig. 1. The experiment lasted for 90 days, and the conditions are described in Tab. 1, experiment #1.

			Experiments								
			1	2.1	2.2	2.3	2.4	3.1	3.2	3.3	3.4
Column	Length	mm	200	60	60	60	60	70	70	70	70
	Section	mm <sup>2</sup>	700	314	314	314	314	570	570	570	570
	Solid	g	88	20	20	20	20	50	53	56	59
	Magnesia	Wt %	100	100	100	100	100	80	60	40	20
	Quartz	Wt.%						20	40	60	80
	Pore vol.	mL	43	6.1	5.9	6.1	5.8	22	23	18	16
	Porosity		0.31	0.32	0.31	0.32	0.31	0.55	0.58	0.45	0.50
	Flow	mL/min	0.2	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
	Darcy flux	m/a	145	100	100	100	100	60	60	60	60
	Residence	min	80	100	100	100	100	360	360	300	260
Inlet	рН		3	2	2	2	2	5.5	5.5	5.5	5.5
	Zn	mg/L	100	75	-	-	-	75	75	75	75
	Cu	mg/L	50	-	75	-	-	-	-	-	-
	Pb	mg/L	-	-	-	75	-	-	-	-	-
	Mn	mg/L	-	-	-	-	75	-	-	-	-
	AI	mg/L	10	-	-	-	-	-	-	-	-
	Fe	mg/L	20	-	-	-	-	-	-	-	-
	Ca	mg/L	360	-	-	-	-	-	-	-	-
	SO <sub>4</sub>	mg/L	960	960	960	960	960	1000	1000	1000	1000

Tab. 1: Summary of the initial conditions of the different column experiments

The initial pH value around 12 correlated with high Ca concentrations and was attributed to the dissolution of a minor amount of lime present in the caustic magnesia sample. After lime exhaustion, the Ca concentration dropped to the inflowing limit. Then, the Mg concentration reached a steady value between 20 and 25 mg/L, and the pH is maintained between 9 and 10. This is attributed to the dissolution of brucite, which coats the magnesia grains. Brucite dissolved sufficiently fast to reach equilibrium during most of the experiment run, and is able to maintain the pH. After 160 pore volumes, however, the flow was increased to 2 ml/min. The magnesia present in the column was not able to attain equilibrium, and the pH dropped to 6.0. This demonstrates that a thickness of magnesia exceeding 0.2 m is necessary to neutralize very high fluxes of acid water (>4 m/day). When the initial flow of 0.2 ml/min was restored the pH rose again to values between 9 and 10. After 400 pore volumes, the flow dropped, and the Mg and pH decreased. This is attributed to the partial clogging of the column and the formation of preferential flow paths due to the precipitation of new solid phases.

The concentration of metals was below the detection limit of the analytical technique (ICP-AES), with the exception of occasional increases in Zn and Cu. The concentration of metals correlated strongly with pH. For pH exceeding 8.5 the outflowing solution had a very low metal content, and for pH between 8.0 and 6.0 the concentration of Zn and Cu increased significantly. It should be noted that Fe and Al concentrations were always below the detection limit regardless of the pH. This experiment demonstrates that caustic magnesia can reduce the concentration of metals down to regulatory levels, for fluxes of polluted water characteristic of permeable aquifers.



*Fig. 1.* Evolution of pH, Ca, Mg and metal concentration of the outflowing solution in the multicomponent experiment.

After the experiment, green, white and red precipitates were observed throughout the column. The column was dismounted and half of the solid was digested and analyzed. Distribution of the different heavy metals retained did not show a homogeneous distribution along the column. The mass of metal in the outflowing solution plus that in the digested samples resembled that in the inflowing solution with errors below 10 %.

SEM-EDS observations showed a crust that was not crystalline in appearance and covered the brucite surface. The different components of the inflowing solution were detected in this crust: Al, Fe, O, Zn, and Cu. In addition to crusts, aggregates of crystals formed by Cu-O and Zn-O were also abundant. Following their elemental composition, the crystals were interpreted as  $Cu(OH)_2$  and  $Zn(OH)_2$  (H is not detected by EDS). In the case of the hexagonal plates, the  $\eta$ -Zn(OH)<sub>2</sub> polymorph has been reported to have a hexagonal symmetry (card 24-1444; JCPDS, 2001). XRD diffractograms of the samples only showed periclase and brucite.

The dependence of metal concentration on pH can be attributed to the solubility of the hydroxides. Thus, metal ions with electric charge 3+, such as iron and aluminum show low concentrations for any pH value exceeding 6. Minor amounts of Cu and Zn co-precipitated with Fe-Al-hydroxides. According to thermodynamic data, the predicted concentration of Cu in equilibrium with Cu(OH)<sub>2</sub> for pH higher than 8.5 is below the detection limit, which is consistent with the measurements (Fig. 2). By contrast, the predicted concentration of Zn in equilibrium with Zn(OH)<sub>2</sub> is higher than 2.5 g/L (log C= -4.4 mol/L). This is inconsistent with the analytical values below the detection limit and warrants further investigation.



*Fig. 2:* Variation of the metal concentration in equilibrium with selected solid phases. Thermodynamic data from the Wateq4f database (Ball et al., 1987). In the absence of a solid phase, the maximum concentration assumed is 0.1 mol/L. D.L. accounts for detection limits.

#### Column experiments #2: unicomponent solutions

The previous experiment using a multicomponent solution showed that metal removal is in part linked to the precipitation of a crust of iron and aluminum oxy-hydroxides. Since these two metals are not necessarily present in polluted waters, a series of assays using single component solutions of Zn, Cu, Pb and Mn were carried out (Tab. 1, experiments #2).

The experiments lasted for 10 months. The outflowing solution from the columns treating Zn, Cu and Pb showed a trend similar to that described for the multicomponent experiment (Fig. 3). Owing to lime dissolution, pH started with values close to 12, and then decreased to values close to 9, indicating brucite control. After a number of pore volumes which differed in each experiment, the pH dropped to values between 6 and 7 and the experiment was cancelled. Mass balance considerations show that only 40 wt.% of the magnesia was consumed at that point The fall in pH could be due to the armoring of the periclase-brucite surface with precipitates or to the switch from pore to fracture flow caused by precipitates. The pH decrease below 8 is accompanied by a significant increase in the metal content in the outflowing solution. It is interesting to note that Zn, and especially Cu showed concentrations exceeding the inflowing value (75 mg/L). This is attributed to the dissolution of the solids formed in the previous step. Therefore, a remediation system based on the reactions described must be removed when symptoms of exhaustion appear. After 10 months the column treating Mn was still working with high efficiency (Fig. 3).


*Fig. 3.:* Evolution of pH (right hand scales), Zn, Cu, Pb and Mn concentration of the outflow in column experiments with unicomponent inflowing solutions.

SEM-EDS observations of the precipitates from experiment 2.1 showed the ubiquitous presence of Zn-O hexagonal plates which were interpreted as  $\eta$ -Zn(OH)<sub>2</sub>. For experiment 2.2, in contrast to multicomponent experiment 1, aggregates of monoclinic crystals made up of S-O-Cu were the main component of the precipitates. They were identified as brochantite (Cu<sub>4</sub>SO<sub>4</sub>(OH)<sub>6</sub>) by XRD. The predicted concentration of Cu in equilibrium with brochantite at pH 8.5 is higher than 0.60 mg/L (log C= -5.0 mol/L), which is inconsistent with analytical values below the detection limit (Fig. 2).

Under SEM-EDS observation, the precipitates from experiment 2.3 were made up of a Pb-O matrix with no clear crystallinity. Aggregates of hexagonal plates were occasionally observed. Hydrocerrusite,  $Pb_3(CO_3)_2(OH)_2$ , was identified by XRD, and could correspond to the hexagonal-shaped crystals. In accordance with the measurements, the predicted concentration of Pb in equilibrium with  $Pb(OH)_2$  is below the detection limit for pH values higher than 8.5 (Fig. 4). Hydrocerrusite equilibrium, however, would yield Pb concentration in solution well above the detection limit. Hence, we attributed most precipitate to  $Pb(OH)_2$ , whereas hydrocerrusite would correspond to a quick carbonation in contact with the atmosphere.

