The ADVOCATE Project

Newsletter no.1: Autumn 2012

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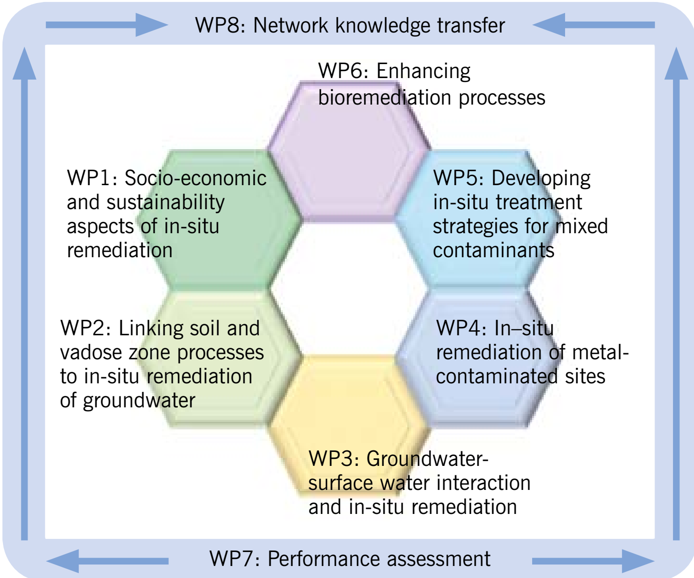
The ADVOCATE Project (**Adv**ancing Sustainable *In Situ* Remediati**o**n for **C**ont**a**minat**e**d Land and Groundwa**t**er) is now under way. This Marie Curie Initial Training Network is an exciting collaboration between leading European institutions, providing advanced training to young researchers in this field. The network aims to develop innovative in-situ approaches for the sustainable management and remediation of soil and groundwater contamination, in ways that traditional methods have not been as successful. The inter-disciplinary and multi-scale research will provide solutions for improved decision-making, management strategies and technology applications, putting in-situ remediation at the forefront of sustainable contaminated land management in Europe.



Delighted with the progress of ADVOCATE

Project co-ordinator Dr Steve Thornton is delighted with the progress of ADVOCATE as the project reaches its halfway point. The research is being carried out by a cohort of young researchers from all around the world, linked together via projects in work packages which examine different themes, such as socio-economic aspects, process understanding, concept appraisal and technology development.

You can find out more about the projects undertaken by our Research Fellows within this newsletter.

We have held several **training workshops** and a **summer school** since the project began, where the Marie Curie Research Fellows have been joined by researchers from other European universities and participants from international consultancies. Our workshop hosted at AGH University of Science and Technology in Krakow, Poland, focused on the analysis and interpretation of biodegradation in soils and groundwater using physicochemical and molecular microbiological methods. Participants were also able to enjoy a tour of the city in a Trabant car!

Other workshops have focused on project management skills and, more recently, advanced techniques for site characterisation and contaminant flux measurement in the subsurface. This workshop was held at the Helmholtz Centre for Environmental Research (UFZ) in Leipzig, Germany, and was combined with a summer school which examined contaminant source identification and remediation performance using stable isotope analysis. A highlight was a series of field trips to view innovative sustainable wastewater treatment technologies and demonstration sites for novel in-situ remediation concepts.

Our training events are open to all interested participants from outside the ADVOCATE network. Information on future events and details on how to apply for these is provided on the project website.

AGH · CL:AIRE · eawag aquatic research · Hydrogeotechnika Sp. z o.o. · Université de Liège · Helmholtz Zentrum für Umweltforschung UFZ · unine Université de Neuchâtel · The University Of Sheffield. · vito vision on technology

Juan Peña (Université de Liège, Belgium)

"Field-scale reactive tracer experiments for performance assessment of natural attenuation of groundwater pollution"

