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Consistent assessment of trace metal contamination in surface sediments and suspended particulate matter: A case study from the Jade Bay in NW Germany

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ABSTRACT

Recently, within the framework of European directives, the importance of marine monitoring programs has increased. In this study, a dense sampling grid was applied for a detailed assessment of the metal contents of surface sediments and suspended particulate matter from the Jade Bay, one of the tidal basins in the southern North Sea. The local lithogenic background was defined and compared with average shale, a common reference material. Based on the calculated non-lithogenic fraction and a cluster analysis, the metals are distributed in two groups: (i) elements of mainly natural origin (Co, Cr, and a major portion of Cd) and (ii) elements associated with anthropogenic activity (As, Cd, Cu, Ni, Pb, Sn, and Zn). However, even the metals of the second group are enriched by at most a factor of two relative to the local background, suggesting minimal anthropogenic impact. Spatial distribution maps show that the harbor area of Wilhelmshaven may be a particularly important source of metal.

1. Introduction

Nature conservation requires knowledge of the conditions of the ecosystems and the manner in which they change. Therefore, human-induced deterioration and changes in ecosystems are the main subjects of monitoring surveys. The information obtained in those surveys may serve as a baseline for policy makers for assessment and improvement of environmental conditions by imposing appropriate measures to protect the environment. However, in most environmental systems, an initial system condition in the absence of human interference cannot be assessed in present times. As a result, the objectives of protection measures are often aimed at a commonly accepted status, for example, well-defined thresholds. These thresholds are based on conditions that are believed to describe either a system that is considered unaffected by anthropogenic forces or a status in which no negative impacts are to be expected with any significant likelihood. To document the gradual changes in the ecosystems, comparison of new data with that of former studies is an essential tool. Our contribution focuses on the Wadden Sea, a tidal flat area stretching along the coastline of the southern North Sea. Due to its outstanding ecological importance and the increased pressure induced by human action, previous studies have documented the past metal contents of sediment and suspended particulate matter (e.g., Danis et al., 2004; Dellwig et al., 2000; Duinker et al., 1974; Little-Gadow and Schäfer, 1974; Schwedhelm and Irion, 1985; Van Alsenoy et al., 1993) and can be used to identify gradual changes.

Coastal regions across the world are subject to manifold monitoring strategies because they suffer from various negative environmental effects of human activity. To construct a comprehensive view of the changes in the marine ecosystem, those strategies include physical, biological and chemical parameters, among others. The neighboring states of the Greater North Sea must fulfill the obligations stipulated in international treaties such as ICES or OSPAR. European directives, including the Water Framework Directive (WFD, Directive 2000/60/EC) and the Marine Strategy Framework Directive (MSFD, Directive 2008/56/EC), are the main outcomes of the European Union's efforts to harmonize protection measures for the marine environment. On a national level, marine monitoring programs were established in Germany in the early 1980s when the pollution of coastal areas such as the German Bight became obvious (Rat von Sachverständigen für Umweltfragen, 1980). The Wadden Sea, which has appeared on the World Heritage List since 2009 due to its unique nature (Stock and Wilhelmsen, 2009), is included in several of these agreements. Furthermore, Denmark, Germany and the Netherlands have worked together on the Trilateral Cooperation on the Protection of the Wadden Sea, which took effect in 1978.

Monitoring programs often must focus on a few sampling sites chosen as representatives of larger study areas. The selection of such representative sites may be difficult, especially in highly

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dynamic environments such as the Wadden Sea, where sediment relocation frequently occurs due to tidal currents and storm surges. One possible approach to improve the informative value of monitoring efforts may be to describe the *status quo* of the system using a sampling grid that is as dense as possible.

In this contribution, we describe the *status quo* of a tidal basin of the Wadden Sea, the Jade Bay, with respect to potential metal contamination. A highly dense sampling grid was used to characterize the spatial pattern of sedimentary metal contents in detail. The results of this detailed investigation may serve as a guide for monitoring authorities in making proper decisions on representative sampling sites and may assist in re-evaluating the results of previous monitoring campaigns based on a smaller number of sampling sites. In this work, we report the contents and spatial pattern of metals in surface sediments and suspended particulate matter from the Jade Bay, identify the non-lithogenic metal fraction to assess potential anthropogenically induced contamination, and provide a first evaluation of possible biological effects via common thresholds.

2. Materials and methods

2.1. Study area

The Wadden Sea is one of the largest tidal flat areas worldwide and stretches along the coastline of the southern North Sea. The region is divided into several tidal basins, each connected to the North Sea by a tidal inlet that permits the inflow of North Sea water during flood tide and the outflow of Wadden Sea water during ebb tide. One of the largest tidal basins located close to the city of Wilhelmshaven (NW Germany) is the Jade system, which is composed of Jade Bay, Inner Jade, and Outer Jade (from south to north).

The Jade Bay was primarily created by storm surges that occurred between the 12th and 16th centuries (Behre, 2004). The constructions of dikes in the Middle Ages resulted in higher storm surge levels due to the loss of former flood plains. When the dikes broke and the hinterland was flooded, several new bays were formed along the coastline, for example, the Jade Bay. Between the 16th and 19th centuries, large parts of the Jade Bay were reclaimed.