Hausmannite ( $Mn_3O_4$ ), manganite (v-MnOOH) and ( $\eta$ -MnOOH) were identified by XRD in precipitates from experiment 2.4. The SEM-EDS observation showed hexagonal plates on a microcrystalline mass with a botriodal appeara1nce. Both the mass and the crystals were made up of Mn and O (H is not detected). The plates could correspond to feitknechtite, of hexagonal symmetry (Bricker, 1965). Feitknechtite has been described as part of the 'hydrohausmannite' formed by oxidation of this mineral. The removal of manganese is a very interesting phenomenon. The concentration of Mn(II) in equilibrium with Mn(OH)<sub>2</sub> is high at any

pH (Fig. 4). However, Mn(II) is oxidized to Mn(III). The concentration of Mn(III) in equilibrium with manganite is very low (similar to hausmannite, which is not represented), and this phase could explain the experimental concentrations below the detection limit (Fig. 4). Unlike iron, the oxidation of Mn(II) is sufficiently fast only at pH exceeding 9 (Stumm and Morgan, 1981, pp 465-468). Therefore, the high pH values caused by caustic magnesia dissolution are essential to remove manganese from solution.



*Fig. 4:* Variation of the metal concentration in equilibrium with selected solid phases. Thermodynamic data from the Wateq4f database (Ball et al., 1987). In the absence of hydroxide, the maximum concentration assumed is 0.1 mol/L. D.L. accounts for the detection limit.

We demonstrated that a column of 0.07 m of a mixture of caustic magnesia (>40 wt.%) and quartz was able to remove the metal content from a flux of 0.06 mL/s of polluted water at least for 10 months. Therefore, a passive system, either a barrier or an infiltration pond, 2 m thick with a similar mixture could treat a flux of 60 m/a for more than 20 years. Although caustic magnesia can neutralize very acid waters, it is more economical to raise pH first to neutral-slightly acid values with calcite and/or organic matter.

As regards organic matter-based treatments, the dissolution of magnesium oxide and metal hydroxide precipitation is very fast, whereas sulfate reduction and sulfide precipitation is slow and dependent on kinetic and bacteriological factors. Therefore, the residence time of the water in the filter is lower for the caustic magnesia with the result that larger fluxes of water can be treated with thinner systems. As regards carbonates, the pH range obtained from magnesium oxide allows the precipitation of divalent metals. This process does not take place for pH values between 6 and 7, commonly resulting from carbonate dissolution. With respect to lime, magnesium oxide is less soluble and more lasting, and it occurs in several permeable grain sizes. Moreover, the pH resulting from magnesium oxide dissolution (8 to 10) is closer to natural values, and is more efficient in precipitating most metals than the pH resulting from lime dissolution (12). Many metal compounds re-dissolve at such high pH values.

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### Contact

Carlos Ayora Institut de Ciencies de la Terra (Jaume Almera), CSIC Lluis Sole i Sabaris, s/n 08028 Barcelona Phone: 34-93-4095410; Fax: 34-93-4110012 Email: ayora@ija.csic.es http://www.ija.csic.es/geologia/hidro

# LONG-TERM PERFORMANCE OF PERMEABLE REACTIVE BARRIERS – RESULTS OF THE PEREBAR PROJECT

Project PEREBAR, Long-term Performance of Permeable Reactive Barriers used for the Remediation of Contaminated Groundwater

 Authors K.E. Roehl<sup>1</sup>, M. Cs vár<sup>2</sup>
 <sup>1</sup> Department of Applied Geology (AGK), Karlsruhe University, Kaiserstrasse 12, D-76128 Karlsruhe, Germany
 <sup>2</sup> Mecsek Ore Environment Corp., Pécs, Hungary

Keywords Groundwater, remediation technology, permeable reactive barrier

### Abstract

Permeable reactive barriers (PRB) are used for passive in-situ groundwater remediation. In the PEREBAR project supported by the European Union the long-term behaviour of PRBs has been studied with the main emphasis on reactive material properties and physico-chemical processes. The following aspects are included in the project work:

- #Reactive materials for permeable reactive barriers: Macroscopic to nano-scale properties and characteristics.
- #Innovative barrier materials: Tailored ligands selectively targeting specific contaminants, in a stable and robust reactive matrix.
- #Attenuation processes in reactive barriers: Study of relevant sorption and degradation mechanisms.
- #Geochemical aspects: Influence of soil and groundwater composition on the barrier performance.
- #Long-term behaviour: Factors inhibiting the barrier efficacy and their significance.

PEREBAR is part of the IMAGE-TRAIN Accompanying Measure and supports IMAGE-TRAIN's ongoing activities. This paper gives an overview of the PEREBAR project and its current status and describes the implementation of an experimental reactive barrier at the project's test site in Pécs, Southern Hungary.

### Introduction

The European research project "Long-term Performance of Permeable Reactive Barriers Used for the Remediation of Contaminated Groundwater" (Acronym: PEREBAR, contract no. EVK1-CT-1999-00035) will conclude its work in spring 2003. A comprehensive presentation of the project's objectives and workplan has been given at the IMAGE-TRAIN Cluster Meeting in Karlsruhe in November 2001 (Roehl & Czurda, 2002). The intention of this paper is to update on the project's current status and describe the installation of an experimental reactive barrier at the project's test site in Pécs, Southern Hungary.

The focus of the PEREBAR project is on the use of permeable reactive barriers (PRBs) for passive groundwater remediation. There are numerous examples worldwide for the application of such systems in urban environments. PRBs can be used in brownfield remediation

projects, such as the industrial park "Campus 21" in Brunn am Gebirge outside Vienna, Austria. At this site, a groundwater cleaning facility has been installed consisting of a hydraulic barrier and activated carbon in-situ reactors, removing a mixture of organic compounds from heavily contaminated groundwater (Niederbacher, 2002). Another example of an activated carbon system in a densely built-up area is located in Karlsruhe, Germany, where a Funneland-Gate system has been installed between various buildings of a former slaughterhouse area, intercepting a PAH plume originating from a former gas works site. The system consists of a sheet piling wall and 8 activated carbon gates (Schad et al., 2000). Installation of PRBs is possible in certain cases even inside buildings, as implemented in Reichenbach in Germany, near Stuttgart. The PRB, consisting of non-overlapping bore-holes filled with activated carbon, was built inside a manufacturing hall (Edel & Vigt, 2001). PRBs are also suitable to implement groundwater remediation schemes in residential areas or on other sites with uses typical in urban areas such as shopping centres, parking lots, industrial parks etc.

Although the use of PRBs is limited to certain site conditions, in places where the application is feasible they appear to be a good choice with good acceptance by end-users, especially in urban environment and built-up areas. Reasons for this can be seen in, e.g., little land use, little visibility, no additional impact on the landscape by equipment such as containers, water tanks, pumps, or by noise from running machines etc.

### Scope of the PEREBAR Project

Two test sites form the central points of the project. One of them is the former uranium ore mining and processing area in Pécs, Southern Hungary. The second site is in Brunn am Gebirge, Austria with an activated carbon PRB system. Especially due to the conditions at the first site the project had its focus on uranium contamination. Reactive materials for PRBs and contaminant attenuation processes in these materials, such as sorption and degradation mechanisms, and geochemical processes in the barrier material that are governing the efficiency of PRB systems on the long-term, especially the influence of groundwater constituents, have been studied. To investigate the long-term performance of PRBs, the properties of the reactive material itself and the geochemical processes taking place inside the porous matrix of the reactive material have been looked into. Therefore, the project has been primarily dealing with the reactive material and not touching in a wider sense hydrogeological aspects such as hydraulics, catchment zones etc. Details on the work plan have been given by ROEHL & CZURDA (2002).