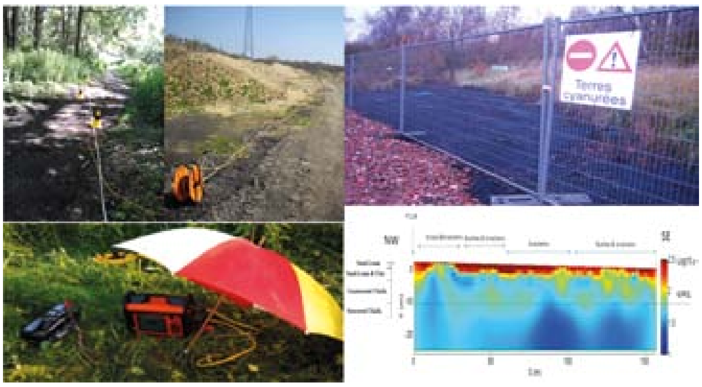
The fate of contaminants in soils and groundwater is influenced by many physico-chemical processes, particularly on complex contaminated sites. Contaminants, as well as tracers, behave very specifically in groundwater, in relation to the porous medium properties and their own physico-chemical properties. Different tracers sample different properties of the subsurface. Therefore, using reactive tracers as contaminant surrogates we can obtain valuable information about the fate and transport of contaminants and properties of the subsurface medium.

Juan's research focuses on characterization of the subsurface medium, which will lead to new conceptual ways of modelling that account for the properties of, and interactions between, selected reactive tracers and soil/aquifer materials, and on developing optimized single and multiple-well tracer techniques. Monitoring techniques will in particular include geophysics, to target specific processes, and tracers for a greater spatial coverage (see Figure 1).

An extensive literature review of existing technologies on reactive tracers and tracer techniques has already been completed, and a field site selected which has a cyanide-contaminated chalk aquifer. Field work for site characterization has included multiple geophysical surveys using self potential, electric resistivity tomography and induced polarization methods.

Existing piezometers at the contaminated site have been re-surveyed to confirm their location on the site and their current groundwater level. Some piezometers have been equipped with divers to obtain temperature, water level and pressure head data. Once the conceptual site model has been completed an experimental setup will be built on site, consisting of multiple wells where tracer experiments can be made at a the field-scale.

Figure 1. Working on the field site



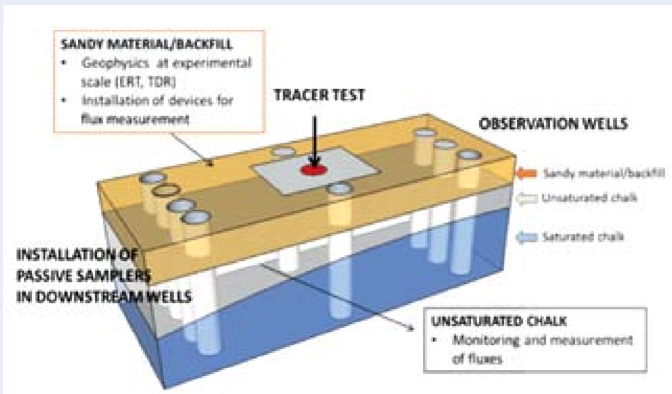
Natalia Fernandez (Université de Liège, Belgium)

"Integrated approach for contaminant fluxes assessment in the heterogeneous soil-groundwater continuum using geophysical, tracer and passive sampling techniques"

Also at the Université de Liège, Natalia is exploring links between soil and vadose zone processes for *in situ* remediation of groundwater. The vadose (or unsaturated) zone is located between the source (surface) and the target of contamination (groundwater). Risk analysis and mitigation programmes for polluted soil and groundwater are based on a detailed understanding of pollutant fate and transport in the soil-groundwater continuum and on the characterization of pollutants at the site-scale. However, difficulties in characterization arise from spatial and temporal variability in the physical, chemical and biological properties of soil and aquifers and the variety of reactive processes therein. This project will develop an efficient and robust procedure for assessing pollutant transport from the pollution site to the groundwater body.

To support this research, an experimental setup has been designed to simulate transport processes in soil and groundwater. The experiment will take place on an industrial contaminated site where preliminary studies have been carried out, including several intensive geophysical campaigns and hydrogeological studies. The next step will consist of installing the experimental setup on-site and starting the simulations by injecting a non-pollutant tracer that can emulate the transport of contaminants in the subsurface.

