

CHEMICAL CHARACTERIZATION OF SUSPENSIONS AND SEDIMENTS IN THE NORTH SEA AND SCHELDT ESTUARY.

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SUMMARY

From December 1987 to July 1988, more than 80 sediment and 20 suspension samples were collected in the river Scheldt and along the Belgian coast. The concentration in the bulk and the clay/silt fraction of the following elements was determined using X-ray fluorescence and atomic absorption spectrometry: K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Cd and Hg. The relative abundance of the fractions $<63 \mu\text{m}$ and $<20 \mu\text{m}$ was determined using wet sieving after drastic deflocculation. This method showed to give the most realistic approximation for the real distribution, as well as the most accurate concentrations of the elements in the clay/silt fraction.

For 10 selected samples the total granulometric distribution was obtained by means of dry sieving, wet sieving and Coulter counting. Although the obtained number distributions were all quadratic functions, significant differences in mass distributions were found for samples from different areas. These differences were detected both in the sand and the clay/silt fraction.

The obtained concentrations were interpreted as a function of time and area and normalized to the clay/silt fraction. This results in the identification of two major different populations of sediments in the Belgian coastal zone and the river Scheldt, each ruled by different pollution factors.

Automated electron probe X-ray micro-analysis was used to characterize the individual suspension and sediment particles. The abundance variations of some specific particle types with salinity and as a function of location and time, provide information about geochemical and physical processes. It appeared that 80 % of all the investigated particles contained mostly silicon ($\text{SiO}_2 > 40 \%$) and probably consisted of quartz or diatoms, and K-, Ca- or Fe-rich alumino-silicates. The less abundant particle types were identified as rich in Ti, Fe+P, Fe+S, Fe or Ca. The mixing ratio of marine suspensions with estuarine suspended matter can be estimated by the relative abundance of the calcite particle type. The occurrence of the Fe-rich particle type is important with respect to pollution studies, as it is assumed that high amounts of trace elements are adsorbed and/or coprecipitated with these particles.

RESUME

Une quatre-vingtaine d'échantillons de sédiments et une vingtaine d'échantillons de suspension prélevés dans l'Escaut et dans la Mer du Nord, ont été analysés de manière détaillée pour évaluer les concentrations en matière organique et métaux lourds. Les éléments suivants ont été dosés par fluorescence de rayons X et/ou absorption atomique: K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pd, Cd and Hg, aussi bien dans les échantillons complets que dans la fraction $< 63 \mu\text{m}$. Les contributions relatives des fractions $< 63 \mu\text{m}$ et $< 20 \mu\text{m}$ ont été déterminées par tamisage humide, précédé par une défloculation forte. Cette méthode donne l'approximation la plus réaliste de la distribution réelle.

Pour une dizaine d'échantillons sélectionnés, la distribution granulométrique totale a été déterminée par tamisage à sec, tamisage humide et comptage à l'aide d'un Coulter Counter. Toutes les distributions numériques étaient des fonctions quadratiques, mais

les distributions de masse étaient différentes pour les différentes stations. Les différences en distribution de masse se manifestaient dans les échantillons de sable et d'argile.

Les concentrations obtenues ont été interprétées en fonction du temps et de la location et ont été normalisées par rapport à l'abondance de la fraction $< 63 \mu\text{m}$. Il en résulte l'identification de deux populations majeures des sédiments de la Mer du Nord belge et de l'Escaut, chacune gouvernée par des facteurs de pollution différents.

Des particules individuelles du sédiment et de la suspension ont été caractérisées par des analyses automatiques à l'aide d'une probe-électronique. Les variations des contributions des types de particules spécifiques en fonction de la salinité, la location et le temps, permet d'étudier l'influence des procès géochimiques et physiques. Quatre-vingt pourcent des particules étudiées contenaient principalement Si ($\text{SiO}_2 > 40 \%$) et consistaient probablement de quartz, diatomées et aluminosilicates riches en K, Ca ou Fe. La contribution relative des suspensions marines avec la matière estuarienne peut être estimée par l'abondance relative des calcites. L'occurrence des types de particules riches en Fe est importante pour ce qui concerne les études de pollution, si on envisage les quantités des éléments de traces absorbées ou coprécipitées par ce type de particule.

1 INTRODUCTION

During the transport from their source to the oceans, water-borne heavy metals are influenced by several processes. Sediments act as a reservoir for these metals, even though they can be remobilised by changes in the environmental conditions. Annually millions of tons of sediments are removed artificially from the Scheldt estuary and Belgian coastal waters, and dumped elsewhere, on land or in the sea. These dredged materials require a close and detailed characterization. Special attention was given to metals of the black and the gray list.

2 SAMPLING and ANALYTICAL TECHNIQUES

2.1 Sampling methodology

During four campaigns between December 1987 and July 1988, 80 sediment and 20 suspension samples were collected at 20 different stations along the Belgian coast and in the river Scheldt (Figure 1a). Sediment samples were taken with a box-corer. Only some sub-samples, taken in the central part of the box-corer, with cylindrical tubes of approximately 5 cm diameter, were used, in order to minimize the contaminating effects of the edges of the box-corer. The upper two cm of the sediments in the tubes were analyzed.

The suspension samples were filtered on Nuclepore filters, until an amount of 0.6 - 1.2 mg/cm² was collected on the filter. All samples were immediately frozen.

For the individual particle analysis small aliquots of water, one drop to a few milliliter, were filtered over a 47 mm diameter 0.4 μm pore-size Nuclepore membrane. Care was taken to obtain a sufficient loading for efficient analysis, while maintaining a low percentage (less than 5 %) of overlapping particles (Kelly et al.,

Figure 1a. Sampling locations in the North Sea and the river Scheldt (1987 - 1988).

