

BEHAVIOUR OF PARTICULATE POLYCHLORINATED BIPHENYLS AND POLYCYCLIC AROMATIC HYDROCARBONS IN THE SCHELDT ESTUARY

R. VAN ZOEST¹ and G.T.M. VAN ECK²

¹Department of Geochemistry, Institute of Earth Sciences, University of Utrecht, P.O. Box 80021, 3508 TA Utrecht, The Netherlands

²Ministry of Transport and Public Works, Tidal Waters Division, P.O. Box 8039, 4330 EA Middelburg, the Netherlands

ABSTRACT

Temporal and spatial variations in PolyChlorinated Biphenyl (PCB) and Polycyclic Aromatic Hydrocarbon (PAH) contents were studied in the Scheldt estuary during a one-year period (August 1987 - June 1988). Concentration levels in the Scheldt river (up to 206 ng-g⁻¹ for individual PCB congeners and 14.6 µg-g⁻¹ for individual PAH compounds) were higher than in any other river in the North Sea area. The annual input into the estuary was approximately 160 kg for total PCBs (10 congeners) and 12 000 kg for total PAHs (13 compounds). A small fraction of the riverine PCB and PAH load (10%) was transported to the North Sea, whereas most organic pollutants were stored in estuarine sediments. Particulate PCBs and most particulate PAHs behaved conservatively in the Scheldt estuary. PCB and PAH contents decreased when salinities increased, as a result of the mixing of riverine with marine particulates. Moreover, the PCB patterns gradually shifted in that the fraction of less chlorinated biphenyls increased compared to more chlorinated congeners. Possible mechanisms are discussed. It is suggested that emissions of PCB mixtures enriched in less chlorinated congeners took place in the proximity of the mouth of the estuary. Low molecular weight PAHs (phenanthrene, anthracene and fluoranthene) were removed in the lower salinity range. This observation may be explained by microbial degradation at low salinities under (near) anoxic conditions, favoured by the long residence time of the particulates in the high-turbidity zone.

1. INTRODUCTION

The occurrence of PolyChlorinated Biphenyls (PCBs) and Polycyclic Aromatic Hydrocarbons (PAHs) has been proved within all abiotic compartments and most biota in the aquatic environment (e.g. BORNEFF & KUNTE, 1983; DUINKER *et al.*, 1984; PHILLIPS & SPIES, 1988; OLIVER & NIIMI, 1988). Impact on marine

organisms has been shown for both groups (REIJNDERS, 1980; MALINS *et al.*, 1988). PCBs and PAHs are very persistent and are bioaccumulated to a great extent (BRUGGEMAN, 1983). Their hydrophobic nature leads to strong sorption onto particulates. Sorption mainly takes place onto the Particulate Organic Matter (POM) phase (KARICKHOFF *et al.*, 1979).

Organic pollutants may be supplied to the sea through: rivers, atmospheric deposition, spills and the dumping of dredging material. Estuaries in particular may accumulate large amounts of polluted riverine particulate matter. In such cases, organic pollutants will contribute to the environmental stress on the estuarine ecosystem, both now and in the future.

Among others, READMAN *et al.* (1982), HERRMANN & THOMAS (1984) and DUINKER (1986) studied the estuarine behaviour of PCBs and PAHs. Generally, pathways and fate of PCBs and PAHs were largely determined by the particulate matter dynamics in the estuary, whereas no major differentiation was detected between PCB congeners and between PAH compounds. An exception was the behaviour of low molecular weight (M.W.) PAHs in the Tamar estuary (READMAN *et al.*, 1982), which were more susceptible to microbial degradation and volatilization than high M.W. PAHs.

DUINKER (1986) found that small/low density particulates, having higher sorption capacity than the 'bulk' particulates in the estuary, escaped from the estuarine circulation and predominated in the coastal area (particulate matter concentrations < 1 mg-dm⁻³).

The Scheldt estuary (Fig. 1) is heavily contaminated with heavy metals and organic micropollutants (RIZA, 1982). The large organic matter load causes oxygen depletion in the Scheldt river and in the upper estuary (from Rupelmonde to buoy 87, Fig. 1).

In this study, we determined PCBs and PAHs in the particulate matter of the Scheldt estuary. The main aims were: firstly, to assess PCB and PAH contents in the Scheldt estuary during different seasons; secondly, to study pathways and fate of PCBs and PAHs in the estuary, and thirdly, to estimate the PCB

and PAH load from the Scheldt river to the estuary and from the estuary to the North Sea. Only the particulate fractions were studied, since they represent the major parts of the total PCB and PAH concentrations.

Acknowledgements.—We thank the crews of R.V. 'Delta' and R.V. 'Argus' for their skilful assistance during the sampling, and W.H. Pot and W. Wilts for analyzing the samples. We also thank R.W.P.M. Laane, J.P. Boon and C.H. van der Weijden for their valuable comments on the manuscript.

