

Historical input and behaviour of hexachlorobenzene, polychlorinated biphenyls and polycyclic aromatic hydrocarbons in two dated sediment cores from the Scheldt estuary, SW Netherlands

R. Van Zoest^a, G.T.M. Van Eck^{b,*}

^aDepartment of Geochemistry, Institute of Earth Sciences, University of Utrecht, P.O. Box 80021, 3508 TA Utrecht, The Netherlands

^bTidal Waters Division, Ministry of Transport, Public Works and Water Management, P.O. Box 8039, 4330 EA Middelburg, The Netherlands

(Received 11 December 1991; revision accepted 8 February 1993)

Abstract

Hexachlorobenzene (HCB), individual polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) were measured in the less than 63 μm fraction of two dated sediment cores from the salt marshes of the Scheldt estuary, S.W. Netherlands, in order to determine their historical input and post-depositional behaviour.

The recent input of PCBs and PAHs (e.g. 80–280 $\mu\text{g m}^{-2} \text{a}^{-1}$ for PCB 153 and 2–7 $\text{mg m}^{-2} \text{a}^{-1}$ for fluoranthene) was two to three times lower than the maximum input in the mid 1960s. The peak discharge of HCB was recorded around 1972. Contents of organic micropollutants in one core were twice as high as in the other one, although both sites had approximately the same distance to the main pollution source. A high percentage of particles less than 20 μm , probably of marine origin with relatively low pollutant contents in one core, were presumably responsible for this difference.

The PCB profiles show post-depositional congener-selective mobilization caused by advective transport (tailing). The PCB pattern changes, between 1965 and 1975, from less chlorinated to more heavily chlorinated PCBs. This shift coincides with the decrease in the use of PCBs in open systems.

Unlike PCBs, the PAH assemblage is remarkably uniform within a core and between the cores. The PAH ratios indicate that the combustion of coal was the source of PAHs in the Scheldt estuary.

1. Introduction

Estuaries near urbanized and industrialized areas receive and retain large quantities of toxic organic pollutants. Both the amount and number of organic pollutants discharged into the estuarine environment have increased rapidly in recent decades.

Several factors determine the retention and preservation of organic pollutants in estuarine sediments: sorption of the organic compound onto the suspended particulate matter; the

stability of the organic compound both in the water column and the sediment; the hydrodynamical conditions, of which the sedimentary depositional pattern is the most important.

The accumulation of various groups of persistent organic pollutants in lacustrine, estuarine and marine sediments has been studied in several parts of the world. This has provided information on the historical input and on post-depositional mobility and reactivity of these compounds (e.g. Gschwend and Hites, 1981; Barrick and Prahl, 1987; Pavoni et al., 1987; Readman et al., 1987; Oliver et al., 1989). Most

* Corresponding author.

studies have shown that post-depositional mobility and reactivity are not very important. Thus, in most cases some information is obtained about the historical input. Rapaport and Eisenreich (1988) and Oliver et al. (1989), for example, found that with some pesticides, polychlorinated biphenyls (PCBs) and chlorobenzenes, depositional patterns largely conformed to known production records in the United States. Readman et al. (1987) found that the polycyclic aromatic hydrocarbon (PAH) assemblage in a core from the Tamar estuary was very uniform. This suggests that processes like degradation and mobilization, which should act compound-selectively, did not affect the PAH distribution in the sediment. Pruell and Quinn (1985), however, found that the historical record of organic pollutants may be disturbed by smearing because of bioturbation and by dumping and dredging. Finally, in sediments some pollutants can be transformed anaerobically (e.g. *p*, *p'*-DDT to *p*, *p'*-DDD; Oliver et al., 1989).

The Scheldt estuary has been shown to be severely polluted by various groups of organic pollutants (Van Zoest and Van Eck, 1990, 1991). These studies have shown that, within the North Sea area, the PCB and PAH contents of suspended matter are highest in the Scheldt river. Moreover, it was estimated that approximately 90% of the PCB and PAH river input accumulated in the estuarine sediments. This fraction may re-enter the aquatic environment, because of changes in the hydrological and/or geomorphological regime in the future.

In this study we examine the vertical distributions of hexachlorobenzene (HCB), PCBs and PAHs in two dated sediment cores in order both to assess the historical input of these organic pollutants and to investigate their post-depositional behaviour.

