

DISTRIBUTION OF ORGANOCHLORINE RESIDUES BETWEEN DIFFERENT FRACTIONS OF SEDIMENTS AND BETWEEN DIFFERENT PLANKTONIC COMPARTMENTS IN THE SCHELDT ESTUARY AND THE BELGIAN COASTAL ZONE.

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ABSTRACT

PCB levels in sediments (bulk and $< 63\mu m$), suspended matter and zooplankton from the Belgian continental shelf and Scheldt estuary are evaluated in relation to their organic carbon content, lipid content and for sediment also particle size distributions. Geographical and seasonal variations are discussed. A discussion is given on the PCB accumulation mechanisms, considering passive (direct) contamination routes (adsorption- partitioning) and for zooplankton also indirect contamination through food.

1. INTRODUCTION

The ecotoxicological significance of organochlorine residues is a well-known fact since +/- 1960. PCBs, still used in industries (Ascarel), are nowadays, in the Western countries, the most important organochlorine residues to be studied.

The contamination mechanisms of PCBs in marine and estuarine environments have been investigated during the past few years by different research groups. An equilibrium distribution of PCBs between the water and the suspended matter was shown to be based on simple physicochemical adsorption and/or partition mechanisms (f.i. Bruggeman et al., 1985; Duursma et al., 1986, 1989; Delbeke and Joiris, 1988). For the bulk sediments, adsorption on the organic and silt fraction of sediments was demonstrated (Simmons et al., 1980, Duinker et al., 1983). The partitioning of PCBs into the lipid fraction of sediments was furthermore noted during a preliminary investigation of sediments from the Belgian continental shelf

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(Delbeke and Joiris, 1988).

The aim of this study is therefore :

(1) to study the association of PCBs with the different fractions (clay, organic carbon, lipids) of the bulk sediments and of the silt and lutim fractions of the sediments ($< 63\mu m$).

(2) to get a global image of the actual contaminant levels of the sediments from the Belgian continental shelf and Scheldt estuary, considering spatial and temporal variations and

(3) to compare PCB levels between different planktonic compartments and sediments and interpret the results in a more general way.

2. MATERIALS

Samples were collected between February 1986 and March 1988, during different cruises with the R.V. Belgica in the Belgian coastal zone and the Scheldt Estuary (Fig.1). Surface sediments (upper cm) were collected with a stainless steel box corer; suspended matter was collected through pumping of sea water at 3m depth and continuous centrifugation. Zooplankton was sampled on a $250\mu m$ or a $500\mu m$ net with a "high speed" sampler. The fresh samples were immediately deep-frozen, on board.

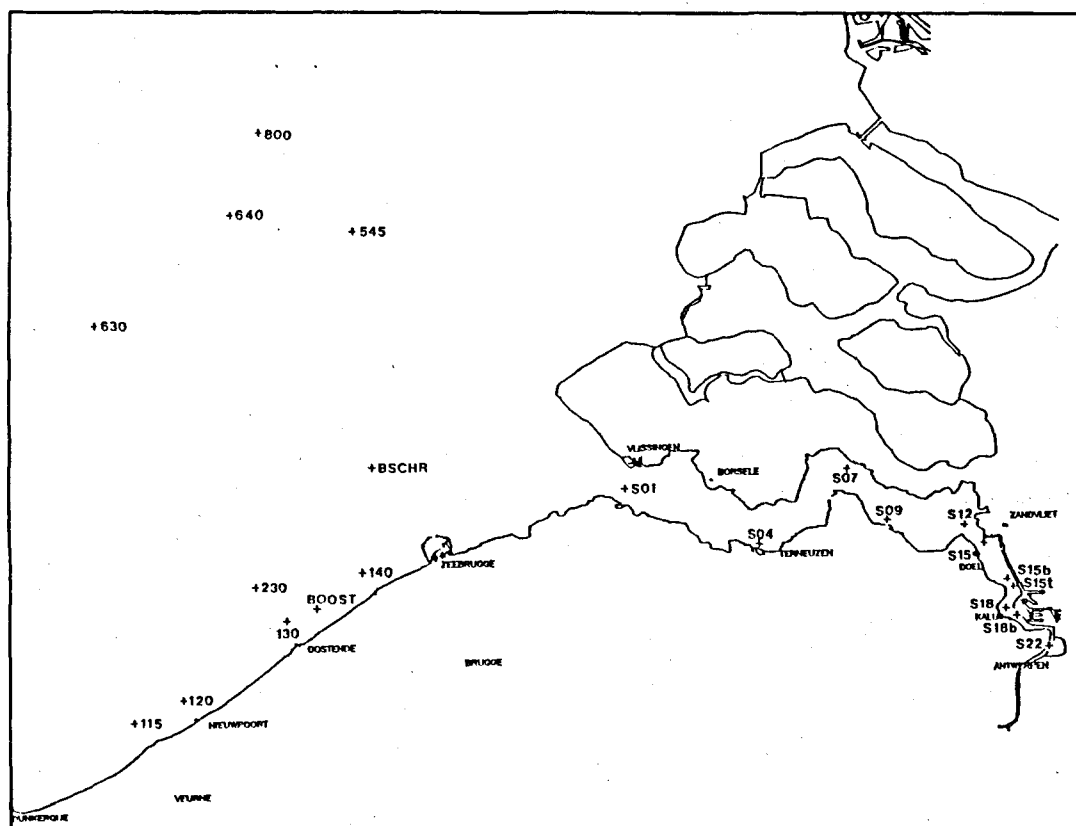


Fig. 1. Sampling stations and areas during different campaigns between 1986 and 1988