### Laboratory Studies

The mineralogical composition and physicochemical properties of selected materials suitable for use in a reactive barrier targeting at the removal of uranium and other metals/metalloids from contaminated groundwater have been studied. The materials chosen were zero-valent iron (Fe<sup>0</sup>), Mg(OH)<sub>2</sub>, natural zeolites, hydrated lime, and phosphate minerals (hydroxyapatite). Mainly uranium but also other heavy metals have been studied in the selected materials.

Column and container experiments have been conducted and are still ongoing to evaluate contaminant removal from the groundwater and its efficiency as a function of time. Accelerated experiments have been performed on uranium in artificial matrix solutions with a composition close to that of groundwater on the test site in Pécs. Geochemical aspects, such as

the influence of major groundwater constituents and/or pH on contaminant (especially uranium) attenuation by the selected reactive materials, have also been studied to evaluate factors inhibiting the barrier efficacy and their significance on the long-term performance.

The experiments showed that zero-valent iron has the best uranium attenuation capability, although U removal is negatively affected by the presence of dissolved carbonates. The removal processes are not yet fully understood. Possible mechanisms of uranium removal from water by zero-valent iron are reductive precipitation, co-precipitation with iron corrosion products, and sorption on to iron oxide surfaces.

Hydroxyapatite also exhibits excellent uranium removal capacity over a wide pH range, and were unaffected by high-concentration dissolved carbonates and sulphates. Slight dissolution of hydroxyapatite can be detected, though. The removal of uranium is taking place by precipitation.

Natural zeolites have an excellent U removal capacity, but are highly influenced by pH and dissolved carbonate. The removal process is adsorption (cation exchange). Lime is also very efficient in removing uranium, but has a high solubility in groundwater. Activated carbon has a very poor U attenuation capacity (predominant mechanism: adsorption).

Innovative barrier materials have been developed for the removal of uranium from groundwater. The new material, named PANSIL, consists of tailored ligands selectively targeting the uranyl ion, bound to a silica matrix, and is currently being tested for its applicability in a robust and stable matrix for use in PRBs or other groundwater remediation efforts. The material proved to be highly effective at sequestering  $UO_2^{2^+}$  from solution when the pH is between 5 and 8. Uranium removal from water is achieved by formation of a stable polyacryloamidoxime uranyl complex.

Electrokinetic experiments have been conducted to evaluate the potential of electrokinetic techniques to improve the performance of PRBs. One of the major problems related to the long-term performance of PRBs seems to be the clogging of pore space and coating of the reactive surfaces by precipitates. An electrokinetic approach is tested in which the concentration of groundwater constituents that might impair the barrier's function is reduced by applying an electric field upstream of the barrier. Laboratory experiments prove that electrokinetic retardation of both anions as well as cations against a hydraulic gradient is possible, and that implementation of an electrokinetic barrier in the field could be promising. Yet the potential positive and negative impacts of electrochemical by-products on the barrier's function have to be investigated in greater detail.

### **Field Studies**

Site characterisation and additional field work at the test sites in Brunn am Gebirge, Austria, and Pécs, Southern Hungary, have been completed.

In Brunn am Gebirge, the monitoring of an existing full-scale PRB system (four in-situ adsorptive reactors filled with activated carbon, in operation since 1999) is continued to evaluate parameters significant for the assessment of the long-term performance of such a system. The activated carbon filling has been sampled and the material analysed using chemical analysis, x-ray diffraction, BET adsorption, and REM to detect possible alterations.

At the site in Pécs, decision on a potential field test site was made and this specific location was further investigated using geophysical and hydrogeological methods. An experimental barrier has been planned and implemented at this site (s. below).

### Overview of the field experiments in Pécs, Hungary

Simultaneously with ongoing laboratory experiments the implementation of the field tests was planned. Goal of the field experiments was to determine the efficiency of various reactive materials in removing uranium from groundwater and to obtain information concerning the alteration of the water composition during the treatment process.

The task has been divided into three subtasks:

#Preliminary column experiments in the existing monitoring wells

#Large-scale column experiments in new wells constructed for this purpose

∉#In situ reactive barrier

Groundwater chemistry at the site is presented in Tab. 1. The data show results of water analysis from a monitoring well of the site for the last two years. The groundwater is considerably contaminated with uranium. The actual uranium concentration varies seasonally and with weather conditions. Other heavy metals are present only in minor concentrations.

Monitoring well number	Components and concentration						
Hb-01/1	Na	К	Ca	Mg	CI	$SO_4$	CO <sub>3</sub>
				mg/l			
	88	20	168	53	43	361	<10
	HCO3	TDS	рН	U	Spec.cond.	Mn	Ra <sup>226</sup>
	mg/l	g/l		σg/l	σS/cm	mg/l	10 <sup>-4</sup> Bq/ml
	474	1,03	7,11	718	1496	<1	1.1

Tab. 1: Groundwater chemistry (field test site, 2000 - 2002, average values)

### Preliminary column experiments in monitoring wells

Objective of the preliminary field experiments was to evaluate whether the most promising reactive material, i.e. zero-valent iron (ZVI) is indeed effective for in situ treatment of the groundwater contaminated with uranium. To answer this question, column experiments were performed using existing monitoring wells containing cylinders filled with reactive material.

Two glass columns of 1 m length and 40 mm diameter were used. One column was used to test steel wire (SW) wastes obtained from tyre recycling. This material is available in large quantities near the site. The column was filled with a SW/sand mixture containing 31 % of SW. The other column was used to test reactive iron of German origin (grain size 0.2-3 mm). Two layers of reactive material were placed in this column: in the first layer, the ZVI content of the ZVI/sand mixture was approximately 10 % by volume, and approximately 50 % in the second layer.

Both columns were placed in the monitoring well below the permanent water level. Water passed through the columns due to the hydraulic gradient between the well and the receiving canal. The flow rate was adjusted from time to time and kept between 5  $(10^{-5} \text{ and } 1 \text{ } (10^{-4} \text{ m/s}, \text{ resulting in a residence time of several hours. The experiments lasted three months (October - December 2001). Water chemistry was monitored during the test at the inflow and the outflow of the columns. Main conclusions drawn from the test were that uranium was re-$ 

moved efficiently from the water (the concentration dropped below 20  $\mu$ g/l in the outflow of the columns). The reactive material proved to be effective in removing uranium from the groundwater at the site. Another valuable information was that iron concentration in the column effluent strongly depends on the residence time of the water in the column.

#### Large-scale column tests

The next step of the field tests is related to the investigation of the chemical processes taking place in the columns. An important question is the influence of the residence time and the ZVI concentration in the mixture (with sand) on the chemistry of the effluent. Therefore a second series of in-situ column tests has been implemented at the site. An open well was constructed in which columns (length: 1.8 m, diameter: 160 mm) filled with ZVI/sand mixtures with various ZVI contents (10 %, 25 %, 50 %, and 100 %) have been placed. The installation of the columns is presented in Fig. 1. It could be concluded from these experiments that the flow rate of the groundwater through the columns has a great effect on the iron concentration in the effluent. The dissolved iron can be kept in the column only at low water flow rate (around  $10^{-6}$  m/s). Therefore, this fact should be taken into account in planning the thickness of a ZVI-based PRB.





#### Experimental permeable reactive barrier

Finally a pilot-scale experimental reactive barrier was installed. The Zsid-valley downstream of a large waste rock pile has been chosen for the PRB construction because of the uranium contamination in groundwater. The cross-section of the PRB is presented in Fig. 2. The PRB consist of four sections in groundwater flow direction:

- 1. Sand (grain size 1 3 mm) drainage for collection and distribution of the contaminated groundwater (10-50 cm)
- 2. ZVI/sand mixture (10 % ZVI, grain size 1 4 mm) for removal of dissolved oxygen (50 cm)
- 3. ZVI/sand mixture (45 % ZVI, grain size 0.2 3 mm) for uranium removal (100 cm)
- 4. Sand drainage for collection and distribution of the treated groundwater (10-50 cm)

The top of the PRB is covered with HDPE, compacted clay (30 cm) and soil (50 cm). The PRB is 6.8 m long, 2.5 m thick (including all sections) and 5.1 m deep including the 0.3 m clay at the bottom and 0.8 m topsoil with clay sealing. At the bottom, the PRB is sealed with clay and a *Bentofix* sealing layer to exclude potential upward flow from the bedrock. The two sides are sealed with HDPE. So the installation is practically a box, with two open sides (upstream and downstream surfaces).

