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THE ROLE OF SMALL, LOW DENSITY PARTICLES ON THE PARTITION OF SELECTED PCB CONGENERS BETWEEN WATER AND SUSPENDED MATTER (NORTH SEA AREA)

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ABSTRACT

The dissolved and particulate suspended concentrations of five PCB congeners (with 3-7 chlorine atoms) in the Southern Bight (North Sea) are interpreted in terms of an equilibrium partitioning model. K_d values for riverine/coastal samples generally increase with chlorine number of the congeners ($K_d = 10^4$–10^6). Values are more than an order of magnitude larger at the low suspended matter concentrations offshore (<1 mg·dm^{-3}). This is interpreted in terms of the presence of different SPM fractions with different contents of PCB: a fraction consisting of low size/density particles carrying high contents of PCBs, dominates at low SPM concentrations. The contribution of particulate forms to the total PCB concentration per unit volume may, therefore, be significant even at low SPM concentrations.

1. INTRODUCTION

Polychlorinated biphenyls (PCBs) are ubiquitous environmental contaminants (COOK, 1972; HUTZINGER *et al.*, 1974; NATIONAL ACADEMY OF SCIENCES, 1979). The North Atlantic may be the dominant sink, accommodating more than half of the environmental burden (NATIONAL ACADEMY OF SCIENCES, 1979). In addition to rivers and direct sources from land, deposition from the atmosphere has been reported to be an important, if not dominant, source in fresh water and marine waters, especially in remote areas (EISENREICH *et al.*, 1981; BIDLEMAN & OLNEY, 1974; HARVEY & STEINHAUER, 1974).

Concentrations in sea water are extremely low (values for total PCB typically in the subng·dm^{-3} range (IOC, 1984)). The extreme sensitivity of the electron capture detector makes it feasible to determine their concentrations at these levels after concentration over many orders of magnitude in an organic solvent or onto an adsorbent and subsequent isolation from interfering compounds.

The class of PCBs consists of 209 compounds with similar, but distinct and specific physico-chemical properties, determined by the number ($N = 1$–10) and relative positions of the chlorine atoms in the molecular framework. They are hydrophobic (lipophilic) and have low (for $N<4$) or non-detectable (for $N>5$) chemical/microbiological reactivity in the marine environment.

The hydrophobic character and persistence in the environment generally increase with increasing chlorine number. Because of these properties, this class of compounds can in principle be used to study transport mechanisms and processes in the marine environment, especially when they are analysed in terms of well characterized, individual compounds, rather than in terms of ill-defined mixtures (DUINKER *et al.*, 1980). Thus, it appears that the compositions of PCB mixtures in marine environmental samples can be rather different from those of commercial mixtures (such as Aroclors or Clophens) as well as from those of ambient compartments (*e.g.* water, particulates, biological tissue). The approach involving the analysis of individual congeners is also essential for understanding the bioavailability of PCBs to organisms (BOON, 1985).

The fate of PCB congeners in the marine environment is affected by their partition between the various compartments. The transport mechanisms of water and particulates (the compartments of our considerations in this paper) are different. Particles with low size/density characteristics (microparticulates, colloids) may be transported like dissolved species. Particles may occur in sea water as large flocs (GIBBS, 1983), with similar properties as dissolved components. Transport of larger particles in estuaries and coastal regions is affected strongly by local

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hydrodynamical and geomorphological characteristics. Larger particles are trapped in many estuaries and coastal regions. Particle trapping mechanisms may also prevent smaller particles from reaching the open sea (WELLERSHAUS, 1981). Particles may alter their composition and/or size under influence of the strong gradients in estuaries (EISMA *et al.*, 1983) and accumulation can take place against the concentration gradients (*e.g.* in the Wadden Sea). Another unexpected feature of particle transport is the mechanism by which particles in estuaries are transported in an upstream direction, even beyond the region of maximum salt intrusion.

Various fundamental aspects of particle transport and behaviour have been observed, developed into models and described by POSTMA (1957, 1961, 1967a, 1967b, 1980, 1981). I should like to dedicate this paper to the recognition of Postma's pioneering work. The field data were obtained when I worked at his institute in Texel, the Netherlands. A description will be given of the role of particles in the distribution of selected PCB congeners in the marine environment (North Sea). Full details, including dissolved concentrations will be described elsewhere (DUINKER & HILLEBRAND, in prep.).

