Comparison of grain size correction procedures for organic micropollutants and heavy metals in marine sediments

J.C. Klamer[1], W.J.M. Hegeman[2] & F. Smedes[1]
[1]*Rijkswaterstaat Tidal Waters Division, PO Box 207, 9750 AE Haren, The Netherlands*; [2]*Dept. of Geochemistry, Inst. of Earth Sciences, University of Utrecht, PO Box 80021, 3508 TA Utrecht, The Netherlands*

Abstract

Four grain size correction procedures were tested for their applicability for comparing concentrations of heavy metals and organic micropollutants (PCBs, PAHs) in sediments. A simple and straightforward procedure proved best: wet sieving of fresh sediment, isolating and analysing the $<63\ \mu m$ grain size fraction and expressing the pollutant concentration as a proportion of the fraction's dry weight. The total analytical errors, expressed as the variation coefficient of the average concentrations, were 3.8–7.6% for heavy metals, 12–24% for PCBs and 5.3–9.9% for PAHs.

Introduction

Marine monitoring programmes are increasingly focussing on the concentrations of micropollutants in bottom sediments instead of in water, because these sediments incorporate water pollution over a number of years and are therefore better suited for monitoring than water itself. It is vital to make accurate assessments of pollutant concentrations, in order to determine temporal or spatial changes properly. However, a major drawback of using sediments is the grain size effect. The coarse components that normally have low levels of heavy metals and organic pollutants produce a downward shift of the concentration in the total sample. Since sediments of different origin vary in grain size composition, this shift is non-uniform between locations. Therefore the contaminant levels of sediments of different origin

can be properly compared only when the data have been corrected for this grain size effect. Various correction procedures have been presented in the literature (de Groot *et al.*, 1971; Förstner & Wittmann, 1979; Ackermann, 1980; Salomons *et al.*, 1981; de Groot, 1982; Schoer, 1982; Ackermann *et al.*, 1983; Hellmann, 1983; Salomons & Eijsink, 1983; Salomons & Kerdijk, 1983; Salomons & Förstner, 1984; Schneider & Weiler, 1984). Almost all refer exclusively to the analysis of heavy metals. As far as we know, this study is the first to compare the performance of several grain size correction procedures for both heavy metals and organic micropollutants.

In general, the grain size fractionation methods mentioned in the literature can be divided into two categories: techniques based on settling velocities and techniques that use fine mesh to trap the sediment. The methods in the first group have the

214

Table 1. Grain size correction procedures tested in this study

Method	Example	Compounds	References #
1. Grain size	$<63\ \mu m$	HM*, PAH	1–6
fractionation	$<20\ \mu m$	HM, PCB, PAH, HCB	3, 7, 8
2. Regression	$50\% < 16\ \mu m$	HM	3, 9–11
3. Organic carbon/		HCB, PCB, OCS**	12
organic matter			
4. Conservative	Cs, Hf, Sc, Al	HM	2, 13, 14
elements			

  * HM = Heavy Metals
** OCS = octa-chloro-styrene
 # 1: Ackermann *et al.*, 1983; 2: Ackermann, 1980; Förstner & Salomons, 1980; 4: Hellmann, 1983; 5: Li, 1981; 6: Lohse, 1988; 7: Marcomini *et al.*, 1986; 8: Salomons & Kerdijk, 1983; 9: Salomons & Eijsink, 1983b; 10: Salomons *et al.*, 1981; 11: Schneider & Weiler, 1984; 12: Schoer, 1982; 13: Stutterheim & Zevenboom, 1988; 14: Turkstra & Fioole, 1987.

drawback that the resulting grain size fractions are not always well defined, since they are based on average densities. The innovative technique of Schneider & Weiler (1984), who used a standardized settling tube, has the serious disadvantage that only 100 mg dried sediment can be treated at a time. In the second group sieving techniques using metal (stainless steel) (Turkstra & Fioole, 1987), brass (Prahle & Carpenter, 1983) or nylon (Ackermann *et al.*, 1983; Turkstra & Fioole, 1987) mesh, with the aid of water to accelerate the process, are most frequently used.