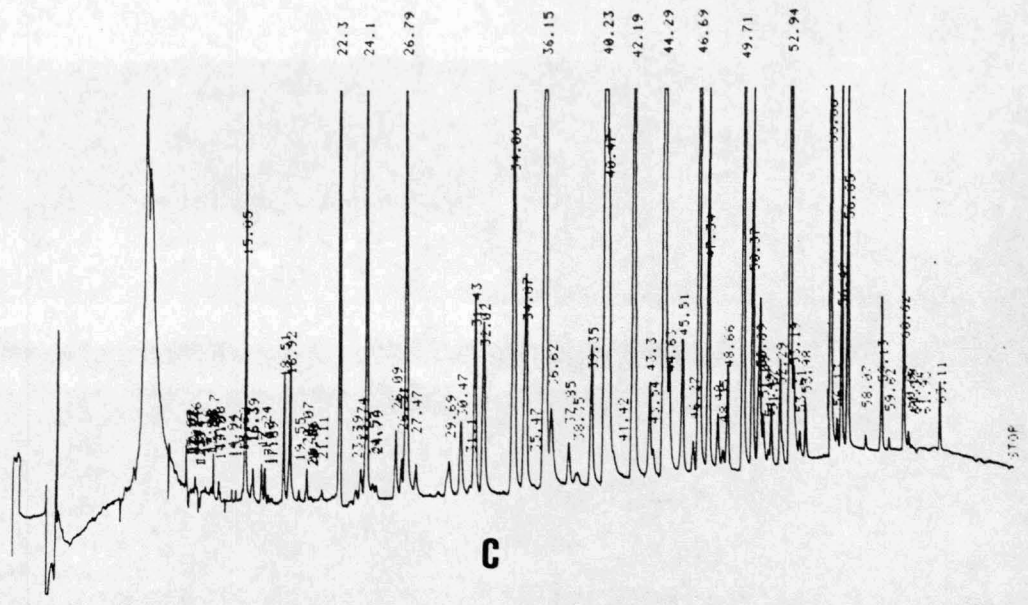
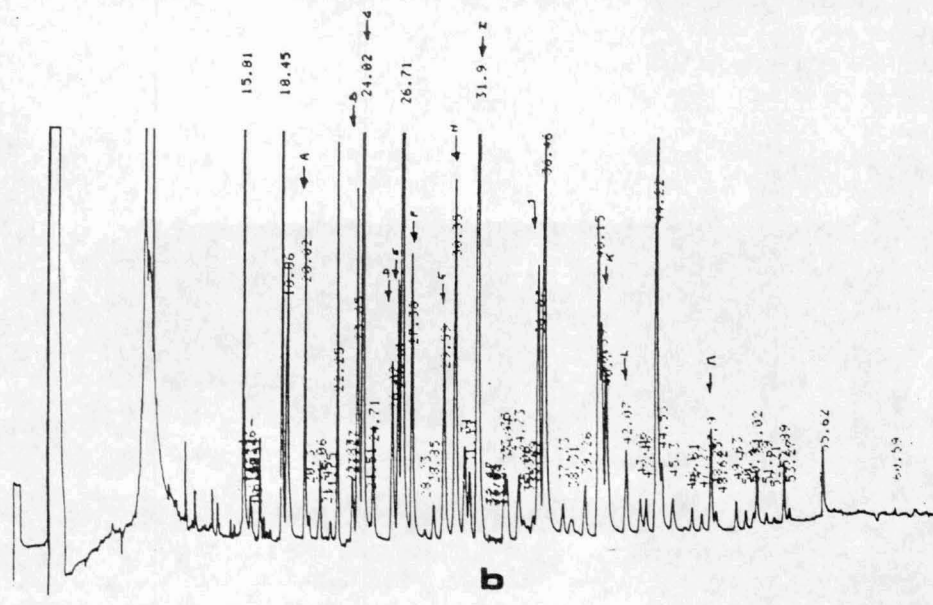
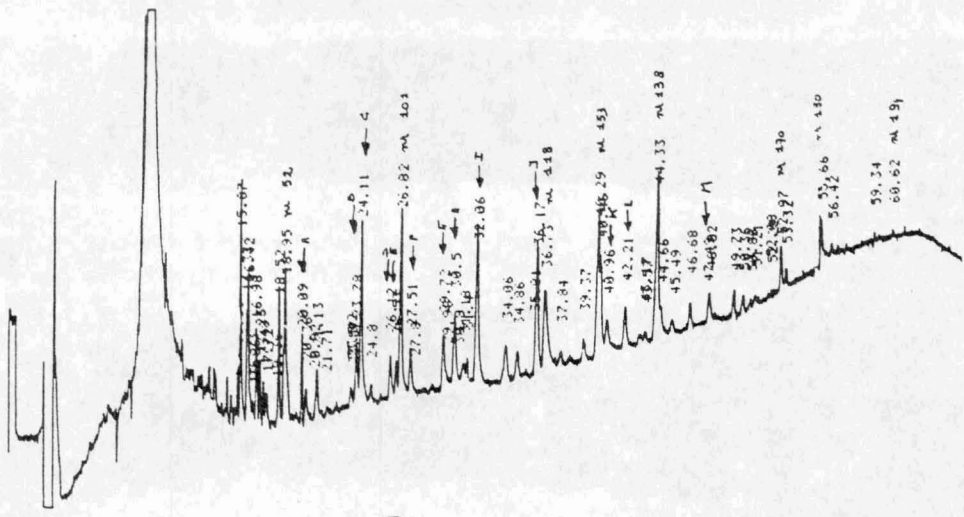


Fig. 2. Comparison of PCB patterns in (a) sediments, (b) Aroclor 1254 and (c) Aroclor 1260. (A-M: peaks used for calculation of "total PCB" values).

3. METHODS

The granulometric distribution of the bulk sediments was analysed after an ultrasonic treatment, on a sedimentation balance. The bulk sediments were wet sieved on $63\mu\text{m}$ to separate the sand from the silt and lutum fraction of the sediments. The bulk sediment, the fine sediment fraction, the suspended matter and zooplankton were further analysed for the lipid contents (after extraction with hexane/acetone (9/1)), the organic carbon content (CH analyzer) and the PCB levels. The latter was measured after soxhlet extraction with hexane/acetone (9/1), clean up on a florisil column and gaschromatographic measurements with an electron capture detector, a capillary column system, an automatic sampler and a plotter-integrator. The conditions used are : splitless injection (splitter closing time : 0.5 min); injector t° : 220°C ; oven t° : $90^\circ\text{C} - 270^\circ\text{C}$ in a temperature program; detector t° : 305°C ; column : fused silica CPsil8CB (25 m, 0.22 mm diameter, $0.12\mu\text{m}$ film-thickness); carrier-gas : 0.6 bar N_2 ; detector-gas : 20 ml N_2/min ; injection volume $1\mu\text{l}$. The quantitative determination of PCB levels is based on individual PCB congeners (IUPAC nrs. 28, 52, 101, 118, 153, 138, 170 and 180) and on the total PCB quantity as compared with the most similar standard mixture : Aroclor 1254 (Fig. 2).

4. RESULTS AND DISCUSSION

4.1. PCB patterns in different sample types.

A constancy in the PCB patterns (it is the relative abundance of the different congeners in the PCB mixture can be seen within a sample type for surface sediments (upper cm.), the silt and lutum fraction of the surface sediments and suspended matter (r^2 : 0.7-0.98) (Fig. 3). In zooplankton, being more heterogeneous, the variations were somewhat bigger (r^2 : 0.1-0.8).

A difference in the relative importance of each congener between the natural samples (f.i. IUPAC nr. 138 in zooplankton, compared to the other sample types) is noted. Higher chlorinated PCB congeners (IUPAC nr. 153 to 180) are more important in natural samples than in Aroclor 1254 (Fig. 4).