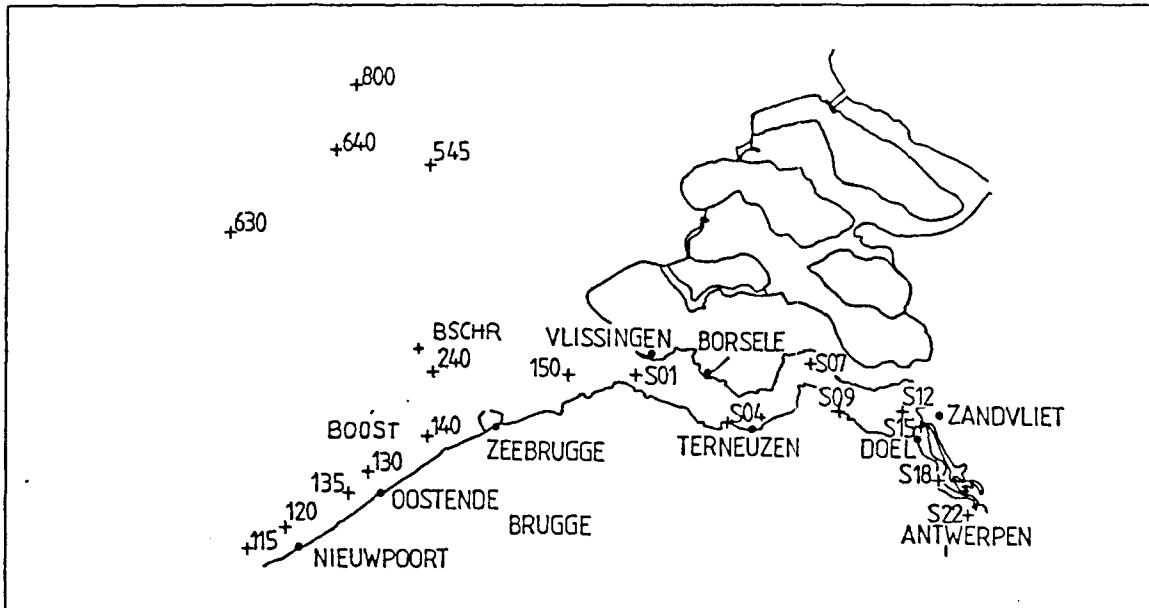
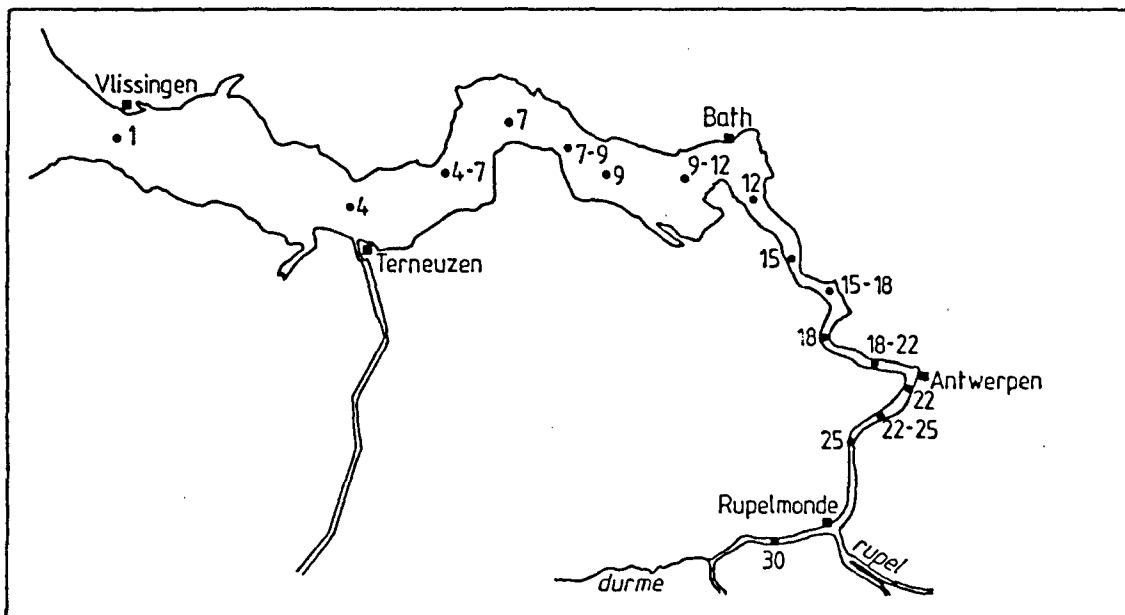


Figure 1b. Sampling locations throughout the Scheldt estuary (Belgium - Netherlands) November 1985, for single particle analysis.



1980). After washing and drying, the filters were coated with carbon. The sampling locations of the longitudinal profile are given in Figure 1b.

2.2 Analytical techniques

(i) X-ray fluorescence: sediment samples were ground in an agate mortar, suspended and filtered on Nuclepore filters up to a loading of 0.6 - 1.2 mg/cm². The sample thickness was determined using the scatter peaks (Van Espen et al., 1979, Araujo et al., 1989). A SPECTRACE 5000 (Tracor Northern) apparatus, with Rh-tube and Rh thin filter was used. The resulting spectra were quantitatively interpreted using two existing computer programs AXIL (Van Espen et al., 1986) and FUND. In the first program the X-ray intensities of the characteristic lines are determined (fitting program) and in the second, intensities are converted into concentrations, absorption phenomena being taken into account.

(ii) Atomic absorption spectrometry: sediment samples were digested with HF, HNO₃ and HClO₄ in Teflon bombs. Fe and Zn concentrations were measured using an air-acetylene flame, at a wavelength and slit of, respectively, for Zn: 213.9 nm, 0.7 nm and for Fe: 248.3 nm, 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-5100 Zeeman instrument. Further analytical specifications are given in Table I. Hg was measured using the cold vapor technique after an amalgamation step.

Table I. Analytical specifications for the AAS measurements.

	Cu	Ni	Pb	Cd
wavelength (nm)	324.8	232.0	283.3	228.8
slit (nm)	0.7	0.2	0.7	0.7
correction	D ₂	D ₂	D ₂	Zeeman
inject. vol.(μl)	5	5-10	20	20
decomp. temp (°C)	1200	1000	750	900
atomis. temp (°C)	2300	2500	2650	1600
matrix modifier	/	/	NH ₄ H ₂ PO ₄	NH ₄ H ₂ PO ₄ , Mg(NO ₃) ₂
graphite tube	pyrol. coated	pyrol. coated	normal	pyrol. coated
platform L'vov	yes	yes	no	yes

(iii) Single particle analysis: the electron probe X-ray microanalysis was performed with a JEOL JXA-733 Superprobe automated with the Tracor Northern TN-2000 system, which is controlled by an LSI 11/23 minicomputer. The microprobe is equipped with a 30 mm² energy-dispersive Si(Li) detector, a wavelength-dispersive detection system, secondary and transmission electron detectors and backscattered electron detectors (for composition and topographic viewing).

For analysis the microprobe was used at an electron energy of 20 keV and a beam current of 1 nA. At these working conditions an optical image resolution of 0.05 μm can be obtained.

The methodology for automated EPXMA of individual particle analysis is described in detail by Raeymakers (1986) and Storms (1988), while the used data treatment methods, for the classification of estuarine particles, were outlined by Bernard et al. (1986).

