Bull. Environ. Contam. Toxicol. (1997) 58:101–107

Archives of Environmental Contamination and Toxicology

Total and Organic Mercury in Greenland and Barents Seas Demersal Fish

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Received: 10 February 1996/Accepted: 23 September 1996

Within the framework of the ecotoxicological study of mercury in Arctic European seas, demersal fish samples were collected in the Greenland and Barents seas, far from direct human activities, and, thus, close to pristine areas which allowed for the evaluation of background (natural) concentrations of Hg in biological material. Pelagic fish from this region show indeed low Hg concentrations (0.04 -0.08 µg/g dw) (Joiris *et al.* 1995a). Another aim is to describe and better understand transfer, accumulation and detoxification mechanisms of Hg in areas with low levels of pollution.

MATERIALS AND METHODS

Samples of demersal fish were collected in the Barents Sea in summer of 1991 during the EPOS 2 cruise of RV Polarstern, by otter trawl and Aggaziz trawl, and of 1992, cruise MMBI/VUB of RV Dalnie Zelentsy. Samples from the Greenland Sea were collected in 1992, on board RV Polarstern. Figure 1 shows the sampling station locations. Main water masses were identified on the base of deep water temperature and salinity determinations. For a direct comparison, samples were also collected in the southern North Sea (Belgian continental shelf) in 1992, on board RV Belgica. Muscle samples were taken in the middle part of the back (latero-dorsal).

Total mercury ($\sum$Hg) was determined by atomic absorption spectrometry (MAS-50 Mercury Analyzer, Perkin-Elmer) after mineralization of fresh samples with sulfuric acid and oxidizing the mercury to Hg^{++}. After reducing the Hg^{++} to Hg^{O} with stannous chloride, the volatile Hg^{0} was bubbled into the closed system of the MAS-50 analyzer and the absorption measured. The method used was that of Hatch and Ott (1968), as described in detail in Joiris *et al.* (1991; 1995a). The mercury content was calculated using an external standard curve. The values obtained were expressed in µg Hg/g dry weight. The absolute detection limit was 0.01 µg, corresponding to about 0.005 µg/g dw.

Organic mercury was determined by gas chromatography with electron capture detector (Westöö 1966), also already described in detail (Joiris *et al.* 1991). The organic Hg detected is mainly methylmercury CH_3Hg (MeHg). The absolute detection limit was 0.02 ng, corresponding to about 0.05 µg/g dw; any reading less

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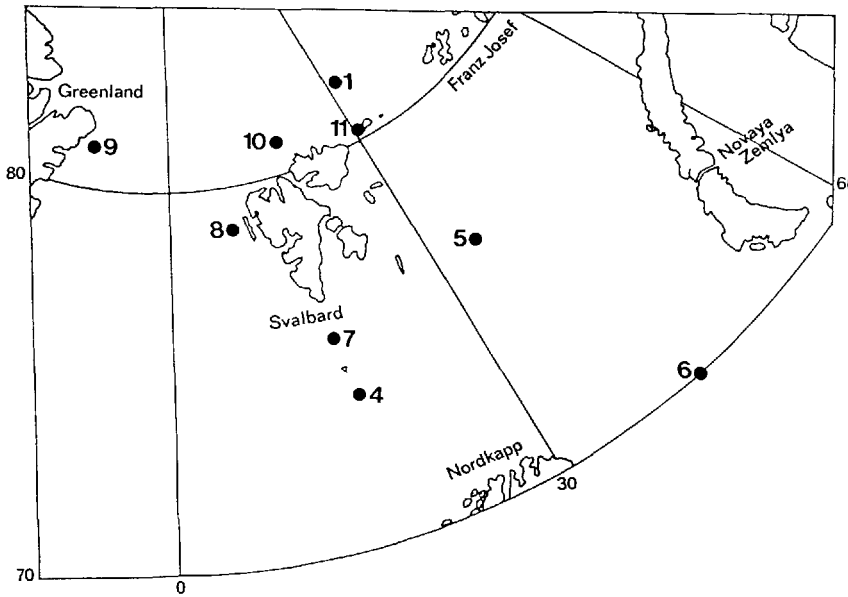

