

ACIDIFICATION AND MECHANICAL DISTURBANCE INDUCED METAL AND METALOID RELEASE AT THE SEDIMENT WATER INTERFACE

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Introduction

In 2014 the authors introduced a microprofiling and micro sampling system (missy) to study pore water concentration of different analytes at the sediment water interface (SWI, (Fabricius et al. 2014)). It enables a direct, automate and low invasive sampling of small water volumes (<500 µL) at a spatial high resolution of a few millimeters. By different sample preparation procedures followed by inductively plasma-mass spectrometry (ICP-MS) analyses, it is possible to address not only the total content of metal(loid)s, but also their fractionation or speciation related analyte distributions in sediment depth profiles (~ -1 above SWI to 2 cm below SWI) in parallel to different sediment parameters (O₂, redox and pH). In 2015 the system was up-scaled to a mesoprofiling and sampling system (messy) to address deeper sediment layers (~ -6 to 16 cm) with a lower resolution of 1 cm, bigger filtration cut-offs and up to 15 ml per sample. In two recent studies an anaerobic sediment was sampled and incubated in the laboratory for more than three month, focusing on the impact of mechanical disturbance and acidification (caused by pyrite weathering) on the metal and metalloid (metal(loid)) release. The presentation will deliver an overview on the two studies including the content < 0.45 µm of Ag, As, Cd, Co, Cu, Fe, Mn, Mo, Sb, U, V and Zn, information on the colloidal distribution (16 µm – 0.45 µm) as well as the As(III/V) and Sb(III/V) speciation, in connection to the pH, O₂ and redox conditions.

Methods

Mechanical disturbance and aeration of anaerobic sediments is an issue in river and lake management practice. The profiling method and basic experimental setup used to study the impact of mechanical disturbance and acidification on the metal(loid) release is detailed in Fabricius et al., 2014.

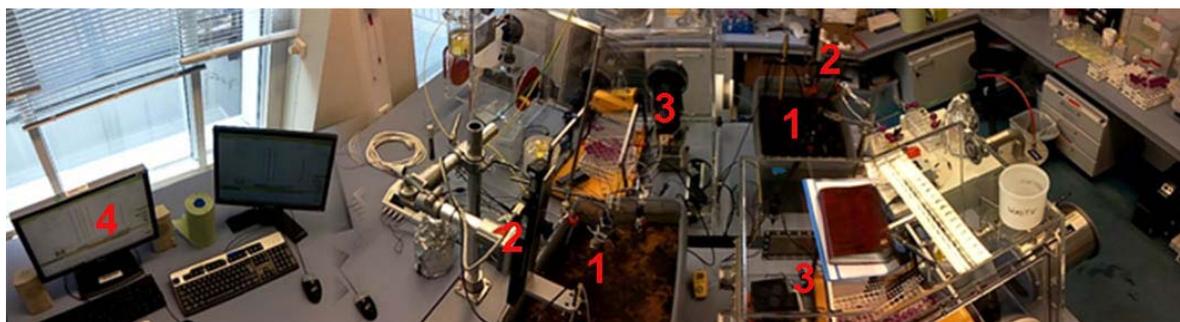


Figure 1. 180° bird eye view on the recent messy setup with: 1. Two incubated sediments (one aerated, one not), 2. profiling motors (Unisense, Denmark), 3. a glove box each with the pump and the fraction collector and 4. the evaluation units.

The sample probe of the messy setup is made of a glass suction cup as a tip (ecoTech, Germany – cut-off 10 – 16 µm), instead of a PES hollow fiber used in the missy setup. This modified suction cup is slowly moved across sediment water interface (22 cm in 6.5 days) and connected via tubing with a peristaltic

pump (Flow ~ 35 $\mu\text{l}/\text{min}$) and a fraction collector, both Lambda Instrument, Czech Republic and both placed in a glove box containing an inert Ar-atmosphere. Figure 1 gives an overview on the recent setup.

The sediment was sampled at an abandoned channel at the river Lahn, Germany. The former mill channel receives fresh water only at high-water events (1-2 times per year) and is strongly impacted by foliage input. The undecomposed foliage layer was removed and the subjacent sediment was sampled (40 – 100 cm depth), brought to the lab and sieved < 5 mm. After homogenizing, the sediment was incubated in polyethylene tanks and let at rest for 2 month. The study was divided into two experiments: In a preliminary experiment conducted to secure and validate the methodological approach and speciation analyses the sediment was disturbed and spiked with Sb_2O_3 powder (Sigma Aldrich). In the second experiment two sediment incubations were run in parallel (figure 1). After the initial resting time and reference profiling, both were mechanically disturbed at the same time, whereas in one experiment from that on air was introduced into the overlaying water (1 l/min) and the other was not further manipulated. This enables to investigate in a direct comparison the acidification impacted release. The O_2 concentration, the redox potential and the pH value were measured with different electrodes and loggers made by Unisense, Denmark or Mansfeld redox-electrodes connected to a data logger made by ecoTech, Germany. The metal(loid)s content was analyzed by ICP-MS (Agilent 7700 and 8800). As and Sb (III/V) speciation was done by coupling an Agilent 1260 HPLC to the Agilent 7700. Therefore, the sample preservation and analyzes were performed comparable to Daus & Wennrich, 2014. All samples taken via the probe tip (< 16 μm) were filtered in the glove with cellulose acetate syringe filters (Sartorius, Germany) < 0.45 μm .

Results

As examples, in Figure 2 the heat plots of As and Ag concentration determined in the <0.45 μm fraction of the preliminary experiment are presented. Arsenic is stronger impacted by the physical disturbance and the connected redox changes, whereas silver is an example for pH impacted metals.

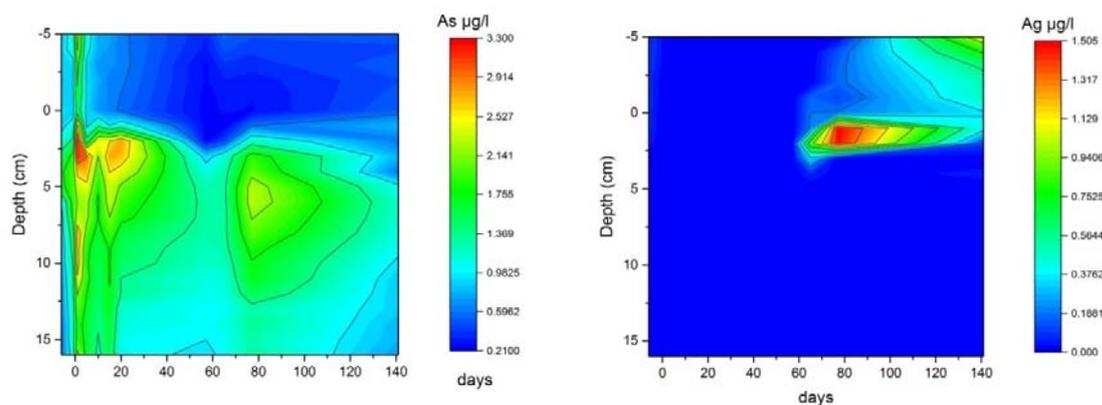


Figure 2. On the left As and on the right Ag concentration: On day 0 the sediment was mechanically disturbed (intensive suspension) and on days -1, 1, 5, 10, 15, 20, 57, 65, 77 and 141 profiles were taken. The pH in the overlaying water decreased from 7.2 on day -1 to 3.5 on day 141. The depth 0 cm indicates the sediment boundary.

References

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