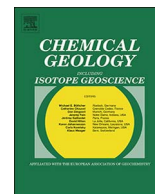




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Molybdenum dynamics in sediments of a seasonally-hypoxic coastal marine basin

Fatimah Sulu-Gambari^{a,*}, Anne Roepert^a, Tom Jilbert^{a,b}, Mathilde Hagens^a,
Filip J.R. Meysman^{c,d}, Caroline P. Slomp^a

^a Department of Earth Sciences (Geochemistry), Faculty of Geosciences, Utrecht University, P.O. Box 80.021, 3508 TA, Utrecht, the Netherlands

^b Department of Environmental Sciences, Faculty of Biological and Environmental Sciences, University of Helsinki, Finland

^c NIOZ Royal Netherlands Institute for Sea Research, Department of Estuarine and Delta Systems, P.O. Box 140, 4400 AC Yerseke, the Netherlands

^d Utrecht University, the Netherlands

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ABSTRACT

Molybdenum (Mo) enrichments in marine sediments are a common indicator of the presence of sulphide near the sediment-water interface and can thereby record historic bottom-water oxygen depletion. Here, we assess the impact of temporal changes in manganese (Mn) cycling and bottom-water oxygen on sedimentary Mo dynamics in a seasonally-hypoxic coastal marine basin (Lake Grevelingen, the Netherlands). High resolution line scans obtained with LA-ICP-MS and discrete sample analyses reveal distinct oscillations in Mo with depth in the sediment. These oscillations and high sediment Mo concentrations (up to ~130 ppm) are attributed to deposition of Mo-bearing Mn-oxide-rich particles from the overlying water, the release of molybdate (MoO_4^{2-}) to the pore water upon reduction of these Mn-oxides, and subsequent sequestration of Mo. The latter process only occurs in summer when sulphide concentrations near the sediment-water interface are elevated. Gravitational focussing of Mn oxides explains the observed increased input of Mo with increasing water depth. Diffusion of MoO_4^{2-} from the overlying water contributes only a small amount to the sediment Mo enrichments. Cable bacteria may indirectly impact sediment Mo dynamics by dissolving Mn-carbonates and thereby enhancing the pool of Mn-oxides in the system, and by contributing to remobilisation of sediment Mo during oxic periods. A sediment record that spans the past ~45 years indicates that sediment Mo concentrations have increased over the past decades, despite less frequent occurrences of anoxia in the bottom waters based on oxygen measurements from water column monitoring. We suggest that the elevated Mo in recent sediments reflects both enhanced rates of sulphate reduction and sulphide production in the surface sediment as a result of increased input of organic matter into the basin from the adjacent North Sea since 1999, and an associated enhanced “Mn refluxing” in the marine lake in summer.

1. Introduction

Molybdenum (Mo) is the most abundant trace metal in the modern ocean (105 nM; Collier, 1985) but is only a minor constituent of the Earth's crust (1–2 ppm; Turekian and Wedepohl, 1961). This discrepancy reflects the fact that molybdate (MoO_4^{2-}) behaves conservatively in oxic seawater, leading to an accumulation of Mo in the oceans and a residence time of $\sim 4.4 \times 10^5$ years (Miller et al., 2011). However, Mo can be removed from seawater to marine sediments in the presence of hydrogen sulphide (H_2S), making sedimentary Mo an important proxy for past redox conditions. Under sulphidic conditions, multiple thiomolybdate intermediates ($\text{MoO}_x\text{S}_4 - x^{2-}$) (Erickson and Helz, 2000; Helz et al., 1996) and complexes of Mo with organic ligands

(Wagner et al., 2017) can form. However, when H_2S concentrations in seawater or pore water exceed $\sim 11 \mu\text{M}$, complete conversion to tetrathiomolybdate (MoS_4^{2-}) is thought to occur (Erickson and Helz, 2000; Helz et al., 1996; Wagner et al., 2017). Molybdenum can subsequently be sequestered through multiple co-occurring pathways involving organic matter, Fe phases and/or authigenic sulphides (Algeo and Tribouillard, 2009). As long as the supply of Mo to the seawater in a given environment is not restricted (Algeo and Lyons, 2006), the redox-sensitive behaviour of Mo allows discrimination between two distinct bottom-water oxygen regimes. More specifically, depositional settings with oxic bottom waters in which sulphide is limited to pore waters throughout the year (sediment Mo < 25 ppm) can be separated from those characterised by permanent anoxic and sulphidic conditions (i.e.

