Marine Chemistry 188 (2017) 6–17

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

Cycling of redox-sensitive elements in a sandy subterranean estuary of the southern North Sea

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ARTICLE INFO

Article history:
Received 22 June 2016
Received in revised form 24 November 2016
Accepted 29 November 2016
Available online 5 December 2016

Keywords:
Redox-sensitive metals
Stable sulfur- and oxygen isotopes
Sandy subterranean estuary
Submarine groundwater discharge

ABSTRACT

The cycling of metals and sulfur plays an important role in beach sediments. We studied the redox-sensitive metals Mn, Fe, U, Re, Mo, and V, in relation to salinity, organic matter-, and sulfur cycling within the subterranean estuary of a barrier island sand beach on Spiekeroog Island, Northern Germany. Pore water samples were obtained along a cross-shore transect down to 5 m below the sediment surface.

Redox conditions range from oxic, close to the base of the dune, to sub- to anoxic towards the low water line. We demonstrate that biogeochemical processes alter not only the pore water concentrations of the trace metals, but are also reflected by the O isotope- and to a minor degree the S isotope composition of dissolved SO_4^{2-}. The deviations from conservative mixing between terrestrial and marine endmembers influence trace metal fluxes into the ocean via submarine groundwater discharge. Redox reactions may be accelerated by the presence of dissolved reactive Mn, which we detected in shallow suboxic pore waters. Changes in the O isotope composition of SO_4^{2-} indicate a cryptic S cycle in the suboxic zone that is fueled by the cycling of Fe and Mn.

Seawater circulation through sediments of the upper beach (duneward part of the intertidal zone) removes U and V from solution, but serves as a source for Mn, Fe, Re, and Mo to the ocean. Pore water discharging from a berm close to the low water line exhibits lower U, V, and Re concentrations than adjacent seawater. This part of the beach thus serves as a sink for U, V, and Re, but as a source for Mn, Fe, and Mo. No significant Mo depletion is found in the pore water, due to the lack of dissolved sulfide. Net flux rates from the subterranean estuary into the ocean are estimated to be 185 mmol for Fe, 48 mmol for Mn, 8.3 μmol for Mo, −24.7 nmol for Re, −8.6 μmol for U, and −24 μmol for V per day and meter of shore line. These fluxes include freshwater flux from the island's freshwater lens and seawater circulation through the beach face. The subterranean estuary therefore serves as V, U, and Re sink, but as a source for Fe, Mn, and Mo to adjacent seawater.

A first comparison of net fluxes of dissolved metals from the Spiekeroog beach system with the island's backbarrier tidal flat margins indicates that the tidal flat area might be of greater importance for the supply or removal of metals to/from the North Sea.

1. Introduction

Sandy beaches comprise more than two thirds of the world's ice free coastline (McLachlan and Brown, 2006) and therefore represent an important part of the land-sea interface. These tide- and wave-dominated sediments play a major role in coastal carbon, nutrient, and trace metal cycling (Anschutz et al., 2009; Charbonnier et al., 2013; Charette et al., 2005; Charette and Sholkovitz, 2006; Kroeger and Charette, 2008; Santos et al., 2008, 2009, 2011, 2012). They are often located in a mixing zone of fresh groundwater and seawater, which is referred to as a subterranean estuary (STE) (Moore, 1999). In such systems, tides, waves, and fresh groundwater flow induce advective fluxes, which lead to the formation of a shallow saline circulation cell in addition to the saltwater wedge. This circulation cell, often called upper saline plume, and the saltwater wedge confine a freshwater discharge tube (Robinson et al., 2007), which serves as a pathway for the exfiltration of terrestrial-derived solutes (Burnett et al., 2003). Seawater circulation through permeable sediments continuously supplies fresh organic matter (plankton remains), oxygen and other electron

