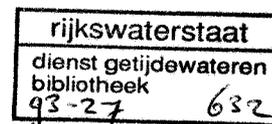


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Geographical Distribution of Chlorinated Biphenyls (CBs) and Polycyclic Aromatic Hydrocarbons (PAHs) in Surface Sediments from the Humber Plume, North Sea

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Concentration distributions of chlorinated biphenyls (CBs) and polycyclic aromatic hydrocarbons (PAHs) were determined in the <math> < 63 \mu\text{m}</math> grain size fraction of surface sediments of the Humber plume, North Sea. Concentration ranges of ΣCB and ΣPAH were 2.92–19.07 $\mu\text{g kg}^{-1}$ and 0.70–2.70 mg kg^{-1} , respectively. The general distribution pattern of CBs and PAHs followed the general path of the Humber plume, with little influence from the Wash. The pattern of lower chlorinated CBs suggested a possible source of these compounds north of the region studied; PAH patterns and PAH-compound ratios demonstrated the influence of urban pollution on offshore sediments. On average, Humber plume sediments had lower CB concentrations than sediments in other areas of the North Sea, while PAH levels were similar or, for some compounds, higher. Concentrations of CBs and PAHs in the Humber mouth, however, showed increased levels.

It has been well established, that organic micropollutants (e.g. CBs, PAHs) have pronounced adverse effects on the health of marine biota (Reijnders, 1986; Malins *et al.*, 1988; Tanabe, 1988). At the Third International Conference on the Protection of the North Sea it was decided to reduce the loads of primary pollutants to the North Sea by 50–70% (Anon., 1990a). To monitor the reduction measures adequately, detailed information on sources (emission), input into the system and actual concentrations is essential. A literature survey on CB

concentrations in the North Sea showed that data on CB levels in English waters are very scarce (Klamer *et al.*, 1990a). However, there are reasons for believing that sediment quality in the area has been adversely effected by industrial activities at e.g. Teesside and Humberside (Grogan, 1984).

The present study aims to fill part of this gap in knowledge, by an investigation of CB and PAH levels in sediments from the Humber plume area. It focuses on determining distribution patterns of individual CB congeners and PAH compounds, and compares concentrations in the area with those found in sediment samples from the rivers Rhine, Scheldt and Ems/Dollard and from sedimentation areas like the Wadden Sea and the Oyster Grounds.

Materials and Methods

The sediment samples were collected during cruise CH 69/90 of the RRS *Challenger* (26 July–7 August 1990), affiliated to UK-NERC's North Sea Project. The location of the sampling stations is shown in Fig. 1. Surface sediment samples were collected using a Day grab. If a relatively undisturbed and muddy top layer existed (0–2 cm), it was subsampled using a PTFE spatula; otherwise, the top 5 to 10 cm were sampled. The subsamples were transferred to pentane-washed polyethylene bottles. All samples were sieved on board, using a specially designed sieving apparatus with 63 μm nylon mesh (Klamer *et al.*, 1990b). The collected fine fractions were kept frozen until further treatment.

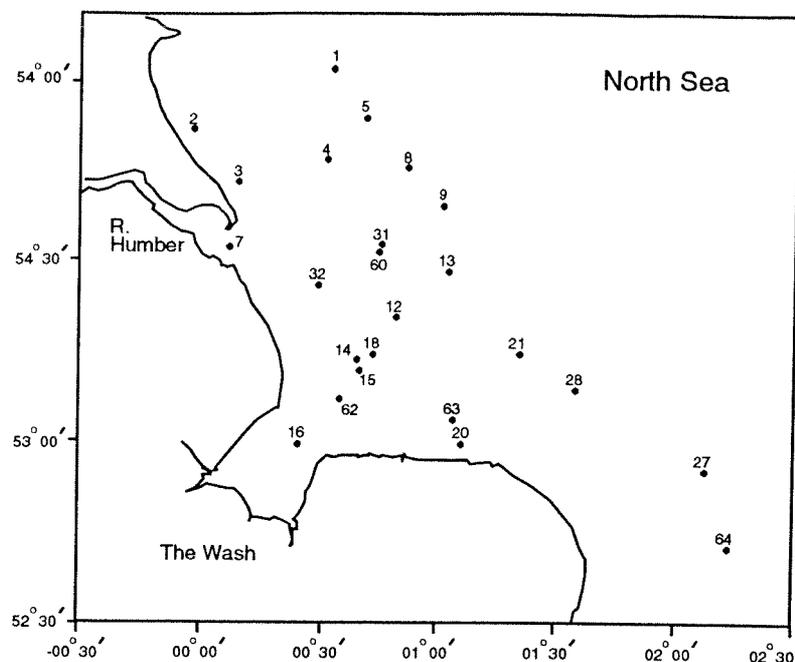


Fig. 1 Sampling stations for sediments around the Humber plume and the Wash, July/August 1990.

