

Optimization of Water Treatment Technology for As and Sb Scavenging by Microbiologically Activated Fe Minerals (MicroActiv)

Kersten M. (1), Daus B. (2), Driehaus W. (3), Haderlein S. (4), Kappler A. (4), Stanjek H. (5), Wennrich R. (2),

(1) Prof. Dr.-Ing. Michael Kersten, Johannes Gutenberg-Universität Mainz, 55099 Mainz, kersten@uni-mainz.de

(2) Dr. Birgit Daus, Dr. Rainer Wennrich, Departments Analytik und Grundwassersanierung, UFZ-Helmholtz-Zentrum für Umweltforschung, 04318 Leipzig, birgit.daus@ufz.de

(3) Dr.-Ing. Wolfgang Driehaus, GEH Wasserchemie GmbH & Co. KG, Heinrich-Hasemeier-Str. 33, 49076 Osnabrück, info@geh-wasserchemie.de

(4) Prof. Dr. Andreas Kappler, Prof. Dr. Stefan Haderlein, Zentrum für Angewandte Geowissenschaften (ZAG), Sigwartstraße 10, 72076 Tübingen, andreas.kappler@uni-tuebingen.de

(5) Prof. Dr. Helge Stanjek, Ton- und Grenzflächenmineralogie, RWTH Aachen, Wüllnerstr. 2, 52062 Aachen, stanjek@iml.rwth-aachen.de

Project homepage: <http://www.geotechnologien.de/forschung/forsch2.10m.html>

Abstract

The main research activity of this collaborative research effort is the optimization of water treatment technology on basis of granulated Fe hydroxides (= GFH, or in German GEH). GFH is applied by the SME-Partner, the GEH Wasserchemie GmbH & Co. KG established in 1997 and now one of the leading providers of iron-based high-capacity adsorbents for use in fixed bed filter process. Over 2000 plants have yet been delivered into more than 20 countries worldwide. Main purpose is treatment of As- and Sb-tainted waters, providing e.g. in India more than half million people with treated tap water. GEH[®] is based on pure synthetic iron hydroxide (β -FeOOH, akaganeite) with a large surface area ($>220 \text{ m}^2/\text{g}$) and an adsorption capacity of up to 55 g/kg As. This enables a simple, low maintenance removal procedure with capacities of up to 300,000 bed volumes over years without producing hazardous As-loaded sludges to be costly deposited. The main practical problem is the yet less well understood efficiency variation between different ground water regimes. Our hypothesis is that these effects are not only due to dissolved inorganic (mainly Si species) but also due to organic compounds interfering with the metalloid oxyanion sorbates. Natural organic matter (NOM) compounds may in particular lead to varying microbial activation of and subsequent more or less intense redox reactions on the surfaces involving redox-sensitive metalloids and trace (chloro-)organic pollutants. An open question to be solved for the SME partner is whether a specific functionalization of the surface may help in optimizing these effects towards a more versatile filter technology, pending a detailed elucidation of the basic mechanisms.

Introduction

Fe(III)-bearing mineral surfaces are an important affiliate of the As species arsenate and arsenite which represent currently the most serious environmental problem with (anoxic) groundwater pollution in many countries all over the world. The environmental relevance of antimonate is currently being increasingly considered. There exist much literature on the As but less on Sb sorption efficiency in pure laboratory batch systems. Not much is known, however, about the molecular mechanisms and kinetics of competing compounds in natural waters such as Si- and NOM bearing species. During a long-lasting practice with natural groundwater, the SME partner has observed complex competition relationships, such as even an antagonistic effect by Ca which may significantly mitigate the Si oxyanion competing effect (Smith and Edwards, 2005; Driehaus 2006). Understanding these effects to a degree enabling their quantitative prediction by adsorption models, however, is a key to optimize appropriate mitigation technologies by applying GEH[®] based filter materials (Meenakshi & Maheshwari, 2006).

Humified natural organic matter (humic substances) is present in most aquatic and terrestrial environments; it is redox-active, can be reduced chemically and microbially and interacts with inorganic contaminants by adsorption, complexation, and redox reactions. However, redox properties of humic substances and its interactions with microorganisms and Fe(III)-minerals are not well described on a quantitative and mechanistic basis. About the consequences of humic substance reduction for their interactions with toxic, redox-active onyanions almost nothing is known at all. In this project, we focus not only on the role of inorganic competitors, but in particular also on humic substances in microbial and chemical electron transfer processes on the Fe-bearing sorbent surface. We hypothesize that humic substances can function as electron acceptor in microbial redox processes and, because humic substances are able to transfer the accepted electrons further to insoluble electron acceptors such as Fe(III)-minerals, represent therefore a main pathway for the electron flow on the sorbent surface.

