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ACCUMULATION MECHANISMS AND GEOGRAPHICAL DISTRIBUTION OF PCBs IN THE NORTH SEA

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Abstract

PCBs were determined in the main compartments of the North Sea ecosystems: suspended particulate matter, zooplankton, fish, sea birds and sediments.

The main PCB contamination mechanisms for each compartment can be better understood by expressing and comparing results in different units: fresh or dry weight, lipid weight and water volume. Accumulation of PCBs in particulate matter is caused by adsorption and partition between water and body constituents (lipids). Zooplankton is seen to be contaminated indirectly mainly through food intake. For fish, evidence exists indicating the importance of both direct partition and indirect PCB contamination. In sediments, the PCB levels are similar to the ones in suspended matter (on a lipid basis), indicating remobilization of PCBs from the sediments to the water column. Hence sediments can not be considered as a sink for PCB residues, as often hypothesized.

Total PCB concentration is similar in particulate matter, zooplankton and fish (on a dry weight basis), but the PCB levels in seabirds are much higher. PCBs are thus essentially bioaccumulated at the level of the seabirds Particulate matter and sediments are of great quantitative importance for the PCB stock.

The PCB levels in particulate matter, net plankton and zooplankton from different geographical places in the North Sea (51°-60°N) finally allow differently contaminated water masses to be distinguished: 1) high PCB levels in the Belgian coast zone decreasing with increasing distance from the coast (51°-53°N); 2) high PCB levels close to the Dogger Bank (53°-54°N) and 3) low PCB levels in the northern water mass (54°-60°N).

Résumé

Mécanismes d'accumulation et distribution géographique des PCB en mer du Nord

Les teneurs en PCB ont été déterminées dans divers compartiments de l'écosystème "mer du Nord": matière particulaire en suspension (surtout phytoplancton), zooplancton, oiseaux de mer et sédiments.

Pour chaque compartiment, les mécanismes de contamination peuvent être compris en comparant les résultats exprimés en différentes unités: par poids frais ou sec, par poids de lipides et par volume d'eau. Dans la matière particulaire, le prélèvement des PCB se fait directement à partir de l'eau, par adsorption et partition vers les lipides. Le zooplancton est contaminé indirectement par sa nourriture. Pour les poissons, il existe des évidences en faveur à la fois d'une contamination directe et indirecte. Les teneurs dans les sédiments, exprimées par poids de lipides, sont comparables à celles de la

matière en suspension, ce qui indique que les PCB sont remobilisés à partir des sédiments lors de l'oxydation des matières organiques (particulièrement de lipides), et donc qu'ils ne constituent pas le piège ("sink") que l'on suppose souvent.

Les niveaux de contamination, exprimés par poids sec, sont comparables dans la matière particulaire, le zooplancton et les poissons. Ils sont plus élevés chez les oiseaux (bioaccumulation).

En valeur absolue (quantités par m^2), les stocks principaux de PCB sont la matière particulaire et les sédiments.

La comparaison des teneurs dans différentes zones de la mer du Nord (exprimées en différentes unités) et dans divers compartiments (matière particulaire, zooplancton) permet de distinguer des masses d'eau à contamination différente: niveaux élevés dans la zone côtière belge (51°-53°N), décroissant vers le large (54°-60°N), avec une nette augmentation vers le Doggerbank (53°-54°N).

INTRODUCTION

The behaviour, distribution and accumulation of stable pollutants in aquatic ecosystems have been the subject of many studies. Three main basic mechanisms are generally involved:

1. Adsorption on the surface of particles, organisms, or more specifically certain organs such as gills, etc., often described by Freundlich adsorption isotherms. For sediments, the adsorption coefficient has been related to the size of the particles and their organic carbon content (Simmons *et al.*, 1980).
2. Also compounds can be absorbed by organisms and partitioned into the body constituents (e.g. as a function of their liposolubility). An equilibrium between the concentrations in the water on the one hand and the particles and organisms on the other hand can be reached through both adsorption and absorption, sometimes called "biosorption" (Bruggeman, 1982). These equilibrium concentrations have been related to the physicochemical properties of the compounds, such as the octanol-water partition coefficient (K_{ow}) (Veith *et al.*, 1980; Kanazawi, 1983).
3. Besides these two direct contamination routes through the water, indirect contamination through food intake can be important as well. This aspect, being dependent on physiological and biological characteristics such as feeding behaviour (diet, feeding rate), contamination of the food, assimilation efficiency and elimination rate, has also been related to the physicochemical properties of the compounds (e.g. liposolubility).

PCBs, due to their high liposolubility, are to a great extent adsorbed and absorbed by the particles and organisms of aquatic ecosystems, partition coefficients often being higher than 10^4 (Duursma *et al.*, 1986).