2. THE SCHELDT ESTUARY

The Scheldt estuary (Fig. 1) drains a densely populated and industrialized area of approximately 22·10³ km² in northern France, western Belgium and south-western Netherlands. The average freshwater input at Rupelmonde is 110 m³·s⁻¹ (range: 20 to 600 m³·s⁻¹). The water residence time is 30 to 90 days and the estuarine water is mostly well-mixed. On average, the influence of the seawater reaches to between Antwerp and Rupelmonde.

The position of the high turbidity zone (HTZ) is strongly dependent on the freshwater discharge (WOLLAST & DUINKER, 1982). Riverine particulates are mixed with marine particulates within the estuary: the percentage of riverine particulate matter decreases from 100 to 10%, when salinity increases from 0.5 to 25 (SALOMONS & EYSINK, 1981). The upper estuary is often anoxic (WOLLAST & DUINKER, 1982). Especially in summer, (near-)anoxic conditions may prevail as far as the Belgian-Dutch border, 55 km upstream from Vlissingen (RIZA, 1982).

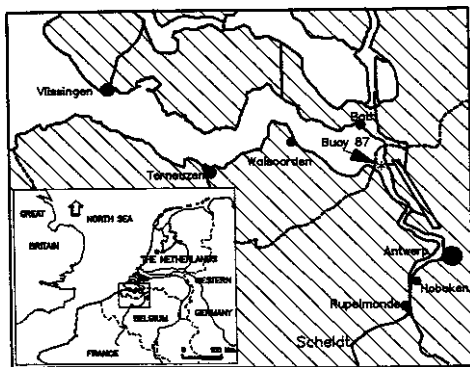


Fig. 1. The Scheldt estuary.

3. SAMPLING AND ANALYSIS

The Scheldt estuary was sampled (irrespective of the tidal phase) 5 times in about one year (25-26 August and 15-16 December in 1987, and 17-18 February, 13-14 April, 15-16 June in 1988). Water depth, salinity, turbidity, temperature, pH and dissolved oxygen concentration were continuously recorded during the cruises.

During each cruise, samples were taken at fixed salinities and always at a depth of 3 m. Particulate matter was collected, using a continuous-flow centrifuge (15000 rpm; 1000 dm³·h⁻¹), on teflon plates (pre-rinsed with acetone and hexane), scraped off and frozen (-20°C) until further treatment in the laboratory. All reagents used were nanograde quality.

The particulate matter samples were freeze-dried and subsequently homogenized and weighed. Particulate Organic Carbon (POC) was analysed gravimetrically with a Coleman C-analyser. Sub-samples (0.5 - 2 g dry weight) were extracted for 4 hours with 150 cm³ hexane-acetone (3/1, v/v) using a Soxhlet apparatus. PCB 29, PCB 155 and benzo(b)chrysene were added as internal standards for recovery determinations. The extracts were concentrated to 5 cm³ using a Kuderna-Danish apparatus and then, gently, to 1 cm³ under a nitrogen flow.

The cleaning-up was performed by eluting the extracts with hexane through a combined SiO₂ (5% water) and Al₂O₃ column (with Na₂SO₃/NaOH burden for sulphur removal, JAPENGA *et al.*, 1987). After a subsequent concentration step, PCBs and PAHs were separated on dry Al₂O₃ (1 g) in a microcolumn. PCBs were eluted with 6 cm³ 3% diethylether in pentane and concentrated to 1 cm³. Before measuring, 100 µg PCB 143 were added as an internal standard. After drying the column under a nitrogen flow, the PAH fraction was eluted with 1 cm³ methanol.

PCB analyses were performed on a Hewlett-Packard 5880 gas chromatograph equipped with two, temperature-programmed, fused-silica capillary columns (SE 54 and CP sil 19 CB, both of 0.32 mm internal diameter and 50 m length) connected to the same injection port, and two ⁶³Ni electron capture detectors.

PAH analyses were performed on a Hewlett-Packard 1090 liquid chromatograph with two Hewlett-Packard 1046a fluorescence detectors, equipped with a reversed phase column (Vydac 201 tpb-5, 4.6 × 250 mm).

Quantification of individual PCB congeners was carried out with PCB 143. The PCB congeners determined were IUPAC nos. 26, 44, 49, 52, 101, 118, 138, 153, 170 and 180 (nomenclature according to BALLSCHMITER & ZELL, 1980). Quantification of PAHs was performed with a mixture of external standards. The PAH compounds determined were: phenan-

TABLE 1

The river discharge (Q, in m³·s⁻¹) and contents (in ng·g⁻¹) of some PCB congeners, Σ10PCB (sum of 10 congeners), some PAHs and ΣPAH (sum of 13 compounds) at Hoboken (average salinity: 0.45) for all cruises.

cruise	Q	PCB 52	PCB 101	PCB 153	PCB 180	Σ10PCB	ANT	FLA	BAP	ΣPAH
25-26 August 1987	114	27.1	49.5	80.3	57.7	396	254	2114	823	10924
15-16 December 1987	135	72.8	148.7	206.0	157.7	1088	3438	13636	1836	60261
17-18 February 1988	293	21.4	31.5	46.2	30.8	245	774	4127	1204	19229
13-14 April 1988	150	16.8	34.3	51.8	34.2	217	1134	7576	1800	32110
15-16 June 1988	95	41.3	88.3	125.1	87.8	542	1517	14628	4645	68683
average	157	35.9	70.5	101.9	73.6	494	1423	8416	2062	38241

threne (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo(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), dibenzo(ah)anthracene (DBA) and indeno(1,2,3-cd)pyrene (INP). The detection limits were 0.1 ng·g⁻¹ for PCBs and 1 to 5 ng·g⁻¹ for PAHs, dependent on the compound and the amount extracted.