Due to these differences in PCB patterns between different sample types and eventually different regions it is important to compare PCB levels on the basis of individual congeners, and to get a more global view of the PCB contamination, on the sum of the individual congeners, even if they only represent a fraction of the total PCB level. For the researches it is however nowadays not clear which congeners ought to be used. Different teams use different congeners and the congeners used change within one research team, according to the gained experience. It therefore seems convenient to additionally express results as total PCB values (in comparison with standard mixtures), to enable the comparison of results in course of time and with literature, even if analyses were executed on glass column systems.

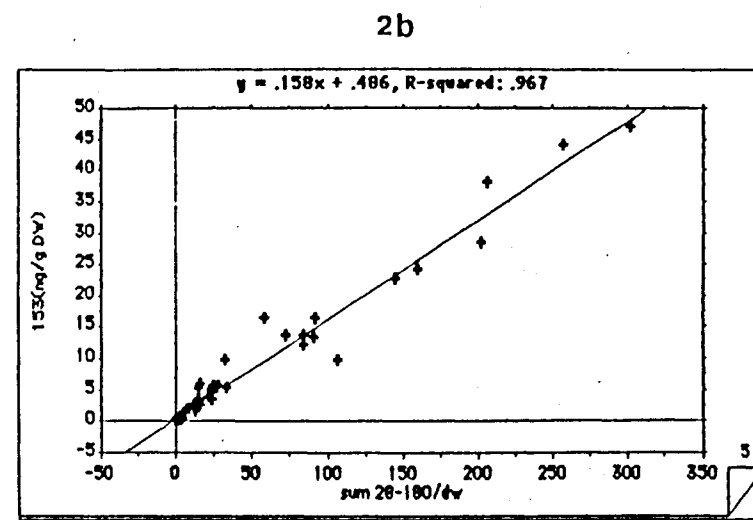
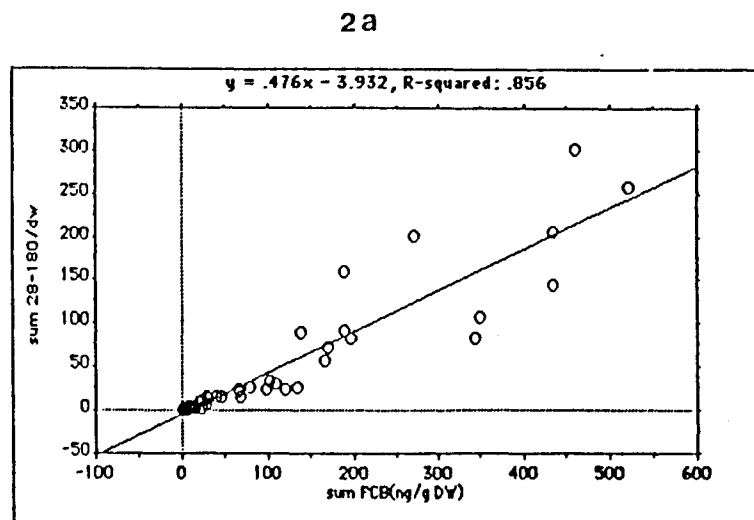
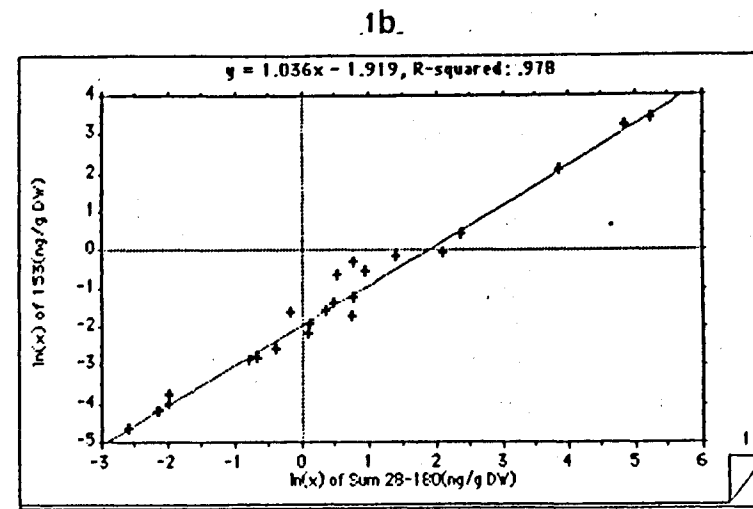
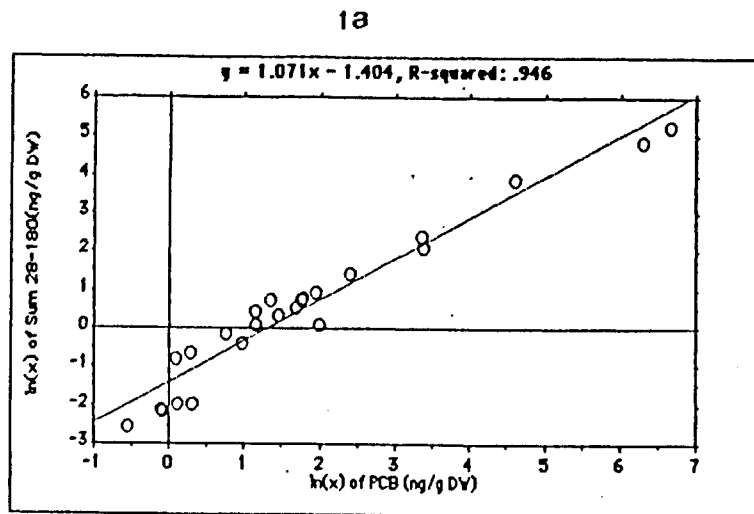


Fig. 3. Relation between (a) the sum of the PCB congeners (IUPAC nrs. 28, 52, 101, 118, 138, 153, 170, 180) and the "total PCB" concentrations in comparison with Aroclor 1254 and (b) the relation between the PCB congener nr. 153 and the sum of the PCB congeners (28 till 180) in f.i. (1) bulk sediments and (2) the silt and lutum fraction of the sediments (< 63 μm) (DW = dry weight).

The PCB results in the further study are essentially compared as the sum of 8 congeners (IUPAC nrs. 28, 52, 101, 118, 138, 153, 170, 180) representing respectively for total sediments, silt and lutum fraction of the sediments, suspended matter and zooplankton : 31%, 43%, 34% and 28% of the total PCB contamination.