The dating of the sediment cores and the historical input and diagenetic processes concerning trace metals are presented in an accompanying paper (Zwolsman et al., 1993-this issue).

2. Materials and methods

Zwolsman et al. (1993 — this issue) described and dated two sediment cores (Konijnenschor and Emanuelschor, further abbreviated as K and E, respectively) from the salt marshes of the Scheldt estuary.

Separate cores were taken at K and E in order to study the historical input and behaviour of organic pollutants. The plastic core liners were pre-cleaned with hot water. The cores, approximately 85 cm long, were frozen at -20°C in the laboratory after collection. They were thawed slightly and sectioned as described by Zwolsman et al. (1993).

Selected samples were wet-sieved on a $63\ \mu\text{m}$ teflon sieve according to the methods of Klamer et al. (1990). In addition some samples were subdivided into three grain size classes (>63 – $1000\ \mu\text{m}$, 20 – $63\ \mu\text{m}$ and $<20\ \mu\text{m}$). The samples less than $63\ \mu\text{m}$ and the subdivided samples were freeze-dried and subsequently homogenized. A subsample was gravimetrically analyzed for POC using a Coleman C-analyzer.

The analytical methods for PCBs, HCB and PAHs have been described previously (Van Zoest and Van Eck, 1990). Briefly, both chlorinated and non-chlorinated compounds were extracted from sediment subsamples with hexane-acetone (3/1, v/v) for 4 h, using a Soxhlet apparatus after adding PCB 29, PCB 155 and benzo(b)chrysene as internal standards for recovery determinations. The clean-up procedure for PCBs was carried out on a combined column with SiO_2 and Al_2O_3 (with Na_2SO_3 and NaOH burden for sulphur removal, Japenga et al., 1987), and on a column with solely Al_2O_3 (also with Na_2SO_3 and NaOH) for PAHs.

PCB analyses were performed after adding PCB 143 as an internal standard, on a Hewlett-Packard (Avondale, USA) gas chromatograph equipped with two, temperature-programmed, fused silica, capillary columns (SE 54 and CPsil19 CB, both of 0.32 mm internal diameter

and 50 m length) connected to the same injection port, and two ^{63}Ni electron capture detectors. PAH analyses were performed on a Hewlett-Packard 1090 liquid chromatograph equipped with a reversed-phase column (Vydac 201 tpb-5, 4.6*250 mm) and two Hewlett-Packard 1046a fluorescence detectors.

Quantification of individual PCB congeners was carried out with PCB 143 as a reference. The 13 PCBs determined were International Union for Pure and Applied Chemistry (IUPAC) numbers: 28, 31, 44, 49, 52, 101, 105, 118, 138, 153, 170, 180 and 187 (nomenclature according to Ballschmiter and Zell, 1980). The quantification of the PAH compounds was performed with a mixture of external standards. The 13 PAH compounds determined were: phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz(a)anthracene (BAA), chrysene (CHR), benzo(e)pyrene (BEP), benzo(b)fluoranthene (BBF), benzo(k)fluoranthene (BKF), benzo(a)pyrene (BAP), benzo(ghi)perylene (BPE), dibenz(ah)anthracene (DBA) and indeno(1, 2, 3-cd)pyrene (INP).

The detection limits were 0.1 ng g^{-1} for PCBs and HCB and $1\text{--}5 \text{ ng g}^{-1}$ for PAHs, dependent on the compound and the amount of sediment extracted. Recoveries for PCB 29 and PCB 155 were, respectively, 93% and 98% (average of both columns). Benzo(b)chrysene proved not to be a proper compound for recovery determinations because another, as yet unidentified, compound with the same retention time was present in the Scheldt estuary samples. The reproducibility, determined by analyzing some samples in duplicate, was satisfactory. Precision was always greater than 85%.

3. Results and discussion

The PCBs, PAHs and HCB content for the two cores K and E as a function of sediment depth and age, are summarized in Fig. 1. Figures 1(a) and 1(b) show total PCB (sum of 13 congeners) as well as two representative PCB

congeners, PCB 52 and PCB 138; Figs. 1(c) and 1(d) show total PAH (sum of 13 compounds) as well as two representative PAH compounds, fluoranthene and benzo(a)pyrene; Fig. 1(e) shows HCB. For 1963–1988 the sedimentation rates 1.7 cm a^{-1} for K and 0.8 cm a^{-1} for E, based on ^{137}Cs were used, for the period before 1963 the rates 1.32 cm a^{-1} for K and 0.9 cm a^{-1} for E, based on ^{210}Pb were used. (Zwolsman et al., 1993).