Figure 2. Experimental setup with the techniques that will be used to assess the transport of contaminants in the soil, vadose zone and groundwater.



Lukasz Cieslak (University of Sheffield, UK)

"Microbial dynamics and biodegradation at the bioreactive fringe of contaminant plumes in groundwater"

Lukasz is exploring interactions between microorganisms in aquifers, which use a range of oxidants to biodegrade organic contaminants. This creates a sequence of zones in contaminated groundwater, which represent different terminal electron accepting processes (TEAP). These redox zones provide an ecological niche for different microorganisms within the in-situ microbial community, and this creates significant spatial variation in contaminant biodegradation potential in plumes. Understanding these environmental and microbiological controls on biodegradation potential at the bioreactive fringe of contaminant plumes will reveal the dynamics of microbiological community, their structure and metabolic functions. Furthermore, it will establish the factors that lead to microbial succession and diversity in the microorganisms at the fringe of plumes.

Lukasz is using a field site at an industrial facility for his research. He has completed an initial sampling programme to characterise the hydrochemistry and microbiology of an organic contaminant plume fringe at the site, using a series of high-resolution multilevel samplers (Figure 3); and further laboratory experiments are planned.

Figure 3. Collection of groundwater samples for hydrochemical and microbiological analysis of contaminant plume fringe, using a high-resolution multilevel groundwater sampler

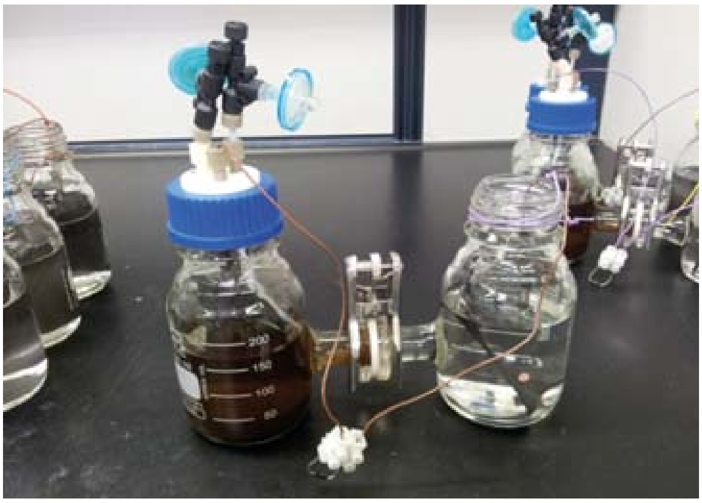
Petra Hedbavna (University of Sheffield, UK)

"Development of microbial fuel cells for enhancement of in-situ bioremediation of soil and groundwater"

Microbial fuel cells are believed to be one of the future sources of sustainable energy. As the name suggests, electricity in these devices is produced by microorganisms. Organic compounds are degraded by microbial metabolism and electrons released during this process are transferred to the electrode of the microbial fuel cell. This can be used in bioremediation technology. Under anaerobic conditions microorganisms sometimes suffer from lack of electron acceptors for their metabolism and therefore the bioremediation rate is too low. Electrodes of microbial fuel cells can serve as inexhaustible and sustainable electron acceptors while helping microorganisms to get rid of "waste" electrons. These are captured, transferred to cathode chamber (where oxygen is reduced) and electricity is produced. Microbial fuel cells could therefore enhance the bioremediation of organic compounds by speeding up microbial metabolism, while producing the energy from organic waste.

The design of the microbial fuel cell affects the amount of electricity produced enormously. An improved H-type microbial fuel cell reactor (Figure 4) was developed during the first stage of the project and tested experimentally. Power of 1.7 mW/m^2 of the electrode surface was produced in the anode chamber, using biosludge from an industrial wastewater (coke) plant as inoculum and phenol as a carbon source for bacteria. This reactor will be used for further experiments introducing phenol-contaminated groundwater as a source of bacteria. Results show that this groundwater composition will be an ideal inoculum for a microbial fuel cell system, to test the concept as a method for the enhanced bioremediation of contaminated groundwater.

