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Mercury pollution in the Ems estuary

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ABSTRACT: From approximately 1960 to 1975 the Ems estuary received several tons of mercury per year from a chlor-alkali plant, a pesticide factory and some minor sources. The discharge has been reduced drastically from 1976 onwards. In 1975 and 1976 measurements were made on the distribution of mercury in the sediment. The horizontal distribution revealed a strong local enrichment of the sediment near the point of discharge. The vertical distribution was found to be in accordance with the local deposition rates. In the water phase no significant change in mercury content from 1975 to 1978/79 could be demonstrated. In 1978/79 a difference between Ems estuary and Dutch Wadden Sea was not significant. In 1978 mercury contents of eelpout *Zoarces viviparus* in the Ems estuary were about twice as high as in the Wadden Sea. In the Ems estuary a decrease of these contents was found between 1974/75 and 1978. A similar decline in the Wadden Sea may be related to a decreased mercury discharge by the River Rhine.

INTRODUCTION

The Ems estuary receives mercury from waste-water discharges from a chlor-alkali plant, a pesticide factory and other minor sources. All discharges occur near Delfzijl (Fig. 1), partly by pipe-line, partly by discharge of surplus fresh water. From approximately 1960 to 1975 the total yearly discharge of mercury amounted to at least 5 tons. This pollution was reflected in the mercury contents of intertidal mussels *(Mytilus edulis)*. In 1971/72 the highest contents along the Dutch coast occurred in the Ems estuary. In fact these contents were the highest along the west European coast from Arcachon (France) to Cape Skagen (Denmark) (de Wolf, 1975).

After 1975 the mercury discharges were reduced drastically to approximately 0.6 ton in 1976, and approximately 0.06 ton in both 1977 and 1978. To obtain information on the effect of this drastic change in mercury discharge on the contamination of the Ems estuary mercury was measured in water and sediments. Furthermore, eelpout *(Zoarces viviparus)*, a resident fish in the Wadden Sea area, was used as an indicator of the contamination of the ecosystem by mercury.

MATERIALS AND METHODS

In 1978/79 surface water samples were taken monthly in the Ems estuary and Wadden Sea at the locations given in Figure 1. Total and dissolved mercury (flameless AAS) and amount of suspended matter were determined. From these the mercury content of the suspended matter was calculated. For the Ems estuary the data for 1978/79

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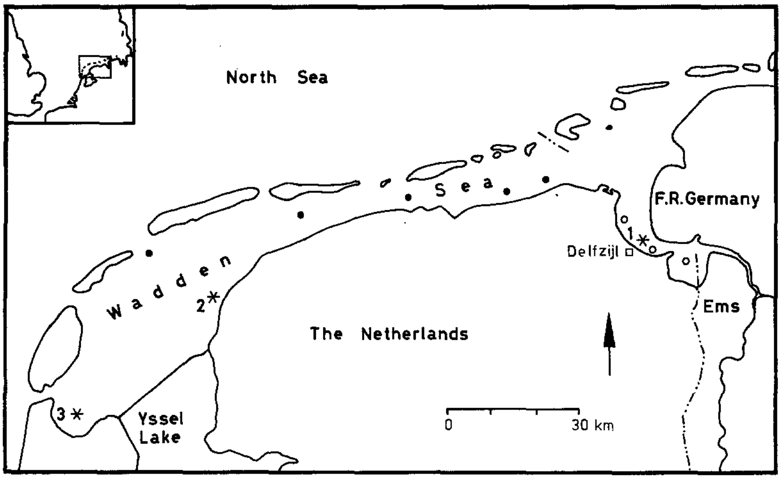

Fig. 1. Map of Wadden Sea and Ems estuary with sampling locations for fish (asterisks) and water (black circles: Wadden Sea; open circles: Ems estuary)

