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Trace metal geochemistry of organic carbon-rich watercourses draining the NW German coast

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A B S T R A C T

Numerous small watercourses are draining the hinterland of the NW German coast. The waters mainly originate from marsh and fen areas and have yellow to deep brownish color. During their flow path, the waters exhibit gradients in salinity (0.2–3), pH (6.2–8.8), particulate organic carbon (5–25%), and iron oxides (7–12%), which alter the concentrations of most dissolved and particulate trace metals. For example, dissolved Fe is rapidly removed from solution at increasing salinities by flocculation, whereas dissolved U is removed in the very low-salinity zone by Fe- and organic-rich colloids. The waters at the flood-gate of Neuharlingersiel, where a composite sample of the entire study area is collected before the freshwater is discharged into the marine-dominated tidal flat area in front of the mainland dike, have the following average trace metal concentrations: dissolved Fe 11 μM, Mn 4 μM, Mo 10 μM, U 1.8 μM, V 75 μM and particulate Fe 7 mg kg^{-1}, Mn 1200 mg kg^{-1}, Mo 2 mg kg^{-1}, U 1.7 mg kg^{-1}, V 140 mg kg^{-1}. After passing the flood-gate most Mo- and U-salinity distributions fit well to the conservative mixing line that connects the seawater of the Wadden Sea to the low-salinity river water entering the tidal flat area. In contrast, dissolved Fe, Mn, and V are removed from solution, especially at intermediate salinities, which may be due to mixing of freshwater with seawater depleted in these elements, flocculation and/or scavenging by particulate matter. In general, processes similar to those in estuarine systems alter the geochemical signatures on transects from land to sea. Compared to average river water, the watercourses are enriched in dissolved and particulate Fe, Mn, Mo, U, and V. Due to the fast removal of dissolved Fe in the salinity gradient and the high concentrations of Mo and U in seawater, the watercourses only form a source for Mn, V, terrestrial organic carbon, and particulate Fe for the Wadden Sea.

1. Introduction

Rivers are carriers of a wide variety of chemical signatures to the oceans. The effect of the transported compounds on the chemistry of the coastal oceans depends on the quantity of dissolved and particulate compounds carried by rivers as well as on the fate of these compounds in the estuarine mixing zone. Estuaries are zones where seawater mixes with freshwater and through which trace constituents must pass when being transported seaward. In the estuarine mixing zone, river-transported compounds are subjected to a variety of physical, chemical, and biological transformation processes, including transfer reactions between the dissolved and particulate phase. For example, some dissolved trace metals such as Fe are generally removed from solution when freshwater encounters saltwater in the natural environment (Eckert and Sholkovitz, 1976; Sholkovitz, 1976; Boyle et al., 1977; Sarin and Church, 1994). In contrast, other dissolved trace metals such as Mn either behave conservatively, are removed from solution, or are added to estuarine waters by pore waters or release from suspended particulate matter (Sholkovitz and Copland, 1981; Eastman and Church, 1984; Ouddane et al., 1997; Klinkhammer and McManus, 2001). The behavior of constituents in the estuarine mixing zone is governed by processes such as adsorption, desorption, complexation, and flocculation, which are induced by variables like salinity, pH, organic carbon, and turbidity (Sholkovitz and Copland, 1981; Gustafsson et al., 2000; Andersson et al., 2001; Lyven et al., 2003). Due to the large variety of processes, globally valid reaction schemes can hardly be defined. Therefore, it is essential to describe each estuarine system separately and to distinguish between globally relevant estuaries and those of more local importance.

Along the coastline of the southern North Sea, several rivers (e.g. Scheldt, Rhine, Ems, Weser, Elbe) transport dissolved and particulate compounds to the coastal ocean (Eisma, 1975; Duinker et al., 1979).

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Besides these large, well-known rivers, numerous significantly smaller watercourses carry chemical constituents to the coastal area. The hinterland of the NW German coast is characterized by a dense mesh of channels and small rivers draining the area behind the mainland dike. The waters of these small rivers confluence at flood-gates, which form part of the dike line permitting the controlled discharge to the coastal zone. The watercourses show a slight salinity gradient with highest values close to the flood-gates. Seaward of the dike, the slightly saline waters are discharged into a fully marine environment. Thus, due to dikes protecting the coastline, the small streams of northern Germany differ from estuaries of large rivers where a continuous gradient of salinity is sustained by mixing of freshwater and seawater. To date, only little is known about the geochemical behavior of elements in these estuary-like watercourses and about the transformation processes these slightly saline waters may undergo when being mixed with marine waters in front of the mainland dike (Dellwig et al., 2002, 2007b).

The present-day coastal landscape of NW Germany started to develop at about 7500 BP and is characterized by barrier islands, tidal flats, and coastal marshlands (Streif, 2004). In the coastal zone between the barrier islands and the Pleistocene hinterland, a wedge-like sediment body accumulated during the Holocene sea-level rise. This sediment body has a thickness of up to 20 m and extends within a 10–20 km wide zone along the coastline. It consists of a basal peat, intercalated peat beds and fine-grained sand, silt, and clay layers (Streif, 2004). The base of the Holocene sedimentary succession is characterized by former river valleys which drained toward the north and reached down to 20 m below the modern sea level (Streif, 1990). Today, this coastal morphology still influences groundwater flow pathways. For example, it may facilitate groundwater flow underneath the dike.

