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Distribution of Total Mercury in Surface Sediments of the Western Jade Bay, Lower Saxonian Wadden Sea, Southern North Sea

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Abstract A total of 114 surface sediment samples was equidistantly collected in the western part of the Jade Bay, southern North Sea, to analyse total mercury contents as well as grain size distribution and total organic carbon (TOC) contents. Total mercury was determined by oxygen combustion-gold amalgamation. Validation, precision and accuracy of the method were evaluated and controlled with two certified reference materials (HISS-1 and MESS-3). Total mercury contents varied between 8 and 243 ng/g dry sediment with a mean value of 103 ng/g dw. The mercury levels in surface sediments showed an inhomogeneous spatial distribution with higher contents in near-dike areas. The values are mostly in the range of natural background values (50–100 ng/g dw) and positively related to TOC and clay/silt contents (<63 µm). The present total mercury contents are compared to those of previous studies, in order to estimate possible temporal trends of mercury contents in the study area over the last decades. Moreover, the comparison to sediment quality guidelines indicated that the surface sediments of the Jade Bay are not mercury contaminated. These results also suggested that the current mercury contents of Jade Bay surficial sediments are mostly affected by atmospheric deposition and re-emission.

Keywords Jade Bay · Wadden Sea · Total mercury · Surface sediments

Mercury (Hg) is one of the most important environmental contaminants. The biogeochemistry of mercury has long been receiving considerable attention because of the extreme toxicity and persistence of its compounds. By natural biological processes the inorganic forms of mercury can be converted into organic compounds, which can bioaccumulate in all levels of the aquatic food web (Dastoor and Larocque 2004). The contamination of mercury in aquatic organisms being consumed by organisms of higher trophic levels and humans has also become a key regional pollution problem (Válega et al. 2006). Therefore, it is important that mercury levels in aquatic ecosystem are determined accurately, in order to understand the environmental impact of this toxic element.

Mercury is an extremely volatile element and emitted to the atmosphere by degassing of the Earth's surface and by re-evaporation of mercury previously deposited on the Earth's surface (Roy and Bose 2008). Currently, the global emission of mercury into the atmosphere from both natural and anthropogenic sources has been estimated to be 7,527 tonnes per year. The predominant sources, accounting for 5,207 tonnes per year, are natural reservoirs and re-emission of previously deposited mercury originating from anthropogenic and natural sources (Pirrone et al. 2010). In the atmosphere mercury can be transported with air masses on a global scale, and deposited in both terrestrial and aquatic environments. Mercury is also washed into aquatic ecosystems by precipitation and subsequently deposited in sediments (Roy and Bose 2008). In particular fine sediments rich in clay minerals and organic matter adsorb heavy metal ions and/or form complex compounds (Little

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Gadow and Schäfer 1974). Actually, the extent of mercury contamination in sediments is counted among the parameters which have been considered important in the bioaccumulation of mercury (Wagemann et al. 1998). For these reasons, determination and monitoring of mercury levels in sediments of aquatic environment is of great importance.

Information on mercury contamination in the Jade Bay, southern North Sea, is scarce and is mainly related to the bioaccumulation of mercury in aquatic organisms such as mussels, fish, or seabirds (Rüdel 2002; Bouquegneau et al. 2004). The Trilateral Monitoring and Assessment Program (TMAP) reported that mercury in Wadden Sea sediments has decreased to a level of 100–400 ng/g dry weight (dw) in the fraction <63 µm, so mercury cannot be considered as being near background (50 ng/g dw) according to OSPAR (Bakker et al. 2009). Although Irion et al. intensively studied mercury and other heavy metals in the Jade Bay (Irion 1986; Irion et al. 1996), recent data for surface sediments are lacking. Hence, the main objective of the present study was to investigate the current contents and the spatial distribution of total mercury in surface sediments of the western part of the Jade Bay. To a better understanding of the factors affecting the distribution of mercury in the Jade Bay the data from this study will be discussed in relation to the grain size distribution and the total organic carbon content. This study also discusses the possible sources of mercury in the Jade Bay.