The PRB is planned for experimental purposes. Therefore it has two wells (upstream and downstream) which can be used to change water flow rate through the barrier maintaining different hydraulic pressure in the wall. These wells are also used for monitoring purposes. Monitoring wells (screened in the whole depth of the reactive zones) are built into the second and third sections. Some additional monitoring wells are also built in different parts of the PRB and its surroundings (not shown in the Fig. 2).



Fig. 2: Principal structure of the experimental PRB

Phases of construction are illustrated by the photographs in Fig. 3. The experimental PRB now is in operation. First results are presented in Fig. 4. It can be seen that uranium is removed with high efficiency from the percolating groundwater. Iron has not been observed in the effluent. Because of high pH, calcium and magnesium are obviously precipitated in the wall. The experiments are continuing.





Fig. 3: Construction of the experimental PRB in Pécs, Hungary





Fig. 4: First monitoring data from the experimental PRB

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### Contact

Dr. K. E. Roehl Karlsruhe University, Dept. of Applied Geology (AGK) Kaiserstrasse 12, D-76128 Karlsruhe, Germany Phone: (49 - 721) 608 3096, Fax: (49 - 721) 606 279 Email: ke.roehl@agk.uni-karlsruhe.de

Dr. M. Cs vári Mecsek Ore Environment Corp. Esztergár Lajos u. 19, HU-7633 Pécs, Hungary Phone: (36 - 72) 253 055 / 3540, Fax: (36 - 72) 256 044 Email: csovarimihaly@mecsekerc.hu

Project Website: http://www.perebar.bam.de/

# MOLECULAR TOOLS FOR ASSESSING THE BIOREMEDIATION POTENTIAL IN ORGANOHALOGEN-CONTAMINATED SITES: STRATEGY TO DETECT REDUCTIVE DEHALOGENASE GENES

Project MAROC, Molecular Tools for Assessing Bioremediation Potential in Organohalogen Contaminated Sites

Authors

C. Regeard<sup>1</sup>, C. Delbes<sup>1</sup>, M. Göbel<sup>2</sup>, L. Görres<sup>3</sup>, D. Janssen<sup>4</sup>, J. Krooneman<sup>5</sup>, J. Maillard<sup>1</sup>, J. Oppentocht<sup>4</sup>, W. Reineke<sup>2</sup>, B.Z. Ruffinen<sup>1</sup>, M. Schlömann<sup>6</sup>, J. Seifert<sup>6</sup>, C. Strömpl<sup>3</sup>, K. Szynalsky<sup>1</sup>, M. van der Velde<sup>5</sup>, J. van de Waarde<sup>5</sup>, F. Wettstein<sup>6</sup>, D. Pieper<sup>3</sup> and C. Holliger<sup>1</sup>

- <sup>1</sup> Laboratoire de Biotechnologie Environnementale, Ecole Polytechnique Fédérale de Lausanne, CH
- <sup>2</sup> Bergische Universität Gesamthochschule Wuppertal, Department of Chemical Microbiology, DE
- <sup>3</sup> Biodegradation Research Group, Division of Microbiology, GBF, DE
- <sup>4</sup> University of Groningen, Department of Biochemistry, The Netherlands
- <sup>5</sup> Bioclear bv, Groningen, The Netherlands
- <sup>6</sup> Bergakademie Freiberg, Interdisciplinary Ecological Center, DE
- Keywords Chloroaliphatics, chloroaromatics, PCE, reductive dehalogenation, dehalogenases, PCR primers

### Abstract

Chlorinated hydrocarbons are the most important and widespread class of soil and water contaminants in Europe. The possible decontamination of these compounds by bacterial activity has been illustrated in many studies. In field situations, stimulated or natural (intrinsic) bioremediation seems to be appropriate for the removal of this pollution. However, in practice it is difficult to predict the bioremediation potential at polluted sites. Hence, there is a need to develop effective, easy to handle tools to predict and monitor the degradative capacity of microbes within a contaminated environment.

These tools should not be dependent on the culturability of the microorganisms of interest but directly assess the genes coding for enzymes that catalyse the key reactions in the degradation pathways of contaminants. It's why mainly PCR based techniques have been set up in this project and used for the characterisation of samples from different industrial sites including those contaminated with **monochlorobenzene**, **chloroethenes** and/or **chlorinated propenes**.

We developed, based on various new isolates, PCR primers for reductive dehalogenases and key genes of the aerobic degradation of haloaliphatics and haloaromatics. Those primers have been successfully applied to follow the catabolic state of microbial communities under environmental conditions. Here we present the detection strategy developed for the peculiar case of reductive dehalogenases.

### Objectives

The **general objective** of the project is the development and optimisation of molecular detection methods to monitor bioremediation processes. A combination of specific microorganism detection, detection of catabolic genes and transformation activity will allow the accurate analysis of in *situ* natural attenuation. The target pollutants of the project are chlorinated compounds such as **chlorobenzenes**, **chloroethenes** and **chloroalkanes**. In order to reach this goal, the **specific objectives** are to characterise a representative amount of sites concerning their pollution profile, to isolate a representative amount of microorganisms with desired metabolic potential, to characterize the genetic information responsible for the metabolic potential of isolated organisms and mixed cultures, to develop primers and probes, based on the previously accumulated information, and to verify their specificity using laboratory strains and new isolates and to obtain genetic information from the environment that is closely and distantly related. A database linking genetic structure to metabolic function for various key enzymes of halogenated hydrocarbon degradation will be constructed. The database will be the basis for the development of specific probes and primers to analyse and quantify the presence and expression of degradative pathways in contaminated samples.

### Results

Samples have been obtained from several different industrial sites including sites contaminated with monochlorobenzene, chloroethenes and/or chlorinated propenes or subject to biotreatment processes. The endogenous degradation potential differed significantly between the sites. DNA extractions from these different samples or from enrichments of these samples have been performed and used for the MAROC project.

### Aerobic degradation of chlorobenzene

Chlorobenzene degrading organisms could be isolated only from a small subset of samples. Chlorobenzene mineralizing capabilities, however, were observed in the majority of samples, evidencing that either complex micobial communities or microorganisms not (easily) cultivable were responsible for degradation and that culture independent approaches are necessary to predict if a bioremediation potential is present (Pieper et al, 2000). The primer design focussed on genes coding for activating (chloro)benzene dioxygenases and ring-cleaving chlorocatechol 1.2- and 2.3-dioxygenase genes as well as genes coding for specific downstream activities. Usually, primers were successfully applied to amplify the respective DNA fragments from new isolates and environmental samples. In isolates sequences most related to previously described todC1, clcB and cbnB genes were dominating. The extended set of new chlorobenzene degraders mineralising chlorobenzene via a new meta-cleavage route was shown to contain special chlorocatechol 2,3-dioxygenases. A completely new route of chlorocatechol mineralization was observed in a Rhodococcus strain. To be capable to relate sequence information to function, metabolic profiling of catabolic genes was performed and fast tests developed to identify differences in substrate specificity. All thus far isolated chlorocatechol 2,3-dioxygenases exhibit very similar sequences and substrate specificities, whereas significant differences in substrate specificity could be observed in chlorocatechol 1,2-dioxygenases and chloromuconate cycloisomerases. Specific amino acids determining regioselectivity of attack on chlorobenzenes were identified. The described primer sets were used to correlate metabolic activity with the presence and abundance of various key genes of chlorobenzene degradation in microcosm studies. Whereas catabolic genes were detected only in a subset of unstimulated samples, during incubation, slurries usually became stimulated and degradation and mineralisation rates increased concomitant with an increase in extractable nucleic acids. Gene sequences probably encoding chlorocatechol dioxygenase were detected in all active samples. The presence of such an activity was confirmed by biochemical grounds. Chlorobenzene dioxygenase gene sequences were usually enriched throughout the incubation, however, it cannot be excluded that alternative routes of substrate activation are important for chlorobenzene mineralisation by the community. CbzE-like genes could be detected by single PCR in one sludge only at the onset of the experiment indicating that the *meta*-cleavage pathway was not active in the enrichments, and suggests that *ortho*-cleaving bacteria outgrew the *meta*-cleaving population. To convert the genetic approach into a method for routine use, DNA extraction protocols were optimized and validated.