Our aim in this study is to describe and understand the accumulation mechanisms of PCBs in the main compartments of the North Sea ecosystem: suspended matter (mainly phytoplankton), zooplankton, fish, seabirds and sediments. We intend to add results on sea mammals later. No measurements were made in the water, due to the very low concentrations encountered and the presence of very small particles in the filtrate making interpretation difficult.

Our approach is made in three complementary stages:

1. Comparison of PCB levels in different compartments;
2. Comparison of PCB levels in different regions and periods;
3. Interpretation of the observed phenomena by integrating results from existing laboratory experiments (Bouquegneau *et al.*, 1985).

MATERIAL AND METHODS

Suspended matter was collected mainly through pumping seawater at a depth of 3 m and by continuous centrifugation. Samples were collected throughout North Sea (51°N-56°N) during some cruises (Fig. 1) and more often in the Belgian coastal zone. Net plankton > 50 µm collected in April-May 1985 consisted mainly of diatoms and some zooplankton inactive in that period (Daro, comm. pers.). Fish (muscle tissue) from the by-catch were sampled when possible. Tissues of seabirds, found dead on the beach, were collected. Sediments were collected with a stainless

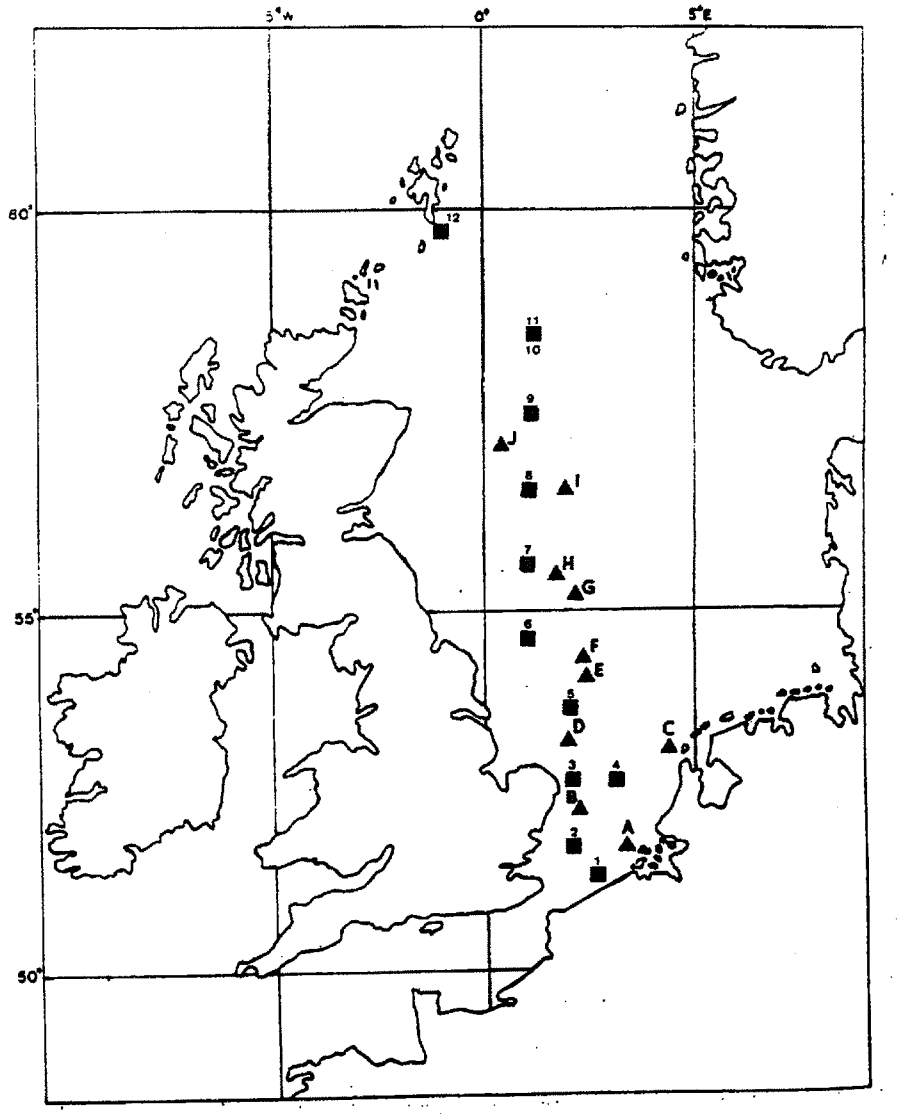
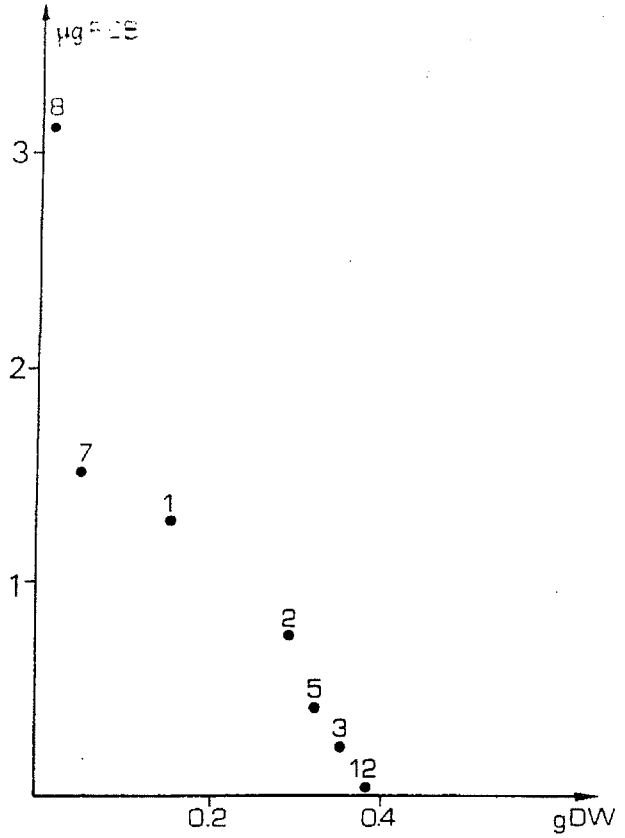