Procedural blanks were performed at regular intervals, and indicated that no significant source of contamination was introduced during the analytical procedures. Moreover, some samples were extracted twice at identical conditions. No PCBs and PAHs could be detected in the second extracts.

Some samples were split up immediately after sampling and further treated as duplicate samples. Precision for all compounds was always better than 18%. Recoveries were 96 and 88% for PCB 29 and PCB 155, respectively (average of both capillary columns). benzo(b)chrysene proved not to be a proper compound for recovery determinations in Scheldt samples. In the chromatogram, another, yet unidentified, compound was present with the same retention time. Results, reported here, were not corrected for recovery.

4. RESULTS

Particulate matter concentrations varied considerably during the sampling period. Highest concentrations (>100 mg·dm⁻³) were measured at the salinity interval 2 to 6 (the High-Turbidity Zone). The location of the HTZ was strongly dependent on the river discharge: at Walsvoorden during high river flow (February), and at Antwerp during low river flow (June), which is in agreement with WOLLAST & DUINKER (1982).

The particulate organic carbon content of the suspended matter in the estuary ranged from 2.1 to 10.1%. Generally, organic carbon contents decreased when salinities increased. Anoxic conditions prevailed in the upper estuary during the summer cruises. At Hoboken, highest dissolved oxygen con-

centrations (4.4 mg·dm⁻³) were measured in February.

Individual PCB congener contents ranged from 0.3 to 206.0 ng·g⁻¹. Individual PAH contents ranged from 11 to 14628 ng·g⁻¹. In Table 1, contents at Hoboken of some PCB congeners, some PAH compounds, as well as total PCB and total PAH contents are presented. PCB and PAH contents at Hoboken (Table 1) varied considerably over time and tended to relate inversely with the river discharge. No obvious relation was found between PCB and PAH contents.

PCB and PAH contents at buoy-87 varied considerably less. In Fig. 2 an example is given in which the contents of PCB 52 at Hoboken are compared to buoy 87 for all cruises, supplemented with measurements in May and June 1986, and January 1987 (unpublished results). Coefficients of variation at Hoboken and buoy-87 were 65 and 13%, respectively.

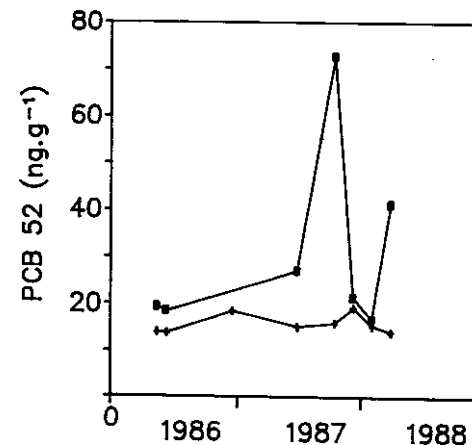


Fig. 2. PCB 52 contents at Hoboken (■) and buoy-87 (▲) during the 1986-1988 period. The coefficients of variation are 65 and 13%, respectively.

PCB and PAH contents expressed in ng per g dry weight, as well as normalized to the POC content, generally decreased with increasing salinities. The latter are presented as a function of salinity, using BAP and PCB 138 as representative examples, in Fig. 3. Steep gradients were observed in the upper estuary, especially in December for PCBs and June for PAHs. During all cruises, PCB and PAH contents tended to show maximum values in the HTZ.

Compared to Hoboken, the fraction of less chlorinated congeners was always considerably higher at Vlissingen, where marine particulates predominate. This shift of the PCB pattern appeared to be a gradual change in the Scheldt estuary. As an example, different PCB contents normalized to PCB 138, of the two end-members (Hoboken and Vlissingen) in February, are compared in Fig. 4. PCB 138 has been chosen as a reference, because this congener is stable and can be determined well (DUINKER *et al.*, 1988).