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http://dx.doi.org/10.1016/j.marchem.2016.11.003
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acceptors. Benthic (micro)organisms degrade this organic matter, a process that is coupled to the reduction of a sequence of electron acceptors. Molecular oxygen (O_2) consumption is followed by nitrate (NO_3^-) reduction, reduction of manganese (Mn) and iron (Fe) (oxyhydr)oxides, sulfate (SO_4^{2-}) reduction, and finally methane (CH_4) formation (Froelich et al., 1979). Organic matter remineralization releases inorganic C, N, and P (macronutrients) and, in the case of suboxic diagenesis, dissolved Mn and Fe (micronutrients) to the pore water. Consequently, nutrient-enriched water discharges into surface seawater during ebb- and low tide and may support coastal primary production (Anschutz et al., 2009; Burnett et al., 2003). On a global scale, this efflux may be as important as river flux, because it has been estimated to be at least of equal volume and typically exhibits higher concentrations of carbon, inorganic nutrients and metals (Kwon et al., 2014; Moore, 2010).

In this study, we focus on the redox-sensitive trace metals (RSMs) uranium (U), rhenium (Re), molybdenum (Mo), and vanadium (V). Since STEs are often characterized by steep redox gradients (e.g., Snyder et al., 2004; Charette and Sholkovitz, 2006; Reckhardt et al., 2015), they are likely sites of intense RSM cycling. The present knowledge of the behavior of these metals in STEs is limited to few contributions: Windom and Niencheski (2003) found U and Mo depletion in well samples, Charette et al. (2005), Charette and Sholkovitz (2006), and Santos et al. (2011) investigated STEs that act as U sink, and Beck et al. (2010) found Mo enrichment in STE pore waters and identified fresh groundwater as potential V source. O'Connor et al. (2015) calculated negative contributions (sink function) for Mo and U and a positive flux from a STE for V. Data on Re in these special systems are lacking, although it is a useful proxy for suboxic conditions (Crusius et al., 1996). Several studies about Re cycling in marine sediments (Crusius et al., 1996; Morford and Emerson, 1999; Sundby et al., 2004; Morford et al., 2009, 2012), however, provide a useful background for the interpretation of Re concentrations in pore water of STEs.

The metals U, Re, Mo, and V are soluble under oxic conditions and are adsorbed or precipitate under reducing conditions (Shaw et al., 1990; Morford et al., 2009). For instance, it was shown that in pelagic surface sediments Fe mobilization and U and Re immobilization occur at similar depths (Crusius et al., 1996). Mo reduction and removal to the solid phase occurs under sulfidic conditions (Crusius et al., 1996) and V also increasingly accumulates in sediments at very low O_2 levels (Shaw et al., 1990). Mo, U, and V are related to Mn and Fe cycling, whereas Re is not (Morford et al., 2005; Chappaz et al., 2008).

