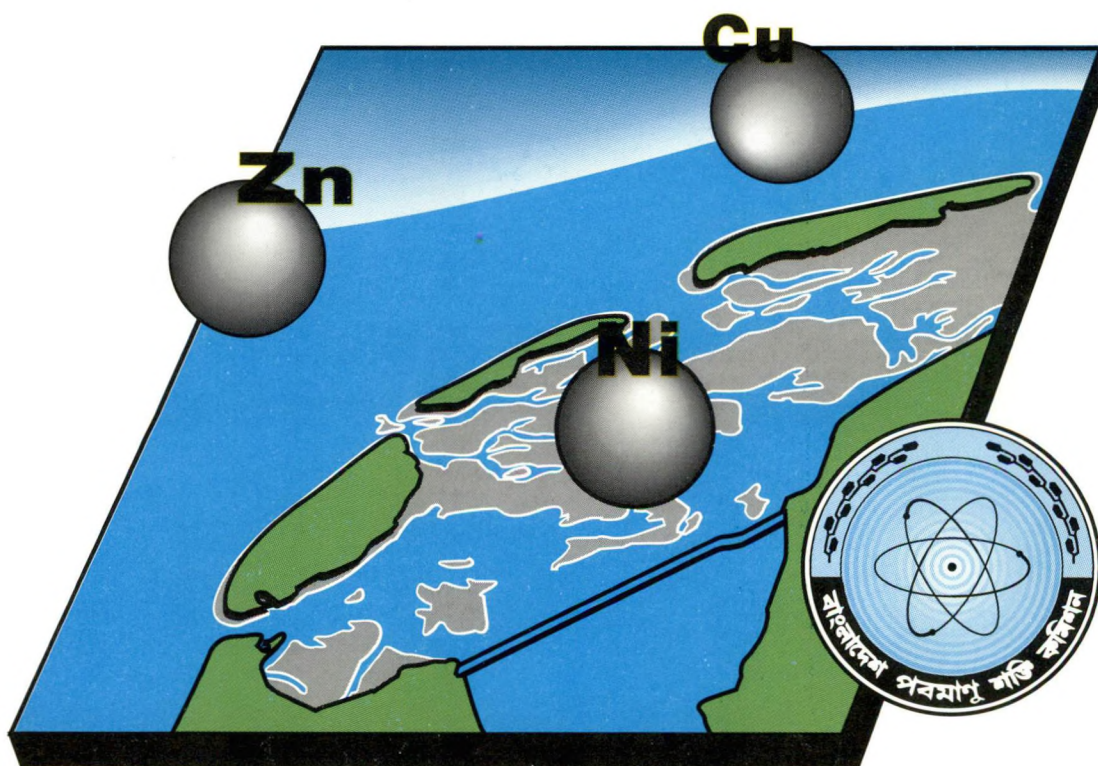


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**TRACE ELEMENT GEOCHEMISTRY AT THE SEDIMENT-WATER
INTERFACE IN THE NORTH SEA AND THE WESTERN WADDEN SEA**

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TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

SUMMARY AND CONCLUSIONS

Trace element geochemistry was studied at the sediment-water interface in the southern North Sea (NS, Frisian Front, Oystergrounds, outer German Bight) and the western Dutch Wadden Sea (WS). The core profiles (0-26 cm) of redox and trace elements (Mn, Fe, Cr, Ni, Cu, Zn, Cd and Pb) in the exchangeable and residual fractions of the sediments and the pore water (Mn, Fe, Cu, Zn, Cd and Pb) were investigated in 1991, in four stations in the NS (38-44 m) and five stations in the WS (2-5 m). The major element (Mg, Al, Si and Ca) composition of the bulk sediments and the clay mineral composition of their fine fractions ($< 10 \mu\text{m}$) were also determined in these two study areas.

From the spatial distribution of trace and major elements in the NS sediments, it is clear that all the stations have individual characteristics and that some of them (NS1 and NS3) have records of Cd and Pb accumulation. The profiles of Mn and Fe of most of the stations indicate approximate steady state conditions of geochemical processes. The oxidized conditions of the sediment is evidenced by the higher proportion of acid leachable fractions of Fe- and Mn-oxyhydroxides.

Organic carbon diagenesis and formation of calcite minerals influence the distribution of Cu and Ni only at some NS stations whereas the diagenetic response of Cr and Zn appears to be similar at all the stations. The Cu and Zn profiles were very homogeneous and no clear vertical trends were observed. Nevertheless, anthropogenic inputs of these elements were recorded at some of the stations.

The profiles of trace metals in the surface sediments of the western Wadden Sea indicate the dynamic states of geochemical processes generally observed in tidal flat areas. All the stations in this estuarine area have strongly varying chemical characteristics and they greatly differ from those in the North Sea. However, two stations of both the areas (WS3, NS2) have comparable records of trace element accumulation indicating equal basical geochemical processes and inputs.

The oxidation of Mn and Fe is very much pronounced in the Wadden Sea resulting in the precipitation of Fe- and Mn-oxyhydroxides in the surface layers. At some stations covariation of redox and trace elements with calcite (CaCO_3) was observed. Apart from WS4, surface enrichment of Cr, Ni, Cu, Cd and Pb was found at all stations.

From the solid phase profiles of Mn, Fe and Cd (WS2-WS5) redox transitions appear at ca. 3 cm below the sediment-water interface. No compression of this boundary towards the surface was observed. This feature is strikingly similar to the diagenetic reactions observed in much deeper marine systems.

In the Wadden Sea, non-steady state redox conditions are reflected in the pore water profiles of Mn and Fe. Near the sediment-water interface, enrichment of Fe in the leachable fraction of the solid phase corresponds to depletion of Fe in pore water near the surface. In the North Sea, weak oxic/sub-oxic conditions were observed at all stations. The observed increase of Cu, Cd and Pb in the pore waters at the sediment-water interface may be due to the release during organic matter decomposition. Below the interface, the concentration of Cu, Cd and Pb are sulphide dependent and their increase in the pore water may be related to release from organic complexes. For Zn some degree of enrichment was found at the interface, possibly originating from the degradation of organic matter. Below the surface, a patchy profile of Zn was obtained for most of the stations.

The association of trace elements with clay minerals present in the fraction $< 10 \mu\text{m}$ of the sediments was studied after two stage sequential extraction (0.5M oxalic acid and 0.1M HCl). Also the clay mineral composition was identified. The extraction results indicate that the trace elements are associated with two groups of minerals: crystalline minerals such as illite, chlorite and possibly smectite and poorly crystalline minerals such as ferrihydrite, akaganeite and opal. The oxalic acid extraction dissolves the amorphous minerals more selectively, thereby removing Cr, Ni, etc. while HCl dissolves the crystalline minerals more favourably and removes trace elements like Cu, Cd and Pb.

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1. INTRODUCTION

Marine sediments are the ultimate depository of many chemical compounds including trace metals from natural and anthropogenic sources. A quantitative analysis of sediments can reflect upon the current features of a marine system. Whether the sediment behaves as a sink or source of metals, depends on the dynamics of the biogeochemical processes that occur at the sediment-water interface under oxic/anoxic conditions (SANTSCHI *et al.*, 1990; FORSTNER, 1983). These processes are particularly pronounced in estuaries and shelf seas where materials moving from the continent to the ocean can be trapped or mobilized. Sedimentary fluxes and remobilization of chemical elements (NRIAGU, 1991) influence global mass balances. Therefore the study of the early diagenesis of trace elements in nearshore environments is important to construct elemental mass balances for the coastal zones as well as the oceans. Pore water trace element chemistry is, however, still not fully understood due to the lack of consistent datasets for solid and liquid phases, including speciation (ELDERFIELD, 1981; SALOMONS & FORSTNER, 1984; HELDER, 1989). The different physico-chemical properties of trace elements and their possible relation to the mineralogy of the sediments determine their (bio)geochemical behaviour including biological uptake (WELLS *et al.*, 1991), adsorption-desorption (FULLER & DAVIS, 1987; BOURG, 1987), sedimentary input and subsequent removal through resuspension, etc.

