The Scheldt estuary revisited

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Abstract

Temporal and spatial variations in particulate PolyChlorinated Biphenyl (PCB) and Polycyclic Aromatic Hydrocarbons (PAH) concentrations were studied in the Scheldt estuary during a one-year period (May 1995-June 1996). This sampling campaign was a recurrence of a campaign held almost a decade ago. Both PCB and PAH concentrations in the Scheldt river were substantially lower in the 90's, but the Scheldt is still one of the most severely polluted rivers in the North Sea area. The annual input into the estuary was approximately 40 kg for total PCBs (sum of 8 congeners) and 3300 kg for total PAHs (19 compounds). The fraction transported to the North Sea is relatively small: 10-20 %.

In the most recent sampling campaign the behaviour of particulate PCBs and PAHs found earlier was confirmed: as a result of the mixing of riverine with marine particulates the concentrations of the micropollutants generally decrease with increasing salinities. The quicker restoration of dissolved oxygen in the upper estuary gave rise to a more intense degradation of organic matter, and, probably as a result of cometabolism, degradation of low molecular weight PAH. Typical calculated half lives were 260 days for pyrene and 390 for fluoranthene.

Introduction

Polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the aquatic environment. Both groups have pronounced adverse effects on the health of marine biota For example, the carcinogenic and mutagenic properties of PAH, due to their metabolic transformation products, and the bioaccumulation of PCBs are well documented in literature (e.g. Malins et al., 1988; Tanabe, 1988). In general accumulation of these substances takes place in estuarine sediments. Thus, with respect to the transport of contaminants from rivers to the sea, the estuary acts as a sink. Moreover, removal processes such as degradation and volatilisation may also account for a substantial reduction for the transport of contaminants from the river to the sea.

Tidal estuaries are characterised by relatively long residence times. In general steep gradients are present and several biogeochemical processes take place affecting the occurrence and behaviour of both particulates and contaminants. Allochtonous sources of particulate matter include riverine and marine inputs, as well as direct inputs from the land. Sources of autochtonous particulates are represented by phytoplankton in the water column and higher plants on the salt marshes.

Sediment/water partitioning depends on the composition of the sediment (Horzempa & Di Toro, 1983). In general, it is assumed that sediments rich in organic matter adsorb nonpolar organic contaminants more strongly than a sediment with a dominant mineralogenic character. Sediments may be defined by an organic carbon partition coefficient (K_{oc}). Most current toxic chemical fate and transport models approach sorption assuming instantaneous equilibrium. Recent studies indicate however that a kinetic approach may be more appropriate, especially concerning the desorption of hydrophobic organic compounds such as PCBs and PAHs (Cornelissen, 1999; Gong et al., 1998; Gong & DePinto, 1998). Experimental results indicate that desorption behaviour can be characterised by two stage behaviour: an initial rapid desorption followed by a prolonged period of a much slower release. Moreover it was found that the extent of possible PAH degradation could be roughly predicted from the initial rapidly desorbing fraction (Cornelissen, 1999).

With respect to PAHs recent studies indicate that a soot phase, present in sediments, may be responsible for a much stronger sorption than expected on the basis of organic carbon-water partitioning (Gustafson et al., 1997; Naes et al., 1998). Pyrogenic PAH may be sequestered during the formation of the soot particles. These strong associations of PAHs with soot particles in sediments affect both the availability for equilibrium partitioning as well as for organisms: they will be lower compared to liquid sources of PAHs such as petroleum or creosote (Pereira et al., 1999).

The Scheldt estuary (Fig. 1) is heavily contaminated with heavy metals and organic micropollutants. Based on measurements executed in 1987-1988, the concentrations in (suspended) sediments of several groups of contaminants were among the highest in European rivers and estuaries (Zwolsman & Van Eck, 1996, 1999, Van Zoest & Van Eck, 1990, 1991). Recently, the governments of the three countries involved (France, Belgium and the Netherlands) agreed to significantly reduce the contaminant load.

The last decade, the Scheldt estuary has been intensively studied. The mixing of marine and fluvial particles was studied indicating that the retention factor of fluvial material amounts 83 ± 4% (Verlaan, 1998). Large quantities of marine particulates enter the estuary at Vlissingen. The retention of marine material is suggested to be dependent on the strength of the estuarine circulation and varied between 31 and 55% (Verlaan, 1998). Middelburg and Nieuwenhuize (1998) found that the organic matter in (suspended) sediments of the estuary can be described by four endmembers: terrestrial, riverine, estuarine and marine, all being characterised by a specific set of the following parameters: $\delta^{13}C$, $\delta^{15}N$ and the C/N ratio. It appeared that in summer, the sedimentary suspended particulate organic pools are rather uncoupled. Moreover, the suspended organic matter composition cannot be explained in terms of conservative mixing of riverine and terrestrial sources on the one hand and

marine sources on the other hand, since autochtonous organic matter contributes significantly to the total suspended matter (Middelburg & Nieuwenhuize, 1998).

The temporal and spatial variations of contaminants within the estuary was measured on several occasions. In the period August 1987-June 1988, the estuary was intensively monitored (Zwolsman, 1999; Van Zoest & Van Eck, 1990). In addition a cruise in January 1989 was carried out (unpublished results). Four sampling points are located in the estuary, where contaminants are routinely determined in the suspended matter at a frequency of (at least) once every quarter or even monthly. These four locations are at the Belgian -Dutch border, Hansweert, Terneuzen and Vlissingen (Fig. 1). The sampling campaign of 1987-1988 was repeated between May 1995 and June 1996. During each cruise 10-12 samples of the suspended sediment were taken between Rupelmonde and Vlissingen. The main aims for the recurrence of these cruises were to assess the occurrence and behaviour of PCBs and PAHs in the suspended matter taking new developments into account: the reduction of contaminant inputs, the gradual improvement in the redox condition and the removal of contaminated sediment in the upper estuary.

Sample collection

The Scheldt estuary was sampled (irrespective of the tidal phase) ten times during a period of about one year (May 1995-June 1996). Waterdepth, salinity, turbidity, temperature, pH and dissolved oxygen concentrations were continuously recorded during the cruises.

During each cruise, samples were taken at fixed salinities (with exception of Rupelmonde as the riverine endmember: fixed location) and always at a depth of 1.5 metres. Particulate matter was collected using a continousflow centrifuge (15,000 rpm; 1,000 $dm^3.hour^{-1}$), on teflon plates (prerinsed with acetone and hexane), scraped off and frozen (-20 °C) until further treatment in the laboratory. All reagents used were nanograde quality.

Sample preparation

The particulate matter samples were freeze-dried and subsequently homogenised and weighed. Particulate organic carbon (POC) was analysed gravimetrically using a Coleman C-analyser. $\delta^{13}C$ was determined using a Fisons CN analyser coupled on line, via a Finnigan con-flo 2 interface, with a Finigan depta S mass-spectrometer. Carbon isotope ratios are expressed in the delta notation ($\delta^{13}C$) relative to Vienna PDB.

Sub-samples (0.5 - 2 g dry weight) were extracted during 4 hours with 150 cm^3 hexane-acetone (3/1, v/v) using a Soxhlet apparatus. The extracts were concentrated to 5 cm^3 using a Kuderna-Danish apparatus and then, gently, to 1 cm^3 under a nitrogen flow.

The cleaning-up was performed by eluting the extracts with hexane through a combined (SiO_2 (5% water) and Al_2O_3 (with activated copper powder for sulphur removal) column. After a subsequent concentration step, PCBs and PAHs were separated on dry Al_2O_3 (1 g) in a microcolumn. PCBs were eluted with 6 cm^3 3% diethylether pentane and concentrated to 1 cm^3. After drying the column under the nitrogen flow, the PAH fraction was eluted with 1 cm^3 methanol.