Sediment contents in Fig. 1 are expressed in $\mu\text{g kg}^{-1}$. The contents are not expressed in $\mu\text{g kg c}^{-1}$ because of the variable nature, and therefore the variable sorption characteristics, of the organic carbon in salt-marsh sediments. The organic carbon in the salt-marsh sediments of the Scheldt estuary originates from (1) the debris of the dense vegetation and (2) the sediment particles accumulating on the salt marshes.

The carbon profile in the less than $63 \mu\text{m}$ fraction of K is essentially constant over depth and varies between $3.0 \pm 0.6\%$ C. The carbon profile in the less than $63 \mu\text{m}$ fraction of E gradually decreases with sediment depth from 4.5% C in the top layer to 2.5% C at the bottom. The micropollutant profiles found (see Fig. 1) cannot therefore be the result of changes in the organic carbon content with a constant associated contaminant burden. An exception has to be made for two high values of the K core which are attributable entirely to the high, non-typical, organic carbon content for these samples. They are not the result of a recent increase in the discharges.

3.1 Input

Peak contents for PCBs and PAHs occurred in the mid 1960s, but the HCB peak content was found in 1972. Unfortunately, no usage data are available for the Scheldt watershed to confirm this.

The results for PCBs are in agreement with other areas (e.g. the lagoon of Venice, Pavoni et al., 1987; Lake Ontario, Oliver et al., 1989). Peak contents were found 5–10 years later in

