



Benthic–pelagic coupling of nutrients and dissolved organic matter composition in an intertidal sandy beach



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ABSTRACT

Subterranean estuaries (STEs) are important biogeochemical land–sea interfaces, where fresh groundwater mixes with seawater in coastal aquifers. However, the sources of dissolved organic matter (DOM) and the connection of its molecular-level processing to pore water chemistry and redox conditions in these ecosystems are still not well understood. We studied the cycling of DOM in the STE of an intertidal sandy beach of the North Sea on spatial and seasonal scales. Ultrahigh-resolution mass spectrometry was used to identify thousands of DOM molecular formulae. These data were interpreted in the context of inorganic pore water chemistry, stable carbon isotope composition of solid-phase extracted (SPE) DOM and chemical tracers for bioavailable (dissolved carbohydrates, DCHOs) as well as biorefractory DOM (dissolved black carbon, DBC). Numerical modelling was used to estimate pore water residence times indicating relatively young pore water in the upper saline plume (USP, <4 years) and decades-old groundwater in the freshwater discharge tube. The detected levels of dissolved Fe and ammonium in the USP at sediment depths exceeding 50 cm demonstrated suboxic conditions. Statistical analyses revealed complex biotic and abiotic DOM processing apart from conservative mixing of marine and terrestrial endmembers. We propose that the input of bioavailable marine and terrestrial DOM, such as DCHOs, by percolating seawater and meteoric groundwater and its degradation by microbes caused oxygen depletion favoring Fe oxide/hydroxide reduction. In the freshwater discharge tube, the presence of highly aromatic compounds, DBC, and ¹³C-depleted SPE-DOM indicated the intrusion of meteoric groundwater containing terrestrial DOM. The discharge of this groundwater appears to be a significant source of nutrients (e.g., ammonium) and biorefractory, e.g. combustion-derived, DOM to the adjacent water column.

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1. Introduction

Sandy shores cover about two-thirds of the ice-free coastlines globally (McLachlan and Brown, 2010). Their positioning at the sea–land interface makes them particularly vulnerable to anthropogenic pressure (Dugan et al., 2010) and sea level changes (Defeo et al., 2009). It is therefore critical to study these systems in order to assess their current status, conceptualize scenarios and make predictions for future developments (Brown and McLachlan, 2002).

Coastal permeable sediments are mainly controlled by nearshore flow processes such as bedform-generated convection, waves and tides. Consequently, fluxes of chemical species across the sediment–water interface are generally higher in permeable compared to fine-

grained sediments (Gibbes et al., 2008; Huettel et al., 1998; Røy et al., 2008; Rusch and Huettel, 2000). Additionally, subterranean estuaries (STEs) are important land–sea interfaces, where fresh groundwater mixes with seawater that has entered the aquifer. STEs control the supply and release of chemical species to coastal oceans by submarine groundwater discharge (SGD, Moore, 1999). Because nutrient concentrations in groundwater may exceed surface water concentrations by several orders of magnitude, the nutrient supply by SGD can be regionally even more important than the supply by rivers (Johannes, 1980; Moore et al., 2008; Slomp and Van Cappellen, 2004).

The Wadden Sea of the coastal North Sea (Fig. 1a) is one of the largest tidal flat systems in the world (Beck and Brumsack, 2012). In this system, pore water advection enhances microbial diversity, biogeochemical processes and the turnover of organic and inorganic compounds (Huettel et al., 2007; Rocha, 2008; Røy et al., 2008; Seidel et al., 2012). SGD from permeable intertidal flats is thus one of the major drivers of nutrient dynamics in the Wadden Sea (Beck et al., 2008; Billerbeck et al., 2006; de Beer et al., 2005; Dellwig et al., 2007;

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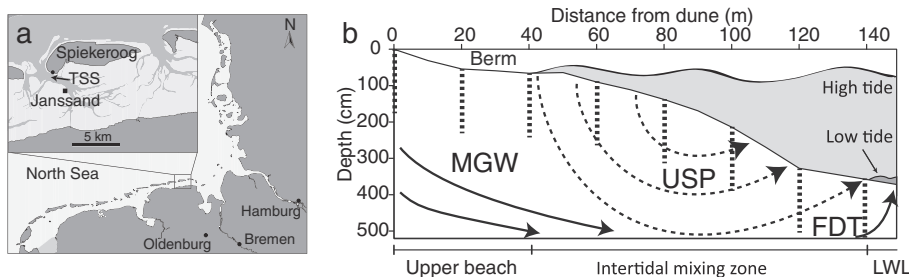


Fig. 1. a) German Wadden Sea with sampling transect (filled circle) at the southern beach of Spiekeroog Island facing the tidal inlet (TSS, time series station). The intertidal flat Janssand (filled square) was subject of an earlier study (Seidel et al., 2014). b) Topography of the intertidal sandy beach with the sampling positions (vertical dashed lines). The main dune line is about 20 m from the first sampling location (‘0 m’). The intertidal zone is ca. 100 m long and includes the fresh-seawater mixing zone. The upper beach (0 to 40 m, includes the berm) generally remains exposed. Fresh meteoric groundwater (MGW, solid horizontal arrows) enters from the island creating a ca. 60 m long subterranean estuary. Tidal forcing leads to the formation of an overlying upper saline plume (USP, dashed arrows) with percolating seawater. The USP confines the freshwater discharge tube (FDT) close to the low water line (LWL). Depths are given relative to the dune base.

Moore et al., 2011). Intertidal beaches, in contrast to tidal flats, have not received much attention yet, because beaches had long been considered to be of minor importance to carbon cycling due to their low sedimentary organic matter (OM) content (Boudreau et al., 2001). However, there is accumulating evidence that sandy beaches are in fact an important part of coastal biogeochemical cycles (Anschutz et al., 2009; Charbonnier et al., 2013; Rocha et al., 2009; Santoro, 2010; Santos et al., 2008).