#### Aerobic degradation of haloaliphatic compounds

Sets of specific primers for the amplification of *dhaA*, *hheA*, *hheB* and *hheC*, genes involved in haloakane and haloalkene degradation (Janssen et al, 2000), have been tested on bacterial strains known to contain the specific genes and on new isolates. All new 1-chlorobutane degraders contained a haloalkane dehalogenase (*dhaA*) gene. Ten of the nineteen isolates that grow on 1,3-dichloropropanol, 2,3-dichloropropanol, or both, contain known dehalogenase genes (*hheA*, *B* or *C*). The remaining nine isolates that grow on 1,3-dichloropropanol may contain a different type of halohydrin dehalogenase or may even use a different degradation pathway. The isolates were distributed among the different soil samples, showing that 1-chlorobutane and dichloropropanol degraders are ubiquitous. This is in sharp contrast to the occurrence of 1,2-dichloro- and 1,2,3-trichloropropane degraders, which were not found at all. Actually, the detection of the halohydrin genes (*hheA*, *B* or *C*) directly in environmental samples is tested.

#### Anaerobic degradation of chloroethenes

Over the last few years, accumulating evidence is available suggesting that the most efficient biological reductive dechlorination of chlorinated compounds such as tetrachloroethelyne (PCE) and trichloroethylene (TCE), correspond to the reaction called dehalorespiration. Organisms involved in the dehalorespiration are able to use chlorinated compounds as catabolic terminal electron acceptor and to couple the dehalogenation reaction with energy conservation (Holliger et al, 2002). Some of these organisms (several Desulfitobacterium, Dehalobacter restrictus, Dehalospirillum multivorans) are only capable to transform PCE to dichloroethene (DCE), whereas until now only one is able to completely dechlorinate PCE through ethene (Dehalococcoides ethenogenes). All these bacteria contain the key enzyme involved in this anaerobic process, the reductive dehalogenase (RdhA). Amino-acid sequences of these proteins reveal that they share common features such as iron-sulfur center, export signature, but that they are quite divergent with only 30 % identity. Moreover, these common features are also found in another class of reductase, the chlorophenol reductive dehalogenase. First attempts to detect the genes pceA encoding the PCE RdhA present in Dehalobacter restrictus, pceA encoding the PCE RdhA present in Dehalospirillum multivorans and tceA encoding the TCE RdhA of Dehalococcoides ethenogenes, directly in environmental samples, were not successful. Therefore, we develop a nested PCR strategy to detect these genes in the DNA extracted from environmental samples. The first step consists in a PCR with degenerate primers designed in order to amplify as many as possible of the dehalogenases presents in contaminated sites. We have tested the efficiency of the primers used in this first step, by working on pure genome of the dehalorespiring bacteria Dehalobacter restrictus,

restrictus, Dehalospirillum multivorans, Desulfuromonas chloroethenica and Desulfitobacterium sp. PCE1. By cloning and sequencing the products obtained after this degenerate PCR, we have not only checked the presence of the known reductive dehalogenase genes of Dehalobacter restrictus and Dehalospirillum multivorans, but we have also discovered new putative genes encoding for chloroethene reductive dehalogenase in Dehalobacter restrictus, Dehalospirillum multivorans and Desulfitobacterium sp. PCE1. The second step consists in a nested PCR with specific primers to detect known reductive dehalogenases. The 23 MAROC samples have been studied for the presence of the Dehalococcoides ethenogenes tcea gene, the pceA gene of Dehalospirillum multivorans and the pceA gene of Dehalobacter restrictus. This study reveals that the pceA gene initially observed in Dehalobacter restrictus is present in 82 % of the 23 MAROC samples tested.

In order to develop a more direct molecular tool to assess the bioremediation potential in contaminated environmental samples, we have set up an SSCP (Single Strand Conformational Polymophism) analysis. We have used a multiplex PCR and analysed the amplifications in an SSCP gel. The advantage of this PCR is to be able to amplify in the same tube four reductive dehalogenase genes: the gene pceA of Desulfitobacterium-Dehalobacter restrictus group, the gene pceA of Dehalospirillum multivorans, the tceA gene of Dehalococcoides ethenogenes and a putative rdh gene isolated previously from Desulfitobacterium sp. PCE1. We have checked the efficacy of this multiplex PCR by testing the reaction on a mixture of the cloned corresponding genes. The SSCP analysis for the rdha genes was applied to the 23 MAROC samples. It was possible to distinguish two kinds of patterns. Some patterns had a low diversity (between 4 and 10 bands) whereas others contained a high diversity (more than 10 bands). It is not yet easy to elucidate general characteristics from the comparison of the MAROC SSCP pattern, but it seems that samples coming from groundwater have a higher diversity than DNA samples extracted from soils. It cannot be excluded, however, that this observation is due to a method artefact. DNA extraction from soil is more problematic than DNA extraction from water. But this molecular tool seems very promising to easily visualize in the field the potential of chloroethenes bioremediation. Indeed, we can expect that a complex pattern which corresponds to a high diversity of reductive dehalogenases, is favorable for natural attenuation of chloroethenes.

#### Dehalogenating protein database

A preliminary version of a database is under construction, which contains information of members of all classes of known dehalogenases involved in aerobic and anaerobic degradation, the organisms, enzymes and gene characteristics. The development of a searchable web-based database system is in progress, wherein information of all dehalogenase genes, enzymes, pathways, compounds and organisms will be integrated as well as links to specific data in existing databases on the internet.

### Conclusions

The major goal of the project was the characterization of new isolates capable to dechlorinate or mineralize the target pollutants, and the optimization and validation of primer sets to follow specific groups of organisms assumed to be important for this process, but especially to follow specific gene families in environmental settings. A set of PCR primers is now available and has successfully be applied to characterize the presence of the respective genes in the environment. Metabolic profiling of catabolic genes has been performed to elucidate sequence (structure)/function relationships in key genes and enzymes. Thus, retrieved sequence information from environmental samples can give a picture of the catabolic properties of the microbial community for metabolizing organohalogen pollutants.

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### Contact

Dr Regeard Christophe EPFL, ENAC-ISTE, LBE CH-B Ecublens 1015 Lausanne, Suisse. Phone: ++ 41 21 693 57 59, Fax: Email: christophe.regeard@epfl.ch

## ON-SITE REMEDIATION OF GROUNDWATER CONTAMINATED BY POLAR ORGANIC COMPOUNDS USING A NEW ADSORPTION TECHNOLOGY

Project	ORGONATE, On Site Remediation of Groundwater Contaminated by Polar Organic Compounds Using New Adsorption Technology
Authors	K. Levsen <sup>1</sup> , H. Kock <sup>1</sup> , A. Preiß <sup>1</sup> , J. Sluys <sup>2</sup> , C. van Strien <sup>2</sup> , B. Heesink <sup>3</sup> and G. Rexwinkel <sup>3</sup>
	<sup>1</sup> Fraunhofer Institute of Toxicology and Aerosol Research, Hannover, Germany
	<ul> <li><sup>2</sup> Akzo Nobel MPP Systems, Arnhem, The Netherlands</li> <li><sup>3</sup> Procede Twente, Enschede, The Netherlands</li> </ul>
Keywords	Groundwater pollution, organic polymers, adsorption, polar pollutants, phenols, explosives

### Abstract

Based on the development of new polymeric adsorbents with improved properties with respect to fouling and based on their characterisation by laboratory studies and mathematical modelling, a pilot plant for the removal of polar pollutants from contaminated ground water was designed and constructed. The results obtained so far demonstrate that (a) the removal of polar pollutants from ground water by adsorption on polymeric sorbents will be possible; (b) the extent of fouling can be reduced using newly produced polymers.