PCB analyses were performed on a Perkin Elmer Autosystem gas-chromatograph equipped with two, temperature programmed, fused silica, capillary columns (SE 54 and Cpsil 19 CB, both of 0.15 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 1100 series HPLC with two Jasco FP-920 fluorescence detectors, equipped with a reverse phase column (C18 Vydac 201 TP5).

Quantification of individual PCB congeners and PAH compounds was carried out using calibration solutions. The PCB congeners determined were: IUPAC nos. 28, 52, 77, 101, 118, 126, 138, 153, 169 and 180. The PAH compounds determined were: naphthalene, acenaphthylene, acenaphtene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, 3,6-dimethylphenanthrene, triphenylene, benzo(b)fluorene, benz(a)anthracene, chrysene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,j)anthracene, dibenzo(a)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, 2-methylcholanthrene, indeno(1,2,3-c,d)pyrene and anthanthrene. The quantification limits were 0.1-0.4 $ng.g^{-1}$ for PCBs and 1-25 $ng.g^{-1}$ for PAHs, dependent on the compound and the amount extracted.

Quality assurance procedures

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. Standard reference material (NIST SRM 1941 for PAHs and NIST SRM 1941 for PCBs) was analysed several times. Recoveries were satisfactory.

Routinely sampled locations

The main features of the methods used for sampling and analysing the suspended at the four routinely sampled locations are similar to the handling mentioned above. Minor variations affect the solvent

and the apparatus used: Accelerated Solent Extraction instead of the Soxhlet apparatus. The same standard reference materials as mentioned above were used.

Results

In Table 1 general water quality features, encountered during ten cruises in 1995/96, are shown. The average river discharge was considerably lower in 1995/96 than in 1987/88. As a result, the average salinity at Rupelmonde, which represents our riverine endmember, is considerably higher than 0.4-0.5. Especially in the warmer period, the river water is anoxic to suboxic, which is similar to the situation in 1987-1988. The net-improved oxygenation of the river water causes the increase of phytoplankton biomass, which is enabled by the chlorophyll-a concentration.

The development in time of contaminant concentrations in the suspended matter of the estuary is shown in Table 2, where the average composition of the endmembers, at Rupelmonde and at Vlissingen is compared. Considering the fluvial suspended matter composition the following changes are apparent between 1987/88 and 1995/96. The concentrations of PCBs and PAHs haven been decreased sharply since 1987/88: respectively 55% and 70%. The organic matter concentration in the fluvial suspended matter has also been decreased.
Considering the marine end member, defined here as suspended matter collected at the mouth of the estuary (Vlissingen), no major changes for PAH between 1987/88 and 1995/96 are observed. For PCBs, slightly lower concentrations in the suspended matter may be present when the results of two cruises, May and July 1995, are kept apart.

Based on sediment balance studies (Salden, 1998), the annual load of particulate PCBs and PAHs, transported by the river Scheldt into the estuary, can be estimated. The amount of particulate matter transported by the Scheldt in 1995/1996 was approximately 220 10^3 tonnes.year^{-1} (Salden, 1998), resulting in a load of 40 kg. year^{-1} for Σ PCBs (8 congeners) and 3,300 kg. year^{-1} for Σ PAHs (19 compounds).

The results of the routinely sampled stations in the estuary enable us to study time-trends in more detail. In Fig. 2 the PCB 138 concentrations measured at the Belgian-Dutch border are shown. Results are presented both expressed as ng.g^{-1} as well as mg.kgOC^{-1}. Approximately 210 measurements have been made between 1988 and 1999. In the figure the results of our own cruises, both in 1987/89 and 1995/96, have been plotted. No overall decreasing tendency is observed with the exception of the period 1988-1991. Afterwards, PCB 138 concentrations in the suspended matter are remarkably constant at 15 ng.g^{-1} or 0.40 mg.kgOC^{-1}. The same pattern is visible for PAH (data not shown).
In Fig. 3 the benzo(a)pyrene concentrations in the suspended matter at Vlissingen are shown (based on approximately 40 measurements between 1988-1999). No time trend is observed, with the exception of a seasonally dependence: relatively high concentrations in the winter and low in summer.

Both in Fig's 2 and 3, it is shown that results from the routinely sampled stations are very well comparable with our own results.

PCB 138 and benzo(a)pyrene show a clear difference in binding with the bulk organic matter in the river (Figure 4). The relation organic matter-PCB 138 is nearly linear, whereas BaP shows no relation with particulate organic matter.

Particulate PCB and PAH concentrations generally decreased with increasing salinities (Fig. 5). Moreover, since positive trends are present between the salinity and $\delta^{13}C$ of the particulate organic matter, it is obvious that the organic contaminant concentration tend to decrease with increasing $\delta^{13}C$ values. In Fig. 6, examples are shown for PCB 138 and BaP. In winter, the relation tends to be linear whereas in summer two populations are present.
In the plots of the salinity against to organic carbon normalised contaminant concentrations, especially during warmer periods, peak values are present. These peaks are not dependent on the salinity or on the sampling location. A distinction occurs between lower and higher molecular weight PAH: the peak is clearly higher for BaP (which represents the higher molecular weight PAH) than for

fluoranthene (which represents the lower molecular weight PAH). In another way this is shown in Fig. 7, where three typical curves of the Fla/BaP ratio as a function of salinity are compared. For all cruises, the Fla/BaP ratio decreases from more than 3 in the river endmember to approximately 1.8-2.0 in suspended matter of the High Turbidity Zone (HTZ, which was present at salinity 5 in 1987/88 and at salinity 10 in 1995/96). Going in a seaward direction the ratio increases again to 2,25-2,5.

Discussion

1.Contaminant load

Although concentrations of organic contaminants have reduced significantly between 1987/88 and 1995/96, the Scheldt river still belongs to the group of most severely contaminated rivers in the North Sea area (Table 3). The North Sea itself does hardly take any advantage of the decreasing river load. This is mainly a result of the intensive mixing of particulate matter in the HTZ (usually located between km 25 and 50) in combination with the resuspension of old contaminated sediment. These old contaminated sediments are heavier polluted than recent sediments (Van Zoest & Van Eck, 1993a). It has been well documented (Salden, 1998) that enormous of amounts of sediments (in majority of a riverine origin) have been removed from the upper estuary in the nineties, starting in 1992. This coincides with the pattern of Fig. 2B. The decreasing trend in PCB and PAH concentrations at the Belgian-Dutch border is completed when the large scale dredging operation commences. For certain months (e.g. August, Fig 5) the observed concentrations are higher in the nineties than in eighties, despite of the substantial reduction in contaminant load that has taken place in the river Scheldt. This has also been observed for heavy metals (Zwolsman, 1999). It is suggested that due to the large-scale removal of relatively recent deposited sediments, older sediment layers become susceptible to erosion and contribute to the burdening of the lower estuary with contaminants.

The remobilization of older sediments, triggered by the large scale dredging operations in the upper estuary, may therefore be 'visible' in the contaminant concentrations in the suspended matter in the zone Antwerp-Hansweert. These remobilised older sediments may (yet) not be deposited before 1970-1975. The reason for this is the lack of influence of the remobilisation on a characteristic ratio such as PCB 52/PCB 138. This ratio did not change in the routinely sampled location at the Belgian-Dutch border after 1992. This would have been the case when sediment deposited before 1970-1975 would have been eroded, since sediments of this age showed a higher ratio characteristic of PCB usage in open systems (Van Zoest & Van Eck, 1993a). From sediment balance studies (Bastin, 1993; Salden, 1998) it is estimated that still 1-2- millions of tonnes of fine grained (old) sediment are present in the upper estuary. So, the lack of improvement in particulate concentrations of contaminants in the lower estuary may be observed for the coming years.

