The
ADVOCATE
Project

Newsletter no.5: February 2015

The ADVOCATE Project

The first addition of our winter newsletters is introducing the work of Alice Badin (University of Neuchatel, Switzerland) and Natalia Fernández de Vera (Université de Liège, Belgium). Happy reading!

Alice Badin is carrying out her PhD thesis titled “Assessing the fate and behaviour of chlorinated ethenes in groundwater using carbon-chlorine isotope analysis”. She is using stable isotopic analysis of chlorinated ethenes to unravel issues related to source delineation and to the characterisation of biodegradation. In this issue, Alice shares her latest results on this topic with us.

Natalia Fernández de Vera is working on vadose zone characterization at industrial contaminated sites. Her PhD is titled “Integrated approach for contaminant fluxes assessment in the heterogeneous soil-groundwater continuum using geophysical, tracer and passive sampling techniques”. Her objective is to develop a conceptual model that accounts for contaminant attenuation in the vadose zone as well as contaminant flux and mixing with the saturated zone. In this issue, Natalia shows us her latest results.

ADVOCATE bulletin

Enhancing bioremediation of groundwater by microbial interaction with a solid state electrode: proof of concept

ADVOCATE bulletin

Balancing the Pillars of Technology Sustainability in Soil and Groundwater Remediation

ADVOCATE bulletin

River flows and riparian vegetation dynamics

ADVOCATE bulletin

Selecting reactive materials for permeable barriers to remediate groundwater contaminated with heavy metals and BTEX: batch and column experiments

ADVOCATE bulletin

Remediation of TCE contaminated groundwater using permeable reactive barriers

CL:AIRE, our knowledge transfer activities and public outreach partner and the Advocate team are busy creating and publishing the **ADVOCATE bulletins**. Every month more and more topics are available at www.theadvocateproject.eu/bulletin. These bulletins describe practical aspects of research which have direct application to the characterisation, monitoring or remediation of contaminated soil or groundwater.

Available topics:

- Remediation of TCE contaminated groundwater using permeable reactive barriers
- Selecting reactive materials for permeable barriers to remediate groundwater contaminated with heavy metals and BTEX: batch and column experiments
- Enhancing bioremediation of groundwater by microbial interaction with a solid state electrode: proof-of-concept
- River flows and riparian vegetation dynamics
- Balancing the pillars of technology sustainability in soil and groundwater remediation

Alice Badin (University of Neuchatel, Switzerland)

Alice attended the National Graduate School of Engineering Chemistry of Lille and graduated as an engineer in Chemistry and Environment in September 2010. During her education, she worked on the effect of polychaetes on the re-establishment of a marine eelgrass at the Institute of Biology at the University of Odense, Denmark. Her masters project, completed in collaboration with the University of Stavanger, Norway, focused on the skin irritation potential and bioavailability of 5 amino-acid based surfactants. After graduating, she worked at the French cosmetics company l'Oréal for one year as a project engineer in a research collaboration between France and Japan.

Alice's research focuses on the use of dual carbon-chlorine stable isotope analysis in chlorinated ethenes for the purpose of source identification and characterisation of biodegradation in groundwater.

Introduction

The inappropriate disposal and accidental spills of chlorinated solvents formerly used in the chemical industry as well as for dry-cleaning or metal-degreasing purposes lead to many contaminated sites throughout industrialised countries which now need to be cleaned up. When dealing with such site remediation, practitioners and regulatory bodies are faced with questions relative to contamination apportionment and contaminant fate. Stable isotopic analysis of chlorinated ethenes has gained interest in the past decade as this method was proven to be a promising tool to unravel issues related to source delineation and to the characterisation of biodegradation. While the sole use of carbon isotopic analysis restricts the range of applicability, it is expected that dual carbon-chlorine (C-Cl) isotopic analysis could strengthen the interpretation of stable isotopic analysis. Our work thus aims at exploring the use of dual C-Cl isotopic analysis for source delineation and characterisation of biodegradation.