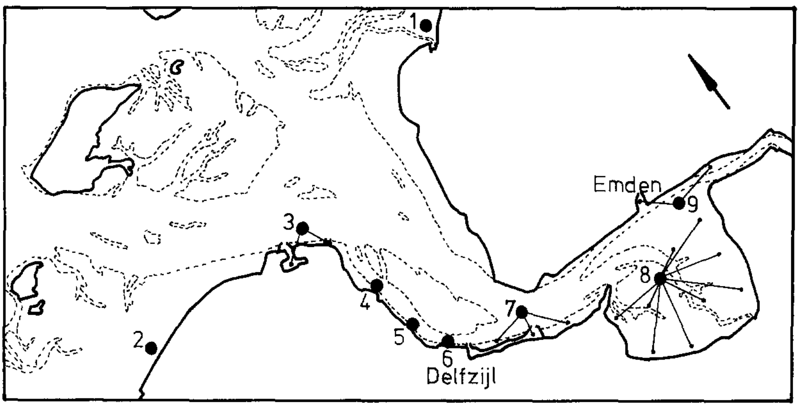

Fig. 2. Map of Ems estuary with locations for surficial sediment samples. (1) Leybucht, (2) N. Groningen, (3) Eemshaven, (4) and (5) Bocht van Watum, (6) Delfzijl, (7) Delfzijl-Termunten, (8) Dollard, (9) Emden

will be compared with data for 1975/76, obtained using neutron activation analysis (van der Sloot & Das, 1974). No data are available from the Wadden Sea for 1975/76. In October and December 1975 surficial sediment samples were taken in the Ems estuary and the adjacent Wadden Sea (Fig. 2). In addition to these samples some sediment cores were taken in October 1976. Mercury was determined by destructive neutron activation analysis (de Groot et al., 1971). The trace metal content in sediments may vary considerably, showing a positive correlation with the amount of finely grained particles. In order to compare the mercury content of sediments from different sample areas, the content (ppm dry weight) at 50 % particles smaller than 16 μm is used (Salomons & Mook, 1977). *Zoarces viviparus* was caught in Ems estuary and Dutch Wadden Sea in March 1978 (Fig. 1, Locations 1 and 2). The fish were anaesthesized with MS 222 and their length measured in half cm. They were packed individually in polythene and stored in deep-freeze. Muscle tissue homogenates were analysed by neutron activation analysis. Mercury contents are given in ppb (fresh weight). These contents are compared with data from 1974/75, obtained from fish sampled at Locations 1 an 3 (Fig. 1).

RESULTS

Water

In the period April 1978–April 1979, i. e. the period with strongly reduced mercury discharges, the average dissolved mercury concentration in the Ems estuary was 0.10 μg/l and in the Wadden Sea 0.08 μg/l. In both areas the observations show a large variation (Table 1). No significant differences – using the *t*-test – between any two stations could be found. The mercury content of the particulate matter is higher in the Ems estuary than in the Wadden Sea. But the variation is very large (Table 1).

In the Ems estuary the average dissolved mercury concentration in 1978/79 was less than in 1975/76. The difference, however, is not significant, due to a large variation of the data in the latter period. The mercury content of the particulate matter is the same in both periods (Table 1).

Table 1. Average mercury content and standard deviation (S. d.) in the water of the Ems estuary and Wadden Sea in the periods Feb. 1975–Jan. 1976 and April 1978–April 1979. N = number of observations

Hg content	Wadden Sea diss. Hg (μg/l) 1978/79	Wadden Sea part. Hg (μg/g) 1978/79	Ems estuary diss. Hg (μg/l) 1975/76	Ems estuary diss. Hg (μg/l) 1978/79	Ems estuary part. Hg (μg/g) 1975/76	Ems estuary part. Hg (μg/g) 1978/79
Average	0.08	0.75	0.31	0.10	1.76	1.77*
S. d.	0.04	1.52	0.30	0.06	1.47	4.54
N	29	25	29	28	45	25

* one value of 724 μg/g was excluded in the calculation.

