Environmental Pollution xxx (xxxx) 113985

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: http://ees.elsevier.com

Elevated mercury concentrations in biota despite reduced sediment concentrations in a contaminated coastal area, Harboøre Tange, Denmark☆

Poul Bjerregaard *, Torben Grau Schmidt, Maria Pedersen Mose

Department of Biology, University of Southern Denmark, Campusvej 55, DK-5230 Odense, Denmark

ARTICLE INFO

Article history:
Received 7 October 2019
Received in revised form 8 January 2020
Accepted 13 January 2020
Available online xxx

Keywords
Mercury
Sediment
Biota
Benthic

ABSTRACT

Metals sequestered in coastal sediments are normally considered to be stable, but this investigation shows – somewhat surprisingly – that mercury concentrations in a previously contaminated area, Harboøre Tange, Denmark, have decreased since the 1980s. Mercury concentrations were determined in sediment and benthic biota and present values were compared to values in the 1980s and values from areas without known; history of mercury contamination. Concentrations in both the upper 20 cm of the sediments and; biota are considerably lower now compared to latest monitoring (1980s). Sediment.concentrations at most locations have decreased from the 100–300 ng Hg g^{-1} dry weight (dw) level to levels below the Background Concentration (BC) of 50 ng Hg g^{-1} dw defined by Oslo-Paris Convention for the Protection of the Marine Environment of the North-East Atlantic; some stations are at the 2–10 ng Hg g^{-1} dw level characteristic of Danish coastal sediments with no known history of mercury contamination. Concentrations of mercury in the benthic biota along Harboøre Tange have also decreased since the 1980s but despite the lowered mercury concentrations in the sediments, concentrations in most samples of benthic invertebrate fauna still exceed those in uncontaminated coastal areas and also the Environmental Quality Standard (EQS) of 20 ng Hg g^{-1} wet weight (≈100 ng Hg g^{-1} dry weight) defined by the European Union's Water Framework Directive. Concentration ranges in selected organisms are: (Harboøre Tange l980s/Harboøre Tange now/uncontaminated areas - given in ng Hg g^{-1} dw): Periwinkles *Littorina littorea* 9000/150–450/55-77, blue mussels *Mytilus edulis* up to 9000/300–500/40–170, cockles *Cerastoderma edule* up to 8000/400–1200/200, brown shrimp *Crangon crangon* 700–2200/150-450/47, eelgrass *Zostera marina* up to 330/25–70/12. The present results - together with a literature review - show that a simple and straight forward relationship between the concentrations of mercury in sediment and benthic organisms does not necessarily exist.

1. Introduction

Coastal and estuarine sediments have long been recognized as sinks for pollutants, and once buried in the sediments, metals and non-degradable, organic contaminants may persist for years or decades (e.g. Baeyens et al., 2005; Ridgway and Shimmield, 2002). Due to its capacity to be methylated and accumulate to harmful concentrations along aquatic food chains (Grandjean et al., 1997; Scheuhammer et al., 2008), releases of mercury to the environment from point sources and on a more global scale have been a major concern for decades (UNEP, 2013).

The western part of Limfjorden, Denmark, Nissum Broad along Harboøre Tange (Fig. 1) was heavily contaminated with mercury during the 1950s and 1960s - mainly due to discharges from the pesticide-producing factory, Cheminova (Lyngby and Brix, 1987). It is estimated that approximately 30 tonnes of mercury were discharged into the Nissum Broad with process waste water, lost by production mistakes and deposited in the vicinity of the factory (Kiorboe et al., 1983).

Thresholds and quality criteria for mercury in sediment and biota have been defined by various organizations. The Background Concentration (BC) and Background Assessment Concentration (BAC) for mercury in sediment are 50 and 70 ng Hg g^{-1} dw, respectively, defined by the Oslo-Paris Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR, 2009). The threshold below which there is a low risk of adverse effects towards the biota (Effects Range Low – ERL) is 150 ng Hg g^{-1} dw sediment (Long et al., 1998; Long et al., 1995; OSPAR, 2009). The Environmental Quality Standard (EQS) of 20 ng Hg g^{-1} wet weight (corresponding to approximately 100 ng Hg g^{-1} dw) in invertebrates and fish defined in the European Union Water Framework Directive (EC, 2008; EU, 2008) is supposed to protect the marine food chains from biomagnifying mercury to harmful concentrations in top predators; the potential toxicity associated with elevated levels of mercury in aquatic food chains is well documented (reviewed by Driscoll et al., 2013). Until 2013

☆ This paper has been recommended for acceptance by Prof. Wen-Xiong Wang.

* Corresponding author.
E-mail address: poul@biology.sdu.dk (P. Bjerregaard)

https://doi.org/10.1016/j.envpol.2020.113985
0269-7491/

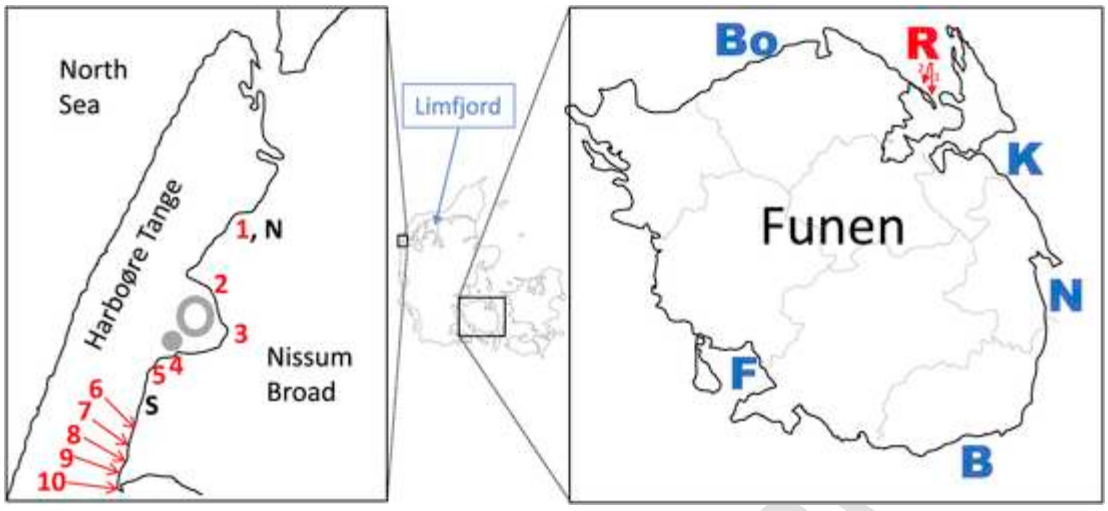

Fig. 1. Maps showing the sampling sites. The left insert shows Harboøre Tange with the sampling stations 1–10 and N and S. The positions of the old, demolished and the present chemical factories are indicated with a grey dot and circle, respectively. The right insert shows the island of Funen with the reference stations.

the Danish environmental authorities used a Norwegian Environmental Classification System (NECS) to assess conditions regarding mercury in the coastal areas (Bakke et al., 2007); NECS focusses on data from sediment, blue mussels *Mytilus edulis*, periwinkles *Littorina littorea* and rock weed *Fucus vesiculosus*.