Ignoring the remobilisation of older sediments in the upper estuary (which may be regarded as an internal source), the Scheldt river is the most important source for PCBs and PAHs. For some compounds however, under specific circumstances additional sources may be present.
Firstly, irrespective of the salinity or tidal phase, in the vicinity of two locations during most cruises, peak values of naphthalene and to a lesser extent other low molecular weight PAH were found, firstly between km 20 and the Kallo-lock and, secondly, at approximately km 60 (Walsoorden, Fig. 1). So, it is believed that PAH sources, enriched in low molecular weight PAH are present in these areas. A possibility may be the leaching of creosote from shore revetments. During some cruises the pattern of acenaphthene, fluorene and benzo(b)fluorene resemble that of naphthalene, confirming the possibility of creosote as a local source (Howsam & Jones, 1998).
Secondly, whereas during our cruises the PCB 52/138 ratio typically varies between 0.3 and 0.5 throughout the entire estuary, as well as very little long-term variation is present at the four routinely sampled locations, in four individual samples strongly deviating ratios haven been observed. This happened in May and July 1995 in the lower estuary and coincided with very low particulate matter concentrations (< 10 mg.dm^{-3}). Normally particulate matter concentrations in the lower estuary exceed 30 mg.dm^{-3}. In the Sloehaven area near Vlissingen, a discharge of PCBs enriched in the less chlorinated congeners was probably present in the past (Van Zoest & Van Eck, 1993b). Due to dredging of sediments influenced by this former discharge and/or subsequent dumping of the dredged material in the lower estuary near Borssele (figure 1) a vast amount of these sediments may contribute to the total particulate matter concentrations in the lower estuary. At times of relatively low suspended solids of riverine and marine origin, this contribution is noticeable, both in concentrations as well as in composition of the PCB-mixture.

2. Behaviour

The most important process in determining fate and behaviour of organic contaminants in the Scheldt estuary is the mixing of riverine with relative high and marine with relative low contaminant concentrations levels (Van Zoest & Van Eck, 1990). This essentially also accounts for the suspended organic carbon. From Fig. 6 it is shown that in winter both bulk organic material and organic contaminants behave conservatively: the pattern is merely a result of the mixing or riverine with marine particulates. In the warmer period however the $\delta^{13}C$ value of the particulate organic matter is more negative than expected on the basis of simple mixing. Three phenomenon's may explain this: a substantial contribution of, firstly, autochtonous estuarine or, secondly, imported or resuspended terrigeneous organic matter (which both have low $\delta^{13}C$ values: respectively -29‰ and -26‰, Middelburg & Nieuwenhuize, 1998) and, thirdly, the degradation of organic matter which leads to more negative values (Laane et al. 1990).

C/N ratios are up to 12 in the HTZ (data not shown). Based on the results of the C/N ratios a quantitatively important contribution of autochtonous estuarine organic matter does not seem the case in this part of the estuary. Considering the C/N ratio, an important contribution of terrigeneous matter seems to possible. But since in summer months the river discharge is generally low, we do not expect a large input of terrigeneous material. The resuspension of bottom sediments (which are rich in terrigeneous matter (Middelburg & Nieuwenhuize, 1998)) may be possible although it is not seen at a glance why this process is relatively more important in summer. This leaves the degradation of organic matter being the most important process taking place in the upper estuary with respect to organic matter.

Autochtonous organic material contributes significantly to the organic pool in the lower estuary in summer. As a result, due to dilution by fresh organic matter, contaminant concentrations are reduced by a factor 2 during spring/summer in the lower estuary. Since the average contribution of phytoplankton to the total amount of suspended matter in the lower estuary may be 25-50 %, another process has to corroborate. This may be the variation in the estuarine circulation during the year. In winter, the river discharge is generally higher than in summer, enabling more riverine sediments to 'escape' from the HTZ and the preferential sedimentation areas to the lower estuary and finally to the North Sea.

From several observations it is obvious that the binding of the contaminants studied here is different from the general idea that organic contaminants are sorbed onto the particulate organic phase and that the compounds are concentrated in the fine grain size fractions:

1. PAHs are not correlated with POC in the river Scheldt;
2. PCBs are correlated with POC. In bottom sediment however the concentration level in the >63 µm fraction is as high (PCBs) or even higher (PAHs) than in the <63 µm fraction (Van Zoest & Van Eck, 1993a, Van Berkel, 1995);
3. Particulate organic matter is degraded in the upper estuary. The contaminants do not seem to be released but quantitatively resorbed onto the remaining organic matter (with the exception of lower molecular weight PAHs, which are co-metabolised, see further).

From grain size fraction measurements it is observed that the <53 µm fraction always exceeds 90% in the collected suspended matter, independently of the tidal phase and the location of the sampling (Salden, 1998). These measurements were performed in organic matter- and calcite-free samples. Thus it is expected that a substantial part of the particulate organic matter is concentrated in the coarse fraction during wet sieving since in the sediment organic contaminants tend be concentrated in this coarse fraction.

Moreover, we feel that within the suspended sediment two organic pools with adsorbed and or occluded contaminants are present:

1. a readily available fraction: contaminants show to a more or lesser extent equilibrium partitioning with the water, possibly with two-stage desorption behaviour since the peak values in particulate concentrations are not or hardly reflected in dissolved contaminant concentrations (Van Zoest & Van Eck, 1993b);

2. a non-available fraction, which may be occluded into the sediment. Non-available contaminant fractions have previously been reported, among others, by Readman et al., 1987 and Gustafson et al., 1997. In the salt marshes of the Scheldt estuary this fraction may dominate the PAH-occurrence, since a remarkably uniform pattern was observed in two sediment cores (Van Zoest & Van Eck, 1993a). No changes in the pattern were observed, although major (biogeochemical) processes take place in these sediments such as: infiltrating water during the food-tide (which causes leaching of PCBs), intermittent aerobic and anoxic conditions and degradation of bulk organic material.

Regarding the PAH, the uniform composition observed in the sediment is already achieved in the suspended matter in the HTZ. For example some characteristic ratios (Pyr/BaP and Fla/BaP) in the sediment cores are exactly the same as found in the long-term average at the Belgian-Dutch border: respectively 1.1 and 1.8, whereas the averages at Rupelmonde are approximately 3.5 and 3.2.
The decrease of (in general) ratios of lower molecular weight PAH (3-4 aromatic rings) to higher molecular weight PAH ($\geq$ 5 aromatic rings) indicates degradation. Since a discharge of a PAH mixture especially enriched in lower molecular weight PAH between km 20 and the Kallo lock, the ratios of these compounds relative to a stable compound like benzo(a)pyrene show more scatter. The contribution of low molecular weight PAH (sum of 2-3 aromatic rings) to total PAH (sum of 19 compounds) in the particulate matter at Rupelmonde shows a temperature dependency. This contribution decreases from 0.25 in winter (typical temperatures 5°C) to 0.15 in summer (typical temperature 20°C). Thus, we suggest that low molecular weight PAH are degraded in the Scheldt river and in the upper estuary under anoxic to suboxic conditions. We can estimate half lives for the degradation of fluoranthene and pyrene in the upper estuary based on two assumptions:
1. benzo(a)pyrene is recalcitrant against degradation and may be used as a reference;
2. the average residence time of the particulates in the upper estuary is approximately one year.