3 RESULTS

(i) Granulometric determinations.

To determine the effectiveness and accuracy of some separations, different techniques were applied to a sample consisting of more than 95 % of material <63 μm . On the freeze dried sample, the following methods were applied:

- dry sieving (method 1)
- wet sieving (method 2)
- wet sieving after long ultrasonic treatment (> 1h) (method 3)
- wet sieving after treatment with H₂O₂ and short ultrasonic treatment (max. 10 min.) (method 4)

The obtained fractions < 63 μm were then analyzed for their heavy metal concentration. The abundances of these fractions as well as the concentrations are listed in Table II.

Table II. Effectiveness and accuracy of the separation methods.

Method	Abundances of the separated fraction < 63 μm	Apparent concentrations in the fraction < 63 μm			
		Pb ppm	Cu ppm	Ni ppm	Cd ppm
1	9%	142	76	37	9.6
2	12%	136	70	35	10.9
3	93%	110	57	22	6.5
4	96%	155	121	42	13.5
bulk	---	178	127	41	15

Methods 1 and 2 give very poor separations while method 3 and 4 result in good separations. The apparent concentrations also differ. The reason for this may be that, within the size fraction $< 63 \mu\text{m}$, the particles are not uniform in concentration and are disaggregated and recovered differently in the different separation methods, as a function of their size. Indeed, when the fractions $< 63 \mu\text{m}$ isolated by methods 1 and 4, were further wet sieved over a $20 \mu\text{m}$ sieve (after H_2O_2 addition and short ultrasonic treatment), values of 0.37 and 1.85, respectively, were found for the ratio of the apparent weight fractions ($< 20 \mu\text{m}$) / ($20\text{-}63 \mu\text{m}$). It is well known that the heavy metal concentration increases with decreasing particle size, which, in this case, leads to a lower and less accurate apparent heavy metal concentration in the dry sieved separated fraction $< 63 \mu\text{m}$. For wet sieving another possible source of error is that some of the elements may dissolve, especially during prolonged ultrasonic treatment. In view of these two phenomena, method 4 is expected to give the most accurate results. All the samples were thus separated, using method 4, to determine the abundance of the fractions $< 63 \mu\text{m}$ and $< 20 \mu\text{m}$.

The abundance of these fractions varies as a function of location as well as time. For example, at sampling station 130, the fraction $< 63 \mu\text{m}$ ranged from 3 % up to 96 %, for the four different campaigns. This variability, more or less pronounced, was found in almost every sampling station, except in the off-shore ones, and in the two Scheldt samples S07-S09 where a maximum of 3% of material $< 63 \mu\text{m}$ was found. In the next paragraph these results are used to normalize the heavy metal concentrations in the sediments.

For ten selected samples the fraction $< 63 \mu\text{m}$ was counted with a Coulter counter, resulting in a quadratic function for all number distributions (see Figure 2a). The mass distributions, however, showed significant variations for different locations (see Figure 2b).

(ii) Composition of sediment and suspension samples

The analyzed bulk samples can be divided in four zones with different types of sediments and pollution degree, as indicated in Table III. The sediment samples taken offshore in the North Sea consist of coarse sand with low pollution level. Along the coastal zones, sand as well as clay samples were found with a significantly higher degree of pollution. The samples taken in the harbour are clay samples with a high degree of pollution. It makes little sense to calculate mean values for the Scheldt because the situation is so variable, as is illustrated by the high standard deviations. The Scheldt can be divided in different zones too (see Figure 3). The samples taken in the mouth of the Scheldt (S01-S04), clay as well as sand samples, have a higher pollution level than the coastal sediments for all measured heavy metals. The adjacent zone (S07-S09) has a pollution level comparable with the offshore samples.

Figure 2a. Number distribution for one selected sample. N= number of particles.

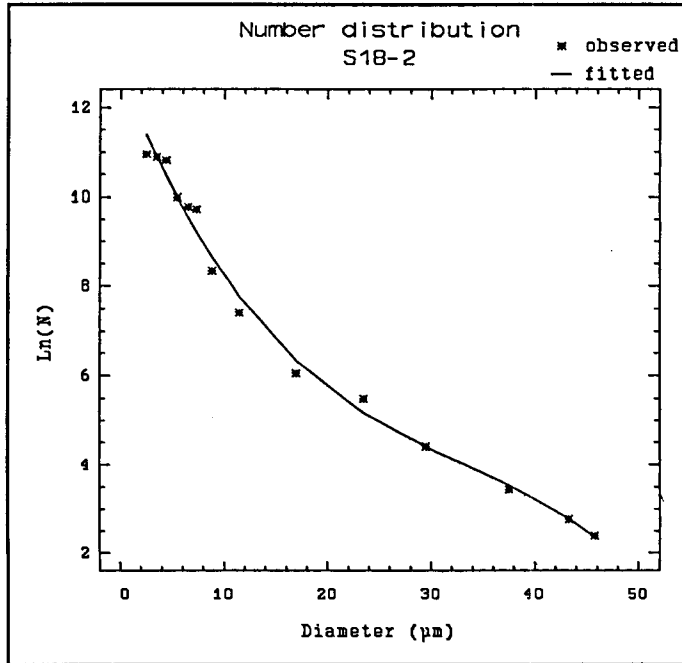


Figure 2b. Mass distributions for two selected shore samples.