Figure 4. New microbial fuel cell reactor design



Oksana Voloschenko (UFZ Leipzig, Germany)

"Microbial nitrogen transformation in horizontal subsurface flow constructed wetlands for treating of contaminated groundwater"

This research explores the role of aerobic and anaerobic microbial processes in the removal of ammonium from contaminated groundwater in constructed wetlands (CWs), using a study site located downstream of the Leuna industrial chemical area in Germany (see Figure 5). The groundwater is contaminated by organic chemicals (BTEX, MTBE) and inorganic compounds (NH_4+, NO_3-). It sits within work package 5 of the ADVOCATE project.

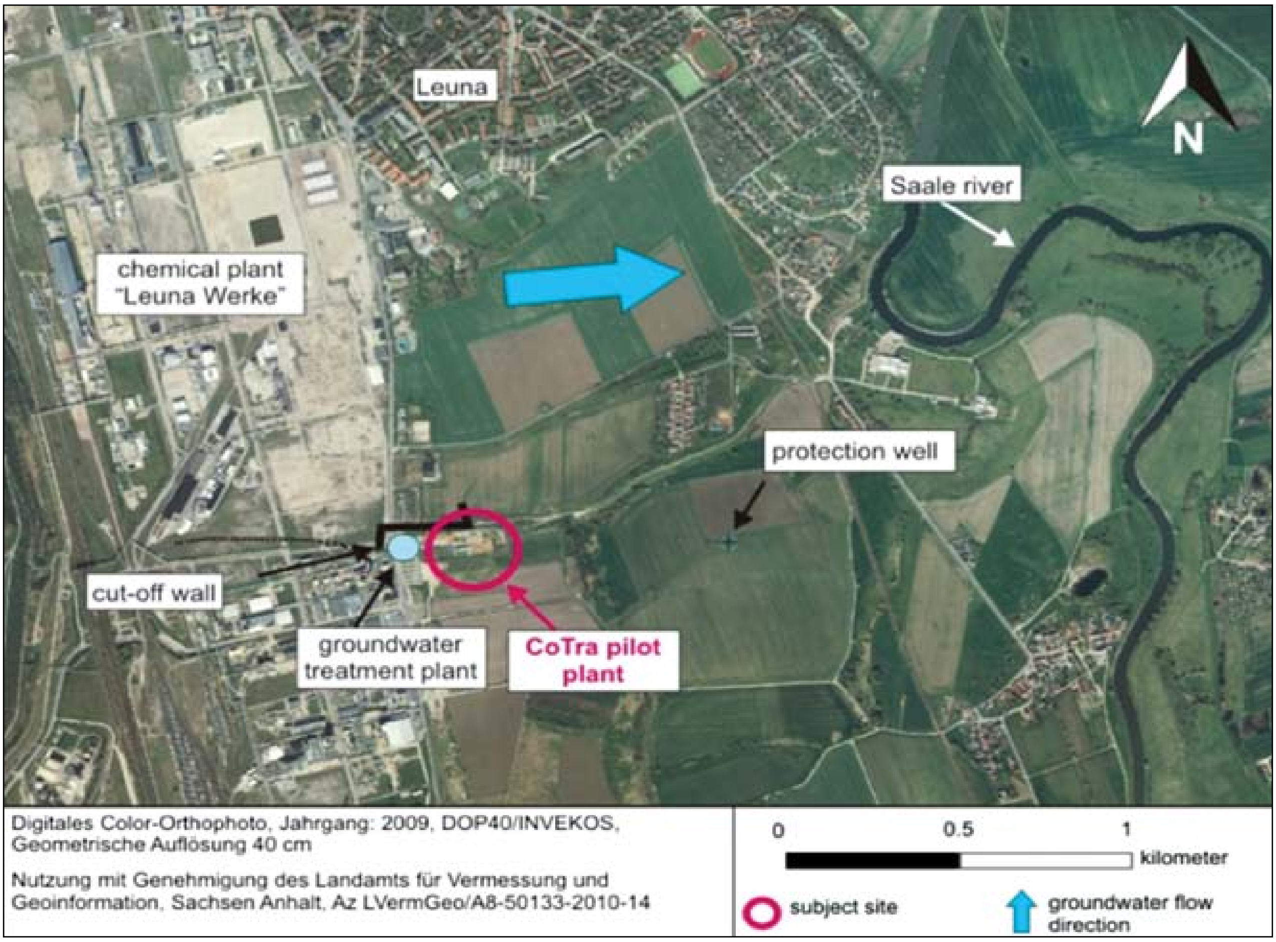
Oksana is focusing on ammonium, which is toxic to organisms and causes bad ecological status of water. The high ammonium load in the groundwater here is due to the intensive former chemical production of amino compounds in the Leuna chemical plant over many decades.

