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Mercury and Polychlorinated Biphenyls in Suspended Particulate Matter from the European Arctic Seas

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During the last few decades with the increase of pollution of the hydrosphere by xenobiotic compounds, scientists in general and ecotoxicologists in particular are in search of "pristine" areas to determine background concentrations for those residues being both of natural origin and anthropogenic. Real backgrounds are difficult to establish since older environmental data often seem to be affected by contamination either during field collection or during analytical procedures (Patterson *et al.*, 1976). To establish such background pristine levels in the marine environment, the polar regions provide ideal areas where the human activity is very low. Of the two, Arctic is recommended: unlike Antarctic, it forms a closed basin; the Antarctic is more open and it is subjected to intense pollution as a result of the activities of developing countries (Joiris and Overloop, 1991). In spite of regular intrusions of polluted air masses known as "Arctic haze", the Arctic region could be proposed to evaluate background concentrations (Mackay and Wania, 1993).
The aim of this study is to determine the concentration of mercury and polychlorinated biphenyls (PCBs) in suspended particulate matter from the Arctic region and to discuss their contamination mechanisms.

MATERIALS AND METHODS

Samples were collected between June and October 1991 from the European Arctic region, during three cruises of RV Polarstern in the Greenland Sea, Barents Sea and the Arctic Basin (ARK VIII 1, 2 & 3). Particulate matter was collected by continuous centrifugation (see details in Joiris and Overloop, 1991). The water was pumped from under the hull of the ship, at a depth of about 11 meters; continuous centrifugation for a period between 36 and 120 hours was necessary to obtained sufficient material for determination of mercury and PCBs. The map (Figure 1) shows the different sampling transects.

Total mercury (ΣHg) was determined with atomic absorption spectrometry: the method was already described in detail (Joiris *et al.*, 1991). The mercury content was calculated using an external standard curve, and the values expressed in μg Hg/g dry weight. To test the reproducibility of the method, a homogeneized fresh sample of particulate matter, was divided into five identical parts. Each was mineralized separately and analyzed for total mercury. The results show a mean and median values of 0.29 μg Hg/ g dw, with a standard deviation of 0.01 (n = 5).

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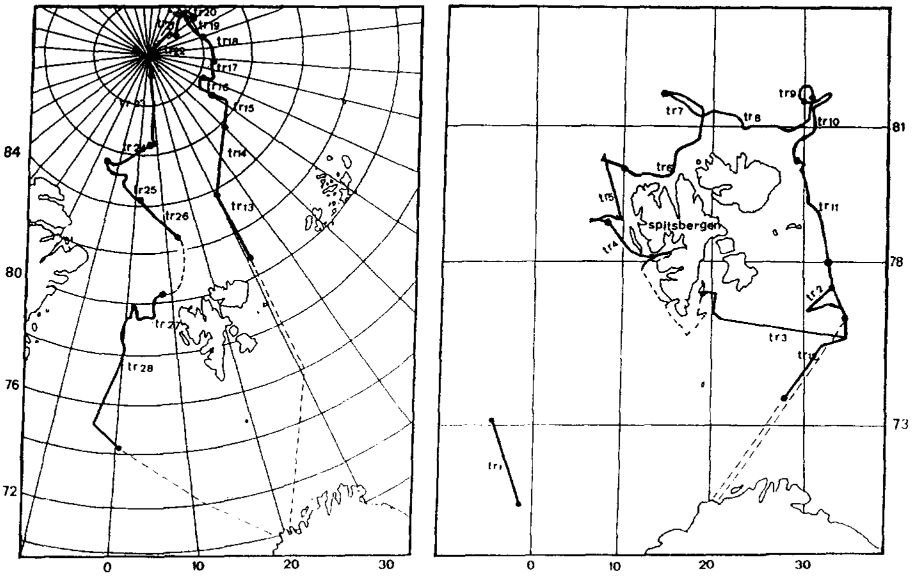

Figure 1. Map showing the route of RV Polarstern during cruises ARK VIII/1, 2 & 3. Transects (thick line) were sampled for particulate matter by continuous centrifugation (see text)