From the point of toxicity, trace element geochemistry of particularly the transition elements, may become relevant in determining primary productivity in coastal zones (SHAW *et al.*, 1990; WINDOM *et al.*, 1991). Moreover, the pore water geochemistry of the upper sediment layers provides the link between the water column and the sedimentary accumulation and burial of trace metals. For many trace metals redox conditions are the key factor controlling geochemistry at the sediment-water interface (PRESLEY *et al.*, 1972; KLINKHAMMER, *et al.*, 1982; KLINKHAMMER, 1980).

In view of the economic importance of coastal regions and the adverse effects of metal pollution on living resources and water quality, it is not surprising that considerable efforts have been devoted in many laboratories to develop a better understanding of the geochemical processes regulating trace metals in marine interstitial waters and solid phases (e.g. LYONS & FITZGERALD, 1982; HELDER, 1989). These studies utilize a variety of specialized and well developed reliable analytical methodologies

(NOLTING & HELDER 1991; CHESTER & VOUTSINOY, 1981), field measurements, controlled laboratory experiments and modelling approaches to quantitatively describe the cycling of trace elements under different environmental conditions (ZUTIC, 1991; GUOHUI *et al.*, 1988; WILHELMY & FLEGAL, 1991; DE BAAR *et al.*, 1988).

The present investigation aims at geochemical processes that influence the distribution of trace elements between sediment and interstitial water under different depositional conditions. Consistent datasets on solid phase and pore water profiles of Mn, Fe, Cr, Ni, Cu, Zn, Cd and Pb from in total 9 stations in the western Wadden Sea and the southern North Sea were obtained. The major element composition of the bulk sediments was identified by analyzing the Ca, Mg, Al and Si contents of the sediments. Both the labile and the non-labile fractions of the solid phase have been measured after acid leaching. The clay mineral composition of the fine fraction (< 10 µm) of the sediments was analyzed to study the association of trace elements with clay minerals.

2. THE STUDY AREA

The locations of the stations in the North Sea (NS) and the western Wadden Sea (WS) are indicated in Fig. 1 and 2, respectively.

2.1. NORTH SEA

The North Sea is of primary economic importance for a large sector of north-west Europe. It receives large volumes of anthropogenic and natural wastes from the highly industrialized countries surrounding this semi-enclosed water body with ill-defined boundaries (ICES, 1974). The mean water residence time of the entire North Sea is ca. 2-3 years. The southern part is shallow and has major fresh water inputs, particularly from the river Rhine. On the basis of water depths, the North Sea can be divided into three regions (EISMA, 1990). The water depth in the southern shallow area reaches 50 m, the deeper central part has a water depth of about 100 m, while in the northern part, the average water depth is about 200 m.

The water from the Rhine disperses in a northeastern direction. The water column in the southern North Sea is well extended from the surface to the sea bed (REID *et al.*, 1988). The suspended particulate matters concentrate and deposit in a few specific areas including the Wadden Sea and the Oystergrounds.

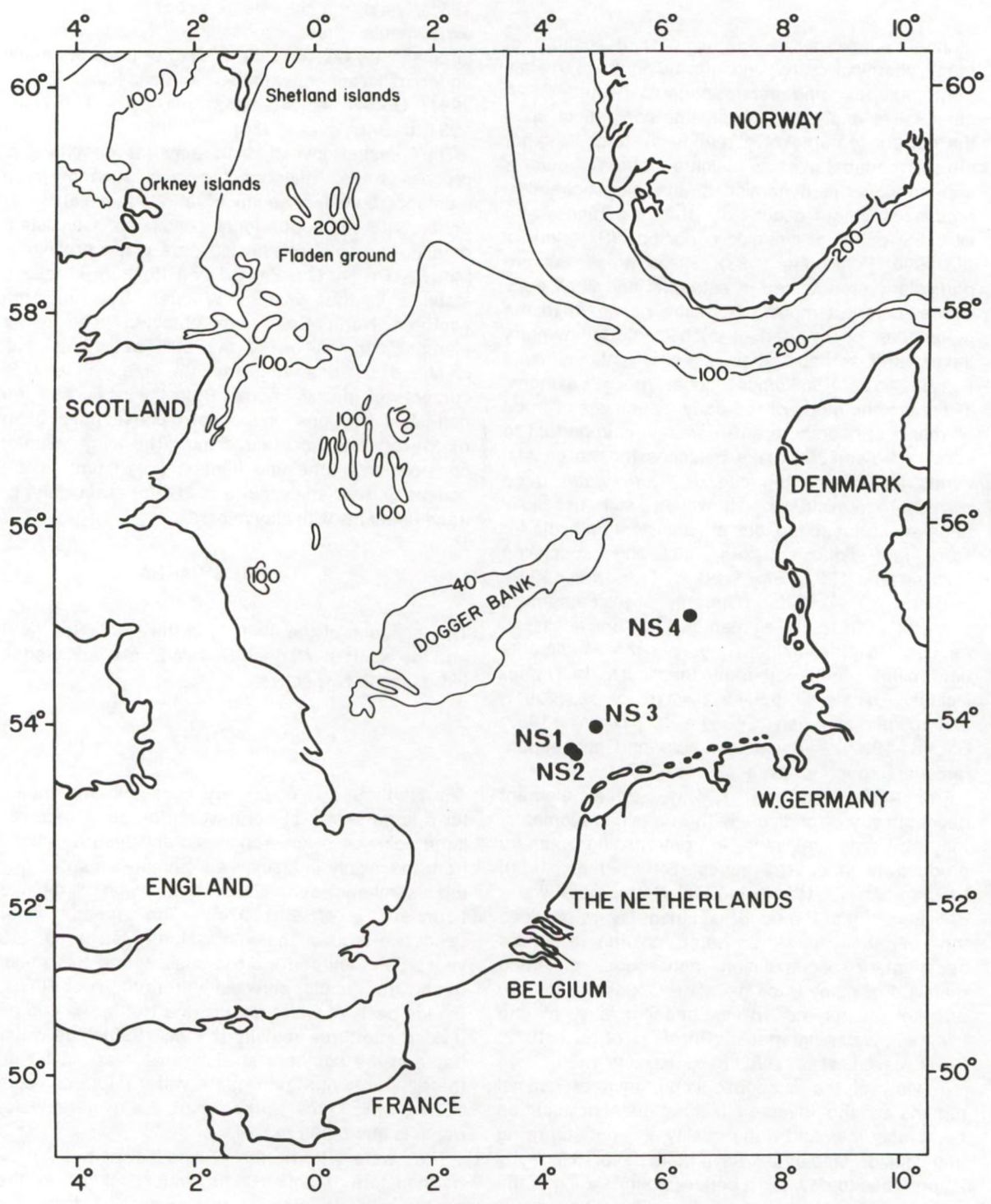


Fig. 1. Locations of the stations in the southern North Sea.