It is assumed that anaerobic ammonium oxidation (ANAMMOX) plays an important role in nitrogen removal in these horizontal subsurface flow CWs (HSSF-CWs). However, interactions between processes of aerobic and anaerobic ammonium oxidation in CWs have still not been satisfactorily investigated. The importance of the ANAMMOX process for nitrogen removal is generally accepted, but the processes in HSSF-CWs are quite unknown.

Monitoring and sampling has begun in pilot-scale CWs at Leuna. Three CWs have been selected: (i) planted horizontal subsurface flow (HSSF-CW), (ii) unplanted HSSF CW, and (iii) floating plant root mat (FPRM). Inflow and outflow water samples are collected in a time interval from 1 to 6 weeks along with pore water samples at different distances from the inlet and at different depths in the systems.

The spatial gradients of nitrogen species (ammonium and nitrate) within the CWs are known. Using an isotope mass-balance approach, it is planned to quantify the relevant N-transformation processes: nitrification, denitrification, and ANAMMOX. Consequently, by combining data for $^{15}N/^{14}N$ variation in nitrogen compounds with physico-chemical parameters (pH, eH, concentrations of N-compounds) and advanced molecular-biological techniques (e.g. FISH and qPCR), a more profound knowledge about the nitrogen removal processes and their controls in CWs will be obtained. The results of this interdisciplinary study will benefit bioengineers in developing new approaches to improve and optimize ammonium removal in CWs.

Figure 5. Location and layout of Leuna research site showing details of pilot-scale remediation infrastructure



Vidhya Viswanathan (EAWAG, Switzerland)

"The influence of surface water-groundwater interactions along a river reach on water quality"

Our two Fellows based at EAWAG in Switzerland are using the same field study site for their research. The river Thur in Switzerland is a tributary of the Rhine. It is a highly dynamic river in a catchment which is 61% agriculture, 30% forest and only 9% urban, and so the biggest problem is pesticides. The river was straightened into a channel in the 1890s, but has now been restored and widened (Figure 6 and 7).

Vidhya Viswanathan's project examines the impact of restoration on the function of the river. This is done by looking at diurnal and seasonal changes in flow and water quality. The research will identify and measure different parameters such as pH, electrical conductivity, dissolved oxygen, total organic carbon (TOC), total inorganic carbon (TIC), and concentrations of major ions (e.g. chloride, nitrate, nitrite, ortho-phosphate, ammonium and calcium) to see how these influence each other, as a descriptor of this interaction between the two environmental systems.

Figure 6.
River Thur before restoration

Figure 7.
River Thur after restoration

Ben Doulatyari (EAWAG, Switzerland)

"Modelling water quantity and natural attenuation processes of mixed contaminants at the catchment-scale"

Ben Doulatyari meanwhile is building a stochastic model to apply knowledge from the local-scale to the catchment as a whole. He is studying the dynamics of the vegetation biomass at different points of the stream, as well as catchment hydraulics, managed aquifer recharge and natural attenuation processes of mixed contaminants on the catchment-scale.

A sustainable approach to water resources management requires consideration of the whole water cycle together with human interventions. We propose that by enhancing the distribution of water during times of high flow (through managed aquifer recharge, artificial reservoirs, river restoration), we can both assist in flood mitigation and provide indispensable resources during times of water scarcity. In this study we aim to create a comprehensive model, that can be used for understanding and predicting the ecohydrology of a fluvial system at the catchment-scale.