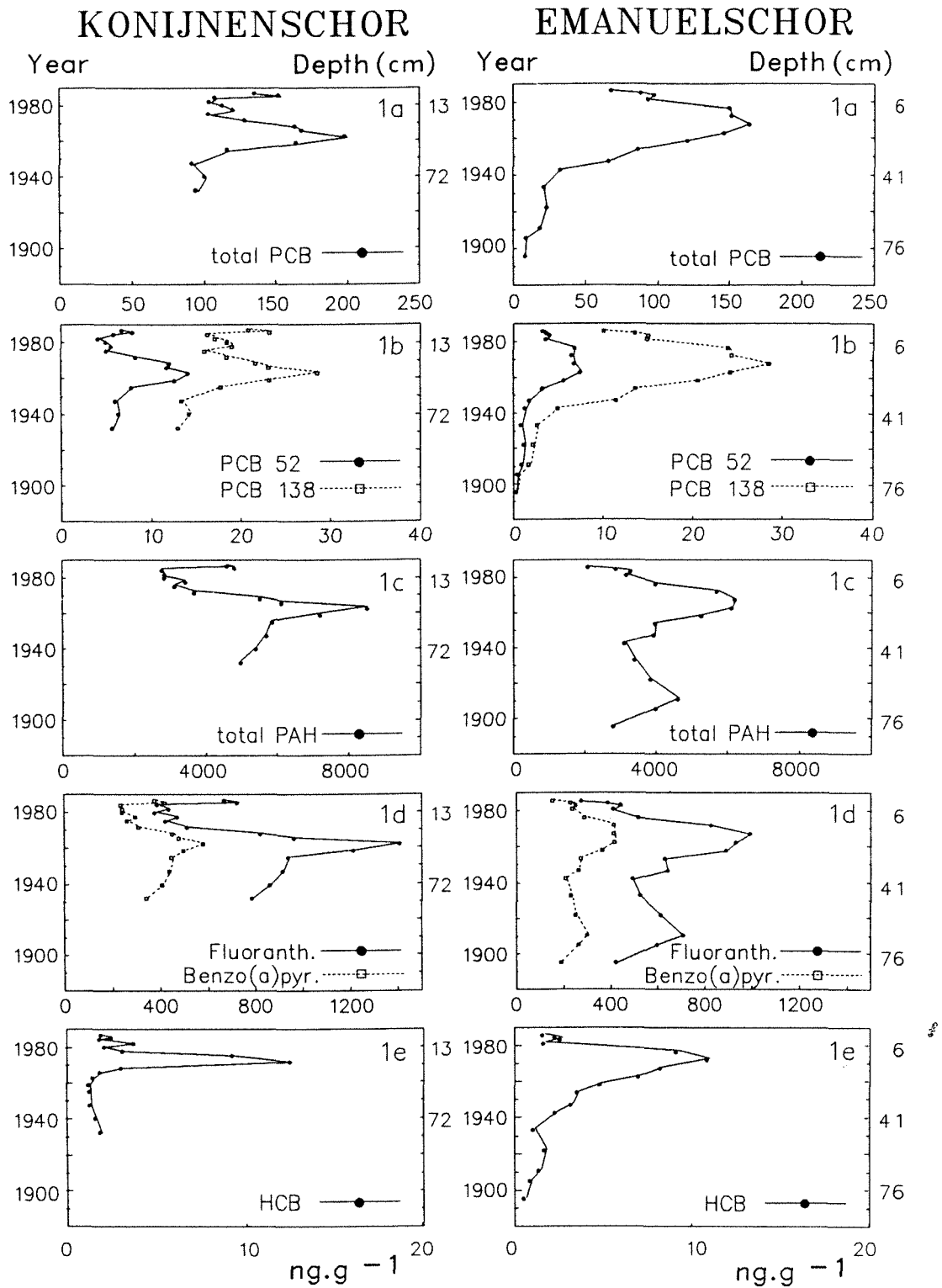


Fig. 1. Total PCB (sum of 13 congeners) (a), PCB 52 and PCB 138 (b), total PAH (sum of 13 compounds) (c), fluoranthene and benzo(a)pyrene (d), and HCB (e), content (in ng g^{-1}) in cores K and E as a function of sediment depth and age.

some other studies (e.g. Rapaport and Eisenreich, 1988). In all cases, however, fast increases in PCB discharges were recorded after 1945–1950, which is in agreement with PCB production and usage records in the United States (Rapaport and Eisenreich, 1988).

A more varied input history (worldwide) is reported in the literature for PAHs. Comparison of the Scheldt estuary with other areas is therefore more difficult. Barrick and Prahl (1987) found maximum PAH contents in the United States in the early 1950s, suggesting that the decrease afterwards reflected the change from coal to oil and gas as domestic heating fuels. In Europe, Pavoni et al. (1987) and Readman et al. (1987) found peak PAH contents in 1960 and 1980, respectively. This variety of input histories probably reflects more specific, region-dependent discharge patterns, in contrast to PCBs.

Less information is available for HCB. In the United States, peak contents found in sediment cores were determined between 1965 and 1970 (Rapaport and Eisenreich, 1988; Oliver et al., 1989), somewhat earlier than in the Scheldt estuary.

Calculations show that the atmospheric contribution to the annual input of organic pollutants is small compared with the sedimentary flux. The atmospheric flux in 1986 for PCB 153 is approximately $0.9 \mu\text{g m}^{-2}$ and for FLA $50 \mu\text{g m}^{-2}$ (KNMI-RIVM, 1987). These are relatively small compared with the present-day sediment flux in the two cores of the Scheldt estuary ($80 \mu\text{g m}^{-2} \text{a}^{-1}$ and $280 \mu\text{g m}^{-2} \text{a}^{-1}$ for PCB 153 in E and K, respectively, and $2 \text{mg m}^{-2} \text{a}^{-1}$ and $7 \text{mg m}^{-2} \text{a}^{-1}$ for FLA in E and K, respectively). The atmospheric PCB 153 flux in the Scheldt estuary is of the same magnitude as the fluxes recently measured in peat cores in the United States (Rapaport and Eisenreich, 1988).

3.2 Behaviour

The two core locations are at the same distance from the main pollution source, i.e.

Table 1

Ratios of some selected PCB congeners and PAH compounds between and within the most recently deposited sediments at K and E

Compound	Ratio in sediment deposited in 1986–1987	
PCBs	$(138/52)_K^a$	3.07
	$(138/52)_E$	3.09
	$138_K/138_E^b$	2.05
	$52_K/52_E$	2.06
PAHs	$(\text{FLA}/\text{BAP})_K$	1.76
	$(\text{FLA}/\text{BAP})_E$	1.75
	$\text{FLA}_K/\text{FLA}_E$	2.41
	$\text{BAP}_K/\text{BAP}_E$	2.40

^a $(138/52)_K$ = ratio of PCB 138 and PCB 52 content at K.

