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OSLO AND PARIS CONVENTIONS FOR THE PREVENTION OF MARINE POLLUTION
WORKING GROUP ON CONCENTRATIONS, TRENDS AND EFFECTS OF SUBSTANCES IN
THE MARINE ENVIRONMENT (SIME)

BONN: 17-21 NOVEMBER 1997

**Evolution of the Concentrations of Trace Metals in
Sediments from the Belgian Continental Shelf (1979-1995)**

Submitted by Belgium



Vlaams Instituut voor de Zee
Flanders Marine Institute

OSPAR CONVENTION FOR THE PROTECTION OF THE MARINE ENVIRONMENT OF THE
NORTH-EAST ATLANTIC

ENVIRONMENTAL ASSESSMENT AND MONITORING COMMITTEE (ASMO)

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Trace Metals and Organochlorines in Sediments from the Western Scheldt

Submitted by Belgium

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EVOLUTION OF THE CONCENTRATIONS OF TRACE METALS IN SEDIMENTS FROM THE BELGIAN CONTINENTAL SHELF (1979-1995)

M. Guns, P. Van Hoeyweghen, H. Baeten, M. Hoenig (Veterinary and Agrochemical Research, Tervuren)
W. Vyncke, H. Hillewaert (CLO Gent, Fisheries Research Station, Oostende)*

Abstract

Results of investigations on thirteen stations on the Belgian Continental Shelf in the period 1979-1995 are discussed. Four of these areas are dumping sites for dredge spoils. Mercury, lead, copper, zinc, chromium, nickel and aluminium were assessed. For the years 1979-1989 nine samples kept in the laboratory as reference material were used (< 2000 μm fraction). From 1990 on, analyses were carried out in the framework of the monitoring programme of the Oslo and Paris Conventions for the protection of the sea and were performed both on the whole sediment (< 2000 μm) and on the fine-grained fraction (< 63 μm).

In most stations, concentrations of trace metals showed a downward trend, indicating lower inputs of contaminants in the marine environment. This strongly suggests that measures to reduce inputs are fruitful, especially when they are taken at an international level (Paris Convention, European Union).

Study of the spatial distribution of metals showed the concentrations to diminish with the distance to the coast.

Comparisons with background concentrations from the pre industrial period allowed to calculate enrichment factors. These were high for mercury, lead and zinc.

Applying ecotoxicological assessment criteria, NOEC (No observed effect concentration) were not exceeded. Nevertheless, on five stations including three dumping areas, contents were higher than the proposed lower toxicity limit (application of a safety coefficient of 10) and should receive special attention.

* Report Nr 242 (1997) of the Fisheries Research Station, Oostende (translation from the Dutch).

1. INTRODUCTION

Sediments can adsorb important quantities of contaminants among which trace metals. This is especially the case in the fine-grained fraction ($< 63 \mu\text{m}$) (Salomons *et al.*, 1988). Sediments act as a sink for these compounds (Skei, 1992). These contaminants, or at least the bioavailable part of it, can be taken up and accumulated by marine organisms. Though metal uptake in biota does not occur directly from the sediment, it has been shown that due to physico-chemical processes in the sediment metals may become available in solution for uptake (Everaarts and Boere, 1989 ; Phelps and Warner, 1990 ; Samant *et al.*, 1990). Depending on the concentrations they can be toxic both for biota and man. Hence, monitoring heavy metals and other pollutants in sediments is important.

In the present report results are given of analyses carried out on 13 sampling stations on the Belgian Continental Shelf in the period 1979-1995. Mercury, lead, copper, zinc, chromium, nickel and aluminium were determined. The samples from the years 1979-1989 were so-called « historical » sediments which were kept in the laboratory als reference material. Their origin is mentioned in table 1.

From 1990 on analyses were carried out on an yearly basis in the framework of the joint monitoring programme of the Oslo and Paris Conventions. Both the whole sediment ($< 2000 \mu\text{m}$) and the silt fraction ($< 63 \mu\text{m}$) were used. From that year on, four sampling points were added *i.e.* Dumping site Ostend, Westhinder, Oostendebank and Steendiep (table 2).

2. METHODS AND MATERIALS

2.1. Sampling stations and technique

The thirteen stations are shown in figure 1. Four stations situated in the outer estuary of the river Scheldt are disposal sites for dredge spoils from the harbours of Ostend and Zeebrugge and from the approach routes to these harbours and to Flushing. Station « Oost Dyck » is located in a sand extraction area.

On each monitoring area three samples were taken in a radius of about 100 m with a Van Veen grab sampler. They were bulked and kept at $- 28^{\circ}\text{C}$ until further analysis. After defrosting, the sediment was dried at 105°C to determine the dry matter content. The fraction smaller than $2000 \mu\text{m}$ (« total sediment») was separated by sieving. From 1990 on, the fine-grained fraction ($< 63 \mu\text{m}$) was also analysed. For this purpose, the sediment was resuspended in water, separated by wet sieving and dried.

In this study, emphasis was put on trend analyses, although spatial differences may also provide useful information on the state of pollution of the sediments.

2.2. Chemical analysis

Analyses were performed on the $< 2000 \mu\text{m}$ fraction (1979-1995) and on the $< 63 \mu\text{m}$ fraction (1990-1995) respectively.

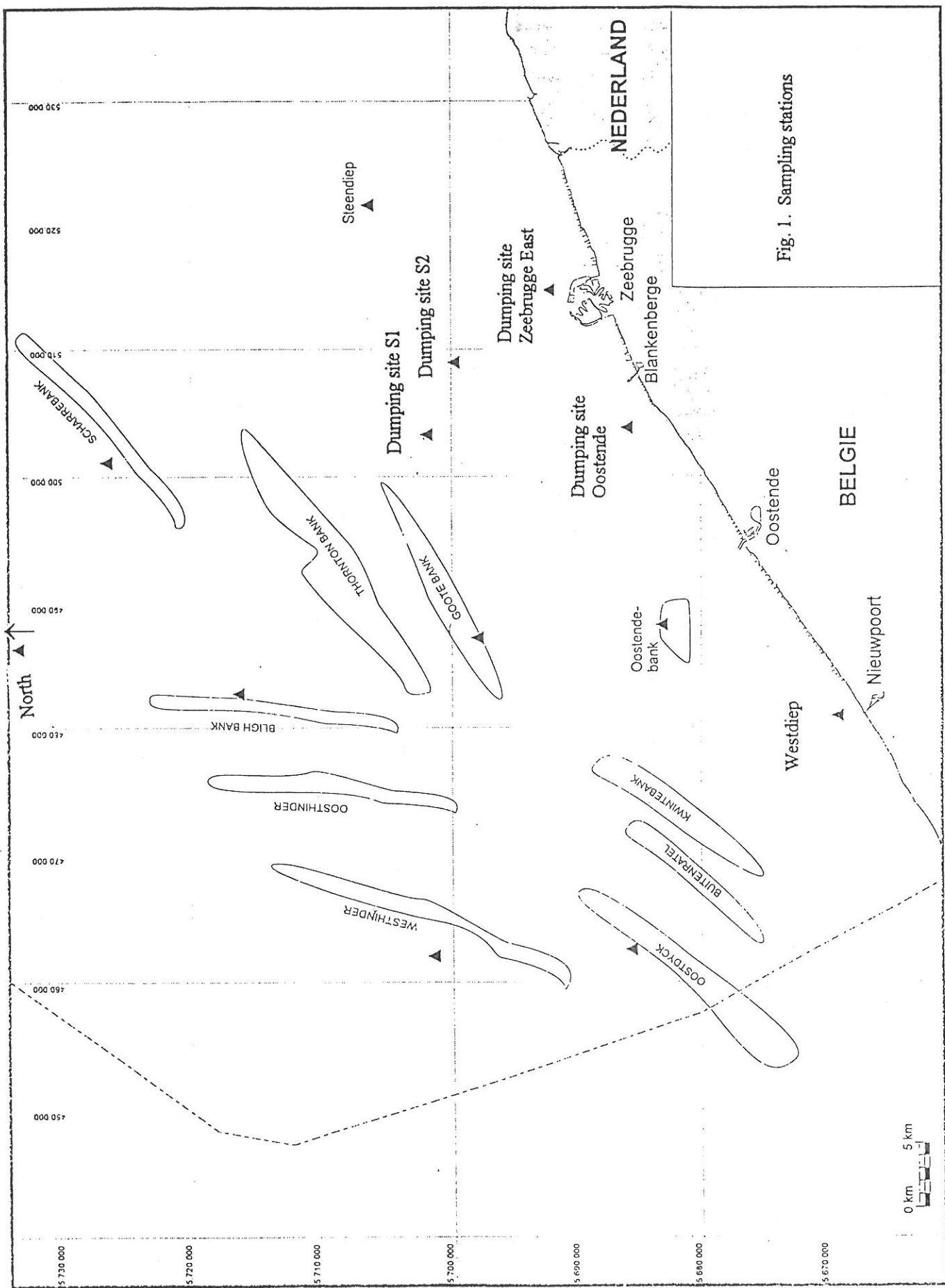


Fig. 1. Sampling stations

Table 1. Concentrations of trace metals in the < 2 mm fraction (mg/kg dry weight) 1979-1995 (a)

MERCURY	ZE	S1	S2	WD	OD	GB	BB	SB	NO
1979	0,28	0,12		0,05		0,03	0,01		
1980	0,47		0,22	0,07	0,02	0,01	0,01		
1981	0,71	0,39	0,03	0,07	0,04	0,01	<0,01		
1982	0,48	0,17	0,03		0,02	0,01	0,02		
1983	0,55	0,23	0,02	0,02	0,02	<0,01	<0,01		
1984	0,66	0,35	0,23	0,05	0,02	0,01	<0,01		
1985	0,50	0,18	0,04	0,01	0,03	0,05	<0,01	0,01	0,02
1986	0,35	0,25	0,03	0,04	0,03	0,02	<0,01	0,01	0,01
1987	0,16	0,08	0,01	0,05	0,03	0,01	<0,01	<0,01	<0,01
1988	0,17	0,07	0,01	0,02	0,04	0,01	0,01	<0,01	<0,01
1989	0,11	0,10	0,16	0,05	0,05	0,01	<0,01	<0,01	0,02
1990	0,25		0,02	0,03		0,01	0,01	0,01	0,01
1991	0,17		0,03	0,03	0,06	0,01	0,01	0,01	0,01
1992	0,17		0,02	0,01	0,02	0,01	0,01	0,01	0,03
1993	0,28	0,06	0,07	0,06	0,02	0,02	<0,01	0,01	0,02
1994	0,11	0,04	0,01	0,03	0,02	<0,01	<0,01	<0,01	<0,01
1995	0,03	0,14	<0,01	0,03	0,02	<0,01	<0,01	<0,01	<0,01
LEAD	ZE	S1	S2	WD	OD	GB	BB	SB	NO
1979	24,5	16,6		7,4	12,6	4,2	5,6		
1980	33,7			17,5	4,1	6,6	4,8		
1981	58,5	46,2	12,9	15,0	4,4	3,9	8,3		
1982	41,2	18,6	15,0		6,1	10,3	4,3		
1983	36,2	27,0	12,8	12,6	6,2	11,1	11,3		
1984	52,3	34,7	12,1	9,9	5,3		7,1		
1985	44,2	23,5	4,5	4,7	3,1	7,2	3,3		3,2
1986		25,8	4,7	8,8		9,8			7,6
1987	26,3	17,3		10,2	10,2		2,9	5,6	3,9
1988	26,4	7,7	4,3	3,0	3,0	6,4	6,8		3,2
1989	18,0	15,5	9,5	11,8	3,8	3,1		2,1	1,9
1990	44,0		8,2	10,0	6,3	6,6	4,4	4,7	4,6
1991	42,0		5,3	13,1	4,5	11,2	2,2	4,2	5,9
1992	35,0		8,2	10,8	6,5	8,6	6,6	5,2	8,2
1993	25,0	6,1	1,9	12,6	1,5	1	1,8	1,3	1,0
1994	18,0	3,3	2,3	5,4	2,3	1,6	3,4	1,3	1,6
1995	13,0	23,0	3,5	5,4	8,3	2,5	2,0		3,2
COPPER	ZE	S1	S2	WD	OD	GB	BB	SB	NO
1979		4,3		3,1	6,0	3,0	3,3		
1980	11,5	2,9	3,3		3,7	4,5	2,6		
1981	16,5		2,4	4,5	4,3	1,0	3,7		
1982	13,3	5,7	2,0		4,7	1,9	1,3		
1983	13,2	10,8	1,4	1,7	4,4	3,4	<1		
1984	15,9	11,2	1,9	2,8	5,3	4,3	1,2		
1985	13,7	7,6	2,5	1,6	3,3		1,4	1,0	2,2
1986			4,6	4,1	6,1	4,6	2,4	3,6	4,2
1987	9,7	4,0		4,3	2,3	5,8	<1	1,8	1,0
1988	9,0		1,3	2,2	<1	<1	<1	<1	3,2
1989	8,1	5,2	2,5	1,0	2,5	1,8	1,3	1,3	2,7
1990	13,4		2,0	1,8	3,2	2,1	2,3	1,5	1,6
1991	11,2		0,8	3,3	1,6	1,8	0,6	0,5	0,9
1992	12,0		3,2	4,3	2,0	3,2			3,4
1993		1,9	0,5	4,4	0,6	0,6	0,3	0,3	0,3
1994	3,8	1,1	0,7	3,3	0,7	0,7	1,1	0,3	0,5
1995	4,4	7,4	1,1	3,2	2,4	1,5	1,0	0,1	1,4