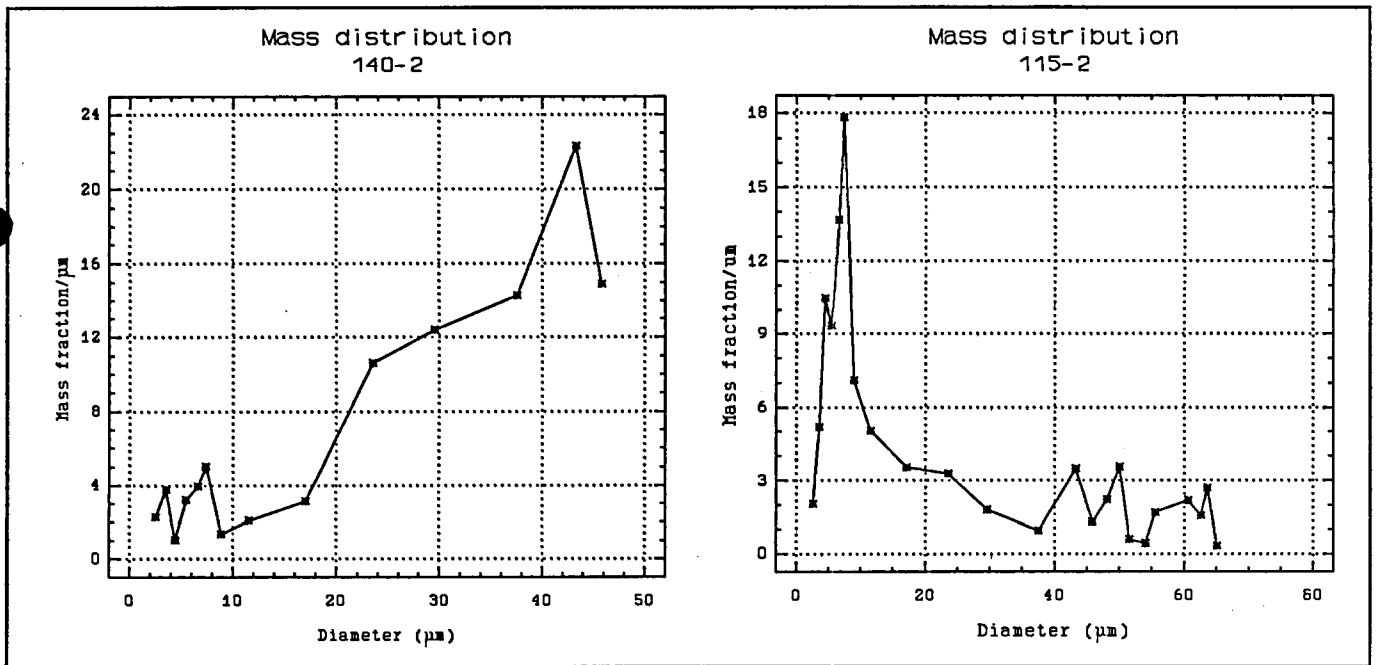
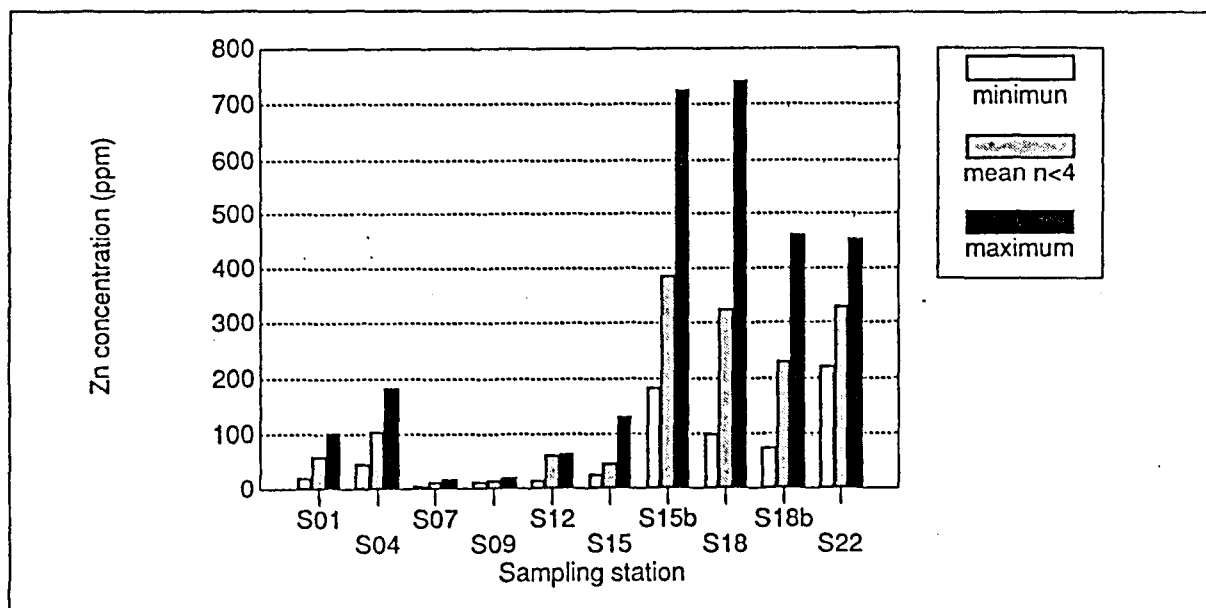


Table III. Different zones in the sampled area.

Location	n	Type	Concentration \pm st. dev. on average				
			Pb ppm	Zn ppm	Cu ppm	Ni ppm	Fe %
sea	16	sand	6 ± 1	9 ± 3	0.74 ± 0.15	2.9 ± 1.1	0.37 ± 0.07
coast	16	clay/sand	14 ± 1	50 ± 14	3.4 ± 0.9	6.8 ± 1.4	0.93 ± 0.24
Scheldt	38	clay/sand	30 ± 32	157 ± 145	19 ± 30	13 ± 14	2.0 ± 0.1
harbour	9	clay	65 ± 40	145 ± 40	14 ± 4	20 ± 7	3.0 ± 0.8

Figure 3. Zn concentration in sediments of the river Scheldt 1987 - 1988.



Closer to the industrial zone, the pollution becomes significantly higher and very variable in time. Comparison of the results with data obtained by the same technique for samples from 1978 to 1984 and data from other laboratories are given in Table IV. However, comparison is not straightforward, due to two main reasons:

- the exact location is very important, especially in the Scheldt
- the data reporting differs from author to author: mean, P_{50} , P_{95} , ranges, bulk, fraction $< 63 \mu\text{m}$, fraction $< 20 \mu\text{m}$, calculated concentration on 50 % $< 20 \mu\text{m}$, etc. are used. This does not allow comparison in detail; however, areas may be compared. This leads to the conclusion that little changes in the concentrations of heavy metals in the sediments of the Scheldt and the North Sea have occurred. The situation has not deteriorated, there may even be an improvement for the coastal zone.

The very variable situation in the Scheldt and some coastal stations leads to local and episodic maxima. Some of them can be explained by granulometric properties, but other by different pollution.