After freeze-drying, CBs 29 and 155 and benzo(b)chrysene were added to the sediment, for recovery measurements (separate laboratory recovery experiments using several different sediment types did not show any loss of CBs or PAHs; Smedes, pers. comm.). The sediments were Soxhlet-extracted with hexane-acetone (3:1). The crude extracts were cleaned up and the CB and PAH fractions obtained by adsorption chromatography using aluminium oxide and silica gel. CBs were determined with capillary gas-chromatography, using two columns of different polarity, and ECD detection at both columns. A laboratory standard of a mixture of CB congeners was used for identification and quantification, using CB 143 as internal standard. CBs determined were: 18, 26, 28, 31, 44, 52, 101, 118, 138, 153, 170, and 180. Detection limits were about $0.1 \mu\text{g kg}^{-1}$, with an analytical error of about 10% and a recovery of 90–100%.

PAH compounds were determined using high-performance liquid chromatography with fluorescence detection, using 2-methylchrysene as internal standard. PAH compounds determined were: fluoranthene (FLU), phenanthrene (PHE), pyrene (PYR), benzo(a)anthracene (BAA), chrysene (CHR), benzo(e)- and benzo(a)pyrene (BEP and BAP), benzo(b)- and benzo(k)fluoranthene (BBF and BKF), benzo(g,h,i)-perylene (BPE) and indeno(1,2,3-c,d)pyrene (INP). Detection limits were about $5 \mu\text{g kg}^{-1}$, with an analytical error of about 10% and a recovery of 80–95%. Biogeochemical markers (e.g. $\delta^{13}\text{C}$) were analysed in the organic carbon fraction of the particulate samples, measuring the $^{13}\text{C}/^{12}\text{C}$ ratio of the combustion product (CO_2) with mass spectrometry (Laane *et al.*, 1990). From $\delta^{13}\text{C}$ the fraction riverine/terrestrial material F_t was calculated, using the formulas from Fry & Sherr (1984) and Fontugne & Jouanneau (1987):

$$\delta^{13}\text{C} = F_t \cdot \delta^{13}\text{C}_t + F_m \cdot \delta^{13}\text{C}_m \quad \text{and} \quad F_t + F_m = 1,$$

where $\delta^{13}\text{C}$ = measured isotopic fractionation; F_t and F_m = fraction riverine/terrestrial and marine organic carbon, respectively; $\delta^{13}\text{C}_t$ and $\delta^{13}\text{C}_m$ = average isotopic fractionation, in moderate climates, of riverine/terrestrial and marine organic carbon, respectively. Values of $\delta^{13}\text{C}_t$ and $\delta^{13}\text{C}_m$ are -29.1‰ and -19.0‰ (Laane *et al.*, 1990; Fry and Sherr, 1984).

Results and Discussion

In this section, results for CB 18 and 153, and for BAP are presented as examples of the general behaviour of lower and higher chlorinated CBs and of all PAHs. Supplementary data on other compounds is available on request. The full cruise data set will be electronically published on CD-ROM in November 1992 by the British Oceanographic Data Centre to whom enquiries should be addressed (BODC, Proudman Oceanographic Laboratory, Bidston Observatory, Birkenhead, Merseyside L43 7RA, UK).

Table 1 gives the concentration ranges of CBs and PAHs. Figure 2 gives the ΣCB and ΣPAH concentrations (both: sum of concentrations from Table 1) for all sampling points. Figures 3a–d give the distribution patterns of CBs 18 and 153, of BAP and of the fraction of terrestrial material F_t of the sediment's organic carbon material, respectively.

CBs

The distribution patterns of all CBs were greatly influenced by the plume from the River Humber; all compounds showed a pronounced decreasing concentration seawards from the Humber mouth, moving south before turning eastward. Examples of the distribution patterns of CB 18 and CB 153 are given in Fig. 3. A characteristic of all lower chlorinated CBs was a decreasing concentration north to south. Standardiza-

TABLE 1

Range in concentrations of CBs and PAHs in Humber Plume surface sediments, fraction <63 μm , in July/August 1990. CBs: nM kg^{-1} , PAHs in $\mu\text{M kg}^{-1}$, ΣCB in $\mu\text{g kg}^{-1}$, ΣPAH in mg kg^{-1} , dry wt.

