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Mercury and Polychlorinated Biphenyls in Zooplankton and Shrimp from the Barents Sea and the Spitsbergen Area

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The continuous production and use of chemicals load the environment with xenobionts that are confronting humanity with very complex ecological problems. At present, about 10 million chemicals are registered, of which a small fraction only has been assessed for their ecotoxicological impact. Research on the distribution of these chemicals in marine organisms is a step towards understanding geochemical and environmental processes and their possible changes due to human activities. Furthermore, in remote areas such as the Arctic, the knowledge on the concentration of stables pollutants in marine organisms, could reveal interesting information on their "background levels" and on the influence that the geochemistry of the site may have on the fate of these xenobionts.

Levels of polychlorinated biphenyls (PCBs), organochlorine pesticides and heavy metals in Arctic marine mammals and fish are relatively well documented (Muir *et al*., 1992), but more information for other compartments is needed.

Two crustaceans, zooplankton and the shrimp *Pandalus borealis*, were used to study the ecotoxicology of mercury and polychlorinated biphenyls (PCBs) in the Barents Sea and Spitsbergen area, and to discuss their transfer and accumulation mechanisms.

MATERIALS AND METHODS

Samples were collected during two different cruises: the shrimp *Pandalus borealis* during the EPOS II cruise of RV Polarstern, in June-July 1991 with Agassiz trawl, and zooplankton during the MMBI/VUB ARCTIC cruise of RV Dalnie Zelentsy, in July-August 1991 with a 150 mu m mesh size net towed vertically from a maximum depth of 80 meters to the surface. The map (Figure 1) shows the different sampling stations. Sometimes, due to the scarcity of zooplankton, the material of some adjacent stations was pooled. Biological samples were immediately deep frozen, and analysed for their mercury and organochlorine concentration a few months later. A microscopic examination of zooplankton samples showed the presence of zooplankton, without phytoplankton. The zooplankton samples were however quite heterogeneous (nauplii, mixture of *Calanus sp., Euthemist libullula*, ctenophores, gasteropods).

The method used for total mercury (ΣHg) determination was already described in detail (Joiris *et al.* 1991). Mercury in sulfuric acid-digested samples was

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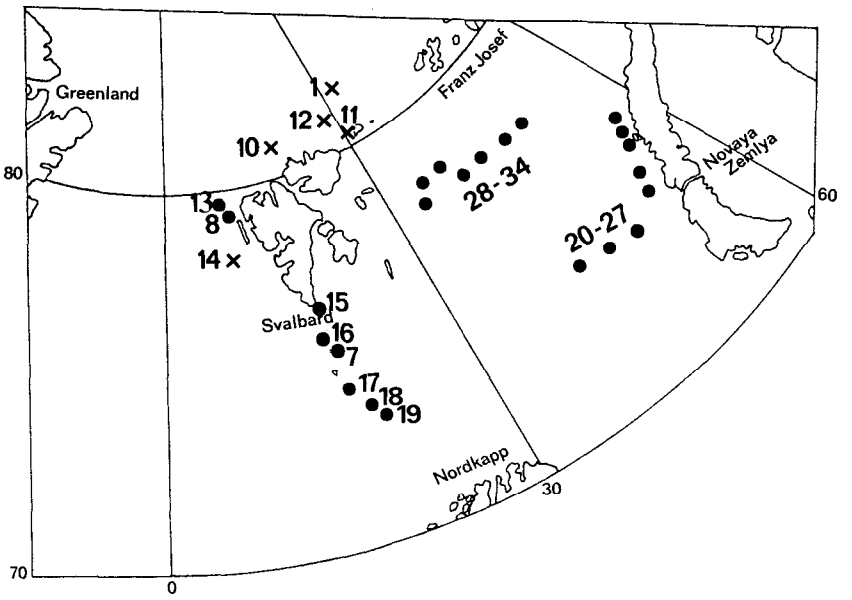