Calculated half-lives of fluoranthene and pyrene are respectively 390 and 260 days.

References

Balls, P.W. & D.C. Campbell, 1999. Organochlorines in sea water and suspended particulates from Scottish coastal sites. Marine Pollution Bulletin, **38**, 142-145.

Bastin, A.L., 1993. Evaluatie van de hoeveelheid slib in de beneden Zeeschelde, evolutie tussen 1964 en 1986. Ministerie van de Vlaamse Gemeenschap, Departement Leefmilieu en Infrastructuur, Administratie Waterinfrastructuur en Zeewezen, Antwerpse Zeehavendienst (in Dutch).

Cornelissen, G. (1999). Mechanisms and consequences of slow desorption of organic compounds from sediments. Thesis. University of Amsterdam, pp 297.

Gong, Y., J.V. De Pinto, G. Rhee & X. Liu, 1998. Desorption rates of two PCB congeners from suspended sediments I. Experimental results. Wat. Res. **32**, 2507-2517.

Gong, Y. & J.V. De Pinto, 1998. Desorption rates of two PCB congeners from suspended sediments II. Model simulation. Wat. Res. **32**, 2518-2532.

Götz, R., O.H. Bauer, P. Friesel, K. Roch, 1998. Organic trace compounds in the water of the Elbe river near Hamburg. Part II. Chemosphere, **36**, 2103-2118.

Gustafson, O., F. Haghseta, C. Chan, J. MacFarlane & P.M. Gschwend, 1997. Quantification of the dilute sedimentary phase: implications for PAH speciation and bioavailability. Environ. Sci. Technol. **31**, 203-209.

Horzempa, L.M. & D.M. Di Toro, 1983. PCB partitioning in sediment-water systems: the effect of sediment concentration. J. Environ. Quality **12**, 373-380.

Howsam, M. & K.C. Jones, 1998. Sources of PAHs in the environment. In: PAHs and related compounds. Chemistry. The handbook of environmental chemistry 3 I. A.H. Neilson, Editor, Springer, Berlin, 137-174.

Klamer, J.C. & R.W.P.M. Laane, 1990. The behaviour of dissolved and particulate PCBs and PAHs in the Rhine estuary, 1988/1989. CEP Consultants Ltd., Edinburgh, 98-100.

Laane, R.W.P.M., E. Turkstra & W.G. Mook, 1990. Stable carbon isotope of pelagic and benthic organic matter in the North Sea and adjacent estuaries. In: Facets of modern biogeochemistry. Eds. V. Ittekkot, S. Kempe, W. Michaelis & A. Spitzy, Springer-Verlag, Berlin, 214-224.

Malins, D.C., B.B. MaCain, 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.

Middelburg, J.J. & J. Nieuwenhuize, 1998. Carbon and nitrogen stable isotopes in suspended matter and sediments from the Scheldt estuary. Mar. Chem. **60**, 217-225.

Naes, K., J. Axelman, C. Naef & D. Broman, 1998. Role of soot carbon and other carbon matrices in the distribution of PAHs among particles, DOC, and the dissolved phase in the effluent and recipient waters of an aluminium reduction plant. Environ. Sci. Technol. **32**, 1786-1792.

Pereira, W.E., F.D. Hostettler, S.N. Luoma, A. van Geen, C.C. Fuller & R.J. Anima, 1999. Sedimentary record of anthropogenic and biogenic polycyclic aromatic hydrocarbons in San Francisco Bay, California. Mar. Chem. **64**, 99-113.

Readman, J.W., R.F.C. Mantoura, & M.M. Rhead, 1987. A record of polycyclic aromatic hydrocarbons (PAH) pollution obtained from accreting sediments of the Tamar estuary, U.K.: evidence for non-equilibrium behaviour. Sci. Total Environ., 66, 73-94.

Salden, R.M., 1998. Het effect van slibverwijdering in de Beneden Zeeschelde op de waterkwaliteit en slibhuishouding in de Westerschelde. RIKZ report 98.015, pp. 104, (in Dutch).

Tanabe, S., 1988. PCB problems in the future: foresight from current knowledge. Environ. Pollut. 50, 5-28.

Van Berkel, N., 1995. Kwaliteit van de waterbodem in de Zeeschelde en de Westerschelde. Rijkswaterstaat-directie Zeeland, Report AXW 95-062, pp.22 (in Dutch).

Van Zoest, R. & G.T.M. van Eck, 1990. Behaviour of particulate polychlorinated biphenyls and polycyclic aromatic hydrocarbons in the Scheldt estuary. Neth. J. Sea Res. 26: 89-96.

Van Zoest, R. & G.T.M. van Eck, 1991. Occurrence and behaviour of several groups of organic micropollutants in the Scheldt estuary. Sci. Total Environ. 103: 57-71.

Van Zoest, R. & G.T.M. van Eck, 1993a. Historical input and behaviour of hexachorobenzene, polychlorinated biphenyls and polycyclic aromatic hydrocarbons in two dated sediment cores from the Scheldt estuary, SW Netherlands. Mar. Chem. 44: 95-103.

Van Zoest, R. & G.T.M. van Eck, 1993b. Behaviour of selected PCBs, PAHs and γ-HCH in the Scheldt estuary, S.W. Netherlands. Neth. J. Aquat. Ecol., 27, 301-308.

Verlaan, P.A.J., 1998. Mixing of marine and fluvial particles in the Scheldt estuary. Thesis, Technical University Delft, pp. 205.

Zhou, J.L., T.W. Fileman, S. Evans, P. Donkin, C. Llewellyn, J.W. Readman, R.F.C. Mantoura & S.J. Rowland, 1998. Marine Pollution Bulletin, 36, 587-587.

Zwolsman, J.J.G. & G.T.M. van Eck, 1996. Spatial and temporal distribution of trace metals in sediments of the Scheldt estuary. Est. Coast. Shelf Sci. 43: 55-79.

Zwolsman, J.J.G. & G.T.M. van Eck, 1999. Geochemistry of major elements and trace metals in suspended matter of the Scheldt estuary, S.W. Netherlands. Mar. Chem. (in press).

Zwolsman, J.J.G., 1999. Geochemistry of trace metals in the Scheldt estuary. Thesis, University of Utrecht, pp. 183.

Table 1: General water quality[1] at Rupelmonde in 1995/96.

No.	Date	Q $m^3.s^{-1}$	Salinity	Temperature °C	SPM $mg.dm^{-3}$	O_2 μM	Chl-a $\mu g.dm^{-3}$
1	950531	108	0.30	18.4	97	0	41
2	950707	67	0.41	22.1	67	23	116
3	950816	37	0.92	23.6	42	26	183
4	950914	51	1.02	18.5	163	9	173
5	951026	48	1.39	15.0	134	14	82
6	951208	52	0.65	5.1	164	43	31
7	960111	76	0.56	4.0	298	31	35
8	960229	128	0.51	4.9	100	77	31
9	980424	51	1.13	13.8	109	8	32
10	960606	51	0.81	19.4	230	15	18

[1] Q = river discharge
SPM = suspended matter concentration
Chl-a = chlorophyll-a concentration

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Table 2: Average composition of the fluvial and marine suspended matter of the Scheldt estuary in 1987/89 (fluvial: n=6; marine n=4) and 1995/96 (n=10).