	18	28	44	52	101	105	118	138	153	170	180	187	ΣCB
Min.	1.36	1.35	0.77	1.12	1.11	0.37	0.81	0.74	1.10	0.22	0.34	0.38	2.92
Max.	7.87	11.55	4.29	7.43	5.67	2.17	3.84	4.83	6.19	1.83	4.11	2.52	19.07

	FEN	ANT	PYR	FLU	CHR	BAA	BBF	BKF	BAP	BEP	BPE	INP	DBA	ΣPAH
Min.	0.67	0.06	0.46	0.42	0.16	0.10	0.21	0.13	0.13	0.22	0.24	0.18	0.03	0.70
Max.	2.32	0.33	1.50	1.86	0.84	0.55	0.89	0.58	0.68	0.90	0.98	0.77	0.13	2.70

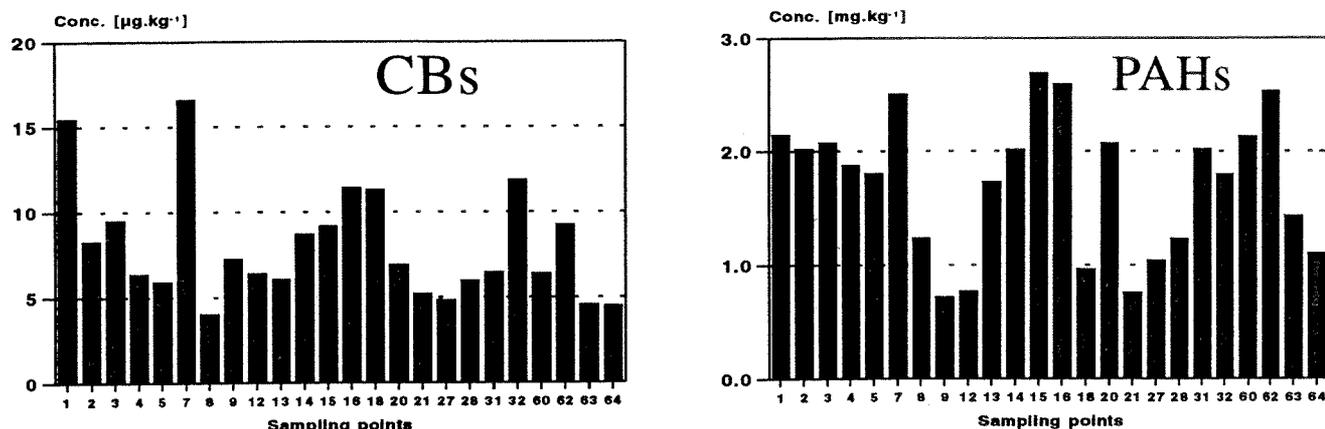


Fig. 2 Concentrations of ΣCB and ΣPAH in Humber plume surface sediments, July/August 1990 ($\mu\text{g kg}^{-1}$ for CBs, mg kg^{-1} for PAHs, dry wt, both in the <63 μm grain size fraction). Sampling points refer to Fig. 1.

tion of CB and PAH levels to F_i (see below) increased this concentration trend. The contribution of these lower chlorinated CBs to ΣCB was generally high: CBs with 5 chlorines or less accounted for 40–80% of ΣCB . Comparison of the CB patterns with those found in different technical formulations (e.g. Clophen mixtures; Duinker and Hillebrand, 1983) and those in sediments from other parts of the North Sea (e.g. Oyster Grounds (Stutterheim and Zevenboom, 1987), Wadden Sea (Duijts, 1990)), gave evidence of a rather unusual distribution. This phenomenon was earlier reported for sediments and polychaetes by Boon *et al.* (1985). Büther (1988) reported a shift in CB pattern in livers of dab, with higher levels of lower chlorinated CBs off the English east coast, compared with samples from the Dogger Bank and German Bight.

This evidence points to the River Humber as the principle source for larger CBs, and suggests that the lower chlorinated CBs could also originate from another source, more to the north/northeast, as was indicated by Schulz-Bull *et al.* (1991). Sources might include leaching of lower chlorinated CBs from polluted sediments around (not necessarily operational) oil/gas rigs (Schulz-Bull *et al.* (1991). On the other hand it is very possible that the influx of CBs from the River Humber merely disturbs a general oceanic/off-shore CB distribution pattern. There are, however, insufficient data available to test either of these hypotheses.