In this study, the performance of four different correction procedures (Table 1), was tested.

Materials and methods

Sampling and chemical analysis

In June and August 1987 samples were taken from three stations on the Balgzand tidal flat area in the western Dutch Wadden Sea (Fig. 1). Eight 2 kg samples with a gradient in grain size composition were taken at station A. At stations B and
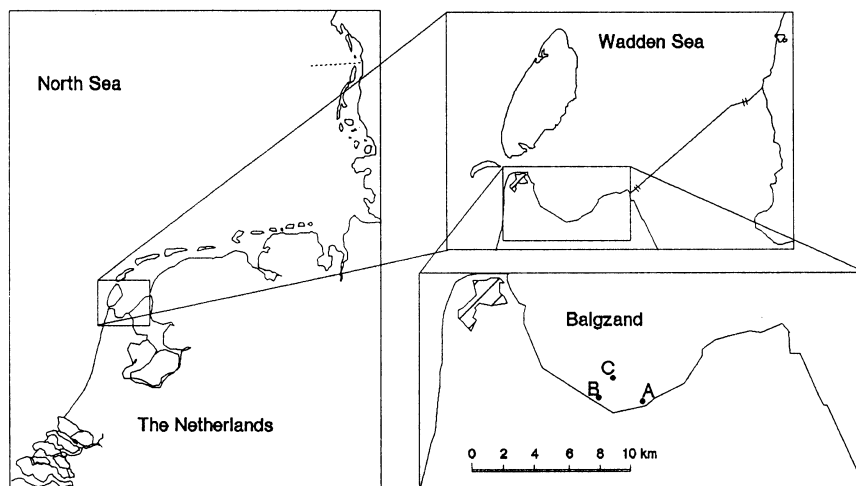

Fig. 1. Location of sampling sites A, B and C on the Balgzand tidal flat, western Wadden Sea.

C, 50 kg bulk samples were taken. Location B is muddier than C. Six subsamples were drawn from B and C. All samples were stored at 4 °C until further treatment.

Specific grain size fractions (< 1000, < 63 and < 20 μm) were separated by sieving the sediments on a device consisting of specially designed Perspex sieve holders, nylon mesh, vibrating platform, aspirator, and a flow through beaker centrifuge (3000 rpm) coated with Teflon. Up to 1 kg wet weight of sediment was put in the uppermost sieve (usually the 1000 μm mesh). The centrifuge, pump and vibrating platform were switched on and the sediment was sieved with the aid of 500–1000 ml circulating water (milli-Q). The < 1000 μm fraction could be collected after ca. 5–10 min., and the < 63 and < 20 μm fractions after 40–50 minutes. The pertinent fractions were freeze-dried and stored at room temperature until further treatment. The average recovery of grain size fractions from the total sediment was 80 to 90%, sandier sediments having higher recoveries than muddier ones.

Grain size distributions of organic carbon and limestone-cleared sediments were determined using a modified Sedigraph. Organic matter was determined gravimetrically by loss-on-ignition (LOI, 45 min. at 600 °C).

The freeze-dried sediments were Soxhlet-extracted with hexane-acetone (3 : 1). The crude extract was cleaned up and the PCB and PAH fractions were fractionated by adsorption chromatography using aluminum oxide and silica gel. PCBs were determined with capillary gas-chromatography, using a laboratory standard of a mixture of PCB congeners for identification and quantification (IUPAC numbers: 26, 28, 31, 44, 52, 101, 118, 138, 153, 170 and 180). PAH compounds were determined using high-performance liquid chromatography with fluorescence detection. A laboratory standard of individual PAH was used for identification and quantification (PAH compounds determined: acenaphtene (ACN), fluoranthene (FLU), phenantrene (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 (BghiP) and indeno(1,3,3-c,d)pyrene (INP)). Of the heavy metals, Cd, Cu, Zn and Pb were determined using flame or furnace atomic absorption spectrometry with high-pressure nitric acid sample-destruction. Other metals were determined using instrumental neutron activation analysis followed by gamma-ray spectrometry. In this study, As is treated as a metal.

