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# Pelagic anomalies and isotope signatures of molybdenum in temperate tidal systems

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The seasonal dynamics of the redox-sensitive trace metal molybdenum (Mo) and its stable isotope signatures were investigated in the water column and in surface sediments of two tidal basins of the German Wadden Sea, North Sea.
Dissolved Mo was assumed to behave conservatively in oxic seawater for a long time. Seasonal observations in the water column of tidal basins of the German Wadden Sea, however, have shown pronounced negative anomalies with decreases down to 50% of the expected salinity-normalized values. This non-conservative behaviour was recognized repeatedly in early summer during the years 2007 to 2011. A shift towards heavier $\delta$98/95Mo values during the depletion period indicates a preferential removal of light Mo isotopes from the aqueous solution. As the Mo depletion coincides with collapsing summer phytoplankton blooms we suggest a tight coupling of Mo with algae derived organic matter. We estimate an isotope enrichment factor from the field data of about -0.3‰ for the removal process which is in agreement with those determined experimentally by Zerkle et al. (2011) during biological Mo uptake, but much less than during the adsorption to metal oxi(hydroxi)des (Wasylenki et al., 2008).
A close association of Mo to organic matter in the tidal ecosystems is further indicated by high contents of Mo in the exterior organic layer (periostracum) of the shell of the invader mussel Ensis americanus displaying an isotope signature below the seawater molybdate value.
Immobilized Mo may be transported to the surface sediments via organic-rich aggregates. After incorporation into the sediment the aggregates may be rapidly decomposed by microorganisms leading to a release of Mo to the pore waters.
A positive anomaly of dissolved Mo was observed in the water column of the tidal area of Sylt Island in 2009. Laboratory experiments demonstrate efficient Mo release from anoxic sediments during sediment re-suspension in oxic sea water. Together with first modelling results, these data lead to the conclusion, that intense sediment re-suspension by high-energy bottom currents and in particular during storm events may cause a significant oxidative release of Mo temporarily enhancing pelagic Mo concentrations.

References

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