Rationale and research carried out

Source apportionment

In nature, carbon and chlorine sources can show different isotopic compositions corresponding to isotopic ratios denoted $\delta^{13}C$ and $\delta^{37}Cl$ for carbon and chlorine, respectively. As different manufacturers synthesise chemicals using raw material originating from different locations and showing therefore different isotopic compositions, an isotopic signature variability can be observed between manufacturers, as reported in former studies[1, 2]. The authors of previous studies pinpointing such isotopic signature variability suggested that source apportionment could hence be performed in the field based on isotopic measurements. Such application however relies on the isotopic signature variability between sites. Our work thus aimed at first at assessing the isotopic signature variability of tetrachloroethene (PCE) between ten sites located in Switzerland. After identifying ten sites contaminated with PCE, groundwater samples were taken and the isotopic composition of PCE was analysed and compared between sites.

Characterisation of biodegradation

PCE can be naturally sequentially degraded in anaerobic conditions by microorganisms through a pathway known as reductive dechlorination. This process occurs via the successive formation and dechlorination of trichloroethene (TCE), cis-dichloroethene (cDCE), vinyl chloride (VC) and can eventually yield the nontoxic compounds ethene or even ethane.

During degradation by a chemical or a biological process, the initial substrate isotopic composition changes. Since it is easier from an energetic point of view to break bonds between light isotopes than between heavy ones, the substrate gets enriched in heavy isotopes over time. This results in an increase of $\delta^{13}C$ and $\delta^{37}Cl$ in the substrate during degradation. Based on these principles, compound-specific single-element isotope analysis (usually $\delta^{13}C$) can be applied in order to identify and characterise biodegradation at the field scale. More specifically, an enrichment factor, which reflects the extent to which the substrate gets enriched in heavy isotopes of one element during the process of degradation, can be determined based on microcosm studies. This enrichment factor (ε) can further help quantifying the extent of biotic degradation in the field.

Looking at dual C-Cl isotopic analysis of chlorinated ethenes is expected to bring more insight into the occurring degradation process than single isotopic analysis, as the dual isotopic approach is believed not to be affected by steps other than the reaction mechanism contrary to the single isotopic approach. While a wide range of single-element enrichment factors associated with PCE reductive dechlorination exists (-0.4 to -16.7 ‰ for carbon), a more confined range is thus expected for dual C-Cl slopes, which could potentially help differentiating biotic from abiotic degradation in the field. Such application would be useful when assessing the efficiency of an applied remediation approach. Our work hence aimed at investigating the variability in dual C-Cl isotopic patterns associated with reductive dechlorination of PCE at the laboratory scale as well as in the field. The dual C-Cl isotopic pattern of PCE was determined during PCE reductive dechlorination by two bacterial consortia and in two sites undergoing PCE reductive dechlorination.