Redox reactions of humic substances with microorganisms and iron minerals may also play an important role in the surface reactivity towards organic pollutants. One important property of iron is the potential of providing Fe(II) cations adsorbed on mineral surfaces to reduce organic pollutants. Dissimilatory metal reducing bacteria like *Shewanella oneidensis* are wide-spread in the environment, and are able to form these surface reactive Fe(II) species. The bacteria mobilize and/or produce proteins that specifically interact with the Fe hydroxide surface as terminal electron acceptor for the oxidation of various carbon substrates, potentially coupled to microbiological alkylation and hence volatilization known as the primary natural attenuation mechanism at least for Sb. The latter reaction, albeit adding to the overall water purification efficiency, may cause serious hazard for plant workers. Not much is known about surface structure-reactivity relationships on a molecular scale triggered by such biogenic surface processes, e.g., in the context of natural organic matter or (co-metabolized) organic disinfection byproduct (e.g. chloramines) degradation on mineral surfaces.

The SME partner expects a major break-through by the scientific deliverables of this collaborative project with potential for optimizing his water treatment technology. This is of particular importance with respect to third-world applications like in Bangladesh with a well known arsenic problem, or for ground water remediation in the framework of superfund sites in

the USA. The project is aimed at resolving these open questions and hypotheses by a collaborative activity according to the complementary methodology and expertise of the participants. These activities are namely concentrating on experiments with water purification units based on Fe oxide phases in laboratory columns and on a field scale with different ground water regimes (WP 1, GEH Wasserchemie GmbH), spectroscopy of the species involved in the surface reactions of the oxoanions sorbates on a molecular scale (WP 2, Geoscience Institute of Univ. Mainz), characterization of redox reactions on microbiologically activated iron mineral surfaces (WP 3, ZAG at Univ. Tübingen), characterization of the sorbent surface structures on a nanoscale by applying X-ray techniques (WP 4, RWTH Aachen), and batch experiments and analytical characterization of potentially formed intermediate organic metalloid species (WP 5, UFZ-Helmholtz Leipzig). A sketch of the structure of this collaborative effort is given in Fig. 1 below.

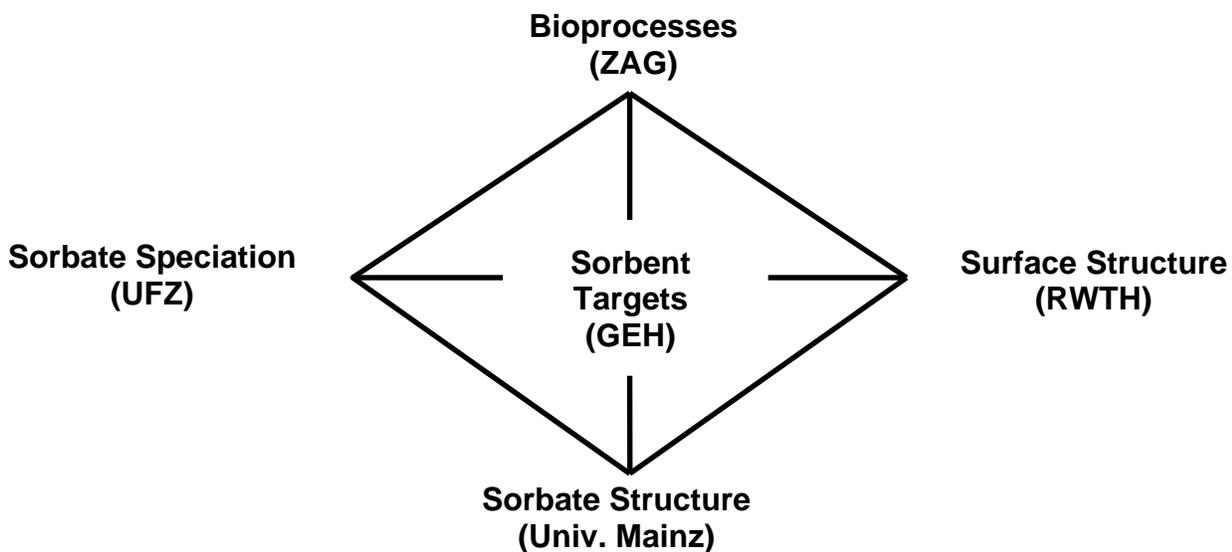


Figure 1: Collaboration scheme of the five partners within this joint research effort

