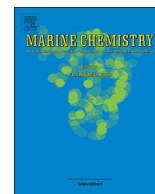




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## Distribution of dissolved and suspended particulate molybdenum, vanadium, and tungsten in the Baltic Sea

Susanne Bauer<sup>a,\*</sup>, Sven Blomqvist<sup>b</sup>, Johan Ingri<sup>a</sup>

<sup>a</sup> Applied Geochemistry, Luleå University of Technology, 971 87 Luleå, Sweden

<sup>b</sup> Department of Ecology, Environment and Plant Sciences, Stockholm University, 106 91 Stockholm, Sweden

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## ABSTRACT

In natural waters, dissolved oxyanions often dominate over the particle-bound element fraction. Still, the scavenging of oxyanions by suspended particles might contribute significantly to their dynamic cycling and distribution. To investigate how oxyanions are affected by manganese (Mn) redox cycling, detailed depth profiles across the pelagic redox zone at the Landsort Deep, Baltic Sea, were collected for molybdenum (Mo), vanadium (V), and tungsten (W), for both dissolved ( $< 0.22 \mu\text{m}$ ) and suspended particulate ( $> 0.22 \mu\text{m}$ ) fractions.

All three oxyanions show a non-conservative behavior in the stratified Landsort Deep. Strong linear correlations with Mn in the particulate fraction in the redox zone of the Landsort Deep suggest that Mn redox cycling influences their distribution. In the dissolved fraction, Mo, V, and W exhibited rather different behavior. Molybdenum was depleted below the redox zone, while V was depleted only within the redox zone. Tungsten concentrations increased within the redox zone, being three times higher in the sulfidic zone than in the surface water. Unlike Mo, W shows no tendency for adsorption or co-precipitation under the prevailing weak sulfidic conditions in the deep water of the Landsort Deep and is, therefore, not exported to the underlying sediment.

The Landsort Deep data were compared with data from the northern Baltic Sea (Bothnian Bay, Kalix River and Råne River estuaries), where particulate iron (Fe) occurs in high abundance. The particulate fractions of Mo, V, and W decreased during mixing in these estuaries. Vanadium showed the most drastic reduction, with a decrease in dissolved and particulate fractions, indicating that different processes influence the distribution of these oxyanions.

### 1. Introduction

Molybdenum (Mo), vanadium (V), and tungsten (W) occur as oxyanions in oxic seawater (Baes and Mesmer, 1976; Collier, 1985; Sadiq, 1988) and show a conservative distribution in the open ocean (e.g., Collier, 1984; Jeandel et al., 1987; Firdaus et al., 2008; Sohrin et al., 1987, 1999). The oceanic distribution contrasts to the non-conservative behavior of these oxyanions that has been reported from estuarine environments (e.g., Dalai et al., 2005; Mohajerin et al., 2016; Strady et al., 2009; Van der Sloot et al., 1985, 1989) and coastal seas (e.g., Dellwig et al., 2007; Wang and Sañudo Wilhelmy, 2009). The non-conservative distribution of these oxyanions is maintained by removal processes, such as biological uptake or scavenging on particles (e.g., Dellwig et al., 2007; Head and Burton, 1970; Shiller and Mao, 1999), which decrease the concentration of the oxyanions in solution.

In the central Baltic Sea, dissolved Mo shows slightly lower concentrations (10–20% less) than would be expected from simple

conservative mixing in the surface water (Nägler et al., 2011; Noordmann et al., 2015). An even higher depletion (about 60% compared to average seawater) has been observed for dissolved V and was attributed to scavenging on terrigenous particles (Prange and Kremling, 1985).

The role of suspended matter for the spatial distribution of oxyanions has been scantily studied. In this context, Fe and Mn (oxyhydr) oxides are crucial scavengers common in the Baltic Sea. Iron oxyhydroxides are particularly abundant in the Bothnian Bay, the northernmost part of the Baltic Sea, due to high riverine inputs (Pohl and Fernández-Otero, 2012; Pontér et al., 1990). Manganese redox cycling creates a large amount of Mn oxides in the pelagic redox zones of the stratified basins of the central Baltic Sea (e.g., Dellwig et al., 2010; Ingri et al., 1991; Neretin et al., 2003).