PAHs

As for CBs, the concentration profiles (e.g. Fig. 3) indicate an emission from the river mouth. The gradients are less pronounced than those of CBs, however. Also, there was no marked difference in concentration pattern between compounds of lower and higher molecular weight; standardization to F_i indicated a slight increase in concentration north of the river mouth. This suggests that next to the River Humber, the atmosphere might be a second dominant source of hydrocarbons. Gschwend & Hites (1981) showed that some PAH ratios in air samples changed going from urban sites to more remote areas. The FEN/ANT ratio especially decreased dramatically in this direction while the FLU/PYR and BEP/BAP ratios increased slightly going from coastal seawater to remote freshwater sites. Table 2 shows PAH ratios, as taken from Gschwend & Hites (1981), and ratios calculated from the Humber plume data. The FEN/ANT ratio in our study changed significantly ($p=0.005$) from 6.9 in coastal areas to 11.8 at locations around 80 km from the coast. The BEP/BAP ratio had the same tendency ($p=0.01$), while the FLU/PYR ratio did not change. These results suggest a possible urban source for PAHs in offshore areas. However, from these ratios no conclusions could be drawn concerning the relative contributions of River Humber water and Humber side air to the PAH pollution of the sediments.

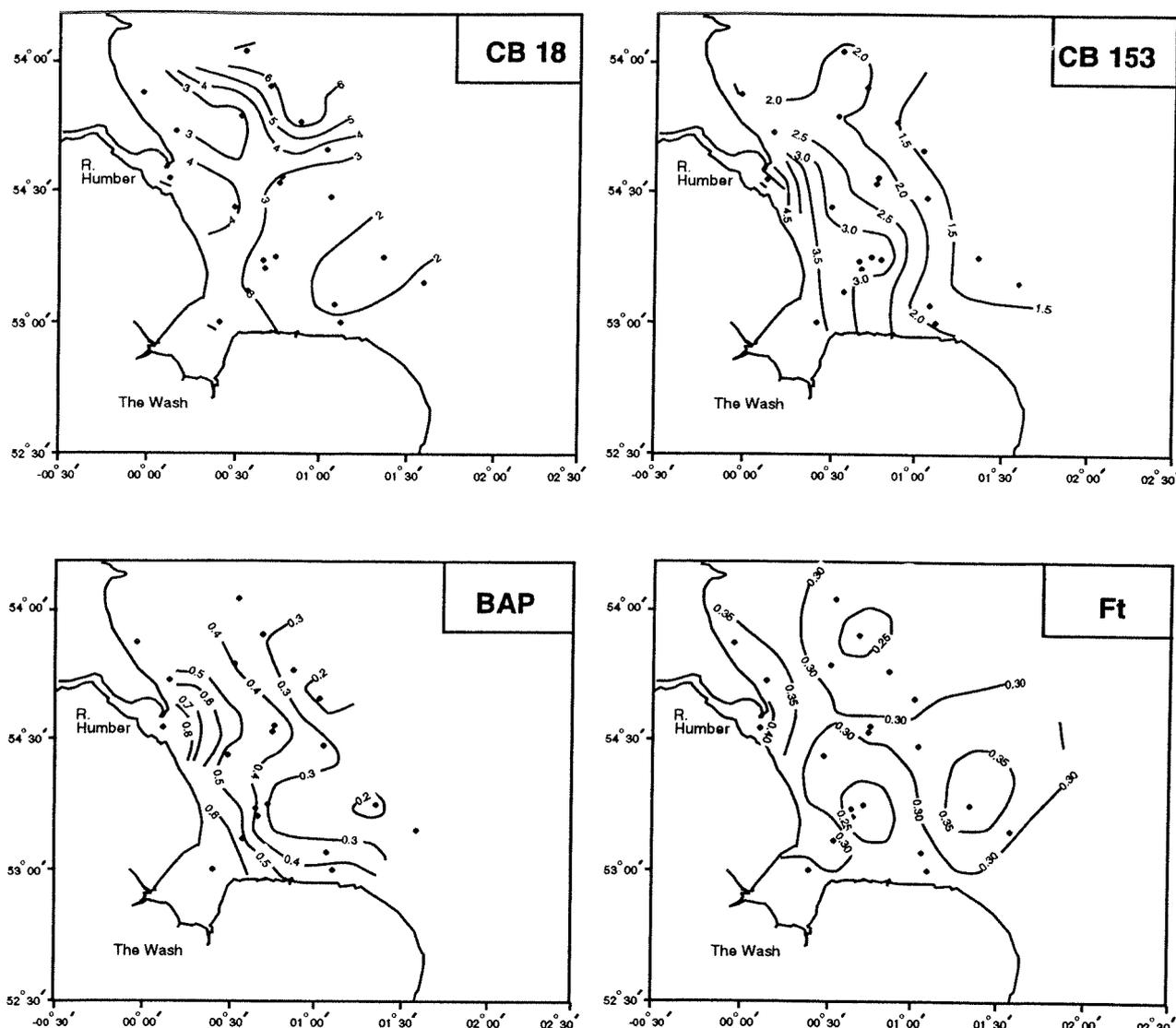


Fig. 3 Concentration profiles of CB 18, CB 153, BAP and F_t in Humber plume surface sediments, July/August 1990 (CBs and BAP in nM kg^{-1} dry wt; fraction $<63 \mu\text{m}$; sampling points are depicted by the black dots).

TABLE 2

PAH ratios in Humber plume surface sediments (refer to Fig. 1), compared with data from Gschwend & Hites (1981).

Location	FEN/ANT	FLU/PYR	BEP/BAP
Coastal area			
Sp. 2	8.1	1.2	1.6
Sp. 3	6.7	1.2	1.3
Sp. 7	6.6	1.0	1.2
Sp. 16	6.0	1.2	1.4
Offshore area			
Sp. 1	9.1	1.2	1.7
Sp. 9	14.3	0.8	1.7
Sp. 21	13.6	0.9	1.7
Sp. 27	9.9	1.2	1.4
Sp. 28	12.3	1.1	1.6
Gschwend & Hites (1981)			
Urban air	8–15	0.7–1.4	1.2–2.0
Wood/coal fire	3	1.0–1.4	0.4–0.8
(Crude) oil	50	0.6–1.4	0.2–3.3

$\delta^{13}\text{C}$