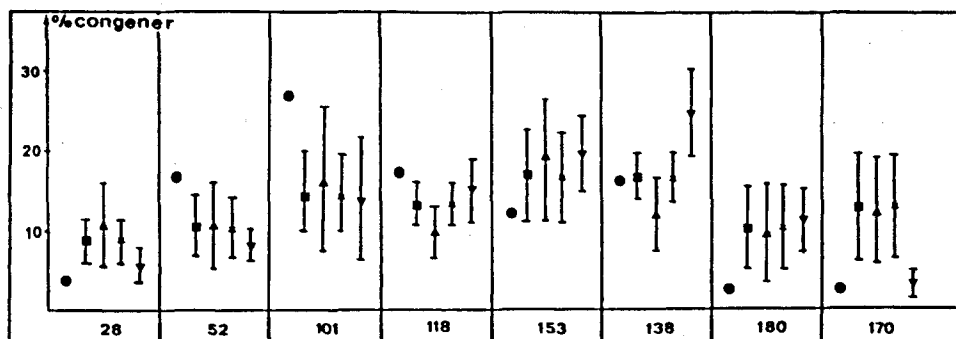


Fig 4 The relative contribution of some PCB congeners in the PCB contamination (as sum of the congeners), in Aroclor 1254 ●. total surface sediment ■, the silt and lutum fraction of the surface sediment (fraction < 63 μm) ▲, suspended matter * and zooplankton ▼ from the Belgian Continental Shelf (mean values and standard deviation error bars).

4.2. Geographical and temporal variation of PCB levels in sediments.

The studied sediments, from the Scheldt estuary and the Belgian coastal zone, have a broad range of geological characteristics (f.i. granulometric distribution) and of organic carbon and lipid contents. Large variations in PCB levels according to the sampling station and sampling period are noted (Fig. 5). It is therefore important, in order to understand and evaluate the noted contaminant levels, to study their association with the silt, the clay, the organic carbon and the lipids of the sediments and thus to standardize the measured PCB levels.

4.3. Association of PCBs with different sediment fractions.

Comparison of the PCB contamination of 15 bulk surface sediments (2ng.g^{-1} dry weight) versus their respective silt and lutum fraction (14ng.g^{-1} dry weight) shows a higher affinity of PCB for the silt, the fine sediment fraction, than for sand

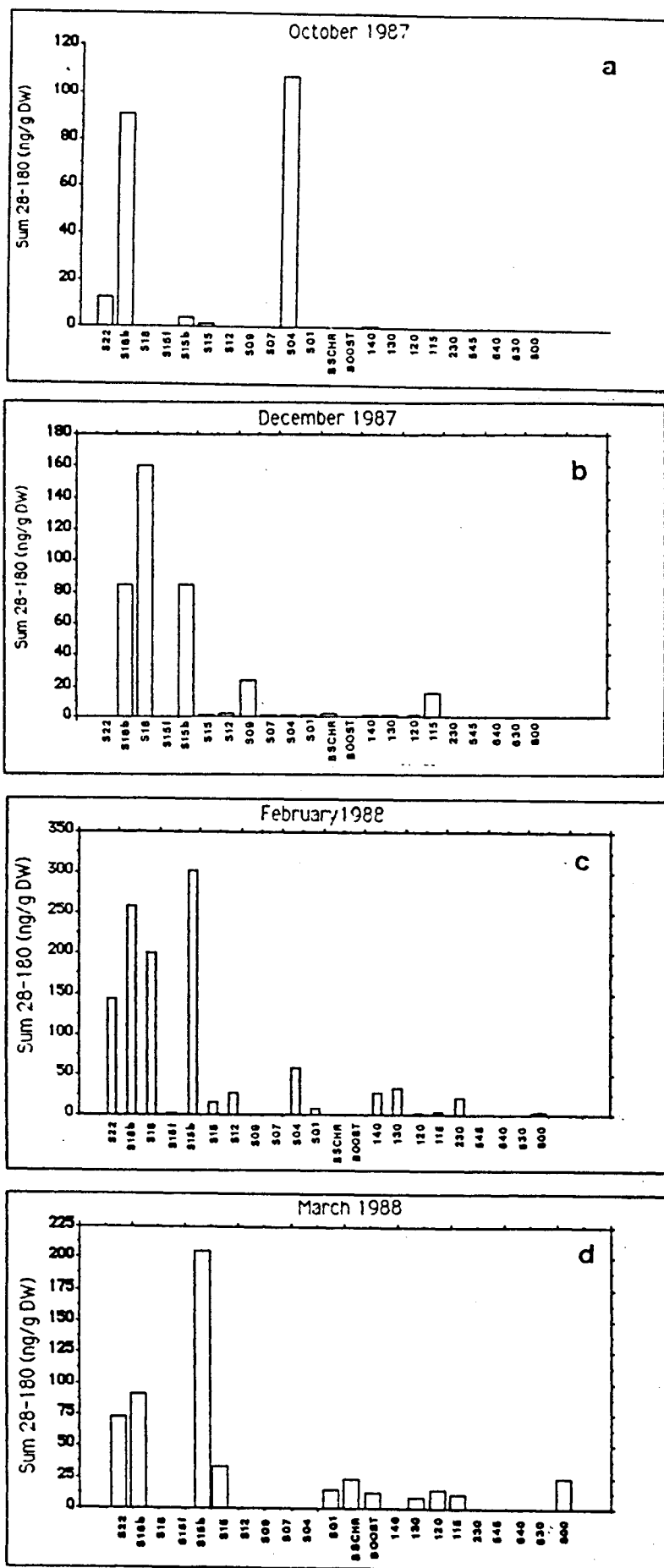


Fig. 5. PCB levels in surface sediments (fraction < 63 μ m) from different places in the Scheldt estuary and the Belgian Continental Shelf in different periods in 1987 and 1988 (μ g.g⁻² dry weight) (see also Fig. 1).

on a lipid weighted base however the PCB levels are much more comparable (Table 1) suggesting already partitioning of PCBs into the lipid fraction of the sediments. Both sediment fractions (bulk < 63 μ m) are therefore, in a first step, separated for a more deeply investigation.

Comparing the geological and chemical characteristics of the bulk sediments, high correlation coefficients are noted between the silt fraction (% < 63 μ m), the organic carbon content and the lipid contents of the samples (Fig. 6).