Materials and Methods

The Jade Bay is situated in south-eastern part of the German Bay, North Sea, and reaches about 45 km into the coastal lowlands. The opening at Wilhelmshaven joins the Jade Bay and the Inner Jade (Kerndorff et al. 1979). Geomorphologically the Jade Bay is mainly characterised by low tidal flats which are crossed by numerous intertidal creeks and channels. The strong tides with an average tidal range of 3.5 m not only facilitate efficient water exchange with the open sea but also bring circa 3.5 × 10^6 m^3 sediment yearly from the North Sea (Irion 1994). These sediments are then distributed in the Jade Bay under the influence of tidal currents, waves and continuous human regulation. In the Jade Bay, water velocities decrease thus allowing deposition of fine-grained sediments especially in the western reaches (Irion 1994). The majority of the sampling sites are located at the low tidal flats of the western part of the Jade Bay, where the sediments are regularly re-deposited by tidal currents. In summer 2007 114 sediment samples were equidistantly collected in an area of ca. 26 × 10^6 m^2 (Fig. 1).

A handheld steel van-Veen-type grab (150 cm^2) was used to collect surface sediments during high tide. This sampler has a maximum penetration in muddy sediments of about 5 cm, less in sandy sediments. Samples were initially frozen at −18°C and then lyophilised (CHRIST-ACPHA 1-4 LSC) at −52°C for at least 50 h. Dried sediments were homogenised with an agate ball-mill ("Pulverisette 5", Fritsch). The finely ground sediments were stored in acid cleaned glass bottles at room temperature.

Directly after sampling, co-parameters were determined. Water content was measured by drying to constant weight at 60°C. The grain size distribution was determined by laser diffraction (Analysette 22 Economy, Fritsch). Carbon analyses (total carbon TC and total inorganic carbon TIC) were carried out using a RC-412 analyser (Leco) with high

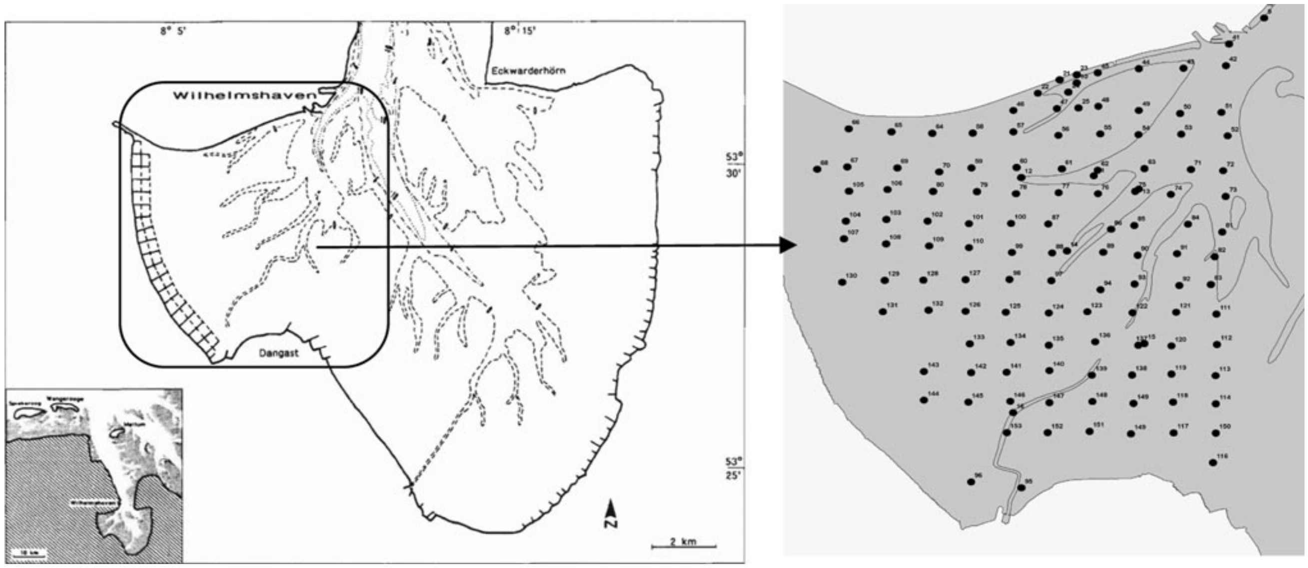


Fig. 1 *Left* study area the western Jade Bay. *Right*: sampling sites

temperature combustion and IR detection. Total organic carbon (TOC) contents were calculated as difference between TC and TIC.