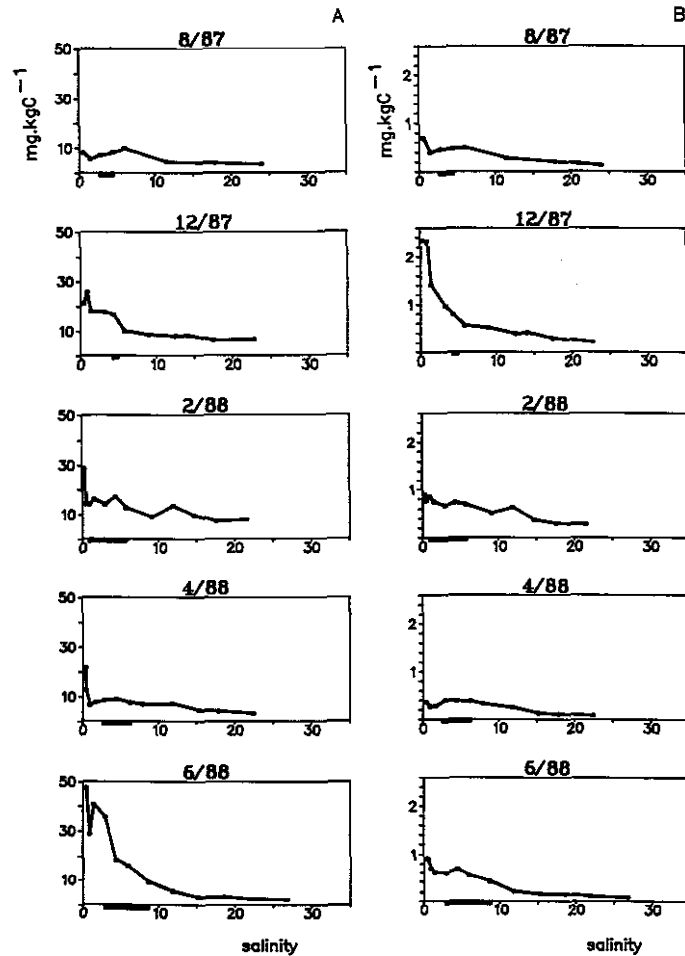


Fig. 3. Contents of (A) BAP and (B) PCB 138 (in $\text{mg}\cdot\text{kgC}^{-1}$) as a function of salinity for all cruises. The salinities with the highest observed particulate matter concentrations are indicated by horizontal bars on the x-axis.

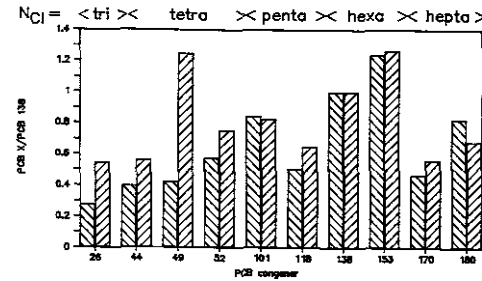


Fig. 4. The particulate PCB patterns at Hoboken (left-hand column of each pair) and Vlissingen (right-hand columns) in February 1988. Contents are normalized to the PCB 138 concentration.

In Fig. 5, the ratio of the sum of the low M.W. PAHs (PHE, ANT and FLA, consisting of 3 or 4 aromatic rings) to total PAHs has been plotted as a function of the salinity for December. The ratio decreased from 0.5 to 0.3, when the salinity increased from 0.4 to 6 and remained constant afterwards. Pyrene (which has the same M.W. as FLA), however, showed behaviour similar to the high M.W. PAHs.

The ratio of (PHE + ANT + FLA) to total PAHs at Hoboken (plotted against the water temperature for all cruises in Fig. 6) tended to decrease with increasing water temperature.

5. DISCUSSION

Table 2 shows that the PCB contents measured in the Scheldt river are higher than those of DUINKER (1986) for the same river, and also that they are higher than those reported for several other rivers in this area (Rhine, Elbe, Weser and Ems). Three explanations for our higher contents in the Scheldt river can be given:

—1. the more efficient extraction by hexane-acetone compared to use of hexane only (summarized by DUINKER, 1986). Reextraction of their samples with

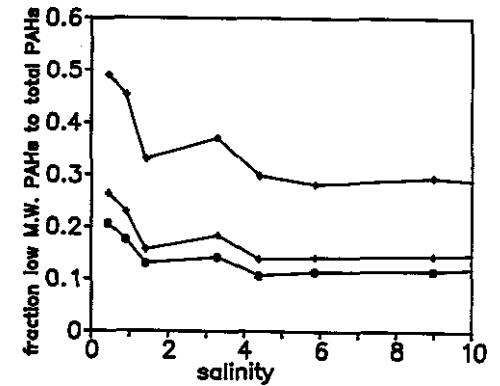


Fig. 5. The ratio of PHE (■), PHE + ANT (+) and PHE + ANT + FLA (◆) to total PAHs, as a function of salinity in the upper estuary in December.

hexane-acetone indicated, however, that the recovery had been (nearly) 100% (Boon, pers.comm.) —2. a recent increase of the PCB pollution, and —3. the samples by DUINKER (1986) were accidentally taken during a period with relatively low PCB levels (*cf.* our April cruise).

To our knowledge, PAH contents in the Scheldt river have never been reported before. PAH contents are very high in the Scheldt river compared to the Rhine and Tamar (Table 2).

PCB and PAH contents at Hoboken (Table 1) strongly varied during the sampling period. A weak inverse relation may exist with the river discharge (December being an exception for PCBs). No dependence on other physical or chemical variables (*e.g.* temperature, O_2) could be detected. The organic pollutant contents in the estuary are probably determined by emissions and variations in hydrological conditions (governing the resuspension of sediments in the Rupel and Scheldt tributaries and the subsequent transport to the estuary).