Statistical analysis

If contaminant levels in a series of samples are plotted against the organic matter content, concentrations generally increase with increasing OM. Using a grain size correction procedure, the regression curve (concentration vs. OM) will level off, resulting in a horizontal line for the ideal correction procedure. In this study, the performance of the procedures mentioned in Table 1 was evaluated with data from location A, using tests on homogeneity of slopes to distinguish between regression lines. The results for locations B and C give information about the total analytical error. In the event of similar levelling off of regression lines, it was decided to opt for the procedure combining smallest analytical error with practicability.

Results and discussion

In this section, results for Cd, PCB 138 and BaP in samples from location A are presented and discussed in detail. Supplementary data on other compounds is available on request.

In Figs. 2a–2c, concentrations of Cd, PCB 138 and BaP in the three fractions isolated are plotted against the organic matter content of the total sample (i.e. < 1000 μm fraction). With increasing organic matter content, the general increase in concentration of the three compounds in the < 1000 μm fraction levels off in the finer-grained fractions. For As (not shown), the levelling off is overdone (becomes a decline) in the case of the < 20 μm fraction.

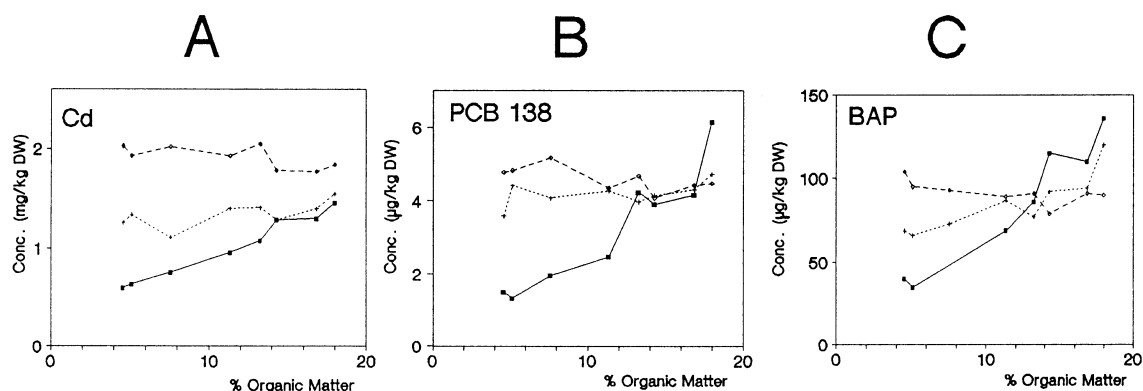Testing the homogeneity of the slopes of the

Fig. 2. Concentrations of cadmium (A), PCB 138 (B) and BaP (C) in various sediment fractions (■–■ < 1000 μm, + · · · + < 63 μm, ◆---◆ < 20 μm) versus the organic matter content of the total sediment, for eight cogenetic samples from location A.

calculated regression lines (concentration vs% organic matter) revealed that in all cases the < 1000 μm fractions behaved differently from the finer fractions ($p < 0.001$). For Cd, Pb and Zn, the levelling off of the regression lines by fractionation to 63 or 20 μm was the same ($p < 0.01$ for Cd and Pb, and $p < 0.05$ for Zn). However, this was not the case for As ($p > 0.1$). For all PCBs, the < 1000 μm fraction behaved differently from the finer-grained fractions ($p < 0.001$) which behave statistically similar ($p < 0.001$). It is important to note that all congeners show a similar behaviour between fractions. For all PAHs, with the exception of BaA and BkF, there was no difference in the behaviour of the two finest fractions ($p < 0.05$ for BaA and BkF, $p > 0.1$ for all other PAHs), compared with the regression line of the < 1000 μm fraction.

