

Elemental concentrations and heavy metal pollution in sediments and suspended matter from the Belgian North Sea and the Scheldt estuary

V. Van Alsenoy, P. Bernard and R. Van Grieken

Department of Chemistry, University of Antwerp (UIA), Universiteitsplein 1, B-2610 Wilrijk, Belgium

(Received January 8th, 1992; accepted February 25th, 1992)

ABSTRACT

The elemental composition of sediment and suspended matter samples from the Belgian coastal and offshore regions of the Southern Bight of the North Sea and from the Scheldt estuary has been determined using X-ray fluorescence and atomic absorption spectrometry. Special attention was given to the heavy metals of the black and the grey lists. The bulk sediment and the clay/silt fraction were analyzed. The average heavy metal contents in the fraction $< 63 \mu\text{m}$ were comparable to the levels in the suspended matter. Different normalization techniques led to the identification of two different populations of sediments. Most of the sediments were enriched in Cd, Cr, Hg, Pb and Zn but no enrichment was found for Cu and Ni. Comparing these data with older data indicates that little changes in the metal contamination of the sediments in the area investigated has occurred over the last 15 years.

Key words: heavy metals; sediments; suspended matter; North Sea; Scheldt estuary

INTRODUCTION

During the last decades several studies have been carried out to determine the heavy metal contamination in the Southern Bight of the North Sea and the Scheldt estuary. Data are available both in the open literature and in internal reports from the Dutch and Belgian ministries and institutions. Many of these works consider dissolved and/or suspended matter samples (Duinker and Nolting, 1976; Duinker and Nolting, 1977; Duinker et al., 1982; Nolting, 1986; Valenta et al., 1986; Baeyens et al., 1987; Nolting and Eisma, 1988). Others include sediments (De Groot and Allersma, 1975; Baeyens et al., 1979; Wollast, 1976; D'Hondt and Baeteman, 1987; Araújo et al., 1988). For the river Scheldt the studies result usually in longitudinal profiles for dissolv-

ed or particulate heavy metal concentrations (Buekens and Dhaese, 1980; Salomons and Eysinck, 1981; Baeyens et al., 1982; Wollast et al., 1985; Temmerman, 1988).

In the work of Araújo et al. (1988), X-ray fluorescence (XRF) analysis results of sediments sampled about 10 years ago were presented. Some normalization and multivariate techniques were used to interpret the data set. In the present paper a similar approach is followed, since this favours later comparison. However, apart from the completely new data set presented, this work is focused on 4 main broader goals:

(1) The samples in the work by Araújo et al. (1988) were analyzed using only XRF, which has rather poor detection limits for some of the heavy metals of interest (1–10 $\mu\text{g/g}$) and does not allow the determination of Cd and Hg. In the present work, several of the heavy metals were determined using atomic absorption spectrometry (AAS) which is more sensitive and accurate for most of the heavy metals and yields Cd and Hg data.

(2) Comparison with older data obtained by the same method allowed an assessment of the evolution of the pollution situation as a function of time.

(3) In the work of Araújo et al. (1988), only four sampling locations in the Dutch Scheldt were investigated. No samples were taken in the Belgian part of the Scheldt. In this work more samples were taken throughout the Dutch and the Belgian Scheldt estuary, including data for the most polluted area, namely the industrial zone around Antwerp.

(4) Suspended matter samples were simultaneously collected and analysed with sediment samples during the last sampling campaign.

SAMPLING AND ANALYTICAL TECHNIQUES

Sampling methodology

Samples of sediments and suspended matter were collected in several stations located in the Belgian North Sea, the river Scheldt and in four harbours (Nieuwpoort, Oostende, Zeebrugge and Blankenberge) along the Belgian coast (Fig. 1). The samples were collected during 4 different cruises with the RV Belgica between December 1987 and July 1988. During each campaign, sampling for all the stations was planned, but due to weather conditions or defects to the sampling equipment, some stations were missed in some campaigns. The number of samples per location varies from 1 to 4. The harbour sediments were only sampled once. The suspended matter samples were simultaneously collected with the sediments during the last campaign. Sediment samples were taken with a box-corer. Only sub-samples, from the central part of the box-corer, taken with PVC tubes, were used, in order to minimize contaminating effects of the edges of the box-corer. The upper 2

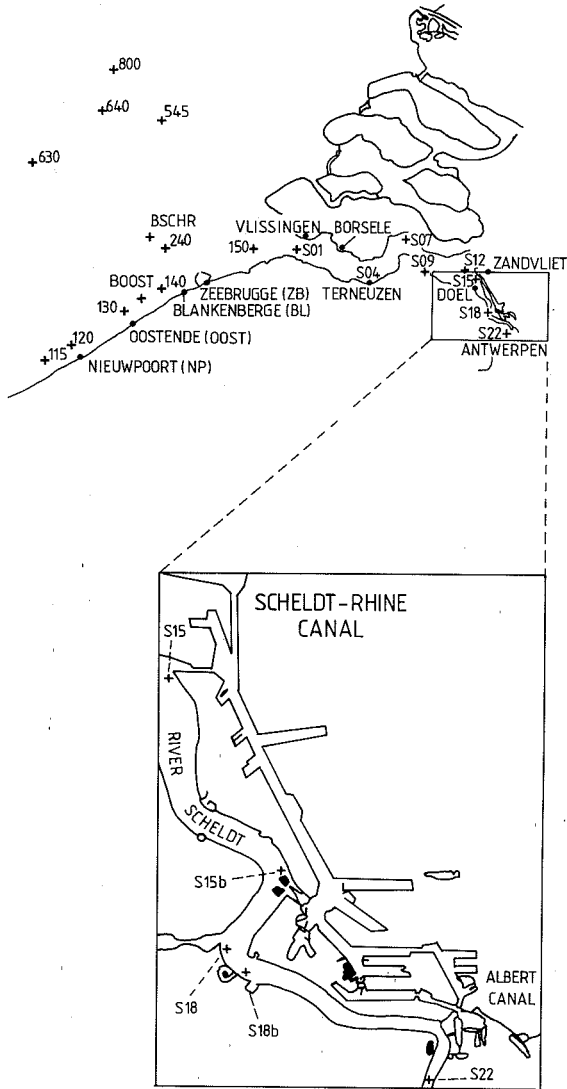


Fig. 1. Sampling stations.

cm of the sediments in the tubes were analyzed. The suspended matter samples were collected on board by filtration of water samples (sampled with Niskin bottles) over Nuclepore filter with a pore diameter of $0.45 \mu\text{m}$. The filters were washed with Milli-Q water to remove sea-salts. All samples were immediately frozen after collection.

Analytical techniques

X-ray fluorescence

Sediment samples were ground in an agate mortar, suspended and filtered over Nuclepore filters (0.45 μm pore size). The sample thickness was determined using the scatter peaks (Van Espen et al., 1979; Araújo et al., 1990). A Spectrace 5000 (Tracor Northern) instrument, with Rh-tube and Rh thin filter was used. The resulting spectra were quantitatively interpreted using the commercially available computer program AXIL (Van Espen et al., 1986). In the calculations absorption phenomena were taken into account.

Atomic absorption spectrometry

Sediment samples were digested with HF, HNO₃ and HClO₄ in teflon bombs. To 0.1–1 g of sediment 8 ml of HF was added and heated slowly to dryness. After cooling 4 ml of 1:1 mixture of HNO₃ and HClO₄ was added and the solution was again heated slowly to dryness. If necessary further digestion of the silicates with HF was performed. After cooling, the residue was dissolved in 2 ml HNO₃ and the volume was made up to 100 ml with Milli-Q deionized water. All reagents were of supra-pure grade. Fe and Zn concentrations were measured using an air-acetylene flame, at a wavelength and slit width of, respectively, for Zn: 213.9 nm and 0.7 nm and for Fe: 248.3 nm and 0.2 nm. A Perkin Elmer PE-AAS-3030 was used. Cu, Ni and Pb were determined electrothermally with a Perkin Elmer PE-HGA-500 unit. Cd was measured using a Perkin Elmer PE-5 100 Zeeman instrument.

For the determination of Hg the samples were digested according to Age-mian and Chau (1976) and Hg was measured using the cold vapour technique after an amalgamation step, at a wavelength of 253.6 nm and a slit of 0.7 nm, with a Perkin Elmer PE-MS-20.

Separation technique

The dry sediments were disaggregated by boiling them for a short time with H₂O₂ and then subjecting them to a short ultrasonic treatment. They were then wet-sieved with a minimum amount of deionized water using plastic sieves with a pore diameter of 63 and 20 μm . Since this separation technique seriously affects the concentration of volatile elements like Hg, the latter element was only determined in the bulk fraction. This method was compared to other methods like dry and wet sieving and gave the best results for separation and metal contents. For these samples, the error induced due to heavy metal mobilization by organic matter digestion was smaller than the error induced by incomplete separation of the different grain size fraction (see Van Alsenoy et al., 1988). Samples containing the highest organic matter

content were used for the optimization. The error induced by this method due to mobilization of heavy metals was $\pm 10\%$ for Pb and Cd and less than 5% for Cu and Ni, while the other methods involve errors $> 10\text{--}20\%$.

RESULTS

The results of the chemical characterization of the bulk samples are given in Tables 1–3; it is clear that the offshore samples (240-BSCHR-545-630-640-800) are all coarse sand samples (fraction $< 63 \mu\text{m}$ is smaller than 5% of the total sample) and that the element concentrations and size distributions show relatively little variability with time and location. The near-shore

TABLE 1A

Element concentrations of the North Sea off-shore bulk sediments. Results are given as mean \pm S.D., ranges between parentheses