The concentration of heavy metals in sediments is a function of the grain-size distribution. The smaller the sand fraction, the higher the concentrations of heavy metals. To minimize this effect, it is common to analyze only the fraction $< 63 \mu\text{m}$. Since there exist quite some internal differences in this group (see Figure 2), and often a very small and probably unrepresentative amount is isolated, interpretation is not always straightforward. Therefore, correlations between the bulk concentrations and the fraction $< 63 \mu\text{m}$ have been calculated instead (see Table V). Considered over all data, the correlation is poor, which means that other factors than the grain-size distribution play a significant role. When one considers only the North Sea and harbour samples, the correlations are significantly better, and high enough to conclude that similar pollution factors are present in the whole area (see Table V). Comparison of the results of the Scheldt sediments with the obtained regression lines, leads to the identification of a second population of polluted sediments, in which the grain-size cannot explain the heavy metal concentration (see e.g. Figure 4). Almost all these samples are taken in the high turbidity zone around Antwerp, where industry and dumping of urban refuse have a high and direct impact on the pollution degree.

Most of the elements in the suspension samples taken in the Scheldt, show a pronounced variation as a function of location (see e.g. Figure 5). Metals as Cr, V, Fe, Cu, Ni, Zn and Pb increase systematically towards the high turbidity zone of Antwerp, which can be explained by the industrial activities in this area. Other elements like Ca, Br and Sr decrease in the same direction, because the influence of the seawater decreases. The suspensions of the off-shore samples contain significantly less trace elements than the ones of the coast samples. In some of the samples Mo, has been detected.

Table IVa. Comparison of our data for the river Scheldt with previous works.

Ref.	Date	Location	Statistic	Pb(ppm)	Ni(ppm)	Cu(ppm)	Zn(ppm)	Cr(ppm)	Cd(ppm)	Fe(%)	As(ppm)
(1)	1959	Saaftingen	mean	126±11	26±2	71±8	520±44	175±10	6.5±0.6	—	61±6
		Zuid Sloe	mean	103±2	28±1	44±1	299±7	135±3	1.08±0.05	—	30±1
		Zwarte Polder	mean	95±6	26±1	35±2	260±15	115±5	0.62±0.03	—	25±2
		Vlaamse Banken	mean	62±7	16±2	21±2	167±16	75±8	0.59±0.06	—	17±2
	1971	Saaftingen	mean	96±10	25±2	51±3	350±14	174±5	7.2±0.8	—	36±3
		Zwarte Polder	mean	55±1	38±3	18±1	161±4	103±3	0.82±0.02	—	17±1
	1974	Saaftingen	mean	68±2	20±1	46±2	229±9	124±3	4.2±0.2	—	29±1
Doel Antwerp		range	122-290	36-62	81-270	480-950	208-380	—	—	—	
(2)	1974 74-78	Rupel Antwerp	calculated	230	66	165	1080	380	26.4	—	—
		Rupel Antwerp	on 50% <16µm	270	61	180	1015	290	35	—	—
(5)	1981	Hansweert Doel(±)		10	—	2.8	23	—	1.1	—	—
				173	—	112	789	—	18.75	—	—
(7)	78-84	Vliss.-Hansw. Doel-Antwerp	mean	14±2	—	8±1	52±10	48±4	—	0.88±0.06	7.6±0.6
			mean	114±8	—	170±90	469±17	267±12	—	—	58±3
(9)	1979	whole river	mean	87	10	26	844	35	3.4	0.40	—
			max	350	42	250	12060	435	32	3.21	—
			min	7	1	0.6	13	0.3	0	0.06	—
(10)	1984	S01-S09 (±)S12	range	<18	1-9	<12	<55	2.5-7.5	0.3-1.3	—	—
			range	35-60	9-20	12-26	140-270	2.5-15	2.7-7.0	—	—
(11)	1985	mouth-Tern.	mean	8.87	5.54	5.07	27.73	18.4	0.34	—	—
		Tern.-Bath	mean	8.93	6.62	2.85	27.64	20.4	0.78	—	—
		Bath-Antwerp	mean	48.26	13.15	31.83	168	39.2	6.5	—	—
(12)	87-88	whole river	mean	30±32	13±14	19±30	157±145	102±22	2.0±0.6	2.0±0.1	11±2
		S01-S12	mean	15±7	8±4	4±3	51±45	51±6	0.23±0.06	1.1±0.1	5.2±0.7
		S15-S22	range	6-207	5-148	1-282	30-740	67-409	0.04-14	1.4-5.5	3-33

— no data reported.

Table IVb. Comparison of our data for the North Sea with previous works.

Ref.	Date	Location	Statistic	Pb(ppm)	Mn(ppm)	Cu(ppm)	Zn(ppm)	Cr(ppm)	Cd(ppm)
(4)	72-73	sea	range	<10->30	<20-500	<5-15	<20-200	—	—
			most abundant	<10	50-100	<5	<20	—	—
		coast	range	<10->30	50->500	<5->50	20->200	—	—
			most abundant	20-25	>500	20-30	100-200	—	—
(7)	78-84	coast	mean	24±4	261±35	8.7±1.3	59±10	44±6	—
(8)	81-84	coast	< 63 μm	—	—	—	223	69	—
			>500 μm	—	—	—	52	27	—
		sea	< 63 μm	—	—	—	318	65	—
			>500 μm	—	—	—	27	12	—
(6)	77-78	mouth Scheldt	mean	60	—	30	169	110	0.4
		coast	mean	73	—	28	82	122	1.0
		whole area	range	52-102	—	16-27	127-220	95-134	0.5-1.2
(12)	87-88	sea	mean	6±1	97±47	0.74±0.52	9±3	18±7	0.03±0.01
		coast	mean	14±1	265±182	3.4±0.9	50±14	45±24	0.23±0.05

Ref.	Date	Location	Statistic	Fe(%)	Ni(ppm)	Ti(%)	V(ppm)	Hg(ppb)	As(ppm)
(4)	72-73	sea	range	<0.5->2.5	—	—	—	—	—
			most abundant	0.5-1.0	—	—	—	—	—
		coast	range	<0.5-2.5	—	—	—	—	—
			most abundant	2.0-2.5	—	—	—	—	—
(7)	78-84	coast	mean	1.0±0.1	11±2	0.12±0.01	48±6	—	9.4±0.8
(8)	81-84	coast	< 63 μm	2.5	—	0.23	90	—	—
			>500 μm	0.97	—	0.13	47	—	—
		sea	< 63 μm	2.4	—	0.23	97	—	—
			>500 μm	0.45	—	0.06	28	—	—
(6)	77-78	mouth Scheldt	mean	—	—	—	—	214	36
		coast	mean	—	—	—	—	545	22
		whole area	range	—	—	—	—	135-545	20-24
(12)	87-88	sea	mean	0.37±0.7	2.9±1.1	0.043±0.004	33±4	21±11	4±2
		coast	mean	0.93±0.25	6.8±1.4	0.13 ±0.02	46±5	140±36	5±2

— no data reported.