The streamflow probability distribution and related flow duration curve at the catchment outlet have been estimated by applying a previously developed stochastic-analytical model, which is able to link the hydrologic regime of a river (and the underlying duration curve) to some key climatic and landscape features of the contributing catchment. In particular, the soil moisture dynamics at basin-scale and the related runoff production are strongly controlled by the temporal variability of rainfall, which is represented by means of a Poisson process, the evapotranspiration rate of the vegetation coverage and residence time of the water particles in subsurface paths.

Rainfall and discharge data series (1970-2011) are used to check the validity of the model assumptions in the case of the Thur catchment, and to assess the ability of the model to estimate the streamflow probability density function at the catchment outlet as well as outlets of five sub-catchments. The model has proven to be very robust at estimating the probability density function at all considered outlets. Furthermore, the results suggest a not-negligible contribution of the fast response of the basin to rainfall events.

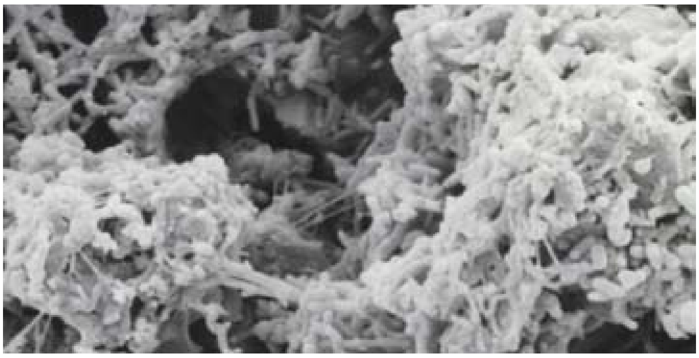
Alice Badin (University of Neuchatel, Switzerland)

"Assessing the behaviour of chlorinated solvents in soil and groundwater using compound-specific isotope analysis"

Sites contaminated with chlorinated solvents are of great concern in many developed countries with industrial activities from the 1940s to the 1970s. Indeed, such chemical compounds, which were mainly used for the degreasing of fatty metals in the automobile or watch industry, and for dry cleaning, are highly toxic. Some of them are known carcinogens. In addition to the need to develop methods for the characterization and remediation of such sites, legal issues also play a big role in resolving these cases. In many countries, those responsible for the pollution have to cover all expenses related to characterization and remediation of spoiled sites, and it is therefore essential to identify the responsible parties.

A useful method of measuring the isotopic signature of solvents (i.e. isotopic ratios of chlorine, noted $\delta^{37}Cl$ and carbon, noted $\delta^{13}C$ in the solvent molecule) could be a great help in providing a rigorous basis to identify the source and timing of chemicals released to soil and groundwater. In the past, it has been shown that isotopic signatures of pure chlorinated solvents such as PCE changed, depending on manufacturer (Figure 8).

Some case studies indicate that it is possible to use this method to identify the origin of groundwater contamination when several sources in the vicinity could be responsible. This research will evaluate the isotopic signature variability within Switzerland.



Throughout Switzerland, 10 sites contaminated with PCE (tetrachloroethylene) have been identified and investigated. These include sites where dry cleaning, metal degreasing or fat extraction from meat previously took place. Chlorine and carbon stable isotope ratios were then measured to give dual carbon-chlorine isotope ratios or isotopic signatures for each site (Figure 9). Due to the sensitivity of the analytical instruments (and therefore measurement precision), some samples initially show a relatively high standard deviation and will therefore be measured again. Current results do not show clear differences between measured sources but we hope that further statistical studies will enable a better interpretation of the results to be made.

