Impact of mechanical disturbance and acidification on the metal(loid) and C, P, S mobility at the sediment water interface examined using a fractionation *meso* profiling ICP-QQQ-MS approach

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HIGHLIGHTS

- Mobility of 12 metal(loid)s, C, P and S, during disturbances at the SWI was studied
- Except for As, Sb, V, mobility of all analytes was more affected by acidification
- Mechanical disturbance promoted the mobility of As, Sb, and V
- Except for Ni, colloids (0.45–16 μm) were not significant for metal(loid)s mobility
- All analytes were quantified by ICP-QQQ-MS in a single run multi-element approach

GRAPHICAL ABSTRACT
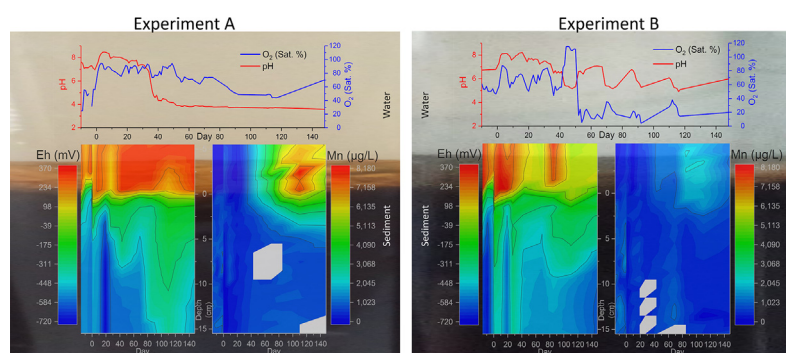
ABSTRACT

The impact of mechanical disturbance and oxygen induced acidification on the concentration and size fractionation of the 12 metal(loid)s As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Tl, V and the polyatomic nonmetals C, P and S in the pore water was studied. Using the *meso* profiling and sampling system (*messy*) 12 pore water depth profiles were sampled from two incubation experiments undertaken in parallel, which were both mechanically disturbed in the lab and subsequently exposed to a different air supply. In parallel to the low invasive, automated sampling process the redox potential, the pH value and the O_2 concentration were detected. Simultaneous quantification of all analytes by inductively coupled plasma-triple quad-mass spectrometry in the two different size classes dissolved (<0.45 μm) and colloidal (0.45–16 μm) showed: i) the predominant influence of the pH on the mobility of metals; ii) the mobility of metalloids was strongly impacted by the mechanical disturbance; and iii) the colloidal release is less important except for Fe, P, and Ni.

1. Introduction

Sediments can serve as sinks, transformation matrix or sources of potentially environmentally harmful substances, depending on the environmental conditions. Processes that determine distribution, cycling, solubility and bio-availability of analytes such as trace metals, nutrients or organic compounds thus depend essentially on parameters such as O_2 saturation, redox potential and pH value. Steep gradients of these parameters characterize sediment water interfaces (SWI), leading to the fact that the analytes speciation and fractionation may vary significantly with depth (Santschi et al., 1990). Therefore, on the one hand

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side it is necessary to study different parameters and analytes in parallel with high spatial resolution, for a comprehensive understanding of the geochemical processes determining distribution and transport of substances at SWI. On the other hand, disturbances, mechanically or chemically, alter existing equilibria and can thus change the partitioning and hence, availability of certain analytes (Eggleton and Thomas, 2004). Such disturbances are often caused by human activities like construction and maintenance measures in waterways. Hence an understanding of processes occurring at the SWI is of interest, especially in the context of environmental risk assessments.

The determination of parameters such as O_2 saturation, redox potential or pH value (next to others) *in-situ* with a spatial high resolution is facilitated by the development of micro-sensors and -electrodes (Stockdale et al., 2009). Contrary, the detection of many contaminants, nutrients and organic matter (OM) can be performed with great accuracy using different state of the art analytical techniques. The extraction of pore water samples, using ex-situ methods such as squeezing and centrifugation (Lourino-Cabana et al., 2012; Scholz et al., 2011) or in-situ methods such as dialyses (Lewandowski et al., 2002; Rigaud et al., 2013) including diffusive gradients/equilibration in thin film (Zhang et al., 2014) or suction based techniques (Duester et al., 2011; Seeberg-Elverfeldt et al., 2005; Vink, 2002) remains the most challenging part, due to its vulnerability to the formation of artefacts.

An option to combine suction based pore water sampling with in-situ measurements on O_2, the redox potential and the pH value for sediment depth profiles was presented by Fabricius et al. (2014). This setup, restricted to high-resolution investigations of the first cm of the sediment, was modified by the authors to sample pore waters to a depth of >15 cm while measuring accompanying parameters in parallel. In a first study the system was tested for the simulation of processes related to sediment handling operations such as re-suspension and oxygenation (Schroeder et al., 2017). The necessity was identified to better distinguish between the processes triggered by the different types of disturbance (mechanical or chemical) by extending the set of analytes and by systematical consideration of the colloidal fraction during metal(loid) releases into the pore and surface water.