^b $138_K/138_E$ = ratio of PCB 138 content at K and PCB 138 content at E.

the rivers Scheldt and Rupel. We therefore expected that at both K and E sediment with more or less the same pollutant content as well as PCB pattern and PAH assemblage is being deposited. Table 1 shows that the PCB pattern (e.g. PCB 138/PCB 52 at K and E) and the PAH assemblage (e.g. FLA/BAP at K and E) in the most recently (1986–1987) deposited sediment of cores K and E, are identical. The absolute contents in the less than $63 \mu\text{m}$ fraction at K and E (e.g. PCB 138 in K/PCB 138 in E), however, vary by a factor 2–2.4.

To resolve this question we determined, in another recent sediment sample from both cores, the PCB contents in three grain-size classes ($63\text{--}1000 \mu\text{m}$, $20\text{--}63 \mu\text{m}$ and $< 20 \mu\text{m}$) (Table 2). Table 2 suggests that particles less than $20 \mu\text{m}$ in E with relatively low PCB content, and therefore probably of marine origin, are responsible for this difference, because the calculated PCB contents (Table 2) in the less than $63 \mu\text{m}$ fraction of the recent K and E sample are similar to the measured contents in other recent K or E samples (see Fig. 1(a)). Table 2 also shows that the $63\text{--}1000 \mu\text{m}$ fraction of core K has the highest total PCB content.

The same as we have found for PCBs, was found for PAHs by Readman et al. (1984).

Table 2
Grain-size distribution and total PCB content (sum of 13 congeners) of three grain-size classes of recently deposited sediments at K and E

Grain-size fraction	Sample E (4–5 cm)		Sample K (2–3 cm)	
	Grain-size fraction (%)	Total PCB content ($\mu\text{g kg}^{-1}$)	Grain-size fraction (%)	Total PCB content ($\mu\text{g kg}^{-1}$)
63–1000 μm	26	95	17	257
20–63 μm	17	107	30	121
< 20 μm	57	69	53	140
< 63 μm	74	78 ^a	83	133 ^a

^a PCB content calculated from the grain-size fractions and PCB content in the fractions.

They found in particulates from the Tamar estuary up to an order of magnitude higher PAH contents in the 53–100 μm fraction. This fraction consisted of low-density organic debris and they concluded that the occlusion of PAH into these particulates, rather than surface area dependent sorption, was probably responsible for their observation.

3.3 PCBs

Inspection of the general PCB pattern in both cores indicates that the PCB pattern changes between 1965 and 1975. Typical changes in the percentages of tetra-, penta-, hexa- and heptachlorobiphenyls are shown in Table 3. The less chlorinated congeners are less abundant after

Table 3
Percentages of tetra-, penta-, hexa-, and heptachlorinated biphenyls between 1945–1965 and after 1975 in the two dated sediment cores K and E

Core	Interval	Chlorinated biphenyls			
		Tetra	Penta	Hexa	Hepta
K	after 1975 ($n = 7$) ^a	13.9%	22.7%	36.1%	27.3%
	1945–1965 ($n = 4$)	19.5%	27.4%	32.7%	20.4%
E	after 1975 ($n = 5$)	13.3%	24.1%	35.5%	27.1%
	1945–1965 ($n = 4$)	17.4%	24.1%	35.5%	23.0%

^a n , number of sediment samples

1975 than before 1965. A shift in usage pattern from less chlorinated to more heavily chlorinated PCBs in more recent years is probably responsible for this. The shift coincides with the decrease in usage of PCBs in open systems (around 1972 in Western Europe), in which less chlorinated congeners were relatively abundant (P. de Voogt, pers. commun., 1989).

The PCBs are also mobilized after deposition. The post-depositional mobilization of PCBs becomes clear when it is realized that PCBs have been produced since 1929 (Oliver et al., 1989), while Fig. 1 shows that PCBs in the E core are present in the sediment deposited before 1929 and that PCB contents in the K core are already quite high in the early 1930s. Moreover, the peaks of PCB 138, a congener with a relatively low solubility, are sharper than the PCB-52 peaks, a congener with a relatively high solubility. It can be calculated for E that the percentage of the total amount in the sediment from before 1929, tends to increase with the solubility of the congener (Opperhuizen et al., 1988; Fig. 2). For calculation of the total amount in the sediment only the period before 1965 was used because of the change in PCB pattern around 1965.