For heavy metals, the < 20 μm fraction for location B (muddy) gave the smallest errors (average variation coefficient (VC, $n = 6$) of 4 metals: 6.1% for < 20 μm and 7.6% for < 63 μm). For location C (sandy) the < 63 μm fraction was the best (average VC: 6.9% for < 20 μm and 3.8% for < 63 μm). The difference in analytical errors between muddier and sandier locations that was apparent for heavy metals was similar for PCBs. Location B: average VC for 7 congeners is 11.4% and 24% for the < 20 μm and < 63 μm fractions respectively, whereas for lo-

cation C VC is 11.3 and 12.1% for < 20 μm and < 63 μm. The differences in VC between locations are not significant for the < 20 μm fraction ($p > 0.1$), and are significant for the < 63 μm fraction ($p < 0.01$). For PAH, the average VC in the < 20 μm and < 63 μm fractions of location B samples (all PAH, $n = 6$) is 3.5% and 9.9%; for location C it is 8.2% and 5.3%, respectively; all VCs are statistically different ($p < 0.001$).

In Figs. 3a and 3b the concentrations of PCB 138 and BaP for location A samples (< 1000 μm fraction) are plotted against the percentage of the fraction smaller than 16 μm in the total sample (Table 1: method 2). For heavy metals, it was calculated that in all cases the concentration at 50% < 16 μm has higher total analytical error than other methods (average VC = 8.0%). The same holds for PCBs (average VC = 12.3%) and PAHs (average VC = 9.6%)

Standardizing the concentrations of organic micropollutants to the organic matter content of the pertinent fractions resulted in statistical similarity of all fractions ($p > 0.1$ for tests on different behaviour) for all PCB congeners and PAH compounds (with the exception of PYR: $p < 0.005$). As an example, the results for PCB 138 and PYR are shown in Figs. 4a and 4b, respectively. For all metals, standardization to Cs, Sc or Al removed the statistical differences
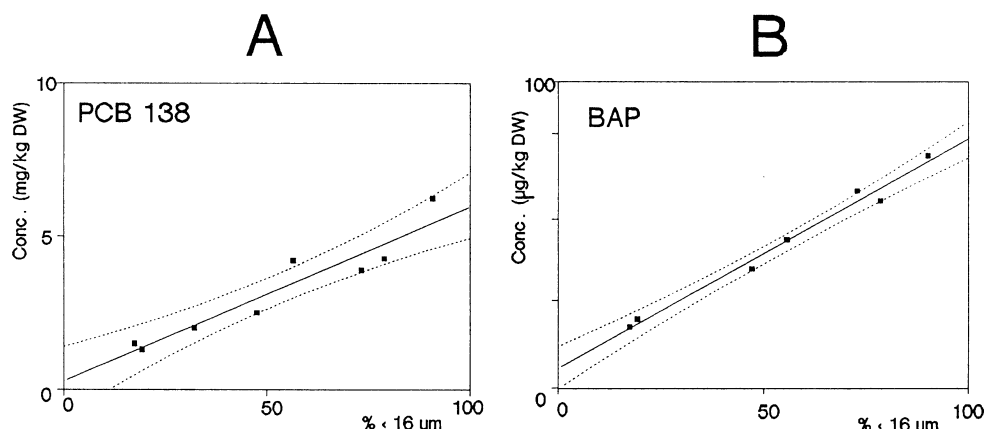
Fig. 3. Concentrations of PCB 138 (A) and BaP (B) versus the percentage of the fraction smaller than 16 μm, for eight cogenetic sediment samples from location A. (... = 95% confidence interval).

between fractions, except for Pb/Sc and Pb/Al ($p < 0.05$). As an example, relative concentrations of Cd/Cs and Pb/Sc are given in Figs. 5a and 5b, respectively. In general, it can be concluded that standardization to Cs or Sc is appropriate to most heavy metals tested.