Investigations during the 1980s documented highly elevated concentrations of Hg in sediment and biota along Harboøre Tange (Andersen, 1992; Brix and Lyngby, 1984; Kiorboe et al., 1983; Lyngby and Brix, 1987; Riisgard, 1984); concentrations in sediment with up to 12 μg Hg g^{-1} dw exceeded the ERL and natural background concentrations by more than 3 orders of magnitude at the most contaminated site; eelgrass (up to 1130 ng Hg g^{-1} dw) and blue mussels (up to 15 μg Hg g^{-1} dw) exceeded natural background concentrations by up to two orders of magnitude (Lyngby and Brix, 1987). Since then, mercury concentrations in sediments and biota in the area have not been monitored.

With the hypothesis that mercury concentrations had remained constant since the 1980s, the main purpose of this investigation was to assess mercury concentrations in sediment and benthic biota in the previously contaminated area and compare these values to previous values from the area and to determine mercury concentrations in areas without known history of mercury contamination. Both sets of data are evaluated against the various thresholds defined in legislations and conventions.

2. Materials and methods

2.1. Field sampling

Sediment samples were collected at the 10 stations along Harboøre Tange indicated in Fig. 1 on October 30, 2014. Stations 1 to 9 are situated at open, coastal locations whereas station 10 is located in a secluded cove with less water exchange and wave action than at the other stations. Triplicate cores were taken at each station by means of Kajak samplers (50 cm polystyrene tube with a diameter of 5.2 cm) except at station 10 where 6 cores were taken because of the expected higher diversity of the sediment in the secluded cove; depth of the individual cores varied between 10 and 24 cm. At station 4, the stony character of the sediment prevented sampling of cores. Further details on the sediment sampling are given in Supplementary Material, Table S1. The method of sediment sampling was the same as used by Lyngby and Brix (1987) with which comparisons are made.

Specimens of the biota in an area up to 15 m from the site of the sediment sample were collected by hand and net; a radius up to 15 m was used to secure enough organisms. If abundant, 5 specimens of each species were collected – otherwise 1 to 4 specimens were collected. Leaves were taken from eelgrass, *Zostera marina*, and top shoots were taken from the macroalgae; the benthic fauna was collected as intact organisms.

On February 4, 2015 similar sampling was carried out at the two reference sites Enebærodde, Funen, Denmark (indicated in Fig. 1, R1 & R2) – without any known history of mercury contamination.

Because the NECS focus species (blue mussels, periwinkles and rock weed) were sparsely abundant at the two reference sites (R1 and R2) it was decided to further characterise background concentrations of mercury in the in areas with no known history of mercury contamination. Benthic biota was sampled twice at 4 reference sites (B: Ballen, F: Faldsled K: Kerteminde and N: Nyborg) around the island of Funen (Fig. 1) during May (B1, F1, K1, N1) and September–October (B2, F2, K2, N2) 2016. Five and approximately 20 specimens of each species were collected from each site in May and September–October, respectively. One further reference site (Bo: Bogense, Fig. 1) was sampled June 3, 2016.

Biota was further collected at two sites along Harboøre Tange (S: Harboøre South and N: Harboøre North, Fig. 1) on June 11, 2016. Reference shrimps were collected at Kerteminde, July 17, 2017 (K3).

Further details on sampling dates, numbers and sizes of specimens collected at the various sampling sites are given in Supplementary Material, Tables S2–S5.

All samples – biota and sediment cores – were collected at walking depths close to the shore at water depths of 20–100 cm. Coordinates for the sampling locations are given in Table S6.

2.2. Treatment of samples

2.2.1. Sediment

The sediment cores were split into 2 cm fractions that were weighed, frozen, freeze dried and weighed again to determine the water content. A subsample of the freeze-dried sediment was heated to 500 °C for 5 h to determine the organic content (Loss on Ignition –LOI). Another subsample of the freeze-dried sediment was used for mercury analysis.

2.2.2. Biota

The biota was transported the 250 km to the laboratory in buckets with aerated water and processed the day after the sampling. The size of the mollusks and shore crabs was determined by measuring the height, width or length of their shell or carapace. The other ani-

mals were weighed. No size estimate was made for plants and macro algae since only the top shoots were collected. The soft parts were dissected from the mollusks and the shore crabs; shrimps and other animals were treated as whole organisms. The samples were frozen and subsequently freeze dried.

2.3. Mercury analysis

Total mercury was determined by means of a Milestone DMA-80 Direct Mercury Analyser. The quality of the determinations was validated by the use of PACS-1 and PACS-3 sediment standards and TORT-standards (lobster hepatopancreas) with certified mercury contents; blanks were included. Values were within ±10% of the certified values. Up to 50 mg dry weight sample was used in the analysis. The mercury concentration was determined in each individual specimen. All concentrations are given on dry weight (dw) basis; sediment concentrations are not normalised with regard to organic content (but data on this are available in Supplementary material, Table S1). This method detects HgS in the anaerobic compartment of the sediment; HgS decomposes at temperatures of 3–400 °C (Azzaria and Aftabi, 1991) - well below the 650 °C the samples are heated to during the analysis.

2.4. Data handling and statistics

Analyses of variance were used to identify differences between sampling sites and times; a few data sets had to be log_{10}-transformed to obtain normal distributions. Tukey's posttest was used for pairwise comparisons. The results of the statistical analyses are indicated in the figures; data points with no common lower-case letter are significantly different. Pearson correlation analyses were used to identify relations between parameters. 0.05 was used as significance level. SYSTAT© ver. 13 was used in the statistical analyses. Because raw data from the 1980s' investigations were not available it was not possible to perform a formal statistical comparison.

3. Results

3.1. Sediments

Mercury concentrations in the sediment at each station are reported to the depth of the shortest of the individual cores in Fig. 2; the content of water and organic material (LOI) is given in Supplementary Material Table S1 together with the mercury concentration based on the organic content.

Most of mercury concentrations in the sediment at the reference sites are in the range 2–5 ng Hg g^{-1} dw with no apparent trends in the depth profile except for an unusually high value at R2 in 4 cm's depth (Fig. 2). At Harboøre Tange stations 1, 6, 7, and 8, Hg concentrations in the sediment were close to background levels and generally below 10 ng Hg g^{-1} dw. Stations 2, 3, 5, and 9 had sediment concentrations between 20 and 40 ng Hg g^{-1} dw while sediment concentrations at station 10 were highly variable with values in individual core sections ranging between 5 and 10,800 ng Hg g^{-1} dw and an average of 592 ng Hg g^{-1} in all of the core sections. For all of the stations with elevated mercury concentrations, mercury appeared to be almost evenly distributed along the depth profiles (Fig. 2).

At most of the stations where comparisons with earlier reported values were possible, mercury concentrations in the upper 5–6 cm of the sediment had decreased considerably since the 1980s (Fig. 3).

3.2. Biota

Besides the 3 NECS focus species (blue mussels, periwinkles and rock weed), 6 additional species were present at a sufficiently high number of sampling stations to allow meaningful comparisons.

