

PCBs and organochlorine pesticides in phytoplankton and zooplankton in the Indian sector of the Southern Ocean

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Abstract: Samples of phyto- and zooplankton were collected in the Indian sector of the Southern Ocean (38–67°S, 18–84°E) and analysed for organochlorine residues (PCBs and pesticides). The PCB concentration in particulate matter (mainly phytoplankton) appeared to be high and similar to that of temperate zones: $0.7 \mu\text{g g}^{-1}$ dry weight. Contamination levels were more constant expressed per water volume than per dry weight, and seven times lower ($1.2 \mu\text{g m}^{-3}$) than in northern temperate zones ($8.8 \mu\text{m}^{-3}$ in the North Sea). The Antarctic ecosystems are thus less contaminated than temperate ones — as expected — but the very low phytoplankton biomass present cause high PCB levels per unit of biomass. These results confirm the necessity of using different systems of units in order to correctly express the contamination levels and to identify the main mechanisms responsible for the accumulation of stable pollutants. PCB levels in netplankton samples (mainly zooplankton) were comparable with phytoplankton on a dry weight basis ($0.7 \mu\text{m}^{-3}$), lower on a lipid weight basis ($5.8 \mu\text{g g}^{-1}$ lw for netplankton, 16.3 for particulate matter) and were much higher per seawater volume ($27.2 \mu\text{g m}^{-3}$ for netplankton, 1.2 for particulate matter). Netplankton contamination is comparable in the Antarctic ($0.35 \mu\text{g g}^{-1}$ dw) and the North Sea (0.70) since zooplankton feeding on phytoplankton has similar levels of contamination in both ecosystems. Lindane, heptachlor epoxide, dieldrin, DDE and DDT were observed in various samples at trace levels. The high DDE/DDT ratio reflects the more recent origin of Antarctic organochlorines.

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Introduction

The discovery of DDT residues in the Antarctic (Sladen *et al.* 1966) provided a first indication of a worldwide distribution of this stable pollutant. Risebrough *et al.* 1976, interpreted their evidence as indicating that atmospheric transport of DDTs and PCBs constitute the most important dispersal route. Since then, other studies have dealt with the geochemical and biochemical behaviour of PCBs and organochlorine pesticides in the open ocean. Concentrations were generally very low in the air and the water (in the range of ppt), but they are widely distributed in the world oceans.

Industrialized countries began to restrict or ban the use of pesticides in the early seventies. In developing countries, especially in the tropical regions of the southern hemisphere, they are however still used on a large scale for agricultural and/or human health purposes (e.g. malaria). However, little information is available on the contamination of the marine biota in the southern hemisphere. Reports on contamination of Antarctic marine organisms concern mainly organisms such as krill (Risebrough 1976, Lukowski 1978a), fish (Subramanian *et al.* 1983), dolphins (Abarnou *et al.* 1985), seals (Hidaka & Tatsukawa 1983) and birds (Risebrough *et al.* 1976, Lukowski 1978b, 1983a, 1983b); no data seem to be available on phytoplankton yet.

We have found it difficult to compare results between studies because of the lack of uniformity in the expression of

the data. There are two aspects to this, first the units used (fresh, dry or lipid weight), and second, the qualitative description of the PCB mixture (complete mixture such as Aroclor 1254 or 1260, or the sum of some selected congeners only). The various approaches make comparisons extremely difficult and indicate an urgent need for standardization to find an acceptable method for reporting PCB contamination which will facilitate comparisons.

In order to describe and understand the pollution and so to be able to predict the evolution of the contamination in marine ecosystems it is necessary to know the main transfer mechanisms of stable pollutants between biological compartments. Results have been gathered in the North Sea ecosystem on PCBs, DDTs and mercury (Delbeke & Joiris 1985, 1988, Delbeke *et al.* 1990). The main conclusions from that study were that contamination of particulate matter by PCBs is caused by adsorption, absorption and partition between water and the phytoplankton intracellular constituents (lipids); one must therefore consider the concentration of suspended matter present when evaluating its PCB levels. Zooplankton was seen to have a comparable contamination level, and was contaminated mainly indirectly, through food intake.