The study area is influenced by semi-diurnal tides with a tidal range of up to 3.8 m (Flemming and Davis, 1994). Therefore, a large water volume (400×10^6 m^3; Götschenberg and Kahlfeld, 2008) flows in and out of the Jade Bay during each rising and falling tide. The large tidal range further explains the occurrence of a wide eulittoral zone in which approximately 75% of the 160-km^2 area becomes dry during periods of low tide (Little-Gadow and Schäfer, 1974). In contrast, the sublittoral zone is limited to the main channels that drain the Jade Bay from south to north. Despite its expansive tidal bay character, freshwater discharge contributes only a small amount to the total water volume (Irion, 1994). Therefore, the salinity generally varies in the range of 26–30 (Böning and Schnetger, 2011) and only occasionally decreases to 18 in the southern Jade Bay (P. Böning, unpublished data).

Construction activities have altered the hydrological and sedimentological conditions in the Jade area. In the late 19th century, a 6-km long training wall was built in the central portion of the Jade Bay to regulate the tidal currents and ensure the accessibility of the Wilhelmshaven harbor. In the Inner and Outer Jade, dredging is necessary to maintain the required depths for the navigation channels. On the west bank of the Inner Jade, an industrial zone stretches along the shore north of Wilhelmshaven and includes four transshipment piers. Furthermore, a new deep-water container terminal became operational in this location in 2012.

2.2. Sample collection

To study metal levels and their spatial distribution patterns, surface sediments were collected during several sampling campaigns in the Jade Bay and Inner Jade in 2009 and 2010 (Fig. 1). In January 2009, samples were collected near high tide using a small van-Veen sampler. A denser sampling grid was applied in a second campaign from April to June 2009, with samples taken in the eulittoral and sublittoral zones. In the sublittoral zone, a van-Veen sampler was used to obtain the samples, whereas the eulittoral zone was sampled at low tide by foot. The latter method permits sampling in the exterior area of the Jade Bay, which is barely accessible by boat due to shallow water depths even at high tide. In April 2010, selected repetitive sampling was performed in the eulittoral zone using the small van-Veen sampler. Furthermore, surface sediments were collected using a box corer in the harbor area of Wilhelmshaven in March 2010. The same technique was used to obtain samples from the east and west banks of the Inner Jade. During all sampling campaigns, the uppermost oxic sediment layer (<2 cm depth) was sampled, except at sites where the anoxic layer began at several millimeters depth and both layers could not be separated. All samples were immediately stored in a cooling box and frozen at the end of the sampling day.

To determine the natural lithogenic background of the study area, a 5-m long sediment core was collected via vibro-coring using aluminum tubes (Ø 8 cm) in the northeastern Jade Bay (Stollhammer Watt) in October 2010. On board, the core was immediately split lengthwise and sampled at 5–10-cm depth intervals.

To study the spatial distribution of the suspended particulate matter (SPM) and its seasonal variations, the water column was sampled in January and July 2010 along transects from the southern Jade Bay to the island of Mellum (Fig. 1). Seawater samples were collected manually with a small PE bucket, and depending on the SPM content, 0.25–1.5 L of water was filtered through pre-weighed Millipore Isopore membrane filters (0.4-μm polycarbonate PC) for multi-element analyses. The filters were rinsed with 60 ml of ultra-pure Milli-Q water to remove salt, dried at 60 °C for 48 h, and re-weighed for determination of total SPM.

2.3. Sample analyses

The sediment samples were freeze-dried, homogenized in an agate mill, and analyzed for major (Al, Fe, Mn, Si, and Ti) and minor (As, Co, Cr, Ni, Pb, and Zn) elements via XRF using a Philips PW 2400 X-ray spectrometer. Before fusion to glass beads, 700 mg of sample were mixed with 4200 mg of dilithium tetraborate and pre-oxidized at 500 °C with NH_4NO_3 (p.a.). International (GSD-3) and in-house standards (loess, sediment from the Peruvian upwelling area) were used to control the analytical precision and accuracy, which were <5% and <10% for major and minor elements, respectively.

Acid digestions of the sediment samples were used to analyze trace elements (especially Cd, Cu, and Sn) via ICP-MS (Thermo Finnigan Element II), and acid digestions of the filter samples were analyzed for Al, As, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn with ICP–OES (Thermo iCAP 5000). The sediment (50 mg) was treated with 0.5 ml of concentrated $HClO_4$ in closed PTFE autoclaves at 180 °C for 2 h to oxidize the organic matter. Next, the sediment was digested with 3 ml of concentrated HF in the same PTFE vessels at 180 °C for 8 h. Subsequently, the acids were evaporated at 180 °C, and the residues were re-dissolved and fumed off three times with 3 ml of semi-concentrated HCl. The residue was dissolved in 1 ml of HNO_3, 10 ml of ultra-pure Milli-Q water was added, and the solution was treated at 60 °C for 60 min. Finally, the acid digestions were diluted with ultra-pure water to a final dilution of 250. The filter samples were digested in a similar