Fig. 1 - Sampling stations during North Sea cruises in September 1983 (triangles) and April-May (squares).

- *Carte des stations d'échantillonnage en mer du Nord en septembre 1983 (triangles) et en avril-mai (carrés).*



Fig; 2 - Relation between PCB levels of net plankton > µm (µg.g^{-1} dry weight) and particle concentration (g dry weight m^{-3}) of net plankton > 50 µm sampled at different stations in the North Sea (51-60°N) in April-May 1985.

- *Relation entre la teneur en PCB dans le plancton > 50 µm (µg.g^{-1} poids sec) et la concentration en particules (g poids sec.m^{-3}) pour l'ensemble de la mer du Nord (51-60°N) en avril-mai 1985.*

steel "Box corer" and by subsequent subsampling to a depth of ± 30 cm. All samples were immediately deep-frozen on board, the PCB levels being analyzed later in the laboratory with gas chromatography equipped with an electron capture detector. The results are expressed as Arochlor 1254 by means of external standardization (for more details, see Delbeke,1986).

RESULTS AND DISCUSSION

PCB levels in suspended matter, sampled in the Belgian coastal zone during different periods, show important fluctuations, especially when the results are expressed in dry weight. The amount of PCBs associated with suspended matter within a given water volume is much more constant (about 6 µg.m^{-3}, excluding one abnormal value) (Table 1). A similar biosorptive equilibrium exists for plankton >50 µm (mainly diatoms), resulting in a negative ratio between the PCB concentration (expressed as µg PCB.g^{-1} dry weight) and the amount of particulate material in the seawater (Fig. 2). This relationship between PCB concentration and particles concentration has already been noted in the laboratory (Biggs *et al.*, 1980) and in a natural ecosystem (Duinker, 1980).

The existence of a relationship between PCB and lipid levels of suspended matter (Fig. 3) indicates furthermore that the PCB accumulation mechanims for suspended matter is more than just adsorption on the sur-

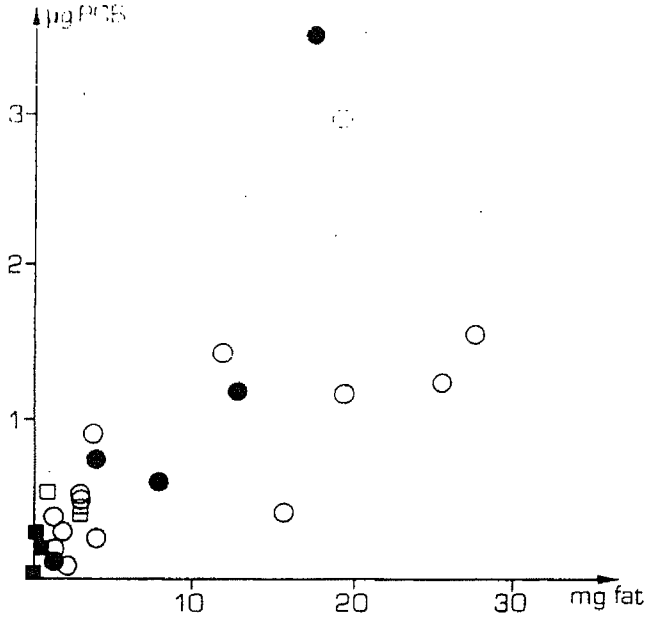


Fig.3 - Relation between PCB and lipid levels of particulate matter (dry weight) collected during cruises in the Belgian coastal zone of the North Sea (open figures) and the English Channel (closed figures)(black and white circles: collected by centrifugation); black and white squares: collected in sediment traps).