Table 1. (continued)

ZINC										
	ZE	S1	S2	WD	OD	GB	BB	SB	NO	
1979	60,6	30,0		17,8		12,1	9,3			
1980	102,0	8,2	22,7	24,7	7,2	11,5	9,4			
1981	135,0	16,4	26,3	25,7	11,5	6,6	21,5			
1982	108,0	47,0	22,9		8,8	11,4	9,3			
1983	112,0	63,3	21,6	15,7	8,2	8,2	6,0			
1984	133,0	86,2	19,7	23,9	8,6	8,4	7,0			
1985	114,0	50,8	18,4	16,2	7,9	15,8	5,0	4,5	5,8	
1986		66,3	20,4	20,7	8,6	12,9	12,6	6,5	9,3	
1987	64,9	38,0	15,1	27,3	8,2	11,3	4,8	5,9	6,0	
1988	67,3	24,9		15,1	8,5	7,8	5,2	8,5	8,3	
1989	54,8	33,4	15,3	25,3	7,4	11,8	5,4	7,4	13,7	
1990	131,0		15,0	20,0	18,0	22,0	19,0	11,0	9,0	
1991	106,0		12,6	23,0	11,0	27,0	9,0	8,0	12,0	
1992	118,0		32,4							
1993	163,0	36,0	19,4		9,5	21,0	11,0	16,0	15,0	
1994	70,0	14,4	13,7	32,0	9,0	8,0	13,0	7,0	6,0	
1995	34,0	57,1	10,8	20,0	7,9	7,6	4,5	4,7	6,8	
CHROMIUM										
	ZE	S1	S2	WD	OD	GB	BB	SB	NO	
1979		15,5		25,7	6,6	4,3	5,6			
1980	39,3	15,9	11,4	13,4	1,3	2,5	4,0			
1981	104,0	54,7	18,4	18,3	9,8	6,9				
1982	42,4	29,6	10,2		8,9	9,3	8,1			
1983	42,6	37,8	11,6	9,5	6,9	2,4	1,4			
1984	50,3	45,0	12,1	13,1	7,4	7,8	7,0			
1985	47,4	27,0	10,7	13,9	6,9	7,6	7,3	6,6	4,6	
1986		34,3	11,5	12,6	16,0	9,9	4,4	5,8	9,9	
1987	39,4	20,0	4,9		4,7	5,9	5,4	11,5	5,2	
1988	37,1	6,8	7,5	9,5	3,7	5,5	12,3	6,4		
1989	39,4	10,0	4	9,9	0,9	4,3	1,2	7,7	4,6	
1990										
1991	62,0			22,0	9,7		4,6	4,5	9,8	
1992	68,6		12,4	16,1	7,2	8,0	5,5	6,1	6,8	
1993	36,2	6,1	6,1	22,0	4,6	4,8	5,5	5,5	4,3	
1994	21,4	6,4	5,6	17,0	15,0	3,7	4,5	2,7	6,6	
1995	28,0		7,2	13,0	8,3	4,9	5,3	4,1	5,6	
NICKEL										
	ZE	S1	S2	WD	OD	GB	BB	SB	NO	
1979	8,0	4,3		8,4	3,0	1,8	2,0			
1980	9,8	3,4	3,1	3,9	2,5	2,5	3,0			
1981				16,8	3,1	3,1				
1982		30,8								
1983	28,0	27,9		15,4	14,0					
1984	12,9	13,6	4,8		2,5	2,4	<1			
1985	13,4	8,6	7,8	3,0	2,1	3,3	<1	1,8	<1	
1986		10,2	3,1	5,4	3,9	1,0	<1	2,6	5,2	
1987	10,0	5,5	<1	5,2	2,5	2,5	<1	2,7	1,6	
1988	10,7	3,8	1,3	2,1	3,1	3,3	1,9	2,9	2,5	
1989	12,6	7,0	2,9	2,0	1,6	3,0	1,9	1,0	6,2	
1990										
1991	20,0		2,5	6,9	3,3		1,7	2,1	4,2	
1992	13,0		1,9	4,8	1,8	3,0	6,3	2,0	2,6	
1993	11,0	5,8	3,1	9,9	2,0	2,6	2,7	3,1	2,6	
1994	11,7	2,8	3,8	8,4	4,5	2,0	2,8	2,9	6,3	
1995	7,3	7,2	0,8	4,3	1,6	1,2	1,0	1,0	1,9	

Table 1. (continued)

ALUMINIUM (%)	ZE	S1	S2	WD	OD	GB	BB	SB	NO
1979	1,83			1,27	0,83	0,74	0,88		
1980	2,09		1,09	1,20	0,91	0,54	0,93		
1981	2,74	3,07	1,35	1,32	1,06	0,71	0,86		
1982	2,34	2,00	1,28		0,98	0,73	1,02		
1983	2,40	2,33	1,21	0,93	0,95	0,56	0,56		
1984	2,89	2,71	1,14	1,31	0,88	0,67	1,09		
1985	2,96	2,10	1,16	1,31	0,78	0,95	0,75	0,72	0,74
1986		2,42	1,20	1,46	0,91	1,11	0,77	0,99	1,21
1987	2,65	1,63	0,68	1,43	0,60	0,69	0,67	0,91	0,92
1988	2,53	1,29	0,89	1,12	0,53	0,61	0,79	1,07	0,70
1989	2,72	1,77	1,23	1,22	0,52	0,73	0,57	0,77	1,32
1990			1,50	1,00	0,90	1,10	1,10	1,10	1,60
1991			0,62	0,78	0,49	0,71	0,37	0,48	0,73
1992					0,73	1,10	1,20	1,30	1,60
1993	1,70	1,50	0,44	1,10	0,44	0,31	0,53	0,64	0,38
1994	2,50	0,56	0,42	1,30	0,61	0,44	0,61	0,62	0,47
1995	2,00	2,00	0,77	1,07	0,61	0,45	0,64	0,75	0,88

(a)

ZE : Dumping site Zeebrugge East

S1 : Dumping site Zeebrugge S1

S2 : Dumping site Zeebrugge S2

WD : Westdiep

OD : Oost Dyck

GB : Gootebank

BB : Bligh bank

SB : Scharrebank

NO : North

2.2.1. Mercury

Ca. 1 g of dried and homogenised sediment is weighed in an 250 ml erlenmeyer flask. Nitric acid 65 % (4 ml), hydrochloric acid 37 % (3 ml) and hydrogen peroxide 30 % (2.5 ml) are added. After refluxing for 15 min, the solution is cooled, filtered and diluted to 100 ml with distilled water. Mercury is measured after reduction with tin (II) chloride in a flameless atomic absorption spectrometer.

2.2.2. Other trace metals

Ca. 0.5 g of sediment is weighed in a PTFE tube and 4 ml of perchloric acid is slowly added. After a four hours' reaction time at room temperature 10 ml hydrogen fluoride 48 % and 1 ml nitric acid are added. The tube is heated overnight on a sand bath at 120°C. One ml of perchloric acid is added and the solution is evaporated to dryness. After cooling, the residue is taken up in 2 ml nitric acid and diluted to 50 ml with distilled water. The determination of Cu, Zn, Pb, Cd, Cr, Ni and Al is carried out with ICP-OES or with atomic absorption with graphite furnace (GFAAS).

2.2.3. Quality assurance of the used methods

Table 2. Concentrations of trace metals in the < 63 µm fraction (mg/kg dry weight)(a)

MERCURY													
	DO	ZE	S1	S2	WD	OD	GB	BB	SB	NO	OB	SD	WH
1990		0,23		0,27	0,74	0,16	0,10	0,17	0,14	0,37	0,29		
1991		0,16		0,26	0,25	0,15	0,15	0,13		0,09	0,27	0,27	
1992	0,19	0,20		0,27	0,21	0,11	0,15	0,11	0,11	0,10	0,26	0,15	0,15
1993	0,08	0,24	0,26	0,08	0,24	0,15	0,14	0,12	0,26	0,12	0,24	0,14	0,23
1994	0,15	0,30	0,29	0,29	0,19	0,32	0,33		0,23	0,48	0,28	0,22	0,34
1995	0,34	0,08	0,33	0,16	0,47	0,30	0,32	0,10	0,27	0,20	0,36	0,25	0,28
LEAD													
	DO	ZE	S1	S2	WD	OD	GB	BB	SB	NO	OB	SD	WH
1990		48,0		36,0	72,0	38,0	41,0	36,0	23,0	26,0	25,0		
1991		42,0		57,7	97,2	47,8	55,4	52,4		46,1	61,0	72,0	
1992	31,2	38,0		44,1	66,2	35,8	34,8	38,3	38,0	30,0	62,6	33,0	33,4
1993	4,6	21,0	32,2	7,8	29,1	17,3	9,2	4,3	6,3	16,0	23,6	6,6	8,1
1994	18,4	26,0	26,1	17,3	26,3	21,5	20,0		17,0	13,0	25,2	14,0	17,7
1995	35,2	16,8	38,7	16,4	56,4	32,6	47,8	23,0	11,4	21,7	36,2	20,7	26,8
COPPER													
	DO	ZE	S1	S2	WD	OD	GB	BB	SB	NO	OB	SD	WH
1990		25,1		47,6	34,4	49,6	76,8	65,9	50,0		34,0		
1991		15,8		17,1	30,1	21,0	21,1	24,8		21,4	27,0	25,0	
1992	14,5	15,2		19,3	43,0	19,0	15,3	23,3	30,0	15,2	48,0	18,0	20,3
1993	2,1	11,4	12,1	3,2	12,0	16,0	9,8	5,3	6,1	20,0	17,0	3,2	12,9
1994	10,7	2,0	2,0	2,4	16,0	20,0	18,0		11,0	2,4	17,0	9,3	21,0
1995	14,7	9,2	16,1	8,8	26,0	16,7	19,7	15,6	17,2	11,4	14,0	13,2	13,6
ZINC													
	DO	ZE	S1	S2	WD	OD	GB	BB	SB	NO	OB	SD	WH
1990		127		154	220	185	222	195	156	419	34		
1991		104		160	247	148	193	216		174	209	180	
1992	131	144		179	233	191	317	221	274	209	350	196	200
1993	55	93	124	59	111	332	103	83	167	136	110	173	220
1994	98	123	124	144	123	132	126		123	159	135	95	120
1995	107	56	114	155	229	123	163	154	115	140	110	128	94
CHROMIUM													
	DO	ZE	S1	S2	WD	OD	GB	BB	SB	NO	OB	SD	WH
1990													
1991		66		109	112	98	116	88		117	105	100	
1992	63	65		75	107	85	70	81	74	63	113	95	64
1993	20	54	52	27	56	63	35	21	24	67	45	18	33
1994	42			63	101	80				58	60	38	
1995	42	52	54	74	64	43	60	50	48	33	31	89	21
NICKEL													
	DO	ZE	S1	S2	WD	OD	GB	BB	SB	NO	OB	SD	WH
1990													
1991		23,1		25,0	33,0	37,5	41,8	37,2		39,3	43,0	34,2	
1992	13,9	17,8		19,2	30,0	28,8	19,1	25,8	26,2	21,2	32,0	15,1	20,7
1993	8,0	21,0	21,0	11,0	18,0	39,3	19,4	17,5	17,7	28,2	19,4	12,0	25,0
1994	46,0	28,0	11,0	31,0	8,4	46,7	49,0		42,7	43,4	35,3	18,7	61,0
1995	14,7	16,5	16,2	11,8	4,3	22,1	16,7	16,0	13,1	16,5	15,3	12,2	16,5
CADMIUM													
	DO	ZE	S1	S2	WD	OD	GB	BB	SB	NO	OB	SD	WH
1990		0,34		0,68	0,64	0,34	0,29	0,23	0,22	0,37	0,33		
1991		0,46		0,58	0,68	0,39	0,24	0,47		0,23	0,75	0,49	
1992	0,31	0,27		0,54	0,63	0,28	0,28	0,42	0,47	0,19	0,54	0,32	0,21
1993	0,18	0,66	0,47	0,17	0,47	0,28	0,34	0,11	0,21	0,45	0,4	0,64	0,26
1994	0,62	0,67	0,61	0,78	0,63	0,36	0,46		0,31	0,37	0,59	0,46	0,38

(a): DO: Dumping site Oostende; ZE: Dumping site Zeebrugge East; S1: Dumping site Zeebrugge S1
S2: Dumping site Zeebrugge S2; WD: Westdiep; OD: Oost Dyck; GB: Gootebank
BB: Bigh bank; SB: Scharrebank; NO: North; OB: Oostendebank;
SD: Steendiep; WH: Westhinder

The methods were also applied on the standard reference material BCSS-1 (Marine sediment, National Research Council Canada). Table 3 reports the results.

Table 3. Analysis of the standard reference material BCSS-1 (\pm standard deviation)

Element	Measured value	Reference value
Hg	0.134 mg/kg	0.129 \pm 0.012 mg/kg
Cu	19.3 mg/kg	18.5 \pm 2.7 mg/kg
Zn	110 mg/kg	119 \pm 12 mg/kg
Pb	20.5 mg/kg	22.7 \pm 3.4 mg/kg
Cd	0.29 mg/kg	0.25 \pm 0.4 mg/kg
Cr	92 mg/kg	123 \pm 14 mg/kg
Ni	53.6 mg/kg	55.3 \pm 3.6 mg/kg
Al	5.92 %	6.27 \pm 0.4 %

2.3. Evaluation of results

Regressions were calculated to detect trends. The significance of the correlation coefficient was set at minimum $p < 0.05$, unless otherwise mentioned. For spatial distribution the means and standard deviations for the years 1993-1995 were determined due to variations in concentrations. These figures were considered to reflect the « actual » situation with regard to the contamination of sediments with trace metals. Concentrations were also normalised against aluminium.