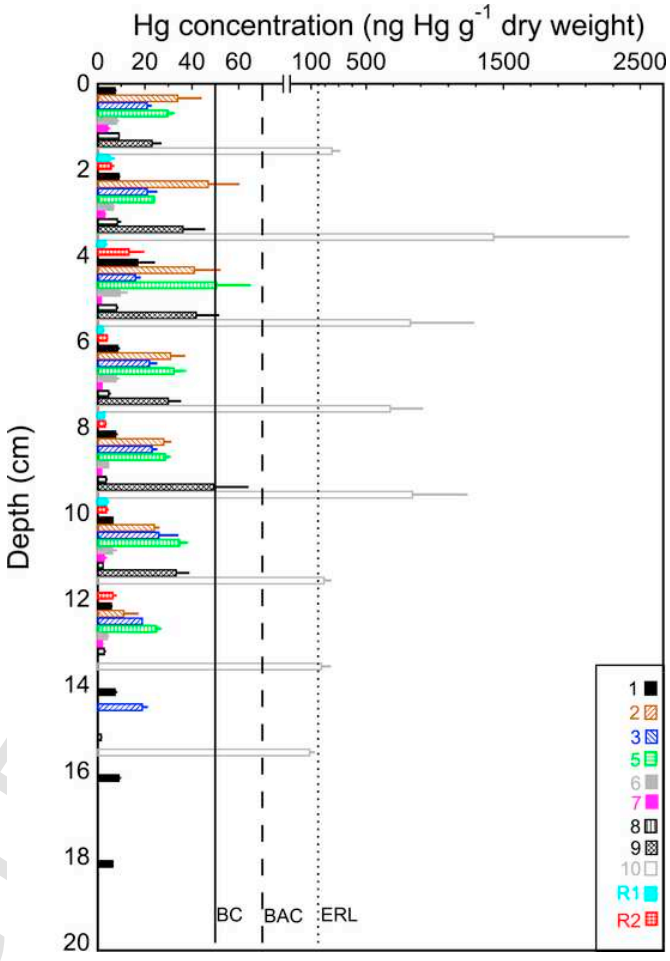

Fig. 2. Depth profiles for mercury from the 2014 sampling. Sampling locations 1–3, 5–10, R1 and R2 are shown in Fig. 1.

These were the cockle *Cerastoderma edule*, three decapod crustaceans (the shore crab *Carcinus maenas*, the brown shrimp *Crangon crangon* and the grass prawn *Palaemon elegans*), eelgrass *Zostera marina* and the slimy whip weed *Chordaria flagelliformis*. These 9 species are termed the main species of the present investigation.

3.2.1. Mollusks

At the 2016 Funen reference sites, mercury concentrations in blue mussels and periwinkles did not differ significantly between the May and September–October samplings and the combined results are shown in Fig. 4AB.

Mercury concentrations in the mussels from the Funen reference sites correlated positively with the size of the animal (length: $r = 0.53$, $p < 0.001$). Average mercury concentrations in blue mussels at B, Bo, K and N were in the range 39–65 ng Hg g^{-1} dw whereas average concentrations at F and R1 were in the range 122–170 ng Hg g^{-1} dw and significantly higher (Fig. 4A); mussels collected at F were larger than at the other sites, explaining the statistically significant difference in mercury concentrations; however, this did not explain the higher values at R1. At the Harboøre Tange sites average mercury concentrations in the range 315–499 ng Hg g^{-1} dw were all significantly higher than at the Funen reference sites (Fig. 4A).

Average mercury concentrations in the periwinkles at the reference sites ranged between 55 and 77 ng Hg g^{-1} dw with no significant difference between the stations (Fig. 4B). There was no statistically significant correlation between the size of the periwinkles and their mercury concentration. Concentrations along Harboøre Tange were signifi-

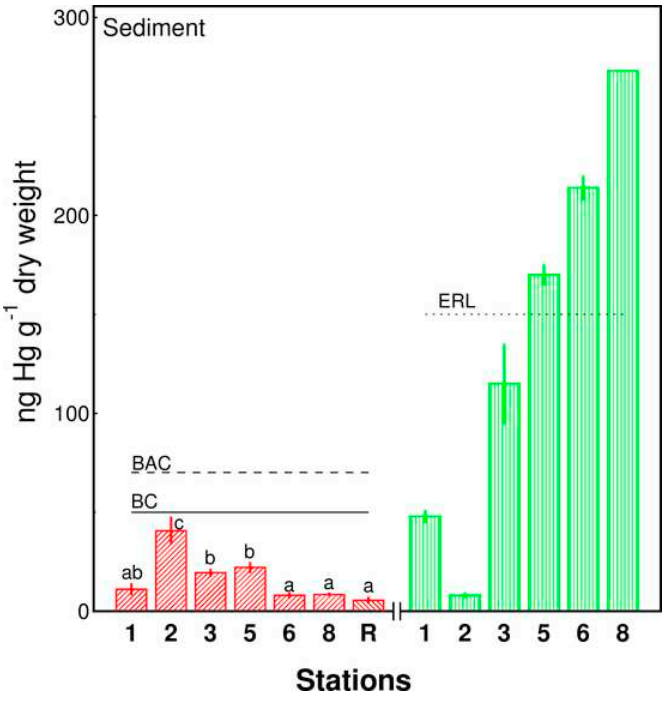

Fig. 3. Mercury concentrations in the upper 5–6 cm of the sediments from Harbøre Tange (////) and reference (\\\\) stations from the 2014 sampling; mean ± SEM, n = 3. Stations with no common lower-case letter show statistically significant ($p < 0.05$) differences. For comparison, mercury concentrations at the same locations in 1983 (Brix and Lyngby, 1984) are shown (|||). Sampling locations are shown in Fig. 1. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

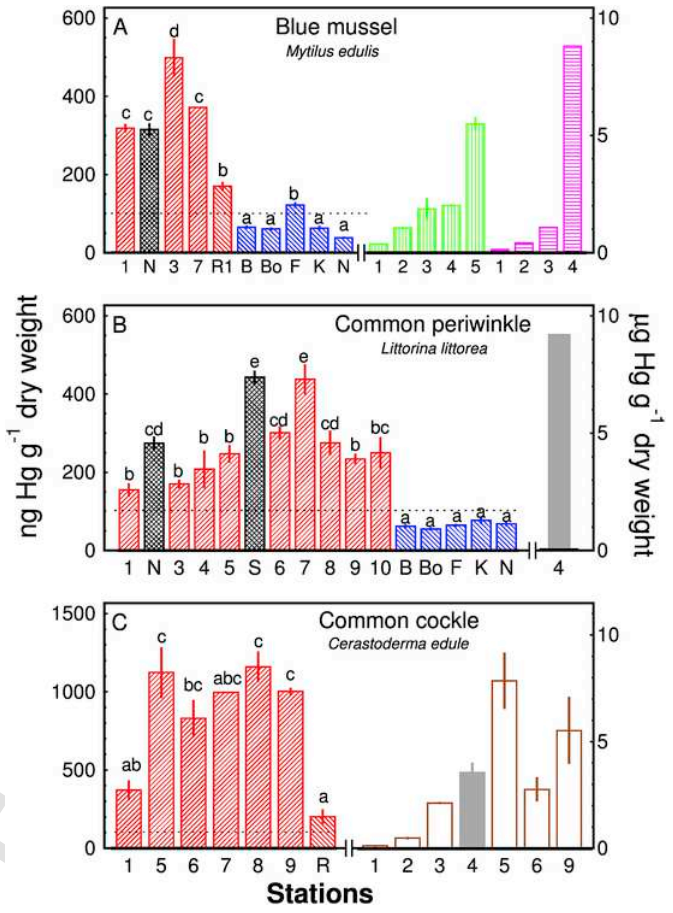

Fig. 4. Mercury concentrations (mean ± SEM; n shown in Tables S2 and S3) in three molluscs along Harboøre Tange (////: 2014; crosshatched: 2016) and at the Funen reference sites (\\\\ & \\\\). Stations with no common lower-case letter show statistically significant ($p < 0.05$) differences. Literature values from the 1980s are indicated on the Y axis to the right. Blue mussels: (Brix and Lyngby, 1984) (|||) and (Riisgard, 1984) (▭); periwinkles: (Kiorboe et al., 1983) (■); Cockles (Kiorboe et al., 1983) (■) and (Mohlenberg and Riisgard, 1988) (□). The Environmental Quality Standard is indicated by the dotted line. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