The tailing of PCBs in sediment cores has also been reported by Rapaport and Eisenreich (1988) and Oliver et al. (1989). In theory, two processes may cause these phenomena: (1) reworking of the sediment by, for example, bioturbation with subsequent selective degradation

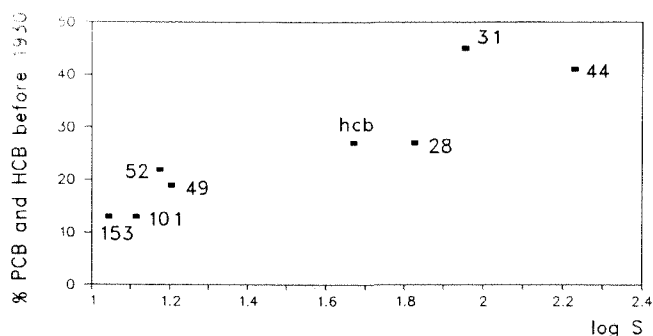


Fig. 2. The fraction in core E of the total amount of HCB and some PCB congeners in sediments from before 1965 found in sediments from before 1929 as a function of solubility (S). Solubility (in $\mu\text{g dm}^{-3}$) of HCB and PCBs from Opperhuizen et al., 1988.

of the higher congeners; (2) migration of PCBs through diffusion and/or advection.

Zwolsman et al. (1993) found no indications for bioturbation. This is in agreement with the fact that salt marshes in general show little or no bioturbation (e.g. Stumpf, 1983).

The migration of PCBs also cannot be explained by diffusion. Diffusion of particulate PCBs is impeded by sorption and their high sediment-water distribution coefficients (K_d). The mean distance that a particle tracer will migrate in the sediment during a certain period (t) is $\sqrt{D_{\text{eff}} * t}$. In this equation D_{eff} is the effective diffusion coefficient, which is inversely related to K_d (Capel, 1986). D_{eff} is less than $1.10^{-10} \text{ cm}^2 \text{ s}^{-1}$ for more chlorinated congeners (Capel, 1986). The mean distance that a PCB congener will migrate in the Scheldt cores in 50 years is therefore only 0.4 cm. Pore-water advection could be more effective to mobilize PCBs in sediments (Tucker et al., 1975). The migration of PCBs is then dependent on the mean water-infiltration rate, the solubility and desorption kinetics. Boderie (personal communication, 1989) measured chlorinity profiles at a salt marsh in the vicinity of our K core and found high advective transport rates. Thus, PCBs are mobilized by infiltrating water.

3.4 PAHs

The composition of the PAH assemblage is

Table 4

Percentage of some individual PAHs to total PAHs (sum of 13 compounds) in the two dated sediment cores K and E

Core	Compound							
	PHE	ANT	FLA	BAA	BEP	BBF	BAP	BPE
K mean	10.1	3.5	15.1	7.2	6.9	11.3	8.0	6.3
s.d.	1.0	0.7	1.1	0.2	0.5	1.0	0.7	0.4
E mean	11.8	3.2	15.0	7.3	6.4	10.7	7.1	6.9
s.d.	1.2	0.4	1.2	0.4	0.3	1.2	0.5	0.7

s.d. = standard deviation.

remarkably uniform within a core and between the cores (Table 4). The ratio of an individual PAH compound to the total PAH contents is very constant over the vertical (i.e. small coefficients of variation) and (nearly) identical in K and E with PHE as the only exception. These results indicate first, that the mobilization process, which affects PCBs, is less effective for PAHs. The reason for this is not clear at a glance, because low molecular weight PAHs should migrate to the same extent as some PCB congeners, since solubilities are of the same magnitude (Miller et al., 1985). Readman et al. (1987), however, also found no mobilization of PAHs and they explained this non-equilibrium behaviour of PAHs by a chemically inert bonding of PAHs. Second, the constancy of the PAH assemblage with depth suggests that other processes like, for example, microbial degradation, which are to be expected to act compound-selectively, are also not important in the Scheldt cores. This is in agreement with the fact that for PAHs microbial degradation under anoxic conditions is seldomly reported in literature.