### Introduction

Ground water is the main source for the production of drinking water in the European community. However, in many areas of Europe this ground water is contaminated by diffuse sources such as agriculture (pesticides) or point sources such as hazardous waste sites. The German Federal Agency of the Environment (UBA) reported that in Germany alone there were more than 150 000 waste sites which represent potential sources for ground water pollution. Up to now, ground water remediation has mainly concentrated on the removal of volatile compounds such as chlorinated hydrocarbons, aromatic (BTEX) and aliphatic hydrocarbons, while polar compounds which are more difficult to remove have received less attention. New methods for the removal of polar compounds are, therefore, developed within the ORGONATE project. The project concentrates on three compound classes or compounds considered to be representative for polar pollutants: Explosives found near ammunition hazardous waste sites (in Germany, for instance, 600 sites are considered to be dangerous), phenols originating in general from processes related to coal mining (coke production) and methyl-*tert.*butylether (MTBE), an additive to fuel (found near gasoline stations).

### **Objectives**

Within this project, a new method for the removal and degradation of polar organic compounds such as explosives and phenols from contaminated ground water is developed and tested. It is based on the adsorption of contaminants on easy to regenerate organic polymer particles. The aim has been to develop such polymers which do not suffer from excessive fouling or pore plugging and can be regenerated on-site using suitable solvents or by chemical degradation. A pilot plant is to be designed and constructed to prove the feasibility of the approach and to demonstrate the performance of this new technique in the field.

### Results

#### Development of new polymeric sorbents

New polymeric sorbents with improved antifouling properties were developed using two concepts: (a) external protection of the pores of the sorbent particles by particle coating; (b) internal protection of the sorbent particles by filling the pores with an (extractive) liquid. During the course of the project, work concentrated on the second concept, i. e. internal protection. New sorbents were developed and tested, consisting of a macroporous polypropylene matrix into which either activated carbon or polymeric resin particles (based on polystyrenedivinylbenzene) are embedded, while the pores are filled with a protective liquid (here termed "oil"). These new sorbents remove pollutants from water by an adsorption and/or extraction mechanism. In order to characterise and optimise these new sorbents, the sorption capacity was determined in the laboratory. The new material was produced in a pilot production plant for extensive field testing. Breakthrough experiments were performed with model pollutants (see below) and simulated using the software developed within the project.



Fig 1.: Electron micrograph of the new polymeric sorbent

#### Laboratory studies on the adsorption of polar pollutants by polymers

The adsorption characteristics of a given polymeric resin can be characterised by thermodynamic and kinetic studies in the laboratory. The capacity is usually derived from <u>adsorption</u> <u>isotherms</u> providing information on the maximum sorbent capacity for an analyte in equilibrium. <u>Breakthrough curves</u> describe the overall kinetics of the adsorption in



Fig. 2. Breakthrough diagram for four compounds in polluted ground water below an ammunition hazardous waste site in Stadtallendorf (Hessia, Germany)

flowing systems such as polluted water flowing through an adsorber bed. Such laboratory studies were carried out on the one hand with model compounds, i. e. phenol and explosives, spiked into water, and on the other hand with real polluted ground water from a former ammunition production plant. The adsorption isotherms and breakthrough behaviour was determined for phenol, the explosives 2,4-dinitrotoluene (2,4-DNT), 2,4,6-trinitrotoluene (TNT) and RDX, the production by-products 2-nitrotoluene (NT) and 2,4-dinitrotoluenesulfonic acid-3 and finally the anaerobic and aerobic degradation products 2-amino-4,6-dinitrotoluene, 2nitrobenzoic acid, 2,4-dinitrobenzoic acid and 2,4,6-trinitrobenzoic acid, using a standard model adsorbent, the polymeric sorbent Ambersorb 563. During the last year, work concentrated on the study of very polar explosives (such as RDX), their polar degradation products (such as trinitrobenzoic acid) and their very polar production by-products (such as dinitrotoluenesulfonic acids). In addition, two large scale laboratory experiments with real polluted ground water from the former ammunition plant at Stadtallendorf, Hessia, Germany, were carried out. These laboratory studies suggest that polymeric resins are well suited for the removal of polar contaminants from polluted (ground) water (with the possible exception of dinitrotoluene sulfonic acids which are present in water in their ionic form and thus show an early breakthrough). Once the contaminants have been removed from the polluted ground water by adsorption on a suitable polymeric sorbent, the sorbent has to be regenerated onsite. Regeneration studies were thus carried out using the model polymer loaded with phenol or explosives. Regeneration was done using steam (phenol) or solvents (phenol, explosives). Based on recovery studies in single experiments combined with the fact that during a series of experiments the adsorbent capacity remained unchanged, it can be concluded that a complete regeneration of the sorbent at least for phenol and the major explosives with common solvents is possible. Methanol appears to be suited best.

In addition, the chemical degradation of explosives in alkaline solutions (after sorbent regeneration with methanol) was studied. These experiments demonstrated that the major explosives (such as TNT and RDX) are readily degraded even at room temperatures and high pH values (>12), but not completely mineralised. Several degradation products of TNT were i-dentified. However, degradation mainly leads to polymeric products which so far could not be identified.

#### Development of a mathematical simulation model

A new software was developed which allows to simulate the adsorption process. The entire simulation model has been developed in modular form. In this model, the adsorption process is described by four stages: (a) the flow of the solute in the bulk phase; (b) the transport through the boundary layer to the polymer particle; (c) the transport of the solute via different mechanisms in the particle; and (d) the final adsorption from the liquid to the adsorbent surface. The entire program has several sub-programs:

The <u>unit operation model</u> predicts the concentration profile in the actual pilot plant for different types of adsorber beds, i. e. the axial packed bed, the radial packed bed and the stirred batch vessel.

The <u>particle transport model</u> describes the physical phenomena occurring inside the heterogeneous porous structure. The particle transport model describes the pore diffusion, the solid diffusion and the pore surface diffusion.

The <u>isotherm model</u> allows the calculation of adsorption isotherms from experimental data. Moreover, the parameters from a single component isotherm can be used to predict multicomponent adsorption equilibria.

The performance of the model was tested using data from the literature and experimental data generated within the project on the above mentioned explosives and related compounds.

#### Design and construction of a pilot plant, benchmark

A process concept evaluation was done during the project, leading to the choice of a pilot plant based on a dual packed adsorber bed. The choice was primarily based on the characteristics of the newly developed sorbents, as the particle diameter limitations in the production process ruled out other alternatives. The laboratory results from both adsorption and desorption studies formed the basis for the design of a pilot plant.

A small mobile pilot plant was constructed (capacity 1 to max.  $5 \text{ m}^3/\text{h}$ ), built inside a container. A first field test was carried on ground water polluted due to a gasoline leakage by aromatic hydrocarbons, BETX (approximately 1 000 µg/l), polycyclic aromatic hydrocarbons, PAHs (approx. 400 µg/l), and methyl-*tert*.-butylether, MTBE (approx. 30 µg/l). After four weeks operation of the pilot plant, the pollutant level was reduced below the detection limit (1 µg/l).

A benchmark was carried out by comparing different water treatment systems for the removal of dichloromethane. The benchmark demonstrates that the technology compares favourably with existing techniques, in particular if the pollutant concentration is high.

