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Thallium dynamics in the southern North Sea

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Abstract

In open ocean waters thallium (Tl) belongs to the group of conservative elements, even though deviations from this trend have been observed in NW German coastal waters. Here, we report on tidal, seasonal and spatial dynamics of Tl along with Mo and Mn in the water column of a backbarrier tidal flat close to the island of Spiekeroog, the Jade system (Inner Jade and Jade Bay) and the adjacent offshore region. Dissolved thallium (Tl_{diss}) displays strong tidal and seasonal variations (~25–60 pM) unrelated to salinity. In all study areas, Tl_{diss} clearly deviates from conservative behavior. In general, Tl_{diss} is low during low tide (with a loss of up to 50%) and inversely related to $Mn_{diss,}$ except in summer. The tidal Tl variations as well as the loss of Tl in the water column may be due to Tl removal from pore waters in reducing sediments and drainage of Tl-free but Mn-rich pore waters into the water column during low tide. The negative Tl anomaly can be traced offshore for more than 40 km to the island of Helgoland.

The redox chemistry of Tl is not well studied, and Tl removal from pore waters was previously suggested to only occur under anoxic/sulfidic conditions. By contrast, our preliminary pore water results suggest that Tl could be removed already under slightly reducing (suboxic) conditions, likely along with microbially induced Mn reduction in the sediments. Therefore, this study supports the biological involvement in the aqueous cycling of Tl. We propose the use of Tl_{diss} next to Mn_{diss} as valuable indicator of suboxic or anoxic pore water discharge to the coastal realm.

Keywords: Thallium; Managnese; Molybdenum; Non-conservative behavior; Pore water; Marine sediment

1. INTRODUCTION

Thallium belongs to those elements, which are significantly enriched in anoxic organic carbon-rich sediments (Brumsack, 2006). But in contrast to its conservative behavior in open ocean waters (Flegal and Patterson, 1985), little is known on its distribution and behavior in coastal waters (e.g. Rehkämper and Nielsen, 2004; Böning and Schnetger, 2011). Thallium is less well studied owing to its very low concentration level in sea water (8–20 ng/l or 40–90 pM) and its rather low economic value. However, it is a US EPA priority pollutant with a toxicity higher than that of the better studied elements Hg, Cd and Pb (Cheam, 2001; Peter and Viraraghavan, 2005).

Thallium has low contents in the Earth's crust (0.5–1 mg/kg) where it replaces potassium (K) in minerals like micas, biotite and K-feldspars and may be part of sulphides like pyrite and sphalerite (e.g. Heinrichs et al., 1980). The element has two oxidation states – Tl(I) and Tl(III) – and a versatile chemistry in aqueous systems. Thallium(I) is predicted to exist predominantly as the free Tl^{+} ion in fresh waters and, additionally, as particle-unreactive $TlCl^{0}$ in saline environments (Matthews and Riley, 1970; Flegal and

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Patterson, 1985; Kaplan and Mattigod, 1998). In general, Tl^+ behaves as a K^+ analog in both living and non-living systems since the ionic radius of Tl^+ is similar to that of K^+ (Heinrichs et al., 1980; Hassler et al., 2007). Field and laboratory experiments suggest that dissolved K competitively inhibits Tl(I) scavenging in natural waters (Twiss et al., 2004; Turner et al., 2010).

Despite of the thermodynamic stability of Tl(I), Tl(III) was detected in the aquatic environment (e.g. Batley and Florence, 1975; Lin and Nriagu, 1999) likely due to the (inadvertent) oxidation of Tl(I) by planktonic bacteria (Twining et al., 2003). Thallium(III) may be present as particle-unreactive $Tl(OH)3^0$ and particle-reactive organic $Tl(CH_3)_2^+$ (dimethylthallium), the latter of which can make up to 50% of total dissolved Tl in surface waters (e.g. Schedlbauer and Heumann, 2000). Uptake of Tl by lake phytoplankton (Twiss et al., 2004) and scavenging of (synthetic) dimethyl-thallium by lake seston (Twiss et al., 2003) as well as elevated Tl contents in marine plankton (Flegal et al., 1986) suggest considerable biological involvement in the aqueous cycling of Tl.

Abiotic interaction of Tl in marine sediments includes enrichment on Mn nodule surfaces through oxidation of Tl(I) (Matthews and Riley, 1970; Bidoglio et al., 1993; Rehkämper et al., 2002), irreversible cation fixation of Tl (I) onto minerals (e.g. illitic clays; Matthews and Riley, 1970; Jacobson et al., 2005) and co-precipitation of Tl(I) with Fe sulfides in reducing saline environments (e.g. Thomson et al., 1995; Schnetger et al., 2000; Böning et al., 2004; Laforte et al., 2005; Böning et al., 2009). Microbially produced Tl(III) may readily be reduced and fixed by sulfides (Lin and Nriagu, 1999; Twining et al., 2003), however, the exact removal and fixation mechanism(s) of Tl in reducing aquatic systems are still largely unknown.