2. THE EQUILIBRIUM MODEL CONCEPT

PCBs are apolar, lipophilic (hydrophobic) compounds, characterized by large octanol-water partition coefficients (log K_{ow} ~4-8, BRUGGEMAN *et al.*, 1982; RAPAPORT & EISENREICH, 1984). Such compounds interact strongly with abiotic and biotic surfaces. The interaction is determined by the organic matter content, the surface area and the nature of the surface.

Hydrophobic organic sorption to natural particulates can be described by an equilibrium model. The relation between the content of a compound in particulates (C_p = mass of compound per g of particulates) and in water (C_w = mass of compound per g of solution) is characterized by the distribution coefficient $K_d = C_p/C_w$. The underlying assumption in this model is that the interactions between solute and particulate matter are weak and non-specific (CHIOU *et al.*, 1979; CHIOU *et al.*, 1983). Thus, ion-exchange reactions and covalent bond formation are not involved.

The amounts per unit volume in each of the compartments are related by a simple expression. Consider 1 dm^3 of water, in which suspended particulates are present at a concentration [SPM] ($g \cdot dm^{-3}$). The amounts of a particular compound in solution and suspension (A_{sol} and A_{susp}), are given by $A_{sol} = c_w$ (c_w = mass $\cdot dm^{-3}$) and $A_{susp} = 10^{-3} \cdot K_d \cdot [SPM] \cdot c_w$. The relation

$$A_{susp}/A_{sol} = 10^{-3} \cdot K_d \cdot [SPM] \qquad (1)$$

allows the evaluation of the relative contributions of the dissolved and particulate forms to the total concentration in any volume of a water body (Fig. 1). For example, compounds with $K_d < 10^5$ are found mainly in solution at suspended matter concentrations < 10 $mg \cdot dm^{-3}$ (*e.g.* 95% in solution for $K_d = 10^4$ at $[SPM] = 5 \times 10^{-3}$.

The equilibrium concept of uptake was developed by various groups (HAMELINK *et al.*, 1971; NEELY *et al.*, 1974; CHIOU *et al.*, 1977; CLAYTON *et al.*, 1977; KARICKHOFF, *et al.* 1979; MEANS *et al.*, 1980; SCHWARZENBACH & WESTALL, 1981). It was confirmed by measurements of PCB in solution and SPM in Puget Sound (PAVLOU & DEXTER, 1979). Several papers have appeared in the literature describing the results of laboratory studies on the mechanisms of uptake of PCB onto sediment particles. Several of these studies have indicated that the sorption isotherms are non-linear and that in fact the distribution coefficient decreases with increasing particulate-to-water ratios (O'CONNOR & CONNOLLY, 1980; VOICE *et al.*, 1983).

Distribution coefficients, if constant, are extremely useful parameters to describe, evaluate and predict the distribution, transport mechanisms and accumulation potential in the marine environment. Quantitative data on partition of PCBs between sea water and suspended particulates are very limited. Reports on concentrations in sea water have usually not distinguished between dissolved and particulate forms. Moreover, virtually no information is available on qualitative and quantitative distributions of individual PCB congeners.

We have studied the distribution of PCB congeners in solution and suspension in the North Sea and some adjacent rivers and estuaries in recent years. Full data will be reported elsewhere (DUINKER & HILLEBRAND, in prep.). Some results will be used in the present paper to investigate the validity of the concept of equilibrium partitioning of specific hydrophobic organic compounds under natural conditions in different suspended matter regimes (0.2-200 $mg \cdot dm^{-3}$). Five selected PCB congeners with 3-7 chlorine atoms per molecule will be investigated.

3. MATERIALS AND METHODS

Data in this paper refer to samples collected in the

Dutch coastal area and in offshore regions (at salinities $>35\times10^{-3}$) in spring and autumn 1981 and 1982 and in the freshwater sections of the rivers Scheldt, Rhine, Ems, Weser and Elbe. The river data have been reported earlier (DUINKER & HILLEBRAND, 1983a; DUINKER *et al.*, 1982a, 1982b, 1985). 100 dm^3 water was taken at halfdepth with a stainless steel gaslift system and introduced into a 100-litre stainless steel container. It was pressure-filtered on board through a $\varnothing$ = 29 cm GF/C filter into another container, from where it was pressed (with tank ultrapure N_2) into a continuous liquid-liquid extractor, using 300 ml n-hexane (DUINKER & HILLEBRAND, 1983b). Pre-weighed filters werd washed with distilled water to remove sea-salt, dried at 90°C and stored for weighing and analysis in the laboratory, where they were extracted by n-hexane. The extracts of water and particulates were concentrated in a Kuderna-Danish concentrator apparatus. The final extract (1 cm^3) was cleaned-up over Al_2O_3, concentrated in a Kuderna-Danish apparatus and eluted on a silica column with n-hexane (this fraction containing PCBs quantitatively). All equipment and glassware was carefully washed and finally rinsed with distilled n-hexane before use. Microcolumns were cleaned with dichloromethane. Procedural blanks were determined at regular intervals. The only step in the procedure that could not be checked appropriately was the sampling procedure, but with the precautions taken, it is considered to be an insignificant source of contamination of the large volume samples analysed (DUINKER & HILLEBRAND, 1983b).