		fluvial SPM 1987/88	fluvial SPM 1995/96	marine SPM 1987/88	marine SPM 1995/96
POC	%	8.1 ± 2.2	6.2 ± 1.7	4.4 ± 1.9	3.2 ± 1.2
FLA	μg/kg	7645 ± 5338	2221 ± 653	383 ± 90	373 ± 88
BaP	μg/kg	1960 ± 1369	702 ± 94	173 ± 33	181 ± 87
Σ 13 PAH[1]	μg/kg	35025 ± 23947	10864 ± 2791	2483 ± 470	2313 ± 704
Σ total PAH[2]	μg/kg	-	14829 ± 3458	-	3389 ± 961
PCB 52	μg/kg	32.4 ± 22.0	13.9 ± 2.7	2.9 ± 1.2	5.1 ± 5.9[3]
PCB 138	μg/kg	80.0 ± 64.1	38.6 ± 15.8	5.7 ± 0.8	5.3 ± 2.8[3]
Σ PCB[4]	μg/kg	454.6 ± 324.4	182.7 ± 44.8	40.6 ± 7.7	50.7 ± 44.6[3]

[1] PAH mixture 1987/89: phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene;
[2] PAH mixture 1995/96: fluorene, phenanthrene, anthracene, fluoranthene, pyrene, triphenylene, benzo(b)fluorene, benz(a)anthracene, chrysene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,j)anthracene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, 3-methylcholanthrene, indeno(1,2,3-c,d)pyrene, anthanthrene;
[3] without the May 1995 and July 1995 cruises respectively: 2.4 ± 0.5, 4.2 ±0.1 and 24.8 ± 4.0
[4] PCB mixture 1987/89: IUPAC no. 26, 44, 49, 52, 101, 118, 138, 153, 170, 180
  PCB mixture 1995/96: IUPAC no. 28, 52, 77, 101, 118, 138, 153, 180

Table 3 Average particulate concentrations (in $\mu g.kg^{-1}$) of PCBs and PAHs in rivers in the North Sea area.

River	PCB 52	PCB 138	Fluoranthene	Benzo(a)pyrene	reference
Rhine	3 - 27	7 - 33	196 - 1420	111 - 655	Klamer & Laane, 1990
Elbe[1]	5	8	361	103	Götz et al., 1998
Weser					
Humber	-	-	51-1560	-	Zhou et al., 1998
Forth	18 - 38	6 - 11	-	-	Balls & Campbell, 1999
Tay	25 - 26	7 - 13	-	-	Balls & Campbell, 1999
Thames					
Scheldt	5 - 14	5 - 39	373 - 2221	181 - 702	this study

[1] concentration calculated from total dissolved concentration

-: not analysed
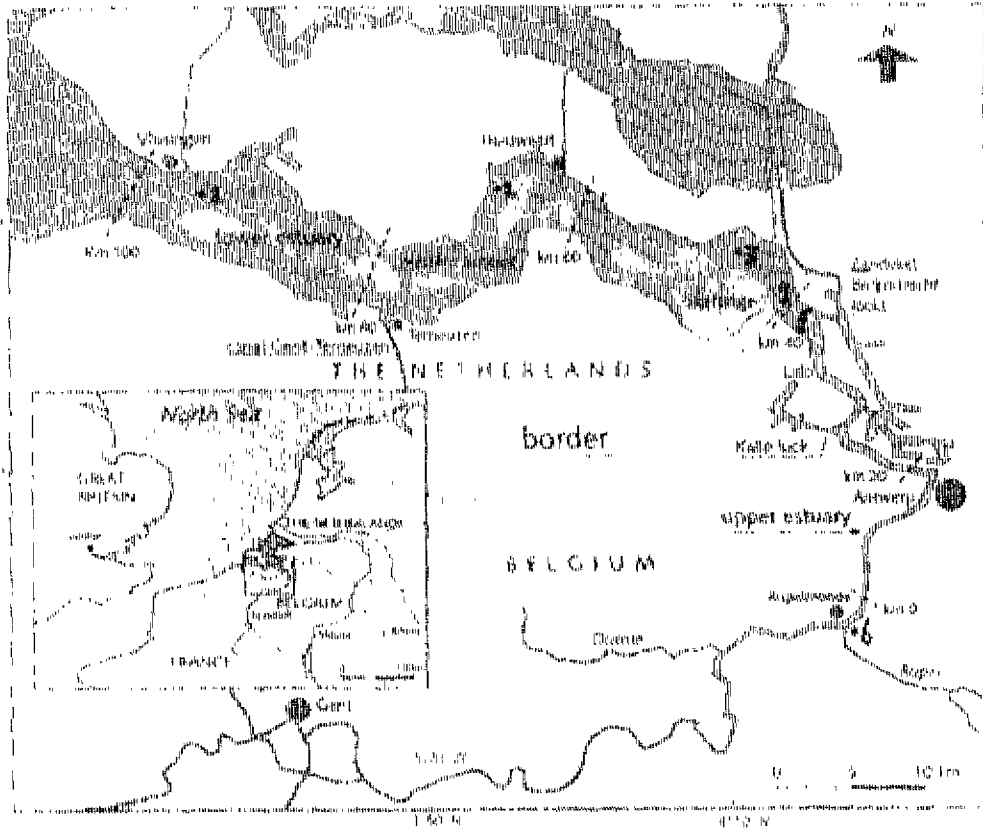
Figure 1: The Scheldt estuary. During 10 cruises 12 samples were taken between Rupelmonde and Vlissingen. The four routine sampling points are denoted by 1. Belgian-Dutch border, 2. Hansweert, 3. Terneuzen and 4. Vlissingen.