The source of the PAHs in the Scheldt estuary can be determined by calculating individual PAH ratios using the method of Gschwend and Hites (1981). The ratios applicable to this study are PHE/ANT, FLA/PYR and BEP/BAP. Plots of these ratios (Fig. 3) confirm the uniform composition of the PAH assemblage throughout the cores. The slopes of the plots (PHE/ANT=2.3 for K and 3.4 for E; FLA/PYR=1.4 for both K and E; BEP/BAP=0.9 for both K and E) have

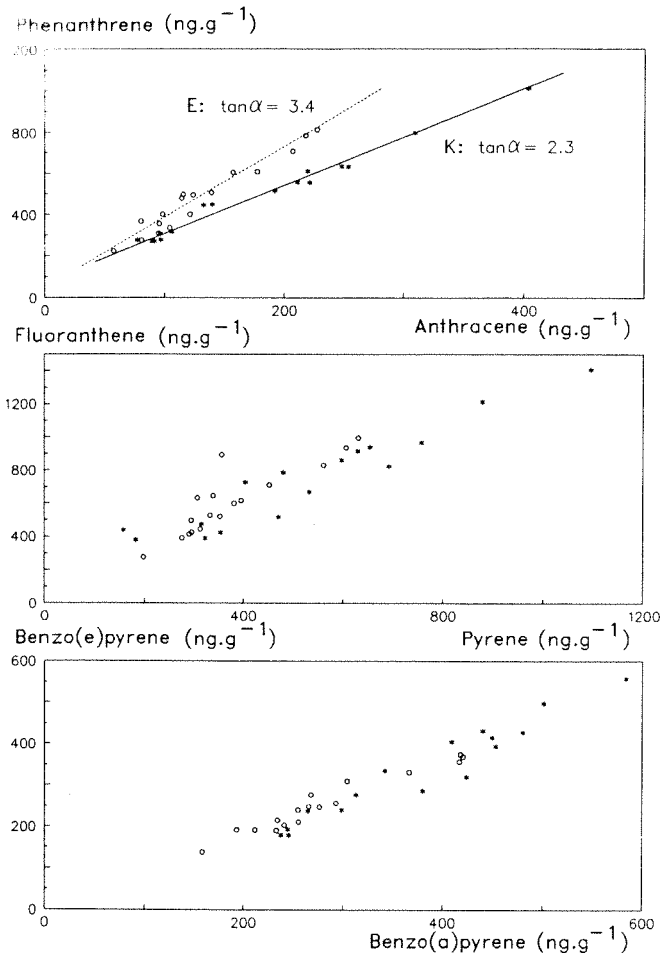


Fig. 3: Plot of phenanthrene vs. anthracene, fluoranthene vs. pyrene and benzo(e)pyrene vs. benzo(a)pyrene in cores K (*) and E (o).

been found before in other sediments and indicate that the most important PAH source in the Scheldt estuary is the combustion of coal (ratios are respectively: 3, 1.3 and 0.84; Gschwend and Hites, 1981). Other sources, such as carbonized coal products (creosote), street-dust runoff and/or fossil fuel combustion are less important in the Scheldt estuary, but were found to be important in other lacustrine and estuarine sediments (Pruell and Quinn, 1985; Readman et al., 1987).

Finally, the higher and constant PHE/ANT ratio in E compared with K (see Fig. 3) has to be explained. The most plausible explanation is a high PHE content in E in the marine derived particles less than 20 μm .

Acknowledgements

We thank F. Steyaert and L. van Geldermalsen for setting up this research, J.J. Siereveld and C.J. Joosse for the sampling and description of the two sediment cores, W. Schreurs, W.H. Pot and W. Wilts for analyzing the samples and J.P.F. Pieters and G. Burger for drawing the figures. We also thank Dr. R.W.P.M. Laane and Prof. C.H. van der Weijden for their valuable comments. The research was commissioned by the Tidal Waters Division (contract DGW-865) and carried out by the University of Utrecht.