- *Relation entre la teneur en PCB et en lipides dans la matière particulaire (en poids sec) dans la zone côtière belge (symboles ouverts) et dans la Manche (symboles fermés) (cercles: récoltés par centrifugation; carrés: par pièges à sédiments).*

face, and that absorption and partition into cell constituents (the lipids) also play an important role. Both mechanisms of adsorption and absorption influence the partitioning of PCBs between suspended matter (phytoplankton) and the surrounding water. The absence of important differences in the contamination of particles of different sizes is another indication fully corroborating this interpretation: 0.4 $\mu g.g^{-1}$ dry weight for suspended matter (almost entirely < 50 µ m) and 0.9 for net plankton > 50 µ m.

The mean PCB level in the sediments of the Belgian coastal zone (70 $\mu g.g^{-1}$ lipids) is comparable to the mean PCB level in particulate matter (120 $\mu g.g^{-1}$ lipids). Differences in PCB levels between different sediment samples (different depths and different places) are clearly related to their lipid content (Fig. 4). These two elements suggest remobilization phenomena of PCBs from the sediments to the water column, in association with the degradation of sediment lipid material. Sediments cannot therefore be considered as a sink for PCB residues, as often hypothesized in the literature.

In zooplankton (>250 µm), consisting mainly of copepods, no clear relation could be observed between PCB levels and lipid content (Fig. 5). Accumulation of PCBs in zooplankton is therefore not ruled by simple adsorption/partition mechanisms. Taking into account both the contamination of the food (suspended material) and their grazing rate (Daro, pers. comm.), the results showing, on a lipid basis, a lower concentration in

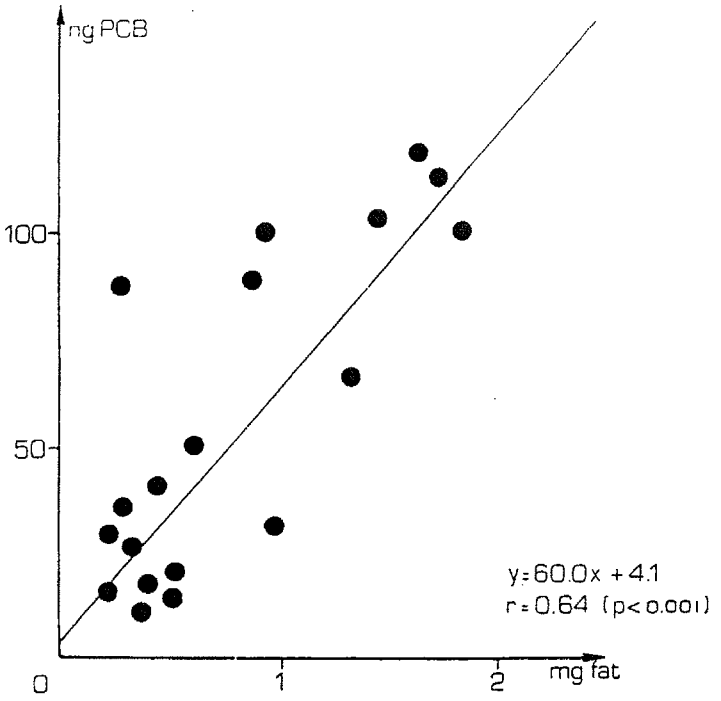


Fig. 4 - Relation between PCB and lipid levels in sediment samples collected in the Belgian coastal zone in 1982 (dry weight).
- *Relation entre teneur en PCB et lipides dans les sédiments de la zone côtière belge, 1982 (en poids sec).*