In the present study the latter setup was used to (i) simulate a resuspension event and the acidification of an oxbow sediment as consequence of aeration. Therefore, two incubation experiments run in parallel were mechanically disturbed in the lab and subsequently either aerated or left untreated. (ii) The impact on the release of 12 metal(loid)s (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Tl, V) was analyzed for 12 pore water profiles sampled across the SWI of both experiments. (iii) Additionally, the pore water concentrations of C, S and P as well as the redox-potential and the O_2 concentration were determined at the same spatial resolution to deliver mechanistic explanations of observed metal(loid) releases. (iv) To examine the potential contribution of the colloidal fraction between 0.45 and 16 μm during the metal(loid) release, a previously presented size fractionation approach (Schroeder et al., 2017) was applied in a systematic manner throughout the whole experiment.

2. Materials and methods

2.1. Incubation experiment

Sediment was sampled at an oxbow (former millstream) of river Lahn in Germany (50°18′56.87″N; 7°37′41.25″E), that only receives fresh water from the stream during flood events (approximately twice a year) and is known for increased metal(loid) concentrations due to former lead and silver mining activities. The sediment was sieved <2 mm to remove coarse (organic) particles such as leaves and branches, split in two 40 × 60 cm large high density polyethylene boxes (Nalge Company, USA) that were each filled to a height of 20 cm and incubated under 10 cm water column.

After an incubation time of 34 days 3 pore water depth profiles were sampled (profile 1–3, day −16, −9 and −1; negative numbers indicate times before the mechanical disturbance at day 0) to characterize the initial conditions at a steady state. On day 0 the sediment of both experiments was completely suspended by mixing sediment and water with a stainless steel stirrer (IKA, Germany) driven by a screw driller (Makita, Germany) for 5 min.

Aeration of the water column of one of the experiments (Experiment A) was started as soon as the main sediment fraction was settled using a glass air stone (JBL, Germany) and a membrane pump (Sera air 110 plus, Germany). This was meant to support oxygen induced slow "natural" pyrite weathering and subsequent acidification as it would take place after re-connecting the oxbow with the stream. Contrary, the reference Experiment B was left unaerated after the disturbance for the best possible comparison to the field conditions.

Pore water depth profiles across the SWI were sampled on day −16, −9, −1, 1, 9, 19, 27, 43, 69, 85, 110 and 148 as detailed in Section 2.2 together with redox potential profiles. Subsequent to every sampling profile a micro profile of the parameters oxygen concentration, redox potential and pH was surveyed as detailed in Section 2.5.

After finishing the last profile, sediment cores were taken using polyethylene terephthalate glycol (PETG) polycarbonate tubes (CT 46.2, ClearTec, Germany) for microwave assisted digestion with reverse *aqua regia* as described in the supplementary material (Section 1).

2.2. Pore water sampling

Profiles of suction based pore water samples were extracted from the experiments as detailed by Schroeder et al. (2017). Basic principle of the sampling process is to move a sampling probe through the SWI in vertical direction by a step motor (Motorized Microprofiling, Unisense A/H, Denmark) while aqueous samples are constantly extracted using a peristaltic pump (REGLO Analog, MS-2/8, ISMATEC, Germany). A fraction collector (Omnicoll, LAMBDA Laboratory Systems, Switzerland), positioned under argon atmosphere to avoid re-oxidation of the samples, is synchronized to gain samples of defined depth intervals. The disturbance of existing gradients is prevented by slow movement of the sampling probe (steps of 100 μm every 270 s.) and the low pumping speed of ~2 mL/h.

12 profiles of 22 samples were taken during each experiment. Starting the profiles 6 cm above and ending 16 cm below the SWI, every sample represents a depth interval of 1 cm. The horizontal offset between individual profiles was about 10 cm. To meet all analytical demands, 15 mL of sample volume were intended to be sampled by pumping at a rate of ~2 mL/h (equals 165 h (~one week) per profile). Contaminations were prevented by cleaning both the 15 mL centrifuge tubes (VWR catalyst Laboratory Services, USA) used to collect the samples and all pipes and tubes with 1.3% nitric acid for >24 h (HNO$_3$, 65%, w/w, p.a. purchased by Merck GmbH, Germany and sub-boiled using a dst-1000 Savillex, USA) and rinsing them with ultrapure water (USF ELGA Purelab Plus system, ELGA LabWater, Germany).

Half of the volume sampled was filtered by syringe filters (pore size 0.45 μm, Minisart NML Syringe Filters, surfactant-free cellulose acetate, Sartorius, Germany) before evacuation from the glove box. The filtrate is regarded as the "dissolved" fraction (<0.45) in accordance to the general convention. The unfiltered fraction (<16 μm) is referred to as total concentration. Until measurement all samples were stored frozen after acidification to a concentration of 1.3% HNO$_3$. Potential sample contaminations were monitored by methodological blank values as described in the supplementary material (Section 3.2).

Some samples in the pore water profiles are missing due to different reasons. If insufficient sample volume was obtained to analyze both size fractions, the focus was targeted to the dissolved fraction. In an event of technical difficulties (e.g. malfunction of the fraction collector), samples are missing in both fractions.