3. RESULTS AND DISCUSSION

All results obtained on the two sediment fractions are mentioned in tables 1 and 2. Due to some changes over the years in the general monitoring programme with respect to sampling stations and metals to be analysed, some data are missing. This should however not strongly influence evaluation and interpretation of results.

3.1. Time trends

The determination of time trends for the period 1979-1995 was carried out on the whole sediment ($< 2000 \mu\text{m}$). It is generally recommended to use the fine grain fraction (*e.g.* $< 63 \mu\text{m}$) as the largest part of contaminants is adsorbed in this fraction (ICES, 1994). When the whole sediment is taken, trace metals are in fact diluted. The sediment samples kept from 1979 to 1989 in the laboratory however were not large enough to allow efficient separation of the fine fraction, especially due to the low amount of this fraction in most sampling stations (fig. 2). Moreover, the applied analytical method appeared to be sensitive enough to determine accurately the concentrations of heavy metals, with the exception of cadmium. For this latter element, only the $< 63 \mu\text{m}$ fraction could be used (from 1990 on). For the sake of completeness the other metals were also assessed in this fraction.

Results of trend analyses are given in tables 4 to 7. In the period 1979-1995 (whole sediment) a general downward trend was observed for all trace metals especially in the dredge spoils disposal areas (table 4). For the other stations this was

Table 4. Significant time trends (regressions) for the < 2000 µm fraction (1979-1995) (a)

Stations	Mercury	Lead	Copper	Zinc	Chromium	Nickel	Aluminium
Dumping site Zeebrugge East	-0,745	-0,491	-0,730	-	-	-	-
Dumping site Zeebrugge S1	-0,576	-0,564	-	-	-0,586°	-0,627°(d)	-0,709
Dumping site Zeebrugge S2	-	-0,765	-0,474°	-0,462°	-0,622°	-	-0,657
North (b)	-	-	-0,519°	-	-	-	-
Bligh bank	-	-0,526	-0,642	-	-	-	-
Scharrebank (c)	-	-0,718	-0,730	-	-0,623	-	-
Oost Dyck	-	-	-0,770	-	-	-	-0,727
Gootebank	-	-	-0,424°	-	-	-	-
Westdiep	-	-	-	-	-	-	-

(a) : p < 0,05 except r° < 0,1.

(b) from 1985 on

(c) from 1987 on

(d) from 1984 on

Table 5. Average procentual decrease per year (fraction < 2000 µm ; 1979 -1995)

Stations	Mercury	Lead	Copper	Zinc	Chromium	Nickel	Aluminium
Dumping site Zeebrugge East	-5,0	-3,1	-3,8	-	-	-	-3,0
Dumping site Zeebrugge S1	-5,1	-4,4	-	-	-5,2	-5,1 (c)	-4,0
Dumping site Zeebrugge S2	-	-5,8	-3,9	-2,4	-3,9	-	-3,8
North (a)	-	-	-6,7	-	-	-	-
Bligh bank	-	-3,7	-4,8	-	-	-	-
Scharrebank (b)	-	-9,2	-10,0	-	-5,3	-	-
Oost Dyck	-	-	-4,9	-	-	-	-3,1
Gootebank	-	-	-3,5	-	-	-	-
Westdiep	-	-	-	-	-	-	-
Average	-5,1	-5,3	-5,2	-2,8	-4,5	-4,3	-3,1

(a) from 1985 on

(b) from 1987 on

(c) from 1984 on

Table 6. Significant time trends (regressions) 1990 - 1995 for the < 63 µm-fraction (a)

Stations	Mercury	Lead	Copper	Zinc	Chromium	Nickel	Cadmium
Dumping site Oostende	-	-	-	-	-	-	-
Dumping site Zeebrugge East	-	-0,946	-0,865	-	-0,915	-	-
Dumping site Zeebrugge S1	-	-	-	-	-	-	-
Dumping site Zeebrugge S2	-	-0,712°	-0,809	-	-	-	-
North	-	-	-	-0,752°	-0,892	-	-
Bligh bank	-0,847	-	-	-	-	-0,885°	-
Scharrebank	-	-	-0,824°	-	-	-	-
Oost Dyck	+0,756°	-	-	-	-0,854°	-	-
Gootebank	+0,872	-	-	-	-	-	-
Westdiep	-	-	-	-	-	-0,983	-
Oostendebank	-	-	-	-	-0,872°	-	-
Steendiep	-	-	-	-	-	-	-
Westhinder	-	-	-	-	-	-	-

(a) p < 0,05 except r° < 0,1

Table 7. Average procentual decrease or increase per year 1990 - 1995 (< 63 µm-fraction)

Stations	Mercury	Lead	Copper	Zinc	Chromium	Nickel	Cadmium
Dumping site Oostende	-	-	-	-	-	-	-
Dumping site Zeebrugge Oost	-	-13,2	-16,2	-	-5,7	-	-
Dumping site Zeebrugge S1	-	-	-	-	-	-	-
Dumping site Zeebrugge S2	-	-15,2	-20,7	-	-	-	-
North	-	-	-	-13,7	-17,2	-	-
Bligh bank	-7,9	-	-	-	-	-15,2	-
Scharrebank	-	-	-17,2	-	-	-	-
Oost Dyck	+3,6	-	-	-	-11,5	-	-
Gootebank	+4,7	-	-	-	-	-	-
Westdiep	-	-	-	-	-	-22,5	-
Oostendebank	-	-	-	-	-18,2	-	-
Steendiep	-	-	-	-	-	-	-
Westhinder	-	-	-	-	-	-	-
Average	0,13	-14,2	-18,0	-13,7	-13,2	-18,9	0

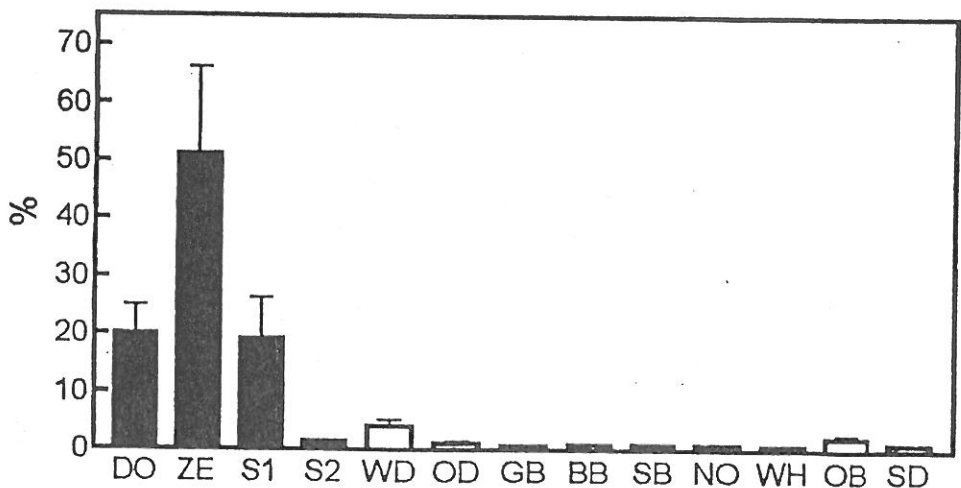


Fig. 2. Percentages of the < 63 μm fraction on the sampled stations (averages and standard deviations ; abbreviations : see table 2)

less the case, with the exception of copper. The average decrease was 3 to 5 % per year (table 5).

The analysis of the < 63 μm fraction in the period 1990-1995 (table 6) confirmed this general decreasing trend with exception of mercury on stations Oost Dyck and Gootebank where an increase of ca 4 % was noted (table 7). This is however possibly due to the occurrence of two high values in 1994 and 1995 (table 2) and should be confirmed the next years. Downward trends were less frequent than in the period 1979-1995 but are probably due to the shorter period of investigation (less data). In this respect it should be mentioned that a number of trend analyses which were considered not significant reached in fact a probability level of min. 85 %. It should also be noted that no significant time trends were found for cadmium.

The decreasing concentrations of trace metals, especially in or in the vicinity of the Scheldt estuary are undoubtedly primarily caused by a decrease in inputs of contaminants but possibly also by the increase in grain size, characterised by diminishing aluminium contents.

The most important inputs in Belgian waters are discharged by the river Scheldt. In 1993 the amounts of trace metals were : 3.5 t cadmium, 37 t lead, 124 t copper, 2.6 t mercury and 243 t zink (Paris Commission, 1995). Concentrations have clearly decreased during the past years (NSTF, 1993), which is in good agreement with the present results on sediments. In the dredge spoils disposal sites, where 6 million m³ harbour sediments (20 % of the total amount) are dumped, this decrease may also be caused by the decrease of contamination of these dredged materials. Accurate figures on the evolution of the concentrations of heavy metals in dredge spoils in the period under investigation are not available unabling comparison with the amounts found in sediments at sea. It can be mentioned however, that in 1987 Van Alsenoy *et al.* found that the sediments in the harbours contained two to three times as much trace metals than those found in coastal stations.

The decrease in aluminium content on several stations (table 4) could result in a lower adsorption capacity of the sediments for trace metals and hence cause a downward trend of their concentrations. As a matter of fact, there was a good relationship between aluminium and heavy metals (see 3.2). Nevertheless, when

computing time trends, only station Zeebrugge S1 (dumping site) showed a significant decrease in the $< 63 \mu\text{m}$ fraction during the same period ($r = -0.752$; $p < 0.001$). Moreover, it should be stressed that the procentual decrease of aluminium per year was mostly lower than the corresponding figures for other heavy metals, that a significant downward trend of these metals did not correspond on all stations with a significant decrease in aluminium content and that aluminium itself is a contaminant, even though a less important one.

Whatsoever, on the whole, the total concentrations of trace metals showed a decreasing trend making it more plausible that the bioavailable part of it for marine biota also diminished. An indication for this assumption is that the decrease in concentrations in sediments corresponded well with the downward trend of mercury, cadmium, lead and chromium noted in benthic organisms in the period 1981-1994 on stations Zeebrugge S1, Zeebrugge S2, Westdiep and Bligh Bank. In brown shrimp (*Crangon crangon*), starfish (*Asterias rubens*), swimming crab (*Liocarcinus holsatus*) and hermit crab (*Pagurus bernhardus*), the decrease was 4 to 8 % per year (Vyncke *et al.*, 1995).

In other areas of the North Sea, decreasing concentrations of trace metals were also observed in sediments and biota (NSTF, 1993). In the same area of the Belgian Continental Shelf, Van Alsenoy *et al.* (1993) did not find marked differences between their results of 1972 and 1987 respectively. This would indicate that the downward trend noticed in the present study occurred only from the eighties on.

3.2. Spatial distribution

To assess possible spatial differences in heavy metal concentrations a normalisation of data is recommended (Windom *et al.*, 1989 ; Loring, 1991 ; Rowlatt and Lovell, 1994 ; ICES, 1994). This normalisation is performed to make a distinction between the concentrations which are naturally present and anthropogenic contamination. Special attention is paid to the influence of grain size, as trace metals mainly occur in the fine fractions ($< 63 \mu\text{m}$). Normalisation can be carried out granulometrically or geochemically. In the latter case aluminium, being the main component of the fine-grained aluminosilicates, is often used. It should be stressed that normalisation was shown to depend on the composition of the sediment (influence of the area) and on the trace metals themselves. This could lead to misinterpretation of data when a normalisation technique is wrongly applied (Bostrom *et al.*, 1978 ; Loring, 1991 ; Din, 1992). This seems especially to be the case with the fine sediment fraction (ICES, 1994b).

For the present investigations normalisation against aluminium was chosen. There was indeed a good correlation between the individual trace metals and aluminium (fig. 3). Intercepts were not significant, with the exception of copper and nickel. Significant intercepts may give misleading normalised data (Rowlatt, 1996). For copper and nickel the values were -0.6 and $+ 1.5 \text{ mg/kg}$ ($p < 0.05$) respectively, resulting in a slight underestimation resp. overestimation of the real concentrations.