Results

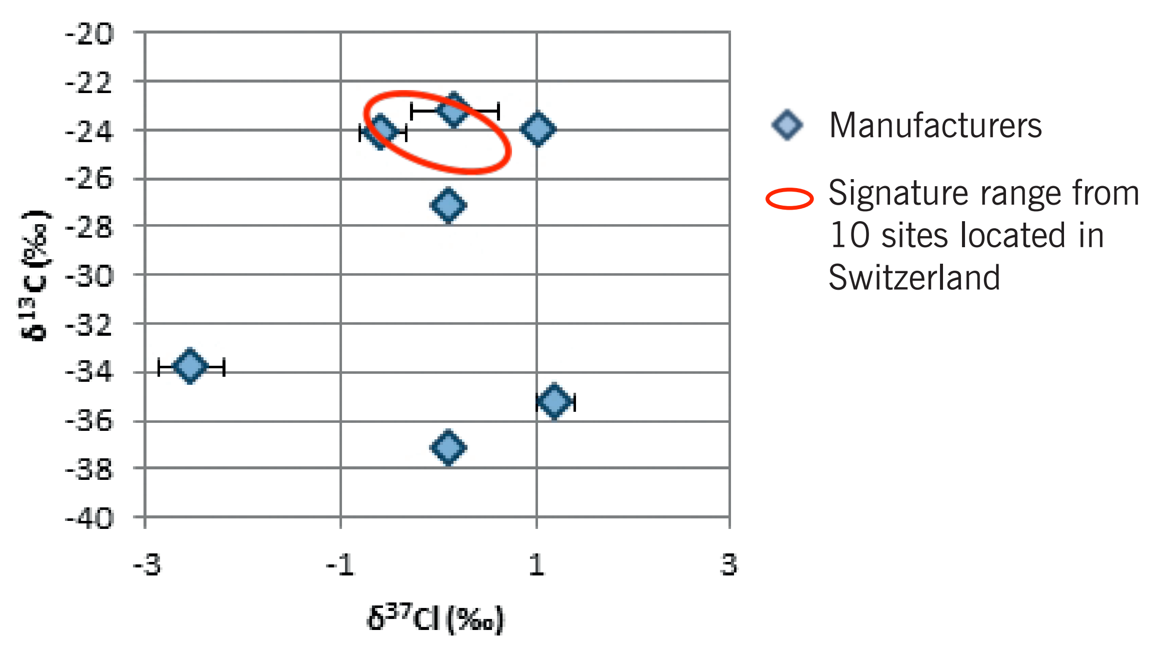

Figure 1 PCE isotopic signature variability between manufacturers[1, 2] and between 10 sites located in Switzerland.

Source apportionment

The PCE isotopic signature variability is less significant between the 10 sites located in Switzerland than between the previously reported values for manufacturers (Figure 1). Some differences can be observed between some sites but some sites could not be differentiated by dual C-Cl isotopic measurements. A few studies however showed the benefits of C-Cl isotopic analysis for source identification[3]. Our results thus suggest that the success of C-Cl isotopic analysis is very site-specific and that little can be predicted before analysing the isotopic composition.

Characterisation of biodegradation

Two different dual C-Cl isotope slopes of 2.7 ± 0.3 and 0.7 ± 0.2 were observed for the two studied bacteria consortia, respectively (Figure 2). At the field scale, two different dual isotope slopes of 3.5 ± 1.6 and 0.7 ± 0.3 were also observed for site Y and site X, respectively (Figure 2). Each slope obtained in the field is statistically similar to one of the two laboratory determined slopes. When taking into consideration the unique other dual C-Cl isotope slope of 2.5 ± 0.8 associated with PCE reductive dechlorination recently published[4], two distinct slope groups can be identified (i.e. slopes of 2.5 to 2.7 and 0.7). Finding two groups of dual C-Cl isotope slopes suggests that PCE can be dechlorinated under reductive conditions according to two different reaction mechanisms. The consequences are that the dual isotope approach should be applied with caution to differentiate biotic from abiotic degradation in the field as several slopes could be found for biotic degradation itself.