Standardization of PCB concentrations to Al was tested, and rejected: for congeners 101, 138, 153 and 180 there was still a difference between the $< 1000\,\mu$m fraction and the $< 63\,\mu$m and $< 20\,\mu$m fractions ($p < 0.05$), although in all

cases differences between the latter factions were eliminated.

It is interesting to compare the contaminant levels obtained by analysing pertinent fractions, with the levels obtained from extrapolation (e.g. 100% < 53 or 16 μm). Table 2 gives the extrapolated levels and the average concentrations in the $< 63\,\mu$m and $< 20\,\mu$m fractions.

The extrapolated concentrations at 100% $< 53\,\mu$m are generally higher than the levels in the $< 63\,\mu$m fraction. With the exception of Cd, Pb
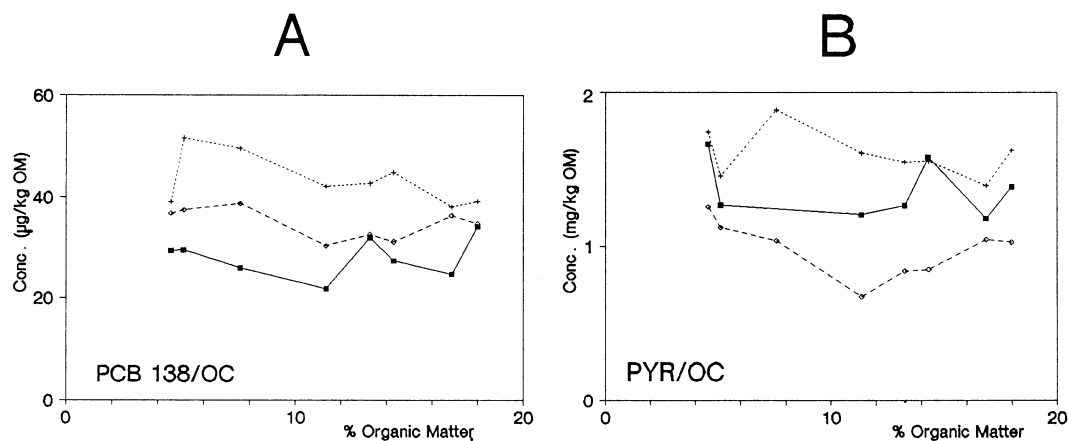

Fig. 4. Organic matter standardized concentrations of PCB 138 (A) and PYR (B) in various sediment fractions (■–■ $< 1000\,\mu$m, $+ \cdots +$ $< 63\,\mu$m, ◆---◆ $< 20\,\mu$m) versus the organic matter content of the total sediment, for eight cogenetic samples from location A.

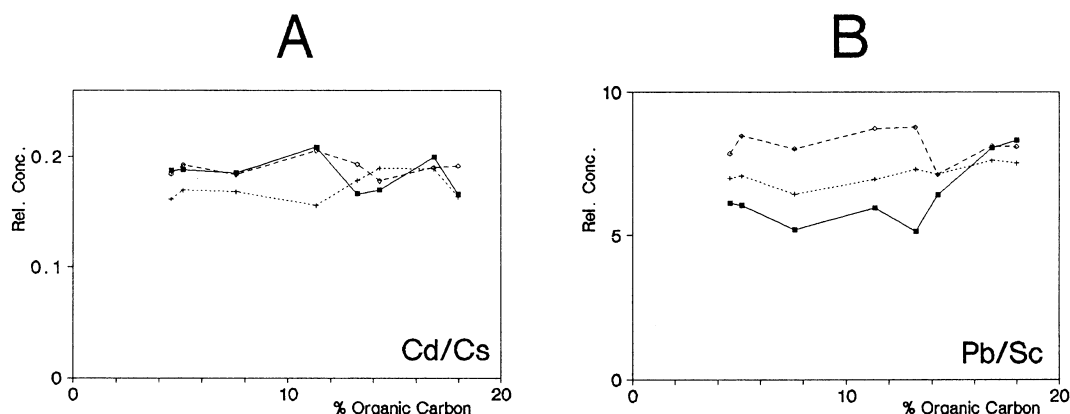*Fig. 5.* Concentrations of cadmium, standardized to Cs (A) and of lead (B), standardized to Sc, in various sediment fractions (■-■ 1000 μm, + · · · + < 63 μm, ◆---◆ < 20 μm) versus the organic matter content of the total sediment, for eight cogenetic samples from location A.