For studies of micropollutant processes, it is necessary to understand the distribution and fate of POC from riverine/terrestrial and marine origin, in estuaries

and adjacent coastal areas. The carbon isotope ratio of POC, $\delta^{13}\text{C}$, has been used frequently to distinguish between different sources (Laane *et al.*, 1990; Fontugne and Jouanneau, 1987; Fry and Sherr, 1984). Riverine/terrestrial POC has a lower (i.e. more negative) $\delta^{13}\text{C}$ than marine POC. In principal, the contribution of fluvial and marine POC in sediments at a certain location can be calculated using simple mixing models. However, complicating factors exist (summarized in Laane *et al.*, 1990). The movement of the plume from the Humber could clearly be distinguished from the fraction of riverine/terrestrial organic carbon (F_t , Fig. 3d). F_t decreased from 0.4 to 0.2 in the area investigated. It appeared that the plume tended to move southward, with very little influence from the Wash. In the coastal area, the F_t pattern gave a good correlation with the CB and PAH distribution ($p=0.01$). The increase in F_t levels, up to 0.38 in the southeastern part of the plume, cannot be explained; this specific pattern was not found for CBs or PAHs, while earlier published data from this cruise did not give any indication of increased terrestrial/riverine influence (as indicated by increased pollutant levels), either (Raymundo & Preston, 1992).

Comparison of CB and PAH Concentrations with Levels in Other Areas of the North Sea

Figure 4 gives the total concentration of respectively CBs 28, 52, 101, 118, 138, 153 and 180, and of the six 'Borneff' PAHs (FLU, BBF, BKF, BAP, BPE, INP), in different sediment samples. In these figures, the total concentration at different locations has been anchored at the overall average value of all locations (Klamer *et al.*, 1990c). Data are from this study ('H1', 'H7' and 'H64', refer to Fig. 1), from Klamer & Laane, 1990 ('R': lower Rhine estuary), Akkerman *et al.*, 1992 ('OG': Oyster Grounds, 'WWS': Western Wadden Sea, 'ED': Ems-Dollard and 'LS': lower Scheldt estuary). Concentrations are in $\mu\text{g kg}^{-1}$ for the CBs, and in mg kg^{-1} for PAHs.