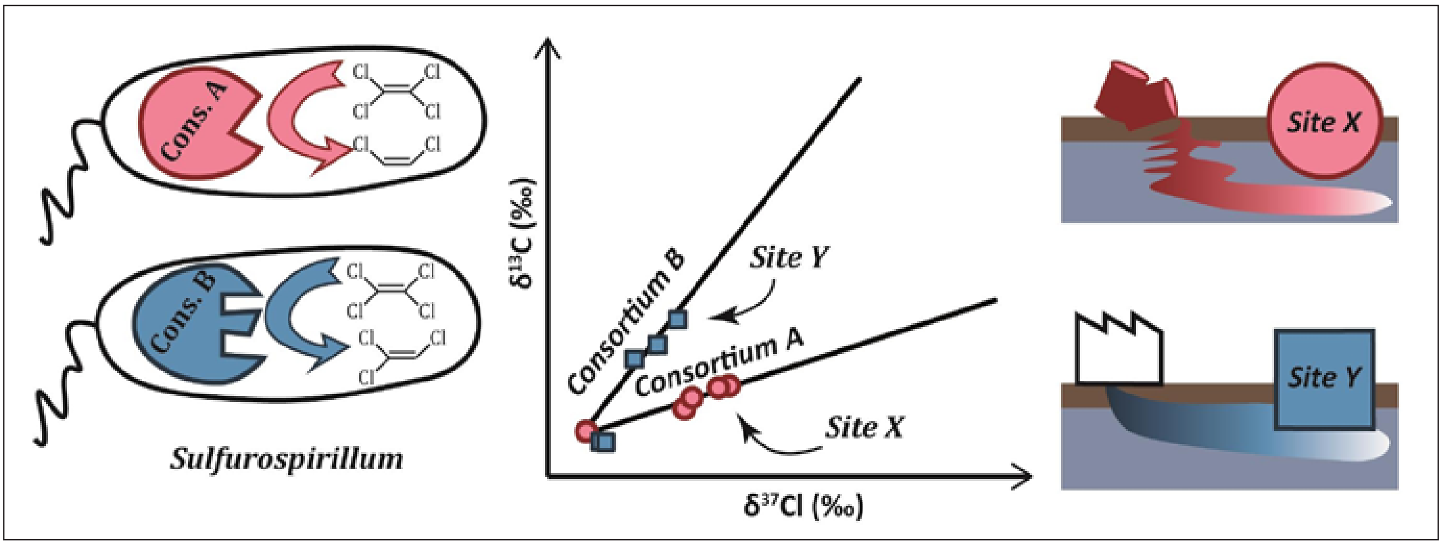

Figure 2 Summary of the results associated with PCE reductive dechlorination - two dual C-Cl slopes have been found for two different bacterial consortia, which are similar to two slopes observed in two different sites. Modified from Badin et al.[5]

Current and next steps

After exploring the use of the dual C-Cl isotopic approach for source delineation and to gain more insight into reaction mechanisms associated with PCE reductive dechlorination, we are investigating to what extent isotopes could help substantiate natural attenuation in the field. This is being assessed based on data previously acquired in a site located in Denmark, which is contaminated with PCE and its dechlorination metabolites TCE, cDCE, and VC[6]. A reactive transport and flow model has been setup in order to investigate the difference in plume fate prediction between a model calibrated with concentration only and a model calibrated with concentration and isotopic data. The data collected during a second sampling campaign carried out in May 2014 are being processed in view of validating the model.

References

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6. Hunkeler, D.; Abe, Y.; Broholm, M. M.; Jeannottat, S.; Westergaard, C.; Jacobsen, C. S.; Aravena, R.; Bjerg, P. L., Assessing chlorinated ethene degradation in a large scale contaminant plume by dual carbon-chlorine isotope analysis and quantitative PCR. Journal of Contaminant Hydrology 2011, 119, (1-4), 69-79.

We are pleased to announce that Franklin Obiri-Nyarko defended his PhD titled ‘Simultaneous removal of heavy metals and BTEX from contaminated groundwater by Permeable Reactive Barriers’.

Franklin has been part of the ADVOCATE Project as an early stage Research Fellow within Work Package ‘Developing in situ treatment strategies for mixed contaminants using sequenced reactive biobarriers’. He developed his doctoral research at Hydrogeotechnika Sp.zo.o. in Poland under the supervision of Dr Tomasz Kasela, PRofessor Grzegorz Malina and Professor Jolanta Kwiatkowska-Malina.

Congratulations, Dr Obiri-Nyarko on you perseverance and success, and we wish you a bright future.

Natalia Fernández de Vera (Université de Liège, Belgium)

Natalia, graduated as a geologist from University of Oviedo (Spain). After finishing her studies she worked on projects related to contaminant hydrogeology, karst geohazards and groundwater protection both at the British Geological Survey and Ireland Geological Survey. In 2009, she was awarded with a Fellowship from the Spanish Ministry of Science within the Operational Support Group at the International Continental Scientific Drilling Programme in Potsdam (Germany).

Since 2011, Natalia is working as an Early-Stage Researcher within the Advocate Marie Curie Initial Training Network doing PhD research on "Integrated approach for contaminant fluxes assessment in the heterogeneous soil-groundwater continuum using geophysical, tracer and passive sampling techniques", linking soil and vadose zone processes to in situ remediation of groundwater.