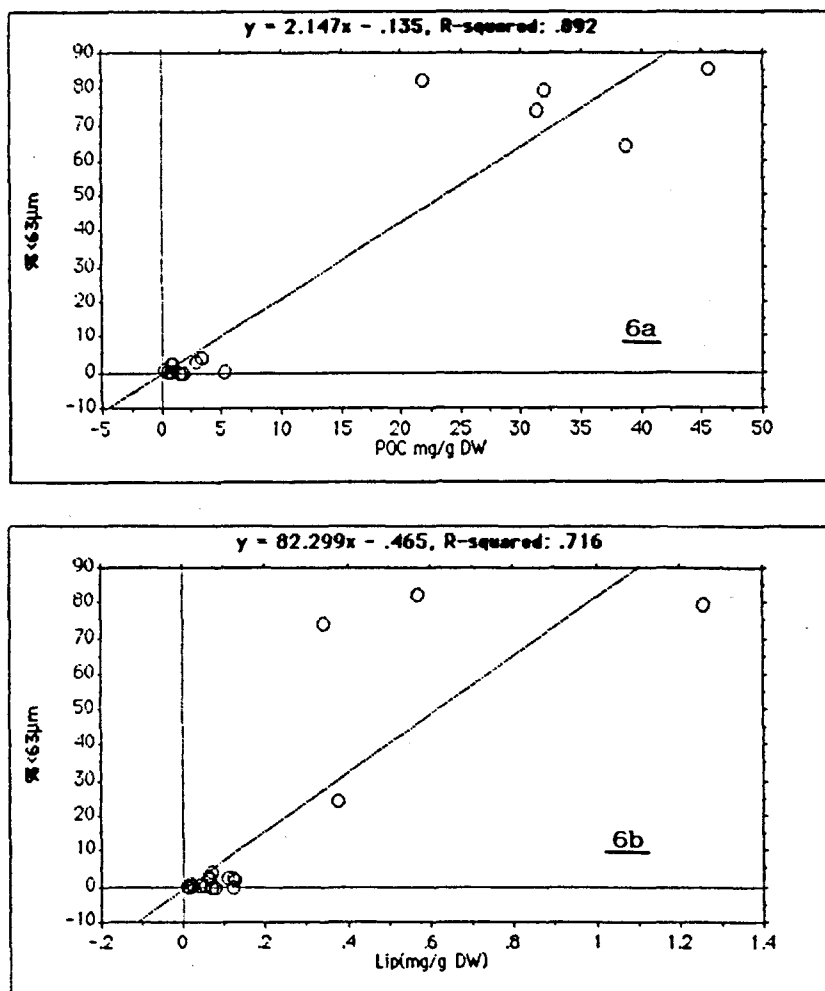


Fig. 6 Relation between silt and particulate organic carbon (6a) or lipid contents (6b) in bulk surface sediments from the Scheldt Estuary and Belgian Continental shelf in 1987 and 1988, excluding one sample from a highly contaminated zone (S18)

TABLE 1

Comparison of PCB levels (as sum of congeners) in different fractions of surfac sediment samples: total sediments and the silt and lutum fraction of the sediment (median levels, n = 15).

Identification	ng.g ⁻¹ dry weight	µg.g ⁻¹ lipid
Total sediment	2	15
Silt and lutum	14	28

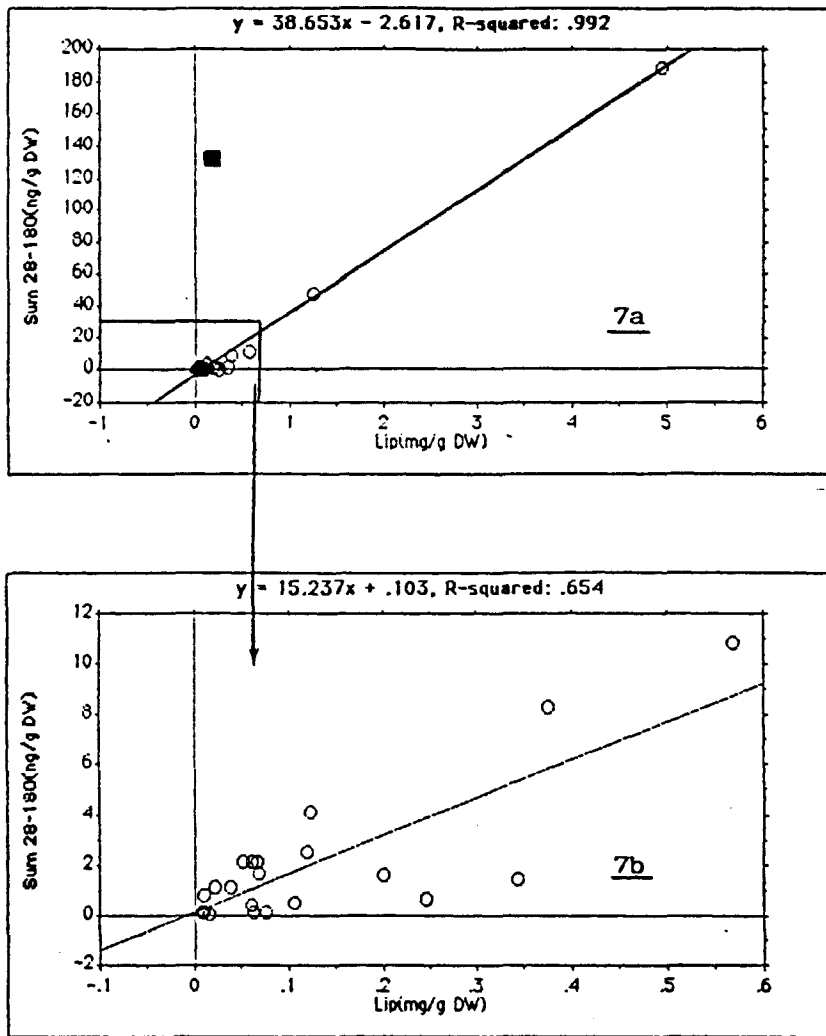


Fig. 7: Relation between PCB and lipid contents of bulk sediments (7b): excluding samples from a more contaminated zone.

■: station 140 in February 1988.

The association between silt and organic carbon and the association between silt or organic carbon and PCBs, indicates the importance of adsorption of PCBs onto sediments, a statement already noted during previous investigations, on bulk sediment samples (Simmons et al., 1980; Duursma et al., 1989). Our study revealed additionally a very high correlation between the PCB and the lipid content of the bulk sediments indicating the importance of partitioning of PCBs into the sediment particles (Fig. 7).

Similar associations were investigated within the silt and lutum fraction ($< 63 \mu\text{m}$) of the sediments : a positive relation between the organic carbon and lipid contents was noted. The lipid and carbon contents of the sediments are however not related to the presence of clay (%) (Fig. 8). The PCBs of the silt and lutum fraction of the sediments, excluding some samples from a particular zone in the Scheldt estuary (see later), are associated with the lipids in the samples, less with the organic carbon and not at all with the clay (Fig. 9). This clearly reveals the association of PCBs with the lipids of the sediments in an equilibrium state with the surrounding water. The non-association with the clay shows evidence for the origin of the PCBs in the sediment : sedimented biological material (essentially suspended phytoplankton).