Table 2. Mercury content (ppm) at 50 % < 16 μm in surficial sediment of the Ems estuary. Inaccurate estimates are given between brackets (locations as in Fig. 2)

Location	Number of samples	Mercury content and 95 % confid. interval
(1) Leybucht	8	0.59 ± 0.11
(2) N. Groningen	10	0.62 ± 0.24
(3) Eemshaven	6	0.61 ± 0.32
(4) Bocht van Watum	2	(1.2)
(5) Bocht van Watum	4	(2.4)
(6) Delfzijl	10	(1 – > 5)
(7) Delfzijl-Termunten	11	1.46 ± 0.54
(8) Dollard	33	0.84 ± 0.10
(9) Emden	18	0.84 ± 0.21

Sediment

In 1975 the mercury content of the surficial sediment of the Ems estuary showed a rather clear gradient (Table 2). The highest contents were found in the vicinity of the town of Delfzijl (Location 6), where the main discharge of mercury occurs. At this location no linear relationship between the mercury content and the fraction of particles < 16 μm in the sediment was present. As a consequence the content at 50 % < 16 μm could not be determined with any accuracy; this value may be between one and a value greater than at least five ppm. The actual contents found at Location 6 range from 1.47 ppm (at 17.8 % < 16 μm) to 154.0 ppm (at 10.9 % < 16 μm). The lowest mercury values were found in the outer part of the estuary, at N. Groningen and Leybucht. The relatively low values in the inner part of the estuary, Dollard and near Emden, are still distinctly higher than those in the outer part (Fig. 3).

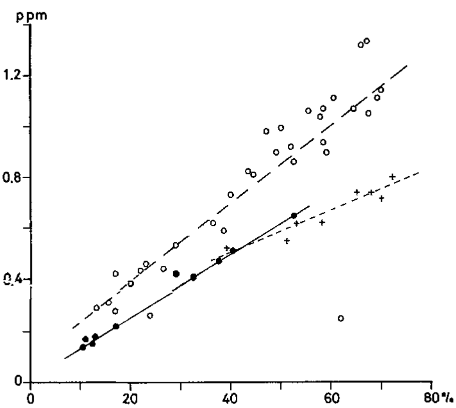

Fig. 3. Relation between fraction of particles < 16 μm (%) and mercury content (ppm) in surficial sediments from Dollard (○), N. Groningen (●) and Leybucht (+) in 1975

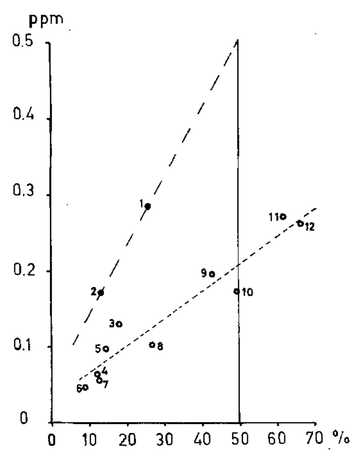

Fig. 4. Relation between fraction of particles < 16 μm (%) and mercury content (ppm) in twelve successive 5-cm sections of sediment Core No. 1 (see Fig. 5). Numbers 1–12 represent 5-cm sections in order of increasing depth

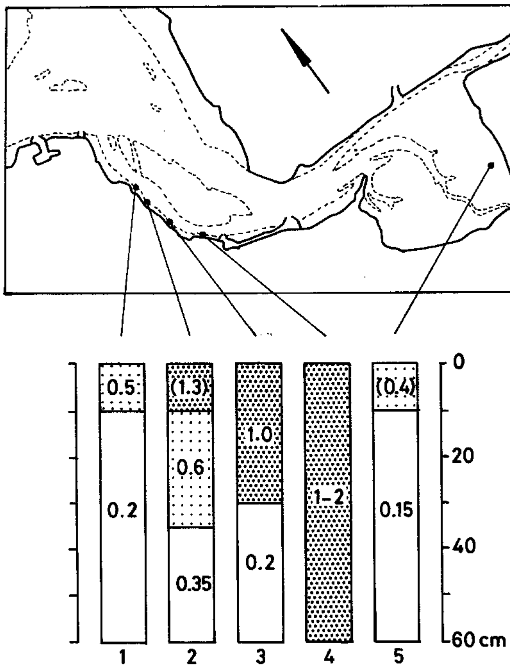

Fig. 5. Vertical distribution of mercury content (ppm) at 50 % < 16 μm in five sediment cores in 1976 (see also text)

In October 1976 five sediment cores to a depth of 60 cm were taken. In each 5-cm fraction the mercury content and grain size were determined. A plot of these data suggests that in most of the cores two or three depth sections can be distinguished, each with different mercury contents. In Figure 4 this is illustrated for Core 1. Figure 5 shows the distribution of mercury contents at 50 % < 16 μm in the cores. The mercury-enriched top layer varies in thickness from 10 cm (Cores 1 and 5) to at least 60 cm (Core 4).