Work package 1 (GEH Wasserchemie GmbH)

The SME partner GEH Wasserchemie (GmbH & Co. KG) is one of the leading manufacturers of iron-based adsorbents which can refer to approx. 2,200 GEH[®] plants worldwide treating an estimated amount of 450,000 m³ of tap water for daily use. In the badly affected areas of India (Meenakshi & Maheshwari, 2006), half a million people are supplied with arsenic-free tap water, thanks to the use of GEH[®]. Scientific work focuses since 2001 on the development of reliable prediction and calculation methods for the adsorption and removal of arsenic from natural (anaerobic) waters. A more recent but prominent site is the Olympic Park athletics residence area in Beijing equipped with our filter plants to clean the water reservoir within the framework of a Chinese-German BMBF research project (Figure 2).

Natural groundwater has a complex composition, affecting and reducing the performance of treatment plants with granular ferric hydroxides as adsorbents for arsenic removal (Sperlich & Werner, 2005). This is especially true for ground water in the tropical regions with its high organic matter content, and in arid regions with its enhanced salt content. Performance

monitoring of treatment plants showed competitive adsorption of silica (H_4SiO_4) and also competition from natural organic matter. Competitive interference can decrease the treatment capacity of such adsorptive treatment by as much as 80%. Current adsorption modelling uses surface complexation models (SCM) fine-tuning the model parameters to get best fit of experimental data (Smith & Edwards, 2005). This is done without a deeper mechanistic understanding of surface structural interactions of the target contaminants, competitors, and the sorbents surface. A better understanding of the mechanism of competitive adsorption is highly required for reliable projections of capacities and improvements of our adsorbents to make them less sensitive for competition, and more selective for the target contaminants arsenic and antimony.

For the investigations by ourselves and by the project partners we will prepare samples of granular ferric hydroxide from the production (GEH[®]) and exhausted sorbent material from long-term applications in water works. So far used materials loaded with arsenic and other contaminants are concerned, a life cycle analysis and description will be done including operating conditions and water profiles. It is also necessary to produce adsorbent samples loaded with arsenic and antimony under strictly controlled conditions using small column adsorption trials in our own laboratory with known but still raw groundwater composition. Contact time will be varied between the trials, and different water qualities with regard to As(V) and As(III) concentration, pH, silica, PO_4 , humic acids, and other water quality parameters will be varied in these trial scenarios. The received samples and laboratory samples need to be characterized for grain size distribution, equilibrium pH, pH_{PZC} , surface area, mineral composition, and chemical composition. The data are needed to interpret results and understand differences from spectroscopic investigations performed by the other WPs. Results of the investigations and the trials will help to develop an advanced SCM for adsorption capacity predictions with regard to water quality parameters. We will also manufacture and supply modified sorbents for investigations to identify versatile improvements of sorbent properties for extreme water treatment.



Figure 2: Water treatment plant with GFH used in four parallel filter containers, designed to treat 4,000 m^2 of water daily like that from the reservoir lake in the Olympic Park in Beijing.

Work package 2 (Mainz University)