We assessed to what degree biogeochemical processes within a STE may alter U, Re, Mo, and V concentrations and evaluated if these sediments represent a net sink or source regarding coastal element budgets. As U, Mo, and V are known to adsorb to Mn and/or Fe oxide phases (Wehrli and Stumm, 1989; Morford et al., 2005; Beck et al., 2010) and may consequently be released during Mn/Fe oxide reduction, and Mo may be fixed with Fe sulfide (Helz et al., 2004), these elements were included in this study. We further used the stable S and O isotope composition of dissolved SO_4^{2-} to evaluate the role of S cycling for trace metal dynamics in these sediments. In particular, the O isotope composition of SO_4^{2-} was shown to be a sensitive tracer for reductive and oxidative reactions in the sedimentary S cycle with special regard to the sulfur-metal interaction (Böttcher and Thamdrup, 2001; Böttcher et al., 1998a, 1998b; Stempvoort and Krouse, 1994). Because of rapid reoxidation of Fe(II) to Fe(III), dissolved Fe may be recycled within the sediment (Caetano et al., 1997). This may have an influence on the escape of associated trace metals via submarine groundwater discharge (SGD). In contrast, the reoxidation of dissolved Mn(II) to particulate Mn(IV) is relatively slow, consequently, there can be a significant Mn flux from reducing sediments into the water column (Balzer, 1982; Dellwig et al., 2007a). The Mn removal rate to the solid phase, however, largely depends on the oxidation state of dissolved Mn in the pore water. In nature, Mn exists in three oxidation states – Mn(II), Mn(III), and Mn(IV). Under suboxic conditions (low O_2 concentrations and no H_2S in the pore water) Mn(III), stabilized by organic or inorganic ligands, can be the dominant dissolved Mn species (Trouwborst et al., 2006; Madison et al., 2013). Dellwig et al. (2012) and Schnetger and Dellwig (2012) identified a fraction of Mn that precipitates within <48 h under oxic conditions and is most likely predominantly consisting of Mn(III). To date, this dissolved reactive Mn (dMn_{react}) has never been investigated in highly dynamic systems like mesotidal sandy beaches. We expect that the extended suboxic zones of the beach sands are favorable for the production and stabilization of dMn_{react}, owing to elevated concentrations of Mn, dissolved organic carbon, and limited net SO_4^{2-} reduction. Since electron transfers between Mn oxidation states are coupled to C, N, S, O, and Fe element cycles (Madison et al., 2013) and the oxidation state of Mn influences the mobility of particle reactive trace metals (Morford et al., 2005), characterizing the Mn species distribution is important to understand the redox system of intertidal sandy beaches.

We hypothesize that the Spiekeroog beach system adds or removes redox-sensitive metals to/from adjacent seawater, that dMn_{react} is present in suboxic zones of the sediments, and that microbial SO_4^{2-} reduction forms part of the redox cycling although net SO_4^{2-} reduction is limited.

2. Material and methods

2.1. Study area

Spiekeroog Island forms part of the East Frisian Barrier Island chain at the German North Sea coast. It is subject to a semidiurnal mesotidal regime with a tidal range of approximately 2.6 m at the western head of the island (Flemming and Davis, 1994; Reuter et al., 2009). As it is common for barrier islands, an underlying freshwater reservoir has developed due to the regular infiltration of rain water into the permeable sediments (Röper et al., 2012).

Sampling was conducted along a cross-shore transect at a beach site, which is exposed to the hydrodynamics of the open North Sea (Fig. 1). During a joint sampling campaign on May 19–22, 2014, sediment, pore water and water column samples were collected. The main transect consisted of five sites, extending from close the dunes (site 0), to the high water line (site 2), to a sand bar (site 3), and finally to the low water line (site 4). Pore water samples for major ion, nutrient and trace metal analyses were sampled at a higher resolution (10 sites between the dune and the low water line), as depicted in Fig. 2. A detailed description of the beach morphology and hydrodynamics of the adjacent North Sea is available in Beck et al. (2016, under review). Pore water samples for dMn_{react} analysis were taken in September 2015 at the same beach site.

2.2. Sample and data collection

Beach topography and study sites were mapped with a vertical and horizontal accuracy of ±2 cm using a Trimble 5800 GPS (Beck et al., 2016, under review). Stainless steel push point samplers were used to sample pore water from 0.5 to 2 m depth (Reckhardt et al., 2015). Samples from greater depths (max. 5.20 m) were collected by elongating a stainless steel tip stepwise with 0.9 m long extension rods, which were pushed into the ground by percussion drilling (Charette and Allen, 2006). Pore water was obtained through a 6 m long Teflon tube, using a vacuum hand pump. Samples from the fresh water observation wells were obtained as described in Röper et al. (2012). Seawater samples were taken during low tide at 0.5 m water depth by submerging pre-cleaned polyethylene (PE)-beakers.

Salinity was measured directly in the field with the Multi 3430 (WTW) conductivity sensor. Sediment cores were retrieved as described in Beck et al. (2016, under review). O_2 concentrations were measured with optode microsensors (Pyroscience, sensor type OXR 430 HS) that were introduced into sediment cores through little holes