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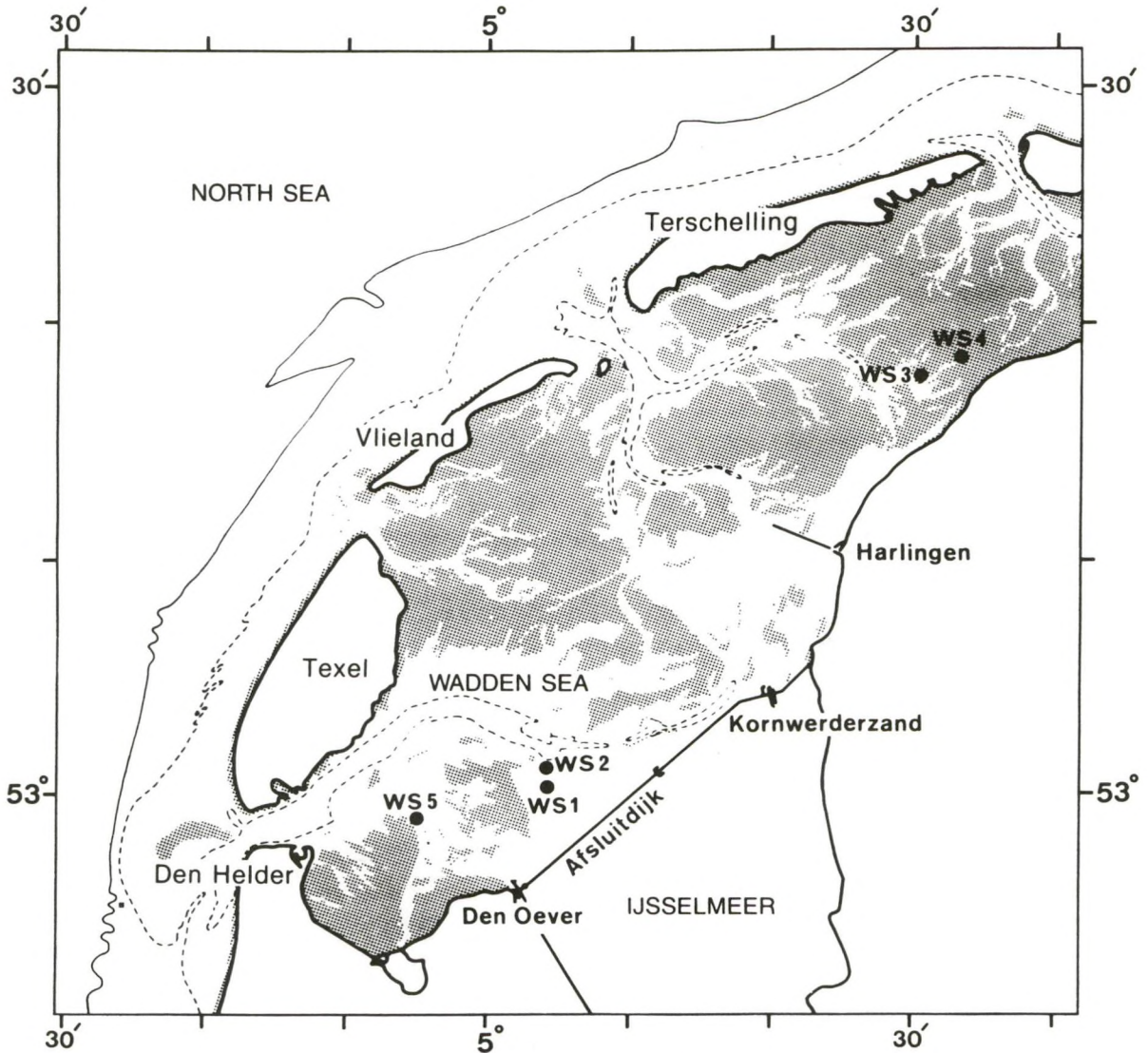


Fig. 2. Locations of the stations in the western Dutch Wadden Sea.

2.2. WADDEN SEA

The Wadden Sea is a shallow coastal sea extending along the coasts of Denmark, Germany and the Netherlands. Of the total area, 30% belongs to the Netherlands. The western part of the Dutch Wadden Sea receives water from the river Rhine through the coastal zone of the North Sea and through discharges from Lake IJssel (WOLF, 1988). The average tidal amplitude varies between 1.36 m near Den Helder, The Netherlands, and 3.43 m at Husum in Germany. At low tides, about 50% of the area emerges. Sediments in the area are largely sandy but particularly at tidal divides, more muddy sediments occur as well.

Five sampling stations in the Dutch Wadden Sea are considered to be suited for studying diagenetic processes of trace elements. The salinity in the area varies between 20 and 30‰ S (WOLF, 1988). The sedimentation (BERGER *et al.*, 1987) rate in this area is known to be high ($6.46 \pm 0.15 \text{ cm.y}^{-1}$ from ^{210}Pb geochronology).

3. SAMPLING METHODS AND ANALYSIS

3.1. SEDIMENT AND PORE WATER SAMPLING

Sediment samples were collected at five stations in the Dutch Wadden Sea (Fig. 2), during a cruise with the RV NAVICULA, from 25 March through 27 March,

1991, using a modified Reineck-Scripps-Type boxcorer designed by the Technical Department of NIOZ. The boxcore (i.d. = 30 cm and h = 50 cm) can be closed both at bottom and top, so that during lifting of the core, no exchange of overlying water with pore water occurs. In the North Sea, sediment samples were collected at four stations (Fig. 1), during a cruise with RV PELAGIA from 27 May through 29 May, 1991. Here, sediment cores were obtained with a Reineck boxcorer, which is rectangular in shape. Before sub-sampling, the overlying water was carefully syphoned off with a plastic tube.

After draining off the overlying water, three sediment sub-cores were collected from each boxcore with plastic pipes (i.d. = 6 cm, h = 30 cm) with sharply tapered ends. The pipes were carefully removed from the main core, capped at both ends with cleaned rubber stoppers and transferred to the cooled laboratory of the research vessel for further processing.

From the top 25 cm of each sub-core, sediment samples were sliced with a PVC slicer at intervals of 0.5 cm at the top, 1-2 cm at the middle and 3-4 cm at the bottom. In this way, 10-12 slices were obtained. Slices of the same depth from 3 sub-cores were pooled in clean teflon squeezers as described by Reeburgh (Reeburgh, 1967). Pore water samples were collected in acid cleaned polyethylene bottles by squeezing the sediments over 0.2 µm cellulose nitrate filters (Sartorius) under nitrogen pressure of 1.5-2.0 bar. The samples (20-50 ml) were acidified to pH=2 with suprapure conc HCl and stored in a refrigerator at 4°C until analysis. After pore water collection the sediment samples were collected in clean plastic bags and stored in a freezer at -20°C until analysis.

Separate sub-cores were sliced down to a depth of 10 cm for porosity measurement.

3.2. DESCRIPTION OF THE CORES

The geographical positions of the stations and the water depths are shown in Table 1. Generally, the cores were brown sandy at the top (0-3 cm) indicating oxic conditions. Blackish horizontal streaks appeared below 7-8 cm probably due to sulphate reduction. The core of station 3 in the Wadden Sea (WS3) was brown from top to bottom. WS4 was built up with both oxic/anoxic layers and below 15 cm, sulphide reduction conditions were observed. WS5 has relatively fine grained sediments with a high porosity. Below 10 cm it was brown, however, with blackish streaks below 12 cm. While sectioning, no serious discontinuity was observed in

any of the cores. At WS3 and WS4 small shells (Ø4-5 mm) were observed on drying and they were removed by sieving.

TABLE 1
Locations of sampling stations in the North Sea (NS, May, 1991) and the Wadden Sea (WS, March, 1991).

Station	Location	Water depth (m)	Core length (cm)
NS 1	53° 42.52'N 4° 29.45'E	38	19
NS 2	53° 41.80'N 4° 30.20'E	38	21
NS 3	53° 57.39'N 4° 58.01'E	40	16
NS 4	54° 59.98'N 6° 26.22'E	44	16
WS 1	53° 00.50'N 5° 04.67'E	2.5	25
WS 2	53° 01.12'N 5° 04.51'E	3.5	20
WS 3	53° 18.24'N 5° 31.51'E	2.0	15
WS 4	53° 19.20'N 5° 34.17'E	2.0	23
WS 5	52° 58.08'N 4° 55.67'E	5.5	26

In the North Sea stations NS1 and NS2 the sediments were more homogeneous than in the Wadden Sea. The colour was brown at the top, gradually becoming more greyish with depth. Distinct sulphide (anoxic) conditions were not visible. The sediments of NS4 showed some horizontal blackish streaks. Benthic fauna was observed in the upper 6 cm of NS2 and at 1-3 cm below the surface at NS3.