TABLE 2

Average contents (in $\text{ng}\cdot\text{g}^{-1}$) of some PCBs and PAHs in the rivers Rhine (Klamer, pers.comm.), Weser and Ems (DUINKER, 1986), Elbe (STURM *et al.*, 1986, average of 9 cruises in 1984-85), Tamar (READMAN *et al.*, 1982) and Scheldt (DUINKER, 1986; this study). -: not analyzed.

	PCB 52	PCB 101	PCB 153	PCB 180	ANT	FLA	BAP
Rhine	27.3	31.1	36.9	15.4	306	1050	521
Weser	4.8	5.9	-	97.6	-	-	-
Ems	4.2	1.8	-	29.0	-	-	-
Elbe	21	25	28	12	-	-	-
Tamar	-	-	-	-	-	-	-
Scheldt	12.8	15.6	-	36.3	-	760	741
This study	35.9	70.5	101.9	73.6	1423	8416	2062

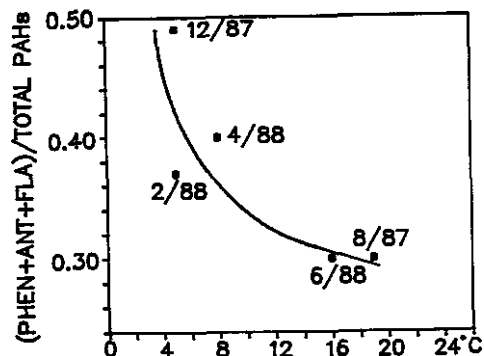


Fig. 6. The ratio of (PHE + ANT + FLA) to total PAHs at Hoboken as a function of water temperature for all cruises. Line fitted by eye.

PCB and PAH contents varied considerably less at buoy 87 than at Hoboken (Fig. 2). The large difference may be explained by the high residence time of the particulate matter in the upper estuary. Riverine particulate matter with varying pollutant contents is thoroughly mixed in the upper estuary (the HTZ being present in the upper estuary), before a further transport takes place. Besides, the marine particulates, expected to have relatively constant contents compared to the riverine particulates, is considerably higher at buoy 87 than at Hoboken.

PCB and PAH contents generally decreased in a seaward direction as a result of the mixing of riverine with marine particulates. Contents normalized to POC tended to show peak values in the HTZ. Due to great variations in the river discharge during the sampling period, the position of the HTZ also varied, so that this phenomenon cannot be attributed to a certain discharge or effluent. We suggest that in the HTZ, POM was partially broken down (Van Zoest *et al.*, in prep.), while subsequently organic pollutants were re-adsorbed onto the remaining organic matter. The observed pattern was most distinct in summer. In December, the pattern was not observed for PCBs. This may be the result of the exceptionally high load, eclipsing the common pattern.

Particulates near Vlissingen have relatively high contents of less chlorinated congeners compared to the riverine source. We can think of 3 mechanisms causing an enrichment of less chlorinated congeners in marine particulates:

—1. atmospheric deposition with PCB mixtures enriched in these congeners. Less chlorinated congeners easily evaporate, and may thus be enriched in the atmosphere, and consequently in the depo-

sition;

—2. degradation of more chlorinated congeners in the lower estuary, and

—3. discharges of PCB mixtures enriched in less chlorinated congeners in the lower estuary. The shift in PCB pattern, however, has not been recognized in the Rhine estuary (Klamer, pers. comm.) and Elbe (STURM *et al.*, 1986), suggesting that marine particulates are not enriched in less chlorinated congeners by atmospheric deposition. Besides, DUINKER & BOUCHERTALL (1989) recently found that the PCB mixture in aerosols and rain was dominated by a high degree of chlorination. In the literature, no evidence has been presented for the degradation of more chlorinated congeners in aerobic environments. The opposite however, (*i.e.* the aerobic degradation of less chlorinated congeners and the anaerobic degradation of more chlorinated congeners) has been reported (FURUKAWA *et al.*, 1979; BROWN *et al.*, 1987, respectively). There is no evidence for the third, most plausible reason, because of the lack of measurements in the harbour area of Vlissingen.

Finally, the behaviour of PAHs in the Scheldt estuary will be discussed. The low M.W. PAHs were removed in the upper estuary (Fig. 5). In general, the differentiation between low and high M.W. PAHs may be explained by several processes: photodegradation, volatilization, desorption and microbial degradation. READMAN *et al.* (1982) found that in the Tamar estuary the low M.W. PAHs (Naphtalene, PHE and ANT) were more susceptible to volatilization and microbial degradation than high M.W. PAHs. FLA was included in the high M.W. group. In the Scheldt estuary, however, the FLA behaviour mostly resembles the PHE and ANT behaviour. HEITKAMP & CERNIGLIA (1987) found that low M.W. PAHs were better degraded by microorganisms than high M.W. PAHs.