Means and standard deviations of the whole sediment ($< 2000 \mu\text{m}$) are shown in fig. 4. For the sake of completeness and comparison the non normalised total concentrations are also indicated. After normalisation, differences in concentrations

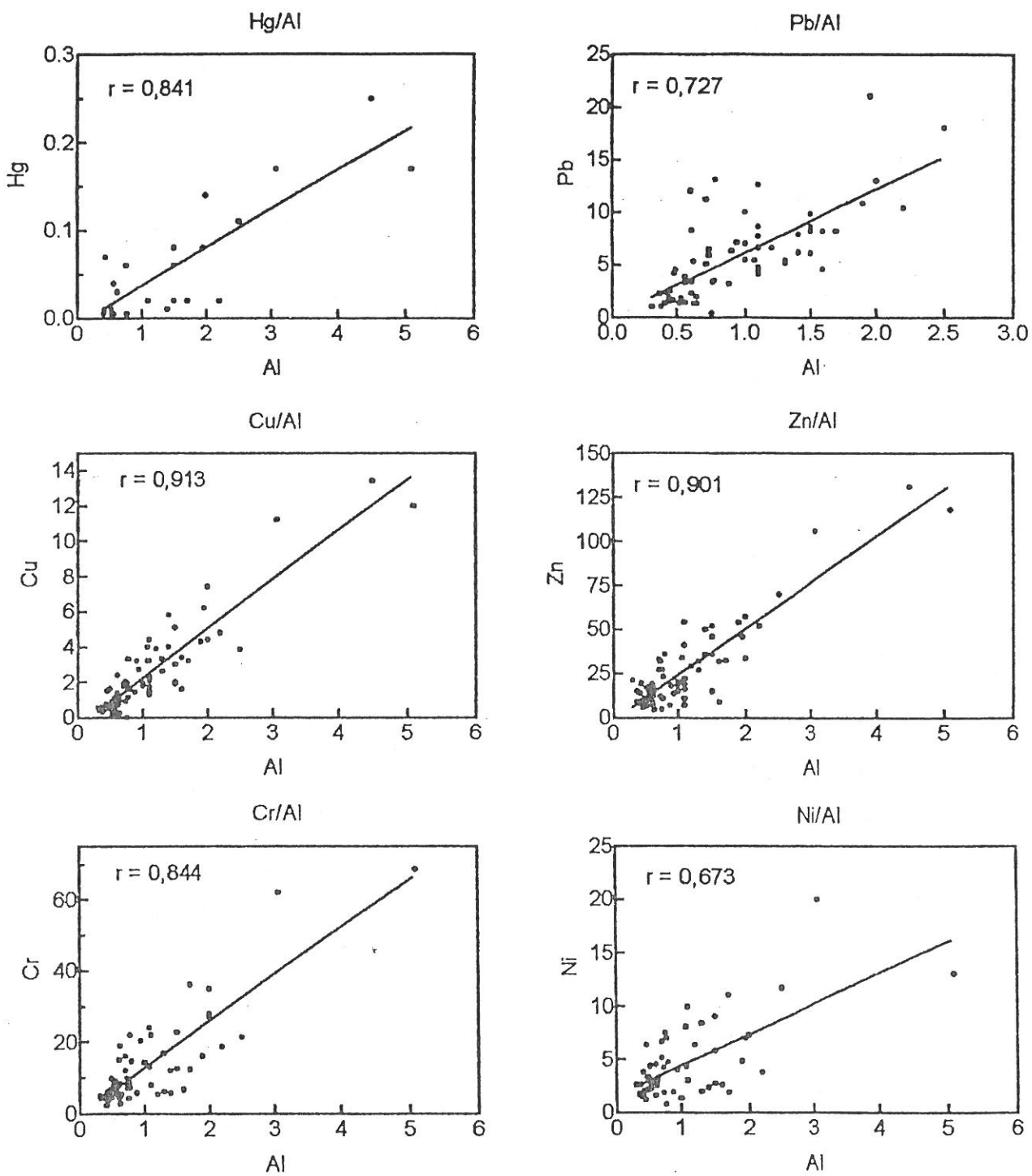


Fig. 3. Correlations between trace metals and aluminium (< 2000 μm fraction)

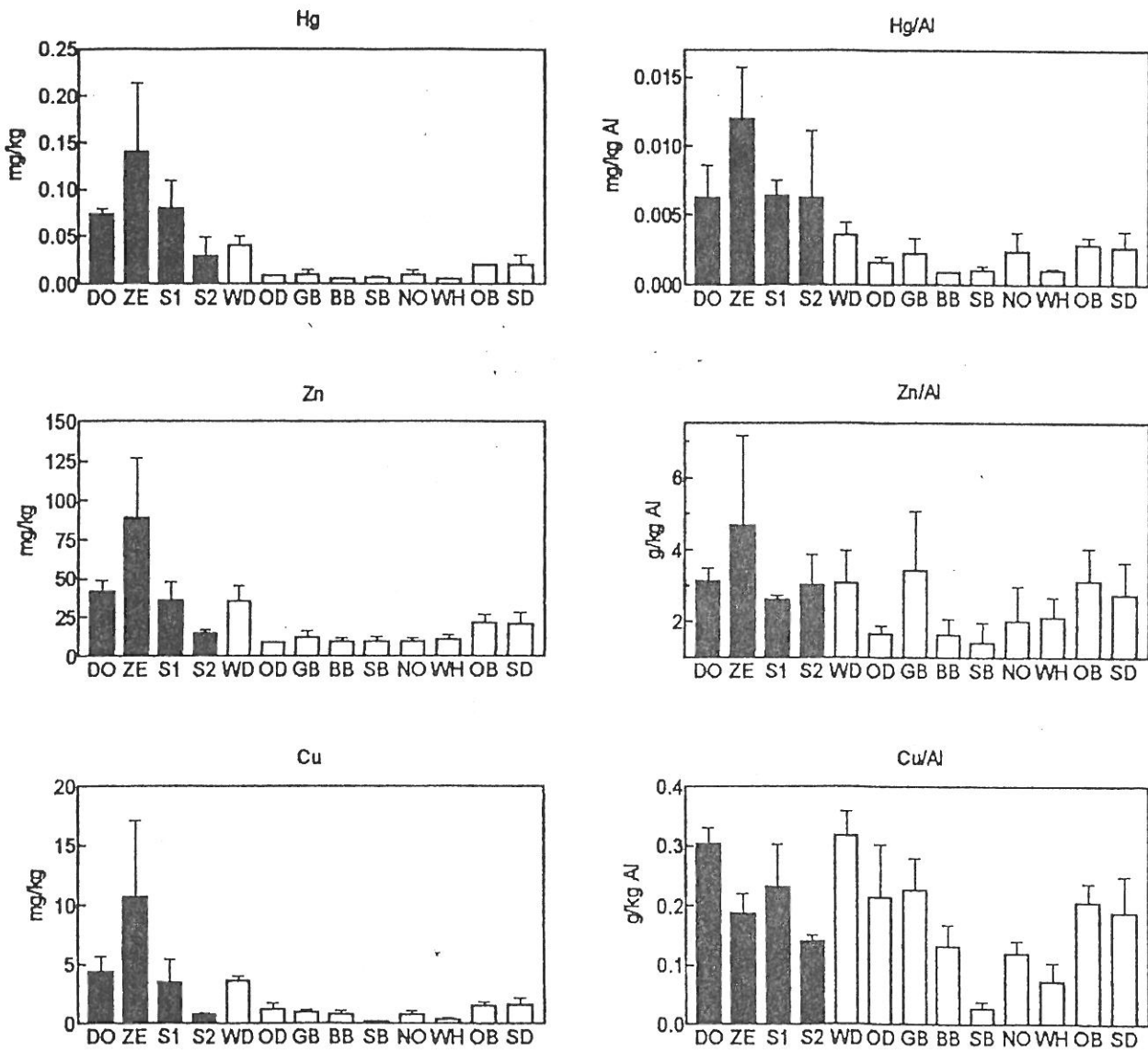


Fig. 4. Concentrations of trace metals and normalised trace metals 1993-1995 (averages and standard deviations) (continued on next page)

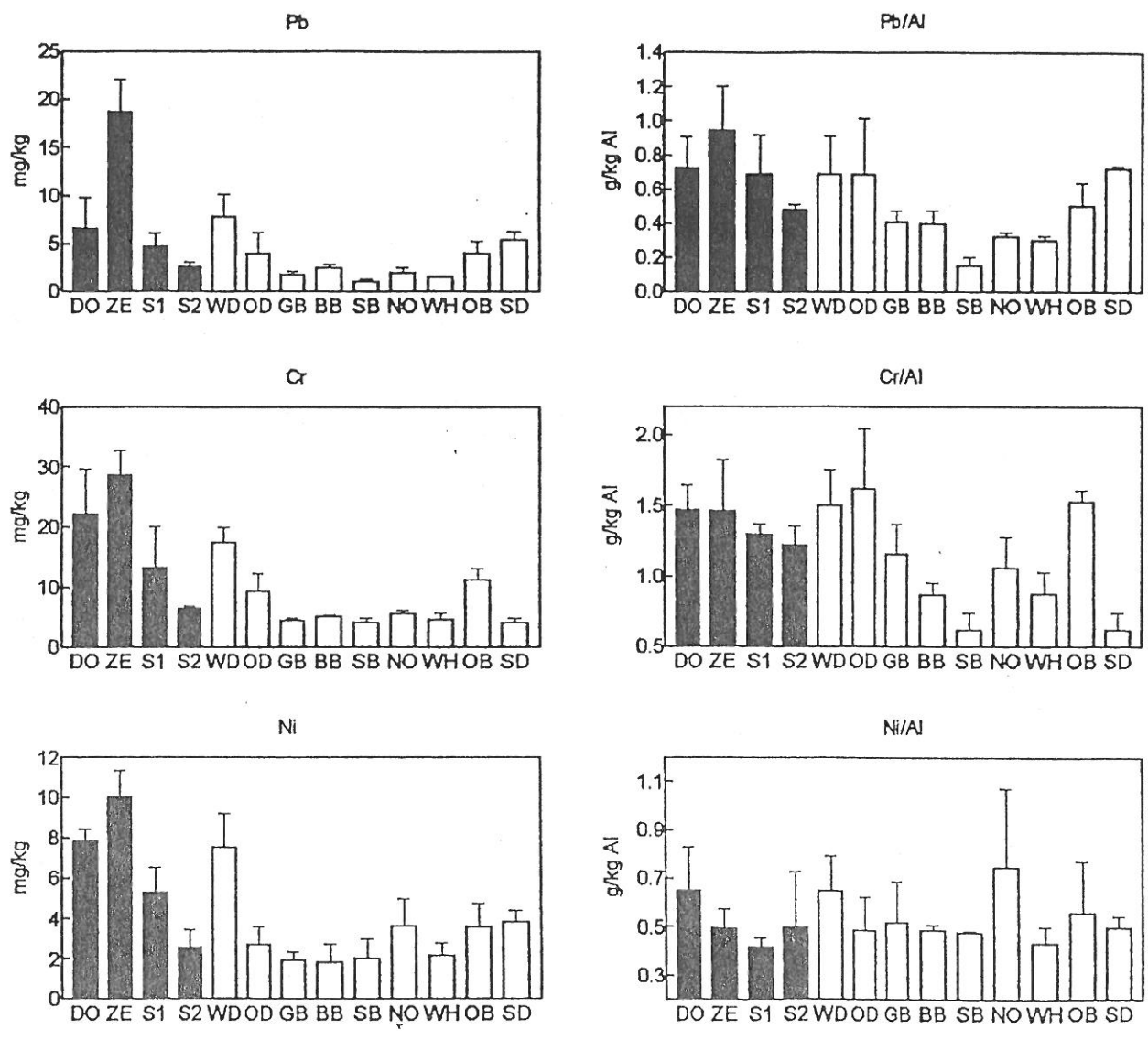


Fig. 4. (continued)
Legends to figures : see table 2

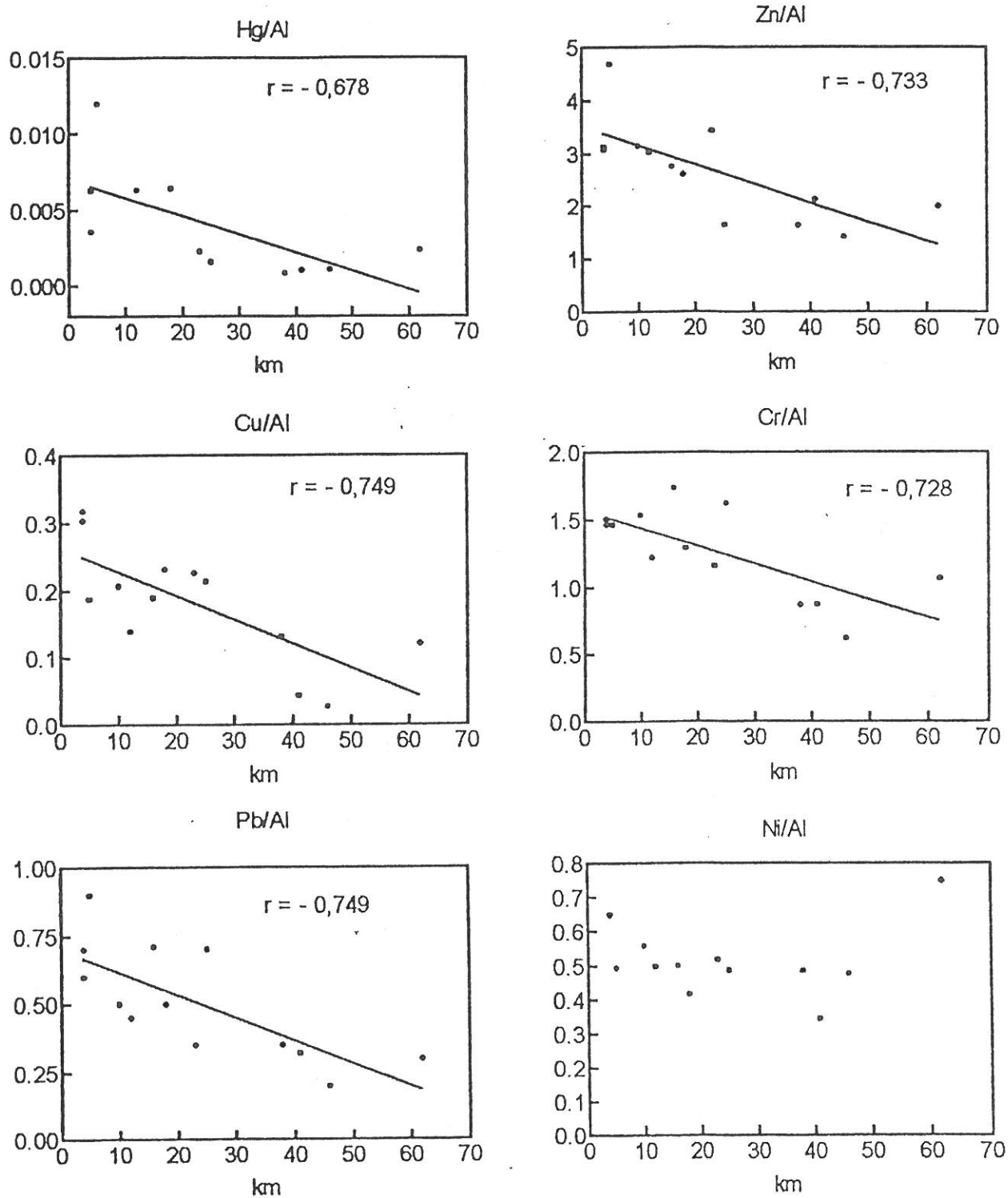


Fig. 5. Correlations between the normalised metal concentrations and the distance to the coast

among the different stations were less pronounced than with non normalised values. In the latter case the dumping sites for dredge spoils (except Zeebrugge S2) and station Westdiep showed markedly higher contents. Normalised data on the other hand appeared to depend on the distance from the coast, so that there was no real contradiction with the previous findings.