The aim of our study in the Antarctic marine environment was to test the generality of the accumulation mechanisms described above in other environments isolated from direct

local influence of human activities. Using on the one hand a coastal system (close to the Antarctic continent), and on the other hand a pelagic system, where much less is known about bioaccumulation, we could compare the data with temperate zones. Additionally, the determination of contamination of the Antarctic biota will increase the knowledge of basic information needed in order to control the pollution on a global scale.

Materials and methods

From 3 January to 27 February 1987 we participated at the INDIGO 3 cruise of the French R.V. *Marion Dufresne*. The cruise track covered the Indian section of the Antarctic Ocean between 38°S to 67°S and 18°E to 84°E (Fig. 1).

The main water masses were identified from their physico-chemical and biological parameters (water temperature, salinity, dissolved oxygen, chlorophyll). The main frontal systems were positioned as follows, from North to South: Subtropical Convergence between 41°S and 43°S; less pronounced Subantarctic Front at 47°S, and Antarctic Convergence or Polar Front at 50°S; Antarctic Divergence at 66°S (Poisson & Caschetto 1989).

Particulate matter (mainly phytoplankton) was sampled by pumping water from under the surface. Continuous centrifugation for a period of about 24 hours was necessary to obtain sufficient material for determination of PCBs and pesticides. This resulted in 37 samples. Netplankton samples were obtained with a 200 μm mesh size net towed horizontally for a period of 20 min at 2 knots at every station (see Fig. 1).

A sample of 1–20 g fresh weight was homogenized, after addition of water-free Na_2SO_4 in order to obtain a completely pulverized and water-free powder. Lipophilic compounds

were extracted with 100 ml hexane for a period of 10 hours (Soxlet extraction). The hexane was evaporated, the extracted lipids were weighed and redissolved in 5 ml hexane. Clean-up was done in a florisil column (the exact quantity of florisil was determined after standardization). The organochlorine compounds were separated by two successive elutions:

- 100 ml of hexane (PCBs and DDE) and
- 100 ml of hexane-ether 1:1 (other organochlorine residues).

Technical procedure

The organochlorine residues were determined with gas-liquid chromatography (Packard Instruments model 437), capillary column electron capture detection, Shimadzu CR 1A integrator, automatic injection LS607, preset temperature programmes.

Injection: splitless with injector flush after 0.5 min (50 ml $\text{N}_2 \text{ min}^{-1}$); injection volume: 1 μl ; injector temperature 250°C; carrier gas 0.6 bar N_2 ; bypass 20 ml $\text{min}^{-1} \text{N}_2$; column fused silica CPSil 8CB (25 m length; 0.22 mm diameter; 0.12 μm film/thickness); oven temperature programme:

first elution	second elution
90°C: 2 min	90°C: 2 min
90°-180°C: 20°C min^{-1}	90°-180°C: 20°C min^{-1}
180°-190°C: 2°C min^{-1}	180°-190°C: 2°C min^{-1}
190°-220°C: 4°C min^{-1}	190°C: 10 min
220°-270°C: 4°C min^{-1}	190°-220°C: 4°C min^{-1}
270°C: 10 min	220°-270°C: 5°C min^{-1}
	270°C: 15 min

PCBs were recognized on the chromatograms as a standard mixture Aroclor 1254 (13 peaks were used) and as nine individual congeners (Fig. 2).

Results and discussion

PCBs

The identification of PCB residues was based on two types of standardization: firstly, comparison with the standard Aroclor 1254 mixture (close to the PCB pattern found in marine samples), and secondly, comparison with nine of the most "classical" PCB congeners, namely IUPAC nrs 28, 52, 101, 118, 138, 153, 170, 180 and 194 in order of increasing chlorine content (Fig. 2). The chromatograms of the first elution showed peaks comparable to the standard mixtures, although more highly chlorinated PCBs were present in the sample than the 1254 mixture. Such a difference could be explained by the distance from the sources of PCBs, more highly chlorinated congeners being slightly more stable than the less chlorinated ones.