Compared with sedimentation areas in the Dutch sector of the North Sea, ΣCB levels in offshore regions of the Humber plume were relatively low (H1, H64; $p < 0.01$). The level at the most remote location 64 was similar to that at the Oyster Grounds. Levels in the Humber mouth were comparable with those in the lower estuaries of the Rhine and the Scheldt, and in the western Wadden Sea. Individual concentrations of CBs

118, 153, 180 were significantly lower than in the Ems-Dollard and western Wadden Sea ($p < 0.001$), and higher than the Oyster Ground values; CB 52 at location 7 (Humber mouth) was higher than in the lower estuaries of the Rhine and Scheldt and in the Ems-Dollard ($p < 0.01$). Comparison of F_1 -standardized CB values (only F_1 -values available in this study and from Klamer and Laane, 1990), showed that standardized CB values from the Rhine were almost twice as high as those from the Humber plume ($\text{CB}/F_1 = 0.43$ for the Rhine, and 0.20, 0.26 and 0.21 for Humber plume samples 1, 7, and 64, respectively).

The total level of the six Borneff PAHs at location 7 (Humber mouth) and at location 1 (north of the mouth) was higher than in the other areas ($p < 0.001$). Of the individual PAH compounds, FLU, BKF and BAP were higher in the Humber plume at location 7 than in the Ems Dollard and western Wadden Sea. Concentration differences for other individual PAH at other locations were not significant with $p > 0.01$. Comparison of F_1 -standardized PAH values showed that standardized PAH values from the Humber were between 2 and 4 times higher than those in the Rhine ($\text{PAH}/F_1 = 1.5$ for the Rhine, and 2.8, 4.7 and 5.5 for Humber plume samples 64, 7, and 1, respectively).

Conclusions

The results of this study indicate that, on average, the Humber plume sediments have lower CB concentrations than sediments in other areas of the North Sea, while PAH levels are generally equal or, for BAP and BKF, higher. Concentrations of CBs and PAHs in the Humber mouth, however, showed increased levels. Standardized on the sediment's fraction of terrestrial organic carbon, CB levels in the Humber plume were almost twice as low as in the lower Rhine estuary, while F_1 -standardized PAH values were 2 to 4 times as high, with maxima at the mouth and to the north.

The general distribution pattern of CBs and PAHs showed evidence that the concentrations follow the general path of the Humber plume with only a slight influence from the Wash. The pattern of lower chlorinated CBs suggested a possible source of these compounds north of the river mouth. PAH-compound ratios showed the influence of urban pollution on offshore sediments, while F_1 -standardized PAH levels also pointed to an unknown source, north of the region studied.

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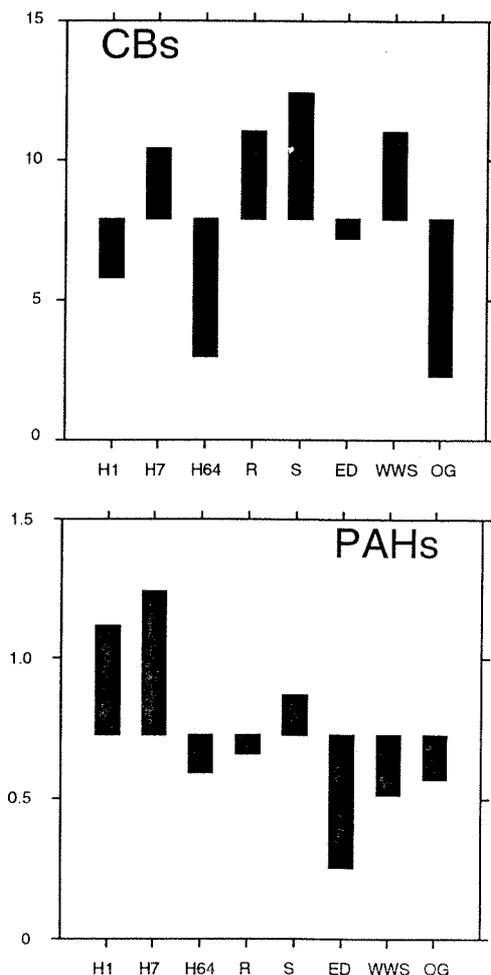


Fig. 4 Total concentration of respectively CBs 28, 52, 101, 118, 138, 153 and 180, and of the six 'Borneff' PAHs (FLU, BBF, BKF, BAP, BPE, INP), in different sediment samples, anchored at the overall average value of all locations. Data are from this study ('H1', 'H7' and 'H64', refer to Fig. 1), from Klamer and Laane, 1990 ('R': lower Rhine estuary), Akkerman *et al.*, 1992 ('OG': Oyster Grounds, 'WWS': Western Wadden Sea, 'ED': Ems-Dollard and 'S': lower Scheldt estuaries). Concentrations are in $\mu\text{g kg}^{-1}$ for the CBs, and in mg kg^{-1} for PAHs.

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