With the exception of nickel, significant correlations were found (fig. 5). Hence, contamination with heavy metals appeared to be highest close to the coastline and decreased seawards. This was also noticed in other areas of the North Sea (Rowlatt and Lovell, 1994 ; Rowlatt and Davies, 1995), although in some regions (e.g. Doggerbank) higher concentrations were found (Everaarts and Fischer, 1992). Similar investigations by Van Alsenoy *et al.* (1993) in the same area of the Belgian Continental Shelf carried out in 1987-1988 gave comparable values.

The higher total concentrations in three of the four dumping sites corresponded well with the results of analyses of trace metals in several benthic organisms. Cut trough shell (*Spisula subtruncata*) and anemone (*Sagartia troglodytes*) contained about twice as much lead in the dumping sites (considered together) as in the other stations. This was also the case with chromium in *Spisula* and in swimming crab (*Liocarcinus holsatus*) (Vyncke *et al.*, 1995).

3.3.Enrichment factors

At the demand of the Commission of the Paris Convention, an ad hoc working group has established a series of provisional background / reference concentrations *i.a.* in sediments for several areas (Anon., 1997). These are concentrations from the pre industrial period (mostly box core data). By dividing the present contents of trace metals by the normalised background values enrichment factors can be determined.

Table 8, Enrichment factors for trace metals in sediment

Metal/Al	Background concentration (ppm/%)	Min.-max.	Median
Mercury	0,004	2.08-29.93	7,33
Cadmium	0,016	-	-
Lead	3,12	0.49-3.03	1,87
Zinc	14,5	0.98-3.24	1,94
Chromium	10,18	0.61-1.59	1,23
Nickel	4,79	0.87-1.56	1,03
Copper	3,61	0.33-0.88	0,59

The enrichment factors which are related to the North Sea are shown in table 8, together with the background values. These results should be evaluated with caution as sandy sediments may influence data (Anon., 1997). However, they provide a general picture of the increase in concentrations of heavy metals in the present industrial period. Especially the enrichment with mercury (x 7), followed by lead and zink (ca .x 2) appeared to be strong. The increase of chromium was moderate (23 %) and nickel and copper did not show marked changes. For copper, the enrichment factor was even below the reference value. Van Alsenoy *et al.* (1993) came to the same

conclusion, although iron was used as normaliser. In several other coastal areas of the North Sea, increases in contents were also noted (NSTF, 1993b).

3.4. Ecotoxicological assessment

Table 9. Stations exceeding lowest EAC (a)

	EAC	DO	ZE	S1	WD	SD
Mercury	0.05-0.5	+	+	+		
Zinc	50-500		+			
Copper	5-50		+			
Lead	5-50	+	+		+	+
Chromium	10-100	+	+	+	+	
Nickel	5-50	+	+		+	

(a) EAC : "Ecotoxicological assessment criterium"
(mg/kg dry weight)

At the request of the Paris Commission, a working group has established a series of provisional ecotoxicological assessment criteria (EAC) *i.a.* for sediments (Anon., 1997b). The lowest concentration below which no toxicological effects were shown to occur (NOEC : No observed effect concentration) is taken as a criterion (upper limit) and a safety coefficient of 10 is applied (lower limit). Table 9 shows these EAC. In none of the stations the upper limits were exceeded. For the lower limits this was the case in five stations. Three of these areas were dredge spoil disposal sites. These regions should further receive careful attention.

4. CONCLUSIONS

In the period 1979-1995 a general downward trend for mercury, lead, zinc, copper, chromium, nickel and aluminium was noticed. This was especially the case in dredge spoil dumping areas which are situated in the outer estuary of the river Scheldt. The average decrease per year was 3 to 5 %. As this was also observed in other regions of the North Sea, this would indicate a reduction of the inputs of contaminants and could be an indication that measures mainly taken at an international level (Paris Convention, European Union) to reduce inputs yield positive results.

With regard to spatial distribution concentrations of trace metals appeared to diminish with the distance to the coast. Also in this case, dumping areas showed the highest values and should receive special attention.

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Agenda Item 4

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NORTH-EAST ATLANTIC

ENVIRONMENTAL ASSESSMENT AND MONITORING COMMITTEE (ASMO)

SPA: 20-24 APRIL 1998

Trace Metals and Organochlorines in Sediments from the Western Scheldt

Submitted by Belgium

TRACE METALS AND ORGANOCHLORINES IN SEDIMENTS FROM THE WESTERN SCHELDT (1990-1995)

W. VYNCKE, P. ROOSE , H. HILLEWAERT (CLO Gent ,Fisheries Research Station, Oostende, Belgium)

M. GUNS, P. VAN HOEYWEGHEN, H. BAETEN, M. HOENIG (Veterinary and Agrochemical Research, Tervuren, Belgium)*

Abstract

Results of a survey on contaminants carried out during the period 1990-1995 on eight stations in the western Scheldt located from Flushing to Antwerp are discussed. Mercury, lead, copper, zinc, chromium, nickel, aluminium, polychlorinated biphenyls (CBs), α - and γ -hexachlorhexane, hexachlorbenzene, dieldrin, p,p'-DDE and p,p' DDD were analysed.

With the exception of mercury and nickel trace metals showed a downward time trend on several stations. No significant trends were found for organochlorines.

Geographically seen a marked upward gradient from the coast to Antwerp was observed. The strongest increase started at about the Dutch-Belgian border. CBs also showed an upward gradient from Flushing to Kallo, in the vicinity of Anwerp, followed by a decrease in Antwerp itself. The other organochlorines did not show any clear spatial differences.

Comparison of background concentrations from the pre industrial period with present values allowed the calculation of enrichment factors for trace metals. Especially the enrichment with mercury and cadmium appeared to be high. For organochlorines reference values from so-called pristine areas were used. The concentration of CBs showed to be strongly increased.

By application of ecotoxicological assessment criteria the "No observed effect concentration" levels for heavy metals were exceeded on two stations in the Antwerp region. For CBs this was the case on all stations. Especially these compounds should received further careful attention.

* Report nr 244 (1997) from the Fisheries Research Station, Oostende (translated from the Dutch).

1. INTRODUCTION

The western Scheldt is known to be a rather heavily polluted river receiving domestic and industrial effluents from cities such as Brussels, Antwerp and Ghent. The tidal difference is 4 to 5 m and the flow varies from 40 to 350 m³ per sec with an average of 90 m³ per sec at Antwerp, which is rather low. Hence, tides and associated variations in flow properties, oxygen and salt contents play an important part in sediment behaviour in this region. Increasing salinity causes sedimentation with adsorbed contaminants, while a supply of fresh water results in desorption of these compounds (D'Hondt and Baeteman, 1987 ; Panutrakul and Baeyens, 1991).

Sediments can adsorb large quantities of contaminants. This is especially the case in the fine grained fraction and the organic phase. They act as a sink for these compounds (Skei, 1992).

The Scheldt is the main input source of contaminants in Belgian coastal waters (NSTF, 1993). In 1993, these amounted to 3.5 t cadmium, 37 t lead, 124 t copper, 2.6 t mercury, 243 t zinc, 207 kg polychlorinated biphenyls and 58 kg lindane (Paris Commission, 1995). For this reason, studying this river and its estuary is important for marine ecology including fisheries. In the framework of ecological monitoring programmes sediments should be regarded as a priority issue.

In the present work concentrations of trace metals and organochlorines were determined in eight stations situated between Flushing and Antwerp. This survey was carried out in the framework of the monitoring programmes established by the Commissions of the Oslo and Paris Conventions (area J02). It was started in 1990 and 1991 for trace metals and organochlorines respectively. Both time trends and spatial distribution were studied.

2. MATERIAL AND METHODS

2.1. Sampling sites and technique

The eight stations are shown in fig. 1. On each monitoring area three samples were taken in a radius of about 100 m with a Van Veen grab sampler. They were bulked and kept at - 28°C until further analysis. After defrosting, the sediment was dried at 105°C to determine the dry matter content. The fraction smaller than 2000 µm (« total sediment») was separated by sieving. The fine-grained fraction (< 63 µm) was also analysed. For this purpose, the sediment was resuspended in water, separated by wet sieving and dried.

Heavy metals were assessed in both fractions. Organochlorines were determined only in the < 63 µm fraction as analysis of the total sediment was shown to be not sensitive enough.

For the study of time trends contaminants were determined in the fine grained fraction, as recommended by ICES (1994), most of them being adsorbed in this fraction. For the geographical distribution trace metals were assessed in the total sediment and, with the exception of iron, normalised against aluminium. It should be

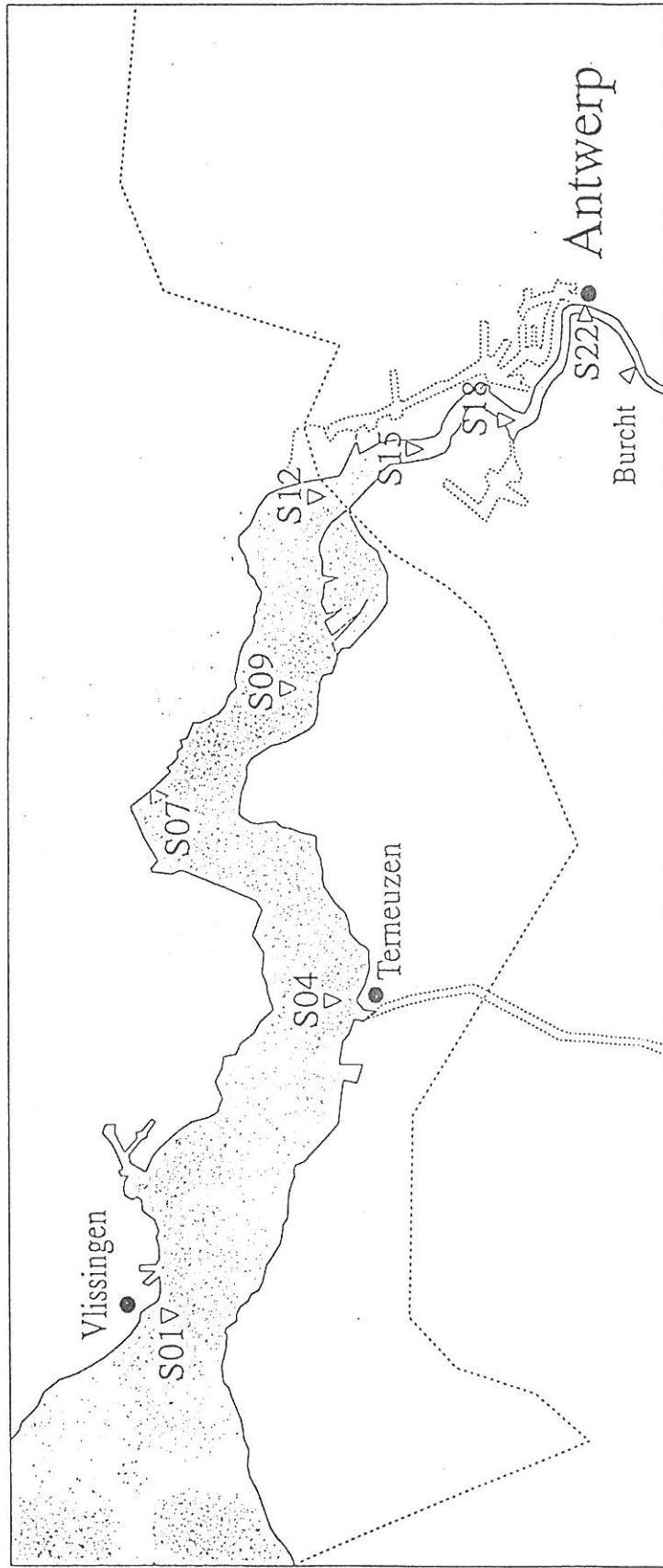


Fig. 1. Sampling stations

4.

remarked that iron itself is used as a normaliser (Van Alsenoy *et al.*, 1993 ; ICES, 1994). The determination of organochlorines was performed only on the fine fraction and no normalisation was applied.

2.2. Chemical analysis

2.2.1. Heavy metals

2.2.1.1. Mercury

Ca. 1 g of dried and homogenised sediment was weighed in an 250 ml erlenmeyer flask. Nitric acid 65 % (4 ml), hydrochloric acid 37 % (3 ml) and hydrogen peroxide 30 % (2.5 ml) were added. After refluxing for 15 min, the solution was cooled, filtered and diluted to 100 ml with distilled water. Mercury was measured after reduction with tin (II) chloride in a flameless atomic absorption spectrometer.