Since the mean and the median are equal and all measurements fall within 1.96 standard deviation from the mean, and the coefficient of variation (cv= standard deviation/mean) is very low (0.03) a normal distribution is assumed and the test of reproducibility is considered as satisfactory. Another means of testing for reproducibility is by comparing the standard deviation of the measurements with the theoretical error calculated from the error on the measuring instrument used (in this case a analytical balance and spectrophotometer). Since the mean calculated theoretical error of 0.01 µg/g dw corresponds precisely with the standard deviation of the measurements, it further confirms the high reproducibility of measurement for total mercury. In order to test the representativity of determination for the whole particulate matter sample, a test of homogeneity was carried out as well: total Hg was measured in 10 different sub-samples of the same sample of suspended particulate matter. The results showed a good homogeneity: mean = 0.29 µg Hg/ g dw, median = 0.29, standard deviation = 0.06 (n = 10). Since all measurements fall within 1.96 standard deviation from the mean, a normal distribution is assumed and the test of homogeneity is considered as satisfactory. A test was conducted to check for the possibility of any interaction between mercury and biological material in which it was analyzed (matrix effect). One sample of suspended particulate matter was homogenized and divided into five identical parts. Sample 1 was prepared for analysis as usual; known quantities of inorganic mercury were added to samples 2 through 5 before mineralization (internal standard: 0.1, 0.15, 0.3 and 0.4 µg). Measured concentrations increase linearly with quantity of mercury added; measured Hg (y) is bound to added Hg (x) by equation $y = 1.006\,x + 0.015$ ($n = 5$; $r^2 = 0.99$; $p < 0.01$), so that no matrix effect had to be taken into account.

Organic Hg was determined by gas chromatography with electron capture detector, as already described in details (Joiris *et al.*, 1991). The organic Hg detected is mainly methylmercury CH_3Hg^+.

Organochlorines (PCBs) were determined by liquid gas chromatography (Shimadzu GC-14A) with capillary column and electron capture detector and "total" lipids after extraction with an hexane/ acetone solution (90-10%) (see descriptions in Delbeke *et al.*, 1990). PCBs were recognized on the chromatograms as a standard mixture Aroclor 1254 and as nine individual congeners. 95% (± 9) of PCB congeners added to suspended particulate matter prior to analysis were recovered.

The determination of chlorophyll a and the organic carbon content in suspended particulate matter were performed by high performance liquid chromatography (HPLC) and coulometric titration, respectively.

Remark: the results discussed here do 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 Mann-Whitney.

RESULTS AND DISCUSSION

Within the suspended particulate matter, a linear relationship was found between suspended particulate matter and particulate organic carbon (POC) concentrations ($y = 3.78\ x + 0.03$; $r^2 = 0.75$; $n = 25$; $p < 0.01$), as well as between POC and chlorophyll a, with a POC/ chlorophyll ratio of 80 ($y = 79\ x + 0.03$; $r^2 = 0.74$; $n = 25$; $p < 0.01$). These data allow to consider that phytoplankton constitutes the most important component of suspended particulate matter. Determination of opal content in the same samples confirms the marine origin of suspended matter, with very limited lithogenic influence only (D. Nürnberg, pers. comm.).

Total mercury concentration, on a dry weight basis, is higher in the Arctic water compared to the Mixed and the Atlantic water masses (Table 1), and this difference between the Arctic and Mixed water masses is statistically confirmed ($p < 0.01$). For the Atlantic water mass, there is one transect only, and no statistical test was applied. In comparison with the North Sea and Antarctic ecosystems (Table 1), the concentration of Hg in suspended particulate matter from the Arctic region is of the same order of magnitude as taht of the heavily polluted North Sea and slightly less than the Antarctic. Such a direct comparison of concentrations (in fresh or dry weight or on the basis of carbon content) is however misleading: data should first be normalized before any discussion; this is why the main factor(s) affecting the transfer and accumulation of the stable residues should be identified first. A negative correlation is observed between the mercury concentration and the concentration of particulate organic carbon, becoming linear on logarithmic scales (Figure 2). The high correlation coefficient for the Arctic and the Mixed water masses respectively, suggest that the concentration of suspended particulate matter in seawater is the main factor explaining the variability of total mercury measurements. Irmer *et al.* (1985) made a similar observation: a negative correlation between phytoplankton biomass and mercury content of suspended particulate matter. Such observations reflect the existence of a direct contamination from water to particulate matter, basically to be understood as an adsorption phenomenon (see further: PCBs). Similar correlations are observed between total mercury and particulate matter, and chlorophyll a, with r^2 ranging between 0.65 and 0.82 (all $p < 0.05$) for the different regression curves.