The quantitative evaluation of PCBs constitutes a complex problem, even if most publications do not mention it and tend to avoid the discussion. The first approach makes use of external standardization with an Aroclor 1254 mixture: this

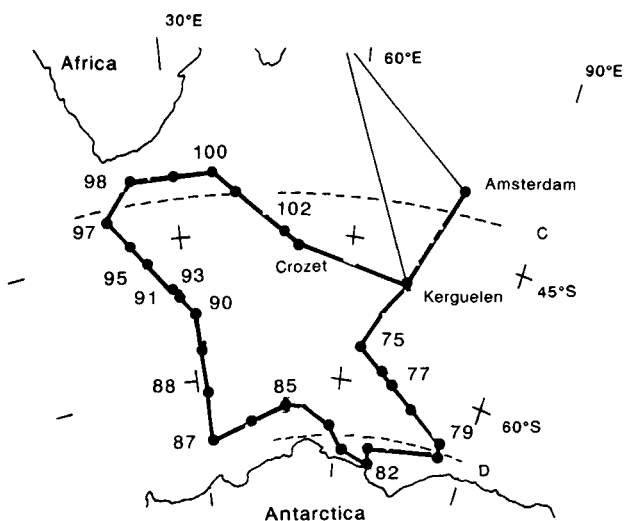


Fig. 1. Cruise track, ship's stations (dots) and location of the sampling stations for particulate matter by continuous centrifugation (thick line) during the INDIGO 3 expedition of R.V. *Marion Dufresne*, 3 January–27 February 1987.

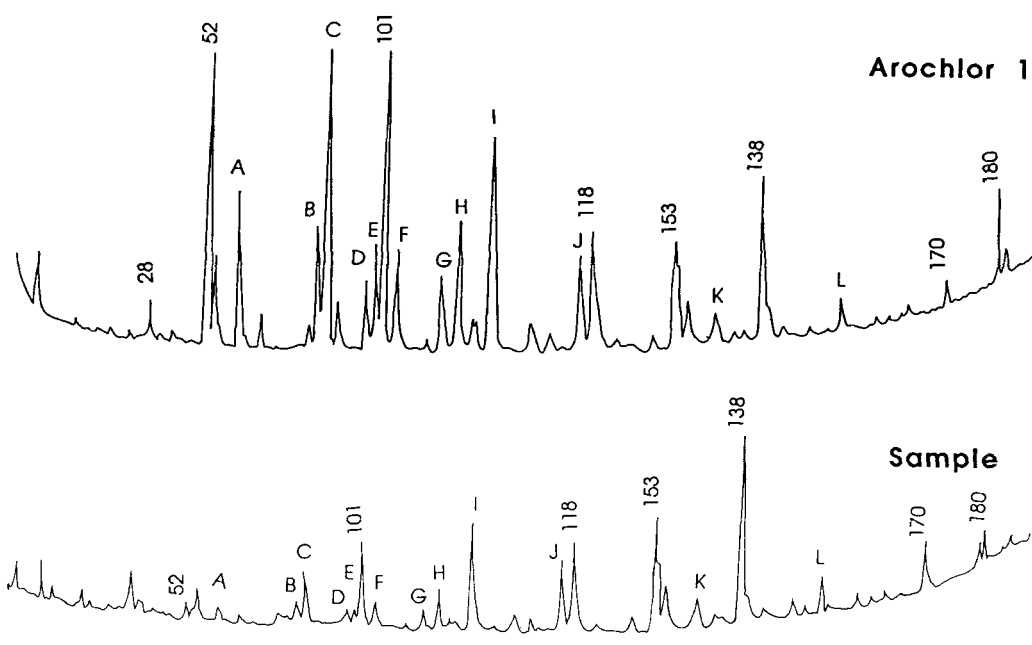


Fig. 2. Chromatograms of PCBs in particulate matter and of the standard mixture Arochlor 1254 (13 peaks: A–L), and nine individual congeners (28–194).