Figure 8: Dual carbon-chlorine stable isotopes plot measured in PCE for different manufacturers (from Van Warmerdam, 1995 and Jedrzejewski , 2001)

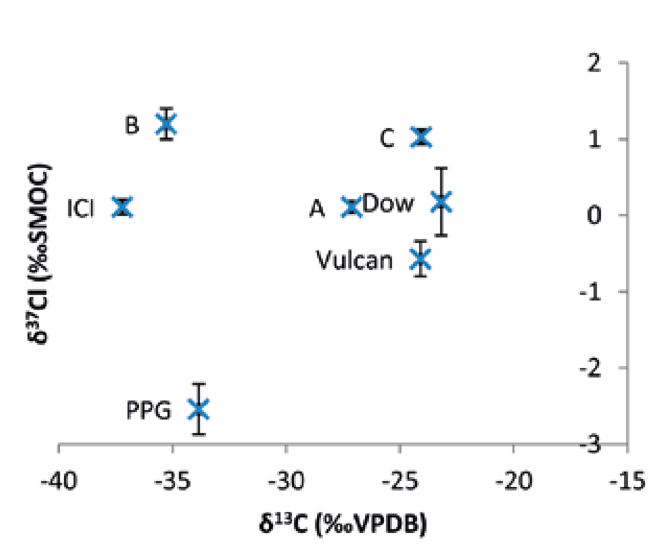
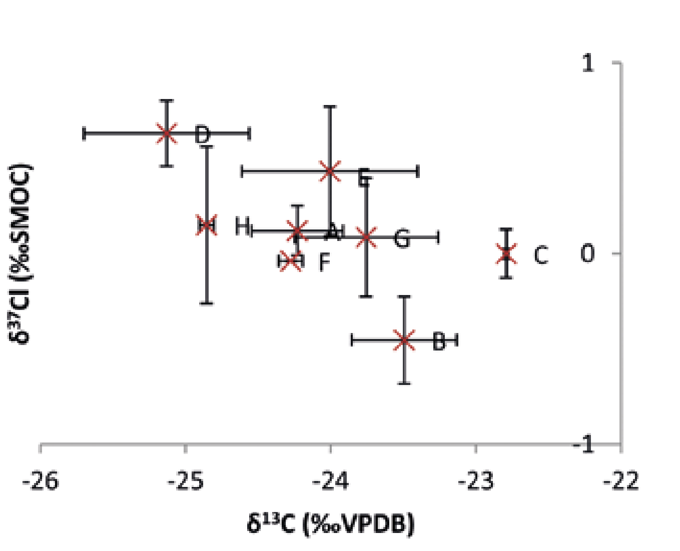


Figure 9: Dual carbon-chlorine isotopes plot measured in PCE for different sites in Switzerland



References

Jendrzejewski, N., H.G.M. Eggenkamp, and M.L. Coleman, *Characterisation of chlorinated hydrocarbons from chlorine and carbon isotopic compositions: scope of application to environmental problems.* Applied Geochemistry, 2001. 16(9-10): p. 1021-1031.

vanWarmerdam, E.M., et al., *Stable chlorine and carbon isotope measurements of selected chlorinated organic solvents.* Applied Geochemistry, 1995. 10(5): p. 547-552.

Franklin Obiri-Nyarko (Hydrogeotechnika, Poland)

"In situ sustainable remediation of groundwater contaminated with mixed organic/inorganic compounds using permeable reactive multi-barrier (PRmB) systems"

The permeable reactive multi-barrier (PRmB) system is a relatively new technology that offers many advantages over other conventional engineered technologies such as 'pump and treat', for example. This research will investigate new and potentially suitable reactive materials for treating specific contaminants, as well as evaluating and enhancing the long-term performance of the PRmB system. The results will play a major role in improving the general understanding and advancing knowledge of both the scientific and technical aspects of this technology. Activities undertaken so far include the screening of two contaminated sites to select a suitable test site for field installation of a PRmB (Figure 10).

Following this, the site at Tuczepy, previously a sulphur mining facility and an important agricultural area, was selected to host the pilot-scale experiment. The groundwater is acidic, with concentrations of BTEX and some heavy metals above environmental quality standards. The site is now the subject of detailed characterization. Laboratory batch and column experiments are currently being designed to screen potentially suitable barrier materials. The focus of these experiments will be the assessment of the removal efficiencies of the reactive materials, understanding the contaminant removal processes, and deducing the key barrier parameters to develop the pilot-scale PRmB system.