Figure 1. Map showing the sampling stations on board RV Polarstern and RV Dalnie Zelentsy, 1991; dots: zooplankton, crosses: shrimp; Arctic water: stations 8, 13, 14, 23 - 31; Atlantic water: stations 1, 10, 12, 17, 18, 19; mixed water: 7, 15, 16, 20, 21, 22, 32 - 43; (same numbering of stations as in preceeding Barents Sea papers)

determined by an atomic absorption spectrophotometer (MAS-50 Mercury analyzer, Perkin-Elmer) using an external standard curve. The detection limit was 0.01 µg Hg. Zooplankton, entire shrimp and shrimp muscle were used for total mercury determination. Several tests were conducted in order to check the reproducibility and the accuracy of the method. The reproducibility was tested on a homogenized sample of zooplankton divided into ten identical subsamples. Since the mean and the median are equal (0.10 µg/dw) and the coefficient of variation (CV= standard deviation/mean) is low (8%), the test of reproducibility was considered as satisfactory. In order to test the representativity of the zooplankton samples, a test of homogeneity was carried out as well. The results showed a good homogeneity: 0.10 µg ΣHg/g dw for mean and median, with a coefficient of variation of 8%. It can be concluded that the variability in the measurements is entirely explained by the reproducibility of the method and the test of homogeneity was considered as satisfactory. A test was conducted to check for the possibility of any interaction between mercury and the biological samples (matrix). One sample of zooplankton and two specimens of shrimps were homogenized separately and divided into five equal parts for each biological sample. Part 1 was prepared for analysis as usual; known quantities of inorganic mercury were added to the other parts before mineralization. Measured concentrations increased linearly with the added mercury; measured Hg (y) is bound to added Hg (x) by equation $y = 0.91 x + 0.04$ ($n = 5$; $r^2 = 0.97$; $p < 0.01$) and $y = 1.07 x + 0.08$ ($n = 5$; $r^2 = 0.99$; $p < 0.01$) for zooplankton and shrimp, respectively. Since a high correlation was obtained and the slope was close to 1, no matrix effect had to be taken into account.

Organic mercury was determined by liquid gas chromatography with electron capture detector as already described in detail (Joiris *et al.* 1991). The organic Hg

detected is mainly methylmercury CH_3Hg^+. A matrix test was conducted on muscle of shrimps. The high correlation between added and measured mercury ($y = 1.10 x + 0.15$; $n = 5$; $r^2 = 0.98$; $p < 0.01$) showed a slope sufficiently close to 1 to consider the matrix effect as negligible.

Organochlorines and neutral lipid extraction was carried out using a Soxhlet extraction with hexane/acetone (9/1) during ten hours. The total neutral lipids were gravimetrically quantified. After drying, the extracted lipids were weighed, re-dissolved in hexane, and transferred to the elution columns for clean-up of PCBs (see description in Delbeke *et al.* 1990). PCBs were recognized on the chromatograms as standard mixture Aroclor 1254 and as 11 individual congeners: IUPAC nrs 28, 32, 52, 101, 118, 153, 138, 156, 180, 170 and 194, in order of increasing chlorine content. 94% (±12) and 100% (±10) of PCB congeners added to zooplankton and entire shrimps prior to analysis were recovered, respectively.

Remark: the results discussed here do not show a normal distribution; thus, median values are presented rather than means, and the significance of differences are tested with non-parametric Mann-Whitney and Kruskal-Wallis tests.

RESULTS AND DISCUSSION

A high correlation exists between mercury concentration in entire shrimp and in muscle (Figure 2). The slope is close to one, and no significant difference was detected between the two samples ($p > 0.05$). Subsequently, the results for both measurements were pooled for further discussion.

Total mercury concentration in crustaceans varies geographically (Table 1). Samples from the Arctic water mass were significantly less contaminated than from Atlantic water: 90 and 150 ng/ g dw for zooplankton and 170 and 340 ng/ g dw for shrimp, respectively ($p < 0.01$). Due to their small size, Hg levels in zooplankton

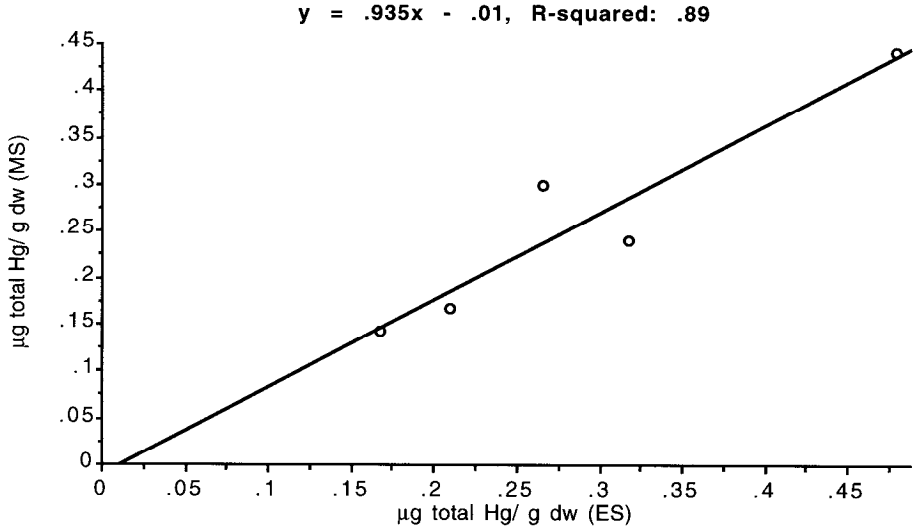

Figure 2. Linear regression of total mercury in entire shrimp (ES) and shrimp muscle (MS) (median value for each station, $p < 0.05$)