cantly higher at all sites than at the reference sites with average values ranging between 155 and 443 ng Hg g^{-1} dw.

Cockles at the reference site generally showed higher mercury concentrations (201 ng Hg g^{-1} dw) than the other two mollusc species and the concentrations at stations – especially along the southern part of - Harboøre Tange were generally higher than at the reference station (Fig. 4C).

No statistically significant correlations were found between the mercury concentrations in the surface (upper 6 cm) sediments at the individual sampling stations along Harboøre Tange and the concentrations in the mollusks; this was true both when the sediment mercury concentrations were expressed on basis of dry weight and organic content.

3.2.2. Decapod crustaceans

C. maenas at the reference site had mercury concentrations of 48 ± 3 ng Hg g^{-1} dw in their soft parts (Fig. 5A) and average values for *C. crangon* and *P. elegans* at reference site K3 were 47 ± 3 and 66 ± 23 ng Hg g^{-1} dw, respectively (Fig. 5BC) with *P. elegans* showing a high variability compared to *C. crangon*. Average concentrations at the sites along Harboøre Tange were up to an order of magnitude higher than at the reference stations but for the shrimps, the difference was not statistically significant at all of the stations (Fig. 5BC) – probably due to the low number of individuals.

No statistically significant correlations were found between the mercury concentrations in the surface (upper 6 cm) sediments at the individual sampling stations along Harboøre Tange and the concentrations in the crustaceans.

3.2.3. Plants

Eelgrass was not found at any of the Funen reference stations. Mercury concentrations in the eelgrass leaves at the Harboøre Tange sites appeared higher (Fig. 6A) than the background values of 12 ng Hg g^{-1} dw for the Limfjord generally (Lyngby and Brix, 1987).

Mercury concentrations in the eelgrass leaves at Harboøre Tange showed a positive correlation ($p = 0.005$) with sediment mercury concentrations; the positive correlation was mainly driven by the high concentrations at station 10.

Average background concentrations of mercury in the seaweeds were approximately 10 ng Hg g^{-1} dw with little variability (Fig. 6BC). The concentrations at the Harboøre Tange sites were generally two-to five-fold higher (Fig. 6BC).

3.2.4. Less abundant organisms

Concentrations of mercury in less abundant species are presented in Tables S4 & S5 and in Figs. S1–3. For these organisms, the limited overlap between presence at reference and Harboøre Tange sites does not allow firm conclusions to be drawn; however, judged from background concentrations extracted from the scientific literature (Table S7), concentrations in some of these organisms along Harboøre Tange do appear to be elevated.

4. Discussion

The overall conclusion from this investigation is that mercury concentrations in the sediment along Harboøre Tange have decreased considerably since the 1980s, but also that the mercury concentrations in the benthic invertebrates are higher than background levels and

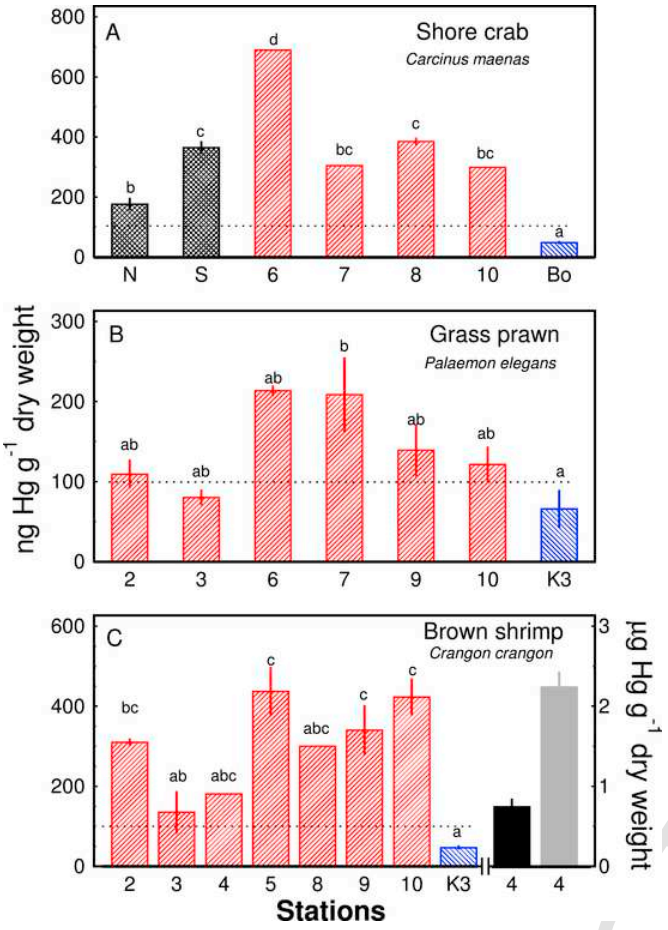

Fig. 5. Mercury concentrations in three species of decapod crustaceans along Harboøre Tange (////: 2014; crosshatched: 2016) and at a Funen reference site (\\\\). Literature values from the 1980s are indicated on the Y axis to the right for *C. crangon* (Riisgard and Famme, 1986) (■) and (Kiorboe et al., 1983) (■). Symbols as in Fig. 4. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