Introduction

Natalia's research focuses on vadose zone characterization at industrial contaminated sites. Characterization is essential to improve risk assessment and decision making for remediation strategies. The objective is to develop a conceptual model that accounts for contaminant attenuation in the vadose zone as well as contaminant flux and mixing with the saturated zone. Such a conceptual model has to be developed directly from field measurements. The main challenge of the research arises from the lack of suitable technologies for vadose zone characterization at field scale. At present, most developed techniques have been designed for agricultural purposes. Such techniques are not suitable for characterizing industrial contaminated sites, as the depth of investigation is generally much deeper than the soil horizon and the types and sources of contamination differ from those in agricultural landscapes.

Technology description

In order to overcome the challenges arising from the lack of suitability of the above described techniques, a Vadose Zone Experimental Setup is proposed (Fig. 1). The setup comprises of two elements: the vadose zone monitoring system (VMS) and crosshole Electrical Resistivity Tomography (ERT) imaging.

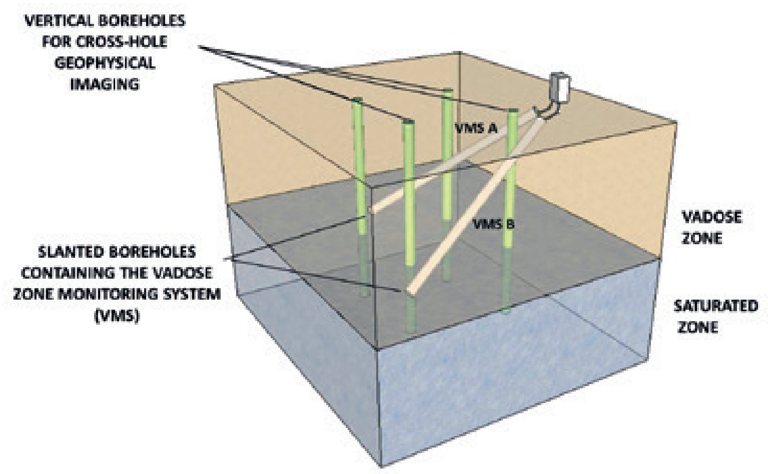


Fig. 1

The VMS is a system that allows continuous measurements of soil water content at different depths of the vadose zone. In addition, water samples can be retrieved. It consists of a flexible sleeve which is installed in a slanted borehole to avoid soil disturbances induced from vertical drilling. The flexible sleeve contains three types of sensors: the Time Domain Transmissometry (TDT), which measures soil water content continuously; the Vadose Sampling Ports (VSP), which are designed to retrieve soil water coming from the soil matrix; and the Fracture Samplers (FS), through which it is possible to obtain water coming from fractures.

Crosshole ERT consists of the injection of electric currents through electrodes installed in boreholes in the ground. From measured potential differences between pairs of electrodes installed in the subsurface an image of the electrical properties of the subsurface is obtained. From such an image, spatial patterns related to the structure of the subsurface as well as to solute and water contents are inferred.

Information obtained from the VMS is combined with crosshole ERT to characterize the vadose zone. This experimental setup is capable of providing a higher range of depth of investigation as well as more accuracy in terms of identification of heterogeneities in the subsurface.


Fig. 2

Research methodology

The system was installed at a former industrial site in Belgium. The legacy of industrial activities led to contamination of soil and groundwater with BTEX, PAH, cyanide and heavy metals. The lithology of the site is formed by 1m of backfill followed by alternation of sand, loam, silex and chalk. The thickness of the vadose zone is 7 m. Two open slanted boreholes were drilled on site. Subsequently, flexible sleeves containing the sensors in their upper wall were inserted in each slanted borehole (Fig.2). A mixture of cement and additives were introduced in the flexible sleeves. The expansion effect of such mixture pushed the sleeve and the sensors against the borehole walls, ensuring good contact with the soil. Four vertical holes were drilled on site and equipped with PVC tubes containing electrodes. Subsequently, the holes were filled with a mixture of bentonite, cement and gravel.

Latest results

The site was monitored under natural recharge conditions. Fig. 3 shows the reaction of the vadose zone to rainfall infiltration in November 2013. In the figure, the upper diagram shows rainfall and evapotranspiration (EPR). Below, five diagrams show water contents registered by the TDTs at different depths. On the bottom of the graph groundwater levels are shown. The TDTs installed at 0.2 and 1.12m respectively show fast wetting and draining reactions. Rain water that infiltrates gradually saturates the matrix. Once the matrix becomes saturated, water flow through fractures is activated, which can be seen in the abrupt water changes observed at TDT3 on the 8/11/13.