1 μl portions of the extracts were analysed by fused silica temperature programmed capillary column (SE-54 0.2 mm $\varnothing_{id}$) GC-ECD. Authentic standards of individual congeners (in appropriate mixtures) were used for identification and quantitation of those PCB congeners that are well-separated from neighbouring ones and can thus be analysed accurately (DUINKER & HILLEBRAND, 1983c; MULLIN *et al.*, 1984). We shall report here on the congeners No. 18, 52, 101, 149 and 180 (a tri-, tetra-, penta-, hexa- and heptachlorobiphenyl, respectively). For identification purposes, we shall use the systematic numbering systems for PCB congeners, suggested by BALLSCHMITER & ZELL (1980).

4. RESULTS AND DISCUSSION

Tables 1-4 summarize the range of concentrations of the PCB congeners 18, 52, 101, 149 and 180 in solution and in suspension (in pg·dm^{-3}), the range of their contents in SPM (in ng·g^{-1}) and the range and average of the K_d values, calculated for the individual samples. Three groups of samples are distinguished for reasons to be discussed below: fresh water from the rivers Scheldt, Rhine, Ems, Weser and Elbe, estuarine and coastal samples with SPM concentrations ([SPM]) above 15 mg·dm^{-3} and offshore samples with [SPM] <15 mg·dm^{-3}.

Considerably higher concentrations were present in the rivers than in the marine samples, especially the offshore ones, where typical concentrations of the individual congeners in solution were up to 100 pg·dm^{-3} and in suspension up to 200 pg·dm^{-3}, depending on [SPM] and the congener considered. It appears that the concentrations in solution and in suspension are strongly related and can be characterized by K_d's. We shall discuss the river and coastal samples first.

4.1. RIVER- AND COASTAL SAMPLES

The concentration levels of PCBs differed between the 5 river systems for each of the congeners, but the calculated individual K_d values were very similar for the rivers, generally increasing with chlorine number (roughly 10^4-10^6, Tables 1 and 2).

PAVLOU & DEXTER (1979) have calculated regional K_d^N values for SPM and sea water in Puget Sound. The PCB constituents were grouped according to the number of chlorine atoms (N), to generate subgroups

TABLE 1

Concentrations in solution (c_w, in pg·dm^{-3}) and contents of individual PCB congeners (identified by their IUPAC number according to BALLSCHMITER & ZELL, 1980)) in suspended particulates (c_p, in ng·g^{-1}) in fresh water of the rivers Scheldt, Rhine, Ems, Weser and Elbe. Data from DUINKER & HILLEBRAND, 1983a[1] and DUINKER *et al.*, 1982a[2], 1982b[3], 1985[4].

	Scheldt[1]		*Rhine*[1]		*Ems*[4]		*Weser*[3]		*Elbe*[2]	
PCB congener	c_w	c_p	c_w	c_p	c_w	c_p	c_w	c_p	c_w	c_p
18	560	4.5	1010	25	220	4.0	170	2.8	290	5.6
52	365	12.8	660	50	90	4.2	130	4.8	170	8.0
101	190	15.6	220	22	30	1.8	60	5.9	70	7.3
149	160	21.3	180	149	30	4.0	70	13.1	60	13.7
180	380	36.3	50	150	100	29	200	97.6	200	95.6

TABLE 2

Water-SPM distribution coefficients (K_d) for individual PCB congeners (identified by their IUPAC number according to BALLSCHMITER & ZELL (1980)), calculated from freshwater concentration data in Table 1, for the rivers Scheldt, Rhine, Ems, Weser and Elbe; the average value is given in the last column.

