

Transformation processes of Mo at the particulate/dissolved interface in the Wadden Sea of NW Germany: An experimental approach

Nicole Kowalski¹, Olaf Dellwig¹, Melanie Beck², Maik Grunwald², Thomas Leipe¹, Thomas Riedel², Michael E. Böttcher¹, Hans-Jürgen Brumsack²

¹ Leibniz Institute for Baltic Sea Research Warnemünde, Seestr. 15, D-18119 Rostock, Germany

² Institute for Chemistry and Biology of the Marine Environment, Carl von Ossietzky University of Oldenburg, D-26111 Oldenburg, Germany



Introduction

In oxygenated ocean water molybdenum generally behaves conservative, i.e. its distribution changes with salinity. Recent investigations carried out in the Wadden Sea of NW Germany showed a non-conservative behaviour of Mo during certain time periods. Almost simultaneously with the breakdown algae blooms dissolved Mo showed dramatic depletion followed by enrichments. Both phenomena seem to be related to microbial activity which will be discussed in this contribution.

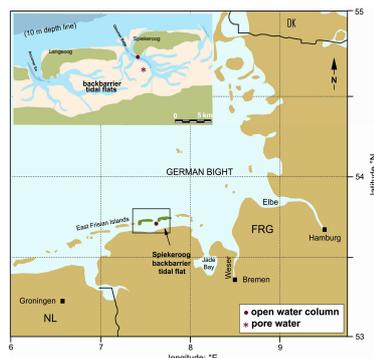


Figure 1: Map of the study area with the sampling sites

Study area

The study area is situated in the backbarrier tidal flat of the Island of Spiekeroog. The sites for open water column and pore water samples are shown in Fig. 1.

Methods

Mo has been measured by HR-ICP-MS. H₂S [1] and Si(OH)₄ [2] are determined photometrically. The structural properties of the aggregates are investigated by SEM-EDX.

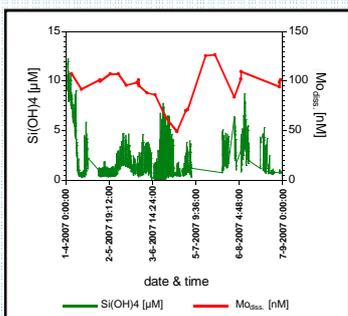


Figure 2: Concentration of dissolved Mo and silica in the water column of the backbarrier tidal flat of Spiekeroog

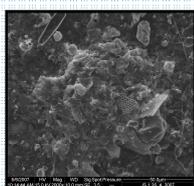


Figure 3: SEM picture of an aggregate

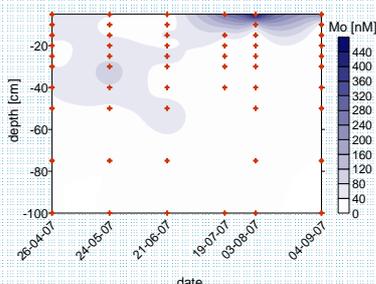


Figure 4: Dissolved Mo in pore waters of the tidal flat sediments

Results and discussion

In July 2005 a remarkable decrease of dissolved Mo along with the breakdown of an algae bloom was observed [3]. The same phenomenon occurred in June 2007 when dissolved Mo decreased from 104 nM down to 52 nM (Fig. 2). An collapsing algae bloom releases organic material (e. g. TEP) which cause the formation of larger aggregates (Fig. 3).

A relation to scavenging of Mo by freshly formed MnO_x phases could not be derived from our data [3]. Thus, we hypothesize that oxygen-depleted micro-zones in the aggregates favour a reduction of MoO₄²⁻ thereby leading to an enrichment of particulate Mo. Deposition of aggregates results in a Mo-enriched "fluffy layer" at the sediment surface. Degradation by micro organisms leads to a release of Mo from the aggregates and a Mo enrichment in the pore water (Fig. 4).

First laboratory experiments

Beyond the field investigations, laboratory experiments are accomplished under controlled conditions. Fig. 5 shows an experiment in 1 L bottles with homogenized oxic tidal flat sediment and a 2.5 cm sea water layer. The sediment of bottle II and III was artificially enriched with organic material (bottle II: C_{org.} 1.4 % by addition of *Spirulina*, bottle III: C_{org.} 0.05 % by addition of *Amphiprora kufferathii*) to increase microbial activity and produce anoxic conditions at the water/sediment interface. The bottles were stored at a temperature of 6 °C.

At the beginning of the experiment a release of dissolved Mo from the sediment was observed in bottle I and III (Fig. 6). Subsequently a gradual decrease of dissolved Mo could be measured. The oxygen depletion in bottle II is apparently more effective because under presence of H₂S (Fig. 7) Mo is rapidly removed from the dissolved phase.

Outlook

The laboratory experiments with artificial and natural sediment cores will be expanded. Under controlled conditions the material input will be manipulated to investigate the effects on microbial activity and trace metal cycles. The manipulation of environmental conditions shall provide information about the influence of abiotic and microbial processes on the release and fixation of Mo in the sediments.



Figure 5: Bottle experiment with tidal flat sediments

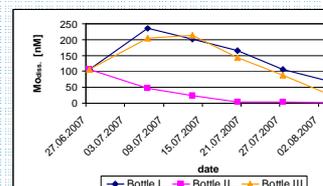


Figure 6: Dissolved Mo in the bottom water of the bottle experiments

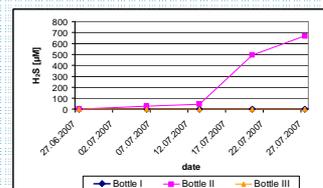


Figure 7: H₂S in the bottom water of the bottle experiments

Acknowledgements

We would like to thank Astrid Ahke (MPI Bremen) for the provision of the ice diatom *Amphiprora kufferathii*. This work is funded by DFG (Research group "BioGeoChemistry of tidal flats").

References

- [1] Cline (1969) Limnology and Oceanography, Vol. 14, No. 3, pp. 454-458
- [2] Grasshoff et al. (1999) Methods of seawater analysis. Wiley-VCH, New York, N. Y.
- [3] Dellwig et al. (2007) Geochim. et Cosmochim. Acta 71, 2745-2761