* Corresponding author.

E-mail address: fatimah.sulu-gambari@uu.nl (F. Sulu-Gambari).

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euxinia) in bottom waters (sediment Mo > 100 ppm; Scott and Lyons, 2012).

Bottom-water hypoxia ($O_2 < 62.5 \mu\text{M}$; Levin et al., 2009; Rabalais et al., 2010) has become increasingly prevalent in coastal environments worldwide over the past decades. This has led to so-called “dead zones”, where the sediment and bottom water are devoid of larger fauna (Diaz and Rosenberg, 2008; Rabalais et al., 2014). The increase in these dead zones is often directly linked to increased nutrient input from land, which fuels algal blooms, thus enhancing the oxygen demand in deeper waters when algal material sinks to the seafloor (Carstensen et al., 2014; Diaz and Rosenberg, 2008). Sediment Mo records can provide valuable information on the timing of the onset of human-induced hypoxia, anoxia or euxinia and its further development (Gooday et al., 2009; Helz and Adelson, 2013). In the deep basins of the Baltic Sea, for example, a strong enrichment of Mo is observed in the upper ~20 cm of the sediment (up to ~220 ppm), in accordance with the establishment of euxinic conditions in the bottom waters of these basins since ~1980 (Jilbert and Slomp, 2013b; Mort et al., 2010; Scholz et al., 2013). Similarly, the expansion of hypoxic bottom waters in Chesapeake Bay since 1960 has been linked to an increased burial of Mo in the sediment (Adelson et al., 2001b; Helz and Adelson, 2013; Olson et al., 2017).

In non-euxinic settings, there are two main sources of Mo to sediments. First, MoO_4^{2-} may diffuse into sediments from the overlying water where it may be sequestered in H_2S -bearing pore waters (e.g. Emerson and Husted, 1991; Tribouillard et al., 2006; Zheng et al., 2000). Second manganese-oxide particles may act as a major carrier of Mo to the sediment (Adelson et al., 2001b; Algeo and Lyons, 2006; Scheiderich et al., 2010). The input of Mo associated with Mn oxides can lead to two vertically-separated sediment enrichments in Mo: (1) an enrichment associated with Mn oxides at or near the sediment-water interface that is only a transient sink for Mo, and (2) an enrichment of Mo associated with sulphur and/or organic matter at depth that acts as a permanent sink (Morford et al., 2007; Scott and Lyons, 2012). Such dual Mo enrichments can be a permanent feature in sediments with oxic bottom waters (Malcolm, 1985). The release of Mo from Mn-oxides near the sediment-water interface may support a flux of Mo from the sediment to the overlying water. Such an efflux of Mo will prevent diffusion of Mo into the sediment (e.g. Scott and Lyons, 2012). In seasonally-hypoxic settings, the remobilisation of dissolved Mn from sediments, formation of Mn oxides in the water column and re-deposition of Mo-bearing Mn-oxides on the sediment in summer may lead to such a high input of Mo that the diffusive loss of MoO_4^{2-} becomes unimportant relative to its input and conversion to tetrathiomolybdate (e.g. Adelson et al., 2001a). This so-called “Mn-refluxing” is thought to contribute to the high Mo burial fluxes in environments with weakly sulphidic bottom waters (Algeo and Lyons, 2006). To our knowledge, there are no detailed seasonal studies of the dynamics of Mo and Mn in both pore waters and sediments of hypoxic systems to confirm the suggested seasonality in coupled Mn-Mo cycling.

Recently, it was discovered that sulphide-oxidising cable bacteria (Nielsen et al., 2010; Pfeffer et al., 2012) may dissolve Fe-sulphides and Mn-carbonates in surface sediments of seasonally-hypoxic systems. Consequently, these bacteria actively contribute to the formation of an oxidised, Fe- and Mn-oxide rich surface layer in winter and spring (Seitaj et al., 2015; Sulu-Gambari et al., 2016b; Sulu-Gambari et al., 2016a). In contrast, sulphur oxidising Beggiatoaceae, present in autumn, had a more limited effect on the formation of Fe- and Mn-oxides in the surface sediment (Seitaj et al., 2015; Sulu-Gambari et al., 2016b; Sulu-Gambari et al., 2016a). Due to the coupling of Mn, Fe, S and Mo cycles in hypoxic systems, the activity of cable bacteria may also be of relevance to the sedimentary dynamics of Mo. More specifically, we hypothesise that cable bacteria activity may amplify seasonal oscillations in sediment Mo linked to bottom-water hypoxia. This hypothesis is based on their role in the efficient re-dissolution of sulphide-associated Mo in winter and spring, and in enhancing the pool of Mn-oxides by dissolving Mn-carbonates (Rao et al., 2016; Sulu-Gambari et al.,

2016b).