	240	BSCHR	545	630	640	800
K (%)	0.68	0.52 \pm 0.06 (0.45–0.56)	0.55 \pm 0.01 (0.54–0.55)	0.43 \pm 0.02 (0.41–0.44)	0.55 \pm 0.01 (0.54–0.55)	0.4 \pm 0.2 (0.33–0.56)
Ca (%)	3.14	5 \pm 15 (2.7–10)	1.4 \pm 0.8 (0.88–1.95)	6 \pm 3 (3.9–7.9)	1.5 \pm 0.9 (0.85–2.1)	1.3 \pm 0.1 (1.2–1.4)
Ti ($\mu\text{g/g}$)	700	460 \pm 60 (400–500)	500 \pm 200 (300–600)	300 \pm 100 (200–400)	450 \pm 70 (400–500)	300 \pm 100 (200–400)
V ($\mu\text{g/g}$)	32	22 \pm 3 (19–24)	36 \pm 1 (35–36)	26 \pm 2 (24–27)	38 \pm 6 (33–42)	40 \pm 10 (24–46)
Cr ($\mu\text{g/g}$)	29	15 \pm 4 (12–19)	20 \pm 10 (13–30)	14 \pm 1 (13–15)	18 \pm 4 (15–20)	11 \pm 5 (7–14)
Mn ($\mu\text{g/g}$)	125	100 \pm 20 (80–118)	65 \pm 9 (58–71)	140 \pm 110 (60–214)	40 \pm 20 (33–55)	60 \pm 40 (29–80)
Fe (%)	0.52	0.38 \pm 0.05 (0.32–0.41)	0.28 \pm 0.03 (0.26–0.30)	0.4 \pm 0.1 (0.30–0.47)	0.28 \pm 0.01 (0.27–0.29)	0.3 \pm 0.1 (0.25–0.45)
Ni ($\mu\text{g/g}$)	5	4 \pm 3 (1.7–7)	2.2 \pm 0.2 (2.0–2.3)	2.4 \pm 0.5 (2.0–2.7)	4 \pm 2 (2–5)	3 \pm 1 (2–4)
Cu ($\mu\text{g/g}$)	0.74	0.7 \pm 0.4 (0.3–1.1)	0.7 \pm 0.2 (0.5–0.85)	0.5 \pm 0.3 (0.3–0.67)	0.8 \pm 0.2 (0.68–0.95)	0.8 \pm 0.2 (0.7–1.0)
Zn ($\mu\text{g/g}$)	15	9 \pm 2 (7–11)	6.5 \pm 0.7 (6–7)	8 \pm 3 (6–10)	9 \pm 3 (7–11)	7 \pm 3 (4.5–10)
Rb ($\mu\text{g/g}$)	43	37 \pm 3 (34–39)	37 \pm 4 (34–39)	28 \pm 3 (26–30)	38 \pm 3 (36–40)	34 \pm 9 (27–40)
Sr ($\mu\text{g/g}$)	186	300 \pm 270 (113–605)	90 \pm 20 (80–101)	380 \pm 130 (280–470)	120 \pm 40 (87–146)	120 \pm 9 (128–115)
Pb ($\mu\text{g/g}$)	7	6 \pm 2 (4.2–8)	7 \pm 2 (5–9)	5 \pm 1 (5–6)	6 \pm 6 (2–10)	6 \pm 3 (4–9)
Hg (ng/g)	7	<5	14 \pm 12 (<5–22)	14 \pm 13 (<5–23)	80 \pm 110 (<5–162)	<5
Cd (ng/g)	40	30 \pm 10 (13–36)	11 \pm 7 (6–16)	18 \pm 17 (6–30)	7 \pm 2 (<5–8)	30 \pm 60 (4–151)
<63 μm (%)	5	3 \pm 1 (3–4)	3 \pm 1 (2–3)	2 \pm 1 (1–2)	2 \pm 1 (1–2)	2 \pm 1 (1–2)
n	1	3	2	2	2	3

TABLE 1B

Element concentrations of the North Sea near-shore bulk sediments. Results are given as mean \pm S.D., ranges between parentheses

	115	120	130	BOOST	140	702	150
K (%)	0.7 \pm 0.2 (0.48–0.96)	0.7 \pm 0.1 (0.57–0.87)	0.9 \pm 0.3 (0.64–1.25)	0.8 \pm 0.4 (0.5–1.2)	0.7 \pm 0.2 (0.54–0.92)	0.87	0.57
Ca (%)	5 \pm 2 (2.2–7.7)	7 \pm 2 (4.5–9.4)	8 \pm 3 (3.9–9.7)	6 \pm 4 (3.5–10)	4 \pm 4 (2.1–8.6)	6.5	1.57
Ti (%)	0.12 \pm 0.08 (0.05–0.19)	0.12 \pm 0.07 (0.05–0.20)	0.17 \pm 0.09 (0.05–0.27)	0.12 \pm 0.1 (0.05–0.25)	0.13 \pm 0.09 (0.07–0.23)	0.21	0.08
V (μ g/g)	40 \pm 20 (30–72)	40 \pm 20 (32–65)	60 \pm 30 (23–106)	50 \pm 30 (25–83)	40 \pm 12 (29–52)	45	17
Cr (μ g/g)	40 \pm 20 (26–69)	40 \pm 20 (24–66)	60 \pm 40 (16–105)	50 \pm 50 (24–103)	40 \pm 10 (23–69)	71	32
Mn (μ g/g)	200 \pm 140 (97–415)	230 \pm 120 (104–370)	420 \pm 250 (155–760)	340 \pm 340 (114–723)	230 \pm 190 (121–450)	430	124
Fe (%)	1.2 \pm 1.1 (0.57–2.85)	0.8 \pm 0.3 (0.51–1.12)	1.2 \pm 0.6 (0.53–1.81)	0.8 \pm 0.8 (0.36–1.7)	1.1 \pm 0.6 (0.46–1.45)	0.95	0.36
Ni (μ g/g)	8 \pm 8 (4–20)	4 \pm 2 (2–7)	8 \pm 5 (2–14)	7 \pm 10 (1–18)	5 \pm 5 (2–10)	6.4	2.5
Cu (μ g/g)	5 \pm 6 (1.6–14)	2.6 \pm 0.6 (2–3.5)	4 \pm 2 (0.43–6.1)	5 \pm 7 (0.52–13)	3 \pm 2 (0.65–5.4)	3.2	1.0
Zn (μ g/g)	60 \pm 60 (26–156)	30 \pm 10 (20–42)	70 \pm 40 (16–100)	60 \pm 90 (7–170)	40 \pm 40 (16–78)	47	12
Rb (μ g/g)	50 \pm 10 (40–69)	46 \pm 7 (38–52)	60 \pm 20 (41–91)	60 \pm 30 (35–94)	50 \pm 10 (37–60)	62	36
Sr (μ g/g)	240 \pm 80 (146–328)	310 \pm 120 (165–458)	370 \pm 130 (207–504)	310 \pm 160 (219–496)	240 \pm 180 (126–448)	343	116
Pb (μ g/g)	30 \pm 30 (11–67)	13 \pm 5 (7–18)	20 \pm 5 (13–26)	20 \pm 30 (2–58)	11 \pm 7 (5–19)	13	5
Hg (ng/g)	200 \pm 190 (35–374)	100 \pm 110 (10–263)	180 \pm 90 (119–287)	230 \pm 350 (14–636)	70 \pm 100 (<5–181)	112	<5
Cd (ng/g)	240 \pm 310 (47–710)	140 \pm 60 (81–202)	320 \pm 210 (50–494)	210 \pm 310 (25–575)	180 \pm 160 (81–371)	200	40
<63 μ m (%)	30 \pm 20 (8–86)	21 \pm 6 (5–31)	60 \pm 20 (3–96)	30 \pm 20 (2–83)	20 \pm 20 (3–63)	78	7
n	4	4	4	3	3	1	1

samples (115-120-130-BOOST-140-702-150), however, show a high variability in size distribution (fraction < 63 μ m, range from 3% to 96%) and element concentrations. The samples taken in the harbours all contain high contents of clay/silt, with relatively high heavy metal content. For the river Scheldt sediments, all samples (except S07 and S09) show high variability in grain size and element content. Since the heavy metal content in sediments is concentrated in the finer fractions (Salomons and Förstner, 1984 and references therein), the fraction < 63 μ m was analyzed. These results can be found in Tables 4–6. The marine samples were all taken in the Southern North Sea (identified as zone IV by Nolting and Eisma, 1988). In this part of the North Sea, the suspended matter concentration and its size composition are similar

TABLE 2A

Element concentrations of the Scheldt bulk sediments. Results are given as mean \pm S.D., ranges between parentheses

	S01	S04	S07	S09	S12
K (%)	0.87 \pm 0.06 (0.80-0.94)	0.5 \pm 0.2 (0.39-0.74)	0.34 \pm 0.11 (0.20-0.45)	0.61 \pm 0.09 (0.54-0.74)	0.7 \pm 0.2 (0.49-1.0)
Ca (%)	4 \pm 2 (2.0-6.3)	3.8 \pm 1.3 (2.2-5.4)	0.6 \pm 0.4 (0.29-0.54)	0.7 \pm 0.3 (0.49-1.1)	3 \pm 2 (0.8-5.1)
Ti (%)	0.17 \pm 0.04 (0.13-0.22)	0.05 \pm 0.02 (0.03-0.07)	0.04 \pm 0.03 (0.02-0.09)	0.06 \pm 0.02 (0.49-1.1)	0.11 \pm 0.07 (0.05-0.20)
V (μ g/g)	50 \pm 20 (42-82)	50 \pm 20 (29-65)	30 \pm 10 (17-47)	37 \pm 8 (26-44)	80 \pm 60 (29-170)
Cr (μ g/g)	70 \pm 10 (57-84)	63 \pm 9 (59-73)	40 \pm 20 (20-63)	29 \pm 8 (21-40)	80 \pm 70 (29-170)
Mn (μ g/g)	320 \pm 140 (151-475)	260 \pm 30 (225-288)	50 \pm 20 (37-80)	80 \pm 30 (46-104)	420 \pm 480 (80-1100)
Fe (%)	1.4 \pm 0.2 (1.11-1.55)	1.8 \pm 0.8 (1.40-2.94)	0.7 \pm 0.3 (0.32-1.09)	0.8 \pm 0.2 (0.58-1.04)	3 \pm 5 (0.4-8.5)
Ni (μ g/g)	10 \pm 6 (6-19)	20 \pm 30 (4-69)	1.5 \pm 0.6 (1-2)	3 \pm 1 (2-4)	4 \pm 3 (2-7)
Cu (μ g/g)	5 \pm 4 (1-10)	9 \pm 10 (3-24)	0.7 \pm 0.2 (0.3-0.9)	2 \pm 3 (0.3-6.7)	2 \pm 2 (1.1-4.1)
Zn (μ g/g)	60 \pm 30 (23-103)	100 \pm 60 (46-184)	13 \pm 5 (7-19)	17 \pm 4 (13-22)	60 \pm 50 (17-65)
Rb (μ g/g)	60 \pm 10 (44-71)	32 \pm 9 (24-43)	23 \pm 7 (14-29)	37 \pm 3 (35-42)	40 \pm 10 (34-60)
Sr (μ g/g)	230 \pm 100 (133-386)	280 \pm 120 (182-415)	60 \pm 20 (36-79)	80 \pm 20 (64-114)	190 \pm 120 (89-325)
Pb (μ g/g)	20 \pm 7 (12-27)	14 \pm 9 (6-26)	5 \pm 2 (2-7)	8 \pm 2 (6-9)	14 \pm 12 (2-26)
Hg (ng/g)	80 \pm 100 (<5-217)	40 \pm 20 (30-62)	40 \pm 80 (<5-162)	<5 (<5-5)	90 \pm 120 (<5-172)
Cd (μ g/g)	0.5 \pm 0.5 (0.063-1.1)	0.4 \pm 0.2 (0.18-0.51)	0.019 \pm 0.009 (0.01-0.03)	0.06 \pm 0.07 (0.01-0.16)	0.2 \pm 0.2 (0.1-0.5)
<63 μ m (%)	30 \pm 10 (4-59)	30 \pm 20 (5-86)	2 \pm 1 (1-3)	2 \pm 1 (1-2)	7 \pm 5 (1-21)
n	4	4	4	4	3

and so are the particulate metal concentration associated with the suspended matter (Nolting and Eisma, 1988). On average, significant agreement is found between the concentrations of the heavy metal content in the fraction < 63 μ m of the analyzed North Sea sediments in this work and those of the suspended matter samples of the North Sea taken in the same period by Nolting and Eisma (1988). An overview follows.