Zoarces viviparus

In March 1978 samples of *Zoarces viviparus* were obtained from the Ems estuary and the Dutch Wadden Sea (Fig. 1, Locations 1 and 2). The mercury content of the muscle tissue shows a significant positive correlation with the length of the fish (Table 3). The difference in regression coefficient between males and females from the Ems estuary was tested (Sokal & Rohlf, 1969) and was found not to be significant. Therefore males and females are taken together for the calculation of the regression of mercury content on length. In the Ems estuary the mercury contents are about twice as high as in the Wadden Sea (Table 3; Fig 6a).

Thanks to the Dutch Organisation for Applied Scientific Research (TNO) our data can be compared with similar data for 1974/75 (W. Chr. de Kock, unpublished) from the same area in the Ems estuary and from Location 3 in the Wadden Sea (Fig. 1). These data, however, do not give mercury contents of individual *Z. viviparus*, but the contents of pooled muscle-tissue homogenates from length classes with a width of some centimetres;

Table 3. Regression formula and correlation coefficient for the relation between length and mercury content of *Zoarces viviparus* in March 1978 from the Wadden Sea and Ems estuary. x = length (mm), y = mercury content (ppb, wet weight)

Sample	n	r	Regression formula
Wadden Sea, ♂♂	42	0.64	$y = 1.87\,x - 116.84$
Wadden Sea, ♀♀	36	0.83	$y = 2.08\,x - 203.52$
Ems estuary, ♂♂	35	0.80	$y = 5.51\,x - 543.51$
Ems estuary, ♀♀	44	0.74	$y = 4.17\,x - 415.72$
Wadden Sea, ♂♂ + ♀♀	78	0.72	$y = 1.85\,x - 131.83$
Ems estuary, ♂♂ + ♀♀	79	0.73	$y = 4.04\,x - 357.68$

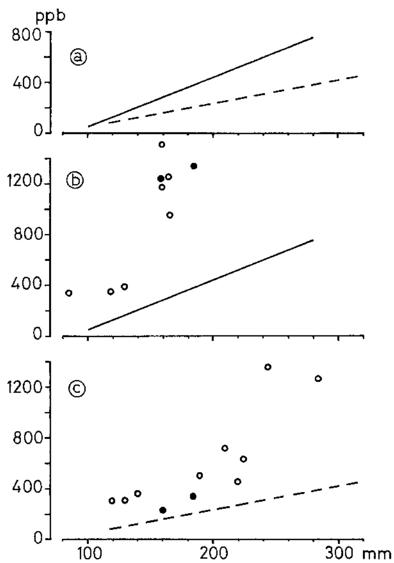

Fig. 6. Relation between length (mm) and mercury content (ppb, fresh weight) of *Zoarces viviparus*. (a) Ems estuary (solid line) and Wadden Sea (broken line) in 1978; (b) Ems estuary in 1974/75 (circles) and 1978 (line); (c) Wadden Sea, Location 3 in 1974/75 (circles), and Location 2 in 1978 (line) (open circles: data from de Kock, unpublished; black circles: methyl mercury data from Stam, unpublished)

they have been plotted as open circles in Figure 6b for the Ems estuary and in Figure 6c for the Wadden Sea. They again indicate a linear relationship between length of the fish and mercury content. In Figures 6b and 6c four data on the methyl mercury content of muscle tissue from 1974 are given (black circles; A. Stam, unpublished). These data fit in rather well with de Kock's data, when taking into account that methyl mercury comprises a major part (on the average about 75 % – W. Chr. de Kock, unpublished) of the total mercury content. A comparison of the data for 1974/75 and for 1978 reveals that in this period the mercury contents of *Z. viviparus* have decreased both in the Ems estuary and in the Wadden Sea (Fig. 6b, c).

DISCUSSION

Water

The dissolved mercury contents in the Ems estuary in 1975/76 compare with some of the higher values found in the Scheldt estuary by Baeyens et al. (1979). The mercury content of the particulate matter, however, is higher in the Ems than in the Scheldt estuary.