The similar relationship (PCB-lipids), with similar regression coefficient, noted in respectively the bulk (Fig. 7) and the fine sediment fraction ($< 63 \mu\text{m}$) (Fig. 9) can be understood considering the origin of the sediment lipids (biological material). All samples can therefore be combined into one general equation and a PCB level of $\pm 20 \mu\text{g} \cdot \text{g}^{-1}$ lipid can then be calculated as an acceptable mean value for the Belgian coastal zone and the Scheldt Estuary for the period October 1987-March 1988 (Fig. 10). The zone Kalo-Doel needs special future attention with some very high, some very low and some "normal" PCB values. Possibly we are dealing with occasional dumping of fatty materials either with or without PCBs. The equilibrium state, depending on the diffusion transport via interstitial water, resuspension of sediment material, bioturbation etc., has in those "special" samples not yet been

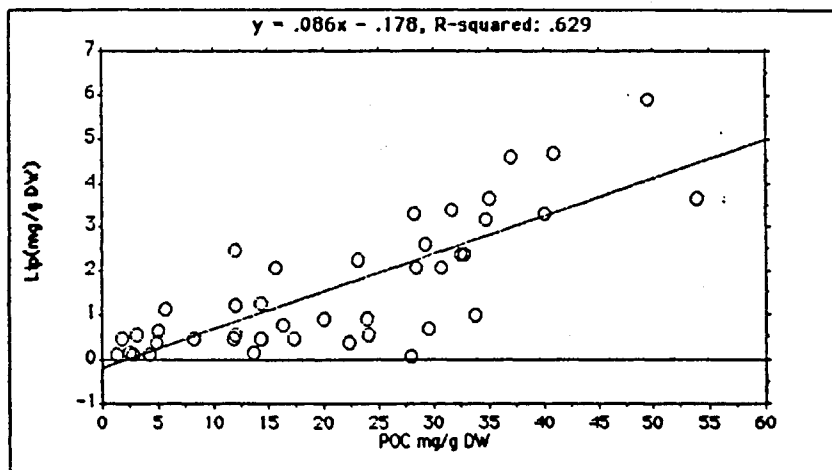
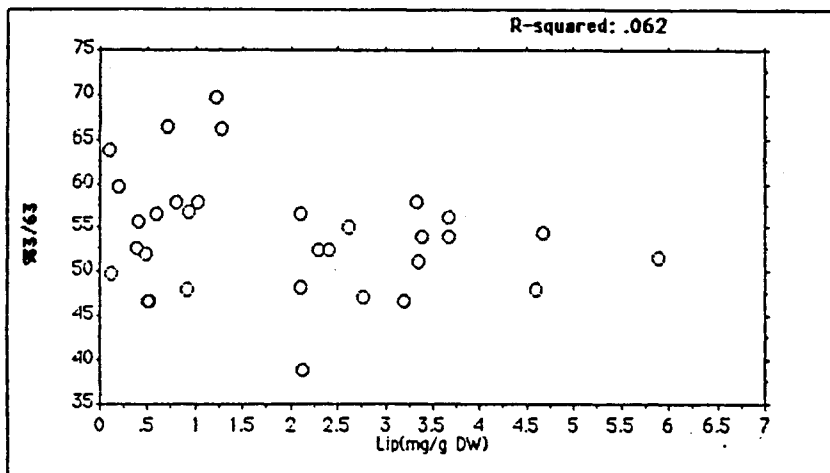
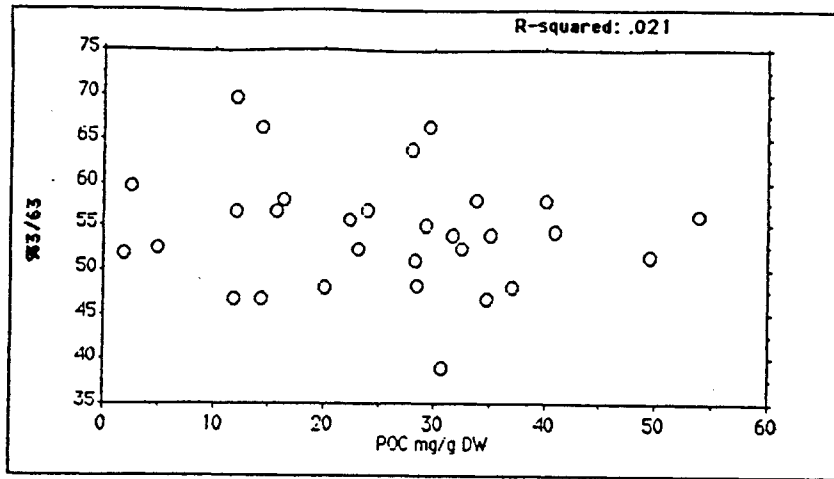


Fig. 8. Relations between the geological and chemical characteristics of the silt and lutum fraction of surface sediments from the Scheldt estuary and the Belgian Continental Shelf in 1987-1988.

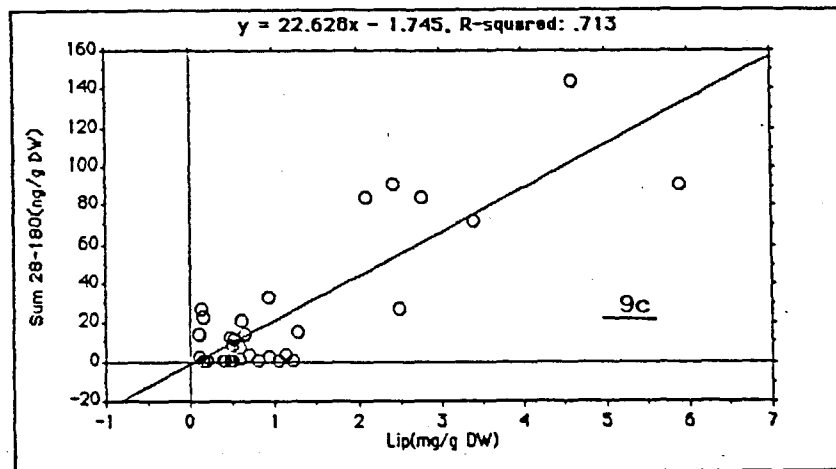
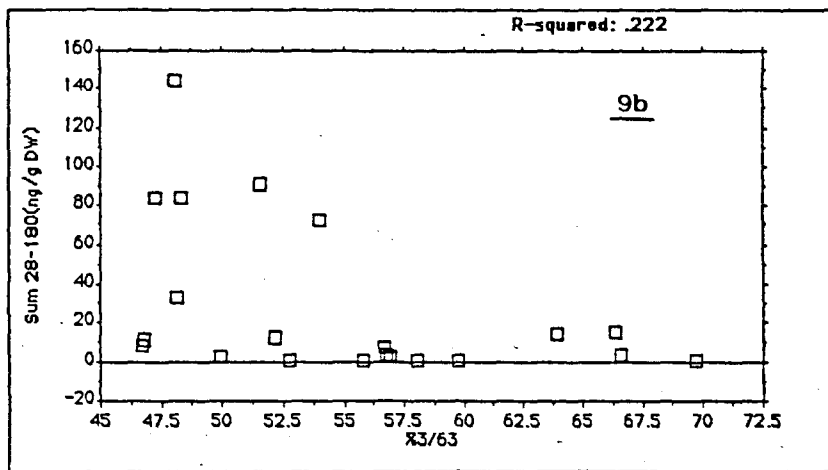
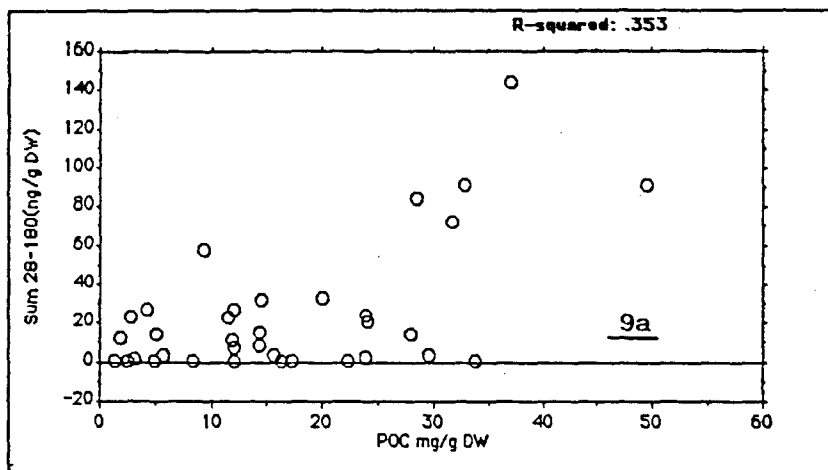