“total” PCB concentration utilizes 13 out of all the detected peaks. Separate congeners can also be used in a second approach: the sum of the nine selected congeners provides an underestimated total PCB load. In our Antarctic samples these congeners account for about 33% of the “total” PCBs for particulate matter and 31% for netplankton: no major qualitative difference could be detected between the two compartments. The relative contribution of the individual congeners to the sum of all congeners was also compared between both compartments (Table I): for the congeners 101 to 170, the differences were relatively small (the levels of the other congeners were too low to be considered here). These results, reflecting a similarity in PCB pattern in the two compartments, allow comparison on the basis of “total” PCBs expressed as Arochlor 1254. Fig. 3 provides a graphical confirmation of these values and shows the strong correlation between the sum of nine congeners and “total” PCBs, as well as between individual congeners and “total” PCBs, both in particulate matter (Fig. 3a) and in netplankton (Fig. 3b).

The PCB levels in netplankton (NP) and particulate matter

(PM) (Tables II & III) are comparable on a dry weight basis ($0.35 \mu\text{g g}^{-1}$ dw for NP, 0.74 for PM or 0.64 without taking into account the high values from the subtropical zone); they are higher in particulate matter on a lipid weight basis ($16.3 \mu\text{g g}^{-1}$ lipid weight in PM, 5.8 in NP), indicating a higher lipid content of netplankton. Per seawater volume, the difference between particulate matter and netplankton contaminations is even more marked ($1.2 \mu\text{g m}^{-3}$ in PM, 27.2 in NP), reflecting the higher abundance of particulate matter than netplankton in Antarctic waters. As stated earlier, the higher homogeneity of results expressed per seawater volume for particulate matter than for netplankton (to be noticed at the level of the ratio between standard deviation and mean) reflects the differences in contamination for zooplankton (through food).

Geographical comparisons

In order to attempt to understand the main transfer mechanism, the PCB concentrations have to be expressed in different systems of units.

Three major zones are compared: subtropical, the zone between the Convergence and Divergence, and south of the Divergence. On a dry weight basis, a slightly higher contamination level seems to exist in the subtropical zone: $1.4 \mu\text{g PCB g}^{-1}$ dry weight compared with 0.7 in the two other zones (see Fig. 4, Table II). When the data are expressed per volume seawater, by multiplying the PCB level per unit of biomass by the amount of biomass present per volume seawater (Fig. 4, Table I), however, no difference appears to exist between the three zones. Mean PCB concentration is $1.2 \mu\text{g m}^{-3}$ for the whole region. These observations are confirmed by application of the non-parametric Kruskal-

Table I. Relative mean contribution (expressed in %) of five individual congeners to the sum of nine congeners in particulate matter, netplankton and the standard mixture Arochlor 1254.

Congener (IUPAC nr)	Particulate matter ($n = 35$)		Netplankton ($n = 14$)		Arochlor 1254
	\bar{x}	sd	\bar{x}	sd	
101	17	7.4	17	6.1	26
118	15	8	15	5.2	18
138	30	8.4	18	6	18
153	15	5.6	12	4.7	12
170	9	5.3	7	2.4	3