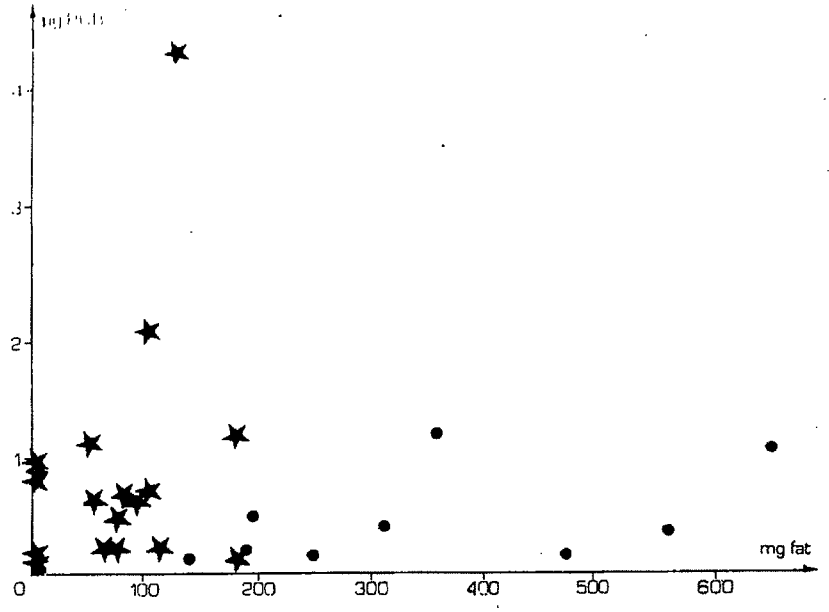


Fig. 5 - Relation between PCB and lipid levels of zooplankton from the Belgian coastal zone (stars) and the northern North Sea (circles) (dry weight).
- *Relation entre la teneur en PCB et en lipides dans le zooplancton de la zone côtière belge (étoiles) et le reste de la mer du Nord (cercles) (poids sec).*

zooplankton (7 $\mu g.g^{-1}$) than in particulate matter (120 $\mu g.g^{-1}$) are quantitatively consistent with an important uptake of PCBs through feeding together with a further "dilution" into autogenically formed, PCB-free, zooplankton lipids. Evidence for the importance of indirect contamination of zooplankton by PCBs is provided by laboratory experiments as well (Wyman & O'Connor, 1980; Brown *et al.*, 1982).

The PCB levels in fish from the Belgian coastal zone are clearly related to their lipid content (Fig. 6). These data concern various species (Delbeke, 1986; Vandamme & Baeteman, 1982; Vandamme, 1984): commercial and by-catch, pelagic and demersal, herbivorous and carnivorous, of different sizes. This suggests the important role of partitioning (sea water/body lipids) in the accumulation of PCBs by fish. This interpretation agrees with other studies (Schneider, 1982; Boon & Duiker, 1985; Duursma *et al.*, 1986) and with laboratory experiments showing a relation

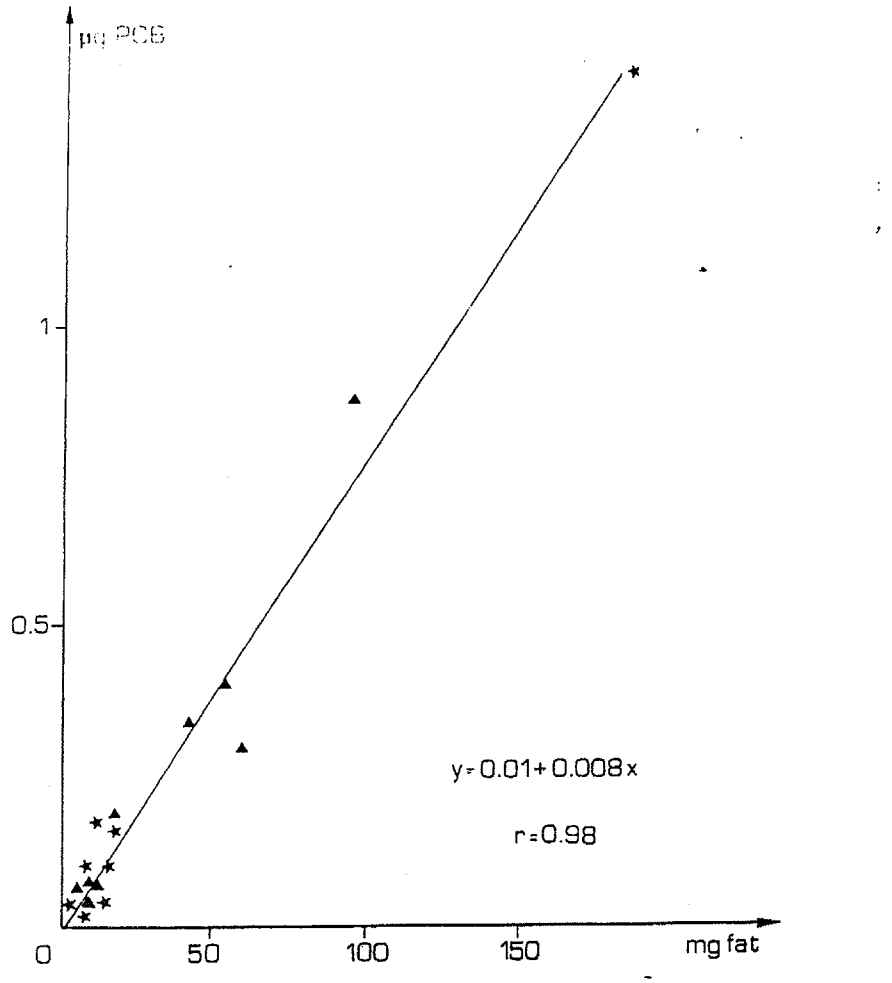


Fig. 6 - Relation between mean PCB and lipid levels in the muscle of different species of fish collected in the Belgian coastal zone of the Southern Bight of the North Sea in 1984 and 1985 (fresh weight). This study : stars; from Vandamme and Baeteman, 1982, 1984: triangles.