3.3. CHEMICAL ANALYSIS

Sediment

About 20 g of squeezed sediment samples were put into a petridish and dried at 60-65 °C for 48 hours. The dried sediments were softly ground to fine powder with both acid cleaned teflon mortar and pestle. Coarse material (shells) was eliminated using a small teflon framed nylon sieve. For determination

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the HCl leachable fraction of the sediments (DUINKER & NOLTING, 1976), 0.1 g of the sediments was quantitatively transferred into acid cleaned 50 ml polypropylene volumetric flasks and leached with 0.1 N HCl (Suprapure, E. Merck) for 18-20 hours. The leachable fraction was separated by filtration on a pre-cleaned 0.45 μm cellulose nitrate filter (Sartorius). The residual fraction of the HCl treated sediments was digested by aqua regia and HF in an acid (7N HNO_3) cleaned teflon bomb at 120 °C for 4 h (RANTALA & LORING, 1977a, 1977b). After digestion the solution was transferred to a 30 ml saturated H_3BO_3 solution in a 50 ml volumetric flask, which was then filled to the mark with distilled water.

Mg, Mn, Fe and Zn were analyzed in both the leachable and residual fractions, Ca, Al and Si only as total contents. All these elements were determined by flame atomic absorption spectrophotometry (FAAS) using air-acetylene or N_2O -acetylene (Al, Si) flames with a Perkin-Elmer 2380 AAS. The method of standard addition or normal calibration curves were used. The trace elements Cr, Ni, Cu and Pb were analyzed by the stabilized temperature platform furnace technique (STPF technique) using a Perkin-Elmer 5000 AAS applied with deuterium background correction. Cadmium was analyzed by the STPF technique with Zeeman background correction (Perkin-Elmer 5100 PC). In all graphite furnace analyses, an external range of calibration standards of the elements in a 1.4 M HNO_3 matrix was used.

In all dilutions and preparations for standards, standard additions and calibrations, gravimetric methods were applied to achieve high accuracy. Titrisol standards of 1000 $\text{mg}\cdot\text{l}^{-1}$ were used for the preparation of the range of standards. The standards for trace elements were stored in acid cleaned teflon bottles, all other standards in acid cleaned polyethylene bottles. Only calibrations within the linear range of absorbance were used for concentration calculations, always correcting for blanks. For sediments, the total contents of the elements (Mn, Fe, Cu, Zn, Ni, Cr, Pb and Mg) were obtained by summing leached and residual fractions. For Al and Si, the leachable fraction, and for Ca the residual fraction was negligible.

Pore Water

Six trace elements (Mn, Fe, Cu, Zn, Pb and Cd) were analyzed in pore water samples, either directly by flame AAS (Mn, Fe) or after appropriate dilutions by graphite furnace AAS (Cu and Zn) equipped with deuterium background correction. For Pb and Cd, the pre-concentration technique of solvent extraction was used. In a 5-ml pore water sample, the pH was

adjusted to 4-5 with ammonium acetate buffer and the metals were extracted into freon (5 ml) after complexation with aqueous 1% APDC/DDDC solution. After phase separation, the metal complexes in freon were destroyed by adding 50 ml of conc. HNO_3 (Suprapure, E. Merck) and back extracted in 0.95 ml of Milli-Q water by shaking for 2 min (DANIELSSON *et al.*, 1978). The samples were thus five times preconcentrated and sea salts were removed. Both Pb and Cd were analyzed by graphite furnace AAS with STPF technique using a Perkin-Elmer 5100 Zeeman AAS and standards having the same acid concentration as the samples. A recovery study for both the elements was performed using cleaned pore water and it was found to be 100% for Cd and 97% for Pb. The slope of the calibration (standard addition) curve in the recovery study was the same as that of the external calibration curve, thus confirming the accuracy of the procedure.

For direct analysis of Zn and Cu, pore water samples after appropriate dilutions (20 μl to 1 ml for Zn and 300 μl to 1 ml for Cu) were directly injected on a PE 5000 AAS with deuterium background correction. The standard addition method for each boxcore was used for concentration calibration so that the salt matrix effects can be properly corrected. All dilution factors were obtained by gravimetry as mentioned before. Milli-Q water was used for dilution.

Standard Reference Materials

In order to validate the analytical procedures adopted in the present study, two standard reference samples, BCR 142 and BCR 277 from the Community Bureau of Reference, Brussels, were analyzed in parallel with the samples for all the concerned elements of interest. BCR 142 is a light Sandy Soil reference while BCR 277 is an Estuarine Sediment, both having matrix composition similar to that of the sediment samples analyzed in this study. The trace element concentrations of the BCR 142 were ideal for comparison with the present results and as such used for analytical quality assurance (QA) purpose. For major elements, however, both the reference samples were found suitable. A very good agreement between measured and certified values almost for all the elements studied assures the accuracy of the results (Appendix 1). The standard deviations are obtained from triplicate or duplicate measurements. Similar accuracy of these analytical procedures for sediments has been reported previously from this laboratory (NOLTING & VAN HOOGSTRAATEN, 1992).

Several analytical blanks were prepared for each element in the same way as the analytical samples. An average of triplicate blanks with minimum standard deviation was used for blank correction. All blanks for the leachable fractions were, however, negligible. For residual fractions where acid cleaned filters were destroyed in acid cleaned teflon bombs, higher blanks were observed for the trace elements, Cu, Zn, Ni, Cr, Cd and Pb. In pore water analysis, the blanks were also negligible.

3.4. MINERALOGICAL ANALYSIS

For mineralogical analysis, the fine fraction (< 10 μm) of sediments was obtained by wet sieving and repeated sedimentation using centrifugation. All glasswares, centrifuge tubes (polypropylene), plastic sieve and other handling tools used in this preparation were acid cleaned. Milli-Q water was used in all preparations. The calcium carbonate content was removed by shaking the sediment for 5 hours with sodium acetate - acetic acid buffer of pH=5. The samples were then subjected to sequential extraction, first with 0.5 M oxalic acid and then with 0.1 M HCl (Suprapure, Merck). After extraction, the samples were Ca exchanged with CaCl_2 (Suprapure, BDH) and the excess of the salt was removed by washing twice with Milli-Q water and once with methanol. After oxalic acid extraction, the samples were cleaned by washing four times with NaCl solution to remove calcium oxalate. The samples were then Ca exchanged as described above. After the methanol wash, the samples were dried at 50°C and the specimens for XRD analysis were prepared by pressing about 12 mg of the sample material in a depression (12x0.5 mm) "off axis" cut monocrystalline silicon disc providing very low background and no diffraction peaks.

The XRD analysis was carried out with a wide angle goniometer (PW 1050/25, Philips) using Co K α radiation from a generator with 40 KV accelerating voltage and 40 mA beam current, equipped with a long fine focus XRD tube, a graphite monochromator and a vacuum-helium device (VAN DER GAAST & VAARS, 1981). The constant irradiated specimen areas were ensured by using a computer aided variable divergence slit. The details of the instrumentation and the methodology have been reported by VAN DER GAAST (1991).

The XRD patterns were recorded digitally. The slit setting was 12 mm for the variable divergence slit and 0.2 and 1 mm, for the receiving slit and the antiscatter slit, respectively. The specimen chamber was flushed with gas at 50% relative humidity. The recording speed was 4 sec/0.02° 2 θ .

In differential XRD, the diffractograms were smoothed over 3 points of equal weights before and after chemical extractions with oxalic and HCl acids. The patterns were normalized in intensity with respect to the quartz (101) peak at 3.343Å. The x-ray patterns after chemical extractions were smoothed over 11 points of equal weights to make the broad bulges better visible.

The trace element concentration of the acid extracts from the fine fractions were analyzed following the analytical procedures described earlier.