Whereas Franklin is working with mixed organic contaminants (BTEX) and some heavy metals (Cu, Pb, Zn, Cd, Ni), Johana Grajales, our other Fellow based in Poland, is also looking at PRmBs, but concentrating on organic contaminants. They have different field sites, but are collaborating on techniques and evaluation.

Figure 10: Site characterisation and collection of groundwater samples for screening evaluation of PRmB system for mixed contaminants

Johana Grajales (AGH University of Science and Technology, Poland)

"In-situ remediation of contaminated groundwater using permeable reactive multi barriers (PRmB) systems"

Johana is using laboratory studies, field work and numerical modeling to test her permeable reactive multi-barrier (PRmB) system as an in-situ remediation technology for removing tetrachloroethylene (PCE) and trichloroethylene (TCE). She is using the Nowa D-ba waterworks in SE Poland as her study site (Figure 11). Suitable active materials to be used in the barrier have been selected from an extensive literature review. These materials will be tested in the laboratory using batch and column experiments to deduce their properties and select the final candidates for a pilot on-site installation. The longevity of the system will be established from the performance of the pilot installation and modeling studies. The results will be interpreted in a full-scale design of the technology.

First results suggest that TCE and PCE migrate at the same rate in the aquifer and comparable to the average groundwater flow rate, suggesting little attenuation by sorption (retardation coefficient $R_f < 2$). Therefore, the prospect for this site is a quick spread of contaminants and thus a high associated risk. The feasibility study indicated that the installation of a PRmB system may be effective to reduce TCE and PCE concentrations under the site specific conditions, diminishing risk and meeting the drinking water standards established in the European Water Directive and the Polish Water Law Act.

Pre-screening batch tests are being undertaken to determine the effectiveness of PCE and TCE removal from groundwater using different potential active materials, such as compost, brown coal, mulch, limestone (separately and in combination), compared with zero-valent iron (ZVI). Reactive materials, which prove to be most effective in the removal of contaminants of interest will then be evaluated in laboratory column tests.

Figure 11: Nowa Deba field site for pilot-scale evaluation of PRmB system for organic contaminants

Alistair Beames (VITO, Belgium)

"Socio-economic and sustainability aspects of in situ remediation"

Alistair is developing a decision-support framework to assist stakeholders in choosing between brownfield revitalization alternatives. Brownfield revitalization planning entails the careful consideration of remediation alternatives capable of reducing contamination levels to the required target values, as well as determining the optimal land-use scenario for the remediated site.

At present, Alistair is developing the Social Impact Assessment component of the eventual decision-support framework. He is also currently reviewing a selection of existing decision-support tools, used to evaluate the sustainability of feasible remediation strategy alternatives. The focus of the review is on whether the social aspect of sustainability is adequately accounted for in these existing tools.

Uwe Schneidewind (VITO, Belgium)

"The influence of subsurface heterogeneities on in-situ remediation of organic contaminants at the groundwater-surface water interface"

The groundwater-surface water interface of lowland rivers often shows increased contaminant attenuation potential compared with the adjacent aquifer, due to its special biogeochemical characteristics. Giving this zone special consideration in water quality management practices could lead to a better conceptual understanding of ongoing processes and more informed management decisions. The natural attenuation potential of this interface is described by hydraulic and biochemical parameters, which can differ with location. This so-called spatial heterogeneity may have a major influence on the attenuation potential. Uwe is investigating which parameters are of importance and how they are related to each other. For this he is conducting modeling studies to determine reaction rates and hydraulic parameters, and their interdependence across different spatial and temporal scales.

Figure 12. Installation of sensors in the riverbed to measure temperatures and heads to help determine fluxes across the groundwater-surface water interface.

You can find our full list of partners on our project website (**www.theadvocateproject.eu**). If you would like any further information please contact Jenny Chambers at j.a.chambers@sheffield.ac.uk.

Contact information for lead scientists at organisations hosting Research Fellows within the ADVOCATE Marie Curie Initial Training Network

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We are also pleased to have a number of associated partner organisations from different commercial and industrial sectors of the contaminated land and groundwater management field within the network, who are helping us with training and technical assistance. You will find details of these partners and their contribution to the network on our website.