Table IVc. Comparison of our data for the harbours with previous works.

Ref.	Date	Location	Statistic	Pb(ppm)	Ni(ppm)	Cu(ppm)	Zn(ppm)	Cr(ppm)	Cd(ppm)	Fe(%)
(1)	1974	Vlissingen	mean	70±4	26±2	35±3	186±9	107±6	0.8 ±0.1	—
		Sloehaven	mean	73±3	27±3	30±3	201±24	106±5	1.5 ±0.3	—
		Handelshaven van Breskens	mean	48±12	17±3	23±5	138±30	87±10	0.9 ±0.2	—
		Veerhaven van Breskens	mean	56±3	21±1	28±2	160±1	90±2	0.93±0.07	—
(3)	75-79	Antwerp	mean	13	—	5.0	344	16	3.0	1.6
			<i>P</i> ₅₀	3	—	0.9	194	1.1	0.7	1.9
			<i>P</i> ₉₅	71	—	21.4	1315	65	15.4	2.4
(12)	87-88	Nieuwpoort	mean	44±16	16±6	32±21	115±34	108±5	0.42±0.02	2.10±0.85
		Oostende	mean	90±1	22±6	40±28	228±92	93±24	1.7 ±0.7	2.61±0.55
		Zeebrugge	mean	69±6	21±1	15±1	170±24	87±20	0.80±0.10	2.86±0.22
		Blankenberghe	mean	58±5	21±2	12±3	176±7	111±6	0.69±0.12	2.97±0.07

— no data reported.

(1) Anonymous, 1975.

(2) Salomons and Eysink, 1981.

(3) Senten and Charlier, 1984.

(4) Wollast, 1976.

(5) Baeyens et al., 1982.

(6) Anonymous, 1983.

(7) Araujo et al., 1988.

(8) D'Hondt and Baeteman, 1987.

(9) Buekens and Dhaese, 1980.

(10) Reynders, 1985.

(11) Termerman, 1988.

(12) This work.

Figure 4. Zn bulk concentration versus the abundance of the fraction < 63 μm . OOST-1 is a sample taken in the harbour of Oostende.

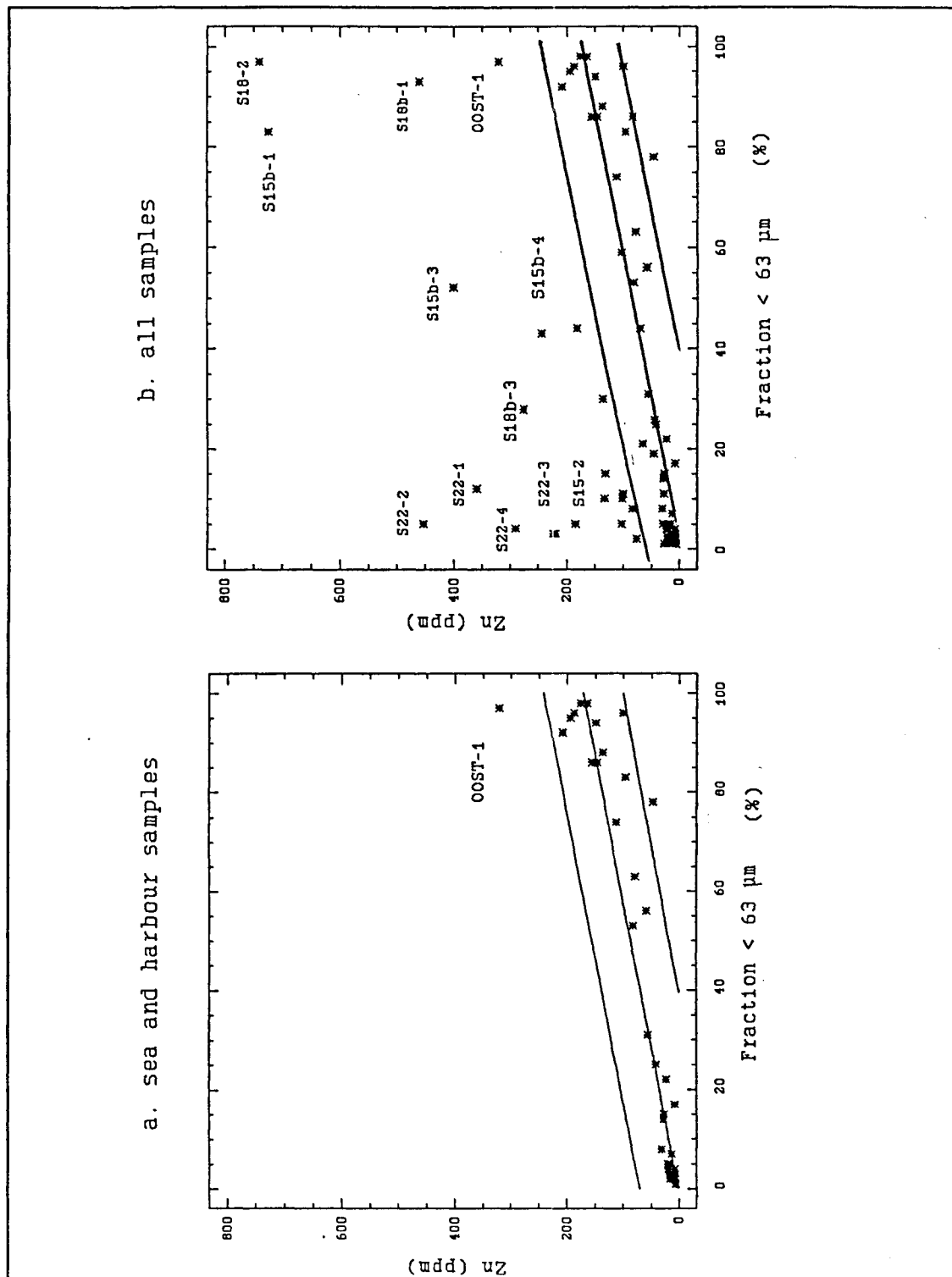
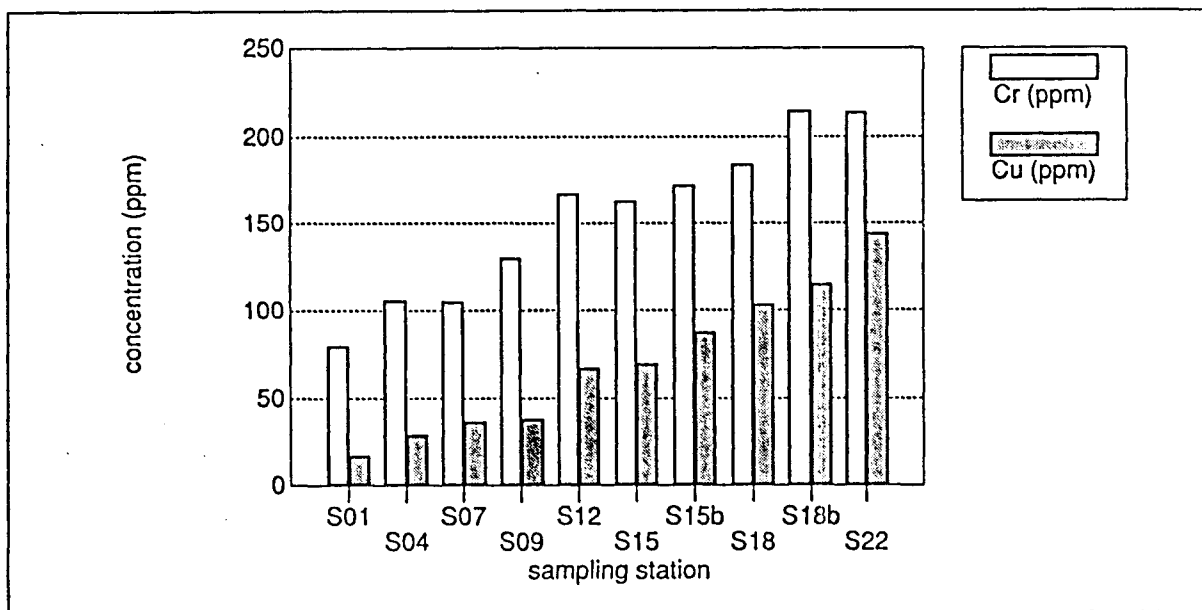