Wet digestion followed by cold vapour atomic absorption spectrometry (CV-AAS) according to Kruse (1979) is the most widely used method for the determination of mercury in environmental samples. CV-AAS and other traditional methods are difficult, time consuming and generate their own hazardous waste. In this study the determination of total mercury in sediment samples is carried out by a rapid, simple and reliable method using oxygen combustion-gold amalgamation. The Direct Mercury Analyser (DMA-80) analyses samples without chemical digestion or other pre-treatment and waste disposal, and allows to perform routine quantitative determination of mercury with a low detection limit. A number of studies applying this technique have certified that the DMA-80 is able to determine low level mercury in a variety of samples with accurate and reproducible results (Maggi et al. 2009; Carbonell et al. 2009).

The equipment used in this study decomposes sediment samples thermally with controlled heating (drying for 30 s at 250°C, and thermal decomposition for 720 s at 700°C). The decomposition products are carried by a continuous flow of oxygen (at a pressure of ca. 4 bar and a flow rate of 100–167 mL/min) through a hot catalyst bed, where halogens and nitrogen/sulphur oxides are trapped. At the same time, all mercury species are reduced to Hg^0. The final reaction gases pass through a gold-amalgamator, which collects Hg^0. The mercury amalgamator is then heated to 700°C and the Hg^0 is released and quantified by cold-vapour atomic absorption spectrometry at 253.7 nm as a function of mercury concentration (US EPA 1998).

The equipment calibration and quality assurance were performed according to US EPA 7473 (1998). For the calibrations two certified reference materials were obtained from the National Research Council Canada, Institute for National Measurement Standards: marine sediment HISS-1 from the Hibernia Shelf with 0.01 mg/kg mercury for the low content range and marine sediment MESS-3 from the Beaufort Sea with 0.091 ± 0.009 mg/kg mercury for the high content range. Before calibration with the standards, the instrument was run several times with empty pre-cleaned metal boats until a very low and stable value (ca. 0.001 ng Hg absolute) was obtained. Both the low range and the high range calibrations were processed with 5 different weights of standard reference materials equivalent five different absolute contents of mercury. To control the accuracy of the method, blanks were carried out throughout the entire analytical process. Pre-cleaned empty metal boats were run after every four samples in each sequence of 40 samples. Furthermore, one MESS-3 standard was analysed in each sequence. Other parameters of the quality assurance, the limit of quantification (LOQ) and the limit of detection (LOD) were also estimated in relation to the absorbance of blanks. In each batch of samples processed, one sample of certified reference material was analysed.

All metal boats used were combusted at 500°C for 30 min. Approximately 0.05–0.1 g of dry sediment was directly weighed into the metal boat using the analytical balance interfaced with the DMA-80. All samples were analysed in duplicate and the relative standard deviation (RSD) was calculated. If the RSD value ≤3%, the results were considered to be in good agreement. Otherwise the corresponding sample was re-analysed.

The DMA-80 instrument was calibrated independently in two concentration ranges (0–2 and 2–20 ng Hg absolute) for a wide range of mercury values in samples and an optimal response over the entire dynamic range, because the calibration range switched over automatically