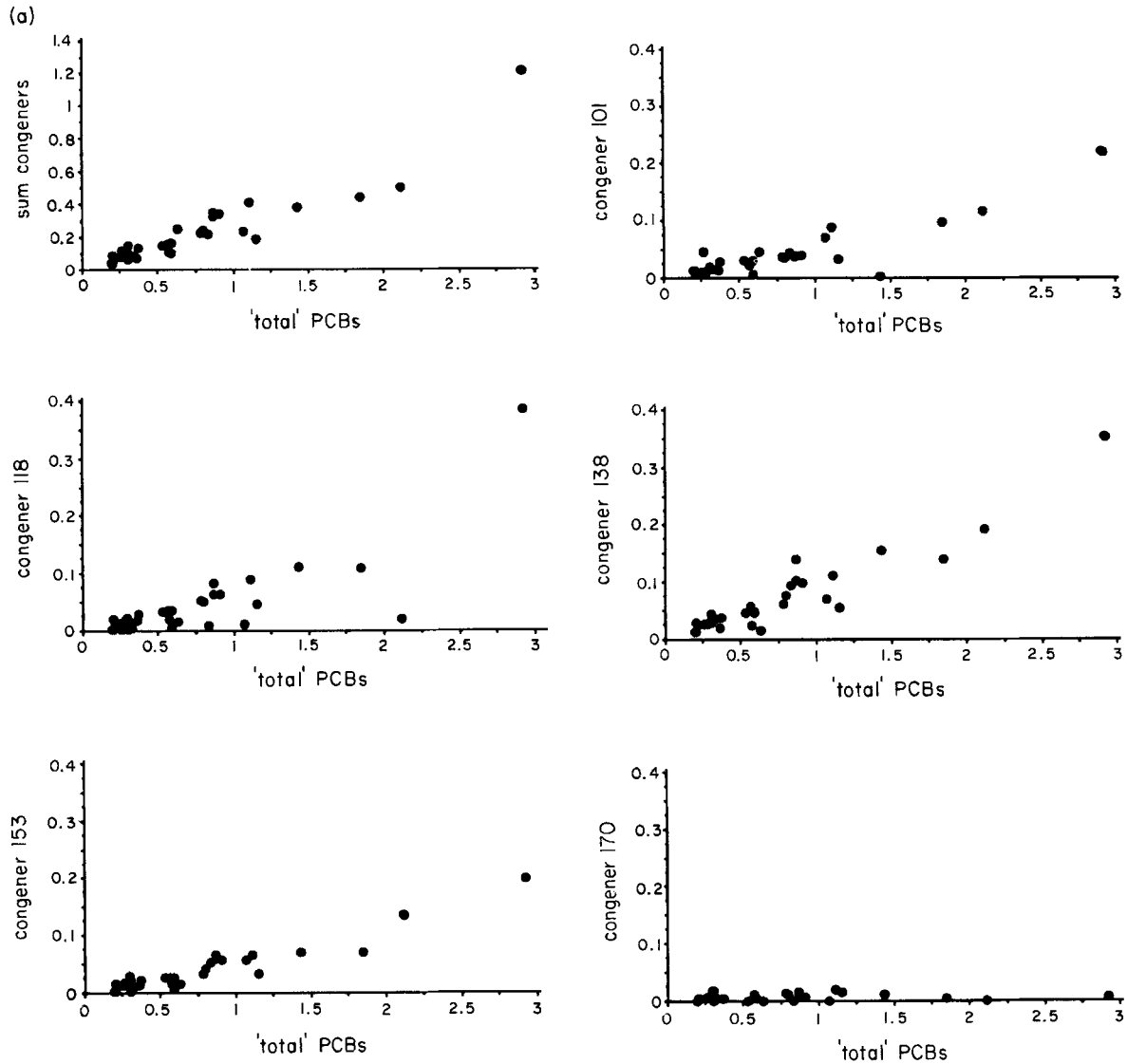


Fig. 3. Correlation between the sum of nine congeners and individual congeners. a. "total" PCBs (as Aroclor 1254) in particulate matter.

Wallis test. No significant difference was detected between zones, but the H value is much lower for the results expressed per m^3 , which reflects the greater homogeneity of this series.