Figure 1. Map of the Greenland and Barents seas, showing the sampling stations for demersal fish, on board RV Polarstern (PS) and RV Dalnie Zelentsy (DZ). Station 1: PS 1991, Atlantic water, long rough dab *(n = 20);* 4: DZ 1991, Atlantic water, long rough dab *(11)* and starry ray *(3);* 5: PS 1991, Arctic water, long rough dab *(26)* and halibut *(1)* 6: DZ 1992, Atlantic water, halibut *(18)* and cod *(12).* 7: DZ 1991, Atlantic water, long rough dab *(7);* 8: PS 1991, Arctic water, Greenland halibut *(10);* 10: PS 1991, Atlantic water, long rough dab *(1);* 11: PS 1991, Arctic water, Greenland halibut (5).
(Note: stations 1, 4, 5 & 6 are the same as in Joiris et al. 1995a).

than this was considered as trace. The reproducibility of the methods and the homogeneity of the fish samples were tested, as well as matrixeffect, recovery and intercalibration using a certified dogfish muscle (DORM-1, Marine Analytical Chemistry Standards Program, Ottawa, Canada): we obtained results representing 93% (n = 15) of the certified value for ΣHg, and 85% (n = 12) for MeHg (Joiris *et al.* 1995a).

The results discussed here did not show a normal distribution; this is why median values are presented instead of mean, and the significance of differences was tested with a non-parametric Kruskal-Wallis test.

RESULTS AND DISCUSSION

For the long rough dab, *Hippoglossoides platessoides,* represented in both Atlantic and Arctic water masses in the Barents Sea and in the Greenland Sea, a clear difference in total Hg content was detected, with low concentration in fish from Barents Sea Arctic water: 0.1 µg/ g dw; higher in fish from Barents Sea Atlantic water: 0.3; and much higher in fish from Greenland Sea Arctic water: 0.9 (Table 1)($p < 0,01$). Comparing Hg concentrations of Greenland Sea fish to

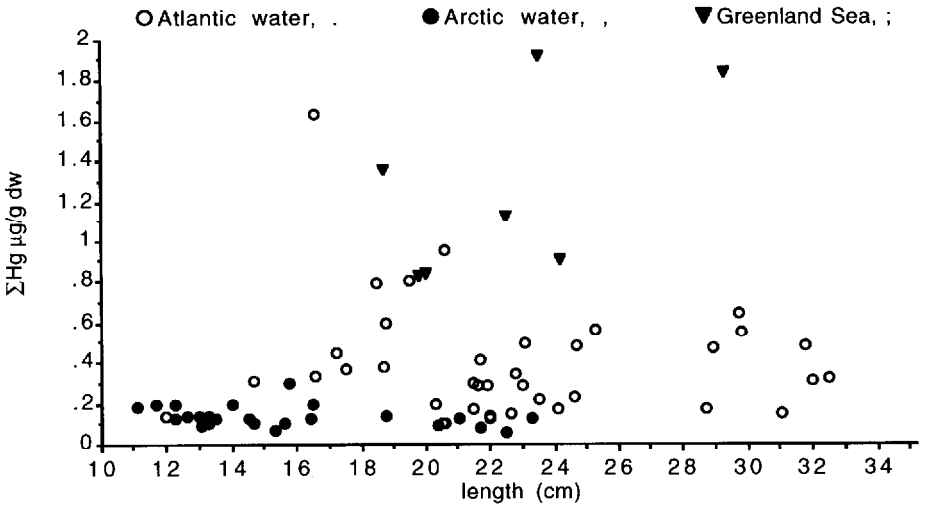

Figure 2. Total Hg concentration (ΣHg, µg/g dw) in muscle of long rough dab, *Hippoglossoides platessoides,* collected in 1991 and 1992, as a function of total body length (cm). Open circles: Barents Sea Atlantic water; solid dots: Barents Sea Arctic water; triangles: Greenland Sea.