PCB congeners	K_d					
	Scheldt	*Rhine*	*Ems*	*Weser*	*Elbe*	*Average*
18	1×10^4	2×10^4	2×10^4	2×10^4	2×10^4	1.8×10^4
52	4×10^4	8×10^4	5×10^4	4×10^4	5×10^4	5.2×10^4
101	8×10^4	1×10^5	6×10^4	1×10^5	1×10^5	8.8×10^4
149	1×10^5	8×10^5	1×10^5	2×10^5	2×10^5	3.0×10^5
180	1×10^5	3×10^6	3×10^5	4×10^5	5×10^5	8.6×10^5

for which the following average K_d^N values were calculated: $K_d^3 = 4.36 \times 10^4$; $K_d^4 = 4.43 \times 10^4$; $K_d^5 = 6.27 \times 10^4$; $K_d^6 = 9.18 \times 10^4$; $K_d^7 = 9.67 \times 10^4$. The present values for individual congeners are very similar to these average data for groups of components analysed from packed column chromatograms.

The relative contributions of suspension and solution to the total concentration of each congener per unit volume can be estimated with the use of equation 1 or from Fig. 1 and the K_d values given in Tables 2 and 3. In practically all cases in the river and coastal samples, the suspended forms dominated the total concentration of each PCB congener.

Water-sediment partition coefficients of hydrophobic compounds have been related to octanol-water partition coefficients (K_{ow}'s) (KARICKHOFF *et al.*, 1979; SCHWARZENBACH & WESTALL, 1981). K_{ow} values for 58 individual PCB congeners have been determined recently by reverse phase C_{18} high-performance liquid chromatography (RAPAPORT & EISENREICH, 1984). A linear relationship appears to exist between presently determined log K_d and their log K_{ow} values, but we feel that more data are required for both properties before the relation might be useful for relating the findings to a physico-chemical interaction model.

The coastal samples discussed here were derived from relatively shallow water depths in dynamic regions where considerable exchange of particles between bottom sediments and the overlying water takes place continuously in response to variations in hydrodynamical and meteorological conditions of relatively large/dense bottom-derived particles (POSTMA, 1967a, 1967b, 1980). Direct comparison of the present data with those of laboratory studies on the uptake of individual congeners onto sediments, and those of field studies of PCB congeners in sediments are thus of interest. The contents of the five congeners in suspended matter ($ng \cdot g^{-1}$) are 1-2 orders of magnitude above the levels detected in the total bottom sediments in the Wadden Sea and North Sea, where a correlation of contents with the $< 63\,\mu m$ size fraction in sediments was found (DUINKER *et al.*, 1983). The small contributions of the $< 63\,\mu m$ fraction in the total sediments account for this large difference, at least qualitatively K_d's also depend on the composition and organic matter content of sediments (MEANS *et al.*, 1980). Obviously more data are required for a better understanding of the relations involved.

4.2. OFFSHORE SAMPLES

An interesting relation was found between the contents of individual PCB congeners in SPM (expressed

TABLE 3

Range of concentrations in solution (c_w, in $pg \cdot dm^{-3}$) and contents of individual PCB congeners (identified by their IUPAC number according to BALLSCHMITER & ZELL (1980)) in suspended particulates (c_p, in $ng \cdot g^{-1}$), and range and average distribution coefficients (K_d) for individual coastal marine samples with suspended matter concentrations $> 15\ mg \cdot dm^{-3}$.

PCB congener	c_w	c_p	K_d	
			Range	*Average*
18	23-130	1.3- 4.4	0.8×10^4-1.3×10^5	4.8×10^4
52	22-132	2.1- 8.2	3×10^4-1.4×10^5	7.1×10^4
101	15- 57	1.5- 6.1	6×10^4-2.1×10^5	8.5×10^4
149	15-181	0.8-25	0.3×10^4-1.3×10^4	9.7×10^4
180	<23- 48	1.8-24.6	4×10^4-3.8×10^5	2.6×10^5

TABLE 4

Range of concentrations in solution (c_w, in pg·dm^{-3}) and contents of individual PCB congeners (identified by their IUPC number, according to BALLSCHMITER & ZELL (1980)) in suspended particles (c_p, in ng·g^{-1}), and range of distribution coefficients (K_d) for individual samples with suspended matter concentrations <15 mg·dm^{-3}.