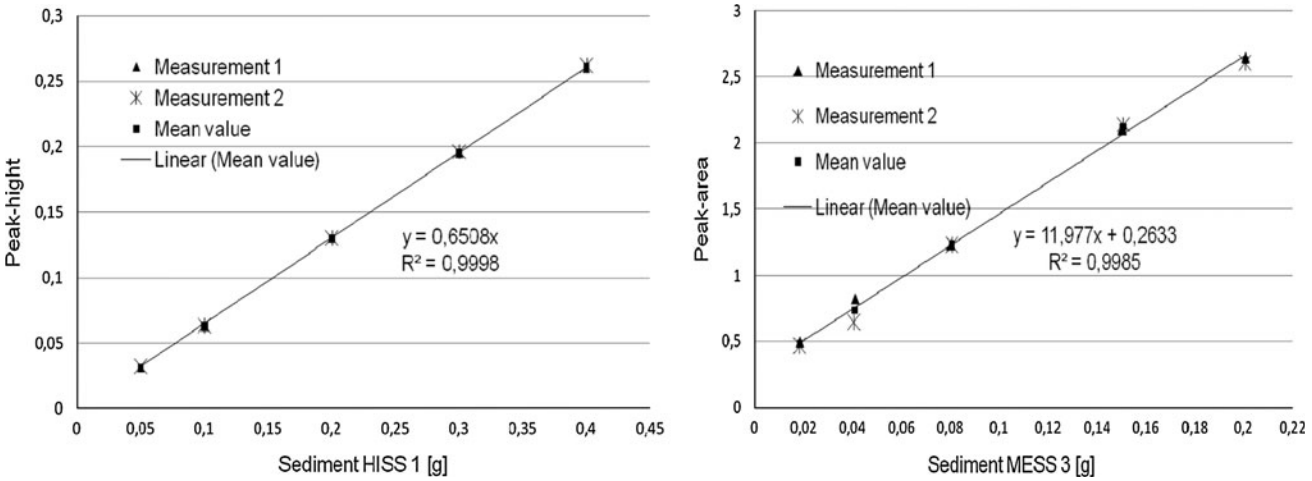


Fig. 2 Calibration curves used in this study. *Left* the calibration using HISS-1 in the range of 0–2 ng Hg absolute. *Right* the calibration using MESS-3 in the range of 2–20 ng Hg absolute

depending on the mercury content of the samples. Both of the calibrations were repeated twice, and the calibration curves shown in Fig. 2 were obtained by linear regression of the mean values.

The absorbance of the method blanks were always less than 10% of the absorbance of any samples. Thus no appreciable mercury contamination could be detected. The limit of detection of the DMA-80 was 0.14 ng Hg absolute, estimated as the mean of 10 blanks plus three times the standard deviation of 10 blanks. The limit of quantification was 0.40 ng Hg absolute, calculated as the mean of 10 blanks plus ten times the standard deviation.

Measured mercury contents in the standard reference materials were compared to the certified values. They varied little over time (RSD $< 3\%$), and were within the certified range for MESS-3 (Table 1). For the HISS-1 standard, significantly lower contents than the given information value were consistently obtained. The reason for this discrepancy is at present unclear.

Table 1 Total mercury (ng/g, dw) in certified reference materials (CRM): certified values and results of own analyses

CRM	Certified value (mean ± SD)	Determined value (mean ± SD)	Replicates number
HISS-1	10[a]	4,6 ± 0.11	9
MESS-3	91 ± 9	90.6 ± 0.02	9

[a] Information value only

Results and Discussion

The spatially comprehensive survey on sediments from the western part of the Jade Bay in 2007 showed THg contents in surface sediment in the range of 35–120 ng/g dry weight (dw). The highest values were observed in the tidal flats near the dikes of the Jade Bay, with contents usually in the range of 100–200 ng/g dw, but values as large as 243 ng/g dw were also observed. In the centre of the study area where the water is deeper, the contents were usually in the range of 8–50 ng/g dw (Fig. 3).

Taking into account that mercury is preferentially bound to fine grain sizes (clay/silt) and organic matter (Little Gadow and Schäfer 1974), the results will be compared with data for grain size distribution and TOC. Both parameters are strongly influenced by tidal currents, resuspension and deposition and hence clay/silt and TOC contents vary significantly in the Jade Bay. Normalisation of the mercury content against clay/silt and TOC contents may thus provide further information The clay/silt normalised mercury contents showed a spatial gradient from the coast towards the open sea similar to the gradient of the