and Zn, the same holds for extrapolating to 100% < 16 μm and the < 20 μm fraction. However, in all cases the extrapolated values are within the same order of magnitude as the values in the pertinent fractions, and, with the exception of BaP(20), BaP(63) and INP(63), fall within each other's range of $x \pm \sigma$. It should be noted that the extrapolated concentrations are calculated for organic carbon and limestone-cleared sediment. Correction for OC will generally result in a better correspondence between the extrapolated and measured concentrations.

It has been reported (Turkstra & Fioole, 1987; Lohse, 1988) that in the coarse-grained fraction of marine and fluviatile sediments, concentrations of PCB and PAH are sometimes greater than in the fine-grained fractions. Therefore, we estimated the ΣPCB and PAH levels in the 63–1000 μm fraction of location A samples by combining the results from PCB and PAH analysis of the < 1000 and < 63 μm fractions, and the grain size composition of the samples (as% > 53 μm). For ΣPCB, it appeared that of the total content in the < 1000 μm fraction, less than 14% was con-

Table 2. Extrapolated contaminant concentrations at 100% < 16 μm and 100% < 53 μm, compared with average concentrations in the < 20 (C-20 μm) and < 63 μm (C-63 μm) fractions. (C in mg kg^{-1} for heavy metals, μg kg^{-1} for PAHs and PCBs; dry weight).

Compound	C(100% < 16 μm)	C-20 μm	C(100% < 53 μm)	C-63 μm
Cd	1.58	1.92	1.39	1.35
Pb	82.1	93.7	69.6	68.2
Zn	253	279	225	217
As	27.2	26.1	23.5	21.4
PCB 28	2.91	2.33	2.43	3.00
PCB 138	6.01	4.60	5.04	4.19
PCB 180	3.24	2.72	2.75	2.47
FLU	40.5	38.6	34.2	31.5
BaP	145	92	123	85
INP	168	144	142	104

tributed by the >63 and $<1000\,\mu m$ grain size fraction. For individual PAH compounds, it was calculated that 1 to 63% (ΣPAH: 11–58%) of the total content was present in this fraction. This phenomenon is important for monitoring, but it should be recognized that by isolating a grain size fraction, one does not measure the total pollutant content.

Conclusions

There are various reasons for not choosing standardizing micropollutant levels to the organic matter or conservative element content of the sample. First, such a procedure needs at least one extra analysis for each sample. Second, concentrations of neither OM nor conservative metals can be determined with absolute precision and therefore add to the total analytical error. Third, since concentrations of micropollutants in the total sample are generally lower than in a finer fraction, extra care has to be taken to avoid contamination. Last, in some cases, concentrations in the total sample could be below detection limits.

The '50% $<16\,\mu m$' procedure, in which standardized concentrations are calculated by regression analysis, is applicable to the sediments tested. However, this is mainly because on a tidal flat it is possible to sample a cogenetic gradient in which the $<16\,\mu m$ fraction is very variable. In North Sea sediments, such a sampling procedure is very likely to fail, partly because in sandy sediments the $<16\,\mu m$ fraction is less than 20% nearly everywhere (Klamer, unpublished results).

Based upon the results described above and the criterion of practicability, we conclude that for the analysis of heavy metals and organic micropollutants (PCBs, PAHs) in sediment, correction for differences in grain size composition can best be effected by isolating and analysing the $<63\,\mu m$ grain size fraction. However, it must be realized that a significant amount of the PAH can be present in the $>63\,\mu m$ fraction.