References

- Ballschmiter, K. and Zell, M., 1980. Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. *Fresenius Z. Anal. Chem.*, 302: 20–31.
- Barrick, R.C. and Prahl, F.G., 1987. Hydrocarbon geochemistry of the Puget Sound region-III. Polycyclic aromatic hydrocarbons in sediments. *Estuar. Coast. Shelf Sci.*, 25: 175–191.
- Capel, P.D., 1986. Distributions and diagenesis of chlorinated hydrocarbons in sediments. Thesis. Graduate School of the University of Minnesota, 209 pp.
- Gschwend, P.M. and Hites, R.A., 1981. Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the north-eastern United States. *Geochim. Cosmochim. Acta*, 45: 2359–2367.
- Japenga, J., Wagenaar, W.J., Smedes, F. and Salomons, W., 1987. A new, rapid clean-up procedure for the simultaneous determination of different groups of organic micropollutants in sediments; application in two European estuarine sediment studies. *Environ. Technol. Letters*, 8: 9–20.
- Klamer, J.C., Hegeman, W.J.M. and Smedes, F., 1990. Comparison of grain-size correction procedures for organic micropollutants and heavy metals in marine sediments. *Hydrobiologia*, 208: 213–220.
- KNMI-RIVM, 1987. Chemical composition of precipitation over the Netherlands. Annual report 1986. Koninklijk Nederlands Meteorologisch Instituut, De Bilt and Rijksinstituut voor Volksgezondheid en Milieuhygiene, Bilthoven, The Netherlands.
- Miller, M.M., Wasik, S.P., Huang, G.L., Shiu, W.Y. and MacKay, D., 1985. Relationships between octanol-water partition coefficient and aqueous solubility. *Environ. Sci. Technol.*, 19: 522–529.

- Oliver, B.G., Charlton, M.N. and Durham, R.W., 1989. Distribution, redistribution and geochronology of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in Lake Ontario sediments. *Environ. Sci. Technol.*, 23: 200–208.
- Oppenhuizen, A., Gobas, F.A.P.C., van der Steen, J.M.D. and Hutzinger, O., 1988. Aqueous solubility of polychlorinated biphenyls related to molecular structure. *Environ. Sci. Technol.*, 22: 638–646.
- Pavoni, B., Sfriso, A. and Marcomini, A., 1987. Concentration and flux profiles of PCBs, DDTs and PAHs in a dated sediment core from the lagoon of Venice. *Mar. Chem.*, 21: 25–35.
- Pruell, R.J. and Quinn, J.G., 1985. Geochemistry of organic contaminants in Narragansett Bay sediments. *Estuar. Coast. Shelf Sci.*, 21: 295–312.
- Rapaport, R.A. and Eisenreich, S.J., 1988. Historical atmospheric inputs of high molecular weight chlorinated hydrocarbons to eastern North America. *Environ. Sci. Technol.*, 22: 931–941.
- Readman, J.W., Mantoura, R.F.C. and Rhead, M.M., 1984. The physico-chemical speciation of polycyclic aromatic hydrocarbons (PAH) in aquatic systems. *Fresenius Z. Anal. Chem.*, 319: 126–131.
- Readman, J.W., Mantoura, R.F.C. and Rhead, M.M., 1987. A record of polycyclic aromatic hydrocarbon (PAH) pollution obtained from accreting sediments of the Tamar estuary, U.K.: evidence for non-equilibrium behaviour of PAH. *Sci. Total Environ.*, 66: 73–94.
- Stumpf, R.P., 1983. The processes of sedimentation on the surface of a salt marsh. *East. Coast. Shelf Sci.*, 17: 495–508.
- Tucker, E.S., Litschgi, W.J. and Mees, W.M., 1975. Migration of polychlorinated biphenyls in soil induced by percolating water. *Bull. Environ. Contam. Toxicol.*, 13: 86–93.
- Van Zoest, R. and Van Eck, G.T.M., 1990. Behaviour of particulate polychlorinated biphenyls and polycyclic aromatic hydrocarbons in the Scheldt estuary. *Neth. J. Sea Res.*, 26: 89–96.
- Van Zoest, R. and Van Eck, G.T.M., 1991. Occurrence and behaviour of several groups of organic micropollutants in the Scheldt estuary. *Sci. Total Environ.*, 103: 57–71.
- Zwolsman, J.J.G., Berger, G.W. and Van Eck, G.T.M., 1993. Sediment accumulation rates, historical input, post-depositional mobility and retention of major and trace elements in two salt marsh sediment cores from the Scheldt estuary, SW Netherlands, *Mar. Chem.*, 44: 73–94, this issue.