Changing redox conditions can affect the distribution of Mo, V, and W, in different ways. Redox-sensitive trace metals are often more soluble under oxic conditions, while they are less mobile in reducing

\* Corresponding author.

E-mail addresses: [susanne.bauer@ltu.se](mailto:susanne.bauer@ltu.se) (S. Bauer), [sven.blomqvist@su.se](mailto:sven.blomqvist@su.se) (S. Blomqvist), [johan.ingri@ltu.se](mailto:johan.ingri@ltu.se) (J. Ingri).

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environments (Tribovillard et al., 2006). Vanadium is reduced if free hydrogen sulfide is present forming more particle reactive components (Wanty and Goldhaber, 1992; Wehrli and Stumm, 1989). Molybdenum and W can be thiolated, which also decreases their mobility (Erickson and Helz, 2000; Helz et al., 1996; Johannesson et al., 2013; Mohajerin et al., 2014, 2016).

Scavenging of Mo, V, and W by Fe and Mn (oxyhydr)oxides have been observed in different environments. Enrichment in ferromanganese concretions is common for all three elements (Calvert and Piper, 1984; Calvert and Price, 1977; Koschinsky and Hein, 2003; Kunzendorf and Glasby, 1992). In marine sediments enrichment of Mo and V is related to Mn redox cycling (Crusius et al., 1996; Morford et al., 2005; Shimmield and Price, 1986), while in lake sediments Fe oxyhydroxides are scavengers for V and W (Harita et al., 2005). In freshwater, V and W show a relation to suspended and colloidal Fe (Johannesson et al., 2013; Pokrovsky and Schott, 2002). Molybdenum distribution is affected by the presence of Mn oxides in more marine settings with changing redox conditions (Berrang and Grill, 1974; Brüggemann et al., 1998; Dellwig et al., 2010).

In the present study, we test the hypothesis that Mn redox cycling affects the distribution of Mo, V, and W, in the Baltic Sea. We measured detailed profiles of dissolved and particulate concentrations across the pelagic redox zone in the Landsort Deep. To the best of our knowledge, our study provides the first detailed vertical profiles of W across a pelagic redox zone. Because it is important for understanding the distribution for Mo, V, and W in the Baltic Sea we also discuss data from the northern Baltic Sea.

## 2. Material and methods

### 2.1. Study area

The Baltic Sea is a large brackish semi-enclosed coastal sea (Fig. 1) with long periods of euxinic (sulfidic) conditions in bottom water in the deeper southern areas. High freshwater input and a restricted water exchange with the North Sea create salinity gradients from North to South and with depth. Inflow events, where higher salinity water from the North Sea intrudes into the Baltic Sea, occur at irregular intervals (e.g., Matthäus et al., 2008; Mohrholz et al., 2015). North Sea water has a higher density than Baltic Sea water and brings oxygen-rich water along the bottom into the deeper, euxinic basins, oxidizing the sulfidic water. A permanent halocline restricts vertical exchange between surface and deep water and promotes conditions for the formation of sulfide in the bottom water mass. A pelagic redox zone with a steep redox gradient separates the oxic water from the sulfidic water (e.g., Neretin et al., 2003; Yakushev et al., 2007).

During our sampling period, no inflow event affected the sampling site at the Landsort Deep (Fig. 1). The Landsort Deep is a narrow, deep trench (459 m). Its water column is stratified, often with sulfidic conditions in the deeper sections. Samples were collected at station BY31 (58°35'N, 18°14'E), which is part of the Swedish national monitoring program, run by the Swedish Meteorological Hydrological Institute (SMHI, Norrköping).

The Bothnian Bay (Fig. 1) is dominated by a riverine freshwater input. The Kalix and Råne rivers are both pristine (unregulated) rivers that drain a boreal environment. Their estuaries show salinities below 3. The main hydrological event is the snowmelt, which usually occurs in May when the water discharge increases up to 10 times over winter base-flow (Pontér et al., 1990).