A
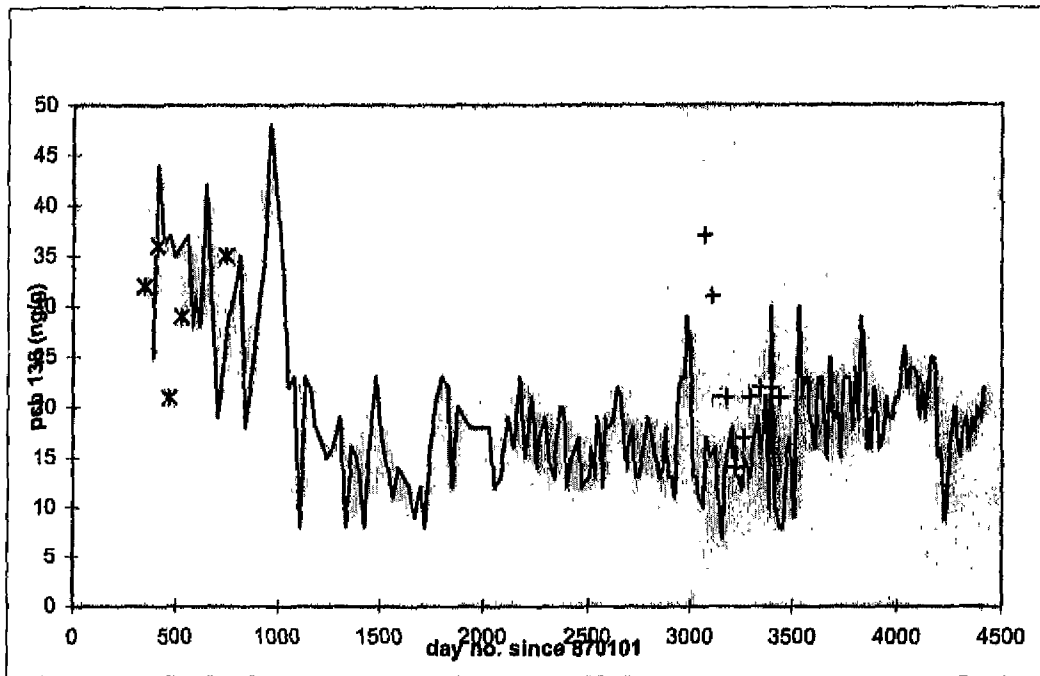
B
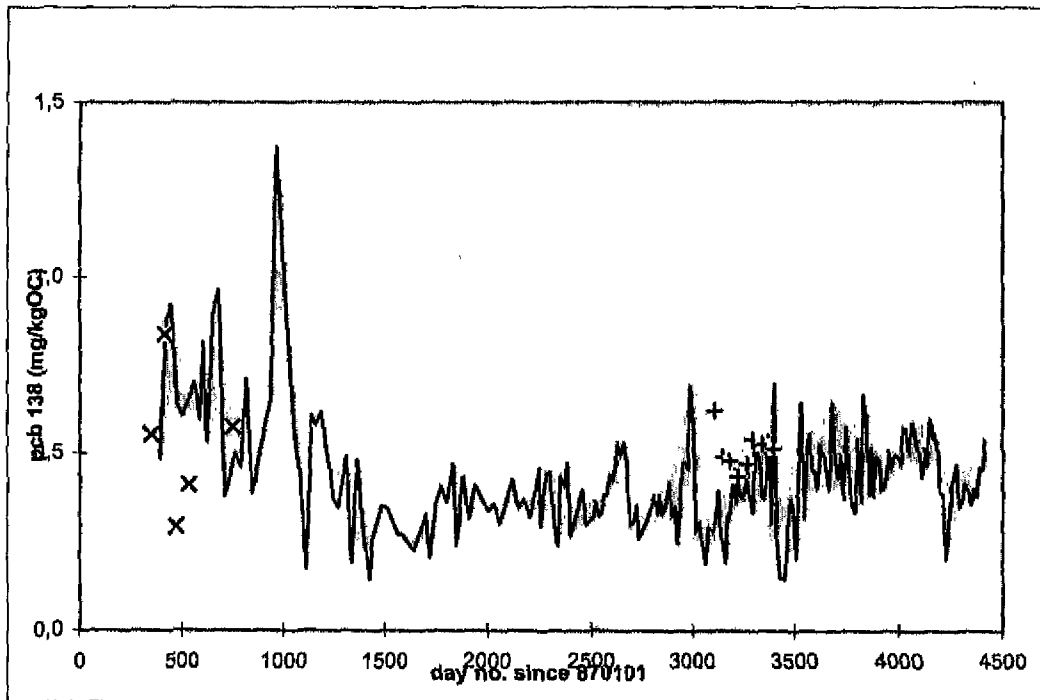
Figure 2: PCB 138 concentrations (A: in ng/g and B: in mg/kgOC)
at the routinely sampled location Belgian-Dutch border.

x cruises 1987/89
+ cruises 1995/96

A
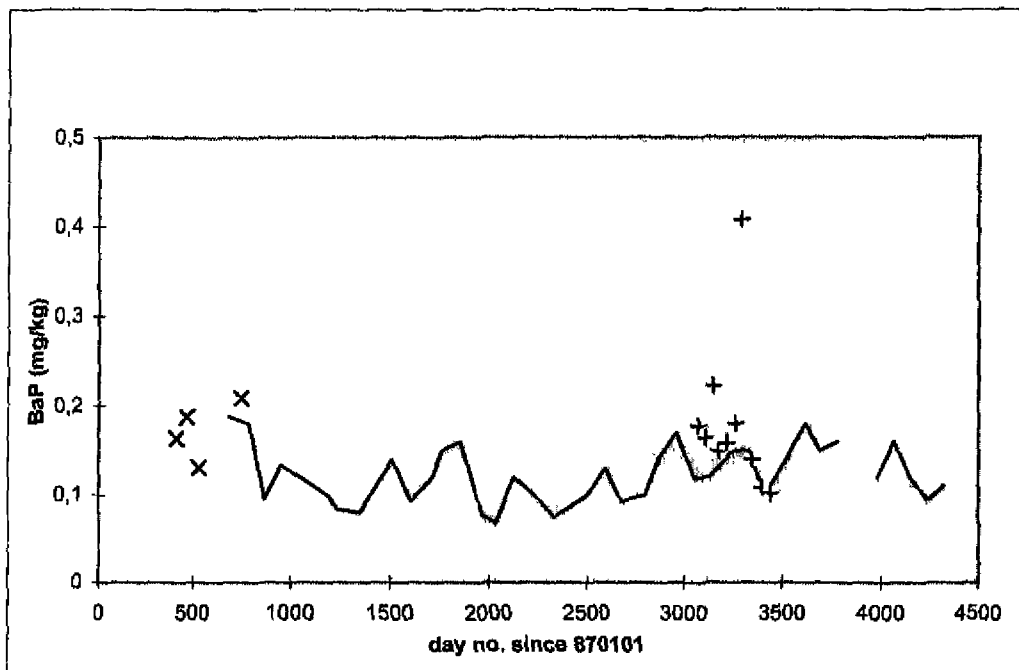
B
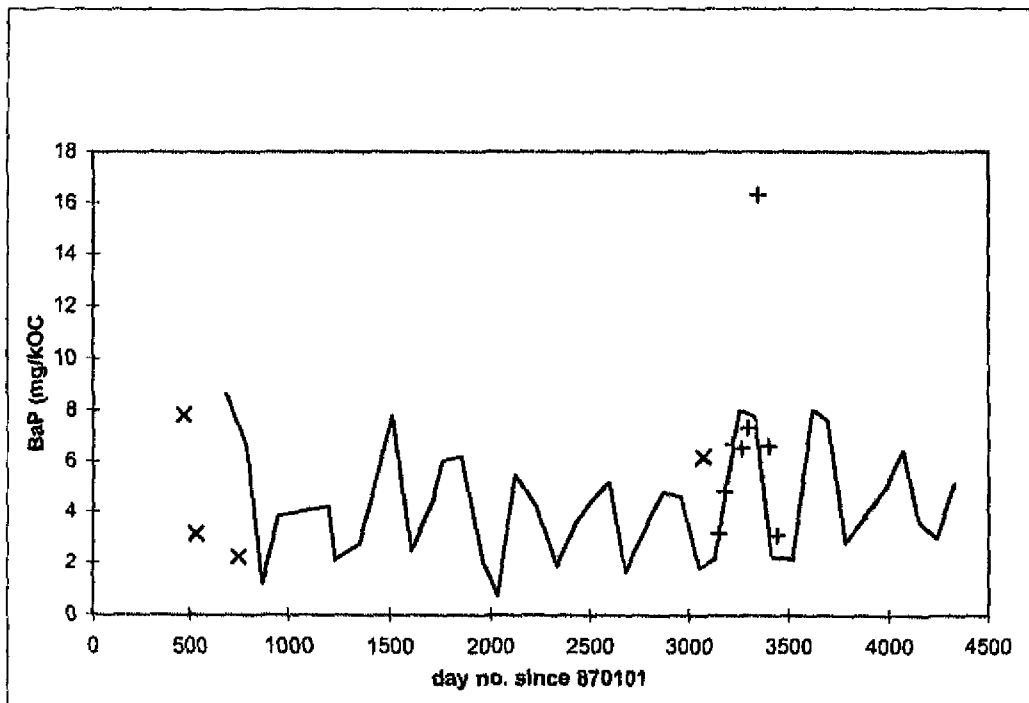
Figure 3: BaP concentrations (A: in mg/kg and B: in mg/kgOC)
at the routinely sampled location Vlissingen.