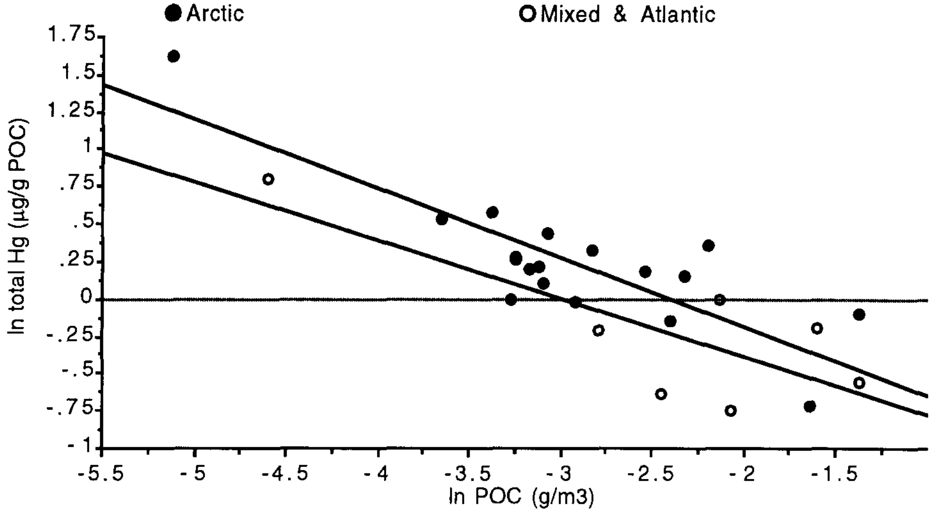

Figure 2. Correlation between total mercury and particulate organic carbon (POC) concentrations in suspended particulate matter (logarithms):
Arctic: $y= -0.464\ x -1.116$; r^2: 0.695; $p < 0.01$
Mixed and Atlantic: $y= -0.389x -1.17$; r^2: 0.624; $p < 0.05$

Taking into account the concentration of suspended particulate matter, the data must be normalized as total load per seawater volume (µg total Hg/ m^3), by multiplying the total mercury level per unit of particulate matter present per seawater. No difference than appears to exist between the Arctic and mixed water (Table 1, right column; $p > 0.10$). Total mercury in Atlantic water with a low mercury concentration on a dry weight basis, becomes very high compared with the others transects. Comparing with data obtained by the same team and techniques, the mercury concentration per cubic meter in the North Sea (Table 1) is strikingly higher than in polar regions, but the low concentration of suspended particulate

Table 1. Median total and methylmercury concentrations in suspended particulate matter expressed in different units (dry weight and per seawater volume) for different regions (note different units)

	total Hg					MeHg		
Water mass	*n*	µg/ g dw	ref	µg/m3	ref	*n*	ng/ gdw	ref
Arctic	*19*	0.30	a	0.05	a	*12*	4.0	a
mixed	*8*	0.17	a	0.05	a	*3*	4.0	a
Atlantic	*1*	0.18	a	0.17	a			
North Sea	*8*	0.16	b	2.20	c			
	-	0.14	d					
Antarctic	*22*	0.51	e	0.30	e			

a: this study; b: Decadt, 1986; c: Delbeke & Joiris, 1984; d: Van Alsoney et al., 1989; e: Joiris & Holsbeek, unpublished.

matter in polar regions (Gordon and Cranford, 1985, Joiris and Overloop, 1991) is the reason for the high value of mercury concentration expressed per dry weight.

Mercury in suspended particulate matter is mainly inorganic, MeHg represent less than 2%. This result confirms observations by Gadner *et al.* (1978) and Topping and Davies (1981). No significant difference is found between the Arctic and mixed water masses on dry weight and lipid basis ($p > 0.05$). The median values for all region are 4 ng MeHg/g dry weight and 285 ng MeHg/g lipid weight (Table 1).