K. The K content is comparable for all the analyzed sediment samples of the Southern North Sea with an average \pm S.D. of 1.2% \pm 0.2% ($n = 32$). The individual concentrations range from 0.74% to 2.0%. Nolting and Eisma found values > 1% in the Southern North Sea with a maximum value of 1.6%. The K content is also rather constant in the sediments of the Scheldt estuary. The average value (1.5% \pm 0.4%) ($n = 39$) is somewhat higher than

TABLE 2B

Element concentrations of the Scheldt sediments. Results are given as mean \pm S.D., ranges between parentheses

	S15	S15b	S18	S18b	S22
K (%)	0.85 \pm 0.04 (0.84-0.90)	1.04 \pm 0.09 (0.96-1.13)	1.2 \pm 0.2 (0.94-1.39)	1.0 \pm 0.3 (0.76-1.35)	0.87 \pm 0.05 (0.8-0.91)
Ca (%)	4 \pm 2 (2.2-6.7)	4.5 \pm 0.3 (4.1-4.7)	4 \pm 2 (2.1-5.9)	2 \pm 1 (1.2-4.0)	2 \pm 1 (1.4-3.9)
Ti (%)	0.09 \pm 0.01 (0.07-0.10)	0.4 \pm 0.2 (0.19-0.59)	0.3 \pm 0.1 (0.23-0.48)	0.2 \pm 0.1 (0.09-0.36)	0.05 \pm 0.02 (0.03-0.07)
V (μ g/g)	60 \pm 20 (40-77)	90 \pm 20 (63-104)	130 \pm 20 (111-148)	90 \pm 60 (41-163)	53 \pm 5 (48-59)
Cr (μ g/g)	73 \pm 4 (67-77)	180 \pm 50 (133-251)	270 \pm 140 (129-409)	170 \pm 90 (88-295)	79 \pm 9 (67-90)
Mn (μ g/g)	210 \pm 20 (185-237)	670 \pm 190 (520-907)	700 \pm 450 (216-1100)	500 \pm 500 (102-1200)	280 \pm 150 (190-490)
Fe (%)	2.3 \pm 1.0 (1.4-3.7)	3.0 \pm 1.3 (2.2-4.9)	3.0 \pm 2.1 (1.6-5.5)	2.4 \pm 0.9 (1.7-3.7)	2.3 \pm 0.3 (1.9-2.7)
Ni (μ g/g)	6 \pm 2 (4-9)	50 \pm 70 (11-148)	20 \pm 20 (6-41)	12 \pm 10 (4-25)	6 \pm 3 (4-10)
Cu (μ g/g)	5 \pm 6 (0.2-12)	100 \pm 130 (21-282)	50 \pm 70 (9-127)	20 \pm 20 (2-32)	8 \pm 6 (4-16)
Zn (μ g/g)	70 \pm 50 (27-131)	390 \pm 240 (180-724)	320 \pm 360 (100-740)	230 \pm 180 (76-461)	330 \pm 100 (220-453)
Rb (μ g/g)	46 \pm 3 (43-49)	63 \pm 9 (56-75)	80 \pm 30 (49-103)	60 \pm 30 (43-111)	45 \pm 1 (43-46)
Sr (μ g/g)	330 \pm 150 (208-520)	300 \pm 60 (261-379)	220 \pm 70 (142-293)	180 \pm 90 (106-291)	180 \pm 90 (94-302)
Pb (μ g/g)	20 \pm 20 (6-58)	110 \pm 70 (50-207)	80 \pm 90 (21-178)	50 \pm 50 (11-132)	70 \pm 30 (31-86)
Hg (ng/g)	150 \pm 170 (<5-390)	640 \pm 580 (<5-1400)	900 \pm 780 (70-1620)	430 \pm 430 (20-1030)	50 \pm 20 (29-70)
Cd (μ g/g)	0.8 \pm 0.9 (0.04-1.7)	8.4 \pm 5.6 (2.9-14.0)	5.0 \pm 7.0 (1.0-13.0)	3.0 \pm 3.5 (0.34-7.9)	1.7 \pm 0.8 (1.1-2.8)
<63 μ m (%)	10 \pm 2 (5-14)	60 \pm 10 (43-83)	40 \pm 30 (10-97)	30 \pm 20 (2-93)	6 \pm 2 (3-12)
n	4	4	3	4	4

the one for the North Sea sediment samples. Concentrations range from 0.8% to 2.6%.

Ca. The Ca content is fairly constant over the analyzed area of the North sea, with a mean value of 11% \pm 2%. Nolting and Eisma found a Ca content in suspended matter in that region \geq 10%. The average Ca content in the river Scheldt samples is lower by almost a factor of 2: 7% \pm 3%.

Ti. The Ti contents are rather constant over the investigated area. For the North Sea samples an average of 0.24% \pm 0.06% was found, compared to Nolting and Eisma's value of 0.2%. The mean value for the sediments of the Scheldt estuary is 0.28% \pm 0.06% with elevated values up to 0.5% around Doel, Antwerp.

TABLE 3
Element concentrations in the harbor bulk sediments

	ZB2	ZB3	OOST1	OOST2	NP1	NP2	BL0	BL1	BL2
K (%)	1.24	1.25	1.16	0.87	0.95	1.35	1.36	1.35	1.23
Ca (%)	8.28	8.55	8.99	11.3	9.90	10.3	9.43	11.6	9.6
Ti (%)	0.25	0.24	0.24	0.18	0.16	0.24	0.27	0.28	0.25
V ($\mu\text{g/g}$)	85	98	93	50	61	83	95	91	95
Cr ($\mu\text{g/g}$)	103	112	117	69	73	101	117	117	98
Mn ($\mu\text{g/g}$)	760	640	460	640	324	523	770	768	797
Fe (%)	2.64	3.08	3.17	2.06	1.34	3.03	3.10	2.95	2.86
Ni ($\mu\text{g/g}$)	20	21	27	16	10	22	24	20	19
Cu ($\mu\text{g/g}$)	14	15		12		11	17	9	9
Zn ($\mu\text{g/g}$)	146	194	104	137	82	149	187	176	164
Rb ($\mu\text{g/g}$)	101	110	104	73	71	115	113	109	111
Sr ($\mu\text{g/g}$)	390	434	420	560	487	463	461	509	497
Pb ($\mu\text{g/g}$)	63	72	90	42	28	59	68	53	54
Hg (ng/g)	367	509	514	277	300	332	413	332	465
Cd (ng/g)	695	898	1020	2339	433	407	707	891	763
<63 μm (%)	86	95	97	88	53	94	96	98	98

TABLE 4A

Element concentrations in the fraction $< 63 \mu\text{m}$ of the North Sea off-shore sediments. Results are given as mean \pm standard deviation, ranges between parentheses

	240	BSCHR	545	630	640	800
K (%)	1.11	1.6 \pm 0.4 (1.3-2.0)	1.2 \pm 0.5 (0.87-1.6)	1.0 \pm 0.3 (0.74-1.23)	0.9 \pm 0.2 (0.83-1.06)	1.0 \pm 0.3 (0.78-1.22)
Ca (%)	10.6	10 \pm 4 (5.0-12)	10.8 \pm 0.4 (10.5-11)	13 \pm 2 (10.9-14.4)	9.6 \pm 0.8 (9.0-10.2)	9.5 \pm 0.7 (9.1-10.0)
Ti (%)	0.23	0.23 \pm 0.12 (0.14-0.37)	0.23 \pm 0.07 (0.18-0.28)	0.18 \pm 0.08 (0.12-0.24)	0.19 \pm 0.06 (0.15-0.23)	0.21 \pm 0.06 (0.16-0.25)
V ($\mu\text{g/g}$)	91	140 \pm 60 (109-207)	110 \pm 20 (90-120)	80 \pm 10 (72-89)	100 \pm 20 (81-115)	100 \pm 20 (87-118)
Cr ($\mu\text{g/g}$)	108	150 \pm 20 (124-161)	150 \pm 70 (98-203)	78 \pm 4 (75-80)	100 \pm 20 (74-115)	100 \pm 20 (56-116)
Mn ($\mu\text{g/g}$)	650	690 \pm 360 (428-1100)	580 \pm 30 (564-604)	480 \pm 240 (313-650)	420 \pm 130 (320-510)	520 \pm 330 (286-746)
Fe (%)	3.2	5.2 \pm 1.0 (4.2-6.2)	3.5 \pm 0.6 (3.1-3.9)	2.8 \pm 0.1 (2.7-2.9)	2.8 \pm 0.5 (2.4-3.1)	3.1 \pm 1.3 (2.2-4.0)
Ni ($\mu\text{g/g}$)	16	40 \pm 30 (16-65)	34 \pm 5 (30-38)	22 \pm 3 (20-24)	30 \pm 6 (25-34)	30 \pm 10 (22-38)
Cu ($\mu\text{g/g}$)	7	15 \pm 3 (12-17)	15 \pm 5 (11-18)	11 \pm 2 (10-13)	10 \pm 1 (9-11)	12 \pm 8 (6-17)
Zn ($\mu\text{g/g}$)	550	260 \pm 210 (119-508)	120 \pm 30 (101-145)	120 \pm 40 (90-140)	340 \pm 370 (77-595)	150 \pm 110 (69-231)
Rb ($\mu\text{g/g}$)	80	120 \pm 40 (92-158)	120 \pm 20 (102-130)	80 \pm 20 (68-95)	90 \pm 10 (77-93)	80 \pm 20 (66-101)
Sr ($\mu\text{g/g}$)	715	660 \pm 250 (377-860)	720 \pm 80 (660-771)	970 \pm 610 (535-1400)	1150 \pm 650 (688-1602)	660 \pm 90 (602-727)
Pb ($\mu\text{g/g}$)	48	130 \pm 50 (78-160)	80 \pm 10 (72-90)	51 \pm 4 (48-54)	47 \pm 7 (42-52)	71 \pm 7 (66-76)
n	1	3	2	2	2	2

V. For the North Sea sediments an average value of $90 \pm 30 \mu\text{g/g}$ was found. The variations on the concentrations per station are rather high. This can probably be related to analytical imprecision since the concentrations were often close to the detection limit. The values found by Nolting and Eisma in this area were mostly $> 50 \mu\text{g/g}$ with a maximum around $200 \mu\text{g}$. Our values for the North Sea range from 58 to $203 \mu\text{g/g}$. The values found for the Scheldt sediments are higher with a mean of $145 \pm 40 \mu\text{g/g}$ and ranging from 68 to $250 \mu\text{g/g}$.