### Contact

Prof. Dr. Karsten Levsen Fraunhofer Institute of Toxicology and Aerosol Research Nikolai-Fuchs-Str. 1, D-30625 Hannover (Germany) Phone: +49-511-5350-0, Fax: +49-511-5350-155 E-mail: levsen@ita.fraunhofer.de Project Website: http://www.orgonate.com/

# A DECISION SUPPORT SYSTEM TO QUANTIFY COST/BENEFIT RELATIONSHIPS OF THE USE OF VEGETATION IN THE MANAGEMENT OF HEAVY METAL POLLUTED SOILS AND DREDGED SEDIMENTS

Project PHYTODEC, A Decision Support System to Quantify Cost/Benefit Relationships of the Use of Vegetation in the Management of Heavy Metal Polluted Soils and Dredged Sediments

Authors M. Barbafieri, National Research Council of Italy (IT)

Keywords Metals, phyto-extraction, bio-availability, chemicals additives

### Abstract

Phyto-remediation for inorganic contaminants is entered as develop strategy using metal hyper-accumulating plant and/or chemical treatments inducing the increasing of metal availability to plant uptake. In fact in many contaminated soils metals are present in not bioavailable chemical forms. The metal bioavailability to plant up-take is the limiting factor in plant uptake. Many test are under evaluation with the goal to increase metal accumulation in plants. In this work are reported preliminary results from two growing season at mesocosm scale, located in the greenhouse of research in the frame of the European project PhytoDec.

The soil used has been collected in a contaminated area of a manufactured gas plant located near Milan. The metals investigated were: Pb and As. These metals present different chemical behaviour and consequently were objects of different mobilizing agents treatments. The selected metal mobilizing agents were: EDTA to mobilize Pb and BAP (biammonium hydrogen phosphate) to mobilize As.

Different plant species have been used. Brassica juncea, Lupinus albus; Holcus lanatus, Helianthus annus, Zea Mais.

Heavy metal mobility in soil has been evaluated by sequential extraction procedure for Pb as followed:  $H_2O$ ,  $KNO_3$ , DTPA. For As only water extraction has been used. An extensive monitoring program (including bioavailability monitoring by soil solution sampling and analysis) is included in the working programme.

### Contact

Dr. Meri Barbafieri Italian National Research Council (CNR) Via G. Moruzzi 1 56124 Pisa, Italy Phone: +39 59 48337, Fax: +39 59 500631 Email: Barbafieri@ict.pi.cnr.it Website: http://www.alterra-research.nl/pls/portal30/docs/folder/phytodec/index.htm

# SESSION 5 SUSTAINABLE MANAGEMENT OF LAND AND GROUNDWATER IN URBAN AREAS

Chairman: Paul Nathanail, Nottingham University (UK)

# SUMMARY

### Purpose of the Workshop

Representatives of the scientific community, investors and land developers, urban planners and policy makers presented their statements concerning the current state of the art within their special field, their interests and how these interests can be integrated in sustainable land and water management. These statements were followed by front table discussions; all participants were invited to involve themselves, for comments, suggestions, and criticism. Final objective of the workshop was to draw conclusions and to recommend further activities (highlighting research needs) to preserve soil and water resources at high quality in urban areas.

### Conclusions

Especially in densely populated areas a high pressure on the resources soil and groundwater can be recognised. Urban areas may be seen in a field of conflict between intensive land use – agglomeration of potential sources for emission of pollutants on the one hand – and the interest in environmental quality in the form of clean drinking water, sufficient land for high-level use, and broad biodiversity on the other hand. Urban areas are subject to continuous and rapid changes offering the possibilities for development and room for improvements.

Management of contaminated land in urban areas means dealing with

#a broad variety and large number of pollutants,

#a broad variety of different polluting substances,

∉#a large number of stakeholders.

Complex problems need complex solutions in a way of balancing existing problems (soil, groundwater contamination, historic and new contamination, point sources and areal contamination) with current and existing requirements for the resources soil and water by respecting interests of various stakeholder groups. Integrated management of problems is required – but how? Current management options mostly focus on individual aspects of the problem – however, integrated approaches are hardly applied.

Changed demands on the resource "land" in a way of more individual, larger and more attractive space lead to increasing use of "greenland" – on the other hand demolition in city centres leave brownfields requiring integration of these pieces of land into urban environment. There is the need to look more carefully at the INPUT signal (sources) and its variability – it matters at catchment scale and not at individual sources. There is further need to learn how to handle

#multiple point sources (dating at different time scales)

∉#multiple areal sources

#and mostly how to handle the combination of point and areal sources within a catchment.

Hand in hand with environmental targets, macro- and micro-economic benefits like

#efficient use of land and existing infrastructure,

#additional jobs and new tax revenues for cities and towns,

∉#quality of life and the environment,

- ∉revitalisation of deteriorated neighbourhoods,
- #solving problems like liability for past contamination, inadequate financing, weaker market conditions, and

#potential for exceptional returns on investment for developers and lenders

are to be defined to find sustainable solutions for urban planning projects. Making use of the broad spectrum of stakeholders involved win-win solutions are to be envisaged as basis for successful project management:

∉#remediation à ecological benefit

∉#employment à social benefit

#financing of projects à economic benefit

A promising approach to handle contaminated land and groundwater can be seen in managing the following aspects in an adequate and integrated way in the sense of a risk based land management:

#### **Risk reduction**

Dealing with historic contamination, choice of technology, Monitored Natural Attenuation, monitoring/controlling, manage source-pathway-receptor,...

#### Land use requirements

Setting and delivering redevelopment/remediation objectives at a regional scale.

#### Using natural resources

Consideration of consumption of natural resources (water, land).

#### Costs

Consideration of all possible costs involved.

#### Involving stakeholders

For reaching a consensus on the protection and remediation objectives under environmental, social and economic view.

#### **Managing uncertainties**

Balancing data availability versus data needs under the aspect of cost effectiveness.

#### Aftercare, liability issues, site management

As regards a further development of integrated management options the following NEEDS can be defined:

#Continue research to improve the knowledge base to develop tools to support the areas of European policy touched by contaminated land and groundwater in urban areas.

#Improving practice by knowledge transfer from scientists to stakeholders.

#Integration of policy approaches in integrated concepts.

Martin Schamann, Federal Environment Agency – Austria

# ADDRESS LIST

#### Alcock (Dr.), Susan

Cranfield Biotechnology Centre Institute of BioScience and Technology Cranfield University Silsoe, Bedfordshire MK45 4DT UK Project: SENSPOL s.alcock@cranfield.ac.uk

#### Auxt (RNDr.), Anton

HES – COMGEO s.r.o. Kostiviarska cesta 4 974 01 Banská Bystrica Slovakia hes@penet.sk

#### Ayora (Prof.), Carlos

Institut de Ciencies de la Terra Jaume Almera, CSIC Lluis Sole Sabaris s/n, 08028 Barcelona Spain Project: PIRAMID cayora@paleo.ija.csic.es

#### Barbafieri (Dr.), Meri

National Research Council of Italy, Institute of Ecosystem Study, Section of Soil Chemistry Via Moruzzi 1, 56124 Pisa Italy Project: PHYTODEC barbafieri@ict.pi.cnr.it

#### Biermann, Vera

BAM, Federal Institute for Materials Research and Testing Unter den Eichen 87, 12205 Berlin Germany Project: PEREBAR vera.biermann@bam.de

#### **Bittens**, Martin

Tuebingen University Sigwartstrasse 10, D-72076 Tübingen Project: IMAGE-TRAIN martin.bittens@uni-tuebingen.de

#### Büsing (Dr.), Jürgen

DG Research 200, rue de la Loi; 1049 Brussels Brussels juergen.buesing@cec.eu.int

#### Cofalka, Piotr

Institute for Ecology of Industrial Areas Kossutha str 6, 40-844 Katowice Poland Project: IMAGE-TRAIN piter@ietu.katowice.pl

#### Csoevari (Dr.), Mihaly

Mecsekerc Kornyezetvedelmi Rt 7633 Pecs, Esztergar I.u. 10 Hungary Project: PEREBAR csovarimihaly@mecsekerc.hu

#### Cyrana-Szram, Mira

Institute for Ecology of Industrial Areas Kossutha str 6, 40-844 Katowice Poland szram@ietu.katowice.pl

#### Debreczeni (Dr.), Ákos

University of Miskolc, Faculty of Earthscience and Engineering Miskolc, Egyetemváros H-3515 Hungary Project: PEREBAR bgtda@gold.uni-misckolc.hu

#### Eiswirth (Dr.), Matthias

Department of Applied Geology Karlsruhe University Kaiserstr. 12, 73128 Karlsruhe Germany Project: AISUWRS eiswirth@agk.uka.de