Fig. 9. Relation between the PCB levels and the silt fraction (9a), the POC content (9b), and the lipid content (9c) of sediment samples from the Scheldt estuary and the Belgian Continental Shelf in 1987-1988. Some samples from the Scheldt estuary with a very particular PCB behaviour (see fig. 10) are excluded from this graph.

reached.

Seasonal variations in PCB contents must also be considered, the highest levels being noted in February (Fig. 5) (see also later).

4.4. Distribution of PCBs between the different compartments of the water column.

Comparing PCB levels between the different planktonic compartments and the sediments from the Belgian coastal zone (1986-1988) shows on a dry weight base increasing PCB levels : bulk sediment, silt and lutum, suspended matter, zooplankton. On a lipid weight base, PCB levels in sediments and suspended matter are comparable; in zooplankton they are lower (Table 2). The similarity in PCB levels (on lipid weighted base) between the sediments and the suspended matter clearly shows the importance of a passive physicochemical equilibrium partitioning between the water, the suspended matter and the sediments. For the sediments, one must therefore consider sorption and desorption phenomenons of PCBs. A redistribution of the contaminants into the water-column in association with the breakdown of organic material clearly exists in agreement with results during laboratorium experiments (Wildish et al., 1980).

The sediments can thus not be considered as a "sink" for PCBs; the sediments represent nevertheless an enormous "stock" of PCBs considering the large amount of organic sediment material present at the bottom of the estuaries and seas.

TABLE 2

PCB levels (as sum of congeners in different natural samples from the Belgian coastal zone.

(median levels, n = numbers of samples).

Identification	Period	n	ng.g ⁻¹ dry weight	µg.g ⁻¹ lipid
Surface sediment	(1987-1988)	9	2	15
Silt and lutum	(1987-1988)	10	8	15
Suspended matter	1986	8	27	21
	1987-1988	3	27	9
Zooplankton:				
> 250 µm	1986	8	154	2
> 500 µm	1987-1988	2	159	6

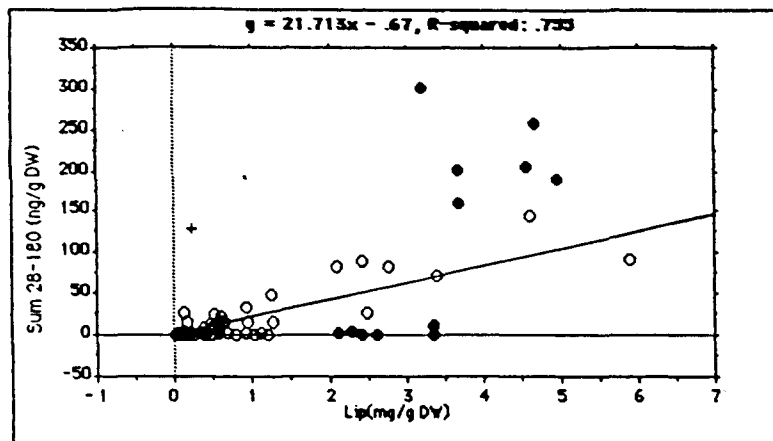


Fig. 10. Relation between PCB and lipid levels of sediments (bulk and silt sediments) from the Scheldt estuary and the Belgian continental shelf (• zone Kalo-Doel and 1 sample from Antwerp, +: 140 February 1988).

4.5. PCB uptake mechanisms in suspended matter and zooplankton.

Considering the planktonic compartments, a positive tendency between PCB levels and lipid contents can be noted for suspended matter, not for zooplankton (Fig. 11).

This again indicates the existence of a passive physicochemical adsorption/partitioning mechanisms of PCB in suspended matter and the importance of biologically regulated uptake and elimination mechanisms of PCBs in zooplankton. In suspended matter (and sediments) one must however also consider the dilution of PCBs into the available lipids and thus evaluate PCB levels considering the biomass levels (Delbeke and Joiris 1988, Joiris et al., 1987). Highest PCB levels, in suspended matter, zooplankton and also in sediments can therefore be noted during the winter (February 1986 and 1987), when the amount of suspended matter is low (Fig. 12 and Fig. 5).

4.6 Geographical differences in PCB levels in the Belgian Continental Shelf.

The geographical comparison of PCB levels in suspended matter and zooplankton reveals, for the different periods considered, higher PCB levels in the near coast area than in the open sea region (Fig. 12). This dilution of PCBs into the sea is related to the transport mechanisms of PCBs : PCBs are, due to their low water solubility essentially associated with the particulate fraction of the water-column (f.i. Verscheuren 1983 and f.i. Duursman et al., 1989) and are therefore to a very high extent deposited on and transported by the sediments. They are only, to a limited extent, transported with the water current, causing lower PCB levels, in remote areas from the dumping origin.