References

Ackermann, F., 1980. A procedure for correcting the grain size effect in heavy metal analyses of estuarine and coastal sediments. Envir. Technol. Lett. 1: 518–527.

Ackermann, F., M. Bergmann & U. Schleichert, 1984. Monitoring of heavy metals in coastal and estuarine sediments – a question of grain size: $<20\,\mu m$ versus $<60\,\mu m$. Envir. Technol. Lett. 4: 317–328.

De Groot, A. J., J. J. M. De Goeij & C. Zegers, 1971. Contents and behaviour of mercury as compared with other metals in sediments from the rivers Rhine and Ems. Geol. Mijnbouw 50: 393–398.

De Groot, A. J., K. H. Zschuppe & W. Salomons, 1982. Standardisation of methods for heavy metal analysis in sediments. Hydrobiologia 92: 689–695.

Förstner, U. & G. Wittmann, 1979. Metal Pollution in the Aquatic Environment. Springer Verlag, Berlin: 486 pp.

Förstner, U. & W. Salomons, 1980. Trace metal analysis on polluted sediments part I. Assessment of sources and intensities. Envir. Technol. Lett. 1: 494–504.

Hellmann, H., 1983. Grain size distributions and organic trace substances in fluvial sediments and soils. Z. Anal. Chem. 316: 286–289.

Li, Y-H., 1981. Geochemical cycles of elements and human pertubation. Geochim. Cosmochim. Acta 45: 2073–2084.

Lohse, J., 1988. Herkunft, Ausbreitung und Verteilung von schwerflüchtigen Chlorkohlenwasserstoffen in Sedimenten der Nordsee. PhD. Thesis. University of Hamburg, 160 pp.

Marcomini, A., B. Pavoni, R. Donazzolo & A. A. Orio, 1986. Combined preparative and analytical use of normal-phase and reversed-phase high-performance liquid chromatography for the determination of aliphatic and polycyclic aromatic hydrocarbons in sediments of the Adriatic Sea. Mar. Chem. 18: 71–85.

Prahl, F. G. & R. Carpenter, 1983. Polycyclic aromatic hydrocarbon(PAH)-phase associations in Washington coastal sediment. Geochim. Cosmochim. Acta 47: 1013–1023.

Salomons, W. & U. Förstner, 1984. Trace metals in the Hydrocycle. Springer Verlag, Berlin, 349 pp.

Salomons, W. & H. N. Kerdijk, 1983. Metalen in boorkernen en oppervlakte sedimenten van de Noordzee. Delft Hydraulics report no. M1676.

Salomons, W. & W. D. Eijsink, 1983. Zware metalen in

sedimenten van de Waddenzee: verslag onderzoek. Delft Hydraulics report no. M1839.

Salomons, W., W. D. Eijsink & H. N. Kerdijk, 1981. Inventarisatie en geochemisch gedrag van zware metalen in de Schelde en Westerschelde: verslag onderzoek. Delft Hydraulics report M1640/M1736.

Schneider, B. & K. Weiler, 1984. A quick grain size correction procedure for trace metal contents of sediments. Envir. Technol. Lett. 5: 245–256.

Schoer, J., U. Nagel, D. Eggersglüss & U. Förstner, 1982. Metal contents in sediments from the Elbe, Weser and Ems estuaries and from the German Bight (southeastern North Sea): grain size effects. Mitt. Geol.-Paläont. Inst. Univ. Hamburg 52: 687–702.

Stutterheim, E. & W. Zevenboom, 1988. Joint Monitoring Programme of the Netherlands. Ministry of Transport and Public Works, Tidal Waters Division report GWWS-88.011: 47 pp.

Turkstra, E. & A. Fioole, 1987. Onderzoek naar verontreinigingsgehalten in sediment fracties in de kader van monitoring. Ministry of Transport and Public Works, DBW/RIZA report 87.100X.