From the 11th century on, dike building influenced the coastal landscape. The mainland along the North Sea coast was protected from flooding, however, this resulted in a loss of former flood plains and thus in elevated sea levels during storm surges. Several new bays were formed along the coastline when dikes broke and the hinterland was flooded (Flemming and Davis, 1994; Behre, 2004). As documented by these authors, the reclamation of the flooded areas by continuous dike building was only completed in the last century. Thus, large parts of the hinterland in NW Germany are reclaimed wetlands.

In the present contribution, we studied the geochemistry of small, yellow to brownish, organic carbon (OC)-rich watercourses in NW Germany. Our objective was to highlight trace metal dynamics in these watercourses and to track the geochemical alterations occurring when these low-salinity waters are discharged into the marine tidal flat area situated in front of the dike. The study focused on trace elements being of geochemical importance in the marine environment in this area, such as Fe, Mn, Mo, U, and V. In the tidal flat area, Mn shows pronounced seasonal variations, which are partly induced by changes in the freshwater input to the marine environment (Dellwig et al., 2007b; Kowalski et al., 2011). Mo and U mostly behave conservatively, but exhibit positive and negative anomalies in Wadden Sea waters (Dellwig et al., 2007a; Kowalski et al., 2009). V was reported to be associated with dissolved organic carbon (DOC) in pore waters (Beck et al., 2008). Finally, particulate Fe and Mn as well as OC are known to control the distribution of trace elements between solid phase and corresponding waters, for example by scavenging.

2. Material and methods

2.1. Study area

This study was carried out in the hinterland of the NW German coast, which is characterized by small natural and artificial watercourses. The water of these channels is flowing to flood-gates which control their discharge into the coastal zone. Our study focuses on the catchment area of the flood-gate of Neuharlingersiel (Fig. 1). This flood-gate forms the only surficial freshwater input into the tidal flat area of Spiekeroog Island. The catchment area of about 125 km^2 experiences a long-term average rainfall of about 830 mm a^{-1} according to the records at the city of Aurich ($\sim$30 km afar). The landscape is characterized by marsh, fen, raised bog, and some woodland areas.

The catchment area is very flat and hardly exceeds elevations of more than 5 m above sea level. Freshwater discharge from the hinterland to the Wadden Sea mainly takes place when the water level in the tidal flat area is low, i.e., especially during low tide. Whether the flood-gates are open and for how long, depends exclusively on the water level in the hinterland. During times of high precipitation, freshwater may even be pumped to the tidal flat area to prevent flooding of the hinterland.

2.2. Sampling sites

The watercourses of the study area were sampled at eight sites in 2002 and 2003 (Fig. 1). Samples were collected at the flood-gate of Neuharlingersiel (I) and in channels close to the villages Kleinholum (II), Anderwarfen (III), Insenhausen (IV), Süd-Stedesdorf (V), Süd-Dunum (VI), Altharlingersiel (VII), and Mullbarg (VIII). Samples were taken monthly, except at the flood-gate of Neuharlingersiel where sampling intervals were more frequent.

Süd-Dunum (VI) and Süd-Stedesdorf (V) are the most inland sites (Fig. 1). When flowing northwards, the waters pass Anderwarfen (V) and Insenhausen (IV) before reaching the coastline at Neuharlingersiel (I). Thus, all these sites are situated along one watercourse draining the catchment area from south to north. The southernmost sites are located in or closely to fen and raised bog areas, whereas the remaining sites are situated in the marshland. Site Kleinholum (II) is located at a watercourse running parallel to the dike line for several kilometers and reaching the former described watercourse at Neuharlingersiel. Other watercourses mainly draining marsh areas, too, are sampled at Mullbarg (VIII) and Altharlingersiel (VII). These watercourses are hardly connected to the streams draining the fen and raised bog area. They merge with the previously described watercourses shortly before reaching the flood-gate at Neuharlingersiel where a composite sample reflecting the whole catchment area is obtained. The numbers of the sampling sites increase with increasing distance to the coastline, except for sites VII and VIII.

At the seaward side, samples were taken at 13 stations along a transect from Neuharlingersiel harbor, located close to the flood-gate, up to some kilometers offshore the barrier islands of Spiekeroog and Langeoog (Fig. 1). Sampling was performed around low tide in April, June, August, and November 2004. Because sampling of river and marine sites was not performed at the same dates, but even in different years, concentration levels on the seaward and landward side cannot be compared directly. However, geochemical processes leading to the measured concentration gradients are expected to be the same. Year-to-year changes in precipitation and temperature may influence seasonal dynamics, but supposedly have little impact on general geochemical dynamics in river compared to marine waters.

2.3. Sample collection and analysis

In-situ water temperature, conductivity, and pH were measured in unfiltered freshwater samples using WTW® LF 196 and a WTW® pH 196 T electrodes (WTW, Weilheim, Germany). The electrodes were calibrated before each sampling campaign.

For the analysis of dissolved trace metals, freshwater samples were filtered through 0.45 μM SFCA (surfactant-free cellulose