#### England (Dr.), Adrian

IMC Consulting Engineers PO Box 18, Common Lane; Huthwaite, Suttonin-Ashfield; NG17 2NS UK UK Project: PIRAMID englanda@imcgroup.co.uk

#### Ertel (Dr.), Thomas

UW, Umweltwirtschaft GmbH Friolzheimer Straße 3; 70499 Stuttgart Germany Project: INCORE thomas.ertel@uw-d.de

#### **Fatulova, Elena** Ministry of the Environment Námestie L'. Štúra 1, 812 35 Bratislava Slovak Republic fatulova.elena@lifeenv.gov.sk

#### Ferber, Uwe

Projektgruppe Stadt + Entwicklung Stiglitzstrasse 84, 04229 Leipzig, DE Germany projektstadt@t-online.de

#### Foelding, G

Mecsekerc Kornyezetvedelmi Rt 7634 Pecs, Esztergar I.u. 10 Hungary Project: PEREBAR foldinggabor@mecsekerc.hu

#### Frauenstein, Jörg

Umweltbundesamt Bismarckplatz 1 D 12193 Berlin Germany Project: EUGRIS joerg.frauenstein@uba.de

#### Godzik (Prof.), Stefan

Institute for Ecology of Industrial Areas Kossutha str 6, 40-844 Katowice Poland Project: INCORE godzik@ietu.katowice.pl

#### Gombkötö, Imre

University of Miskolc, Faculty of Earthscience and Engineering Miskolc, Egyetemváros H-3515 Hungary Project: PEREBAR ejtimreg@gold.uni-miskolc.hu

#### Grathwohl (Prof.), Peter

Center for Applied Geoscience University of Tübingen Sigwartstrasse 10, D-72076 Tübingen Germany Project: SOWA grathwohl@uni-tuebingen.de

#### Gregolec, Gabriele

Karlsruhe University Germany Project: PEREBAR gabi.gregolec@bio-geo.uni-karlsruhe.de

#### Gruber, Sultana

Bank Austria Creditanstalt Landste. Hauptstr. 1, A-1030 Vienna Austria sultana.gruber@ba-ca.com

#### Gyüreová, Daniela

Ministry of the Environment of the Slovak Republic Námestie L'. Štúra 1, 812 35 Bratislava Slovak Republic gyureova.daniela@lifeenv.gov.sk

#### Gzyl, Grzegorz

University of Mining and Metallurgy Poland AGH ggzyl@wp.pl

#### Gzyl (Dr.), Jadwiga

Institute for Ecology of Industrial Areas Kossutha str 6, 40-844 Katowice Poland Project: INCORE gzyl@ietu.katowice.pl

#### Jánová (RNDr.), Vlasta

Ministry of the Environment of the Slovak Republic Námestie L'. Štúra 1, 812 35 Bratislava Slovak Republic janova.vlasta@lifeenv.gov.sk

#### Levsen (Prof.), Karsten

Fraunhofer Institut fuer Toxikologie und Aerosolforschung Nikolai Fuchs Str.1, D 30625 Hannover, Germany Project: ORGONATE k.levsen@t-online.de

#### Mayer (Dr.), Wojciech

University of Mining and Metallurgy Poland AGH wmayer@geol.agh.edu.pl

#### Moraczewska-Majkut, Katarzyna

Institute for Ecology of Industrial Areas Kossutha str 6, 40-844 Katowice Poland Project: IMAGE-TRAIN mor@ietu.katowice.pl

#### Morvai, Balazs

Agruniver Ltd Ganz-Ábraham St 2 (P O Box 56), 2100 Gödöllö Hungary Project: NORISC bmorvai@mail.digitel2002.hu

#### Nahold, Manfred

G.U.T GRUPPE UMWELT + TECHNIK GMBH, A 4040 Linz, Leonfeldnerstrasse 18 Austria Project: PEREBAR m.nahold@gutlinz.at

#### Nathanail (Dr.), Paul

Land Quality Management SCHEME University of Nottingham Nottingham NG7 2RD UK Project: CABERNET Paul.Nathanail@nottingham.ac.uk

#### Padovani, Caterina

Comune di Milano Piazza Duomo, 21; Milano, IT Italy INCORE ambiente.incore@comune.milano.it

#### Podwojewski, Eckehardt

DSK Germany eckehardt.podwojewski@deutschesteinkohle.de

#### Prokop, Gundula

UBA, Austrian Federal Environment Agency, Contaminated Sites Department Spittelauerlaende 5, A-1090 Vienna Austria Project: IMAGE-TRAIN prokop@ubavie.gv.at

#### Ptak (Dr.), Thomas

University of Tübingen Center for Applied Geoscience Sigwartstrasse 10, D-72076 Tübingen Germany Project: INCORE thomas.ptak@uni-tuebingen.de

#### Regeard (Dr.), Christophe

Swiss Institute of Technology, EPFL, ENAC-ISTE, Laboratory for Environmental Biotechnology CH-B Ecublens, 1015 Lausanne, Switzerland Project: MAROC christophe.regeard@epfl.ch

#### Rijnaarts (Dr.), Huub

TNO Environment, Energy, and Process Innovation, PO BOX 342, 7300 AH Apeldoorn the Netherlands Project: WELCOME h.h.m.rijnaarts@mep.tno.nl

#### Roehl (Dr.), Karl Ernst

Department of Applied Geology Karlsruhe University Kaiserstr. 12, 73128 Karlsruhe Germany Project: PEREBAR ke.roehl@bio-geo.uni-karlsruhe.de

#### Schaefer (Dr.), Gerhard

Université Louis Pasteur de Strasbourg 23, rue de Loess, 67037 Strasbourg, FR France Project: INCORE schafer@imf.u-strasbg.fr

#### Schamann, Martin

UBA, Austrian Federal Environment Agency, Contaminated Sites Department Spittelauerlaende 5, A-1090 Vienna Austria Project: IMAGE-TRAIN schamann@ubavie.gv.at

#### Simon (Dr.), Franz

BAM, Federal Institute for Materials Research and Testing Unter den Eichen 87, 12205 Berlin Germany Project: PEREBAR franz-georg.simon@bam.de

#### Šuchová (RNDr.), Marianna

HES – COMGEO s.r.o. Kostiviarska cesta 4 974 01 Banská Bystrica Slovakia

#### Tanda (Prof.), Maria Giovanna

Politecnico di Milano Piazza Leonardo da Vinci, 32; 20133 Milano, IT Italy Project: INCORE mariagiovanna.tanda@unipr.it

### Teutsch (Prof.), Georg

U. Tuebingen Sigwartstrasse 10, D-72076 Tübingen Germany Project: INCORE georg.teutsch@uni-tuebingen.de

#### Track (Dr.), Thomas

DECHEMA e.V. Theodor-Heusse-Allee 25 60486 Frankfurt am Main Germany Project: WATCH track@dechema.de

#### Tsakiroglou (Dr.), Christos

Institute of Chemical Engineering and High Temperature Chemical Processes- Foundation for Research and technology Hellas (ICE/HT-FORTH) Stadiou Street, Platani, P.O. Box 1414, GR-26504 Patras Greece Project: TRACE-FRACTURE ctsakir@terpsi.iceht.forth.gr

#### Valiente (Prof.), Manuel

Universitat Autonoma de Barcelona. Department of Chemistry Edifici CN. Campus de Bellaterra, 08193 BELLATERRA (Barcelona) Spain Project: DIMDESMOTOM manuel.Valiente@uab.es

#### Wolkersdorfer (Dr.), Christian

TU Bergakademie Freiberg, Lehrstuhl für Hydrogeologie Gustav-Zeuner-Str. 12, D-09596 Freiberg/Sachsen Germany Project: ERMITE c.wolke@tu-freiberg.de

#### Younger (Prof. Dr.), Paul

U. of Newcastle NE1 7RU Newcastle upon Tyne UK Project: PIRAMID p.l.younger@ncl.ac.uk