Table V. Correlations between the abundance of the fraction < 63 μm and the bulk elemental concentration.

Correlations			
Element	All samples	North Sea/harbours	Scheldt
Pb	0.56	0.89	0.65
Zn	0.50	0.90	0.65
Ni	0.53	0.85	0.71
Cu	0.41	0.53/0.87	0.66
Hg	0.67	0.89	/
Fe	0.54	0.91	0.53

Figure 5. Cu and Cr concentration in suspensions of the river Scheldt 1987 - 1988.



(iii) Individual particle analysis.

The results of the automated EPXMA are given in Table VI, which lists the average composition of the different particle types identified by cluster analysis, and in Table VII which gives the relative abundance of each of the particle types in every sample.

As seen from Table VI, thirteen particle types were retained. The Si-rich particle types ($\text{SiO}_2 > 40\%$), particle types 1 to 6, account for 81 % of the measured particles. They consist of a quartz and/or diatom group, and a number of aluminosilicate groups. The four last aluminosilicate groups are respectively rich in K, Fe+K, Fe and Ca. Besides these Si-rich particle types, Fe, Ca+Fe+P, Fe+S, Ca and Ti-rich particle types were identified.

None of the identified groups showed systematic abundance variations throughout the estuary, except for the calcite and/or aragonite particle type of which the abundance increases gradually seaward, a phenomenon which was also found in the Ems estuary (Bernard et al., 1986). But while the abundance of the CaCO_3 group at the Ems downstream stations increased steadily, the abundance of the CaCO_3 particle type in the Scheldt fluctuates significantly. For sample station 1, where two samples were taken with a 50 min time difference, significant abundance variations up to 10 % were measured.

At the most upriver sampling station, number 30, the calcite and/or aragonite particle type reaches its minimum while the Fe+K-rich aluminosilicates group, particle type number 4, reaches its maximum. It is however not clear whether this is an indication of the influence of river derived material on the composition of the estuarine suspended matter. Actually sample station number 30 cannot be taken as an end-member as it is not possible to determine the river suspended particulate matter unambiguously. Therefore it is necessary to sample further upriver than station 30, to characterize the pure river material.

Throughout the whole estuary, Fe, Fe+P and Fe+S rich particle types, respectively numbers 12, 7, 8 and 9, have a mean relative abundance below 3 %. No systematic abundance variations were found for these particle types. This is probably a direct result of the abundance variations of the more abundant Si and Ca-rich particle types, influencing relatively the abundance of the other groups. The occurrence and distribution of Fe-rich particles are important with respect to pollution studies, as the iron oxides/hydroxides (Sing and Subramanian, 1984) are scavengers for heavy metals.

Table VI. Average composition of the particle types (normalised to 100%), for the whole Scheldt estuary (1985). MAD = maximum diameter; MID = minimum diameter; AVD = average diameter; SF = shape factor; () = standard deviation on the measurement.