In a comparison with the North Sea ecosystem (Table II), the results indicate a comparable PCB level when expressed per dry weight: the observed difference was not significant at the $p=0.05$ level in a Mann-Whitney test. Per volume water, the contamination of the Antarctic samples is less variable than in the other units (see Fig. 4, Table II) and lower than in the North Sea. These findings reflect again the fact that the most important mechanism for particulate matter contamination are adsorption, absorption and partition.

As a whole (per volume seawater), Antarctica is less contaminated than temperate regions — as expected — but the lower biomass levels cause a high PCB concentration per unit of biomass.

Netplankton consisted mainly of zooplankton, but sometimes included phytoplankton. No difference appeared

when comparing PCB concentrations on a dry weight basis in the three zones (Table III): $0.37 \mu\text{g g}^{-1}$ dry weight, mean value for the whole region, 0.37, 0.38 and 0.30 for the three zones. Expressed per volume seawater, differences appeared between the three zones: 0.01 for the subtropical region; 0.04 for the intermediate region and $0.001 \mu\text{g m}^{-3}$ south of the Divergence, with a mean value for the whole region of $0.03 \mu\text{g m}^{-3}$. A Kruskal-Wallis test confirmed that the differences between zones were not significant.

The PCB levels were of the same order of magnitude in the Antarctic netplankton and the North Sea zooplankton on a dry weight basis (Table III), and no significant difference appeared in a Mann-Whitney test.

Organochlorine pesticides

The level of organochlorine pesticides in netplankton was generally low, and in many samples just above the detection