In the Scheldt estuary, the observations cannot be accounted for by photodegradation, volatilization and desorption, since there is no reason why such a process should only take place in the very low salinity ($S=0$ to 5) range. We suggest that microbial degradation of the low M.W. PAHs occurs in the upper estuary through bacteria thriving in anaerobic or low-oxygen conditions. The low M.W./total PAHs ratios at Hoboken tend to decrease with increasing temperatures (Fig. 6), confirming the suggestion of microbial degradation of low M.W. PAHs.

In general, however, microbial degradation of PAHs is favoured by aerobic conditions (DELAUNE *et al.*, 1981; MILLE *et al.*, 1988), but may take place very slowly in anoxic conditions (HAMBRICK *et al.*, 1980). The long residence time of particulates in the upper estuary may cause low M.W. PAH degradation to be a significant removal mechanism.

6. BUDGET CALCULATIONS

For budget calculations, it is assumed that the particulate pollutant fractions represent the major part of the load: in general, both partition coefficients (*e.g.* DUINKER, 1986) and particulate matter concentrations are high. Our calculations are limited to the area between Hoboken and Vlissingen (Fig. 1).

6.1. INPUT

Table 1, in which the contents of $\Sigma 10\text{PCB}$ and ΣPAH for all cruises are given shows large variations. The annual input of PCBs and PAHs into the estuary at Hoboken can be calculated by multiplying the average contents and the amount of particulate matter transported by the Scheldt river into the estuary ($0.32 \cdot 10^9 \text{ kg} \cdot \text{y}^{-1}$; VAN ECK & DE ROOY, 1990). Thus, the river input (period August 1987-July 1988) is approximately $\Sigma 10\text{PCB} = 160 \text{ kg} \cdot \text{y}^{-1}$ and $\Sigma\text{PAH} = 12 \text{ 000 kg} \cdot \text{y}^{-1}$.

The PCB pattern in the particulate matter at Hoboken resembles Clophen A50 (DUINKER & HILLEBRAND, 1983). The 10 PCB congeners considered here account for approximately 40% of this technical mixture. Thus, the total input of particulate PCBs into the estuary at Hoboken may be estimated at $400 \text{ kg} \cdot \text{y}^{-1}$.

The contribution of the dissolved PCB load is probably small: the partition coefficient of Aroclor 1254 (which shows only minor differences with Clophen A50, DUINKER & HILLEBRAND, 1983) is $100,000 \text{ dm}^3 \cdot \text{kg}^{-1}$ (THOMANN & D'ITORO, 1983). The average dissolved PCB concentration is then $12 \text{ ng} \cdot \text{dm}^{-3}$, corresponding to a dissolved input at Hoboken of $42 \text{ kg} \cdot \text{y}^{-1}$, which is a minor contribution ($\sim 10\%$) to the total PCB input at Hoboken.

6.2. OUTPUT

The same calculation method can be used for the amounts transported to the North sea, since the majority of the particulate pollutants behaved conservatively (*i.e.* PCBs and high M.W. PAHs). STEYAERT & VAN MALDEGEM (1987) estimated that the amount of particulate matter entering the North Sea from the Scheldt estuary is 10% of the amount transported by the river, thus carrying the same pollutant fraction to the North Sea (16 and $1200 \text{ kg} \cdot \text{y}^{-1}$ for $\Sigma 10\text{PCB}$ and ΣPAH , respectively). For PCBs, the estimated load is too low, since a discharge of PCBs probably takes place in the proximity of the mouth of the estuary.

This is a minor contribution for PCBs (compared to *e.g.* the Rhine: $7600 \text{ kg} \cdot \text{y}^{-1}$, DUINKER *et al.*, 1984) to the budget of the North Sea, in spite of the high concentration levels. Although the PCB flux is small, the

PCB concentrations in the estuary cause very high contents in *e.g.* mussels (*Mytilus edulis*: at Terneuzen, the average concentration of $\Sigma 7\text{PCBs}$ (congeners: 28, 52, 101, 118, 138, 153 and 180) was $84 \mu\text{g} \cdot \text{kg}^{-1}$ (wet weight) in 1987, which was 4 times higher than the contents in the Ems-Dollard estuary (STUTTERHEIM & ZEVENBOOM, 1988).