- *Relation entre la teneur moyenne en PCB et en lipides dans le muscle de diverses espèces de poissons dans la zone côtière belge en 1984 et 1985 (en poids frais). Cette étude : étoiles; Vandamme et Baeteman, 1982, 1984 : triangles.*

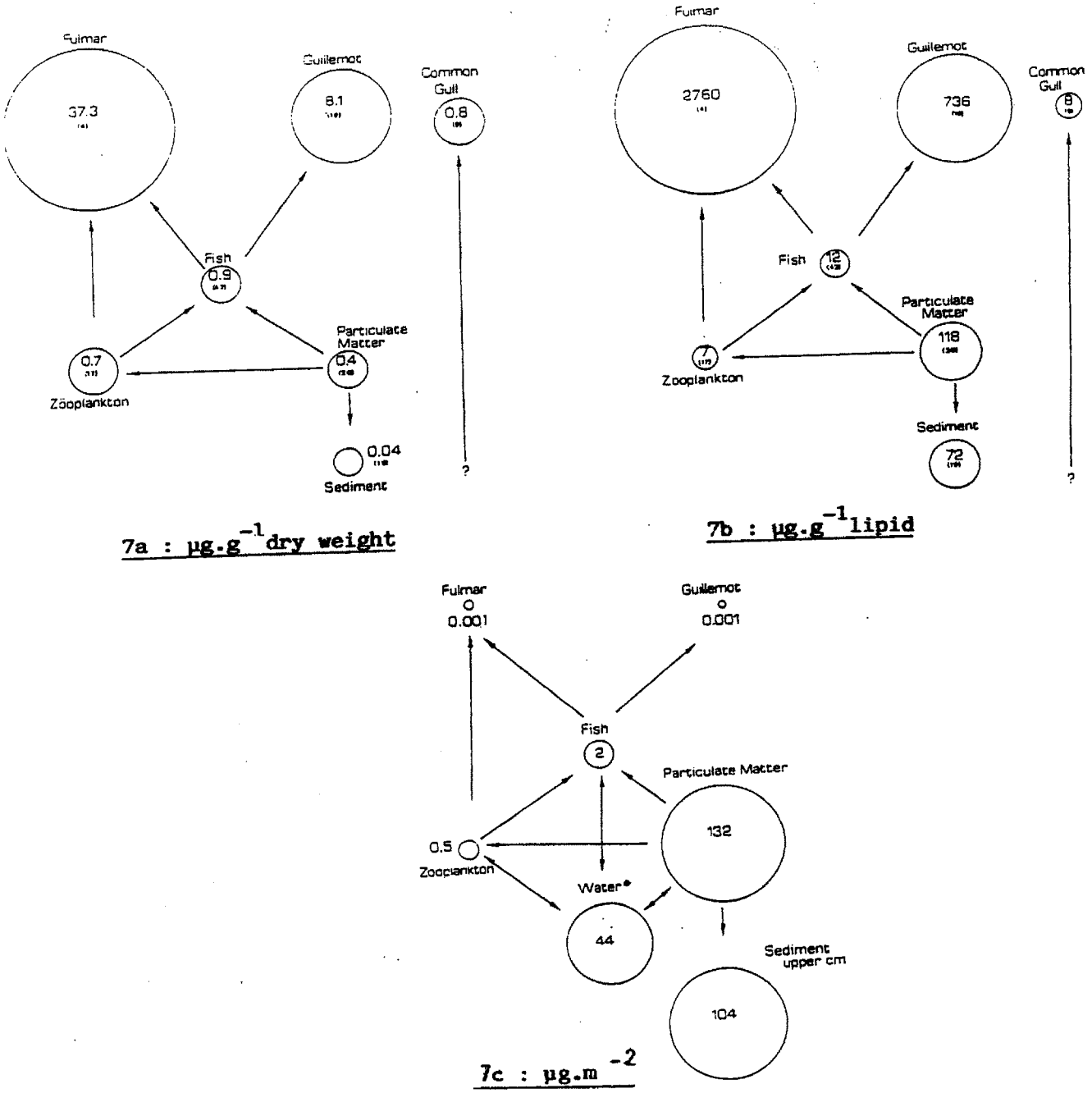


Fig. 7 - PCB levels in the different compartments of the coastal zone of the Southern Bight of the North Sea. Median contamination levels figured by circles. 7a: µg.g^{-1}dry weight; 7b: µg.g^{-1}lipid weight; 7c: µg.m^{-2}.*: Geyer *et al.*, 1984; (*n*), number of samples; biomass figures for particulate matter and zooplankton are obtained from Joiris *et al.*, 1982; for fish recalculated from Yang, 1982 and for seabirds calculated from Joiris, 1983.