PCB congener	c_w	c_p	K_d
18	24-90	2 -67	4×10^4-2.9×10^6
52	13-62	5 -76	9×10^4-5.9×10^6
101	5-56	0.4-20	7×10^4-3.3×10^6
149	4-70	3 -94	1×10^5-3.8×10^6
180	3-25	3 -34	1.7×10^5-3.2×10^6

as mass per weight SPM), and the concentration of SPM (expressed as mass per unit volume). This is represented for three of the congeners in Fig. 2. It appears that considerably higher content values (ng·g^{-1}) were found for several offshore samples with low [SPM], typically below 1-2 mg·dm^{-3}. A

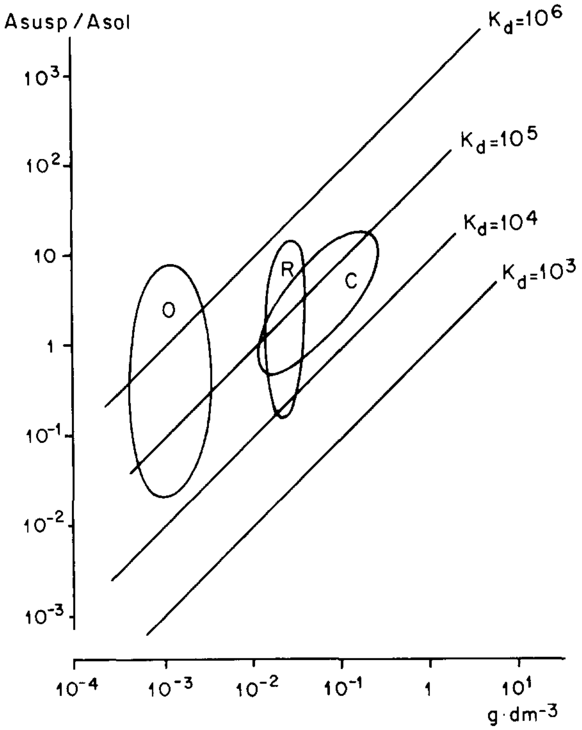


Fig. 1. Ratio of the concentration of any compound C in suspension (A_{susp} in mass of C/unit volume of sample) and in solution (A_{sol} in mass of C/unit volume of sample) against suspended matter concentration (g·dm^{-3}) for different values of the distribution coefficient K_d. The range of values for A_{susp}/A_{sol} for the five PCB congeners considered in this paper, at suspended matter concentrations typical of the rivers (R), coastal region (C) and the offshore (O) areas described here, is indicated by the appropriate boundaries.