Although one expects the higher levels to be found in the Ems estuary, significant differences between the Ems estuary and Wadden Sea with respect to the contamination of the water phase by mercury could not be established, due to the large variation in the data. However, by way of active biomonitoring, using the filter-feeder *Mytilus edulis* harvested from buoys in the central North Sea, de Kock in 1974 could demonstrate a clear difference between the degree of mercury pollution in the Ems estuary and along the West coast of the Netherlands. Even within the Ems estuary a gradient was found with increasing values from the outer part of the estuary towards Delfzijl (Hueck, 1976).

The drastic reduction in the discharge of mercury after 1975 may have led to a decrease in dissolved mercury levels in the Ems estuary from 1975/76 to 1978/79. This decrease, however, is not statistically significant.

Sediment

The contamination of the sediment by mercury appears to be local. High concentrations in the upper sediment layer were found only in the vicinity of Delfzijl (Table 2). Such a local distribution has also been reported elsewhere (Halcrow et al., 1973; Skei, 1978; Jones & Jordan, 1979). In all these localities the hydrographical conditions allow for significant sedimentation of particulate matter contaminated by mercury. In the outer part of the estuary the mercury contents are low; they are considered as base-line values because the concentration of a number of trace metals in these sediments has not changed during the last two decades (Salomons & de Groot, 1977).

The sediment in the Dollard and near Emden is almost entirely of marine origin (Salomons, 1975; Salomons & Mook, 1977). The mercury contents in these sediments are higher than the base-line values just mentioned, due to the sedimentation of particles enriched in mercury content near Delfzijl. It is not likely that significant amounts of mercury are discharged by the River Ems.

With respect to the vertical distribution of mercury in the sediment (Fig. 5) we could make an estimation of the chronology of mercury deposition in the period 1960–1976 for two cores, using sounding and levelling data (Ministry of Public Works, Research Dept. Delfzijl, unpublished). For Core 5, with a mercury-enriched top 10 cm, sedimentation of about 2 decimetres was found for the period 1960–1976. At the location of Core 4, where increased mercury contents were found down to at least 60 cm, sedimentation of about 11 decimetres occurred in the same period. When methodological inaccuracies in the estimation of the sedimentation are taken into account, the obtained results, showing the same order of magnitude, do not contradict the conclusion that the mercury-enriched top layers of the Cores 1–3 and 5, and the entire Core 4 sedimented in the period of high mercury discharges, i. e. 1960–1976. A similar agreement between the downward occurrence of enhanced mercury contents and the depth of deposition since the disposal and discharge of mercury-containing waste commenced was found in the Firth of Clyde (Halcrow et al. & Thornton, 1973) and in Mobile Bay, Alaska (Lindberg & Harris, 1974).

Zoarces viviparus

A significant positive linear relationship between length and mercury content, as was found in *Zoarces viviparus*, has also been found in other fish, e. g. *Esox lucius* (Johnels et al., 1967; Olsson, 1976) and *Gadus morhua* (Jacobs, 1977), in crustaceans, e.g. *Crangon crangon*, and in the gastropod *Littorina littorina* (Zauke, 1977). Especially in organisms with a life span of several years such a relationship represents an integration of possible temporary variations in occurrence in the aquatic environment of substances which accumulate in the food chain (Johnels et al., 1967).

Changes in input of mercury into the aquatic environment will lead to changes in mercury levels in organisms. In Sweden the mercury content of *Esox lucius* showed a 100 % increase from 1964 to 1966 (Johnels et al., 1967), whereas from 1968 to 1972, i. e. after the use of mercury in Swedish paper and pulp industries was banned, the contents decreased (Olsson, 1976). A similar decrease was found in several aquatic organims by Armstrong & Hamilton (1973), Armstrong & Scott (1979) and Bacci et al. (1978). In the Ems estuary the reduction of the mercury emissions from 1976 onwards is considered the cause of the decrease of mercury contents in *Zoarces* from 1974/75 to 1978 (Fig. 6b).