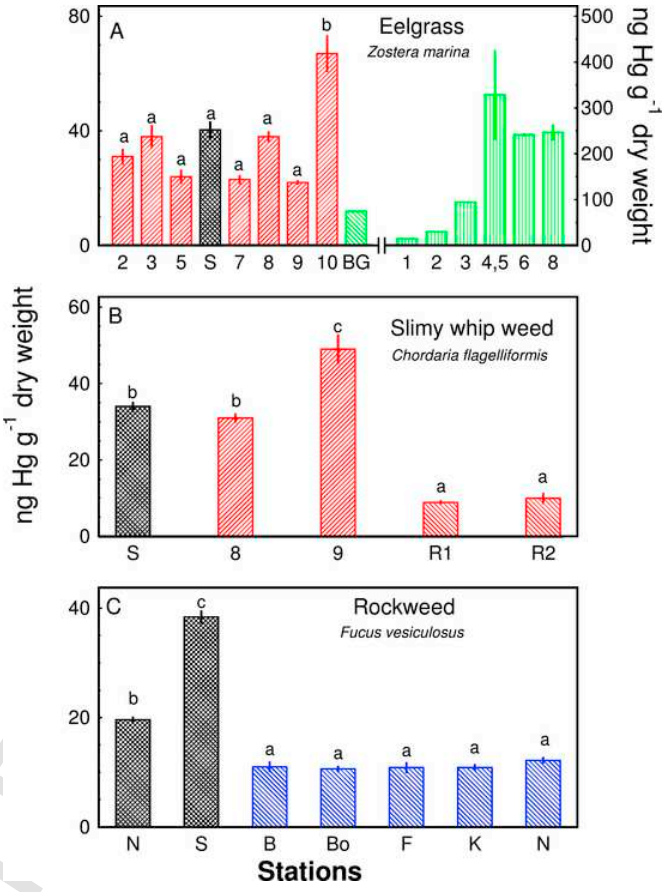

Fig. 6. Mercury concentrations in eelgrass and two seaweeds along Harboøre Tange (////: 2014; crosshatched: 2016) and at Funen reference sites (\\\\ & \\\\). Literature values from the 1980s are indicated on the Y axis to the right for eelgrass (||||) (Brix and Lyngby, 1984). BG is background values from Brix and Lyngby (1984). Symbols as in Fig. 4. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

still exceed the EQS, despite sediment concentrations generally being below the BAC and BC values defined by OSPAR.

4.1. Mercury in sediment

Sediment mercury concentrations determined at the reference stations (generally < 10 ng g^{-1}) agreed well with literature values (6–13 ng g^{-1}) obtained in the Baltic area (e.g. Beldowski et al., 2014) – as such generally much lower than OSPAR's BC/BAC values of 50/70 ng g^{-1} (OSPAR, 2009).

At Harboøre Tange, mercury concentrations in the sediment only exceed the ERL value in the secluded cove at station 10, indicating that at the other stations along the coast there is little risk that the remaining mercury might lead to adverse effects in the biota.

Several investigations have shown that mercury deposited in coastal sediments due to discharges from point sources has the potential to spread.

After dredging of the most polluted sediment (>25 µg Hg g^{-1}) in the Minamata Bay in 1990, the concentrations of total mercury in the surface sediments of the highly polluted bay were reported by the Kumamoto Prefecture (2010) (cited by Matsuyama et al., 2016) to average 4.1 µg Hg g^{-1}. An investigation in 2012 showed that the concentrations changed somewhat during the preceding 25 years where the average concentration of total mercury was determined to 3.0 µg Hg g^{-1} in the total sediment and 2.3 µg Hg g^{-1} in the surface of the sediment (Akito et al., 2014). Tomiyasu et al. (2014) found no significant variation in sediment samples from 2002, 2006, 2008 and 2010 with values in the range of 2.47 and 3.34 µg Hg g^{-1} each of the years. Although a relatively small change of the sediment concentrations have been seen after the dredging, transport of mercury from the Minamata Bay to the Yatsushiro Sea has been documented (Balogh et al., 2015). The transport was suggested to be caused by a slow (~110 m/y) migration of mercury-bearing sediment particles (Kudo et al., 2000). The annual particulate transport of total mercury from the Minamata Bay to Yatsushiro Sea has been estimated to 6 kg (Yano, 2013) and modelled to150 kg (Rajar et al., 2004) hereof 16 kg under normal and 132 kg under storm conditions. For comparison the total amount of total mercury mobilized from the sediment in the Minamata Bay to the water column was estimated to 0.7 kg (Akito et al., 2014). This agrees with results on mercury transport in the contaminated Gulf of Trieste where model considerations and actual measurements showed that most mercury is transported adsorbed on suspended particles and that transport of dissolved total mercury is almost negligible (Rajar et al., 2004). Similarly, mercury discharged to the Bay of Kuwait during 1963–1985 appears to be spreading towards the northern part of the Bay (Al-Zamel et al., 2010). Mercury concentrations in the top 2 cm of the sediments outside a former chlor-alkali plant in Chaleur Bay, New Brunswick, Canada have decreased considerably after the plant closed in 2008 (Walker, 2016) and the author ascribes this decrease to burial by recent sediment deposition.

Mercury concentrations in the sediment along Harboøre Tange appear to have decreased at a faster rate and to lower concentrations than seen in the examples mentioned above. It is not known with certainty which process underlies the decrease in mercury concentrations and where the mercury has gone but 3 explanations have been considered:

Firstly, the mercury might now be buried deeper in the sediment than our Kajak samplers reached. Mercury in the Minamata Bay does not appear to move downwards in the sediments (Tomiyasu et al., 2006) and there is nothing in the depth profiles we have seen at Harboøre Tange suggesting that higher mercury concentrations should be found below our greatest depths for sampling, but the possibility cannot be completely rejected.

Secondly, there might be a possibility that the divalent mercury has been reduced to elemental mercury and evaporated as such. It is known from studies on River Elbe's mercury-contaminated floodplains that divalent mercury is reduced to elemental mercury that may evaporate to the atmosphere (During et al., 2009; Rinklebe et al., 2010; Rinklebe et al., 2009; Rinklebe et al., 2013). Reduction of Hg^{++} to Hg° - mediated by microorganisms - takes place in the free water phase in the marine environment (Monperrus et al., 2007) and this process has also been demonstrated to take place in the sediment in shallow, coastal areas. The values found for the release of elemental mercury from sediment water to the atmosphere range from 0.04 pg Hg m^{-2} $hour^{-1}$ in the St. Lawrence River, Canada (Poissant et al., 2007), to over 80 ng Hg m^{-2} $hour^{-1}$ in a mercury contaminated lagoon in Italy (Covelli et al., 2008; Emili et al., 2012). In the tidal environment in Arcachon Bay, France, Bouchet et al. (2011) reported sediment-water fluxes up to 5.1 ng Hg m^{-2} $hour^{-1}$, sediment-atmosphere fluxes up to 40 ng Hg m^{-2} $hour^{-1}$ and water-atmosphere fluxes up to 14.5 ng Hg m^{-2} $hour^{-1}$. Sharif et al. (2013) and Conaway et al. (2003) reported fluxes up to 15 ng Hg m^{-2} $hour^{-1}$ in the Gironde Estuary, France, and up to 45 ng Hg m^{-2} $hour^{-1}$ in the San Francisco Bay, respectively. It has also been found that e.g. eelgrass can absorb mercury from the sediment and release it to the atmosphere as elemental mercury; rates of 10–40 ng Hg m^{-2} $hour^{-1}$ have been reported (Lindberg et al., 2005; Lindberg et al., 2002) and Bouchet et al. (2011) observed that the presence of eelgrass in the Arcachon Bay increased the mercury fluxes under light conditions. For reduction and evaporation of divalent mercury to explain the decrease in sediment concentrations along Harboøre Tange, calculations show that a flux rate of at least 200 ng Hg m^{-2} $hour^{-1}$ over the 32 years between 1982 (Lyngby and Brix, 1987) and 2014 would have been required. Preliminary experiments with sediment cores from station 10 of the present experiment showed that the flux (with 2–4 cm water phase) to the atmosphere was around 3.4 ng Hg m^{-2} $hour^{-1}$ (Schultz, 2017) – or far less than needed to explain the reduction in the sediment mercury concentrations over the 3 decades.