Group No.	% Abun.	SiO ₂ %	Al ₂ O ₃ %	CaO %	Fe ₂ O ₃ %	MgO %	Na ₂ O %	K ₂ O %	TiO ₂ %	Cl %	S %	P %	MAD μm	MID μm	AVD μm	SF
1	18	92 (5)	1 (2)	0.8 (1.1)	1.0 (1.3)	0.2 (0.5)	0.1 (0.3)	0.9 (1.2)	1 (1)	2 (1)	1.1 (1.2)	0.2 (0.5)	2 (2)	1.2 (1.3)	1.5 (1.6)	1.5 (0.8)
2	11	72 (6)	11 (5)	2.4 (2.6)	5 (4)	0.8 (1.1)	0.5 (0.7)	4 (3)	1 (2)	1 (2)	1 (2)	1.0 (1.2)	3 (2)	1.2 (1.1)	1.7 (1.5)	1.8 (0.8)
3	8	58 (6)	14 (6)	2 (2)	2 (2)	1 (1)	0.1 (0.4)	19 (5)	1 (2)	0.9 (1.7)	1.1 (1.7)	0.6 (0.9)	2.4 (2.3)	1.3 (1.3)	1.7 (1.6)	1.5 (0.6)
4	33	58 (5)	17 (6)	3 (3)	8 (4)	1.3 (1.6)	0.4 (0.6)	5.5 (3.5)	1.3 (2.2)	2 (3)	1.9 (2.4)	1.5 (1.7)	2.8 (2.5)	1.3 (1.2)	1.9 (1.7)	1.7 (0.7)
5	8	47 (7)	13 (5)	4 (4)	21 (7)	3 (2)	0.5 (0.8)	5 (4)	1 (3)	2 (3)	2 (3)	3 (2)	2 (2)	1 (1)	1.6 (1.4)	1.6 (0.6)
6	3	42 (7)	12 (5)	14 (10)	8 (5)	1.5 (1.6)	2 (1)	4 (3)	3 (4)	7 (9)	3 (4)	4 (4)	3.4 (3.4)	1.5 (1.7)	2.3 (2.4)	1.8 (0.9)
7	3	12 (6)	4.1 (2.7)	9 (6)	65 (10)	2 (1)	0.3 (0.2)	1 (2)	1 (2)	1 (2)	1 (3)	3 (3)	2.0 (1.5)	1 (1)	1.5 (1.2)	1.3 (0.3)
8	2	14 (9)	4 (3)	16 (7)	35 (8)	1.5 (1.3)	1.2 (0.9)	2 (3)	1.7 (2.4)	3 (4)	2 (4)	19 (9)	2.0 (1.6)	0.9 (0.9)	1.3 (1.1)	1.8 (0.8)
9	2	3 (4)	0.8 (1.1)	1 (2)	33 (4)	0.1 (0.4)	0.2 (0.5)	0.2 (0.8)	0.3 (0.7)	0.1 (0.7)	61 (5)	0.3 (0.7)	1.3 (1.1)	0.9 (0.7)	1.1 (0.9)	1.2 (0.2)
10	7	4 (3)	2 (1)	88 (5)	0.8 (1.2)	2 (1)	0.2 (0.2)	1 (1)	0.7 (1.1)	0.4 (0.9)	0.9 (1.4)	0.7 (1.3)	3.2 (2.4)	1.7 (1.4)	2.3 (1.7)	1.4 (0.5)
11	1	15 (8)	4 (3)	58 (11)	4 (5)	5 (5)	0.4 (0.5)	1.8 (2.7)	1 (2)	2 (3)	3 (5)	6 (8)	3 (2)	1.3 (1.1)	1.8 (1.5)	1.5 (0.4)
12	1	8 (5)	3 (2)	1.0 (1.5)	3 (4)	0.6 (0.6)	0.3 (0.3)	0.8 (1.3)	81 (9)	0.5 (0.9)	0.7 (1.5)	0.6 (1.1)	1.6 (1.2)	0.9 (0.7)	1.1 (0.8)	1.4 (0.5)
13	0.7	21 (11)	6 (5)	7 (9)	9 (10)	1 (2)	1.3 (1.4)	3 (4)	4 (9)	7 (8)	38 (9)	2 (3)	4 (3)	1 (1)	2.1 (1.6)	1.9 (0.9)

Table VII. Abundance of the particle types at each sample station for the Scheldt estuary (1985). () = standard deviation on the measurement.

Group No.	% Abundance for each sampling station																
	1	1b	1	1-7	7	7-9	9	9-12	12	15	15-18	18	18-22	22	22-25	25	30
1	20 (2)	19 (2)	18 (2)	20 (2)	21 (2)	13 (2)	15 (2)	16 (2)	16 (2)	18 (2)	17 (2)	16 (2)	15 (2)	18 (2)	29 (3)	19 (2)	18 (2)
2	13 (2)	13 (2)	12 (2)	16 (2)	16 (2)	11 (2)	5 (1)	9 (2)	11 (2)	11 (2)	8 (2)	11 (2)	15 (2)	11 (2)	14 (2)	10 (2)	7 (2)
3	8 (2)	7 (2)	9 (2)	6 (1)	10 (2)	8 (2)	8 (2)	10 (2)	8 (2)	7 (2)	9 (2)	10 (2)	5 (2)	7 (1)	9 (2)	9 (2)	7 (2)
4	30 (3)	28 (3)	26 (3)	35 (3)	32 (3)	31 (3)	35 (3)	30 (3)	37 (3)	35 (3)	30 (3)	38 (3)	34 (3)	37 (3)	26 (3)	35 (3)	49 (3)
5	6 (1)	6 (1)	9 (2)	6 (1)	4 (1)	5 (1)	7 (1)	12 (2)	8 (2)	8 (2)	9 (2)	8 (2)	11 (2)	11 (2)	10 (2)	10 (2)	11 (2)
6	2 (1)	4 (1)	3 (1)	2 (1)	3 (1)	1 (1)	9 (2)	2 (1)	2 (1)	3 (1)	2 (1)	1 (1)	2 (1)	4 (1)	2 (1)	4 (1)	1 (1)
7	3 (1)	1 (1)	2 (1)	3 (1)	2 (1)	4 (1)	2 (1)	5 (1)	2 (1)	4 (1)	2 (1)	2 (1)	2 (1)	3 (1)	2 (1)	3 (1)	2 (1)
8	7 (2)	0.4 (0.4)	0 (0)	1 (1)	0.7 (0.5)	2 (1)	4 (1)	2 (1)	3 (1)	2 (1)	5 (1)	5 (1)	3 (1)	1 (1)	0.8 (0.6)	1 (1)	2 (1)
9	0.3 (0.3)	0.7 (0.5)	1 (1)	0.7 (0.5)	2 (1)	0.7 (0.5)	2 (1)	3 (1)	2 (1)	3 (1)	5 (1)	2 (1)	0.3 (0.3)	2 (1)	1 (1)	0.7 (0.5)	0.7 (0.5)
10	7 (2)	16 (2)	17 (2)	7 (2)	6 (1)	15 (2)	8 (2)	8 (2)	7 (2)	5 (1)	7 (2)	4 (1)	6 (1)	1 (1)	0.8 (0.6)	4 (1)	0.3 (0.3)
11	0.7 (0.5)	1 (1)	2 (1)	1 (1)	1 (1)	5 (1)	0.9 (0.5)	1 (1)	2 (1)	2 (1)	3 (1)	0.3 (0.3)	1 (1)	0.7 (0.5)	2 (1)	0.3 (0.3)	0.7 (0.5)
12	0.7 (0.5)	0.7 (0.5)	0.9 (0.5)	0.7 (0.5)	0.3 (0.3)	0.3 (0.3)	0.6 (0.4)	0.9 (0.5)	0.3 (0.3)	0.7 (0.5)	2 (1)	1 (1)	2 (1)	1 (1)	3 (1)	0.7 (0.5)	0.3 (0.3)
13	0.3 (0.3)	3 (1)	0 (0)	0 (0)	0.3 (0.3)	0 (0)	0.3 (0.3)	0.9 (0.5)	1 (1)	0.3 (0.3)	0.7 (0.5)	0 (0)	2 (1)	0.3 (0.3)	0 (0)	0.7 (0.5)	0.3 (0.3)

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