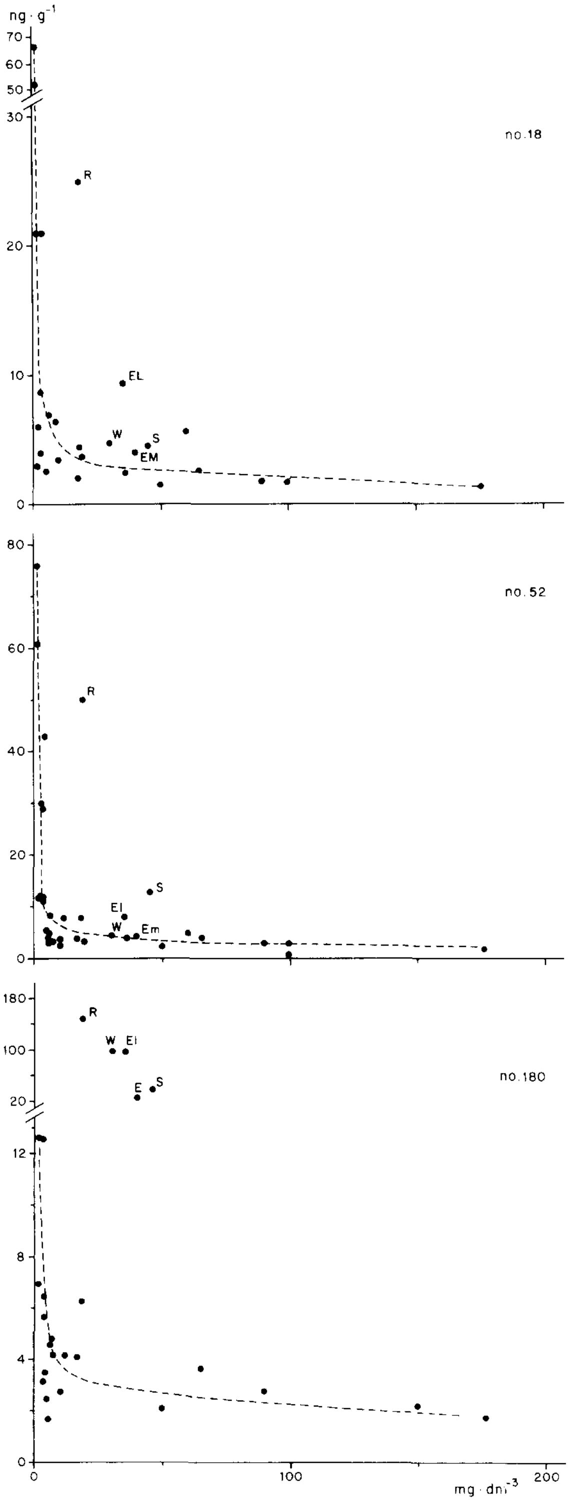
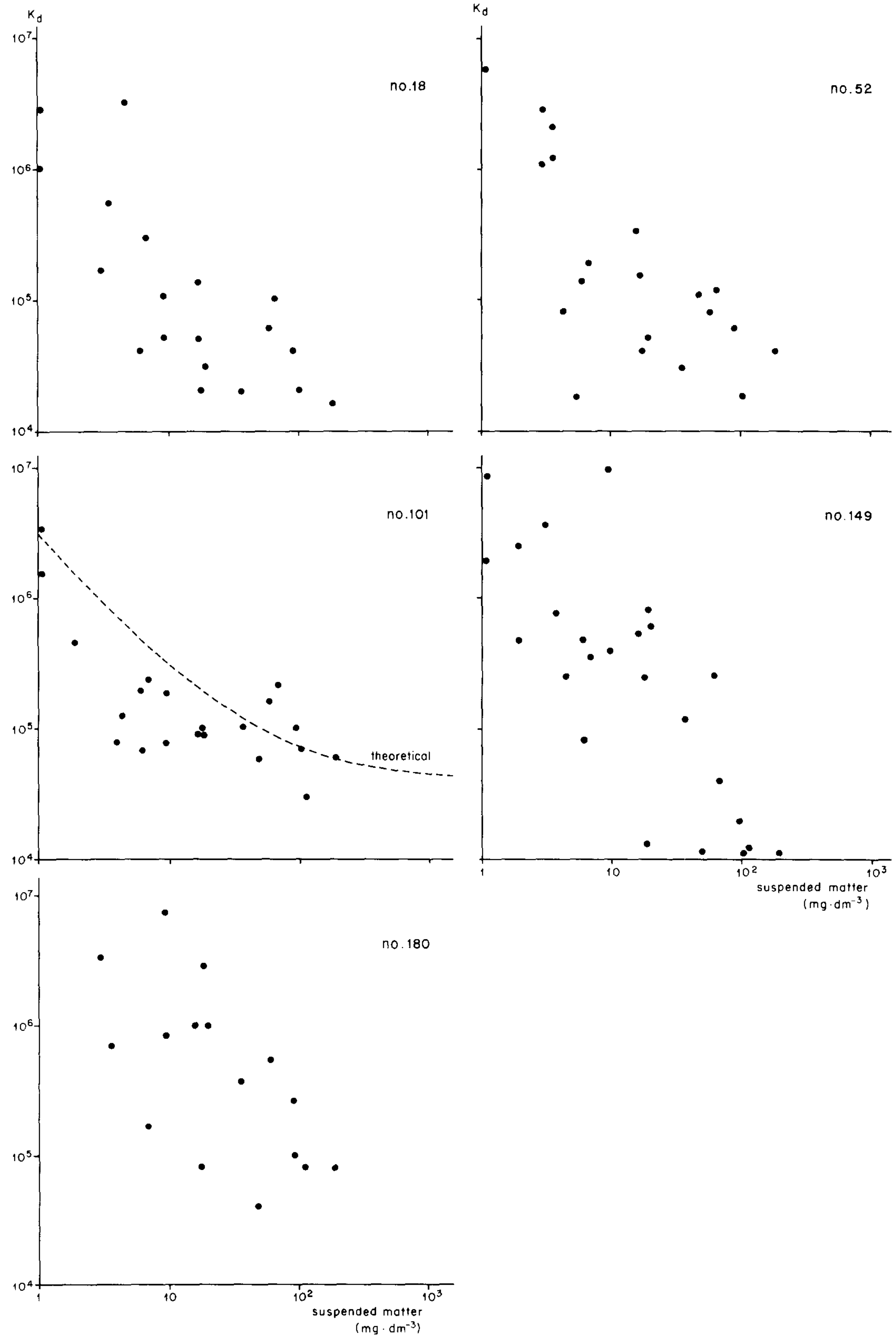


Fig. 2. Contents of PCB congeners 18, 52 and 101 in SPM (ng·g^{-1}) in relation to the suspended matter concentration (mg·dm^{-3}) in all river, coastal and offshore samples considered in this paper. The freshwater data are identified for the Scheldt (S), Rhine (R), Ems (E), Weser (W) and Elbe (El).