Aerobic OM degradation is important in intertidal beaches, because oxygen can be replenished by the pore water flow resulting from tides and waves (Anschutz et al., 2009). The organic carbon content of permeable sands is generally very low (<0.5%, e.g. Huettel and Rusch, 2000). Benthic organisms, including microbes (Santoro, 2010) and macrofauna (Defeo and McLachlan, 2005; Degraer et al., 2003) therefore depend on organic carbon inputs from percolating seawater and fresh groundwater. OM can be supplied, for instance, from pelagic phytoplankton (Huettel and Rusch, 2000), benthic microalgae and stranded organic detritus from the surf zone or dune vegetation (McLachlan and Brown, 2010; Spilmont et al., 2005).

When microbial oxygen consumption exceeds the oxygen supply, the pore water becomes anoxic and diagenesis proceeds through anaerobic metabolism (McLachlan and Brown, 2010). Redoxclines are often observed where fresh groundwater and seawater with different oxygen concentrations mix which in turn largely affects the cycling of N and P (Santoro, 2010; Slomp and Van Cappellen, 2004) as well as of trace metals (Charette and Sholkovitz, 2002, 2006). In general, three oxygen-depleted redox zones can be distinguished, (i) non-sulfidic suboxic, when nitrate, Mn and Fe oxides/hydroxides are used as electron acceptors but sulfate is not, (ii) sulfidic, when sulfate is used as electron acceptor thereby producing sulfide, and (iii) non-sulfidic methanogenic, when OM decomposition leads to the formation of methane (Chester and Jickells, 2012). Active methanogenesis, although a main OM remineralization pathway in anoxic intertidal flats (Beck and Brumsack, 2012), is typically not found in STEs of beaches (Santoro, 2010).

DOM consists of molecules that can be characterized by a reactivity continuum (Hansell, 2013). While reactive labile to semi-labile DOM is rapidly consumed and bioavailable within hours/days to weeks/months, there is a less reactive, biorefractory DOM pool with turnover times of years to millennia (Hansell, 2013). Complications of defining DOM reactivity arise from observations that the stability of DOM compounds can depend on the environmental conditions (Schmidt et al., 2011b). For instance, combustion-derived polyaromatic DOM is resistant to biodegradation in the deep ocean (Dittmar and Paeng, 2009) but it becomes labile in the surface ocean when exposed to photodegradation (Stubbins et al., 2012).

The cycling of bulk dissolved organic carbon (DOC) in sandy beaches is controlled by a complex combination of environmental and seasonal parameters (Avery et al., 2012; Heymans and McLachlan, 1996; Santos

et al., 2008, 2009). Labile DOC can be rapidly consumed, but there may also be an export of less reactive DOC to the coastal ocean which may vary seasonally (Avery et al., 2012; Santos et al., 2009). Although these previous studies have given valuable insights into the bulk DOC cycling, the molecular level processing of DOM, its connection to marine or terrestrial sources as well as to redox conditions is still poorly understood. The lack of studies is due to the molecular complexity of OM which makes it an analytical challenge to characterize it (Hedges et al., 2000). However, the recent advance of ultrahigh-resolution Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) allows resolving thousands of molecular formulae in the complex DOM mixtures. Consequently, ultrahigh-resolution mass spectrometry has been applied to study the transformation of DOM in a wide range of habitats, including terrestrial and marine aquifers (Einsiedl et al., 2007; Longnecker and Kujawinski, 2011; Schmidt et al., 2009; Seidel et al., 2014) as well as the water column (Kim et al., 2006; Koch et al., 2005; Medeiros et al., 2015; Seidel et al., 2015; Sleighter and Hatcher, 2008).

This study extends our earlier research of a mainly anoxic intertidal flat close to the current study site which is subject to extensive seawater circulation (Seidel et al., 2014). In the intertidal flat, microbial activity, especially sulfate reduction, strongly enriched the pore water with metabolic end products such as trace metals, nutrients and DOC (Seidel et al., 2014). The intertidal sands of <100 cm sediment depth were found to be strongly affected by tidal flushing and seasonal changes in DOM input such as algal blooms. These sediments appeared to be effective filters for bioavailable DOM such as dissolved carbohydrates (DCHOs) from algae that are transported with the percolating seawater. The deeper sediments, in contrast, were decoupled from seasonality and found to be relatively enriched in highly aromatic compounds suggesting accumulation of DOM that was not readily biodegradable under anoxic conditions. We hypothesize that differences in hydrogeology and sedimentology affect redox-conditions and thus DOM cycling at contrasting sites. We therefore compare the results from the sulfidic to methanogenic intertidal flat showing seawater salinity at all sampling depths, to an intertidal beach nearby. The dune side of the beach receives meteoric groundwater from the dune ridge and its intertidal zone is exposed to high-energy waves (Fig. 1). The studied beach transect covers oxic to anoxic redox-conditions (Reckhardt et al., 2015).

In this study, we aim to characterize the molecular composition of the DOM and the processing of nutrients in the beach sands. We sampled the intertidal beach transect at the four seasons down to 2 m depth (Fig. 1) to answer the following questions: i) what is the seasonal and spatial variability of the molecular DOM composition, ii) what are potential DOM sources and biotic/abiotic removal processes at the beach, and iii) which hydrological and biogeochemical factors potentially control the redox state of the pore water? We identified the DOM sources (marine vs. terrestrial) using stable carbon isotope analysis of solid-phase extracted (SPE) DOM and we aimed to evaluate the DOM

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