Any attempt to understand solid-water interaction in aqueous environments necessitates studies of the inherent processes on a molecular scale. X-ray absorption spectroscopy (XAS) and attenuated total-reflection infrared spectroscopy (ATR-FTIR) are currently the most productive techniques to study on a molecular level oxyanion sorption phenomena including formation of complexes, heterogeneous nucleation and co-precipitation on oxide surfaces (e.g., Marcus et al. 2004). ATR-FTIR spectra can be collected *in situ* during the surface reactions, by which molecular information can be gained on the kinetics of these processes. FTIR spectroscopy is a fast, sensitive, and noninvasive benchtop method that provides structural information on tetrahedral coordinated oxyanions. A major problem with environmental surface analysis is, however, that H₂O is a strong IR adsorber. The penetration depth d_p , at which the light intensity decays to $1/e$ is in the order of only one μm at 1100 cm^{-1} . A relatively new technique that conveniently provides the equivalent of such short path lengths is „Attenuated Total Reflection“(ATR)-FTIR (Figure 3). The spectroscopic signature of infrared interrogation of wet oxide slurry on an ATR crystal can provide insight into the nature of the bonding networks of oxyanions. An IR-translucent crystal prism (e.g., Germanium) is covered by a fluid cell, while the IR beam is passing from below the prism and is reflected by the wet particle layer sediment at the bottom of the cell. After recording a background spectrum with layer and solvent, spectral changes are monitored *in situ* during titration of a sorbate and/or adding (natural or pollutant) organics and/or microbes to the solution. The resulting sets of IR spectra measured as a function of time and solution monitoring parameters (concentrations, pH, redox, cell density, etc.) allow a direct link between spectral information and theoretical models. ATR-FTIR is also used as a screening tool to collect the most promising samples for the XAS experiments, which are commonly hampered by the scarce synchrotron beamtime allotted to the measurement campaigns. XAS spectra are obtained by measuring the X-ray absorption as a function of energy in eV-resolution at synchrotron facilities. XAS data have provided important insight into chemical processes on a molecular scale at the solid-water interface between the oxide surface and oxoanion species (e.g., As on goethite: Marcus et al. 2004, As on akaganeite: Guo et al. 2007). However, experiments with laboratory and field samples cannot be readily compared, because other oxyanions common in nature like silicate could compete with arsenate for the same inner-sphere surface sites. We will therefore perform As, Fe, and Si K-edge EXAFS analyses with samples from the collaborative partners.

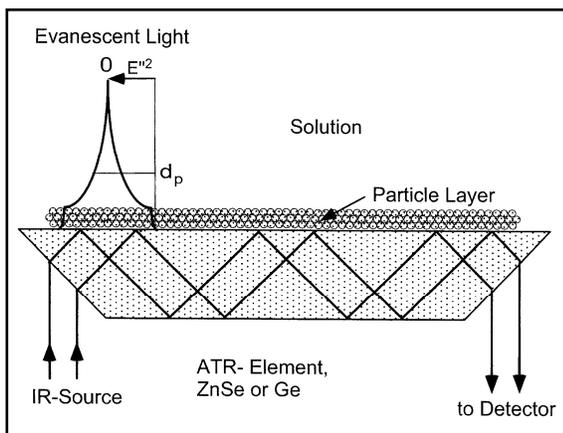


Figure 3: Scheme of the ATR cell. Upon each reflection on passing through the ATR crystal, the evanescent light interacts with the sorbent particle layer sediment in the aqueous suspension cell.

Based on the possibility to gain atomistic models, recent advances in steady-state surface complexation modeling (SCM) will be employed, where it is now possible to include spectroscopic information (Kersten and Kulik, 2005). For this, a series of classical pH-dependent titration experiments with oxyanionic species of As and Sb in akaganeite particle suspensions with and without addition of competing ions will be performed. The new SCM approach can be used to model the sorption continuum applying the nanostructure information available from the spectroscopic measurements on fits to titration data from the batch sorption experiments. This new development will be extended to competing multi-component systems such as those identified by the SME partner, and with experimental data from other partners within this collaborative effort (e.g., for silicate by WP 4, or for organic As and Sb species by WP 5).

Work package 3 (Tübingen University):

Motivated by the ubiquity of microbe-mineral interactions and by the lack of detailed understanding of these complex processes, we propose to investigate the mechanisms of microbially catalyzed redox processes involving iron mineral surfaces, and the consequences of these redox processes for the fate of (in)organic pollutants. The overall goal of the proposed research is to identify the effects of biogenic iron surface coatings at minerals (oxides, clays, carbonates) representative of those present in bank filtration systems and water purification filters on surface mediated reactions with i) organic micropollutants, and ii) arsenic(V). Members of our research team have experience in studying the precipitation and dissolution of Fe minerals by Fe(II)-oxidizing and Fe(III)-reducing microorganisms, and the role of reactive minerals and humic compounds on the fate of (in)organic pollutants in the environment (Kappler and Straub, 2005). In this project we will focus on how the properties of minerals produced either by microbial reduction of Fe(III) minerals by the iron-reducing microorganism *Shewanella oneidensis* strain MR-1 or by oxidation of Fe(II) by the iron-oxidizing microorganism *Acidovorax* sp. Strain BoFeN1 compare with non-biogenic minerals in terms of redox reactions with organic compounds and arsenate (Chen et al., 2008). One key question here is to what extent cultivation conditions commonly used in geomicrobiological lab experiments (Kappler et al., 2005) affect the properties of biogenic minerals, especially with regard to the presence of phosphate. Further, we propose to clarify to what extent redox active natural organic matter (humic substances) that serves as electron acceptor for bacteria and as electron shuttle to Fe(III) minerals, influences the identity and reactivity of the Fe minerals. We will determine to what extent the reactive mineral species produced during these microbial redox processes react with redox sensitive pollutants (metalloids, disinfection byproducts). First, we will choose a set of iron(II)-containing iron minerals (produced either by microbial Fe(III) reduction of common natural iron(III) oxides like ferrihydrite, goethite, and hematite or by Fe(II) oxidation), clay minerals like nontronite, as well as poorly crystalline akaganeite phases from natural settings delivered by the SME partner. We will then follow their redox reactions with As(V) and organic compounds that occur as byproducts during drinking water treatment. More specifically, we will focus in our research on the following objectives:

- Determination of the effect of adsorbed phosphate and DOM on the formation and properties of biogenic minerals (during microbial reduction of Fe(III) by *Shewanella oneidensis* strain MR-1 and oxidation of Fe(II) by *Acidovorax* sp. strain BoFeN1) as

compared to abiotic systems. From these experiments we expect to gain also insights to what extent results from model systems can be transferred to complex natural conditions.

- Investigations on pure iron minerals as compared to mixtures of different minerals to determine the effects of mineral templates on mineral formation and activation during microbial reduction of Fe(III) and oxidation of Fe(II).
- Quantification of the reactivity of microbially activated mineral surfaces with respect to the oxidation of chloramines and reduction of As(V) and halomethanes in the presence and absence of phosphate and humic substances and comparison to abiotic systems.

We propose to address these goals by studying oxidation and reduction reactions of the organic and inorganic target compounds in well defined laboratory model systems (mineral suspensions) of different degrees of complexity (combinations of setups with and without microorganisms, pure and mixed mineral systems, absence and presence of phosphate and humic substances). We shall therefore investigate our own relatively simple model systems, as well as samples delivered by the SME partner. For each subtopic we will evaluate on a mechanistic level how environmental factors including pH and ionic strength affect the surface mediated reactions of the target compounds. The studies with phosphate and NOM will be complemented by the sorption modeling studies done in WP 1 and 2. In order to understand these complex systems and to follow and identify the processes we will use a set of modern analytical tools such as μ -X-ray diffraction, Mössbauer spectroscopy, scanning and transmission electron microscopy, HPLC, GC-MS, GC-isotope-ratio-MS, electron microscopy techniques (STXM) and X-ray techniques (XANES).

The major goal of this WP is also to investigate the rates of heterogeneous redox reactions in pure and poised (NOM, phosphate) systems as a function of environmental conditions and mode of formation of the mineral coatings involved. The proposed work includes (i) reactivity studies in aqueous suspensions of biogenic and abiogenic iron-(hydr)oxides (both from WP2 and SME partner), (ii) comparison of the rates with control experiments in suspensions of non-redox active minerals (quartz, alumina) and in homogenous solution (O_2 as oxidant), and (iii) establishment of structure-reactivity relationships on pollutant transformation rates by studying model compounds. The organic analyses will be performed in our laboratories and the As redox state will be determined by wet-chemical analysis (collaboration with WP 5) and synchrotron-based XAS spectroscopy (in collaboration with WP 2).

Work package 4 (RWTH Aachen)

As has already been outlined in the introduction, oxyanions such as phosphate, silicate, and sulfate may compete with both As species for sorption sites. The most relevant oxyanion in many groundwaters, especially those with alkaline pH, is silicate. In water plants operated by our industry partner, concentrations up to 50 mg/L were observed and decreased the sorption capacity of the akaganeite filter material significantly. Furthermore, the specific adsorption of silicate will shift the point of zero charge and subsequently the sorption behaviour. Adsorption isotherms for silicate on akaganeite are to the best of our knowledge not known. For tuning the sorption behaviour in water plants using akaganeite, equilibrium models based on isotherms will not be sufficient, because kinetic aspects are also to be considered.

For the sorption and kinetic experiments larger amounts of homogeneous samples of akaganeite have to be synthesized. Crystal shape and size distribution can be tuned by various recipes (e.g., Sugimoto et al., 1993). Since the biologically controlled mineralization of iron oxides by bacteria (see WP2) produces iron phases in amounts being too small for large-scale sorption experiments, a further emphasis will be on syntheses as close to the biological conditions as possible. The known uptake of carbonate into iron oxides requires all works to be performed in a controlled atmosphere within a glove box.