Table 1. Median total and methylmercury concentrations in zooplankton and shrimp from different regions (ng/ g dw)

Species	Water mass	ref	ΣHg	*n*	MeHg	*n*	%MeHg
mixed zooplankton	European Arctic: Arctic	a	90	*9*	5	*4*	6
	mixed	a	120	*8*	7	*3*	6
	Atlantic	a	150	*3*	13	*2*	9
	North Sea	b	320*	*13*			
	Antarctic	c	240	*15*			
Pandalus borealis	European Arctic: Arctic	a	170	*15*	140	*2*	100
	Atlantic	a	340	*42*	210	*13*	77
Crangon crangon	Belgian North Sea coast	d	410*				

a: this study; b: Delbeke & Joiris, 1984; c: Joiris & Overloop, unpublished; d: Guns & Van Hoeyweghen, 1992; *: mean.

were determined on homogenized mixed assemblages. So that the differences in Hg concentrations in zooplankton might partially be due to differences in species composition and trophic levels.

No correlation was detected between Hg concentrations and body size for shrimps, in contradiction with data of other authors, but the size range in our samples was limited and we could not take other biological factors such as sex into account. On the other hand, many populations of *Pandalus borealis* can be encountered in Arctic Seas, and their growth is linked to the water temperature (Teigsmark 1981). This also could be a cause of heterogeneity in the results.

Mercury in zooplankton was mainly inorganic; MeHg represents less than 10 % (Table 1). No difference was detected between the three water masses ($p > 0.05$): the median values for all regions were 6 ng MeHg/ g dry weight and 20 ng MeHg/ g lipid weight. In contrast, MeHg in the muscle of shrimp represented the majority of total Hg (77-100 %). Similar data were found for *Crangon crangon:* 60-90% (Riisgard and Famme, 1986). Fowler *et al.* (1978) explained the high methylmercury content in shrimp muscle by the transfer of MeHg which, once taken up between certain tissues, is ultimately accumulated in the muscle.

The comparison of mercury in crustaceans from Arctic regions with other regions can be done although it is very rough since zooplankton is composed of mixed species and shrimps' data were not corrected for size, and thus provide orders of magnitude only. The mercury concentration in zooplankton from the Arctic region is two and three times lower than the North Sea and the Antarctic respectively (Table 1). The same observation is valid for the shrimp from the Arctic water mass.

The identification of PCB residues was based on two types of standardization: a comparison with the standard Aroclor 1254 mixture (close to the PCB pattern found in marine samples), and the sum of 11 congeners. These congeners account for 32% and 25% of "total" PCBs for zooplankton and entire shrimp, respectively. There was a similarity in PCB pattern when visually comparing the chromatograms of samples with the standard Aroclor 1254. The similarity was confirmed by comparing the mean relative contribution of the most important congeners 52 to 156 of samples with Aroclor 1254 versus 1260 (Table 2). Moreover, Table 3 shows the strong relationship between the concentration of sum

Table 2. Relative mean contribution (expressed in % of the sum of congeners) of the six important individual congeners in zooplankton, shrimp and the standard mixtures Aroclor 1254 and 1260

Congener (IUPAC nr)	Zooplankton (n = 15)	Shrimp (n = 16)	Aroclor 1254	Aroclor 1260
52	9	8	15	2
101	24	24	26	8
118	20	21	18	2
138	18	19	18	17
153	17	17	12	23
156	3	3	5	5

Table 3. Correlation between "total" PCBs (expressed as Aroclor 1254), sum of congeners and individual congeners in zooplankton (n = 15) and shrimp (n = 16)

	Correlation coefficient (r) between "total" PCBs and:						
Sample	Σcong	52	101	118	138	153	156
zooplankton	0.94	0.80	0.90	0.89	0.96	0.91	0.86
shrimp	0.95	0.82	0.85	0.95	0.94	0.94	0.90