2.2.1.2. Other trace metals

Ca. 0.5 g of sediment was weighed in a PTFE tube and 4 ml of perchloric acid was slowly added. After a four hours' reaction time at room temperature 10 ml hydrogen fluoride 48 % and 1 ml nitric acid were added. The tube was heated overnight on a sand bath at 120°C. One ml of perchloric acid was added and the solution was evaporated to dryness. After cooling, the residue was taken up in 2 ml nitric acid and diluted to 50 ml with distilled water. The determination of Cu, Zn, Pb, Cd, Cr, Ni and Al was carried out with ICP-OES or with atomic absorption with graphite furnace (GFAAS).

2.2.2. Organochlorines

The following compounds were analysed : the ten polychlorinated biphenyls CBs 28, 31, 52, 101, 105, 118, 138, 153, 156 and 180, α -HCH (hexachlorhexane), γ -HCH (lindane), HCB (hexachlorbenzene), dieldrin, DDE (p,p'-dichlordiphenyldichlorethene) and DDD (p,p'-dichlordiphenyldihlorethane).

2.2.2.1. Extraction of the organochlorines

Four to twenty g of sediment were extracted during six hours with a hexane/acetone (3/1) mixture in a soxhlet still. Small pieces of copper, treated beforehand with diluted nitric acid, were introduced in the extraction flask to avoid a slowing-down of the boiling process and to precipitate a first amount of inorganic sulphur. The extract was then reduced to ca 1 ml in a Rotavapor with a stream of nitrogen and poured on a column filled with 4 g desulphurising agent ($\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_3$). The compounds were eluted with 25 ml hexane and the eluate was reduced by evaporation to ca 1 ml. This solution was poured on another column filled with siliciumdioxide (5 % water). A first fraction was eluted with 17 ml hexane (CB fraction), followed by a second with 20 ml hexane/diethylether (9/1) (other organochlorines). One ml iso-octane containing the internal standard tetrachloronaphtalene was added to both fractions which were then reduced by evaporation to 1 ml and analysed by gas chromatography.

2.2.2.2. Gas chromatography

A Carlo Erba 8160 gas chromatograph fitted with a DB-1701 or DB5 capillary column (J & W Scientific) of 60 m with an internal diameter of 0.25 mm and a phase thickness of 0.25 μm , a splitless injector and a Ni^{63} electron capture detector were used. The temperature of the injector was 230° C and that of the detector 410° C. Hydrogen was used as carrier gas and nitrogen or Ar/Me as make-up gas. The temperature programme was as follows : 90° C during 3 min, followed by an increase from 90 to 150° C at a speed of 15° C per min, again followed by an increase to 265° C at 3° C per minute. This last temperature was maintained during 10 min. Finally the column was heated at a speed of 15° C per min to 275° C. This temperature was kept for 10 min.

2.2.2.3. Quality assurance of the used methods

For heavy metals the analytical methods were also applied on the standard reference material BCSS-1 (Marine sediment, National Research Council Canada). Table 1 reports the results.

Table 1. Analysis of the standard reference material BCSS-1 (\pm standard deviation)

Element	Measured value	Reference value
Hg	0.134 mg/kg	0.129 \pm 0.012 mg/kg
Cu	19.3 mg/kg	18.5 \pm 2.7 mg/kg
Zn	110 mg/kg	119 \pm 12 mg/kg
Pb	20.5 mg/kg	22.7 \pm 3.4 mg/kg
Cd	0.29 mg/kg	0.25 \pm 0.4 mg/kg
Cr	92 mg/kg	123 \pm 14 mg/kg
Ni	53.6 mg/kg	55.3 \pm 3.6 mg/kg
Al	5.92 %	6.27 \pm 0.4 %

For organochlorines internal reference materials with known concentrations were analysed regularly. The quality of the analytical methodology was also checked by participating in different intercomparison exercises organised by ICES or QUASIMEME.

2.3. Processing of results

Time trends were assessed by computing regressions. The significance of the correlation coefficient was set at $p < 0.05$ unless otherwise mentioned. For spatial distribution the averages and their standard deviations for the years 1993-1995 were calculated. This procedure was chosen because of the large variations between the concentrations and the occurrence of several significant trends. These values were considered to represent the actual situation with regard to contaminants in sediments.

Table 2. Trace metals in sediment (< 2000 µm-fraction) 1990-95
(mg/kg dry weight, except Fe en Al : %)

Mercury	S01	S04	S07	S09	S12	S15	S18	S22
90	0,03	0,02	0,01	0,01	0,36	0,25	1,18	0,16
91	0,01	0,01	0,01	0,01	0,04	0,10	0,94	0,17
92	0,12	0,02	0,01	0,01	0,01	0,40	1,41	0,17
93	0,04	0,06	0,03	0,03	0,08	0,22	1,32	1,10
94	0,04	0,04	0,07	0,01	0,1	0,36	1,55	
95	0,14	0,02	0,01	0,01	0,03	0,24	0,46	0,07
Lead								
90	1,9	7,3	5,6	6,8	35,0	11,0	139,0	130
91	10,0	14,3	5,7	7,4	22,2	25,1	35,0	35,2
92	21,1	11,8	5,5	7,6	10,2	49,6	127,0	43,1
93	8,8	9,8	1,9	2,8	4,5	21,7	137,0	78,3
94	9,0	5,9	4,5	3,6	12,1	36,8	181,0	
95	21,3	8,1	4,1	4,8	9,1	61,1	47,9	79,2
Cadmium								
90	0,19	0,38	0,16	0,10	2,46	0,05	8,69	0,37
91	0,05	0,11	0,02	0,03	0,32	0,63	2,36	2,44
92	0,37	0,16	0,08	0,83	0,18	2,01	9,73	0,73
93	0,21	0,17	0,06	0,15	0,24	0,56	11,90	8,70
94	0,14	0,15	0,73	0,03	0,65	2,50	10,70	
95	0,25	0,25	0,25	0,25	0,25	2,75	1,88	0,73
Copper								
90	2,8	5,0	1,5	1,8	47,9	6,7	82,0	27,4
91	1,2	2,3	0,7	1,6	11,0	11,1	27,7	25,9
92	8,0	4,8	2,9	7,2	3,8	35,0	96,7	11,1
93	3,9	7,7	0,2	0,4	2,2	9,8	122,0	30,6
94	3,1	2,4	5,4	0,5	7,3	31,4	94,0	
95	7,8	5,6	2,0	2,0	5,5	40,6	26,8	15,4
Zinc								
90	26	26	19	21	239	48	479	208
91	19	33	14	16	66	75	457	531
92	82	64	42	36	64	238	605	196
93	46	58	18	23	46	120	739	312
94	22	14	39	7	41	107	658	
95	57	32	16	21	44	259	187	154
Nickel								
91	3,3	5,6	2,1	2,2	10,1	6,8	40,4	10,6
92	7,4	3,9	1,7	2,3	5,2	10	37,4	5,0
93	13,0	32,0	8,1	8,4	13,8	32,6	158,0	49,0
94	5,4	4,5	6,2	2,4	7,8	23,4	38,2	7,2
95	8,0	4,4	1,9	5,8	4,3	16,5	13,4	7,7
Chromium								
91	29,2	28,0	22,3	9,7	49,0	67,2	42,8	39,0
92	45,3	54,5	17,8	8,5	30,0	66,8	164,0	49,3
93	21,8	44,1	19,3	9,8	24,2	37,7	195	54,4
94	16,6	17,7	20,0	7,8	19,9	40,2	96,3	
95	26,2	14,1	11,3	6,3	15,8	75,4	62,4	21,3
Iron								
94	1,0	1,1	1,4	0,7	0,7	3,4	4,5	1,3
95	1,3	0,9	0,9	1,0	1,4	2,1	1,9	1,6
Aluminium								
90	1,3	0,9	1,5	1,1	2,7	3,5	2,6	0,9
91	0,8	0,6	0,5	0,5	1,0	1,4	1,1	0,8
92	3,3	2,3	1,3	1,1	2,0	2,9	6,0	1,1
93	1,4	3,2	0,6	0,5	1,0	3,3	5,9	1,7
94	1,3	1,2	1,2	0,51	1,4	2,1	5,6	
95	2,1	0,6	0,7	0,7	1,1	2,5	2,3	0,8

Table 3. Trace metals in sediment (< 63 µm-fraction)
1990-1995 ; mg/kg dry weight (Fe : %)

Mercury	S01	S04	S07	S09	S12	S15	S18	S22
90	0,38	0,67	0,51	0,51	0,74	0,8	2,82	2,13
91	0,26	0,28	0,15		0,36	1,18	1,12	1,10
92	0,30	0,33		0,08	0,75	0,78	1,36	0,94
93	0,32	0,30	0,45	0,06	0,32	0,86	1,62	1,10
94	0,36	0,39	0,35		0,69	0,88	1,99	0,90
95	0,46	0,39	0,54	0,64	0,51	1,00	0,99	0,74
Lead								
90	46	64	28	52	88	130	250	250
91	55	59	52		146	217	197	169
92	11	42	74	64	79	101	189	250
93	31	29	8	16	34	80	147	110
94	34	30	19		65	89	244	73
95	28	69	43	60	60	104	103	90
Cadmium								
90	0,75	1,33	0,55	0,77	4,65	2,18	14,6	15,9
91	0,75	0,83	0,48		2,10	6,90	7,20	5,40
92	0,87	0,87	2,69	0,57	3,03	6,39	10,80	8,82
93	0,53	0,76	0,56	0,43	1,71	4,28	14,80	10,10
94	0,69	1,18	0,87		3,75	5,41	4,86	4,16
95	0,25	0,25	0,25	1,53	2,38	4,45	5,25	4,24
Copper								
90	25	33	41	133	94	83	144	179
91	21	23	28		83	129	145	135
92	12	26	26	24	52	77	102	119
93	15	23	11	12	29	54	112	100
94	11	26	21		50	81	118	62
95	12	26	30	34	40	77	79	59
Zinc								
90	159	226	153	308	389	430	859	1018
91	160	200	316		275	544	561	585
92	91	218	303	452	356	465	610	814
93	139	223	160	178	233	356	755	585
94	132	171	175		331	489	918	367
95	85	237	224	231	269	408	393	323
Nickel								
91	29,3	31,3	47,2	34,2	50,0	52,0	56,1	51,9
92	7,0	18,6	21,3	26,6	23,3	27,6	30,2	44,3
93	23,8	22,8	10,8	26,3	26,2	43,0	57,9	41,6
94	34,2	40,1	29,0		61,0	46,3	45,7	49,8
95	12,9	28,9	20,8	25,4	22,3	28,0	28,3	24,4
Chromium								
91	94	118	154		157	220	252	203
92	27	100	120	95	116	165	123	110
93	63	66	30	85	91	107	176	134
94	94	76	61		102	103	121	93
95	47	60	66	83	85	97	84	78
Iron								
94	2,4	2,5	3,8		7,7	3,4	3,4	3,2
95	1,6	2,9	2,7	2,9	5,1	2,8	2,9	2,5

Table 4. Concentrations of CBs in sediments from the Scheldt 1991 - 1995
($\mu\text{g}/\text{kg}$ dry weight)

Total CBs	SO1	SO4	SO7	SO9	S12	S15	S18	S22
91	7,82					57,15	54,21	
92	9,83		19,49	26,70	55,27	71,21	179,65	90,90
93	29,72	66,38	57,01	157,03	73,36	149,26	430,03	
94				17,22	34,84	79,65	35,76	72,73
95	10,78			46,03	44,93	45,91	67,49	
CB 153								
91	1,10					11,20	10,73	
92	2,04		3,81	5,61	12,37	14,95	32,05	18,97
93	4,97	13,29	10,60	32,01	14,76	30,08	92,04	
94				2,71	7,84	18,75	7,56	16,03
95	1,75			9,74	9,79	9,26	14,76	
CB 138								
91	1,72					11,24	11,65	
92	1,85		4,17	5,82	12,59	15,34	31,61	19,66
93	6,59	13,12	12,01	33,69	14,60	31,40	60,74	
94				2,72	6,89	15,77	6,52	12,44
95	1,44			8,36	7,65	7,34	11,18	
CB 52								
91	0,10					5,03	4,24	
92	0,65		1,21	1,40	0,60	5,22	17,59	6,61
93	1,11	4,64	3,77	9,93	5,51	10,60	42,32	
94				1,39	3,75	7,34	3,83	6,77
95	0,81			3,68	3,6	3,9	5,77	

Table 5. Concentrations of organochlorines (exc. CBs)
in sediments from the Scheldt 1991-1995 ($\mu\text{g}/\text{kg}$ dry weight)

γ HCH	S01	S04	S07	S09	S12	S15	S18	S22
91	0,38					1,86	1,46	
92	0,49		1,08	2,46	2,40	1,97	3,72	3,69
93	1,52	1,30	1,33	2,78	2,03	2,46	3,66	
94							0,20	
95	0,66			1,45	0,82	0,57	0,45	
HCB								
91	0,32					0,50	0,36	
92	0,32		0,53	0,79	5,32	1,41	2,01	1,52
93	1,03	3,08	1,33	4,61	1,09	1,61	1,85	
94					0,39	0,79	0,43	
95	0,32			0,56	0,66	0,59	0,59	
DIELDRIN								
91	0,40					0,72	1,55	
92	0,21		0,30	0,45	0,82	0,88	1,50	0,32
93	1,18	1,44	1,64	1,93	1,36	1,73	2,59	
94							0,36	0,92
95	0,16			0,71	0,76	0,62	0,91	
α HCH								
91	0,21					0,27	0,38	
92	0,27		0,31	0,34	0,19	0,12	0,18	0,08
93	0,08	0,08	0,08	0,80	0,63	0,80	0,94	
94								
95	0,26			0,24	0,82	0,27	0,22	
DDE								
91	0,41					2,23	1,73	
92	0,34		0,69	0,67	2,07	2,45	2,35	4,35
93	1,73	3,03	2,80	11,93	3,47	5,81	2,59	
94				0,81	3,38	7,43	2,52	3,67
95	0,5			2,18	1,86	2,49	3,36	
DDD								
91	0,52					0,57	0,62	
92	0,20		0,28	0,38		1,96	1,07	0,84
93	0,08	0,08	0,08	1,60	0,08	0,08	1,74	
94								1,86
95	1,19			2,87	1,72	2,81	2,65	

3. RESULTS AND DISCUSSION

All data are reported in tables 2 to 5. Fig. 2 shows the average percentages of the < 63 µm fraction. These appeared to be strongly depending on the sampling location.