4. RESULTS

4.1. CHARACTERISTICS OF THE SEDIMENTS

The porosities, grain size distribution, total organic carbon and nitrogen contents of the sediments are given in Tables 2 and 3.

The porosity of North Sea (NS) sediments is very uniform with depths (0-10 cm). The porosity of NS3 was ca. 50% higher compared to the nearby stations NS1 and NS2. A wide range of variations in porosity was observed for the Wadden Sea stations (WS) as well with depth of the sediments as between different stations. Especially WS3 and WS5 show high porosities in the upper layers (0.77 and 0.81, respectively). Stations WS1 and WS4 have similar porosities as the North Sea sediments.

C:N ratios were measured at three different depths (Table 2). Apart from NS1 and WS3, C:N ratios were increasing with depths from 6.5-10.0 in the upper 5 mm's to 10.0-13.4 in deeper layers. At NS1 and WS3 the lowest ratios were observed at 10 cm depth. The most pronounced vertical profile of org. C and N contents was observed at WS3 with very high contents in the surface layer as compared to the deeper layers.

The results from the granulometric analysis are given in Table 3. Two sediment cores from both Wadden Sea and North Sea were considered as representative. Only the top and the bottom layers were determined. The top layers of the sediments were found to contain higher proportions of the > 63 μm fraction (94-99%) than the bottom layers (83-86%), except WS2 where the proportions were equal (89% at the top and 92% at the bottom). The fine fractions of the sediments (< 10 μm) are generally present in higher percentages at the bottom (1.3-6.0%) than in the top layer (0.2-2.7%). WS2 was again different, 1.4% at 0.25 cm and 0.6% at 18 cm depth.

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TABLE 2
Physicochemical characteristics of the North Sea and Wadden Sea sediments.
NS = North Sea; WS = Wadden Sea; D = depth interval, nd = not determined.

Station	D(cm)	Porosity (wt/wt)	C(%)	N(%)	C:N (wt/wt)
NS 1	0-0.5	0.33	0.34	0.021	16.5
NS 1	5-7	0.29	0.64	0.046	13.9
NS 1	9-12	0.27	0.73	0.053	13.7
NS 2	0-0.5	0.24	0.39	0.040	9.7
NS 2	5-7	0.25	0.56	0.056	10.0
NS 2	9-12	0.25	0.69	0.051	13.4
NS 3	0-0.5	0.43	0.46	0.049	9.4
NS 3	6-8	0.42	0.57	0.056	10.2
NS 3	8-12	0.47	0.60	0.052	11.7
NS 4	0-0.5	0.28	0.30	0.035	8.8
NS 4	6-8	0.22	0.42	0.044	9.6
NS 4	8-12	0.21	0.45	0.045	10.0
WS 1	0-1	0.27	0.21	0.033	6.5
WS 1	9-13	0.25	0.70	0.063	11.0
WS 1	21-25	nd	0.72	0.060	12.0
WS 2	0-0.5	0.57	0.57	0.075	7.6
WS 2	8-12	0.22	0.46	0.050	9.2
WS 2	14-22	nd	0.40	0.035	11.4
WS 3	0-0.5	0.77	1.64	0.155	10.6
WS 3	7-9	0.19	0.05	0.004	12.9
WS 3	11-15	nd	0.08	0.009	9.4
WS 4	0-0.5	0.25	0.18	0.018	10.0
WS 4	9-11	0.45	0.15	0.015	9.9
WS 4	19-23	nd	0.42	0.036	11.7
WS 5	0-1	0.81	0.05	0.005	9.5
WS 5	10-12	0.45	0.37	0.036	10.2
WS 5	20-24	nd	0.25	0.022	11.3

TABLE 3
Grain size distribution of some North Sea and Wadden Sea sediments.

Station	Depth interval (cm)	>63 μm (%)	10-63 μm (%)	<10 μm (%)
NS 1	0-0.5	94	4.3	1.6
NS 1	15-19	83	10.8	6.0
NS 3	0-0.1	95	2.4	2.7
NS 3	12-16	84	10.7	4.8
WS 1	0-1	99	1.1	0.2
WS 1	21-25	86	12.5	1.3
WS 2	0-0.5	89	9.9	1.4
WS 2	14-22	92	7.1	0.6

TABLE 4

Clay minerals (<10 µm fraction) of sediments extracted by in oxalic and hydrochloric acids. D = depth interval.
See also Table 7.

Station	D(cm)	Opal	Akagoneite	Ferrihydrite	Smectite	Illite/MiCa	Chlorite	Kaolinite
Oxalic acid extractable (0.5 M, 18 h, 35 mg, 35 ml acid volume)								
NS 1	0-0.5	++	++	++	?	-	+	-
NS 1	15-19	+	+	+	-	-	+	-
NS 3	0-0.5	-	+	+	?	+	+	+
NS 3	12-1	+	+	+	+	+	+	+
WS 1	21-25	-	-	?	?	+	+	+
Hydrochloride acid extractable (0.1 M, 18 h, 25 mg, 15 ml acid volume)								
NS 1	0-0.5	-	-	-	-	+	+	+
NS 1	15-19	?	-	-	-	-	-	-
NS 3	0-0.5	+	+	+	-	-	+	-
NS 3	12-1	+	+	?	+	+	+	+
WS 1	21-25	-	?	?	-	-	-	-

++ = present; + = less present; - = no detectable amounts

4.2. MINERALOGICAL COMPOSITION OF THE SEDIMENTS (< 10 µm FRACTION)

Sediments from two stations in the North Sea (NS1 and NS3) and one station in the Wadden Sea (WS1) were analyzed for clay mineral composition. The sequential dissolution characteristics of these minerals in subsequently oxalic acid and in 0.1 M hydrochloric acid are shown in Table 4. The ray diffraction patterns after oxalic acid and HCl sequential extractions are illustrated in Figs 3-5. The differential XRD patterns (DXRD) of the sediments were analyzed to quantify the soluble minerals during the 2 sequential extraction steps. This quantification has been done after normalizing their peak intensities with respect to the quartz (101) peak at 3.343Å.

From the XRD patterns, clay mineral reflections of chlorite, illite/mica, kaolinite, probably some smectite and other minerals such as quartz, feldspar and amphibole were identified (Table 4). Apart from these minerals, a strong bulge occurred with the maximum at 3.3Å representing poorly crystallized materials, and possibly confirming the presence of the iron(III)-oxide akaganeite. After oxalic acid extraction, other poorly crystalline components as opal (4.2Å) and ferrihydrite (2.5Å) were confirmed by DXRD.

Chlorite, which holds Fe in its structure, was partly

removed from the sediment matrix by oxalic acid extraction. In the subsequent extraction with HCl this mineral was not removed in measureable quantities. Hydrochloric acid extraction, however, significantly removed amorphous materials (opal, ferrihydrite and akaganeite). Mica and kaolinite also partly dissolved in 0.1 M HCl.

The North Sea sediments contained much higher proportions of non-crystalline materials than the Wadden Sea sediments. After the oxalic acid extraction, amorphous materials were partly removed from the sediments of both the study areas. Some specific features were observed at the Frisian Front and Oyster Grounds (NS1-3) in the North Sea. All clay minerals, except smectite in the top layer (0-0.5 cm) of the sediments in NS1 could be attacked with HCl after extraction with oxalic acid. At station NS3, only chlorite from the surface layer could be dissolved. At a depth of 12-16 cm in NS3, all clay minerals were dissolved by HCl. At WS1 (2-25 cm) all non-crystalline materials could be dissolved in HCl after oxalic acid extraction.

The influence of the above features of the minerals on the leachable characteristics of the redox elements (Fe and Mn) and trace elements (Cu, Cr and Ni) will be discussed in later sections. The possible association of different trace elements with clay minerals is illustrated in Table 5 as a reference (after LORING, 1991).