Here, we investigate the evolution of sediment and pore-water Mo profiles over one year in a seasonally hypoxic marine basin (Lake Grevelingen, the Netherlands). We focus on identifying the relationship between seasonal and spatial differences in bottom-water oxygen and the dynamics of Mo and Mn in the sediment. We assess whether sulphide-oxidising cable bacteria and Beggiatoaceae, which are both known to be present in our study basin for at least part of the year (Seitaj et al., 2015; Sulu-Gambari et al., 2016b; Sulu-Gambari et al., 2016a) can impact the sequestration of Mo in the sediment. Our results reveal strong annual oscillations in sedimentary Mo content driven by seasonal hypoxia and amplified by Mn refluxing and the activity of sulphide-oxidising bacteria. Furthermore, using an extended sediment record for the past 45 years we show how the long-term evolution of sedimentary Mo content reflects changes in pore water sulphide concentrations and Mn refluxing.

2. Methods

2.1. Study sites and sample collection

Lake Grevelingen (Fig. 1) is a former estuary of the rivers Rhine and Meuse. The lake was formed by the construction of a landward dam (1965) and seaward dam (1971) in response to flooding caused by a storm surge (1953). The shallow lake covers an area of 115 km² and has an average depth of 5.1 m but is intersected by several channels, of which the deepest (main channel) has a maximum water depth of 48 m (Fig. 1; Hagens et al., 2015; Sulu-Gambari et al., 2016b). The salinity of the lake falls within a stable range of 29 to 32 that is maintained via an exchange with the saline water from the North Sea through an underwater sluice in the Brouwersdam (Paulij et al., 1990). In spring and summer a temperature-dependent stratification develops in the main channel (Hagens et al., 2015). Bottom-water hypoxia has developed in the main channel in summer since 1971 (Wetsteyn, 2011).

Three sites, located along a water-depth gradient (sites 1–3, with water depths of 34, 23 and 17 m respectively) in the Den Osse basin in the main channel of Lake Grevelingen (51.747°N, 3.890°E; 51.749°N, 3.897°E; 51.747°N, 3.898°E), were sampled monthly in 2012 on board R/V Luctor (Fig. 1). Sediment accumulation rates at sites 1, 2 and 3 were previously estimated at ~2, 0.8 and 0.4 cm yr⁻¹, respectively (Malkin et al., 2014; Sulu-Gambari et al., 2016b; Sulu-Gambari et al., 2016a). Discrete water column samples were collected at 8 water depths (1, 3, 6, 10, 15, 25 and 32 m) using a 12-litre Niskin bottle and gas-tight Tygon tubing. Oxygen concentrations were measured in the collected samples using an automated Winkler titration procedure (Hagens et al., 2015).

Bottom-water oxygen concentrations between 1978 and 2011 were available for site 1 through a monthly monitoring programme operated by the Ministry of Infrastructure and the Environment (RWS) (Wetsteyn, 2011). Oxygen concentrations were assigned to specific time intervals each year and assumed to start and end in the middle of the interval between consecutive sampling dates. Each time interval was classified as ‘anoxic’ (< 1 μM oxygen), ‘hypoxic’ (1–62.5 μM oxygen), ‘oxic’ (> 62.5 μM oxygen) or ‘not determined’, depending on the oxygen concentration and whether or not sampling was conducted.

Short sediment cores (~40 cm) with ~20 cm of overlying water were collected at the three sites with a gravity corer (UWITEC, Austria) using Plexiglas® core-liners (6 cm inner diameter; 60 cm length). In addition to monthly sampling, a long core capturing the upper 90 cm of the sediment was obtained with the UWITEC corer (6 cm inner diameter; 120 cm liner length) at site 1 in May 2012. With an average sediment accumulation rate of ~2 cm yr⁻¹ and duration of the lake phase of ~41 years, since the closure of the system, the estuarine-lacustrine transition in this core is expected near a depth of 82 cm.

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