- *Synthèse des niveaux de PCB dans les différents compartiments de la zone côtière belge. Les valeurs médianes sont proportionnelles au volume des sphères représentées. 7a : µg.g^{-1} poids sec ; 7b : µg.g^{-1} lipides ; 7c : µg.m^{-2} (c'est-à-dire valeur intégrée sur une colonne d'eau sous 1 m^2). (n): nombre d'échantillons; *: Geyer* et al., *1984; les valeurs de concentration en matériel particulaire (phytoplancton) et en zooplancton proviennent de Joiris* et al., *1982; celles des poissons ont été recalculées à partir de Yang, 1982, et celles des oiseaux de mer à partir de Joiris, 1983.*

between the octanol-water partition coefficient of various chemicals and their bioconcentration factor from water into fish (Verschueren, 1983). Other data, however, indicate the importance of indirect contamination: PCB levels are higher and show a higher amount of highly chlorinated constituents in fish than in suspended matter. On the other hand, an increase in fish contamination as a function of age (length) cannot merely be due to a simple partition mechanism.

In the seabirds , different PCB levels between species (Table 2) are related to differences in feeding habits and/or metabolic capacities of birds (Knight & Walker, 1982).

A comparison of PCB concentrations (on a dry weight or lipid weight basis) between the different compartments (Fig. 7a and 7b) shows no important bioaccumulation between phytoplankton (particulate matter), zooplankton and fish, but an important bioaccumulation by the seabirds .