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

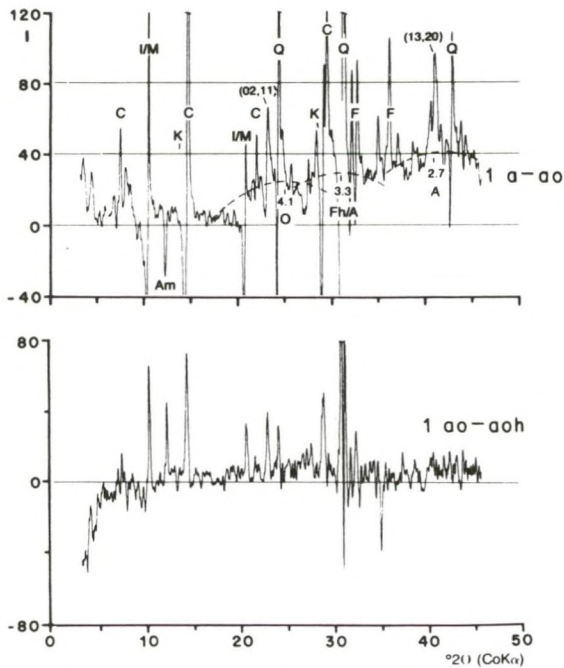
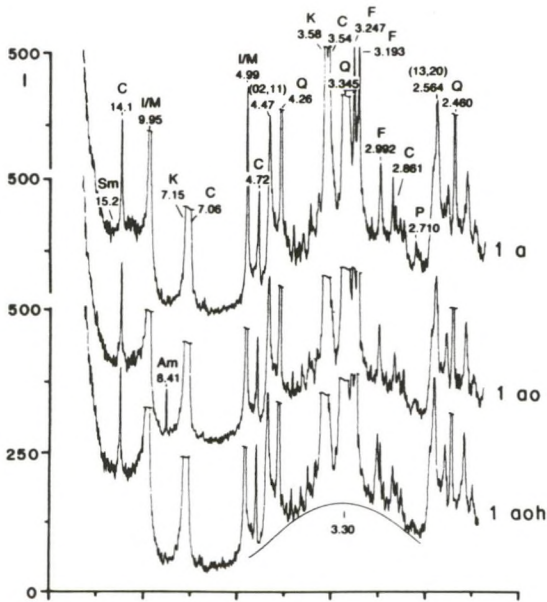


Fig. 3 left (1). XRD and DXRD patterns of the < 10 μm fraction of sample NS1, 0-0.5 cm. a = pattern after acetic acid extraction; ao = pattern after sequential extraction with acetic acid and oxalic acid; aoh = pattern after sequential extraction with acetic acid, oxalic acid, and hydrochloric acid. a-ao = DXRD pattern, pattern of ao has been subtracted from that of a; aoh-ao = DXRD pattern, pattern of aoh has been subtracted from that of ao. sm = smectite; C = chlorite; K = kaolinite; I/M = illite/mica; Q = quartz; F = feldspar; Am = amphibole; P = pyrite; O = opal; Fh = ferrihydrite; A = akaganite. The (02,11) and (13,20) reflections at 4.47 and 2.56Å respectively, are non-diagnostic clay mineral reflections.

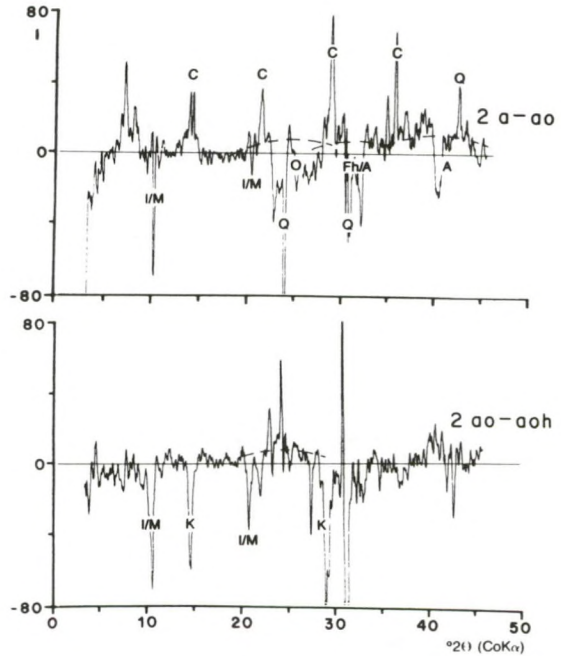
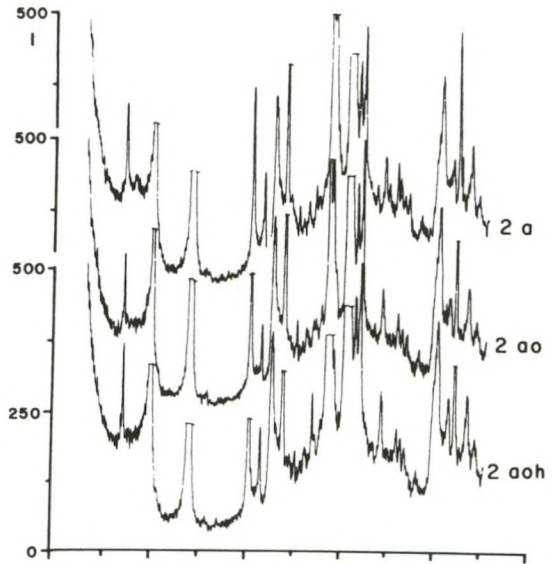


Fig. 3 right (2). XRD and DXRD patterns of the < 10 μm fraction of sample NS1, 15-19 cm. For explanation of symbols etc. See Fig. 3 left.

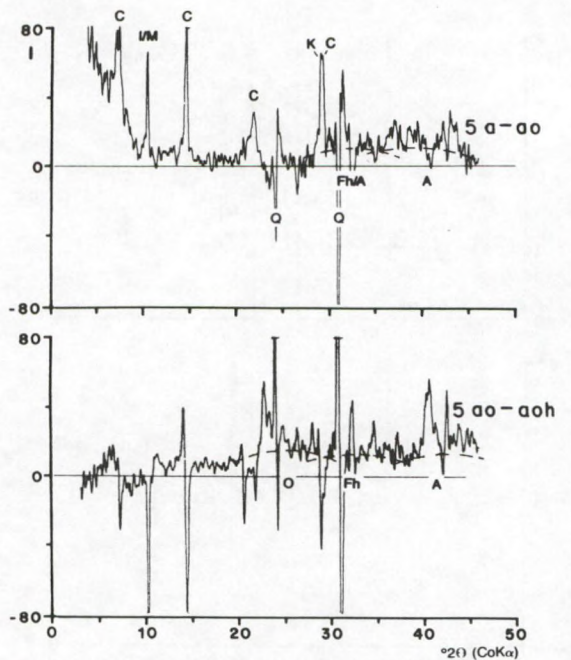
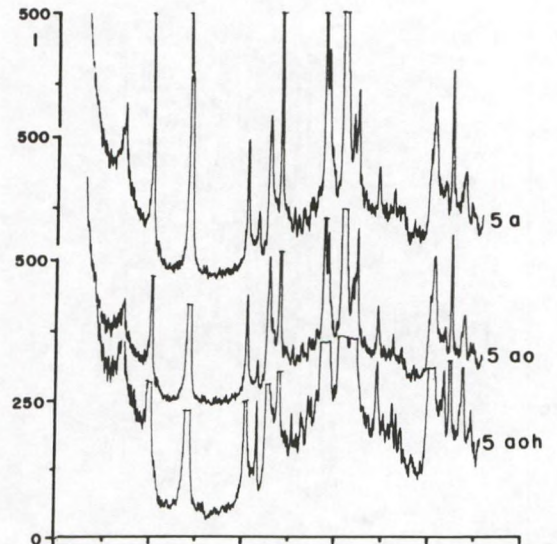
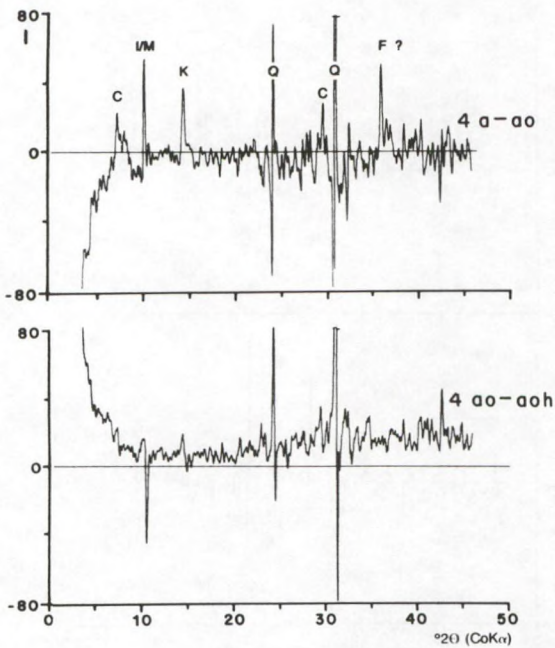
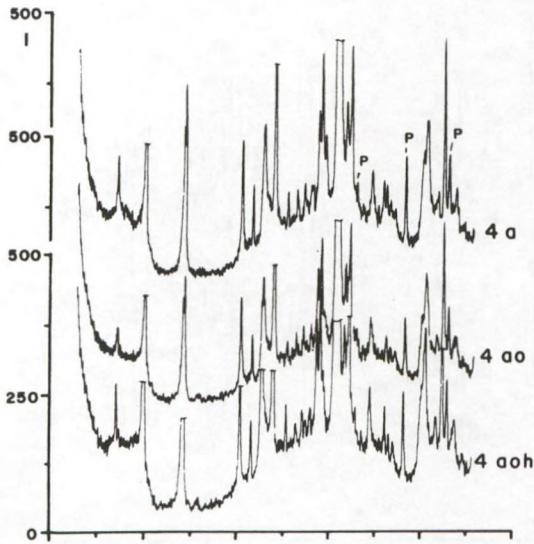