This work aims at contributing to the basic understanding of Tl behavior in the coastal marine environment. While some geochemical studies on dissolved Tl exist for estuaries like the Amazon and Kalix (Nielsen et al., 2005), Tamar (Anagboso et al., 2013) and Weser (Böning et al., 2017), studies on the behavior of dissolved Tl geochemistry in the coastal realm are essentially lacking (Böning and Schnetger, 2011; Böning et al., 2017). Here, for the first time, an extensive data set is presented for Tl from two tidally influenced areas in NW Germany. The data on Tl will be discussed in context with the trace metals Mo and Mn, the behavior of which is much better known in this environment. Essentially, dissolved Mn (Mn_{diss}) serves as a tracer for reducing conditions in pore waters, which drain during low tide from the tidal flats stretching along the coastline of the southern North Sea (Dellwig et al., 2007a; Moore et al., 2011). On the other hand, dissolved Mo (Mo_{diss}) shows significant deviations from conservative behavior in the water column of the tidal flat area, which seems unrelated to Mn cycling (Dellwig et al., 2007b; Kowalski et al., 2013). In summer, a Mo_{diss} loss was ascribed to the association of Mo with particulate organic matter (presumably after bloom breakdowns of the flagelate *Phaeocystis*) and its corresponding transfer into the sediment. In fall, the organic matter incorporated in the sediment was decomposed, leading to enrichments of liberated Mo in pore waters. Increased resuspension led to episodic positive Mo_{diss} anomalies in the water column.

Here, we hypothesize that dissolved Tl (Tl_{diss}) shows non-conservative behavior in coastal waters. Furthermore, we test whether Tl dynamics in the coastal zone are linked to those of Mn and/or Mo, and try to identify possible biogeochemical reactions.

1.1. Study area

The Wadden Sea forms one of the largest tidal flat areas worldwide and has been inscribed on the World Heritage List in 2009 due to its unique nature. The region is divided into several tidal basins, each connected to the North Sea by a tidal inlet permitting inflow of North Sea water during high tide and outflow of Wadden Sea water during low tide. Some study sites are located in the tidal area close to back-barrier island Spiekeroog (Fig. 1) where numerous biogeochemical studies were already conducted (e.g. Dellwig et al., 2007a,b; Beck et al., 2008; Al-Raei et al., 2009; Stanev et al., 2009; Grunwald et al., 2010; Moore et al., 2011; Kowalski et al., 2013; Reckhardt et al., 2015). The area is characterized by semi-diurnal tides with a range of about 2.6 m (e.g. Dellwig et al., 2007a,b).

One of the largest tidal bays of the German Wadden Sea is the Jade system comprising Jade Bay, Inner Jade and Outer Jade (from south to north) (Fig. 1). The Jade area is influenced by tides with a range of up to 3.8 m resulting in a large water volume ($400 \cdot 10^6$ m^3; Götschenberg and Kahlfeld, 2008) flowing in and out of the Jade Bay during each rising and falling tide. About 75% of the 160 km^2 area fall dry during low tide (Little-Gadow and Schäfer, 1974). Freshwater discharge through local flood gates contributes only a small water volume ($\sim 0.25 \cdot 10^6$ m^3 per tide; Irion, 1994).

2. MATERIAL AND METHODS

This work is a follow-up to the methodological work of Böning and Schnetger (2011) who presented a fast and reliable method for the measurement of dissolved Tl in seawater. In the forementioned work, Tl_{diss} data were shown for a time-series (48 h) and a subsequent transect in January 2010 for the Jade area. In this contribution we extend this data set with (i) Tl_{diss} data from April, July and November 2010 from the Jade area (ii) Tl_{diss} data from the pile station close to Spiekeroog Island over most of the year 2010, and (iii) Tl_{diss} data for a time-series (13 h) close to Spiekeroog Island and a transect to Helgoland in September-October 2015. The whole Tl data set is complemented with Mo_{diss} and Mn_{diss} data. Additionally, for the Jade data set, particulate Tl and Al (Tl_{part}, Al_{part}) for the water column, surface sediments and a 4.5 m long sediment core as well as pore water Tl_{diss}, Mn_{diss}, and Mo_{diss} were determined.

2.1. Sampling

Time-series sampling in the Jade area was done hourly for about 48 h in January, April, July and for 24 h in November 2010 at a fixed station located close to one of