7. REFERENCES

- BALLSCHMITER, K. & M. ZELL, 1980. Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography.—*Fresenius Z. Anal. Chem.* 302: 20-31.
- BORNEFF, J. & H. KUNTE, 1983. Polycyclic Aromatic Hydrocarbons in river and lake water, biota and sediments. In: A. BJORSETH. Handbook of polycyclic aromatic hydrocarbons. Marcel Dekker inc., New York: 629-652.
- BROWN JR, J.F., R.E. WAGNER, H. FENG, D.L. BEDARD, M.J. BRENNAN, J.C. CARNAHAN & R.J. MAY, 1987. Environmental dechlorination of PCBs.—*Environ. Toxicol. Chem.* 6: 579-593.
- BRUGGEMAN, W.A., 1983. Bioaccumulation of polychlorobiphenyls and related hydrophobic chemicals in fish. Thesis, University of Amsterdam: 1-160.
- DELAUNE, R.D., W.H. PATRICK JR & M.E. CASSELMAN, 1981. Effect of sediment pH and redox conditions on degradation of benzo(a)pyrene.—*Mar. Pollut. Bull.* 12: 251-253.
- DUINKER, J.C., 1986. The role of small, low density particles on the partition of selected PCB congeners between water and suspended matter (North Sea area).—*Neth. J. Sea Res.* 20: 229-238.
- DUINKER, J.C. & F. BOUCHERTALL, 1989. On the distribution of atmospheric polychlorinated biphenyl congeners between vapor phase, aerosols, and rain.—*Environ. Sci. Technol.* 23: 57-62.
- DUINKER, J.C. & M.TH.J. HILLEBRAND, 1983. Characterization of PCB components in clophen formulations by capillary GS-MS and GC-ECD techniques.—*Environ. Sci. Technol.* 17: 449-456.
- DUINKER, J.C., J.P. BOON, & M.TH.J. HILLEBRAND, 1984. Organochlorines in the Dutch Wadden Sea. Netherlands Institute of Sea Research-publication series 10: 211-228.
- DUINKER, J.C., D.E. SCHULTZ & G. PETRICK, 1988. Selection of chlorinated biphenyl congeners for analysis in environmental samples.—*Mar. Pollut. Bull.* 19: 19-25.
- ECK, G.T.M., VAN & N.M. DE ROOY, 1990. Development of a water quality and bioaccumulation model for the Scheldt estuary. In: W. MICHAELIS. Estuarine water quality management. Springer Verlag, Heidelberg: 95-105.
- FURUKAWA, K., N. TOMIZUKA & A. KAMIBAYASHI, 1979. Effect of chlorine substitution on the bacterial metabolism of various polychlorinated biphenyls.—*Appl. Environ. Microbiol.* 38: 301-310.
- HAMBRICK, G.A., R.D. DELAUNE & W.H. PATRICK, 1980. Effect of estuarine sediment pH and oxidation-reduction potential on microbial hydrocarbon degradation.—*Appl. Environ. Microbiol.* 40: 365-369.

- HEITKAMP, M.A. & C.E. CERNIGLIA, 1987. Effects of chemical structure and exposure on the microbial degradation of polycyclic aromatic hydrocarbons in freshwater and estuarine ecosystems.—*Environ. Toxicol. Chem.* **6**: 535-546.
- HERRMANN, R. & W. THOMAS, 1984. Behaviour of some PAH, PCB and organochlorine pesticides in an estuary, a comparison - Exe, Devon.—*Fresenius Z. Anal. Chem.* **319**: 152-159.
- JAPENGA, J., W.J. WAGENAAR, F. SMEDES & W. SALOMONS, 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.
- KARICKHOFF, S.W., D.S. BROWN & T.A. SCOTT, 1979. Sorption of hydrophobic pollutants on natural sediments.—*Water Res.* **13**: 241-248.
- MALINS, D.C., B.B. MCCAIN, J.T. LANDAHL, M.S. MYERS, M.M. KRAHN, D.W. BROWN, S.L. CHAN & W.T. ROUBAL, 1988. Neoplastic and other diseases in fish in relation to toxic chemicals: an overview.—*Aquat. Toxicol.* **11**: 43-67.
- MILLE, G., M. MULYONO, T. EL JAMMAL & J.C. BERTRAND, 1988. Effects of oxygen on hydrocarbon degradation studies *in vitro* in surficial sediments.—*Estuar. coast. Shelf Sci.* **27**: 283-295.
- OLIVER, B.G. & A.J. NIIMI, 1988. Trophodynamic analysis of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in the lake Ontario ecosystem.—*Environ. Sci. Technol.* **22**: 388-397.
- PHILLIPS, D.J.H. & R.B. SPIES, 1988. Chlorinated hydrocarbons in the San Francisco estuarine ecosystem.—*Mar. Pollut. Bull.* **19**: 445-453.
- READMAN, J.W., R.F.C. MANTOURA, M.M. RHEAD & L. BROWN, 1982. Aquatic distribution and heterotrophic degradation of polycyclic aromatic hydrocarbons (PAH) in the Tamar Estuary.—*Estuar. coast. Shelf Sci.* **14**: 369-389.
- REIJNDERS, P.J.H., 1980. Organochlorine and heavy metal residues in harbour seal (*Phoca vitulina*) population in the Dutch Wadden Sea.—*Neth. J. Sea Res.* **14**: 30-65.
- RIZA, 1982. De waterkwaliteit van de Westerschelde in de periode 1964-1981. Reportnr. 82-063, RIZA, Lelystad: 1-111 (in Dutch).
- SALOMONS, W. & W.D. EYSINK, 1981. Pathways of mud and particulate trace metals from rivers to the southern North Sea. In: S.D. NIO, R.T.E. SCHUETTENHELM & T.C.E. VAN WEERING. Holocene marine sedimentation in the North Sea basin. Blackwell, Oxford: 429-450.
- STEYAERT, F. & D. VAN MALDEGEM, 1987. Research of mud transport Westerschelde. Poster presented at the 'Scheide symposium', 26-27 May 1987, Terneuzen.
- STURM, R., H.D. KNAUTH, K.H. REINHARDT & J. GANDRASS, 1986. Chlorkohlenwasserstoff-Verteilung in Sedimenten und Schwebstoffen der Elbe.—*Vom Wasser* **67**: 23-38.
- STUTTERHEIM, E. & W. ZEVENBOOM, 1988. National comment of the Netherlands on the Dutch joint monitoring programme 1987. Reportnr. GWW5-88.011, Tidal Waters Division, Den Haag: 1-47.
- THOMANN, R.V. & D.M. D'ITORO, 1983. Physico-chemical model of toxic substances in the Great Lakes.—*J. Great Lakes Res.* **9**: 474-496.
- WOLLAST, R. & J.C. DUINKER, 1982. General methodology and sampling strategy for studies on the behaviour of chemicals in estuaries.—*Thalassia Jugosl.* **18**: 471-491.