Cr. The average Cr content of the North sea samples was found to be $104 \pm 6 \mu\text{g/g}$. This value is twice as high compared with the amount found in the suspended matter ($\pm 50 \mu\text{g/g}$) by Nolting and Eisma. The average value for the Scheldt sediments is even higher: $220 \pm 60 \mu\text{g/g}$.

Mn. Large local and temporal variations have been found for the Mn contents in the North Sea sediments. Concentrations range from 313 to 1500

TABLE 4B

Element concentrations in the fraction $<63 \mu\text{m}$ of the North Sea near-shore sediments. Results are given as mean \pm S.D., ranges between parentheses

	115	120	130	BOOST	140	702	150
K (%)	1.2 \pm 0.2 (1.0-1.4)	1.29 \pm 0.06 (1.21-1.35)	1.1 \pm 0.1 (1.0-1.3)	1.2 \pm 0.2 (1.0-1.2)	1.1 \pm 0.1 (0.96-1.22)	1.6	11.5
Ca (%)	12 \pm 2 (9.8-14.7)	13 \pm 1 (12.5-14.2)	13 \pm 3 (10.5-16)	11 \pm 1 (10-12.8)	12 \pm 3 (9.6-14.4)	11	8.8
Ti (%)	0.27 \pm 0.04 (0.23-0.30)	0.25 \pm 0.02 (0.23-0.27)	0.28 \pm 0.07 (0.18-0.36)	0.28 \pm 0.12 (0.16-0.29)	0.21 \pm 0.07 (0.14-0.36)	0.28	0.23
V ($\mu\text{g/g}$)	90 \pm 20 (72-120)	90 \pm 10 (77-109)	90 \pm 30 (71-141)	90 \pm 20 (72-110)	70 \pm 10 (52-79)	120	85
Cr ($\mu\text{g/g}$)	100 \pm 20 (75-118)	100 \pm 20 (72-123)	90 \pm 40 (58-155)	90 \pm 10 (75-104)	110 \pm 20 (87-133)	203	78
Mn ($\mu\text{g/g}$)	700 \pm 400 (437-1200)	600 \pm 80 (505-700)	1300 \pm 1400 (488-3400)	1000 \pm 500 (650-1500)	640 \pm 80 (561-706)	604	547
Fe (%)	3.1 \pm 0.6 (2.5-3.9)	3.2 \pm 0.5 (2.7-3.7)	3.3 \pm 1.6 (1.8-6.0)	2.6 \pm 0.2 (2.3-2.7)	2.8 \pm 0.8 (1.9-3.5)	3.9	2.7
Ni ($\mu\text{g/g}$)	21 \pm 4 (15-25)	20 \pm 2 (17-22)	18 \pm 6 (11-25)	20 \pm 1 (20-21)	15 \pm 1 (15-16)	38	13
Cu ($\mu\text{g/g}$)	13 \pm 2 (11-15)	13 \pm 2 (11-15)	10 \pm 2 (7-12)	17 \pm 4 (13-21)	11 \pm 3 (8-13)	11	8
Zn ($\mu\text{g/g}$)	170 \pm 20 (144-203)	170 \pm 50 (118-230)	190 \pm 140 (74-390)	150 \pm 50 (101-202)	170 \pm 60 (107-213)	145	119
Rb ($\mu\text{g/g}$)	100 \pm 10 (83-112)	90 \pm 20 (70-108)	80 \pm 20 (59-98)	93 \pm 3 (90-95)	74 \pm 5 (70-80)	130	82
Sr ($\mu\text{g/g}$)	600 \pm 100 (475-720)	700 \pm 100 (553-820)	600 \pm 100 (513-819)	700 \pm 300 (490-1000)	600 \pm 200 (417-835)	660	540
Pb ($\mu\text{g/g}$)	90 \pm 40 (52-140)	70 \pm 30 (42-107)	110 \pm 120 (30-287)	70 \pm 20 (50-93)	70 \pm 30 (45-102)	72	82
n	4	4	4	3	3	1	1

$\mu\text{g/g}$. The averages for the Scheldt sediments ($940 \pm 250 \mu\text{g/g}$) were higher than those for the North Sea ($730 \pm 500 \mu\text{g/g}$).

Fe. The average Fe content in the North Sea sediment was $3.0\% \pm 1.1\%$ with a max of 6.2%. Nolting and Eisma found values $>3.0\%$ with a maximum of 6.46% in the suspended matter. The average value for the Scheldt sediments is twice as high: $6.4\% \pm 2.5\%$.

Ni. The Ni contents range from 11 to 65 $\mu\text{g/g}$ with a mean of $23 \pm 11 \mu\text{g/g}$. Those values are comparable to Nolting and Eisma's values of 20-80 $\mu\text{g/g}$. For the Scheldt the mean values are $31 \pm 13 \mu\text{g/g}$. There is, however, a clear difference between lower values ($23 \pm 8 \mu\text{g/g}$) in the lower estuary (S01-S12) and higher values ($39 \pm 18 \mu\text{g/g}$) in middle estuary (S15-S22).

Cu. The average Cu contents for the North Sea sediments ($15 \pm 6 \mu\text{g/g}$) are much lower than those reported by Nolting and Eisma for the suspended matter (mostly $>100 \mu\text{g/g}$). For the sediments of the Scheldt estuary averages

TABLE 5A

Element concentrations in the fraction $< 63 \mu\text{m}$ of the Scheldt sediments. Results are given as mean \pm S.D., ranges between parentheses

	S01	S04	S07	S09	S12
K (%)	1.6 \pm 0.4 (1.3-2.2)	1.3 \pm 0.3 (0.9-1.6)	1.9 \pm 0.6 (1.2-2.5)	1.6 \pm 0.6 (1.1-2.2)	1.3 \pm 0.4 (1.0-1.8)
Ca (%)	7 \pm 2 (5.0-9.3)	7 \pm 4 (1.7-11.1)	6 \pm 2 (4.3-8.0)	7 \pm 2 (5.3-8.9)	8 \pm 3 (5.2-11.4)
Ti (%)	0.28 \pm 0.03 (0.25-0.31)	0.30 \pm 0.10 (0.17-0.43)	0.25 \pm 0.08 (0.17-0.32)	0.24 \pm 0.03 (0.17-0.27)	0.26 \pm 0.06 (0.19-0.32)
V ($\mu\text{g/g}$)	130 \pm 40 (90-270)	130 \pm 40 (81-176)	150 \pm 50 (87-198)	150 \pm 30 (103-181)	140 \pm 40 (92-171)
Cr ($\mu\text{g/g}$)	170 \pm 80 (99-270)	160 \pm 60 (105-241)	250 \pm 100 (137-373)	260 \pm 90 (134-323)	200 \pm 70 (128-302)
Mn ($\mu\text{g/g}$)	750 \pm 50 (673-792)	1500 \pm 1200 (313-3000)	700 \pm 200 (483-1000)	820 \pm 70 (753-875)	670 \pm 6 (664-676)
Fe (%)	5 \pm 2 (2.7-7.2)	6 \pm 3 (3.0-10.0)	7 \pm 3 (4.5-10.2)	8 \pm 2 (4.7-10.0)	7 \pm 3 (3.3-9.9)
Ni ($\mu\text{g/g}$)	22 \pm 4 (19-28)	30 \pm 10 (19-54)	17 \pm 6 (10-16)	26 \pm 8 (11-29)	24 \pm 6 (24-40)
Cu ($\mu\text{g/g}$)	20 \pm 10 (12-35)	34 \pm 16 (18-54)	13 \pm 2 (10-16)	19 \pm 8 (11-29)	33 \pm 7 (24-40)
Zn ($\mu\text{g/g}$)	300 \pm 200 (150-622)	300 \pm 180 (153-514)	170 \pm 40 (121-206)	230 \pm 40 (180-265)	320 \pm 60 (227-367)
Rb ($\mu\text{g/g}$)	100 \pm 20 (89-135)	100 \pm 20 (77-119)	100 \pm 30 (73-141)	140 \pm 40 (85-168)	90 \pm 10 (81-111)
Sr ($\mu\text{g/g}$)	420 \pm 50 (351-480)	420 \pm 230 (160-729)	370 \pm 140 (172-514)	480 \pm 90 (390-613)	580 \pm 210 (340-852)
Pb ($\mu\text{g/g}$)	90 \pm 30 (52-125)	80 \pm 40 (36-121)	120 \pm 80 (59-235)	110 \pm 40 (66-155)	120 \pm 30 (75-144)
n	4	4	4	4	4

of 24 ± 13 in the lower estuary and 77 ± 35 in the middle estuary were found.

Zn. The mean content found for the North Sea sediments is $190 \pm 120 \mu\text{g/g}$ and is higher than those in the suspended matter analyzed by Nolting and Eisma (mostly below $100 \mu\text{g/g}$). The contents in the sediments in the lower Scheldt estuary are slightly higher: $260 \pm 130 \mu\text{g/g}$ and much higher in the middle estuary: $890 \pm 760 \mu\text{g/g}$.

Pb. The average Pb content for the North Sea sediments is $80 \pm 50 \mu\text{g/g}$. Nolting and Eisma found a mean of $50 \mu\text{g/g}$ for the Southern North Sea suspended matter samples. The lower estuary has a comparable mean content with $100 \pm 50 \mu\text{g/g}$ and the middle estuary has a much higher content with $260 \pm 250 \mu\text{g/g}$.

