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Seasonal and event-driven changes in the cycling and isotopic composition of molybdenum in tidal systems of the North Sea

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Seasonal dynamics of the redox-sensitive trace metal molybdenum (Mo) and its stable isotopic composition were investigated in the water column and surface sediments of two tidal systems of the southern and northern parts of the German Bight: The backbarrier area of Spiekeroog Island and the tidal basin of Sylt Island.

Mo is generally assumed to behave conservatively in oxic seawater following solely changes in salinity. In recent years, however, decreases in Mo concentration as low as 50 % of normal values were observed during certain periods in summer without accompanying changes in salinity. This non-conservative behaviour was recognized repeatedly in the water column of the tidal areas of the North Sea. The corresponding $\delta^{98/95}$Mo values show a trend towards a heavier isotope composition in the residual Mo fraction indicating isotopic fractionation during the depletion period and the removal of a light Mo isotope fraction from the aqueous phase. As this period coincides with summer phytoplankton blooms we suggest a tight coupling to algae derived organic matter and transport of Mo into the sediments by organic-rich aggregates. After burial, these aggregates are rapidly decomposed by microorganisms and Mo is released to the pore water. In agreement with this, pore waters are enriched in the lighter Mo isotope compared to the water column. An interesting observation was made regarding the Mo isotopic composition of the exterior organic layer (periostracum) of the shell of the invader mussel *Ensis americanus*. Distinct enrichments of the lighter isotope and max contents of 160 mg kg^{-1} Mo were observed thus supporting a possible association of Mo to organic matter in the Wadden Sea.

By contrast, significant enrichments of dissolved Mo were observed in the water column of the Sylt area in early summer 2009, which is likely attributed to benthic-pelagic cycling, e.g., Mo liberation from (suboxic) reduction of sedimentary Mn oxides.

Laboratory experiments with anoxic sediments demonstrate that Mo is efficiently released during sediment re-suspension in oxic waters. Therefore, intense sediment re-suspension by high-energy bottom currents and in particular during storm events likely causes effective oxidative release of Mo, thereby accelerating benthic-pelagic Mo cycling. The experimental data will be used in a modelling approach, which simulates sediment re-suspension to estimate the importance of these processes on Mo cycling.