Table 1. Median body length and total Hg concentration in muscle of demersal fish from the Greenland and Barents seas (*n:* number of samples).

species/ origin	*n*	body length (cm) *(min - max)*	total Hg (µg/g dw) *(min - max)*
long rough dab			
Barents Sea: Arctic water	*26*	14.6 *(11.1 - 23.3)*	0.13 *(0.06 - 0.30)*
Atlantic water	*39*	21.9 *(12.0 - 32.5)*	0.31 *(0.10 - 1.63)*
Greenland Sea	*9*	22.5 *(18.7 - 29.3)*	0.90 *(0.60 - 1.84)*
Greenland halibut			
Barents Sea: Arctic water	*5*	29.8 *(21.7 - 33.6)*	0.25 *(0.07 - 0.49)*
Atlantic water	*5*	37.7 *(35.5 - 40.0)*	0.44 *(0.24 - 0.85)*
Greenland Sea	*10*	43.5 *(29.5 - 48.3)*	1.24 *(0.73 - 2.50)*
halibut			
Barents Sea: Atlantic water	*18*	20.0 *(19.0 - 29.9)*	0.24 *(0.16 - 0.41)*
Arctic water	*1*	41.7	1.13
starry ray			
Barents Sea Atlantic water	*3*	43.5 *(18.0 - 50.0)*	0.37 *(0.20 - 0.40)*
Atlantic cod			
Barents Sea Atlantic water	*6*	20 *one size class*	0.11 *(0.07 - 0.13)*
	6	45 *one size class*	0.15 *(0.12- 0.19)*
plaice			
Southern North Sea	*17*	25.0 *(11.0 - 34.0)*	0.30 *(0.18 - 0.52)*

concentrations in those from Barents Sea Atlantic water, it is possible that the difference was ecological since both had a similar length distribution but ΣHg levels in Greenland samples were about three times higher than those from Atlantic water. Within the Barents Sea samples, it is very difficult to attribute the difference in ΣHg levels to either biological or ecological factors: Arctic fish were smaller than the Atlantic ones and showed lower Hg concentrations which did not correlate with length (age) graphically (Fig. 2), possibly as a result of the limited number of size classes in our sample, compared to maximum adult size of 50 cm. This is why fish of similar length, between 14 and 24 cm, were selected from both water masses and their ΣHg content compared. After such a normalization allowing direct comparison, it became evident that the difference in Hg contamination of fish from the Arctic (0.1 µg/g dw) and Atlantic (0.4 µg/g dw) water masses was ecological.

A similar conclusion was drawn, and similar Hg concentrations found, for the Greenland halibut, *Reinhardtius hippoglossoides:* 0.25 µg/g dw in samples from the Barents Sea Arctic water, 0.4 in Barents Sea Atlantic water fish, and 1.2 in the Greenland Sea ($p < 0.01$).

For the Atlantic cod, *Gadus morhua,* the actual length was unfortunately not measured on board, and, thus, the individuals were put into two length classes. A significant difference was noted between both classes ($p < 0.01$) (0.11 µg/ g dw for 20 cm, 0.15 for 45 cm); the total Hg concentration was 0.13 for the pooled samples (Table 1).

Total Hg was higher in halibut, *Hippoglossus hippoglossus,* from the Arctic (1.1 µg/g dw) than the Atlantic water (0.2), but this result should be treated with great caution since the Arctic sample was just one and consisted of a fish much larger (i.e., older) than all the Atlantic samples. No correlation between total Hg and length was detected in halibut and might be due to the sample distribution (19-29 cm) compared to the maximum attainable length of 180 cm for males and 230 cm for females (Pethon 1985). Halibut grow slowly, sexual maturity being achieved after 10 years (Johnels *et al.* 1979); hence the halibut samples could be fish of the same age class.