DISCUSSION

In general the contents of the elements K, Ca, Ti, V, Cr, Fe and Ni in the

TABLE 5B

Element concentrations in the fraction $< 63 \mu\text{m}$ of the Scheldt sediments. Results are given as mean \pm S.D., ranges between parentheses

	S15	S15b	S18	S18b	S22
K (%)	1.2 \pm 0.3 (0.9–1.6)	1.24 \pm 0.09 (1.2–1.37)	1.4 \pm 0.2 (1.3–1.5)	1.4 \pm 0.4 (1.1–1.9)	1.8 \pm 0.3 (1.5–2.2)
Ca (%)	10 \pm 4 (6.7–16.2)	5.3 \pm 0.7 (4.9–6.4)	4.6 \pm 1.2 (3.3–5.5)	5.8 \pm 2.4 (3.8–8.9)	7 \pm 3 (3.2–10.9)
Ti (%)	0.22 \pm 0.07 (0.12–0.26)	0.36 \pm 0.08 (0.29–0.48)	0.37 \pm 0.11 (0.31–0.50)	0.33 \pm 0.08 (0.23–0.41)	0.20 \pm 0.06 (0.14–0.28)
V ($\mu\text{g/g}$)	150 \pm 70 (110–250)	130 \pm 30 (110–170)	180 \pm 50 (135–238)	130 \pm 50 (68–170)	160 \pm 30 (130–188)
Cr ($\mu\text{g/g}$)	220 \pm 50 (190–288)	200 \pm 30 (170–228)	250 \pm 60 (209–318)	200 \pm 90 (78–269)	250 \pm 40 (210–303)
Mn ($\mu\text{g/g}$)	1050 \pm 440 (740–1700)	930 \pm 180 (820–1200)	1070 \pm 250 (804–1300)	760 \pm 180 (500–914)	1020 \pm 220 (851–1300)
Fe (%)	8 \pm 3 (5.6–12.8)	4.4 \pm 0.8 (3.8–5.6)	5.6 \pm 0.7 (4.8–6.2)	5.2 \pm 1.5 (4.3–7.5)	9 \pm 2 (7.1–10.7)
Ni ($\mu\text{g/g}$)	25 \pm 5 (19–30)	30 \pm 10 (22–45)	40 \pm 10 (30–55)	35 \pm 16 (12–46)	60 \pm 20 (42–82)
Cu ($\mu\text{g/g}$)	37 \pm 27 (14–65)	80 \pm 30 (61–117)	100 \pm 20 (80–126)	70 \pm 40 (9–115)	100 \pm 30 (42–135)
Zn ($\mu\text{g/g}$)	350 \pm 300 (84–705)	530 \pm 170 (393–778)	720 \pm 120 (588–804)	640 \pm 350 (120–846)	2200 \pm 700 (1700–3100)
Rb ($\mu\text{g/g}$)	91 \pm 14 (71–102)	90 \pm 20 (78–112)	113 \pm 17 (95–129)	100 \pm 20 (76–128)	100 \pm 30 (57–127)
Sr ($\mu\text{g/g}$)	830 \pm 400 (472–1400)	340 \pm 70 (280–434)	320 \pm 100 (213–401)	360 \pm 100 (270–450)	480 \pm 190 (248–725)
Pb ($\mu\text{g/g}$)	100 \pm 60 (50–175)	160 \pm 40 (116–198)	207 \pm 50 (156–240)	180 \pm 100 (46–282)	650 \pm 310 (227–964)
n	4	4	3	4	4

fraction $< 63 \mu\text{m}$ of the sediments of the Southern Bight of the North sea are comparable to those found in suspended matter by Nolting and Eisma (1988) during a comparable sampling period. The contents of Cr, Zn and Pb are higher in the sediments and the suspended matter contains more Cu. It must be emphasized, however, that these values are averages and neglect small scale differences. Some authors have pointed out that the metal content in the bottom sediments differs from that in the suspended matter, even after grain size correction, which makes the extrapolation from suspended matter to bottom sediment impossible (Duinker et al., 1974, Duinker and Nolting, 1976). For the last campaign, suspended matter samples were simultaneously collected with the sediment samples. The heavy metal contents in the sediment fraction $< 63 \mu\text{m}$ are of the same order of magnitude compared with those in the suspended matter. However, correlation analysis shows that there is no or only a weak significant correlation between the metal content in the suspended matter and the metal content in the sediment for K, Ca, Ti,

TABLE 6
Element concentrations in the fraction $<63 \mu\text{m}$ of the harbor sediments

	ZB2	ZB3	OOST1	OOST2	NP1	NP2	BL0	BL1	BL2
K (%)	1.52	1.52	1.41	1.41	1.45	1.57	1.26	1.29	1.28
Ca (%)	11.5	11.2	16.2	10.3	13.7	12.6	10.8	11.8	10.9
Ti (%)	0.35	0.34	0.28	0.31	0.30	0.27	0.29	0.29	0.29
V ($\mu\text{g/g}$)	132	122	98	98	104	128	85	91	77
Cr ($\mu\text{g/g}$)	119	119	94	128	97	108	102	97	92
Mn ($\mu\text{g/g}$)	900	840	723	917	608	685	549	838	817
Fe (%)	3.43	3.54	2.91	3.4	3.18	3.29	3.22	2.9	2.95
Ni ($\mu\text{g/g}$)	26	27	18	18	27	27	21	16	15
Cu ($\mu\text{g/g}$)	14	21	13	18	14	17	15	15	12
Zn ($\mu\text{g/g}$)	174	204	181	183	189	145	317	164	168
Rb ($\mu\text{g/g}$)	112	118	82	119	102	120	105	107	102
Sr ($\mu\text{g/g}$)	531	509	622	509	607	540	476	552	511
Pb ($\mu\text{g/g}$)	55	68	55	75	57	56	78	63	73

V, Br, Rb, Sr and Pb ($r < 0.4$). For Cr, Fe and Zn a low correlation ($r \approx 0.6$) was found. This confirms the statement that the metal content in the bottom sediment cannot be derived from that in the suspended matter for the Southern North Sea and the Scheldt estuary, due to the different processes controlling the concentrations of the heavy metals in sediment fractions and in the suspended matter; the average metal content in the fraction $< 63 \mu\text{m}$ of the sediment is comparable to that of the suspended matter (Salomons and Förstner, 1984). This data set shows that the observation of Nolting and Eisma (1988) about the particulate metal concentrations being similar for the suspended matter of the Southern North Sea can be extended to the sediment fraction $< 63 \mu\text{m}$.

Variability per location.

The variability in heavy metal content per station before and after grain size correction is the largest for the middle Scheldt estuary. This is due to the location of heavy industry, waste water discharges and a high turbidity zone where large amounts of suspended matter flocculate. Also the other samples

TABLE 7

Comparison of the clay-silt composition derived by extrapolation to 100% of the fraction $< 63 \mu\text{m}$ and the values measured in the isolated fraction $< 63 \mu\text{m}$ for the North Sea and Harbor sediments

Element	Measured values	Extrapolated values	Correlation coeff. regression lines
K (%)	1.23 ± 0.25	1.24	0.93
Ca (%)	11.5 ± 2.2	10.3	0.76
Ti (%)	0.25 ± 0.06	0.25	0.90
V ($\mu\text{g/g}$)	90 ± 20	86	0.90
Cr ($\mu\text{g/g}$)	100 ± 20	105	0.94
Mn ($\mu\text{g/g}$)	700 ± 300	674	0.93
Fe (%)	3.2 ± 0.6	2.6	0.91
Ni ($\mu\text{g/g}$)	23 ± 4	18	0.85
Cu ($\mu\text{g/g}$)	13 ± 4	12	0.87
Zn ($\mu\text{g/g}$)	190 ± 120	172	0.90
Rb ($\mu\text{g/g}$)	95 ± 3	99	0.93
Sr ($\mu\text{g/g}$)	660 ± 40	492	0.74
Y ($\mu\text{g/g}$)	37 ± 2	33	0.94
Zr ($\mu\text{g/g}$)	280 ± 40	280	0.69
Pb ($\mu\text{g/g}$)	80 ± 60	57	0.87

show a considerable variability as a function of time; for an illustration see Tables 1, 2, 4 and 5 where the ranges are given. The variability of the element content of the bulk samples is mainly due to grain size. The fraction $< 63 \mu\text{m}$ still shows large variations at the same stations. Sampling exactly the same spot during different campaigns is not possible which can explain part of this variation. Another possibility is that for coarse sand samples often very small and probably unrepresentative amounts of the fraction $< 63 \mu\text{m}$ were isolated, with consequent implication on the measured elemental concentrations. Due to the fact that often only very small amounts could be isolated, it was only possible to analyze the fraction $< 63 \mu\text{m}$ by XRF.

Granulometric normalization

Analyzing the fraction $< 63 \mu\text{m}$ normalizes an important part of the grain size variations. However, often a very small and probably unrepresentative amount is isolated and the separation techniques may affect the metal concentration. Since these factors might cause uncontrollable inaccuracies, correlations between the bulk concentrations and the abundance of the fraction $< 63 \mu\text{m}$ have been calculated (Salomons and Förstner, 1984 and references

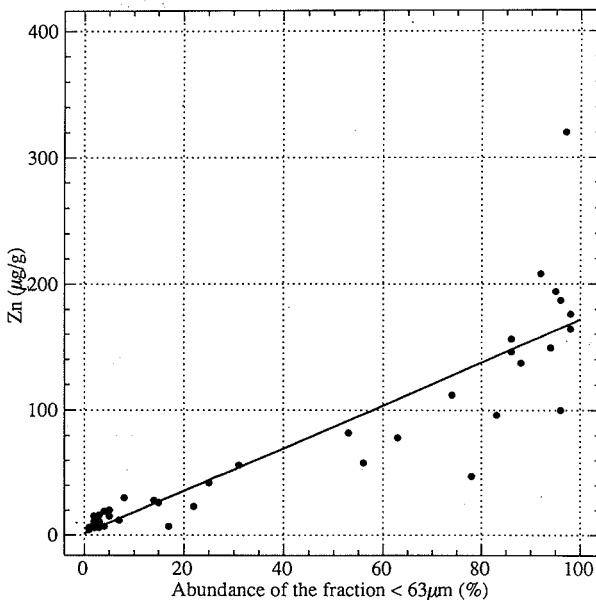


Fig. 2. Relation between the Zn content in the bulk sediments of the North Sea and the harbour samples as a function of the abundance of the fraction $< 63 \mu\text{m}$.

therein). Linear regression was performed on the data set of the North Sea and harbour samples. High correlations were found (See Table 7). An illustration is shown in Fig. 2 which gives the Zn content as a function of the abundance of the fraction $< 63 \mu\text{m}$ for the North Sea and harbour samples. For the river Scheldt no such correlations were found between the heavy metal content and the abundance of the fraction $< 63 \mu\text{m}$. These linear relationships make it possible to characterize the content of a whole group of co-genetic sediments by a single value being obtained by extrapolation to 100% of the fraction $< 63 \mu\text{m}$ (De Groot and Allersma, 1975). In the literature extrapolation to 50% is also often used. The resulting composition has been compared with the value measured in isolated fractions $< 63 \mu\text{m}$ and satisfactory agreement is found (Table 7). For most of the elements the difference between the extrapolated value and the measured one is $< 10\%$, which offers an a posteriori validation that the separation technique used is valid for these sediments. The agreement is poorer for Ca and Sr. The extrapolated values for Ca and Sr are based on poorly correlated regression lines ($r = 0.74-0.76$). Those elements are related with the carbonate fraction, which does not change systematically with grain size. Pb also gives a rather poor agreement. The extrapolated values are obtained from AAS measurements, which are very accurate, while the fraction $< 63 \mu\text{m}$ was measured using XRF and these results are less accurate because there is a peak overlap between the Pb-L lines and the As-K lines. In view of these factors, the agreement between extrapolated and measured values is acceptable.