Fig. 4 left (4). XRD and DXRD patterns of the < 10 μm fraction of sample WS1, 21-25 cm. For explanation of symbols etc. See Fig. 3 left.

Fig. 4 right (5). XRD and DXRD patterns of the < 10 μm fraction of sample NS3, 0-0.5 cm. For explanation of symbols etc. See Fig. 3 left.

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

4.3. MAJOR ELEMENT COMPOSITION OF THE SEDIMENTS

The core profiles of the major elements, Mg, Si, Al and Ca were analyzed in the 0.1 M HCl leachable fraction and the residual fraction (solid phase after acid extraction). They are given in the Appendix 10 and 11 for NS and 20-23 for WS sediments, respectively. The sum of the two fractions gives the total elemental composition. For refractory elements like Al and Si, the acid leachable fractions contained negligible amounts compared to the residual fractions. On the contrary, the Ca content was negligible in the residual fractions of all the sediments, and Mg occurred in both fractions at almost equal proportions.

The elemental composition of the top 2 cm layer, expressed as MgO, Al₂O₃, SiO₂, CaCO₃ and Fe₂O₃ is given in Table 6. The organic matter content of the upper 0-0.5 cm is included in Table 6. The Wadden Sea stations have strongly varying contents with the exception of the SiO₂ content (72.9-76.7%). The composition of the North Sea sediments appeared to be more uniform. The CaCO₃ content is relatively low at NS4 (4.32% within the overall range of 4.32-7.14%). The sum of all contents ranges from 85.7% (NS4) to 107.2% (WS5). On average, totals of the North Sea sediments were close to 100%, while those of the Wadden Sea showed larger deviations.

4.4. TRACE ELEMENT COMPOSITION OF THE SEDIMENTS AND INTERSTITIAL WATERS

The concentration profiles of the redox elements Mn and Fe, and those of the trace elements Cr, Ni, Cu, Zn, Cd and Pb are compiled in Appendix 2-23. The distribution patterns of Mn, Fe, Cu, Cr, Zn, Cd, Pb in the solid phase and the pore water are illustrated in Figs. 6-9 (NS2, NS3, NS4 and WS2, WS3, WS5).

Some trace elements (Mn, Fe, Cr, Ni and Cu) were analyzed only in the 0.5 M H₂C₂O₄ and subsequently 0.1 M HCl leachable fractions of the fine sediment (< 10 μm fraction) to quantify the association with the clay minerals. The results of this analysis are shown in Table 7.

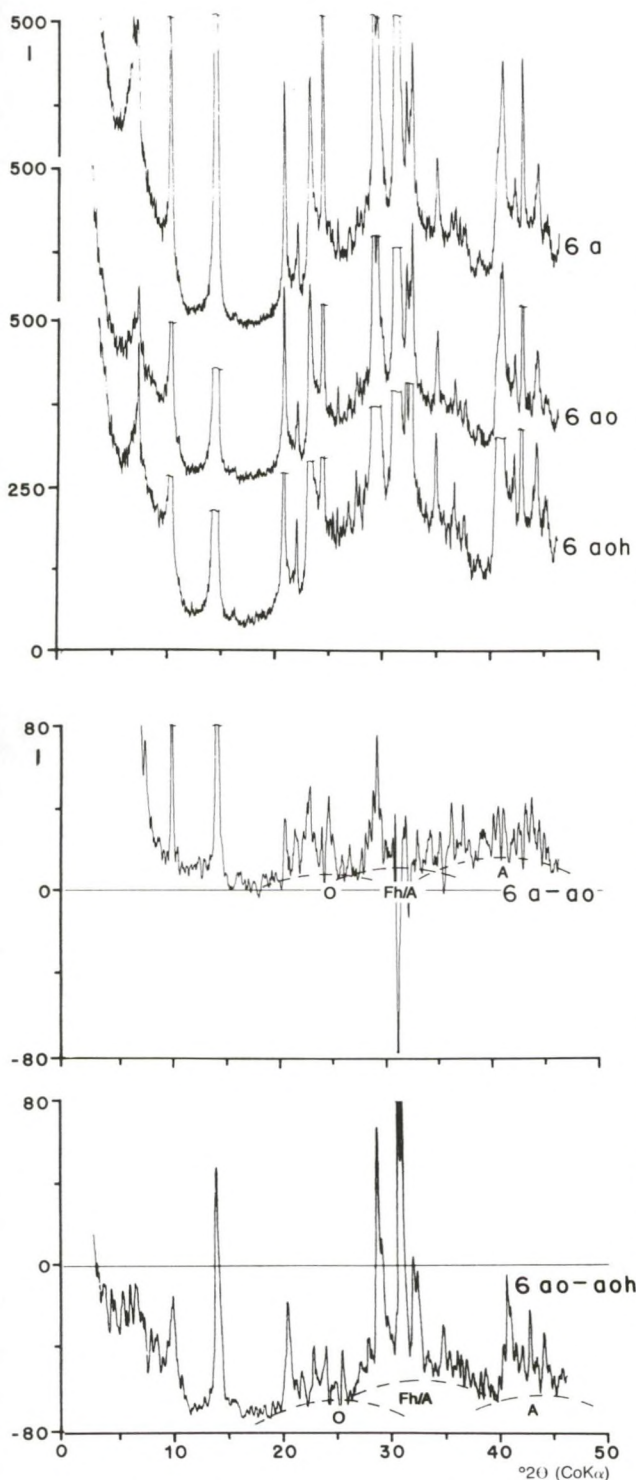


Fig. 5 (6). XRD and DXRD patterns of the < 10 μm fraction of sample NS3, 12-16 cm. For explanation of symbols etc. See Fig. 3 left.

TABLE 5
Incorporation of trace metals in different minerals (after LORING, 1991).