K_d
10^7
10^6
10^5
10^4
no.18
no.52
no.101
theoretical
no.149
no.180
1
10
10^2
10^3
suspended matter
(mg·dm^-3)

similar dependence on [SPM] was also found for K_d's (Fig. 3). Although artefacts in the analytical data at the extremely low concentrations in solution and in suspension in the offshore samples cannot be totally excluded, the quality of solvent and procedural blank determinations, the high extraction efficiency and the oceanographically reasonably consistent distribution of concentrations in the North Sea suggest that the observed effects are real. The large volumes of water analysed (100 dm^3) compensate to a large extent for errors associated with the analysis of low-volume samples. The filtration step is normally a weak link in the procedure as the discrimination between dissolved and particulate matter is operationally defined. However, the danger that particles smaller than the nominal filter pore size can still be retained by the filter is larger at high than at low [SPM], and K_d values at low [SPM] would be lower by this mechanism, and not higher, as is observed here.

A similar relation between contents in total suspended matter and [SPM] contents was also found for a series of major elements and trace elements (Cu, Zn, Fe, Al, Mn . . .) in several estuaries and offshore regions of the North Sea (DUINKER *et al.*, 1979; VAN DER SLOOT & DUINKER, 1981). On the basis of the interpretation given for the partition between different suspended forms of these elements, a PCB congener in total particulate suspended matter is distributed between a continuously suspended, non-settling fraction, consisting of small/low density particles (defined as the fine fraction) and a fraction consisting of particles with larger size/density properties (defined as the coarse fraction). The latter is suspended in the water column or deposited on the bottom, depending on hydrodynamical and meteorological conditions. The first and second fractions dominate at low and high [SPM], respectively. The relation between the content of any congener in total SPM and [SPM] will be different from a horizontal line in the corresponding plot, if the contents in the two fractions are sufficiently different. The data suggest that the continuously suspended fraction has strongly increased contents. The relation can be expressed quantitatively as follows:

Consider a fine and coarse fraction and one congener with contents in the fractions defined by mass F/mass of fine, and mass C/mass of coarse, respectively. The concentration in the ambient water is given by W/mass of water.

Distribution coefficients for the partition between water and the fine and coarse fractions individually, are K_d^f = (F/mass of fine) (W/mass of water)$^{-1}$ and K_d^c = (C/mass of coarse) (W/mass of water)$^{-1}$.

The observed distribution coefficient for the partition between water and a mixture of fine and coarse fractions is given by K_d^{obs} = [(C + F)/(mass of fine + mass of coarse)] (W/mass of water)$^{-1}$. This can also be expressed as

$$K_d^{obs} = K_d^c \left(1 + \frac{\text{mass of fine}}{\text{mass of coarse}}\right)^{-1} + K_d^f \left(1 + \frac{\text{mass of coarse}}{\text{mass of fine}}\right)^{-1} \qquad (2)$$

K_d^{obs} can thus be calculated as a function of the ratio of fine and coarse fractions in total suspended matter for selected values of the respective distribution coefficients. A few examples are given in Fig. 4. Actual concentrations under natural conditions will depend on the situation and will require a particular value for the concentration of the continuously suspended fraction. This defines the concentration of the coarse fraction (and thus total [SPM]) for each fine:coarse ratio.

The theoretically expected values for K_d^{obs} for congener 101 in total SPM on the basis of an assumed set of values of $K_d^f = 3 \times 10^6$ and $K_d^c = 4 \times 10^4$ have, at least qualitatively, the same features as the set of experimental data points (Fig. 3). Similar plots can be constructed for the other congeners. Ideally, K_d^f and K_d^c could be calculated by a best-fit procedure, but the scatter in the data is too large to allow an accurate determination.

The results suggest that the distribution of PCB congeners in sea water is affected by a fraction of microparticulates that remain in suspension continuously. These particles can be collected at least partly by filtration and by centrifugation. They carry considerably larger contents of PCB congeners than the larger particles that settle readily. The increased sorption properties of particles with smaller size and, consequently, larger specific surface area have been suggested by several groups working with PCB sorption on sediments (CHOI & CHEN, 1976; DUINKER & HILLEBRAND, 1979; HIRAIZUMI *et al.*, 1979; BOPP *et al.*, 1981). We have found additional evidence that such fractionation is also important in suspended matter, by separating and analyzing separately four SPM fractions with different size/density properties, ob-

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Fig. 3. Water-SPM distribution coefficient (K_d) values calculated from dissolved and particulate suspended concentration data of PCB congeners 18, 52, 101, 149 and 180 in relation to suspended matter concentrations in all river, coastal and offshore samples considered in this paper. The theoretical relation, calculated from equation (2) for $K_d^c = 4 \times 10^4$ and $K_d^f = 3 \times 10^6$, is indicated for PCB congener 101 as an example.