The identification of PCB residues was based on two types of standardization: comparison with the standard mixture Aroclor 1254 (close to the PCB pattern found in marine samples), and comparison with nine congeners: IUPAC nrs 52, 101, 118, 153, 138, 156, 180, 170, 194. For both water masses, these congeners account for 32% of 'total' PCBs. There was a similarity in PCB pattern when visually comparing the chromatograms of particulate matter samples with the standard Aroclor 1254, confirmed by comparing the mean relative contribution of the most important congeners 101 to 170 in suspended particulate matter with Aroclor 1254 versus 1260 (Table 2). Moreover, there is a strong relationship between the concentration of sum of nine congeners and 'total' PCBs (as Aroclor 1254) on one hand and the most important congeners considered individually and 'total' PCBs, on the other hand (Table 3), reflecting the absence of important heterogeneity in the PCBs patterns of the various samples.

Table 2. Relative mean contribution (expressed in % of the sum of congeners) of five individual congeners in suspended particulate matter and the standard mixtures Aroclor 1254 and 1260.

Congener (IUPAC nr)	Particulate matter *(n= 24)*	Aroclor 1254	Aroclor 1260
101	21	26	8
118	18	18	2
138	17	18	17
153	23	12	23
156	3	5	5
170	4	2	9

Table 3. Correlation between 'total' PCBs (expressed as Arochlor 1254), sum of congeners and individual congeners in suspended particulate matter*; n = 24

	Correlation coefficient (r)					
	Σ cong	101	118	138	153	156
'total' PCBs	0.94	0.83	0.83	0.89	0.80	0.82

* Correlation coefficients based on logarithmic (ln) transformations

Σ cong: sum of PCB congeners 52, 101, 118, 138, 153, 156, 170, 180 and 194

On a dry weight basis, there is no significant difference between Arctic and mixed water masses ($p > 0.05$). The contamination of the Atlantic sample is of the same order of magnitude (Table 5). As for Hg (see higher), a negative correlation exists between PCBs concentration and amount of particulate organic carbon (Figure 3). This relationship has already been noted in the North Sea (Delbeke and Joiris, 1988) and the Antarctic (Joiris and Overloop, 1991), and also during laboratory studies (Biggs *et al.*, 1980; Brown *et al.*, 1982). The same pattern is observed when the particulate is used, or chlorophyll a (r^2 between 0.65 and 0.92; all $p < 0.05$). Taking this effect into account, the data should be expressed per volume

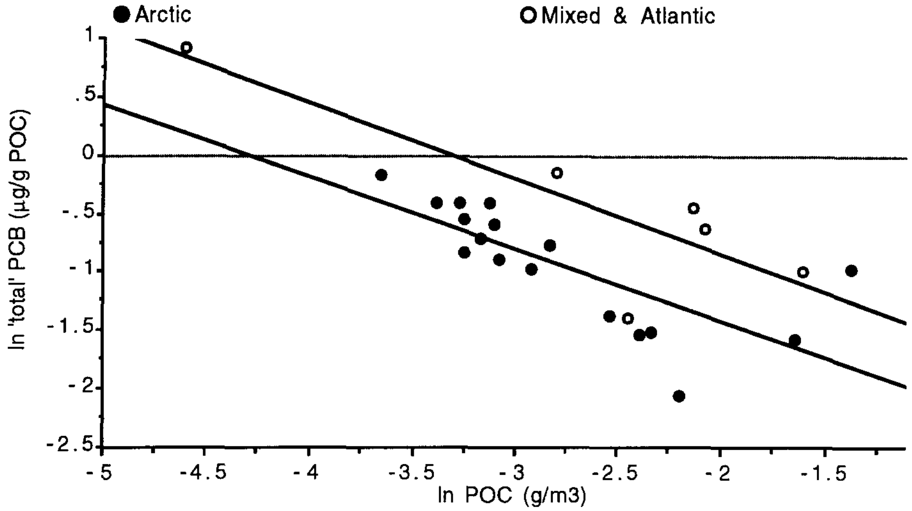

Figure 3. Correlation between 'total' PCBs and particulate organic carbon (POC) concentrations in suspended particulate matter (logarithms):
Arctic: $y = -0.62 x - 2.66$, r^2: 0.559; $p < 0.01$
Mixed and Atlantic: $y = -0.645 x - 2.133$, r^2: 0.722; $p < 0.05$

seawater.The PCB level per cubic water in the Arctic is lower (twice) than theMixed water ($p < 0.05$), while the Atlantic water mass with the lowest concentration of PCBs per dry weight becomes the highest per cubic meter (Table 4).