x cruises 1987/89
+ cruises 1995/96
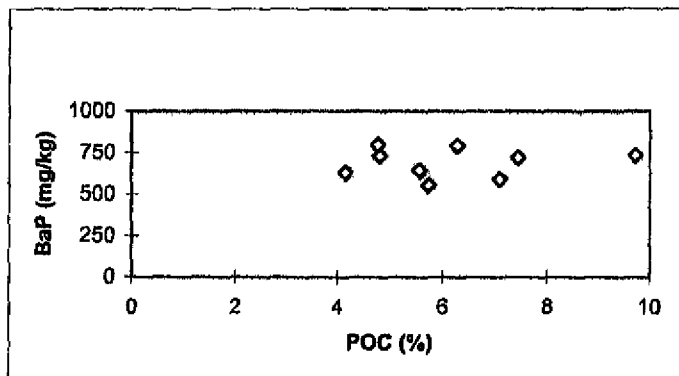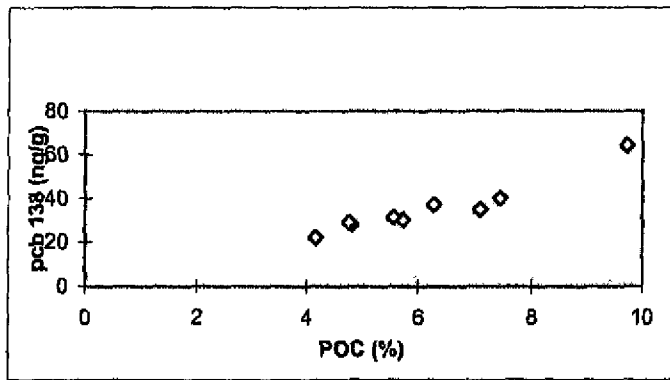
Figure 4: Variations of pcb 138 and BaP concentrations on SPM with POC content at Rupelmonde in 1995/96..
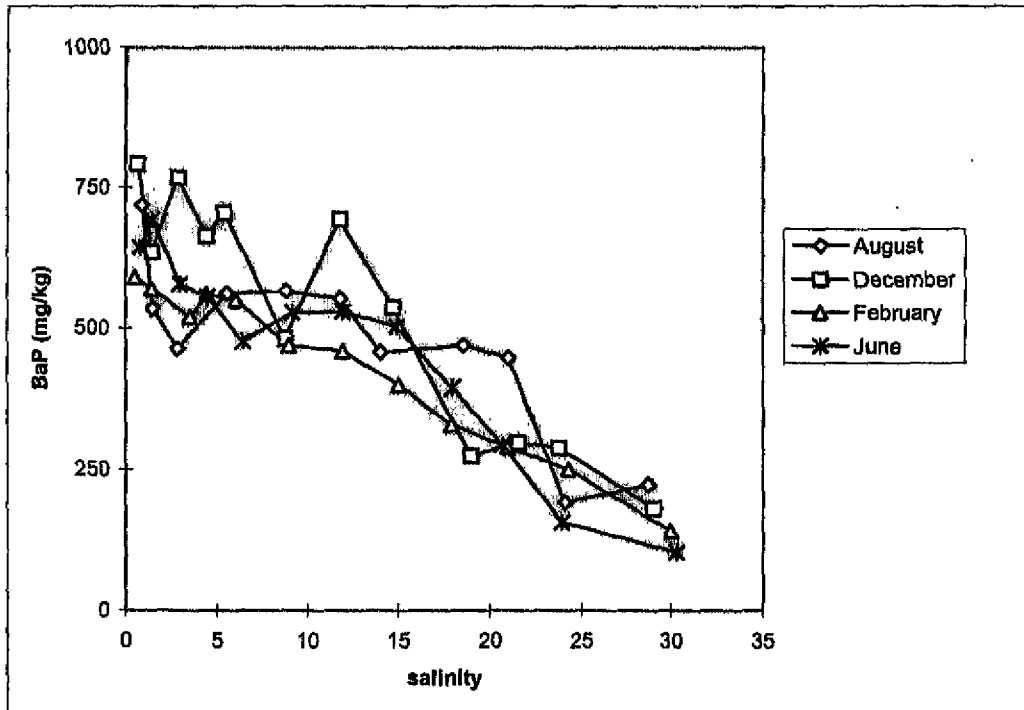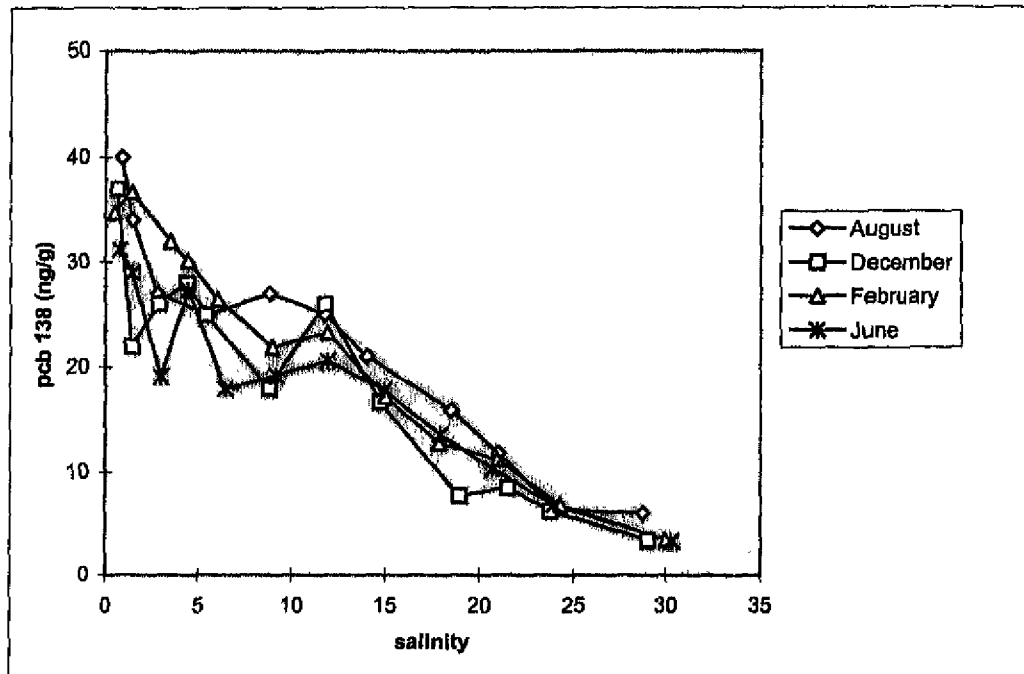
Figure 5: Variations of pcb 138 and BaP concentrations on SPM with salinity for four different cruises in 1995/96.
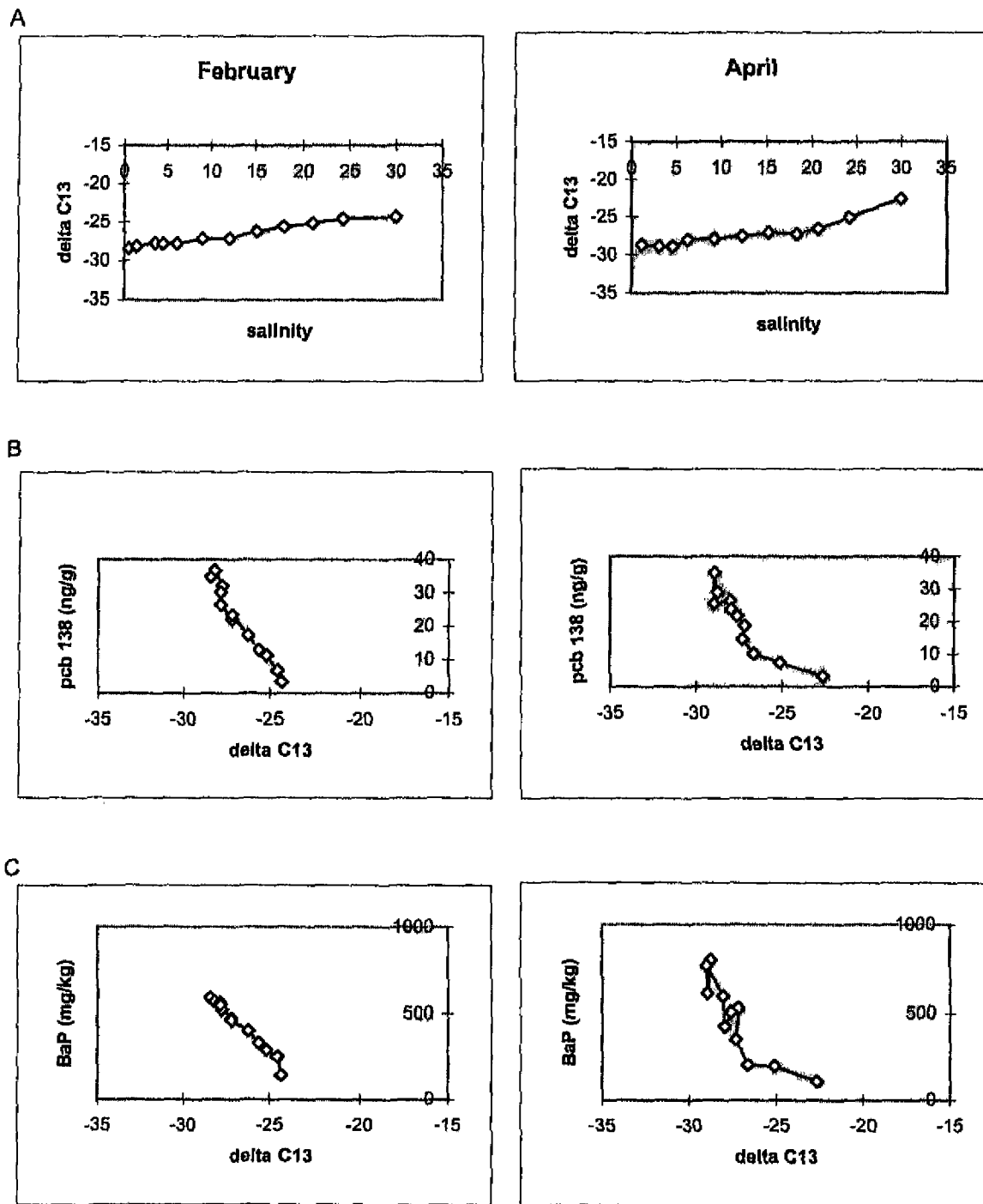
Figure 6: Variations of delta C13 on SPM with salinity in February and April 1996.(A).
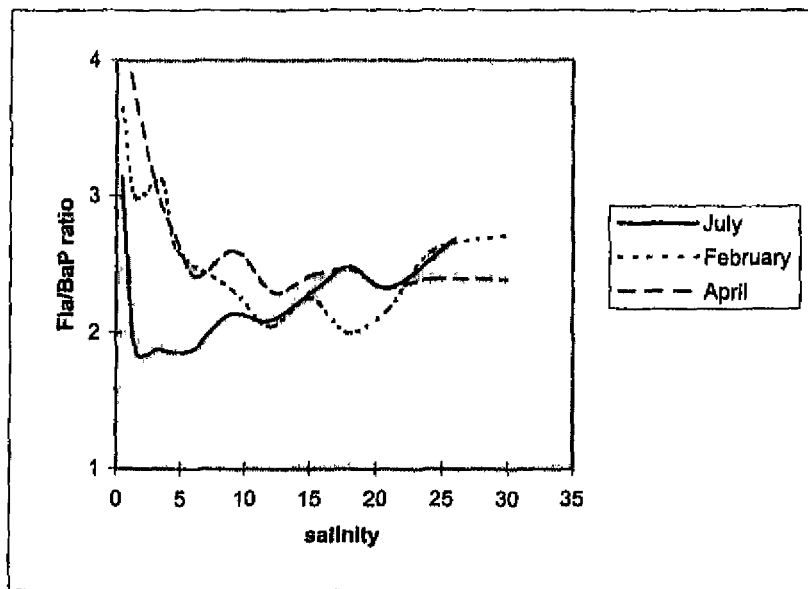In B and C respectively, pcb 138 and BaP variations with delta C13 on SPM.