The third possibility is that mercury has been removed with transport of sediment and water. The water currents in Nissum Broad are mainly driven by the 30–40 cm tidal changes in the North Sea at this location and there is a net flow in the Limfjord from west to east of 300–400 m^3 s^{-1} but the actual inflow and outflow from and to the North Sea are approximately 10 times higher (DTU-Aqua, 2017). All of the sampling stations of the present investigation were situated in areas with shallow water affected by wave action. It is possible that wave action may bring especially the minor organic particulates with the highest mercury content (Kudo et al., 2000; Rajar et al., 2004; Yano, 2013) into suspension whereby the water currents may have transported the mercury both to the North Sea and eastward in the Limfjord. This is probably the most plausible explanation for the decrease in the sediment concentrations along Harboøre Tange; this hypothesis also appears to be corroborated by the fact that sediment mercury concentrations have remained high at station 10, situated in a secluded cove with less wave action than at the other stations. Confirmation of this hypothesis would, however, require an intensive monitoring programme.

4.2. Mercury in biota

At most of the reference stations, the mercury concentrations in the soft parts of the blue mussels are in the range of 'low concentrations' (50 ng Hg g^{-1} dw) defined by OSPAR (2009) and they rarely exceed OSPAR's (2009) BAC (90 ng Hg g^{-1} dw). Judged from the average Hg concentrations in soft parts of blue mussels, the NECS classification system (Bakke et al., 2007) would characterise the area along Harboøre Tange as 'moderately contaminated' (values between 200 and 500 ng Hg g^{-1} dw), whereas the values for periwinkles and rock weed would result in a characterisation as 'uncontaminated' (below 500 and 50 ng Hg g^{-1} dw for the periwinkles and rock weed, respectively). It is obvious that the NECS thresholds for the classification 'uncontaminated' are well above the background levels at the Danish reference sites for all of these 3 focus species. It is also apparent that all of the benthic invertebrates collected along Harboøre Tange have mercury concentrations exceeding the EQS of approximately 100 ng Hg g^{-1} dw – and thereby also exceeding the blue mussels BC and BAC values of 50 and 90 ng Hg g^{-1} dw. Although mercury concentrations in the present-day benthic fauna along Harboøre Tange still exceed the EQS, BC and BAC values it is apparent that a major decrease has taken place since the 1980s.

4.3. Relationship between concentrations of mercury in sediment and biota

Although mercury concentrations in the surface sediments at 9 out of the 10 stations along Harboøre Tange can be characterized as background according to both OSPAR and NECS, the benthic fauna in the area show elevated mercury levels.

Most data on the relationship between concentrations of mercury in sediment and benthic organisms exists for various species of blue mussels *Mytilus* sp. Both inorganic and organic mercury in the sediments have been shown in laboratory experiments to be available for uptake in blue mussels (Gagnon and Fisher, 1997) but field investigations show variable results.

Clear correlations between sediment mercury concentrations in the Limfjord area and mercury concentrations in blue mussels were identified by Lyngby and Brix (1987) and statistically significant correlations were also found in investigations in Galicia, Spain (Beiras et al., 2003; Beiras et al., 2002) and Narragansett Bay, New England, USA for bivalves (including *M. edulis*) (Taylor et al., 2012) whereas Spada et al. (2012) only saw a trend ($p = 0.067$ – calculated from data in their Table 2) in the Taranto Bay, Italy. Correlation was not found for blue mussels in the present investigation – probably caused by the low number of sites where blue mussels were found; failure to demonstrate statistically significant correlations in areas in which such is actually present may be caused by too limited sample size or too low variability in the mercury levels.

Also for the other benthic animals no such correlations were found in the present investigation and judged from the information present in the scientific literature presented below, the relationship between sediment and animal concentrations does not appear to be straight forward.

Periwinkles were obtained from 9 sampling stations in the present investigation with surface sediment concentrations in the top 2 cm between 4 and 251 ng Hg g^{-1} dw and it is slightly surprising that not even a trend of correlation is seen – indicating that the concentration in the periwinkles is not dependent solely on the sediment concentration. A similar conclusion can be drawn from the investigation of mercury in sediment and periwinkles of the contaminated Stour and Orwell UK estuaries (Wright and Mason, 1999): mercury concentrations in the upper 10 cm of the sediment at 29 sampling stations ranged from 60

to 840 ng Hg g^{-1} dw and average mercury concentrations in the periwinkles at 17 of the stations ranged between 60 and 990 ng Hg g^{-1} dw and there is no correlation between the concentrations in sediment and periwinkles ($r = 0.33$; $p = 0.17$ [calculated from data read from Figs. 2–4, 6 in Wright and Mason (1999)]). Also for the polychaete *Nereis diversicolor* the data from Wright and Mason (1999) reveals no correlation between the mercury concentrations in sediment and animal. Contrary to this, Taylor et al. (2012) found clear correlations between the total mercury (normalised with regard to organic content) in sediment and both polychates (*Nereis* sp.), gastropods (*L. littorea* and *Nassarius obsoletus*) and shrimps (*Crangon septemspinosa* and *Palaemontes pugio*) in Narragansett Bay with total mercury concentrations ranging between 35 and 2629 ng Hg g^{-1} dw. Casado-Martinez et al. (2008) found mercury concentrations in lugworms *Arenicola marina* from Spanish ports between 10 and 140 ng Hg g^{-1} dw at sediment concentrations between 50 and 32,000 ng Hg g^{-1} dw without any clear correlation between the two. Correlation becomes apparent only at higher sediment – and lugworm – concentrations when expressed on a dry weight basis (Casado-Martinez et al., 2008). However, if mercury concentrations in the sediment are expressed on the basis of organic content, a correlation ($p = 0.002$; data read from Casado-Martinez, Fig. 2b) becomes apparent in the entire concentration range. Chen et al. (2009) found that mercury concentrations in *C. maenas*, *M.edulis* and *L. littorea* varied no more than a factor 2 to 4 among sites in the Gulf of Maine where sediment concentrations varied from 8 to 1135 ng Hg g^{-1} dw and concluded that sediment concentration is a poor predictor for concentrations in the benthic biota.

Clear correlations between sediment mercury concentrations in the Limfjord area and mercury concentrations in eelgrass leaves and roots were identified by Lyngby and Brix (1987); mercury concentrations in the leaves also showed a correlation with sediment mercury concentrations in the present investigation.

5. Conclusion

Mercury concentrations in sediments and biota along Harboøre Tange are considerably lower now than at the latest monitoring during the 1980s with most sediment concentrations being below the Background Concentration (BC) of 50 ng Hg g^{-1} dw defined by OSPAR. Despite the fact that some stations now have sediment concentrations at the 2–10 ng Hg g^{-1} dw level, characteristic of Danish coastal sediments with no known history of mercury contamination, concentrations in most samples of benthic biota along Harboøre Tange still exceed those in uncontaminated coastal areas and also the Environmental Quality Standard (EQS) of 20 ng Hg g^{-1} wet weight (~100 ng Hg g^{-1} dry weight) defined by the European Union's Water Framework Directive.