CONCLUSION

The investigation of the PCB concentrations in sediments, suspended matter and zooplankton from the Belgian Continental Shelf and Scheldt Estuary in comparison with chemical parameters (particulate organic carbon, lipid contents) and for the sediments also geological parameters (particle size distribution) indicates the existence of an equilibrium partition between the water, the suspended matter

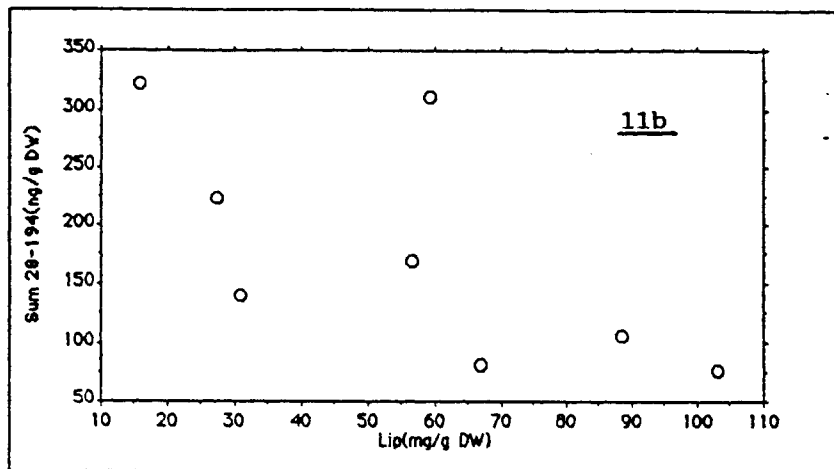
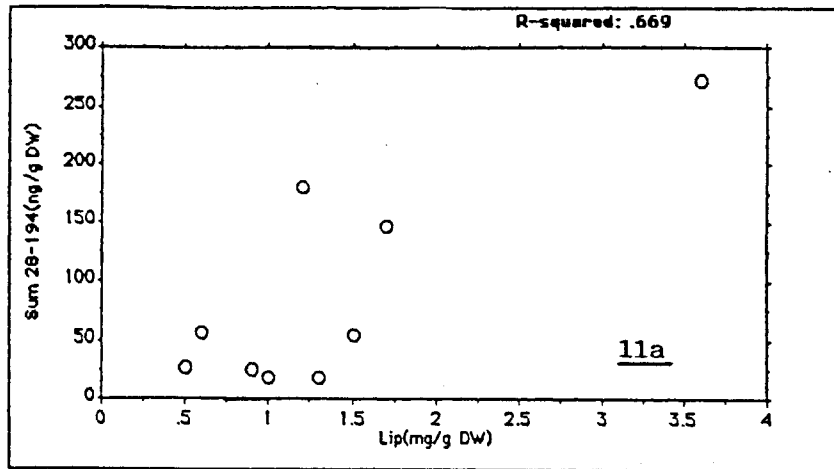


Fig. 11. Relation between PCB and lipid levels of suspended matter (11a) and zooplankton (11b) from the Belgian Continental Shelf and Scheldt estuary in 1986.

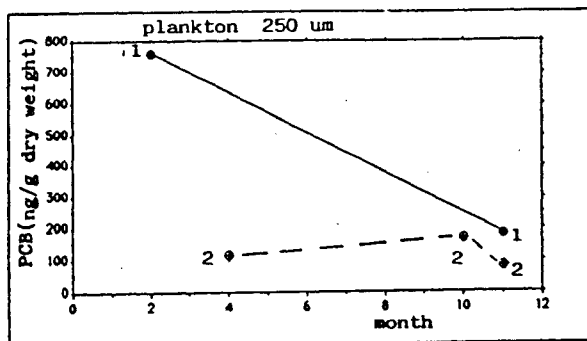
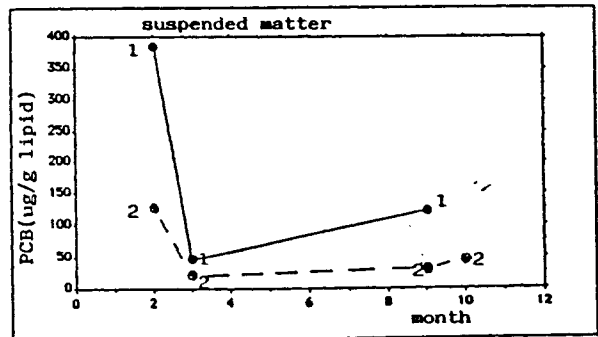
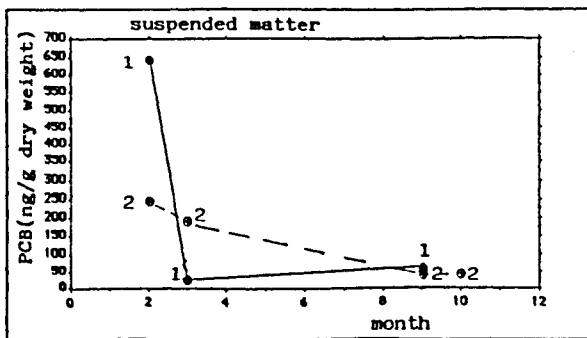


Fig. 12. Seasonal and geographical differences in PCB levels (as total PCBs, compared to Aroclor 1254) in suspended matter and zooplankton from the Belgian Continental Shelf and Scheldt estuary in 1986. —, 1: near coast area; ---- 2; open sea area.

and the sediments.

The partitioning coefficient, being different for the different PCB congeners, causes different PCB concentration factors for the congeners in the natural samples. Differences in "PCB patterns" are therefore encountered between standard solutions, sediments, suspended matter, and zooplankton. PCB congeners with high chlorination (138, 153, 170, 180) are more important in natural samples compared to standard mixtures especially in zooplankton. It thus seems important to compare PCB levels as sum of congeners. To be able to compare with literature it is however still important to measure the "total PCB" concentrations, as compared to the standard mixture. An estimation still valuable within a compartment and geographical region.

The pollutants are essentially associated with the lipid fraction of the particulates, in an equilibrium state. Stable ratios can be noted between the PCB levels and the lipid levels in suspended matter and sediments : $\sim\sim 20\mu\text{g PCB} \cdot \text{g}^{-1}$ lipid (as sum of the congeners, 28, 52, 101, 118, 138, 153, 170, 180) for the Belgian coastal zone and Scheldt Estuary during the period October 1987-March 1988. The similar contaminant levels (on a lipid base) in sediments compared to suspended matter indicates sorption and desorption phenomenons of PCBs in the sediments and redistribution of the contaminants in the water-column. Sediments can therefore not be considered as a sink for PCB compounds.

The sorption and desorption speed of PCBs in the sediment is however dependent on diffusion transport, resuspension of bottom material, bioturbation Local dumping of PCB rich and PCB poor silt could thus be noted in a particular region of the Scheldt Estuary : between Antwerp and Doel. The elevated PCB levels could not be related to particle size or chemical characteristics (organic carbon and lipid concentrations) of the sediments.

A dilution of PCBs from the near-coast area into the open sea area is noted, in different periods, for suspended matter and zooplankton. This transport phenomenon is related to the low water solubility and therefore to the association of

PCBs with the biological particles from the water-column and sediments. The PCB levels in zooplankton are superior on a dry weight base inferior on a lipid weight base to the ones in suspended matter and sediments and not related to the lipid contents of the zooplankton, indicating uptake of these organochlorine residues through food intake and dilution of these organochlorines in the autogenically formed zooplankton lipids.

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