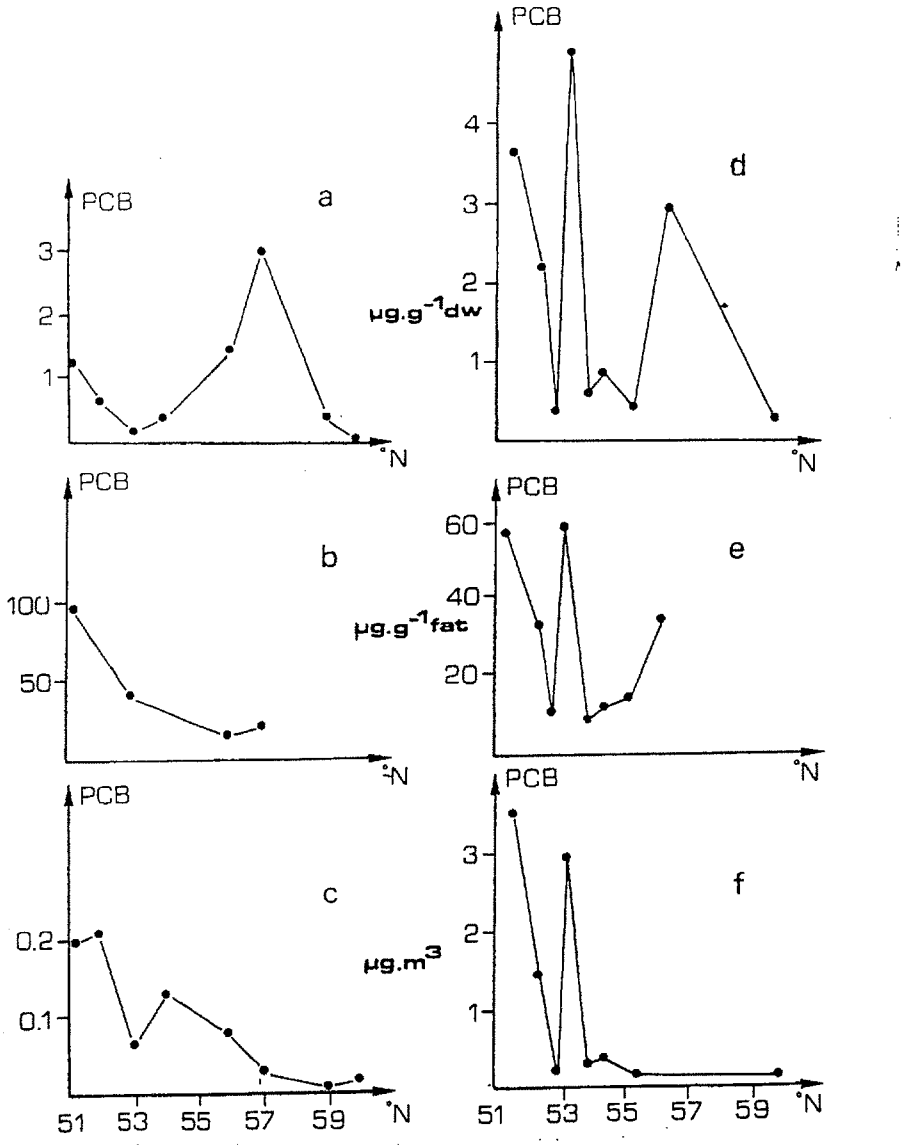


Fig. 8 - Geographical variations in PCB contamination of net plankton (> 50 µm (a, b, C) and of particulate matter collected in the North Sea by centrifugation (d, e, f) in April 1985.

- *Variations géographiques des PCB dans le plancton (>50 µm) (a, b, c) et dans la matière particulaire (d, e, f) de la mer du Nord en avril 1985.*

A comparison of PCB levels associated with each compartment in a given volume of sea water clearly indicates the importance of particulate matter and sediment in the main PCB stocks (Fig. 7c).

In order to compare the PCB contamination of different water masses (or its evolution in time), suspended matter (phytoplankton) can be chosen as representative material, since its contamination is directly dependent on the concentration in sea water. The results then have to be expressed per water volume in order to avoid variations in PCB concentration due to differences in the amount of suspended material. A similar geographical pattern (on a dry weight basis) can be expected for zooplankton, its indirect contamination being dependent on the levels in its food, suspended matter. In the North Sea (51°-60°N : see Fig. 1) differently contaminated water masses have thus been distinguished for suspended matter, net plankton and zooplankton (Figs. 8 and 9):

1. High PCB levels in the Belgian coastal zone, decreasing in the northern direction: such results are consistent with an input of PCBs from the coast and a progressive dilution at increasing distances from the coast.
2. High PCB levels around the Dogger Bank (53°-54°N), possibly related to dumping and the transport of contaminated particles with the current towards the Bank. This abnormal situation is parallel with low zooplankton activities (Daro, pers. comm.) and high fish disease rates (Dethlefsen, 1984). The link between these phenomena deserves further studies.
3. Much lower PCB levels in a northern water mass (54°-60°N) corresponding to different oceanological characteristics (salinity, temperature) and ecological structure (Joris, 1978, 1983).

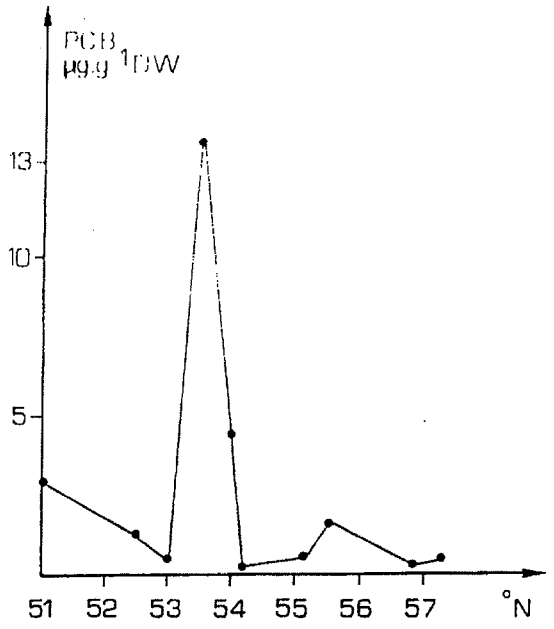


Fig. 9 - Geographical variations in PCB contamination of zooplancton in the North Sea in September 1983 ($\mu g.g^{-1}$ dry weight).

- Variations géographiques des PCB dans le zooplancton de la mer du Nord en septembre 1983 ($\mu g.g^{-1}$ poids sec).

CONCLUSION

In order to identify the main contamination mechanisms for stable pollutants in aquatic ecosystems, it is necessary to express all results in different units: fresh or dry weight, lipid weight and water volume. The comparison leads to the conclusion that the accumulation of PCBs in suspended matter and sediments is caused by adsorption and absorption and a partitioning into lipids. Zooplankton is seen to be mainly contaminated indirectly, through its food. For fish, some results give evidence of a partition mechanism, but other data point to the role of other mechanisms, such as indirect accumulation. In seabirds , the importance of feeding habits and metabolic capacities of the birds is stressed. Bioaccumulation is only evident at the seabird level.

A comparison of contamination between geographical zones and in time must also make use of results expressed in different units.

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