The slightly surprising observation that the mercury concentrations in the benthic fauna exceed the EQS value despite sediment mercury concentrations generally falling below the OSPAR BC and BAC thresholds should be interpreted with care – especially in the light of our incomplete understanding of the precise relation between mercury concentrations in sediment and organisms.

CRediT authorship contribution statement

Poul Bjerregaard: Investigation, Writing - original draft. **Torben Grau Schmidt:** Data curation, Formal analysis. **Maria Pedersen Mose:** Data curation, Formal analysis.

Declaration of competing interest

The authors declare no conflict of interests.

Acknowledgement

We thank Annette Duus, Anna-Katharina Semmler and Bente Frost Holbech for assistance with the 2014-sampling. The investigation was supported by a 50,000 D.Kr. grant (95-306-73551) from Lemvig Kommune, Denmark, which holds the legal responsibility for the environmental management of the area.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.113985.

References

Akito, M., Shinichiro, Y., Akihiro, H., Michiaki, K., Ikuko, S., Akihide, T., Hirokatsu, A., 2014. Reevaluation of Minamata Bay, 25 years after the dredging of mercury-polluted sediments. Mar. Pollut. Bull. 89, 112–120.

Al-Zamel, A., Bou-Rabee, F., Lesniewska, E., Szynkowska, M., Dlugosz, M., Bem, H., 2010. Total mercury distribution in sediment cores from Kuwait Bay. Int. J. Environ. Stud. 67, 505–513.

Andersen, H.B., 1992. The expansion of mercury contamination, 5 years after discovery. Mar. Pollut. Bull. 24, 367–369.

Azzaria, L.M., Aftabi, A., 1991. Stepwise thermal-analysis technique for estimating mercury phases in soils and sediments. Water Air Soil Pollut. 56, 203–217.

Baeyens, W., Leermakers, M., De Gieter, M., Nguyen, H.L., Parmentier, K., Panutrakul, S., Elskens, M., 2005. Overview of trace metal contamination in the Scheldt estuary and effect of regulatory measures. Hydrobiologia 540, 141–154.

Bakke, T.O., Kibsgaard, A., Breedveld, G., Eek, E., Helland, A., Källqvist, T., Ruus, A., Hylland, K., 2007. In: Forurensningstilsyn (Ed.), Revidering Av Klassifisering Av Metaller Og Organiske Miljøgifter I Vann Og Sedimenter. Norwegian.

Balogh, S.J., Tsui, M.T.K., Blum, J.D., Matsuyama, A., Woerndle, G.E., Yano, S., Tada, A., 2015. Tracking the fate of mercury in the fish and bottom sediments of Minamata bay, Japan, using stable mercury isotopes. Environ. Sci. Technol. 49, 5399–5406.

Beiras, R., Fernandez, N., Gonzalez, J.J., Besada, V., Schultze, F., 2002. Mercury concentrations in seawater, sediments and wild mussels from the coast of Galicia (NW Spain). Mar. Pollut. Bull. 44, 345–349.

Beiras, R., Fernandez, N., Bellas, J., Besada, V., Gonzalez-Quijano, A., Nunes, T., 2003. Integrative assessment of marine pollution in Galician estuaries using sediment chemistry, mussel bioaccumulation, and embryo-larval toxicity bioassays. Chemosphere 52, 1209–1224.

Beldowski, J., Miotk, M., Beldowska, M., Pempkowiak, J., 2014. Total, methyl and organic mercury in sediments of the Southern Baltic Sea. Mar. Pollut. Bull. 87, 388–395.

Bouchet, S., Tessier, E., Monperrus, M., Bridou, R., Clavier, J., Thouzeau, G., Amouroux, D., 2011. Measurements of gaseous mercury exchanges at the sediment-water, water-atmosphere and sediment-atmosphere interfaces of a tidal environment (Arcachon Bay, France). J. Environ. Monit. 13, 1351–1359.

Brix, H.L., Lyngby, J.E., 1984. In: Limfjordskomiteen (Ed.), Tungmetaller. Limfjorden 1982. 1. Kviksølv. Tungmetaller i Limfjorden, Danish, p. 139.

Casado-Martinez, M.C., Branco, V., Vale, C., Ferreira, A.M., DelValls, T.A., 2008. Is *Arenicola marina* a suitable test organism to evaluate the bioaccumulation potential of Hg, PAHs and PCBs from dredged sediments? Chemosphere 70, 1756–1765.

Chen, C.Y., Dionne, M., Mayes, B.M., Ward, D.M., Sturup, S., Jackson, B.P., 2009. Mercury bioavailability and bioaccumulation in estuarine food webs in the Gulf of Maine. Environ. Sci. Technol. 43, 1804–1810.

Conaway, C.H., Squire, S., Mason, R.P., Flegal, A.R., 2003. Mercury speciation in the san Francisco bay estuary. Mar. Chem. 80, 199–225.

Covelli, S., Faganeli, J., De Vittor, C., Predonzani, S., Acquavita, A., Horvat, M., 2008. Benthic fluxes of mercury species in a lagoon environment (Grado lagoon, northern Adriatic Sea, Italy). Appl. Geochem. 23, 529–546.

Driscoll, C.T., Mason, R.P., Chan, H.M., Jacob, D.J., Pirrone, N., 2013. Mercury as a global pollutant: sources, pathways, and effects. Environ. Sci. Technol. 47, 4967–4983.

DTU-Aqua, 2017. Hydrodynamics of the Limfjord. (in Danish).

During, A., Rinklebe, J., Boehme, F., Wennrich, R., Staerk, H.-J., Mothes, S., Du Laing, G., Schulz, E., Neue, H.-U., 2009. Mercury volatilization from three floodplain soils at the Central Elbe river, Germany. Soil Sediment Contam. 18, 429–444.

EC, 2008. In: Union, E. (Ed.), Directive 2008/56/EC of the European Parliament and the Council of 17 June 2008 Establishing a Framework for Community Action in the Field of Marine Environment Policy (Marine Strategy Framework Directive), 164. Official J. Eur. Union L, p. 19.

Emili, A., Acquavita, A., Koron, N., Covelli, S., Faganeli, J., Horvat, M., Zizek, S., Fajon, V., 2012. Benthic flux measurements of Hg species in a northern Adriatic lagoon environment (Marano and Grado Lagoon, Italy). Estuar. Coast Shelf Sci. 113, 71–84.

EU, 2008. Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on Environmental Quality Standards in the Field of Water Policy, Amending and Subsequently Repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and Amending Directive 2000/60. EC of the European Parliament and of the Council.

Gagnon, C., Fisher, N.S., 1997. Bioavailability of sediment-bound methyl and inorganic mercury to a marine bivalve. Environ. Sci. Technol. 31, 993–998.

Grandjean, P., Weihe, P., White, R.F., Debes, F., Araki, S., Yokoyama, K., Murata, K., Sorensen, N., Dahl, R., Jorgensen, P.J., 1997. Cognitive deficit in 7-year-old children with prenatal exposure to methylmercury. Neurotoxicol. Teratol. 19, 417–428.

Kiorboe, T., Mohlenberg, F., Riisgard, H.U., 1983. Mercury levels in fish, invertebrates and sediment in a recently recorded polluted area (Nissum Broad, western Limfjord, Denmark). Mar. Pollut. Bull. 14, 21–24.