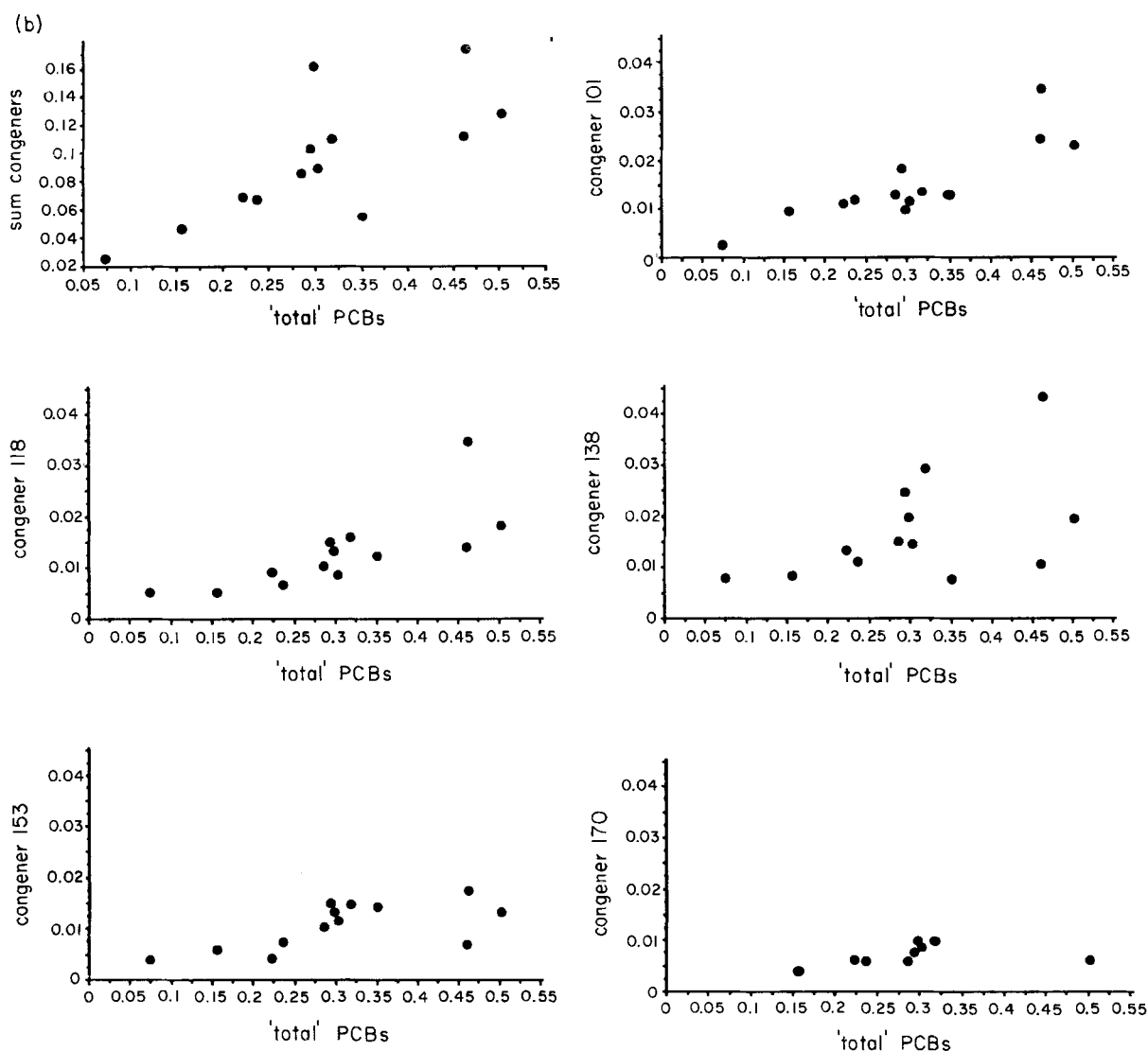


Fig. 3. Correlation between the sum of nine congeners and individual congeners. **b.** in netplankton ($\mu\text{g g}^{-1}$ dry weight).

limit (trace) or not detected at all. The following pesticides were present in most samples: lindane with average values of 19 ng g^{-1} dry weight and 340 ng g^{-1} lipid weight, heptachlor epoxide 27 and 340, and dieldrin 9 and 153. Heptachlor and aldrin were not detected (Table IV). No geographical differences were noticed.

DDT and DDE were present as traces only or were not detected at all in particulate matter. 50% of the netplankton samples contained very low concentrations of DDT and DDE, with an average of 4 ng DDT g^{-1} dw and 7 ng DDE g^{-1} dw. The DDT to DDE ratio provides useful information on the age of the residues, since DDT is slowly metabolized into the more stable DDE. In our results, it had a mean value of 2.55 and varied between 0 (DDE present, DDT not detected) and 8, within a small series of six positive samples. Such findings are confirmed by the analyses of Antarctic seabirds (Lukowski 1978b, 1983a, 1983b) and dolphins (Abarnou *et al.* 1986), with DDT to DDE ratios

ranging up to 10. In North Sea plankton samples, DDT was never detected: this clear difference reflects the recent use of DDT in southern countries, while in Europe it was significantly reduced or stopped in the seventies.

Conclusions

The PCB contamination of oceanic particulate matter is of the same order of magnitude in the Antarctic waters as in the North Sea when expressed as a concentration per dry weight. One expects, however, Antarctic ecosystems to be much less contaminated than temperate ones, especially the heavily polluted North Sea, since the direct local contamination is extremely limited and the stable pollutants have to be imported from adjacent inhabited zones. In order to understand these high levels, one must consider the contamination mechanisms and express the results in different unit systems: per volume of seawater, the PCB level is seven times lower