Normalization to a reference element

The method is based on the assumption that for natural sedimentation conditions, there exists a linear relationship between the conservative element and the heavy metal. If the concentration of the conservative element changes, due to changes in mineralogy, granulometry or other natural phenomena, the concentration of the other metals will change with a constant relation to the conservative element. The choice of conservative element is crucial and Al, Fe, Ce, Sr, Sc and Li have been suggested (Hirst 1962a,b; Bruland et al., 1974; Trefry and Presley, 1976; Rehm et al., 1984; Windom et al., 1986, 1989; Rule, 1986; Loring, 1990; and others). In the work of Araújo et al. (1988) Al has been used as a conservative element. Al was measured using XRF, which has a low accuracy for low-Z elements including Al. Therefore in this work we chose a more accurately determined element: Fe. The origin of Fe may be both natural and anthropogenic, which may cause problems when using Fe as a conservative element. The use of Fe as a conservative element in this case can be justified: e.g. Regnier et al. (1989) found in comparable sediment samples from the most polluted area

TABLE 8

Correlation coefficients between the total metal concentration and the total Fe concentration

Element	All samples (<i>n</i> = 80)	North Sea and harbor samples (<i>n</i> = 42)
Ni	0.64	0.87
Cu	0.63	0.91
Zn	0.83	0.93
Pb	0.83	0.94
Hg	0.57	0.74
Cd	0.57	0.81

of the Scheldt at the harbour of Antwerp, a Fe-Al correlation coefficient of 0.98, which allows the use of Fe and Al equivalently as conservative elements for these sediments. Two different normalizations are discussed below.

One way of normalization uses the regression of the bulk metal concentration versus the bulk Fe concentration and the 95% confidence intervals are calculated (Trefry and Presley, 1976; Rule, 1986). All the points between this interval are considered to have natural metal concentrations while the other ones have anthropogenic influence. The advantage of this method is that no reference material is needed to establish the pollution degree. The major limitation is in the uncertainties about the conservative behaviour of the chosen element. For this data set, considering all samples, the correlation is rather poor and many samples (of the middle estuary) do not fit in the 95% confidence interval. Considering only the North Sea and harbour samples, the correlation is much better and almost all samples are situated in the 95% confidence intervals. By this method two populations could be identified. The North Sea samples, harbour samples and the samples of the lower estuary form one geochemical population. The samples outside the 95% confidence interval belong to a different population; these samples were almost all taken in the middle estuary where high amounts of industrial and domestic waste water are released in the river Scheldt. The correlations for the regression are given in Table 8. Comparing these values with those of Table 7 shows that the correlations with Fe are higher than those with the abundance of the fraction < 63 μm . This proves that normalizing to Fe in this case is superior since not only granulometric variations are normalized but some geological too, which justifies a posteriori the use of Fe as a conservative element.

Another method calculates the enrichment factors (EF) (Zollar et al.,

1974; Sinex and Helz, 1981, Rule 1986), defined for this data analysis for element X by:

$$EF = \frac{\left(\frac{X}{Fe}\right)_{\text{sediment}}}{\left(\frac{X}{Fe}\right)_{\text{earthcrust}}}$$

Reference materials are to be used which is the major limitation of this method. When $EF > 1$ there is an enrichment of that element compared to the average earth crust concentrations. This enrichment can be due to natural phenomena or anthropogenic pollution. In the definition of EF, the earth crust is used as a reference. It may seem more appropriate to compare with mean sediment concentrations. This is done in Table 9 for four different average sediment concentrations. Cu has an EF below 1 in almost all areas except the harbours and the Scheldt and compared to all reference materials. Ni shows only slight enrichment in the North Sea and the harbours when shallow water sediments are used as a reference. These low EF for Ni and Cu have been reported before, although other conservative elements were used (Baeyens et al., 1982; Araújo et al., 1988). Remobilization of these elements was given as the explanation. Mn can be seen as slightly enriched in the North Sea, but not in the Scheldt estuary.

Cr, Zn, Cd, Hg and Pb are highly enriched in the whole analyzed area. The enrichment of Zn, Cd, Hg and Pb is most pronounced in the industrial part of the Scheldt and the harbours due to anthropogenic pollution. Cr, however, has a similar EF all over the area and no pronounced maxima are found either in the industrial part, or the harbours; this might suggest that the Cr enrichment is due to geological properties of the sediment. The average EF may not seem very dramatic ($\langle EF \rangle \approx 2-10$), but when single samples are regarded, EFs of e.g. 130 are found for Cd. These maxima are not persistent in time and occur only in the industrial part of the Scheldt.

Multi-variate analysis

The data set has been subjected to correlation and factor analysis. Correlations between all variables for the bulk samples were poor, when considering the complete data matrix. However, with the aid of simple regression analysis, different populations could be identified and this confirmed the results of the normalization to Fe.

The first population contains all the North Sea samples, the harbour samples and most of the samples of the first five Scheldt stations. In this

TABLE 9

Enrichment factors for metals compared to different reference material

	Shallow water sediment ^a	Mean sediment ^b	Fossile river sediment ^c	River suspended sediment ^d
Cr (shore)	5.3 ± 0.5	2.8 ± 0.3	—	—
Cr (off-shore)	6.2 ± 0.5	3.2 ± 0.3	—	—
Cr (harbors)	4.1 ± 0.1	2.2 ± 0.1	—	—
Cr (S01-S012)	5.2 ± 0.5	2.7 ± 0.3	3.3 ± 0.3	—
Cr (S15-S22)	6.6 ± 0.9	3.5 ± 0.5	4.2 ± 0.6	3.5 ± 0.5
Mn (shore)	2.0 ± 0.3	1.4 ± 0.2	—	—
Mn (off-shore)	2.3 ± 0.3	1.6 ± 0.2	—	—
Mn (harbors)	1.8 ± 0.1	1.2 ± 0.1	—	—
Mn (S01-S12)	1.1 ± 0.1	0.8 ± 0.1	0.49 ± 0.06	—
Mn (S15-S22)	1.4 ± 0.2	1.0 ± 0.1	0.60 ± 0.09	0.8 ± 0.1
Ni (shore)	1.11 ± 0.07	0.47 ± 0.03	—	—
Ni (off-shore)	1.5 ± 0.2	0.65 ± 0.07	—	—
Ni (harbors)	1.36 ± 0.05	0.58 ± 0.02	—	—
Ni (S01-S012)	1.0 ± 0.2	0.42 ± 0.10	0.37 ± 0.09	—
Ni (S15-S22)	1.1 ± 0.3	0.45 ± 0.11	0.40 ± 0.10	0.30 ± 0.07
Cu (shore)	0.36 ± 0.04	0.19 ± 0.02	—	—
Cu (off-shore)	0.27 ± 0.04	0.14 ± 0.02	—	—
Cu (harbors)	1.1 ± 0.4	0.6 ± 0.2	—	—
Cu (S01-S12)	0.28 ± 0.06	0.15 ± 0.03	0.18 ± 0.04	—
Cu (S15-S22)	1.1 ± 0.3	0.6 ± 0.9	0.7 ± 0.2	0.5 ± 0.2
Zn (shore)	2.9 ± 0.3	1.7 ± 0.2	—	—
Zn (off-shore)	1.9 ± 0.1	1.1 ± 0.1	—	—
Zn (harbors)	4.6 ± 0.4	2.8 ± 0.2	—	—
Zn (S01-S12)	2.5 ± 0.5	1.5 ± 0.3	1.0 ± 0.2	—
Zn (S15-S22)	6.9 ± 0.8	4.4 ± 0.5	2.7 ± 0.3	1.3 ± 0.2
Cd (shore)	/ ^e	4.8 ± 0.5	—	—
Cd (off-shore)	/	1.7 ± 0.5	—	—
Cd (harbors)	/	2.8 ± 0.2	—	—
Cd (S01-S12)	/	1.5 ± 0.3	1.0 ± 0.2	—
Cd (S15-S22)	/	4.4 ± 0.5	2.7 ± 0.3	1.3 ± 0.2
Hg (shore)	/	3.2 ± 1.0	—	—
Hg (off-shore)	/	1.3 ± 0.5	—	—
Hg (harbors)	/	3.1 ± 0.4	—	—
Hg (S01-S12)	/	0.6 ± 0.2	0.5 ± 0.2	—
Hg (S15-S22)	/	3.5 ± 1.2	2.6 ± 0.9	6.0 ± 1.4
Pb (shore)	5.0 ± 0.4	3.7 ± 0.3	—	—
Pb (off-shore)	5.3 ± 0.6	3.9 ± 0.4	—	—
Pb (harbors)	6.4 ± 0.4	4.7 ± 0.3	—	—
Pb (S01-S12)	2.7 ± 0.3	2.0 ± 0.2	1.0 ± 0.1	—
Pb (S15-S22)	6.8 ± 0.8	5.0 ± 0.6	2.5 ± 0.3	0.74 ± 0.09

^aWedepohl (1969, 1978).^bBowen (1979) after Wedepohl (1968).^cForstner and Wittman (1981).^dMartin and Maybeck (1979).^e/, no standard available.

population the correlations are very high for almost all the elements. This was expected since similar pollution factors are ruling in this area and the grain size is the most important factor controlling the bulk concentration. This was confirmed by factor analysis: two factors were found. The first one explains 82% of the measured variance, with a high correlation (0.75–0.95) for almost all the elements, except Ca, Sr and Br. The latter three elements were highly correlated with the second factor, explaining 5% of the total variance and related to the carbonate fraction.

The second population, including mostly samples from the industrial part of the Scheldt, gave rather low correlations. Significant (0.8–0.9) correlations were found among the element groups K, Ti, V, Cr and Mn and Ni, Cu, Zn, Pb and Cd. The former group of significant correlation is found in all fractions (sand and clay) and populations (North Sea or Scheldt) and therefore attributed to geological properties of the sediment. However, correlations among the second group are most pronounced in the industrial part and therefore associated with the industrial activities and domestic and urban waste water discharge.

Factor analysis for the industrial zone gives 4 factors. One, highly loaded for the anthropogenic elements Ni, Cu, Zn, Pb and Cd, explains 51% of the total variance. The second factor is highly correlated for As and Hg, the third one for Ti, Zr and Y. The second factor explains 11.5% of the total variance and the third 8.8%. They are probably related to specific industrial activities and soil properties, respectively. A fourth factor is highly correlated with Ca and Sr and represents the carbonate fraction.

For the fraction $< 63 \mu\text{m}$ generally very low correlations are found between the concentrations in the fraction $< 63 \mu\text{m}$. Only for two small groups, relatively high correlations are found: V, Cr and Fe (0.7–0.9) and Cu, Ni and Zn (0.7–0.8). These values were compared with values when only sand samples (defined as minimum 80% $> 63 \mu\text{m}$) are considered. V-Cr correlations were found but the Fe correlations are much lower. This can be explained by the co-precipitation and adsorption capacity of Fe-hydroxides, which is much more important in the smaller fraction. These V-Cr correlations are attributed to geological properties since they occur in all fractions and all populations and the Ni, Cu and Zn correlations are due to industrial activities and/or discharge of domestic waste waters. The correlations are, however, much lower than in the bulk sediment.

Evolution as a function of time

The results from this work have been compared with data obtained by the same analysis method for samples from 1978 to 1984 and with data reported by other authors for the last 15 years (see references in the Introduction).