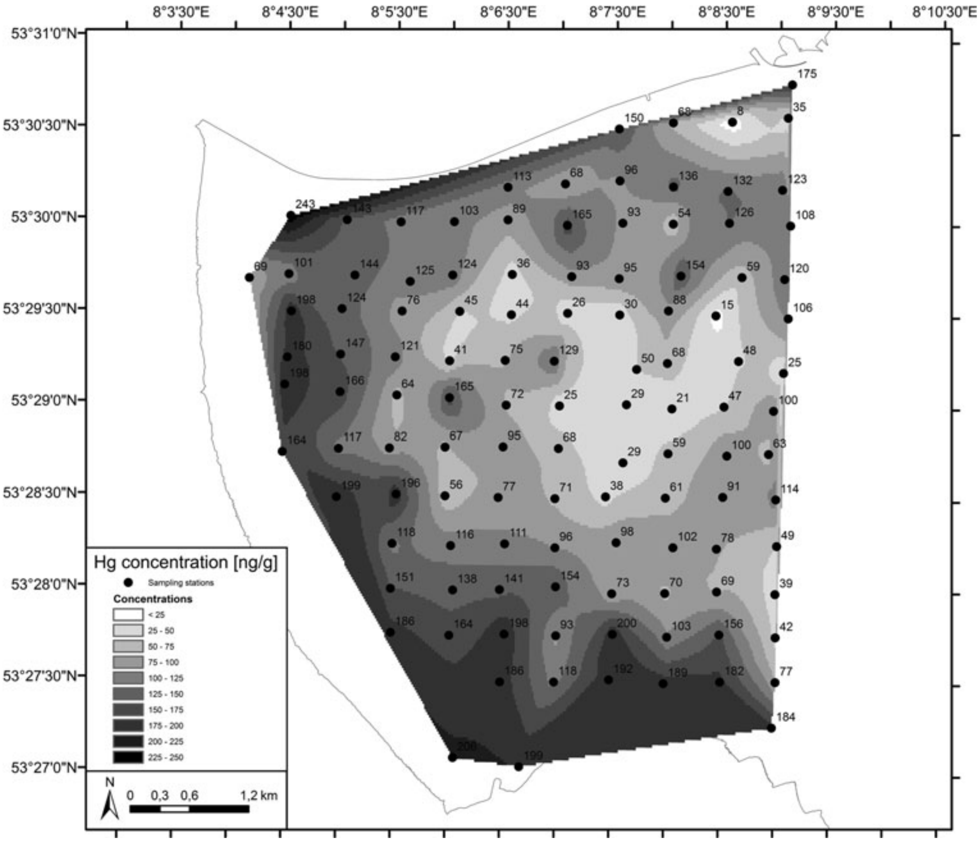
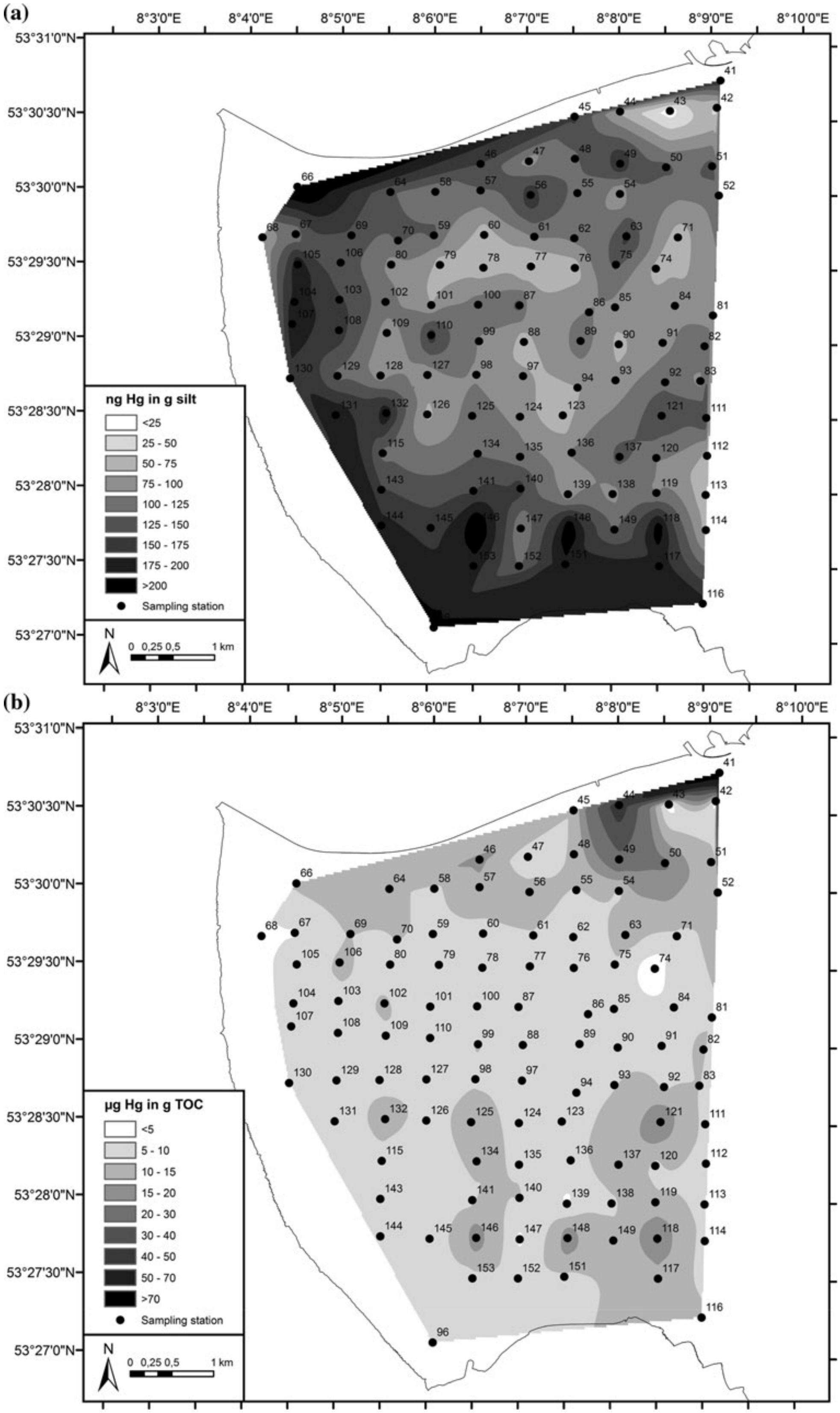