Netherlands Journal of Sea Research
26 (1): 97-109 (1990)

BACTERIA, AUTO- AND HETEROTROPHIC NANOFLAGELLATES, AND THEIR RELATIONS IN MIXED, FRONTAL AND STRATIFIED WATERS OF THE NORTH SEA*

F.C. VAN DUYL, R.P.M. BAK, A.J. KOP and G. NIEUWLAND

Netherlands Institute for Sea Research, P.O. Box 59, 1790 AB Den Burg, Texel, The Netherlands

ABSTRACT

1. INTRODUCTION

The horizontal and vertical distributions of bacteria and bacterial productivity were compared with nanoflagellate densities in the southern part of the central North Sea. Mixed, frontal and stratified waters were sampled in transects during summer 1988.

High bacterial abundance, 2.7 to $4.5 \cdot 10^6$ cells \cdot cm $^{-3}$, distinguished coastal from offshore waters. Bacterial production and nanoflagellate densities were also high in the coastal zone but reached comparable or even higher values further offshore in frontal systems. We crossed two conspicuous fronts: the Frisian Frontal zone and a frontal zone along the northern slope of the Dogger Bank. These fronts were characterized by enhanced bacterial production and/or enhanced bacterial specific growth rates. In fronts as well as mixed waters, nanoflagellate densities covaried with bacterial specific growth rates and reached highest numbers in fronts, e.g. heterotrophic nanoflagellate densities peaked in the Frisian Front with 6000 to more than 10 000 cells \cdot cm $^{-3}$. These high densities were accompanied by low bacterial abundances ($0.45 \cdot 10^6$ cells \cdot cm $^{-3}$) suggesting a regulation of bacterial numbers by heterotrophic nanoflagellates. A comparable pattern was found in the Dogger Bank front. Biomass of autotrophic nanoflagellates was significantly correlated with biomass of heterotrophic nanoflagellates. A maximum of nanoflagellates was present in the thermocline in stratified waters.

The carbon distribution between bacteria and nanoflagellates over the water column was always dominated by flagellates, except in the coastal zone. Offshore, in mixed waters, bacterial biomass made up 30 to 51% of the bacterial plus auto/heterotrophic nanoflagellate biomass. In fronts and stratified waters the biomass of heterotrophic nanoflagellates alone exceeded bacterial biomass.

Bacterial production amounted to a fraction of 3 to 31% of the primary production.

Since STEELE (1974) proposed a structure and carbon budget of the food web in the North Sea, our insight into the functioning of such ecosystems has undergone drastic changes. Fundamental is the importance now ascribed to the microbial food web in the trophic structure. Heterotrophic bacteria appear to utilize significant fractions of the primary production in planktonic marine ecosystems (VAN ES & MEYER-REIL, 1982). Estimates of the fraction of primary production passing through bacterioplankton are in the 10 to 50% range (FUHRMAN & AZAM, 1982; AZAM *et al.*, 1983). This means that at 50% growth efficiency, 5 to 25% of the primary production is converted into bacterial biomass.

Bacteria concentrate energy by converting DOM (dissolved organic matter) not available to other secondary producers into biomass. Subsequently this energy can be transferred to higher trophic levels such as heterotrophic nanoflagellates and ciliates. To what extent the biomass of secondary producers in the microbial loop is transferred to higher trophic levels and links up to the conventional food web is unknown. The process may depend strongly on size class distribution in the food web and on the number of trophic transfers involved (e.g. POMEROY & WIEBE, 1988).

So far only modest efforts have been undertaken to study the small-food web in the North Sea. GEIDER (1988) and NIELSEN & RICHARDSON (1989) studied the structure of auto- and heterotrophic nanoplankton in parts of the North Sea. The role of bacteria in the North Sea was recently reviewed by BILLEN *et al.* (1990). They emphasize the lack of data on the microbial food web in the Central North Sea.

Our investigation aimed to fill in some of these gaps and to supply data on the functioning of the microbial loop in mixed, frontal and stratified water masses.

Acknowledgements.—We are grateful to the technical crew on board the R.V. 'Holland' and R.V. 'Tyro' for