TABLE 10

Comparison of heavy metal content as a function of time

Element	Period	Coast	S01-S12
Ti (%)	78-84	0.12 ± 0.06	0.15 ± 0.04
	87-88	0.12 ± 0.07	0.09 ± 0.06
V (µg/g)	78-84	50 ± 40	50 ± 20
	87-88	40 ± 20	50 ± 40
Cr (µg/g)	78-84	40 ± 40	50 ± 20
	87-88	40 ± 30	60 ± 40
Mn (µg/g)	78-84	260 ± 220	120 ± 80
	87-88	250 ± 170	220 ± 250
Fe (%)	78-84	1.0 ± 0.6	0.9 ± 0.3
	87-88	0.9 ± 0.6	1.1 ± 0.6
Ni (µg/g)	78-84	11 ± 7	/
	87-88	6 ± 5	8 ± 15
Cu (µg/g)	78-84	9 ± 8	8 ± 5
	87-88	3 ± 3	4 ± 6
Zn (µg/g)	78-84	60 ± 60	50 ± 30
	87-88	40 ± 40	60 ± 50
Pb (µg/g)	78-84	20 ± 20	14 ± 9
	87-88	15 ± 14	12 ± 8
Clay (%)	78-84	32 ± 33	35 ± 36
	87-88	35 ± 34	14 ± 23
n	78-84	39	20
	87-88	20	19

Comparison is not straightforward due to two important factors: (i) the exact location is very important, especially in the Scheldt; (ii) the data reporting differs seriously among the authors: mean, P_{50} , P_{95} , ranges, bulk, fraction $< 63 \mu\text{m}$, calculated values to $50\% < 20 \mu\text{m}$, etc. are all used. Since these limitations result in an unsystematical and hardly comparable overview, the comparison is based on the results of Araújo et al. (1988) since in this work the same analysis method has been used (see Table 10). Very similar element contents are found for most of the elements in the bulk sediments for the two sampling periods. To compare pollution levels it is, however, better to compare the slopes of the regression curves calculated in the section on Granulometric normalization. In Figs. 3a and 3b regression lines for Fe and Pb are illustrated. Fe shows a significant difference in slope for the two periods, but for Pb no significant difference in slope was detected nor for the elements Cr, Mn, Zn, Cu and Ni. These results lead to the conclusion that for the investigated area, few changes have occurred in the average heavy

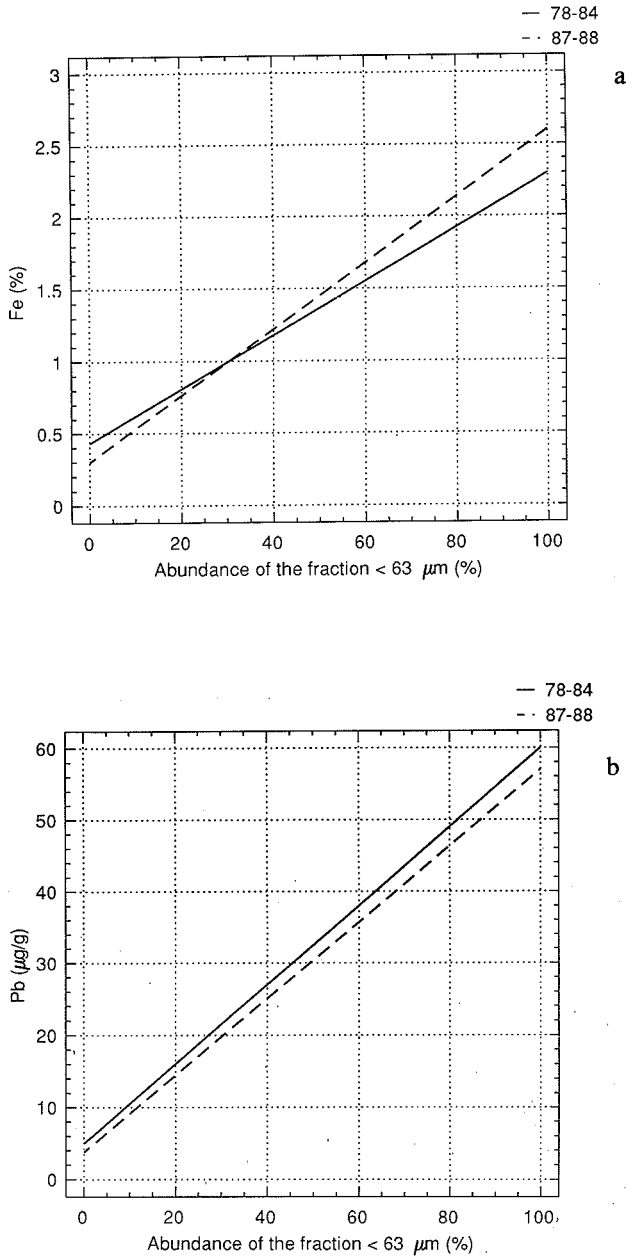


Fig. 3. (a) Comparison of Fe content of the sediments using regression curves for the periods 1978-1984 and 1987-1988. (b) Comparison of Pb content of the sediments using regression curves for the periods 1978-1984 and 1987-1988.

TABLE 11A

Element concentrations in the suspended matter samples of the North Sea

	115	120	130	BOOST	140	702	545	630
K (%)	0.77	0.63	0.77	0.94	1.28	1.37	0.33	0.24
Ca (%)	8.96	7.22	8.37	9.93	10.8	9.92	2.4	2.46
Ti (%)	0.19	0.18	0.23	0.25	0.28	0.29	0.14	0.07
V ($\mu\text{g/g}$)	54	88	65	87	107	124	118	57
Cr ($\mu\text{g/g}$)	115	124	96	91	80	79	144	89
Mn ($\mu\text{g/g}$)	355	400	578	661	717	918	671	353
Fe (%)	2.03	1.81	2.07	2.14	2.46	2.84	1.32	0.74
Ni ($\mu\text{g/g}$)	18	41	31	8.4	9.5	12	21	24
Cu ($\mu\text{g/g}$)	334	224	99	132	48	21	217	262
Zn ($\mu\text{g/g}$)	218	289	578	171	184	219	276	323
Sr ($\mu\text{g/g}$)	461	356	399	528	522	455	276	783
Pb ($\mu\text{g/g}$)	215	275	1116	123	128	157	285	143

TABLE 11B

Element concentrations in the suspended matter samples of the Scheldt estuary

	S01	S04	S07	S09	S12	S15	S15b	S18	S18b	S22
K (%)	1.27	1.23	0.77	0.94	1.28	1.22	1.09	1.16	1.14	1.00
Ca (%)	9.5	7.8	8.8	7.2	6.4	5.5	4.5	4.5	4.3	3.0
Ti (%)	0.29	0.29	0.34	0.30	0.33	0.30	0.30	0.31	0.30	0.30
V ($\mu\text{g/g}$)	159	159	190	165	198	187	176	174	174	185
Cr ($\mu\text{g/g}$)	97	114	128	124	190	168	189	210	227	241
Mn ($\mu\text{g/g}$)	970	1400	2000	2600	2400	2000	1000	1100	1300	1300
Fe (%)	3.2	3.3	4.3	4.1	5.5	4.9	4.7	5.3	5.3	5.0
Ni ($\mu\text{g/g}$)	30	31	44	41	46	42	45	50	48	51
Cu ($\mu\text{g/g}$)	24	36	54	47	94	89	110	140	148	166
Zn ($\mu\text{g/g}$)	179	239	305	299	487	447	570	685	750	882
Sr ($\mu\text{g/g}$)	455	415	457	397	393	358	320	319	305	233
Pb ($\mu\text{g/g}$)	100	130	84	140	166	172	163	204	235	264

metal contaminations in the sediments of Belgian North Sea. However, extreme variability in several sampling sites, over a short sampling period, especially for the Scheldt estuary, shows the existence of local and temporal maxima. Some of these maxima can be explained by granulometric properties, others cannot. In the latter case an excess of pollution is found and it can be attributed to industrial activities and/or domestic and urban waste waters discharge.

Suspended matter

The results of the analysis of the suspended matter are given in Table 11. The largest difference with the contents in the sediments is found for Cu; the Cu content of the suspended matter is much higher than those in the sediments. The suspended matter samples taken in the Scheldt show a pronounced profile throughout the estuary, which in this case correspond to a tendency as a function of salinity (S) and dissolved oxygen (DO). Ti and K have constant concentrations over the whole estuary (Ti: $0.30\% \pm 0.01\%$ and K: $1.3\% \pm 0.1\%$). The elemental concentrations of Cr, Fe, Ni, Cu, Zn

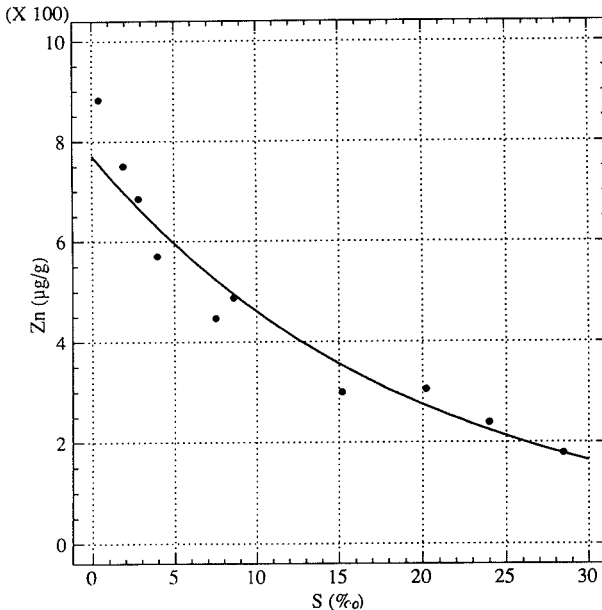


Fig. 4. Relation between Zn content in the suspended matter and salinity in the river Scheldt.

and Pb increase systematically upstream, or increase with decreasing salinity and DO of the water (e.g. see Zn Fig. 4). Most of these elements are related to the industrial activities. Ca, Br and Sr concentrations decrease with decreasing salinity and DO since the influence of the seawater decreases. The Mn profile is a function of DO and its behaviour can be explained by taking into account the reduction and oxidation behaviour of Mn. In anoxic conditions or for low redox potentials, Mn occurs as Mn(II) which is soluble in water, but at higher redox conditions Mn is precipitated as Mn(IV)-oxides. These observations are well in agreement with earlier ones (Duinker et al., 1979, 1982; Wollast et al., 1979). It can be seen that, from station S15b on, anoxic or almost anoxic conditions were present, which could explain the decrease of the Mn concentration in the suspended matter by a factor of 2.