The existence of a positive relationship between PCB levels and lipid contents of suspended particulate matter (Figure 4) indicates that PCB accumulation mechanisms for suspended particulate matter is more than just adsorption on the surface and that absorption and partitioning into the cell constituents (lipids) also play an important role. Both mechanisms of adsorption and absorption influence the partitioning of PCBs between suspended particulate matter (phytoplankton) and surrounding water. The same conclusion was noted by Bruggeman (1982), Duursma *et al.,* (1986, 1989), Delbeke *et al.,* (1990), Joiris and Overloop (1991).

Table 4. Median 'total' PCBs contamination of particulate matter expressed as Aroclor 1254 in different units (dry weight; lipid weight; per seawater volume) for different water masses

water mass	ref	ng/ g dw	*n*	µg/ g lw	*n*	µg/ m3	*n*
Arctic	a	110	*18*	7.09	*18*	22	*18*
mixed	a	157	*5*	7.50	*5*	52	*5*
Atlantic	a	81	*1*	7.61	*1*	74	*1*
North Sea*	b	675	*20*	118.0	*20*	8800	*20*
Antarctic	c	630	*32*	16.3	*35*	1180	*22*
Canadian Arctic*	d	26	*4*	0.12	4	4.3	*4*

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

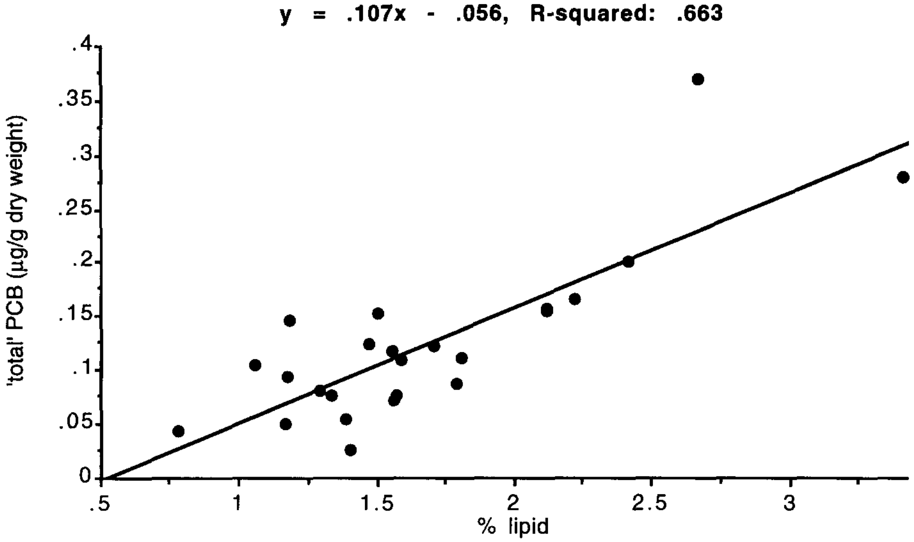

Figure 4. Correlation between 'total' PCBs and lipid content (g/100 g dry weight) in suspended particulate matter; $p < 0.001$

In order to compare the concentration of stable residues in suspended particulate matter between different regions and water masses, it is necessary to identify the main contamination mechanisms, e.g. by expressing the results in different units. The comparison leads to the conclusion that the accumulation of mercury and PCBs in particulate matter is mainly caused by adsorption. One must therefore consider the concentration of suspended particulate matter when evaluating mercury and PCBs, by presenting the result by volume load. Moreover, the existence of a relationship between PCBs and lipid levels of suspended particulate matter indicates that the PCB accumulation mechanisms for suspended matter is more than just adsorption on the surface, and absorption and partitioning into lipids are very important. After normalization for the amount of particulate matter present in the different water masses (data expressed per m^3), the Arctic zones show clearly lower concentrations of Hg and PCBs not only than Atlantic water or the North Sea, but also than the Antarctic: Hg - mainly inorganic - level is 80 times lower in the Arctic than the North Sea, and 6 times lower than in the Antarctic. PCBs contamination is 500 times lower than in the Antarctic, and 4000 times lower than in the North Sea. Hence, the Arctic can be proposed as close to pristine for Hg levels, as already concluded from the study of pelagic fish contamination (Joiris *et al.*, 1995).