In the Wadden Sea a reduction of mercury levels in *Zoarces* also occurred (Fig. 6c). There cannot be any relation with the reduced emissions in the Ems estuary because of the eastward residual water movement in the Wadden Sea and along the coast. The influence of the River Rhine on the Wadden Sea has been shown with respect to sediments (de Groot, 1973), pesticides (Koeman, 1971) and mercury (de Wolf, 1975). Therefore the reduction of mercury contents in *Zoarces* in the Wadden Sea from 1974/75 to 1978 may be a result of the greatly decreased mercury discharge by the Rhine during 1973 (Fig. 7). This decrease continues (Dijkzeul, unpublished).

Both Koeman (1971) and de Wolf (1975) demonstrated a gradient of decreasing levels of contaminants from west to east in the Wadden Sea. It is then reasonable to

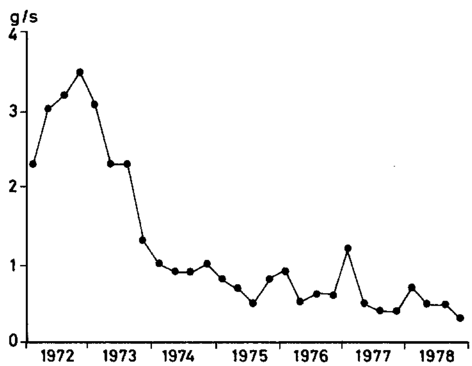

Fig. 7. Mercury load (three-monthly averages) of the River Rhine (after Dijkzeul, unpublished)

expect that in both 1974/75 and 1978 the mercury contents of *Zoarces* were higher at Location 3 than at Location 2 (Fig. 1). As data from Location 3 in 1974/75 have been compared with data from Location 2 in 1978, the decrease of the mercury contents of *Zoarces* from the Wadden Sea reported in this paper may therefore be an overestimation.

Fish are known to accumulate mercury both from water and food (Krenkel et al., 1973). In the Ems estuary we have not been able to demonstrate a significant decrease in the mercury contamination of the water phase, nor do we have at our disposal data on possible decrease of mercury contents of prey organisms of *Zoarces*. *Zoarces* preys upon many benthic organisms (Kühl, 1961). Their mercury contents may therefore be linked to the content of the sediment. We do not know, however, the extent to which the content of the sediment changed after 1975. But, as Armstrong & Hamilton (1973) report a much slower decrease of mercury contents in benthic than in free-swimming organisms after reduction of mercury discharges, it is not likely that in the period concerned the mercury contents of the Ems estuary sediments decreased to such an extent that this could explain the observed decrease in mercury content of *Zoarces*. So the question remains along which route the decrease in the mercury contamination of *Zoarces* in the Ems estuary was produced. New data on a possible decrease of mercury contents in the sediment will be obtained in 1980.

Data on the effects of the mercury pollution upon *Zoarces* and other organisms in the Ems estuary are not available. In the area near Delfzijl where the higher mercury contents in the sediment have been found intertidal macrozoobenthos was absent (Essink, unpublished). This might be caused by the presence of high concentrations of mercury. At least, the fact that the top 30–50 cm of the sediment consisted of very soft mud does not make it unsuitable for benthic animals to live in, as Michaelis (1973) showed for the Blexen area of the Weser estuary.

The difference in mercury content between female and male *Zoarces* from the Ems estuary – though not statistically significant – may nevertheless have some meaning. It may indicate that during gestation females transfer a significant amount of their body burden of mercury to the embryos. This is believed to occur in some marine mammals with respect to organochlorines, which leads to females having lower contents than males (cf. Duinker & Hillebrand, 1979). In *Mytilus* de Wolf & Lewis (1972) found a sharp decrease in mercury content after spawning. They suggest that part of the mercury leaves the mussel with the gametes. Indeed *Zoarces* is neither a bivalve nor a mammal, but as in mammals the embryos obtain their nutrition mainly from the female body. To that end the ovary of *Zoarces* has special, placenta-like structures (Duncker & Mohr, 1928). In this context some preliminary laboratory observations on the survival of newly-born *Zoarces* are of interest. The results suggest that there may be reduced survival in young fish born from Ems estuary parents, as compared with fish from the Wadden Sea. Further investigation into this matter is planned.

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