Figure 7: Ratio of fluoranthene and benzo(a)pyrene
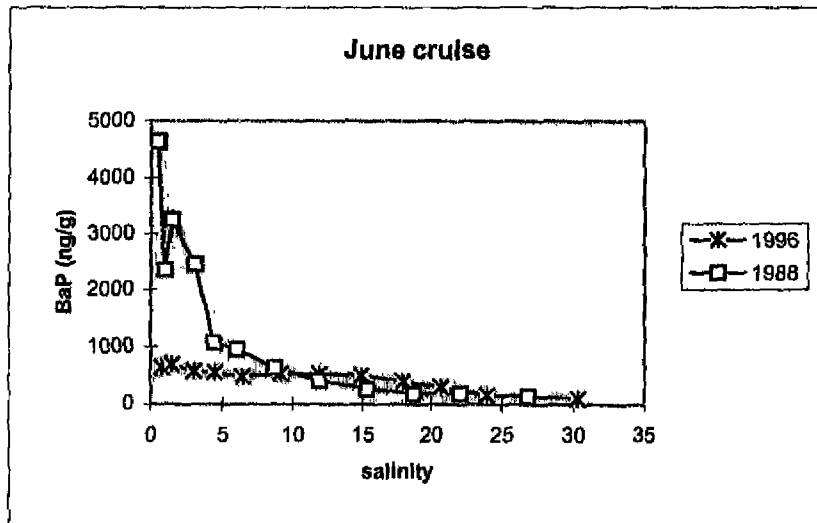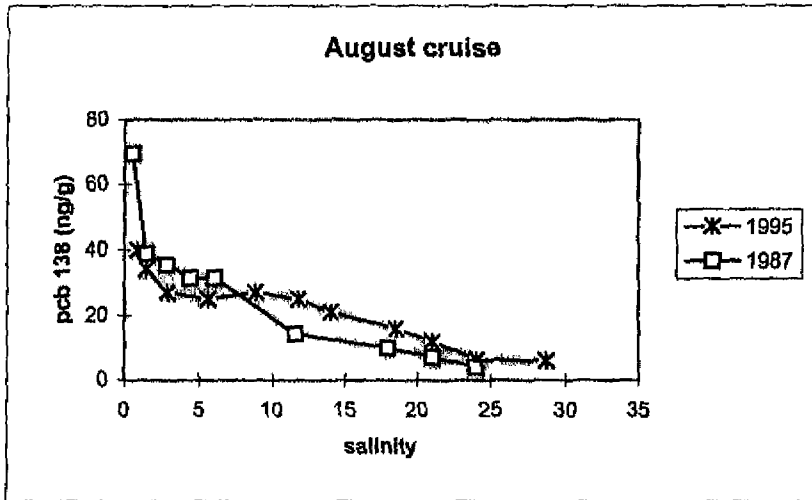on SPM as a function of salinity for three different cruises in 1995/96.

Figure 8: Concentrations of pcb 138 and BaP on SPM
as a function of salinity. Comparison between 1987/88 and 1995/96.

Verantwoording

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