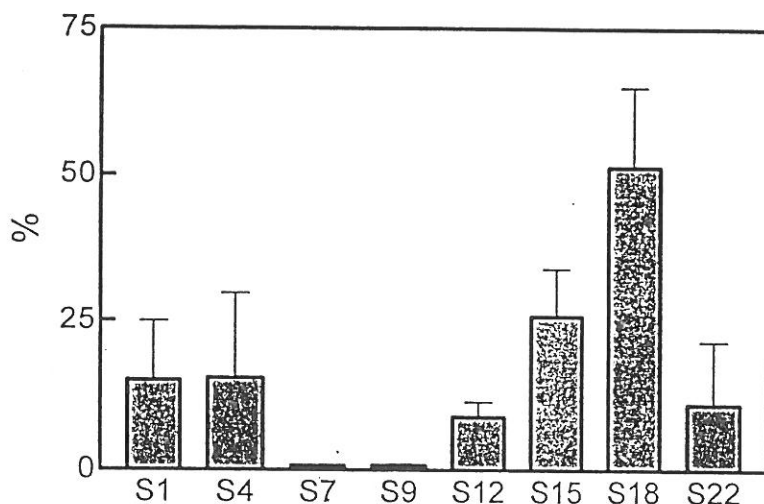


Fig. 2 Percentage of the < 63 µm fraction on the different stations (averages 1993-95 and standard deviations)

3.1. Time trends

3.1.1. Trace metals

Significant time trends are shown in table 6. Table 7 reports the average procentual decreases per year. No differences were found for mercury and nickel. With regard to the heavy metals themselves, especially the concentrations of copper and chromium showed downward trends.

Table 6. Significant time trends (regressions) for trace metals (1990 - 1995 ; < 63 µm-fraction) (*)

	Mercury	Lead	Cadmium	Copper	Zinc	Nickel	Chromium
S01	-	-	-0,731°	-0,859	-	-	-
S04	-	-	-	-	-	-	-0,908
S07	-	-	-	-	-	-	-
S09	-	-	-	-	-	-	-
S12	-	-	-	-0,830	-	-	-0,870
S15	-	-	-	-	-	-	-0,915
S18	-	-	-	-0,836	-	-	-0,820
S22	-	-0,831	-0,715°	-0,979	-0,880	-	-0,861

(*) p < 0,05, except r° < 0,1

From a geographical point of view most downward trends were noted in station S22 (Antwerp). In general, most metals showed a decrease of about 14 % per year on locations where a decrease was noted, which is in accordance with values in different

points of the Belgian Continental Shelf, where diminutions of 13 to 19 % were noticed (Guns *et al.*, 1997). This general downward trend was in good agreement with the reduction of inputs of contaminants from the river Scheldt (NSTF, 1993b).

3.1.2. Organochlorines

In contrast to trace metals, no significant time trends were found for organochlorines. With respect to these compounds no clear improvement or deterioration of the quality of the environment was to be observed.

Table 7. Average procentual decrease of concentrations per year (1990-1995 ; < 63 μm fraction)

	Mercury	Lead	Cadmium	Copper	Zinc	Nickel	Chromium
S01	-	-	-10.1	-11.6	-	-	-
S04	-	-	-	-	-	-	-12.5
S07	-	-	-	-	-	-	-
S09	-	-	-	-	-	-	-
S12	-	-	-	-13.2	-	-	-11.3
S15	-	-	-	-	-	-	-15.4
S18	-	-	-	-15.4	-	-	-15.6
S22	-	-14.0	-14.4	-15.3	-13.5	-	-15.3
Average	-	-14.0	-12.2	-13.9	-13.5	-	-14.0

3.2. Spatial distribution

3.2.1. Trace metals

The averages for 1993-1995 and the standard deviations are reported in fig. 3. All trace metals showed a clear upward gradient from the coast to Antwerp. In this respect, largest differences were noted for zinc, mercury, lead, cadmium and copper. The strongest increase started at about station S12 (Dutch-Belgian border). Station S22 (Antwerp) which is situated in the area with the highest flocculation (D'Hondt and Baeteman, 1987) was the most contaminated, except for iron. This lower concentration of iron was probably due to the lower percentage of the silt fraction in this region (fig. 2) which has a repercussion on the aluminium content, the most important component of aluminosilicates and also on the iron concentration, as a good correlation between aluminium and iron was found (fig. 4).

Similar gradients were observed by Dutch investigators between locations corresponding with stations S01 and S07 (Heesen and van Zeijl, 1995). Also in the Thames a seaward decreasing trend over a distance of 110 km was noted (Attrill and Thomes, 1995).

3.2.2. Organochlorines

Total CBs showed an upward gradient from Flushing (S01) to Kallo (S18) followed by a decrease in the last station investigated (S22-Antwerp). This was also noted between stations S01 and S07 by Heesen and van Zeijl (1995). CB 153 is one of the most persistent compounds and is often regarded as the most representative CB. With the exception of CB 152, all others in North Sea sediments showed a good

12.

correlation with CB 153 (NSTF, 1993 ; Rowlatt and Davies, 1995). The present study indicated that this was also the case with sediments from the western Scheldt. CB 153 was highly correlated ($r = 0.997$) with ΣCBs_{10} and other CBs (e.g. CB 138) (fig. 6). Although CB 152 is less chlorinated and hence less persistent due to a higher water solubility a high correlation was found in Scheldt sediments (fig. 6). Compared with the open sea, observed CB values could be considered as high. This was also noticed in other estuaries (Ems, Elbe) (NSTF, 1993)

For the other organochlorines, no clear gradients could be observed, except for α -HCH and TDE (fig. 7).

3.3. Enrichment factors

At the demand of the Commission of the Paris Convention, an ad hoc working group has established a series of provisional background / reference concentrations *i.a.* in sediments for several areas (Anon., 1997). These are concentrations from the pre industrial period (mostly box core data). By dividing the present contents of trace metals by the background values enrichment factors can be determined.

3.3.1. Trace metals

For heavy metals concentrations normalised against aluminium were used. The enrichment factors which are related to the North Sea are shown in table 8, together with the background values. These results should be evaluated with caution as sandy sediments may influence data (Anon., 1997). However, they provide a general picture of the increase in concentrations of heavy metals in the present industrial period. Especially the enrichment with mercury and cadmium was found to be very high (up to 191 times) followed by lead and zinc. It should be emphasised that the lowest values, which were all measured in the mouth of the river are in good agreement with the medians found on the Belgian Continental shelf (Guns *et al.*, 1997).

Table 8. Enrichment factors for trace metals in sediment

Metal/Al	Background concentration (ppm/%)	Min.	Max.	Median
Mercury	0,004	7,00	92,50	12,50
Cadmium	0,016	7,50	190,6	20,63
Lead	3,12	1,38	24,29	2,40
Zinc	14,5	1,79	13,38	2,37
Chromium	10,18	1,35	2,97	1,86
Nickel	4,79	1,21	4,09	1,77
Copper	3,61	0,42	5,35	1,19

3.3.2. Organochlorines

Theoretically the background concentrations of these anthropogenic compounds should be zero. In practice however reference values from so-called pristine areas are taken *i.e.* the Iceland/Norwegian Sea, Barents Sea and Spitzbergen/Greenland Sea (Anon., 1997). Table 9 reports the average values for these regions and

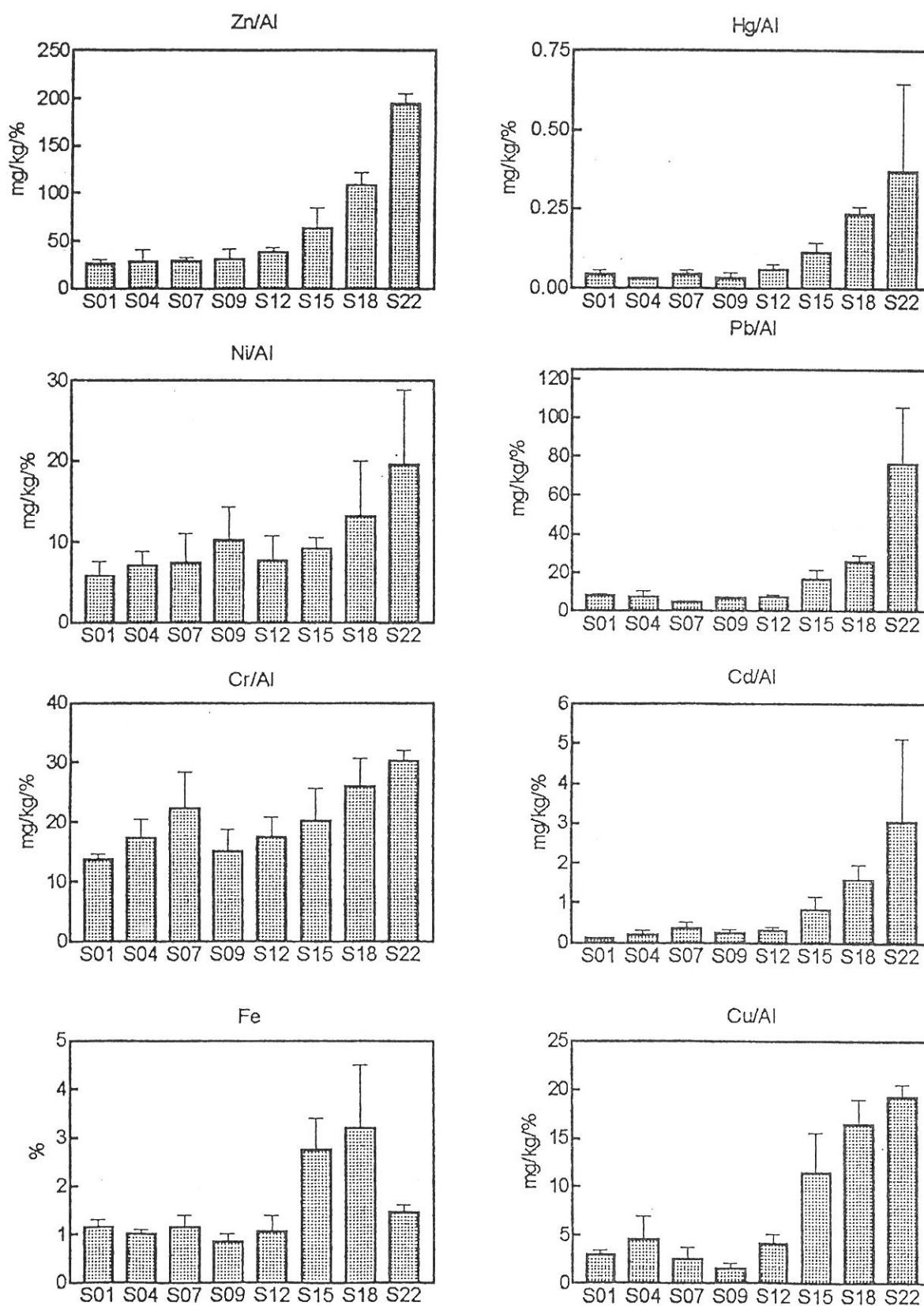


Fig. 3. Normalised concentrations (except iron) on the different stations (averages 1993-95 and standard deviations)