Fig. 3 Mercury contents (ng/g dw) in surface sediments collected in 2007 from south-western part of the Jade Bay

Fig. 4 Normalized mercury contents in surface sediments collected in 2007 from the south-western part of the Jade Bay, **a** as ng Hg/g silt and **b** as ng Hg/g TOC



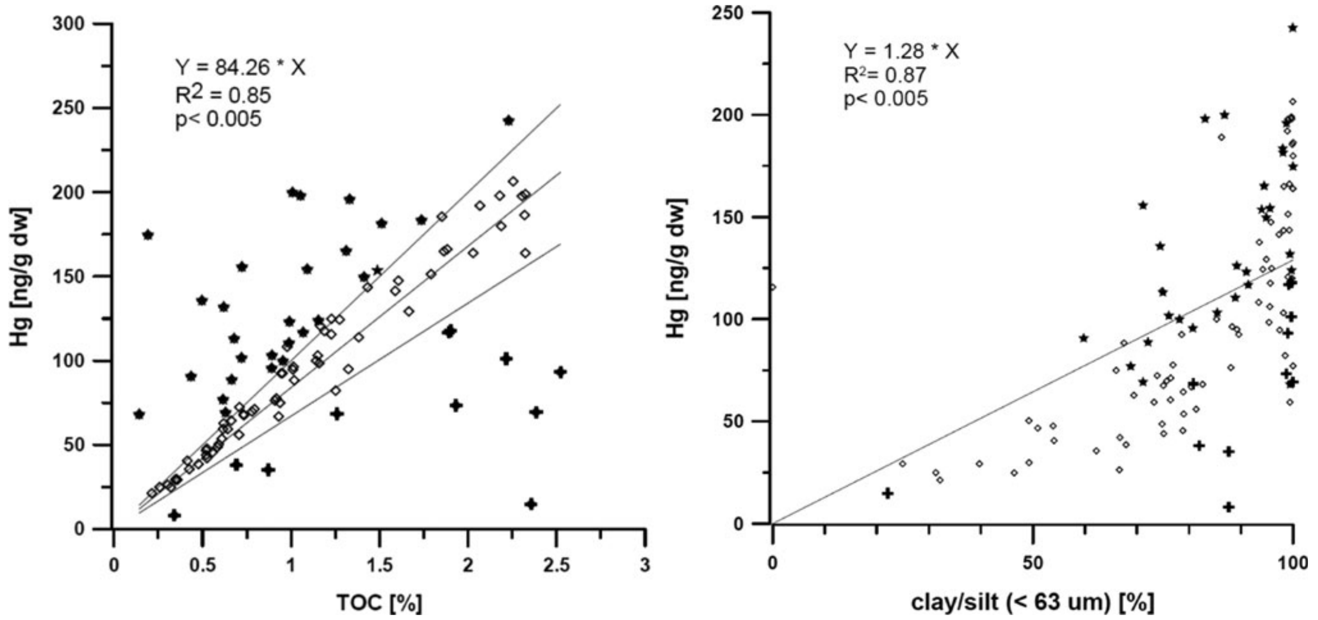


Fig. 5 *Left* correlation between mercury and TOC in surface sediments. The points above and below the 95% confidence-lines stand for outliers. *Right* correlation between mercury and the clay/silt (< 63 µm) in surface sediments. *Back points* correspond to the outliers in the *left* scatter plot (*star* for the points above the upper confidence-line and *plus* for the points below the lower confidence line)

absolute values (Fig. 4a). For TOC normalisation, this trend is not obvious, instead the highest mercury values were found near Wilhelmshaven and Dangast (Figs. 4b).