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REFERENCES

Biggs D C, Powers C D, Rowland R G, O'Connors H B, Wurster C F (1980) Uptake of polychlorinated biphenyls by natural plankton assemblages: Field and laboratory determination of ^{14}C-PCB particle-water index of sorption. Environ Pollut Ser 22: 101-110

Bruggeman W A (1982) Hydrophobic interactions in the aquatic environment Environ Chem 2B: 83-102

Brown M, Mc Laughin J, O'Connor J, Wyman K (1982):A mathematical model of PCB bioaccumulation in plankton. Ecol Model 15: 29-47

Decadt G (1986) Contribution to the Study of the Biogeochemical Cycle of Mercury in the Southern Bight of the North Sea. PhD thesis. Vrije Univ Brussel. Belgium.

Delbeke K, Joiris C (1984) Transfer mechanisms of organochlorine residues and mercury in the coastal zone of the North Sea. Symposium: "Contaminant fluxes through the coastal zone". Nantes, France:14-16

Delbeke K, Joiris C (1988) Accumulation mechanism and geographical distribution of PCB's in the North Sea. Oceanis 14: 399-410

Delbeke K, Joiris C, Bossicart M (1990) Organochlorines in different fractions of sediments and in different planktonic compartments of the Belgian continental shelf and the Scheldt estuary. Environ Pollut 66: 325-349

Duursma EK, Nieuwenhuize J, Hillebrand MTH (1986) Partitioning of organochlorines between water, particulate matter and some organisms in estuarine and marine systems of the Netherland. Neth J Sea Res 20: 239-251.

Duursma EK, Nieuwenhuize J, Liere JM (1989) Polychlorinated biphenyls equilibria in an estuarine systems. Sci Tot Environ 79: 141-155

Gadner W S, Kendall D R, Odem R R,Windons H L, Stephens JS (1978) The distribution of methylmercury in a contaminated salt marsh ecosystem. Environ Pollut 15: 243-251

Gordon DC, Grandford P (1985):Detailed distribution of disolved and particulate organic matter in the Arctic Ocean and comparison with other regions. Deep-sea Res 32: 1221-1232

Hargrave BT, Harding GC, Vass WP, Erickson PE, Fowler BR, Scott V (1992) Organochlorine pesticides and polychlorinated biphenyls in the Arctic Ocean food web. Arch Environ Contam Toxicol 22: 41-54

Irmer U, Knauth H, Weiler K (1985) Formation of particulate suspended matter and its influence on bounding and distribution of ecotoxic heavy metals in the tidal influenced Elbe River. Vom Wasser 65: 37-61

Joiris CR, Holsbeek L, Bouquegneau JM, Bossicart M (1991) Mercury contamination of the harbour porpoise *Phocoena phocoena* and other cetaceans from the North Sea and the Kattegat. Water, Air Soil Pollu 56: 283-293

Joiris CR, Overloop W (1991) PCBs and organochlorine pesticides in phytoplankton and zooplankton in the Indian sector of the Southern Ocean. Antar Sci 3: 371-377

Joiris CR, Ali BI, Holsbeek L, Tapia G (1995) Total and organic mercury in Barents Sea pelagic fish. Bull Environ Contam Toxicol in press

Mackay D, Wania F (1993) Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions. Ambio, 22: 10-18

Patterson CC, Settle D, Glover B (1976) Analysis of lead in polluted coastal seawater. Mar Chem 4: 305-306

Topping G, Davies IM (1981) Methylmercury production in the marine water column. Nature 290: 243-244

Van Alsenoy V, Van Put A, Bernard P, Van Grieken R (1989) Chemical characterization of suspensions and sediments in the North Sea and Scheldt estuary. In: G. Pichot (Ed), Progress Belgian Oceano Res 1989: 351-36