Σcong: sum of congeners 28, 32, 52, 101, 118, 138, 153, 156, 170, 180, and 194

of 11 congeners and "total" PCBs (as Aroclor 1254) on one hand and the most important congeners considered individually and 'total' PCBs, on the other hand, reflecting the absence of any significant heterogeneity in the PCBs pattern of the various samples. On a dry weight basis, no difference was observed between the three water masses for zooplankton ($p > 0.05$) and the median value for all region was 260 ng "total" PCB/ g dw. For the shrimp, the Arctic specimens were less contaminated than the Atlantic ones (Table 4, $p < 0.01$). This difference disappeared on a lipid weight basis ($p > 0.05$) and the median values were 1100 and 6500 ng "total" PCB/ g lipid for zooplankton and shrimp, respectively. Comparing with data obtained by the same team and techniques, the PCB levels were of the same order of magnitude in the Arctic zooplankton and the Antarctic zooplankton on a dry weight basis ($p > 0.05$, Table 4); and were 3 times less contaminated than those of the North Sea. Expressed on lipid weight basis, the Arctic is 5 and 6 times less contaminated than the Antarctic and North Sea zooplankton, respectively. But the zooplankton from the European Arctic seas is more contaminated than from the Canadian Arctic. For shrimps, the comparison will be restricted for *Crangon crangon* from the Belgian Coast and for the sum of congeners only. This comparison is rough however because it concerns different species. On a dry weight basis, *Crangon crangon* is twice more contaminated than Arctic water shrimps: 60 and 30 ng Σcongeners/ g dry weight, respectively; and it has the same PCBs levels as the Atlantic ones (60 ng Σcongeners / g dry weight). On a lipid base, the Arctic specimens are twice more contaminated than those of North Sea: 2000 and 1000 ng Σcongeners/ g lipid weight, respectively. Knowing that the Arctic ecosystem (especially Arctic water) is less contaminated by PCBs than the North Sea, this apparent contradiction can be explained by the relatively high contamination of particulate matter (and the food of the shrimp), due to the low biomass present in polar systems, and causing a high contamination on a dry or lipid weight base (Joiris and Overloop 1991).

Table 4. Median "total" PCBs contamination of zooplankton and shrimp *Pandalus borealis* as Aroclor 1254 in different units (dry weight and lipid weight) from different regions

Species	Water mass	*n*	ng/ g dw	ng/ g lw	ref.
mixed zooplankton	European Arctic: Arctic	*6*	230	890	a
	mixed	*6*	220	1020	a
	Atlantic	*3*	320	1330	a
	North Sea	*20*	700*	7000*	b
	Antarctic	*14*	300	5500	c
	Canadien Arctic	*9*	40*	150*	d
phytoplankton	European Arctic seas	*8*	90	590	c
Pandalus borealis	European Arctic: Arctic	*3*	130	6800	a
	Atlantic	*13*	200	6090	a

a: this study; b: Delbeke *et al.*, 1988; c: Joiris & Overloop, 1991; d: Hargave *et al.*, 1992; e: Joiris *et al.*, 1995; *: mean value

No relationship was detected between PCB levels and lipid content for zooplankton and shrimp. The same observation was made for zooplankton from the North Sea by Delbeke *et al.* (1990). The absence of relationship between PCB's and fat content of crustaceans suggests a greater uptake of PCBs through food (indirect uptake) than through water (direct uptake), confirming the experimental studies done by Brown *et al.* (1982). The comparison of PCBs in zooplankton and suspended particulate matter (composed mainly of phytoplankton) from the polar region confirms this hypothesis (Table 4). On a dry weight basis, PCB levels were higher in zooplankton than in suspended particulate matter; they were lower in zooplankton on a lipid weight base. Kattner and Graeve (1990) showed that for Arctic zooplankton there is a biosynthesis of a large amount of lipids in summer as energy reserves. These newly formed lipids are different from that of phytoplankton, confirming the existence of new autogenic fat in zooplankton. They are free of PCBs and may cause an apparent dilution of PCBs observed on a lipid weight basis. This is qualitatively consistent with an important uptake of PCBs through feeding together with a further dilution into autogenically formed PCB-free, zooplankton lipids.

In general, water and food represent the major routes of chemical uptake by marine invertebrates, the order of importance varying with many factors including species, food type, relative concentration (or strictly bioavailability) of chemicals in food and water, and physico-chemical parameters of the aquatic environment. Our results support the hypothesis that the major route of uptake of PCBs in zooplankton and shrimp *Pandalus borealis* is food, with a further dilution in newly formed autogenic lipids in the case of zooplankton.

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