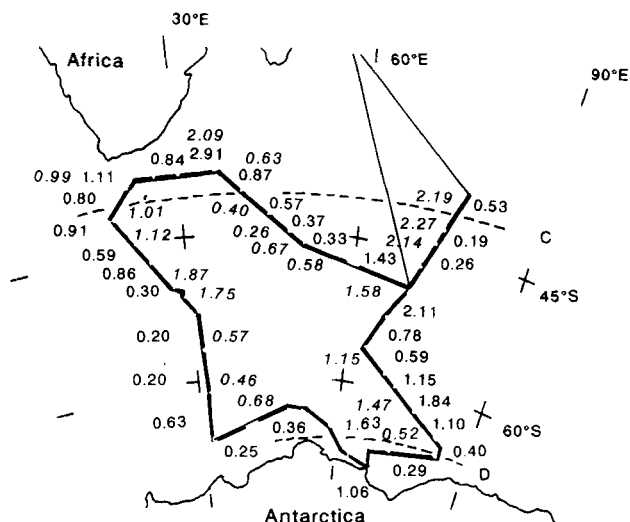


Fig. 4. Geographical distribution of "total" PCBs in particulate matter ($\mu\text{g PCB g}^{-1}$ dry weight: roman figures; $\mu\text{g PCB m}^{-3}$ seawater: italic figures).

in the Antarctic than in the North Sea. This is the figure to be used in order to compare the contamination mechanisms of particulate matter - adsorption, absorption and partition — recognizing that the much lower biomass present in the Antarctic gives similar levels per unit of biomass. The fact that the contamination expressed per lipid weight is lower in Antarctic particulate matter, reflects the latter's higher lipid content. This leads to the paradoxical consequence that, even if the Antarctic ecosystem is six times less contaminated by PCBs than the North Sea, its biological components might be as contaminated or even more contaminated — than in the North Sea.

At the zooplankton level, indeed, the PCB contamination of the Antarctic and North Sea ecosystems are comparable. The presence of organochlorine pesticides: lindane, heptachlor

Table II. Total mean PCB contamination of particulate matter expressed as Aroclor 1254 in different units (dry weight; lipid weight; per seawater volume) for the different zones.

Zone	PCBs								
	ng g ⁻¹ dry weight			µg g ⁻¹ lipid weight			µg m ⁻³		
	x	n	sd	x	n	sd	x	n	sd
Subtropical	1433	4	994	24.6	4	16.6	1.24	3	0.76
Convergence									
to Divergence	677	23	522	15	26	11.2	1.19	17	0.68
South of									
Divergence	678	2	544	10	2	4.1	1.08	2	
Kerguelen (**)	356	3	257	20.7	3	4.9			
Mean	741	32	617	16.3	35	11.6	1.18	22	0.66
North Sea (***)	675	20		118	20		8.8	20	

** Very coastal samples from the Bays of Rhodes and Port aux Français

*** Delbeke & Joiris 1988.

Table III. Total PCB contamination of netplankton (see Table I).

Zone	PCBs								
	ng g ⁻¹ dry weight			µg g ⁻¹ lipid weight			µg m ⁻³		
	x	n	sd	x	n	sd	x	n	sd
Subtropical	370	3	114	6.2	3	1.2	0.01	3	0.007
Convergence to									
Divergence	381	10	332	6.0	10	2.4	0.04	7	0.06
South of									
Divergence	30	1		3.0	1	4.1	0.001	1	
Mean	354	14	295	5.8	14	2.2	0.03	11	0.05
North Sea (**)	700	20		7.0	20		0.02	20	

** Zooplankton (Delbeke & Joiris 1988).

Table IV. Organochlorine pesticides in Antarctic netplankton (see Table II; nd not detected).

Pesticide	n	ng g ⁻¹ dry weight		ng g ⁻¹ lipid weight	
		x	sd	x	sd
lindane	11	19	4	340	7
heptachlor	11	nd		nd	
heptachlor epoxide	11	27	10	340	60
dieldrin	9	9	2	153	20
aldrin	9	nd		nd	
pp'-DDT	6	4	2	99	30
pp'-DDE	9	7	5	115	60

epoxide, dieldrin, DDE and DDT was noticed in various samples at levels varying between traces and low concentration or were not detected. The high DDT/DDE ratio reflects the recent origin of Antarctic organochlorines.

Since the use of organochlorines is still increasing in the southern hemisphere while it is strongly limited or forbidden in the northern countries, one may expect further increases in Antarctic contamination. This suggests an urgent need to improve our knowledge of the levels and the fate of stable pollutants in the southern regions and more especially in the Antarctic.

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