Statistical analysis indicates the mercury concentrations to be positively correlated with both the clay/silt and the TOC contents. The outliers below the lower confidence-line (Fig. 5, left) might indicate a considerable occurrence of peat materials which accumulate particularly at the ports with still water. That is why some sediment samples contain high amounts of organic carbon but little mercury. The outliers above the upper confidence-line dashed line could be the result of relatively high clay/silt contents. As it is shown in Fig. 5 (right), these samples consisted of more than 80% clay/silt fraction. Correspondingly they were collected from the sampling sites in the tidal flats near the dikes.

Sediment quality guidelines developed by Long et al. (1995) from a biological effects' database suggest that at mercury contents <150 ppb adverse biological effects are rarely observed while at levels of >710 ppb such effects occur frequently. Since most of the Jade Bay samples had mercury levels <150 ppb and the maximum mercury concentration did not exceed 250 ppb, the surface sediments of the Jade Bay can be considered to be not contaminated.

In fact, the present mercury levels in surface sediments of the Jade Bay are comparable to pre-industrial sediments of Norway, i.e. older than 400 years, measured as "reference sediments" with mercury contents in the range of 50–100 ng/g dw (Berg et al. 2006). Moreover, sediments of deep cores in the catchment area of the Jade Bay were also analysed as pre-industrial background sediments (Jin and Liebezeit, in prep.). Total mercury contents at ca. 5 m depth were in the range of 14–31 ng/g dw. Through this comparison with the pre-industrial sediments it can be concluded that in most surface sediments analysed mercury contents are within the range of natural background values, while in sampling sites near the dikes the surface sediments might be influenced by mercury of anthropogenic origin.

The results above indicate that there are no significant point sources for mercury in the catchment area of the western part of the Jade Bay. The area is dominated by agriculture and tourism while direct discharges to the Inner Jade and further transport by flood currents into the Jade Bay are limited to treated sewage from the city of Wilhelmshaven, a PVC plant and an oil refinery as well as discharge of brines from leaching of Zechstein salt deposits.

The only significant sediment source for the Jade Bay is the North Sea. Together with organic matter originating in the coastal North Sea inorganic material is transported towards the tidal flats. The increasing tendency of mercury contents in the direction from the middle of the Jade Bay towards the coast indicates that particulate material with a higher mercury load from the North Sea is mixed with less polluted sediments of the tidal flats (Schindler 1994; Zoellmer and Irion 1993).

Besides, our results are in good agreement with the data of a study by Dörjes (1972) showing that the heavy metal contents in sediments of the tidal flats much greater than those in the middle of the Jade Bay. So the “heavy metal depot model” developed by Dittme (1982) can also be applied: mercury adsorbed to fine clay minerals and organic matter suspended in the water column settles and is deposited on the tidal flats. Thus mercury in the water column is transferred to the sediment of tidal flats near the dikes. These sediments function as a sink and decontaminate coastal waters. In fact, the mercury levels in coastal surface waters of the North Sea (1.6–69 ng/L) are significantly larger than those in the offshore water column (0.25–41 ng/L, Sheahan et al. 2001).

On the other hand, a great part of mercury is transported in gaseous form in the atmosphere. According to studies of the OSPAR Commission and the Mercury Species over Europe (MOE) project, mercury contents in the coastal environment of the North Sea area are affected to a large extent by the hemispherical background levels in the atmosphere (Wängberg et al. 2007; Munthe et al. 2003). Furthermore, negative values of the net mercury flux over the coastal waters of Europe indicated the considerable effect of the re-emission in this region (Gusev et al. 2008). Thus, both depositions of mercury in the atmosphere and re-emissions of mercury from water surfaces (Gårdfeldt et al. 2002) could also be potential sources of the mercury in the Jade Bay.

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