Starry ray, *Raja radiata,* were sampled in Atlantic water only, and had a total Hg concentration of 0.4 µg/g dw.

To allow a broader geographic comparison (same techniques, same team), data on the plaice, *Pleuronectes platessa,* from the southern North Sea were collected as well. The median total Hg concentration in plaice (0.3 µg/ g dw) was comparable to that of demersal fish from Barents Sea Atlantic water, and clearly lower than in the Greenland Sea.

The relative concentration of organic mercury - essentially MeHg - is often expected to be high and constant in fish (around 80%: see synthesis in Thompson (1990), or higher (Bloom 1992)). In Barents Sea demersal fish, however, it varied between 3 % and >100 % of total Hg (Table 2). For long rough dab, MeHg concentrations were 0.05 µg/g dw in Barents Sea Arctic and Atlantic water, and 0.44 in the Greenland Sea. Similar conclusions were drawn again, and very similar concentrations found, for the Greenland halibut with a smaller sample: 0.01, 0.04 and 0.5, respectively. In cod, MeHg concentration was very constant with length, while total Hg was clearly increasing with length. This resulted of course in a decreasing relative MeHg concentration with length (i.e., with age). Such data

Table 2. Median total (ΣHg) and organic mercury (MeHg) concentration (µg/g dw) and relative MeHg concentration (% of total Hg) in muscle of demersal fish from the Greenland and Barents seas (*n:* number of samples).

species/ origin	*n*	ΣHg	MeHg *(min - max)*	% MeHg *min - max*
long rough dab				
Barents Sea: Arctic water	*4*	0.16	0.047 *(0.01 - 0.13)*	*9 - 67*
Atlantic water	*14*	0.29	0.047 *(0.01 - 0.40)*	*3 - >100*
Greenland Sea	*9*	0.90	0.44 *(0.10 - 0.93)*	*16 - 49*
Greenland halibut				
Barents Sea: Arctic water	*1*	0.07	0.013	*19*
Atlantic water	*2*	0.31	0.040 *(0.04)*	*1-17*
Greenland Sea	*8*	1.36	0.53 *(0.26 - 1.63)*	*24 - 53*
halibut				
Barents Sea: Atlantic water	*8*	0.21	0.080 *(0.07 - 0.20)*	*24 - >100*
Arctic water	*1*	0.20	0.76	*68*
starry ray				
Barents Sea Atlantic water	*1*	0.20	0.008	*4*
Atlantic cod				
Barents Sea Atlantic water	*6*	0.11	0.021 *(0.01 - 0.05)*	*11 - 57*
	6	0.15	0.015 *(0.01 - 0.04)*	*6 - 30*
plaice				
Southern North Sea	*5*	0.30	0.15 *(0.12 - 0.44)*	*43 - 100*

suggest the existence of a slow demethylation (mineralization) process, as already noted for Barents Sea pelagic fish, and are reflected in the heterogeneity of % MeHg values, varying from very high in small (young) fish to very low in the larger (older) ones (Joiris *et al.* 1995a). In the plaice from the southern North Sea, organic Hg concentration was higher than in demersal fish from Barents Sea Atlantic water: 0.15 µg/g dw, and the percentages of organic Hg were high as well: 43 to 100%. Mercury concentration in demersal fish from the Barents Sea was relatively high compared with Barents Sea pelagic fish (0.04 -0.08 µg/ g dw) (Joiris *et al.* 1995a), with Antarctica (0.13- 0.66) (Joiris *et al.* unpublished) and with the North Sea (0.4 - 1.5) (Guns *et al.* 1992; this study).