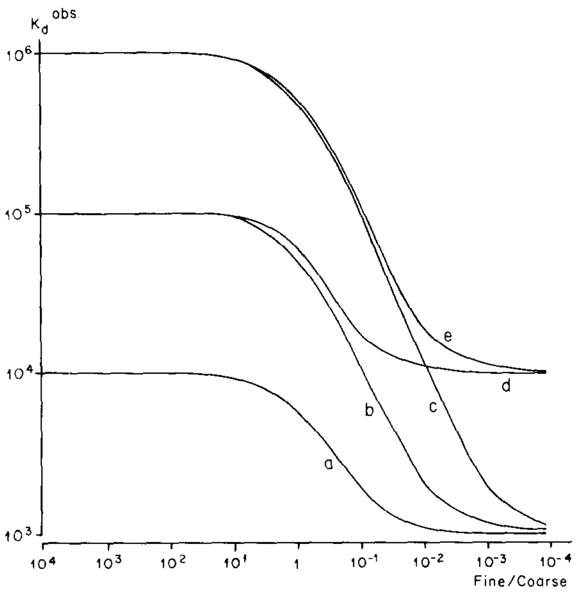

Fig. 4. Relation between the water-SPM distribution coefficients K_d^{obs} calculated for suspended matter, composed of a "coarse" (c) and a "fine" (f) fraction in different mass ratios ("coarse/fine"). The fractions are characterized by distribution coefficients K_d^c and K_d^f, for an arbitrary model compound. The relations, calculated from equation (2), are given for the following combinations of K_d^c and K_d^f values: a) $K_d^c = 10^3$, $K_d^f = 10^4$; b) $K_d^c = 10^3$, $K_d^f = 10^5$; c) $K_d^c = 10^3$, $K_d^f = 10^6$; d) $K_d^c = 10^4$, $K_d^f = 10^5$; e) $K_d^c = 10^4$, $K_d^f = 10^6$.

tained with a modified continuous centrifuge (van der Sloot & Duinker, 1981). It appeared that contents of total PCB (sum of individual congeners) increase typically with decreasing particle size/density: *e.g.*, 81, 294, 963 and 1394 $ng \cdot g^{-1}$, respectively.

This observation on the presence of a SPM fraction with strongly increased K_d's for PCB congeners has important consequences for the distribution and transport mechanisms of these components in the marine environment. If the K_d value for a PCB congener, derived from data in the coastal region, is used for estimating the relative contributions of solution and suspension to the total concentration of the congener in offshore waters with low SPM concentration, a large error may be introduced. For example, a value for $K_d = 5 \times 10^4$ for PCB No 18, results in $A_{susp}/A_{sol} = 0.185$ (or 15% in suspension at a [SPM] = 3.7 $mg \cdot dm^{-3}$. The experimental value for A_{susp}/A_{sol} was 1.9 (*i.e.* 65% in suspension).

It is usually assumed that in offshore samples practically all PCBs are present in solution, which is the justification for not filtering water samples. This may not be justified if strongly increased K_d values are associated with these particulates (which may also contain or even consist mainly of organic macromolecules).

Gschwend & Wu (1985) reported their findings on the role of microparticles or organic macromolecules in batch equilibrium sorption experiments involving sediments. The non-linearity of adsorption isothermes found by others (O'Connor & Connolly, 1980; Voice *et al.*, 1983) was explained by them in terms of incomplete phase separation of dissolved components and those associated with non-filterable or non-centrifugable microparticulates released from the solids. Considerable evidence was presented to support their conclusion that the observed partition coefficients of the PCB congeners studied actually remain constant over a wide range of solid-to-solution ratios. These findings would also weaken the arguments presented to show that sorption is a non-reversible process (di Toro & Horzempa, 1982; Peck *et al.*, 1980).

It can, therefore, be concluded that the distinction between fractions with different settling characteristics has to be taken into account when the partition of PCBs over solution and particulates is considered. The present results suggest that the sorption processes involving these fractions are characterized by quite different distribution coefficients.

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