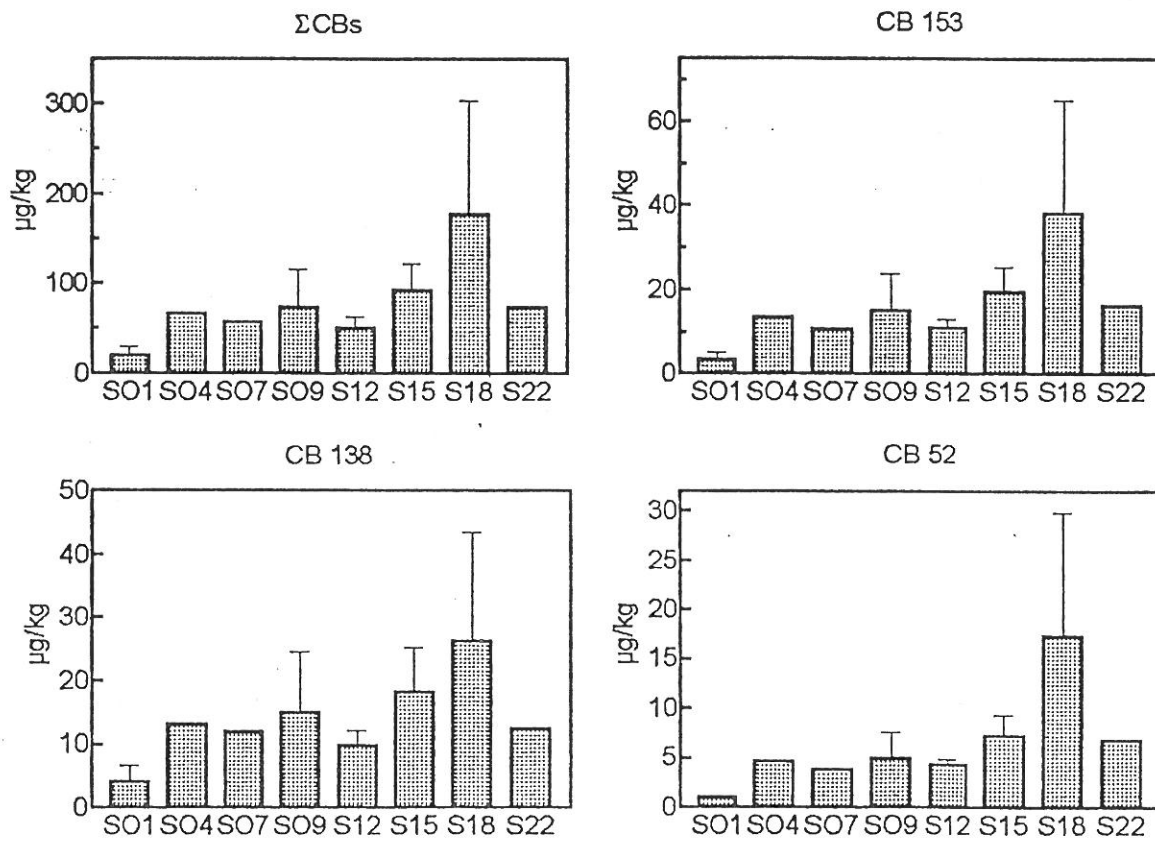


Fig. 5. Concentrations of CBs in sediments from the Scheldt (averages 1993-95 and standard deviations)

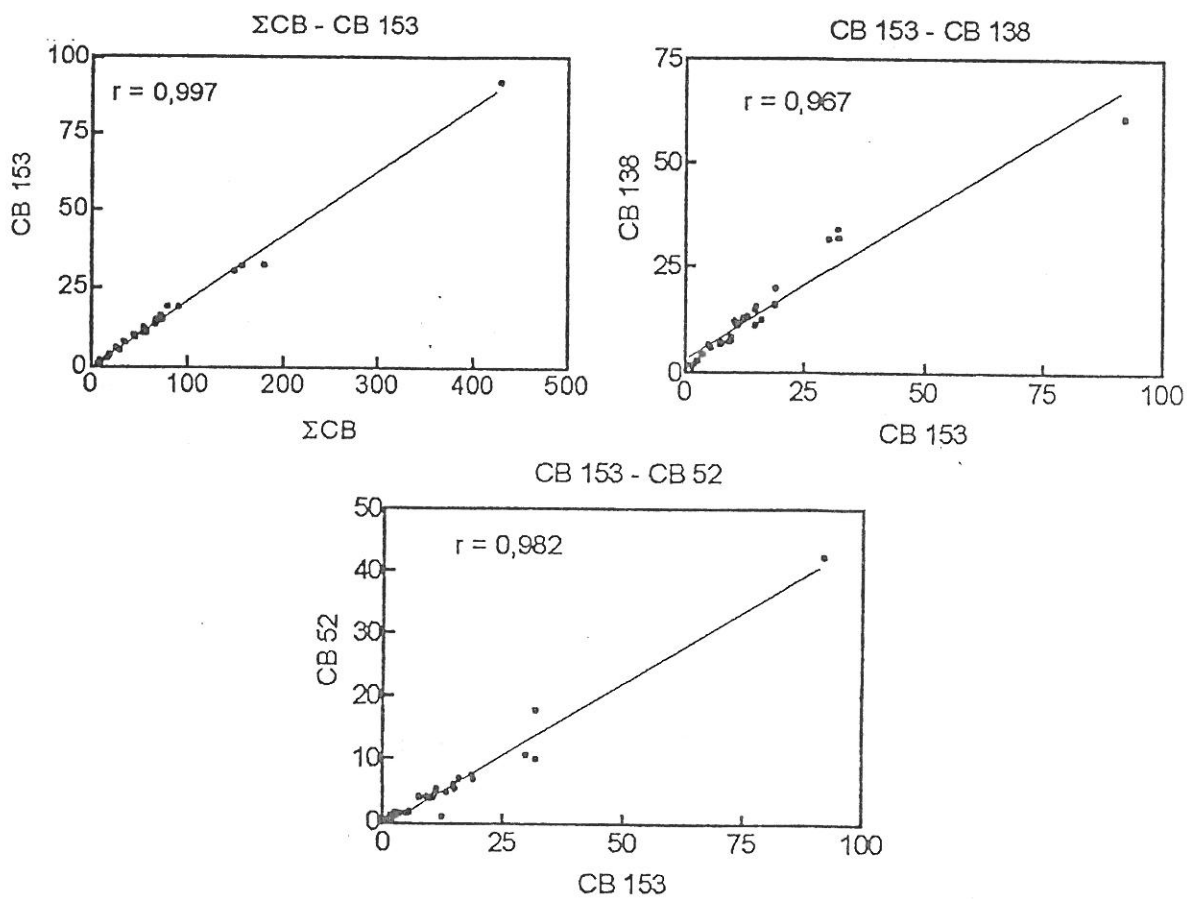


Fig. 6. Correlations between ΣCBs, CB 153, CB 138 and CB 52 (1991-95).

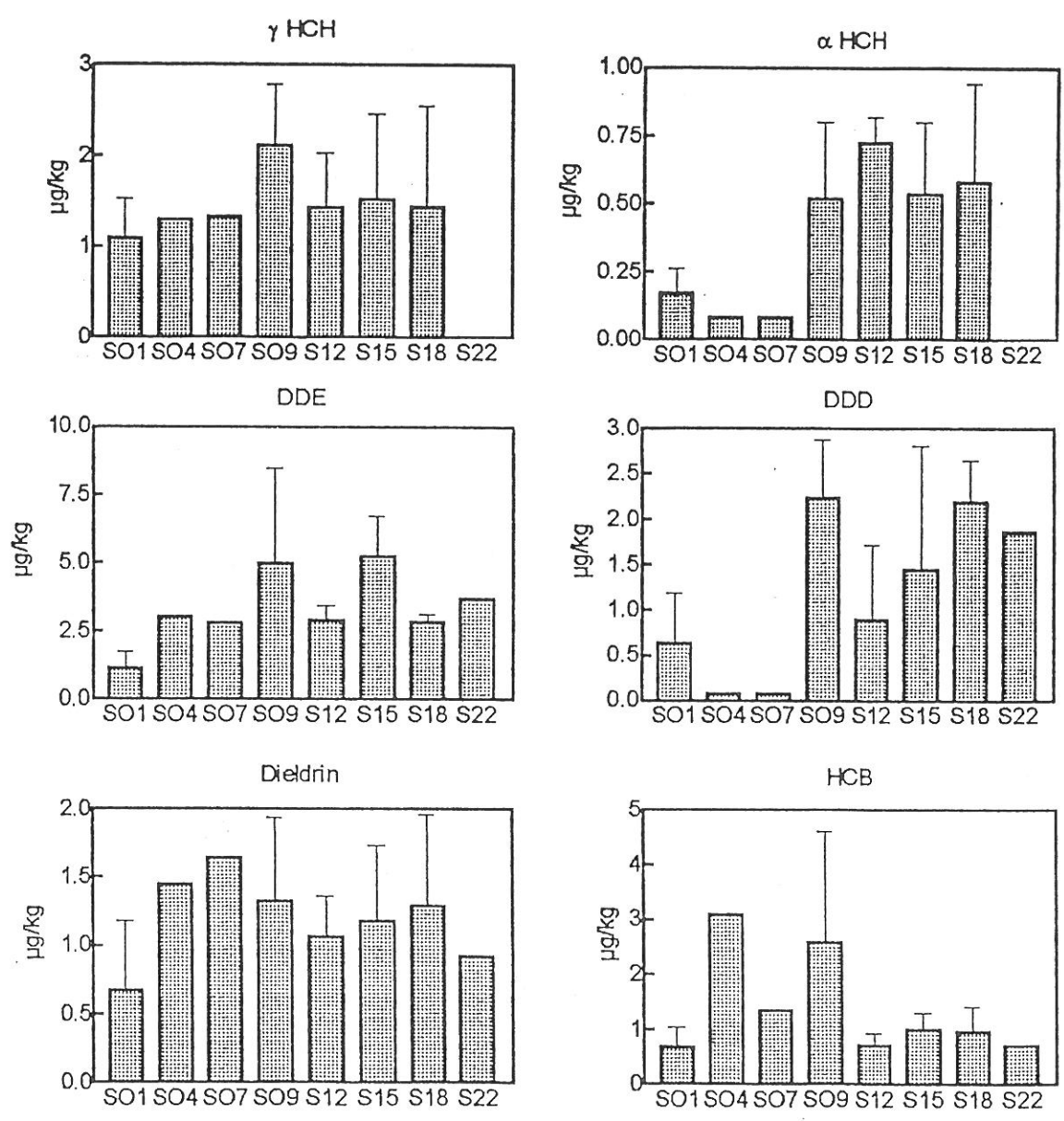


Fig. 7. Concentrations of organochlorines (except CBs) in sediments from the Scheldt (averages 1993-1995 and standard deviations).

the increase in concentrations for CB 153, HCB and DDE (the only compounds available for comparison) in sediments from the Scheldt. It is clear that the contents of these organochlorines are high and that especially CBs are strongly enriched.

Table 9. Comparison of concentrations of organochlorines with reference values

	Reference value ($\mu\text{g}/\text{kg}$ dry weight)	Sediment (increase)
CB 153	0,06	55 - 630 x
HCB	0,14	5 - 21x
DDE-pp	0,10	11 - 52 x

3.4. Ecotoxicological assessment

At the request of the Paris Commission, a working group has established a series of provisional ecotoxicological assessment criteria (EAC) *i.a.* for sediments (Anon., 1997b). The lowest concentration below which no toxicological effects were shown to occur (NOEC : No observed effect concentration) is taken as a criterion (upper limit) and a safety coefficient of 10 is applied (lower limit).

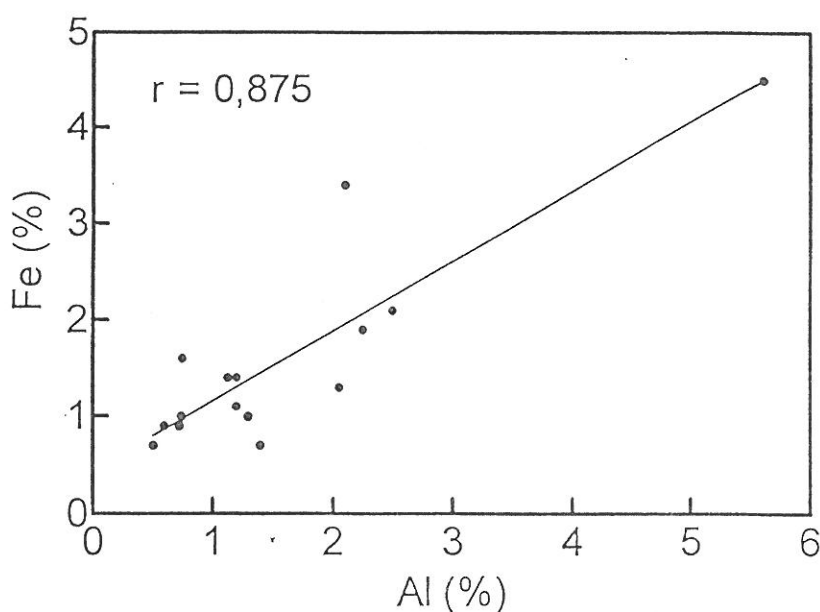


Fig. 4. Correlation between iron and aluminium (< 2000 μm fraction)

3.4.1. Trace metals

Table 10 shows the stations where EAC values were exceeded. For the highest EAC this was only the case on stations S18 and S22, stressing again the fact that this part of the Scheldt, which is situated in an industrial area, is the most polluted. The lowest EAC were exceeded almost everywhere. Only with mercury and zinc this was not the case in the downstream area from station S09 on.

Table 10. Stations exceeding EAC (*)

	EAC	Lowest EAC								Highest EAC								
		SO1	SO4	SO7	SO9	S12	S15	S18	S22	SO1	SO4	SO7	SO9	S12	S15	S18	S22	
Mercury	0.05-0.5					+	+	+									+	
Zinc	50-500																+	+
Copper	5-50		+														+	+
Lead	5-50	+	+														+	
Chromium	10-100	+	+	+														+
Nickel	5-50	+	+	+	+												+	+

(*) EAC : "Ecotoxicological assessment criterium" (mg/kg dry weight)

3.4.2. Organochlorines

For ΣCBs_7 (28, 52, 101, 118, 138, 153, 180) EAC values vary between 1 and 10 $\mu\text{g}/\text{kg}$, corresponding with 1.2 and 12 $\mu\text{g}/\text{kg}$ respectively for the ΣCBs_{10} used in the present survey. These limits were clearly exceeded by the assessed average concentrations (fig. 5). For DDE and dieldrin EAC values are 0.5 and 5 $\mu\text{g}/\text{kg}$ respectively. The lowest value was exceeded but not the highest one (fig. 7). In this respect CBs are again raising the most important problems with regard to contamination of sediments.

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