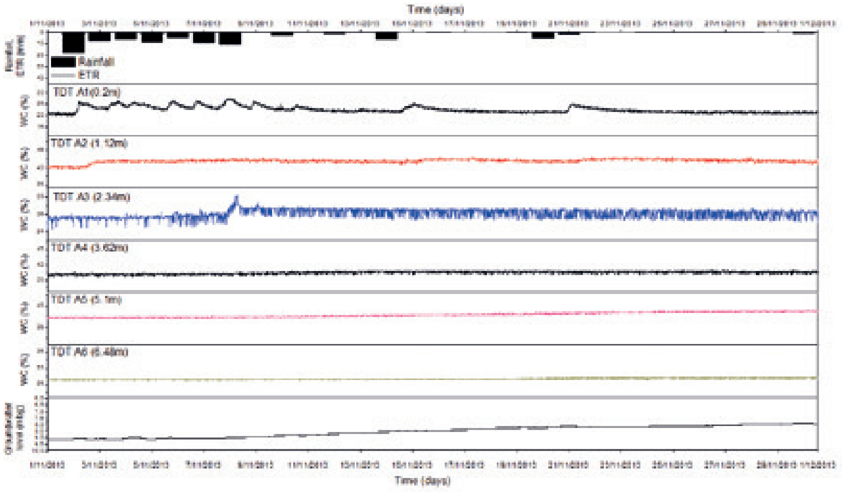


Fig. 3

Fig. 4 shows a Piper diagram with the chemical facies of the water samples retrieved from VSP sensors in November 2013. Three types of facies are observed (calcium-magnesium bicarbonate, sodium-potassium bicarbonate and calcium magnesium sulfate chloride facies), indicating an evolution of water chemistry with depth in the vadose zone.

Fig. 5 shows subsurface images obtained from crosshole ERT in December 2013. The highly conductive subsurface (blue areas in the figure) is coincident with the high mineralization of soil water as measured on the samples collected with the VSP. Heterogeneities are also observed. This is a case of resistive area observed at 4-5m depth, which corresponds to a layer of silex.