Kudo, A., Fujikawa, Y., Mitui, M., Sugahara, M., Tao, G., Zheng, J., Sasaki, T., Miyahara, S., Muramatsu, T., 2000. History of mercury migration from Minamata bay to the Yatsushiro Sea. Water Sci. Technol. 42, 177–184.

Kumamoto Prefecture, 2010. In: Kumamoto Prefecture (Ed.), Mercury Monitoring Report of Minamata Bay (In Japanese). (Kumamoto City).

Lindberg, S.E., Dong, W.J., Meyers, T., 2002. Transpiration of gaseous elemental mercury through vegetation in a subtropical wetland in Florida. Atmos. Environ. 36, 5207–5219.

Lindberg, S.E., Dong, W.J., Chanton, J., Qualls, R.G., Meyers, T., 2005. A mechanism for bimodal emission of gaseous mercury from aquatic macrophytes. Atmos. Environ. 39, 1289–1301.

Long, E.R., Macdonald, D.D., Smith, S.L., Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manag. 19, 81–97.

Long, E.R., Field, L.J., MacDonald, D.D., 1998. Predicting toxicity in marine sediments with numerical sediment quality guidelines. Environ. Toxicol. Chem. 17, 714–727.

Lyngby, J.E., Brix, H., 1987. Monitoring of mercury and cadmium in coastal areas, using aquatic organisms and sediment. Water Sci. Technol. 19, 1239–1241.

Matsuyama, A., Yano, S., Hisano, A., Kindaichi, M., Sonoda, I., Tada, A., Akagi, H., 2016. Distribution and characteristics of methylmercury in surface sediment in Minamata Bay. Mar. Pollut. Bull. 109, 378–385.

Mohlenberg, F., Riisgard, H.U., 1988. Partitioning of inorganic and organic mercury in cockles *Cardium edule* (L) and *Cardium glaucum* (Bruguiere) from a chronically polluted area - influence of size and age. Environ. Pollut. 55, 137–148.

Monperrus, M., Tessier, E., Amouroux, D., Leynaert, A., Huonnic, P., Donard, O.F.X., 2007. Mercury methylation, demethylation and reduction rates in coastal and marine surface waters of the Mediterranean Sea. Mar. Chem. 107, 49–63.

OSPAR, 2009. In: OSPAR (Ed.), Background Document on CEMP Assessment Criteria for the QSR 2010. p. 23.

Poissant, L., Constant, P., Pilote, M., Canario, J., O'Driscoll, N., Ridal, J., Lean, D., 2007. The ebullition of hydrogen, carbon monoxide, methane, carbon dioxide and total gaseous mercury from the Cornwall Area of Concern. Sci. Total Environ. 381, 256–262.

Rajar, R., Zagar, D., Cetina, M., Akagi, H., Yano, S., Tomiyasu, T., Horvat, M., 2004. Application of three-dimensional mercury cycling model to coastal seas. Ecol. Model. 171, 139–155.

Ridgway, J., Shimmield, G., 2002. Estuaries as repositories of historical contamination and their impact on shelf seas. Estuar. Coast Shelf Sci. 55, 903–928.

Riisgard, H.U., 1984. Mercury pollution in the waters around Harboore Tange and Limfjord, Denmark. Mar. Pollut. Bull. 15, 129–133.

Riisgard, H.U., Famme, P., 1986. Accumulation of inorganic and organic mercury in shrimp, *Crangon crangon*. Mar. Pollut. Bull. 17, 255–257.

Rinklebe, J., During, A., Overesch, M., Wennrich, R., Staerk, H.-J., Mothes, S., Neue, H.-U., 2009. Optimization of a simple field method to determine mercury volatilization from soils-Examples of 13 sites in floodplain ecosystems at the Elbe River (Germany). Ecol. Eng. 35, 319–328.

Rinklebe, J., During, A., Overesch, M., Du Laing, G., Wennrich, R., Staerk, H.-J., Mothes, S., 2010. Dynamics of mercury fluxes and their controlling factors in large Hg-polluted floodplain areas. Environ. Pollut. 158, 308–318.

Rinklebe, J., Wennrich, R., Du Laing, G., Staerk, H.J., Mothes, S., 2013. Mercury emissions from flooded soils and sediments in Germany are an underestimated problem: challenges for reliable risk assessments and management strategies. In: Pirrone, N. (Ed.), Proceedings of the 16th International Conference on Heavy Metals in the Environment.

Scheuhammer, A.M., Basu, N., Burgess, N.M., Elliott, J.E., Campbell, G.D., Wayland, M., Champoux, L., Rodrigue, J., 2008. Relationships among mercury, selenium, and neurochemical parameters in common loons (Gavia immer) and bald eagles (Haliaeetus leucocephalus). Ecotoxicology 17, 93–101.

Schultz, V., 2017. The Fate of Mercury in Danish Coastal Systems: May Divalent Merury Be Reduced to Elementary Mercury I Sediments? (In Danish) Master thesis. Department of Biology, University of Southern Denmark, p. 52.

Sharif, A., Tessier, E., Bouchet, S., Monperrus, M., Pinaly, H., Amouroux, D., 2013. Comparison of different air-water gas exchange models to determine gaseous mercury evasion from different European coastal lagoons and estuaries. Water Air Soil Pollut. 224.

Spada, L., Annicchiarico, C., Cardellicchio, N., Giandomenico, S., Di Leo, A., 2012. Mercury and methylmercury concentrations in Mediterranean seafood and surface sediments, intake evaluation and risk for consumers. Int. J. Hyg Environ. Health 215, 418–426.

Taylor, D.L., Linehan, J.C., Murray, D.W., Prell, W.L., 2012. Indicators of sediment and biotic mercury contamination in a southern New England estuary. Mar. Pollut. Bull. 64, 807–819.

Tomiyasu, T., Matsuyama, A., Eguchi, T., Fuchigami, Y., Oki, K., Horvat, M., Rajar, R., Akagi, H., 2006. Spatial variations of mercury in sediment of Minamata Bay, Japan. Sci. Total Environ. 368, 283–290.

Tomiyasu, T., Takenaka, S., Noguchi, Y., Kodamatani, H., Matsuyamab, A., Oki, K., Kono, Y., Kanzaki, R., Akagi, H., 2014. Estimation of the residual total mercury in marine sediments of Minamata Bay after a pollution prevention project. Mar. Chem. 159, 19–24.

UNEP, 2013. Global Mercury Assessment 2013. Sources, Emissions, Releases and Environmental Transport. United Nations Environment Programme, Geneva, p. 36.

Walker, T.R., 2016. Mercury concentrations in marine sediments near a former mercury cell chlor-alkali plant in eastern Canada. Mar. Pollut. Bull. 107, 398–401.

Wright, P., Mason, C.F., 1999. Spatial and seasonal variation in heavy metals in the sediments and biota of two adjacent estuaries, the Orwell and the Stour, in eastern England. Sci. Total Environ. 226, 139–156.

Yano, S., 2013. In-situ measurement of mercury transport in the sea water of Minamata bay. In: Matsui, K., Kramadibrata, S. (Eds.), International Conference on Earth Science and Technology Proceedings. pp. 448–456.