CONCLUSIONS

Several normalization methods showed that the sediments of the Belgian North Sea and the Scheldt estuary are polluted with the heavy metals Zn, Cd, Pb and Hg, with average enrichment factors between 2 and 10. This pollution becomes extreme in the industrial part of the Scheldt where EFs for a single sample can reach 130 for Cd. These maxima occur for each of these four elements. Cu and Ni do not show such an enrichment in most of the sediments of the area.

The pollution level of the North Sea and harbour sediments seems to be controlled by the same factors; these sediments form a population for which grain size is the more important factor controlling the heavy metal content. This was proven by the obtained regression lines, correlation analysis and the analysis of the fraction $< 63 \mu\text{m}$.

For a second population, the industrial part of the Scheldt, grain size becomes a minor factor and the pollution is very variable with time and location. Industry and discharge of urban and domestic waste water are the most likely cause for this.

The newly obtained data have been compared with older data to establish the trends with time. Comparison of the slopes of the regression curves suggests that little changes in the metal contamination have occurred during the last 15 years.

ACKNOWLEDGEMENTS

This work was partially supported by the Belgian Ministries of Science Policy (project 84-89/69) and of Public Health and Environment, Management Unit of the North Sea and the Scheldt Estuary Mathematical Model (under contract BH/87/25).

REFERENCES

- Agemian, H. and A. Chau, 1976. An improved digestion method for the extraction of mercury for environmental samples. *Analyst*, 101: 91-95.
- Araújo, F., P. Bernard, P. and R. Van Grieken, 1988. Heavy metal contamination in sediments from the Belgian coastal North Sea and the Scheldt Estuary. *Mar. Poll. Bull.*, 19: 269-273.
- Araújo, F., P. Van Espen and R. Van Grieken, 1990. Determination of sample thickness via scattered radiation in X-ray fluorescence spectrometry with filtered continuum excitation. *X-Ray Spectr.*, 29-33.
- Baeyens, W., G. Decandt and I. Elskens, 1979. A study of the distribution of mercury in the various compartments of the North Sea and the Scheldt estuary ecosystem. *Oceanol. Acta*, 2: 4, 447-457.
- Baeyens, W., S. Wartel, F. Dehairs, G. Decadt, M. Bogaert, G. Gillain and H. Dedeurwaarder, 1982. The river Scheldt as a transport route for heavy metals in the sea. In: I. Elskens and A. Disteché (Eds.), *Geconcerteerde Onderzoeksakties. Progr. Pol. Sci., Bruxelles*, Vol. 2, part 4, pp. 87-108.
- Baeyens, W., G. Gillian, G. Decandt, and I. Elskens, 1987. Trace metals in the eastern part of North Sea. I: Analyses and short-term distributions. *Oceanol. Acta*, 10: 2, 169-179.
- Baeyens, W., G. Gillian, F. Runday and F. Dehairs, 1987. Trace metals in the eastern part of North Sea. II: Flows of Cd, Cu, Hg, Pb and Zn through the coastal area. *Oceanol. Acta*, 10: 3, 301-309
- Buekens, A.G. and A. Dhaese, 1980. Technische problemen bij het bergen van baggerslib onder meer in verband met de toxiciteit. *Breewa*, 4: 7-18.
- Bowen, H., 1979. *Environmental Chemistry of the Elements*. Academic Press, London.
- Bruland, K., K. Bertine, M. Koide and E. Goldberg, 1974. History of metal pollution in southern California coastal zone. *Environ. Sci. Technol.*, 8: 425-432.
- De Groot, A.J. and E. Allersma, 1975. Field observations on the transport of heavy metals in sediments. In: P.A. Krenkel (Ed.), *Heavy Metals in the Aquatic Environment*. Pergamon Press, Oxford, pp. 85-101.
- D'Hondt, P. and M. Baeteman, 1987. *Evaluatie van de toestand van de Noordzee*. Ministerie van Volksgezondheid en Leefmilieu, Beheerseenheid Mathematisch Model van de Noordzee, Brussel.
- Duinker, J.C., G.T.M. Van Eck and R.F. Nolting, 1974. On the behaviour of copper, zinc, iron and manganese and evidence for mobilization processes in the Dutch Wadden Sea. *Neth. J. Sea Res.*, 8: 214-239.
- Duinker, J.C. and R.F. Nolting, 1976. Distribution model for particulate trace metals in the Rhine estuary, Southern Bight and the Dutch Wadden Sea. *Neth. J. Sea Res.*, 10: 1, 71-102.
- Duiker, J.C. and R.F. Nolting, 1977. Dissolved and particulate trace metals in the Rhine estuary and the Southern Bight. *Mar. Poll. Bull.*, 8: 3, 65-71.
- Duinker, J.C. and R.F. Nolting, 1978. Mixing, removal and mobilization of trace metals in the Rhine estuary. *Neth. J. Sea Res.*, 12: 2, 205-223.
- Duinker, J.C., R. Wollast and G. Billen, 1979. Behaviour of manganese in the Rhine and Scheldt estuaries. II Geochemical cycling, *Est. Coast. Mar. Sci.*, 9: 727-738.
- Duinker, J.C., R.F. Nolting and D. Michel, 1982. Effects of salinity, pH and redox conditions on the behaviour of the Cd, Zn, Ni and Mn in the Scheldt estuary. *Thal. Jugoslav.*, 18: 191-202.
- Förstner, U. and G. Wittmann, 1981. *Metal Pollution in the Aquatic Environment*. Springer-Verlag, Berlin.

- Hirst, D.M. 1962a. The geochemistry of modern sediments from the Gulf of Paria: 1. The relationship between the mineralogy and distribution of major elements. *Geochim. Cosmochim. Acta*, 26: 309–334.
- Hirst, D.M. 1962b. The geochemistry of modern sediments from the Gulf of Paria: 2. The location and distribution of trace elements. *Geochim. Cosmochim. Acta*, 26: 1147–1187.
- Loring, D.H., 1990. Lithium — a new approach for the granulometric normalization of trace metal data. *Mar. Chem.*, 29, in press.
- Martin, J. and M. Meybeck, 1979. Elemental mass balance of materials carried by major world rivers. *Mar. Chem.*, 7: 173–206.
- Nolting, R.F., 1986. Copper, zinc, cadmium, nickel, iron and manganese in the Southern Bight of the North Sea. *Mar. Poll. Bull.*, 17: 3, 113–117.
- Nolting, R.F. and D. Eisma, 1988. Elementary composition of suspended particulate matter in the North Sea. *Neth. J. Sea Res.*, 22: 3, 219–236.
- Regnier, P., R. Wollast and M. Hoening, 1989. The potential use of sediments and suspended matter as a monitoring tool for pollution in estuaries and coastal regions, 1989. In: G. Pichot (Ed.), *Progress in Belgian Oceanographic Research 1989*. Ministry of Public Health and Environment, Brussels, pp. 341–350.
- Rehm, E., M. Schulz-Baldes and B. Rhem, 1984. Geochemical factors controlling the distribution of Fe, Mn, Pb, Cd, Cu and Cr in the Wadden areas of the Weser estuary (German Bight). *Veroff. Inst. Meeresforsch.*, 2: 75–102.
- Rule, J., 1986. Assessment of trace element geochemistry of Hampton Roads Harbor and Lower Chesapeake Bay Area Sediments. *Envir. Geol. Water Sci.*, 8: 204–219.
- Salomons, W. and W. Eysink, 1981. Pathways for mud and particulate trace metals from rivers to the southern North Sea. *Spec. Pub. Int. Ass. Sediment.*, 5: 429–450
- Salomons, W. and U. Förstner, 1984. *Metals in the Hydrocycle*. Springer-Verlag, Berlin, pp. 1–349.
- Sinex, S. and G. Helz, 1981. Regional geochemistry of trace elements in Chesapeake Bay sediments. *Environ. Geol.*, 3: 315–323.
- Temmerman, I., 1988. De kwaliteit van het Schelde sediment. *Water*, 43: 200–204.
- Trefry, J. and B. Presley, 1976. Heavy metal transport from the Mississippi river to the Gulf of Mexico. In: H.L. Wisdom and R.A. Duce (Eds.), *Marine Pollution Transfer*. Health and Co., Lexington, MA, pp. 39–76.
- Valenta, P., E.K. Duursma, A.G.A. Merks, H. Rützel and H.W. Nurenberg, 1986. Distributions of Cd, Pb and Cu between the dissolved and particulate phase in the Eastern Scheldt and Western Scheldt estuary. *Sci. Tot. Environ.*, 53: 41–76.
- Van Alsenoy, V., A. Van Put, P. Bernard and R. Van Grieken, 1988. Chemical characterization of suspensions and sediments in the North Sea and Scheldt estuary. In: G. Pichot (Ed.), *Proceedings of the North Sea Symposium*, 14 Feb. 1989. Ministry of Public Health and Environment, Brussels, pp. 351–368.
- Van Espen, P., L. Van 't dack, F. Adams and R. Van Grieken, 1979. Effective sample weight from scattered peaks in energy dispersive X-ray fluorescence. *Anal. Chem.*, 51: 961–967.
- Van Espen, P., K. Janssens and J. Nobels, 1986. AXIL-PC, software for the analysis of complex X-ray spectra. *Chemometr. Intell. Lab. Syst.*, 1: 109–114.
- Wedepohl, K., 1968. In: L. Ahrens (Ed.), *Origin and Distribution of the Elements*. Pergamon, Oxford.
- Wedepohl, K., 1969: 1978. *Handbook of Geochemistry*. Springer, Berlin.
- Windom, H., 1986. Geochemical and statistical bases for assessing metal pollution in estuarine sediments. Florida Dept. of Environ. Regulation (DER), pp. 1–225.
- Windom, H., S. Schropp, F. Calder, J. Ryan, R. Smith, Jr., L. Burney, F. Lewis and C.

- Rawlinson, 1989. Natural trace metal concentrations in estuarine and coastal marine sediments of the southeastern U.S. *Environ. Sci. Technol.*, 23: 3, 314–320.
- Wollast, R., 1976. Propriétés physico-chimiques des sédiments et des suspensions de la mer du Nord. In: J.G.J Nihoul and F. Gullentops (Eds.), *Project Mer, Prog. Nat. Rech. Dev. Brussels*, Vol. 4, pp. 139–159.
- Wollast, R., G. Billen and J.C. Duinker, 1979. Behaviour of manganese in the Rhine and Scheldt estuaries. I Physico-chemical aspects. *Est. Coast. Mar. Sci.*, 9, 161–169.
- Wollast, R., G. Devos and M. Hoening, 1985. Distribution of heavy metals in the sediments of the Scheldt estuary. In: R. Van Grieken and R. Wollast (Eds.), *Progress in Belgian Oceanographic Research*. University of Antwerp, Antwerp, pp. 147–159.
- Zollar, W., E. Gladney, G. Gordon and J.H. Bors, 1974. Emissions of trace elements from coal fired power plants. In: D. Hemphill (Ed.), *Trace Substances in Environmental Health*. University of Missouri-Columbia, MO, 8, pp. 167–172.