Sorption and kinetic experiments require markedly pure phases. Especially impurities with high specific surface area (notably ferrihydrite) need to be removed or at least quantified. X-ray diffraction on spiked samples and Rietveld analysis will quantify even minor contributions of impurities, and may then prompt selective dissolution treatments for removing such impurity phases. Since sorption is a surface area-dependent property, specific surface areas by N₂ and Kr sorption have to be determined. Apart from measuring BET surfaces, the contributions of micro- and mesoporosity need to be quantified, because these pores exert major influence on the dynamics of sorption. For phosphate sorption, the importance of the multidomainic character of many synthetic iron oxides with its concomitant microporosity has long been known (e.g., Strauss et al., 1997). The crystal morphology will be determined by SEM (WP 3) and by TEM (this WP).

With the suite of akaganeite samples (including the industrially used product from WP 1), ad- and desorption isotherms within the relevant pH range will be measured in stirred batch experiments. From the material balance between silicate remaining in solution and initial silicate amounts the isotherms can be constructed and modeled. Select samples will be investigated within WP 2 by FTIR-ATR and XAS spectroscopy.

In a mixed-flow reactor (MFR), solutions with select inlet concentrations of arsenate are pumped through the reactor by a HPLC pump. Such a pump ensures precise flow rates. Output concentrations are then a measure of the reaction progress and provide a data base for a kinetic evaluation of the sorption process. The possibility to vary single parameters and to test the reversibility of reactions will enable us to identify rate-determining steps and parameters in the sorption process. The solution concentrations are measured by ICP-OES. For calibrating and cross-checking the analytical procedures, a set of 50 samples will be measured by speciation techniques available from WP 5. The kinetic experiments will also be extended to the silicate sorbate.

Work package 5 (UFZ Leipzig):

This WP will investigate the sorption processes of selected species of arsenic and antimony from waters onto iron bearing phases using species analysis techniques (Daus et al 2002). The main hypothesis to follow is that there are species-specific factors disturbing the overall sorption efficiency. The following questions have to be answered in this context:

- Are there differences between the different species in their sorption behaviour onto the relevant Fe-bearing mineral phases?
- Is there a potential change in the aqueous speciation pattern which has a direct influence on the sorption process, and what triggers such a change?

- Which possible biogenic reactions (oxidation, reduction, alkylation) influence the species transformation processes? Can these processes result in a remobilisation of metalloids subsequent to sorption?

First, adsorption isotherms of the most important alkylated species of As and Sb onto the relevant sorbent phases will be determined, with and without interfering ions. The adsorption equilibrium constants of alkylated species (monomethylarsonic acid, dimethylarsinic acid, trimethylantimony) will be determined by surface complexation models fits (FITEQL 4.0 code) from batch experiment data in cooperation with WP 2. Sorbent samples for the experiments will be selected in cooperation with WP 1 (abiogenic formed akaganeite of GEH Wasserchemie GmbH) and WP 3 (microbially formed akaganeite) in order to trace any differences in the sorbent preparation route.

A new method („rotation coiled columns“, RCC) using centrifugal forces will allow the fast and detailed investigation of the interaction of the metalloid species and the Fe-bearing sorbent materials (Fedotov et al., 2002). The technique is based on the retention of the solid phase in RCC under the action of centrifugal forces while the other liquid (mobile) phase is being continuously pumped through. A very strong interaction between the stationary phase (sorption material) and the liquid phase (model groundwater) is forced by the planetary centrifuge system. There are two aims in applying this novel technique, (i) forced kinetic investigations by the intensive contact of the solid and the liquid phase, and (ii) the possibility to investigate (re-)mobilisation or disturbing processes on a small scale (creating reducing conditions, variation of pH, etc...), in short experiment time and under well defined (pH, eH, geochemical) conditions. A novel experimental setup using a micro-sampling system will allow a high spatial resolution for, e.g., sampling along a steep redox potential gradient. Such micro-sampling enables us to take samples near the sorbent surface to analyse and quantify possible transformation products of the added species (arsenite, arsenate, antimonite, antimonite) near the surface electrical double layer. The analysis of all species will be done by chromatographic hyphenation systems coupled with an element-specific and highly sensitive ICP-MS detector.

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