If demersal fish were used as bioindicators directly reflecting Hg levels in marine ecosystems, the apparent conclusion could be that Hg concentrations are highest in the Greenland and North seas, and much lower in the Barents Sea. In the North Sea, this is not only noted for the plaice, but also for dab, *Limanda limanda,* and flounder, *Platichtys flesus* (Guns *et al.* 1992). Such conclusions are, however, misleading, since Hg concentrations in the biota, including fish, are not directly dependent on Hg concentration in the system. The main factor influencing Hg concentration in the biota is primary production: the higher the particulate matter (phytoplankton) concentration, the lower its Hg concentration for a same Hg level in the water. This "biomass effect" is typical for a direct contamination from the water (adsorption on the particles, possibly followed by absorption and partition on intracellular lipids). This phenomenon was already described for PCB contamination in the North Sea (Delbeke and Joiris 1988; Delbeke *et al.* 1990), in the Barents Sea (Joiris *et al.* 1995b), and in the Antarctic, where a low PCB contamination of the ecosystem resulted in high concentration in phytoplankton, due to a very low primary production (Joiris and Overloop 1991).

Mercury concentration in Barents Sea and Greenland Sea phytoplankton were also shown to be dependent on phytoplankton concentration (i.e., on primary production) (Joiris *et al.* 1995b), with lower Hg concentrations in Arctic than in Atlantic water. Taking this into consideration, our interpretation is that Hg concentrations are the lowest in Arctic water, possibly reflecting pristine levels, and apparently characterized by low relative organic Hg concentration in older fish, due to a slow mineralization process very clearly described in pelagic fish (Joiris *et al.* 1995a). The higher concentration in Greenland Sea fish maybe due to low primary production, and not reflecting any significant anthropogenic Hg contamination; organic Hg relative concentration does not seem to be higher than in the Barents Sea. In European Arctic seas, primary production is low, resulting to low concentrations of particulate organic matter (POM = 0.2 g dw/ m^3), and Hg concentration is very low as well (0.05 µg Hg/ m^3 in POM)(Joiris *et al.* 1995 b). In the North Sea, on the contrary, primary production is high (POM = 14 g dw/ m^3) and Hg concentration is high (2,2 µg Hg/ m^3 in POM)(Delbeke and Joiris 1984), which reflects an important anthropogenic contamination; the percentage organic Hg is also clearly higher.

By comparison with older data from the same region, no obvious temporal change of Hg concentration in fish muscle could be detected: in 1975, levels of 0.2 µg/ g dw were noted in Greenland halibut from the NE Atlantic Ocean (ICES 1977), and 0.25, 0.44 and 1.24 in this study, for Greenland halibut collected in the different water masses. From a similar comparison based on pelagic fish (Joiris *et al.* 1995a), similar conclusions were drawn. From both the low levels determined, and the lack of important change of concentrations in Barents Sea fish between 1975 and 1991, it was concluded that concentrations of Hg could be considered as pristine, close to background levels, even if large-scale atmospheric transport probably influenced Hg levels at a global scale.

In demersal fish from the Canadian Arctic, similar ∑Hg concentrations were detected (0.01 -0.21 µg/g fw: Muir *et al.* 1992) to the ones obtained in this study. In the heavily polluted North Sea, on the contrary, Hg concentration in demersal fish decreased from the early seventies (0.45 µg/g dw: ICES 1974) to actual values of 0.30 (this study), probably reflecting a decrease in pollution following European Community legal measures to reduce Hg output. The same conclusion was drawn by Guns *et al.* (1992), who followed Hg levels in plaice from 1971 to 1990. Another interpretation, however, could be that a drastic decrease in the length distribution of the fish due to overfishing took place in between, resulting in smaller fish which normally show lower ∑Hg levels.

Acknowledgments. Barents Sea fish were collected in summer of 1991 during the EPOS 2 cruise of RV Polarstem by CJ, and during the MMBI/VUB cruise of RV Dalnie Zelentsy by LH, J. Tahon and D. Vangeluwe. Greenland Sea fish (Polarstern, 1992), were provided by C. von Dorrien (Kiel). Plaice were collected in 1992, by K. Delbeke (RV Belgica). Research partially funded by the Belgian National Science Foundation (NFWO). Research proposed for funding to the European Commission (DG XI), but classified C “without scientific value”.

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