### 2.2. Sampling and sample processing

Sampling at the Landsort Deep (station BY31) was conducted during a cruise with *M/S Fyrbyggaren*, in cooperation with the Swedish environmental monitoring program. Samples were obtained in 2013, during June, July, August, and October. Twelve Niskin-bottles (5 L,

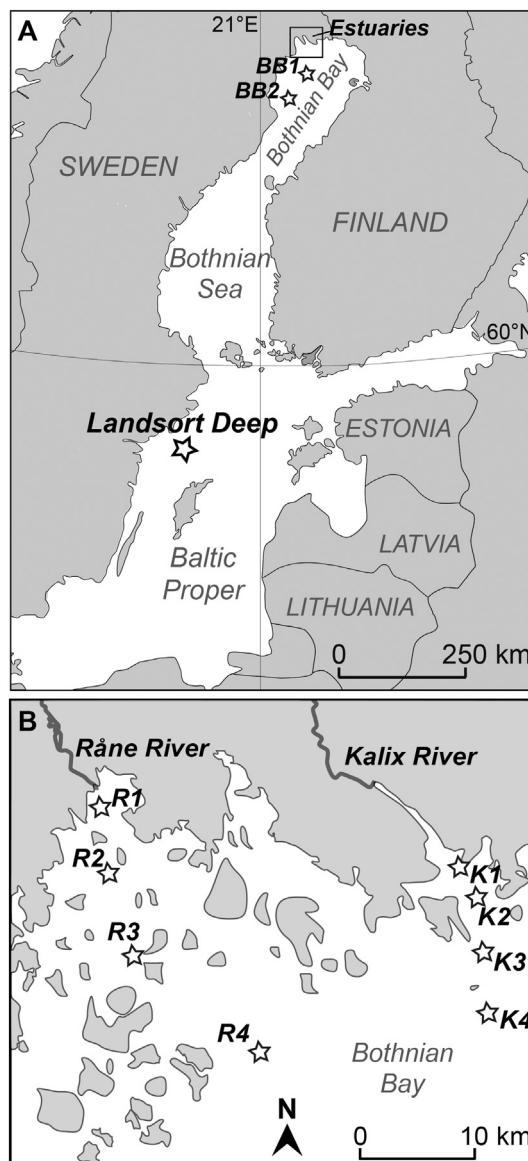


Fig. 1. Map of the Baltic Sea showing sampling locations, the Landsort Deep in the Baltic Proper, two stations in the Bothnian Bay, and the location of the estuaries of Råne River and Kalix River (A). In each estuary four stations were sampled (B).

Hydro-Bios, Kiel, Germany) were placed in line on a wire with a defined spacing. Five meters and 40 m depth were sampled for oxic surface water and 150 m depth for the sulfidic zone. Across the redox zone, the bottles were spaced 2 m apart for a more detailed profile. Before sampling, the position of the redox zone was determined with a CTD cast for recording salinity, oxygen, and temperature.

Once retrieved, the bottles were immediately emptied in argon-filled containers by purging argon gas through the Niskin bottles to avoid oxidation. Samples were taken for oxygen and hydrogen sulfide. Water samples were then stored in argon-filled boxes until processing in the laboratory on land. In the laboratory, the water was filtered through 0.22  $\mu\text{m}$  pore size filter (nitrocellulose, Millipore) with a peristaltic pump. This step defined our sample fractions dissolved ( $< 0.22 \mu\text{m}$ ) and particulate ( $> 0.22 \mu\text{m}$ ). All materials were pre-cleaned according to Ödman et al. (1999). Water samples were acidified by adding ultrapure  $\text{HNO}_3$  to a  $\text{pH} < 2$  and stored at  $+4 \text{ }^\circ\text{C}$ , and filters were stored at  $-18 \text{ }^\circ\text{C}$  until analysis.

Samples from the Råne estuary, Kalix estuary, and Bothnian Bay were collected with LIMNOS water sampler (two polyethylene 1 L

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