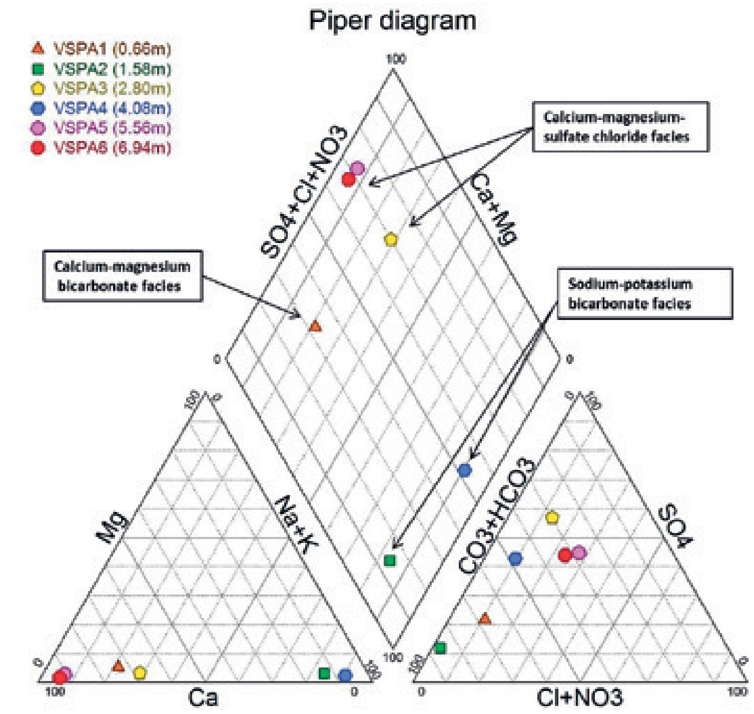


Fig. 4

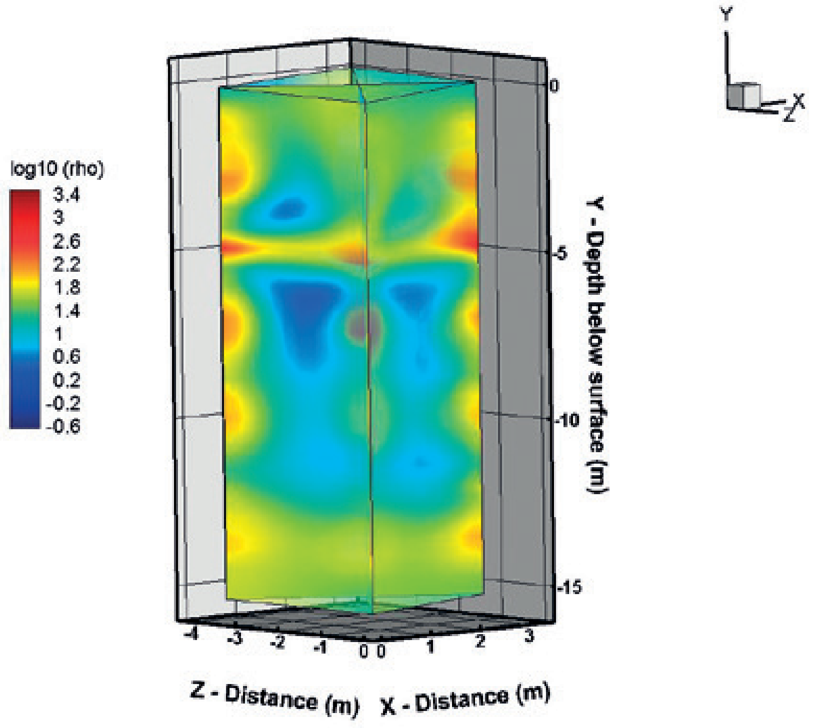


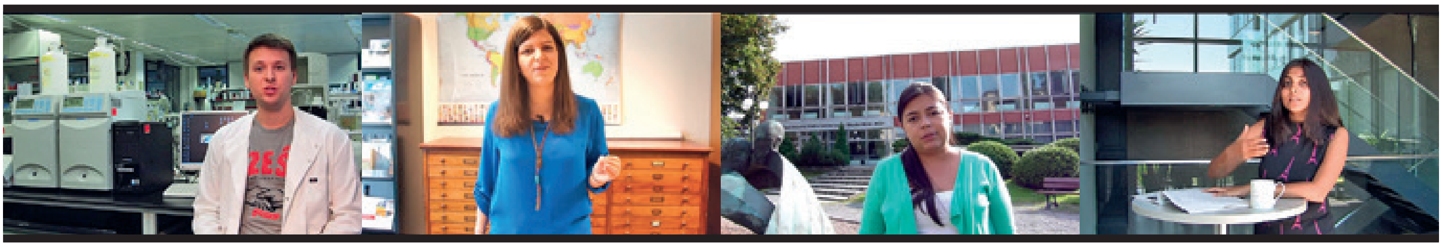
Fig. 5

Conclusion

The Vadose Zone Experimental Setup is an efficient tool for vadose zone characterization at industrial sites. Results have provided information about infiltration mechanisms and water content at depths below the soil horizon. In addition, chemical evolution of water through time and depth has been observed in the vadose zone. The combination of the VMS and crosshole geophysics was used to identify subsurface heterogeneities, essential for vadose zone characterization.

Come and explore further on our website to see the short videos presented by our Fellows discussing their work

www.theadvocateproject.eu



Happy New Year to all Advocate Fellows, Partners and Followers!

Thank you for your collaboration, teachings, presence and for creating a fun and inspiring atmosphere.

The Advocate management team

You can find our full list of partners on our project website (**www.theadvocateproject.eu**). If you would like any further information please contact Gabriella Kakonyi at g.kakonyi@sheffield.ac.uk.

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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.

Created by Ruth Garcia de la Calle