Mineral	Predominant grains	Metals with abundance (%)			
		X	0.X	0.0X	0.00X
Quartz	sand/silt	Si	-	-	-
Plagioclare feldspar	sand/silt/clay ⁺	Na,Ca,Al,Si	-	-	V,Zn,Ni,Al, Pb,Cu
Potash feldspar	sand/silt/clay ⁺	K,Si,Al	-	-	V,Zn,Ni,Pb, Cu
Muscovite	silt/clay	K,Si,Al	Li	Cr,Mn,V,Cs	Zn,Cu,Sc
Biofite	silt/clay	Si,Al,Fe,Mg	Mn	Zn,V,Cr,Li,Ni,S c	Cu,Pb,Co
Pyroxenes	sand/silt/clay ⁺	Ca,Fe,Mg, Si,Al	K,Mn	Cr,V,Ni	Cu,Co,Zn, Li,Sc
Amphibole	sand/silt/clay ⁺	Si,Al,Ca,Fe	K,Mn	Zn,Cr,V	Cu,Co,Pb, Sc
Clay minerals					
Illite	clay	K,Al,Si	Na,Fe,Mg	Zn,Cu,Pb,Cr,Li, V	Co,Ni
Chlorite	silt/clay	Si,Al,Fe,Mg	Mn	Zn,V,Cr	Cu,Pb,Co
Fe-Oxides	sand/silt/clay ⁺ Fe	Mn	Zn,Cu,Pb	Cr,V	
Sulphides ^{**}	clay	Fe,Zn	Co,Ni	-	-
Al-silicates [*]	-	Cu,Pb	-	-	-
Chromite	silt/clay	Cr	-	V	-
Magnetite	sand/silt	Fe,Cr	Mn,V	Zn,Cu,Ni	Co,Pb

* inclusions

** fine grains of Zn, Cu and Pb sulphides

+ derived from igneous rocks

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

TABLE 6

Major element composition (%) of the upper layer (0-2 cm) of sediments from the southern North Sea and the western Wadden Sea. The organic carbon content (expressed in CH₂O) is for the 0-0.5 cm top layer.

Station	CH ₂ O	MgO	CaCO ₃	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	Sum
NS 1	0.85	-	6.67	8.60	76.9	3.42	96.4
NS 2	0.75	-	7.14	11.0	76.7	4.05	99.6
NS 3	1.15	-	6.67	10.3	71.6	4.32	94.0
NS 4	0.75	-	4.32	10.2	76.3	3.39	95.0
WS 1	0.53	1.03	6.16	6.56	73.5	0.86	88.6
WS 2	1.42	0.39	6.09	8.74	72.9	1.21	90.8
WS 3	4.10	0.69	6.77	9.48	77.4	3.18	101.6
WS 4	0.45	0.20	2.35	6.32	74.9	1.50	85.7
WS 5	0.13	0.86	13.2	12.0	76.7	4.33	107.2

TABLE 7

The extractable amounts of Mn, Fe, Cr, Ni and Cu in the fine sediment fraction (< 10 µm) (sequential extraction).
See also Table 4.

Extractant	Station	Interval depth (cm)	Mn (µg/g)	Fe (%)	Cr (µg/g)	Ni (µg/g)	Cu (µg/g)
0.5M oxalic acid	NS1	0-0.5	207	1.95	17.6	14.5	14.7
	NS1	15-19	146	1.87	19.7	15.6	15.5
	NS3	0-0.5	192	2.06	19.5	16.0	23.6
	NS3	12-16	159	2.01	21.8	16.3	21.1
	WS1	0-1	154	1.48	48.7	12.4	29.6
0.1M HCl	NS1	0-0.5	12.0	0.05	0.89	1.58	9.45
	NS1	15-19	9.31	0.04	0.89	1.59	2.97
	NS3	0-0.5	< 6.00	0.06	1.14	1.32	3.77
	NS3	12-16	< 6.00	0.05	1.12	1.83	3.42
	WS1	0-1	11.0	0.07	2.57	1.51	5.40

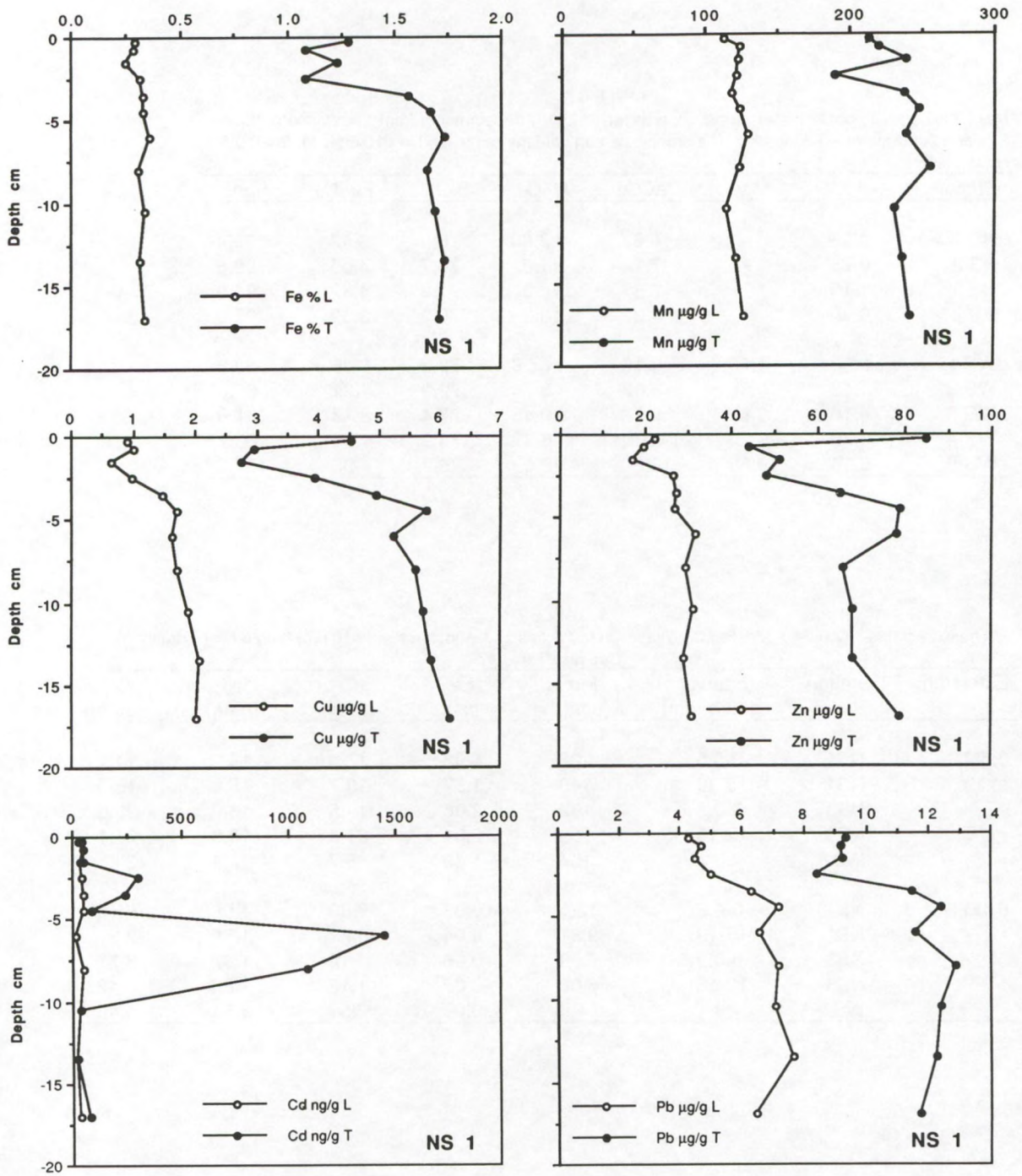


Fig. 6. Solid phase profiles of Mn, Fe, Cu, Zn, Cd, Pb in the NS1, NS3 and NS4 stations (L= leachable, T= total).

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

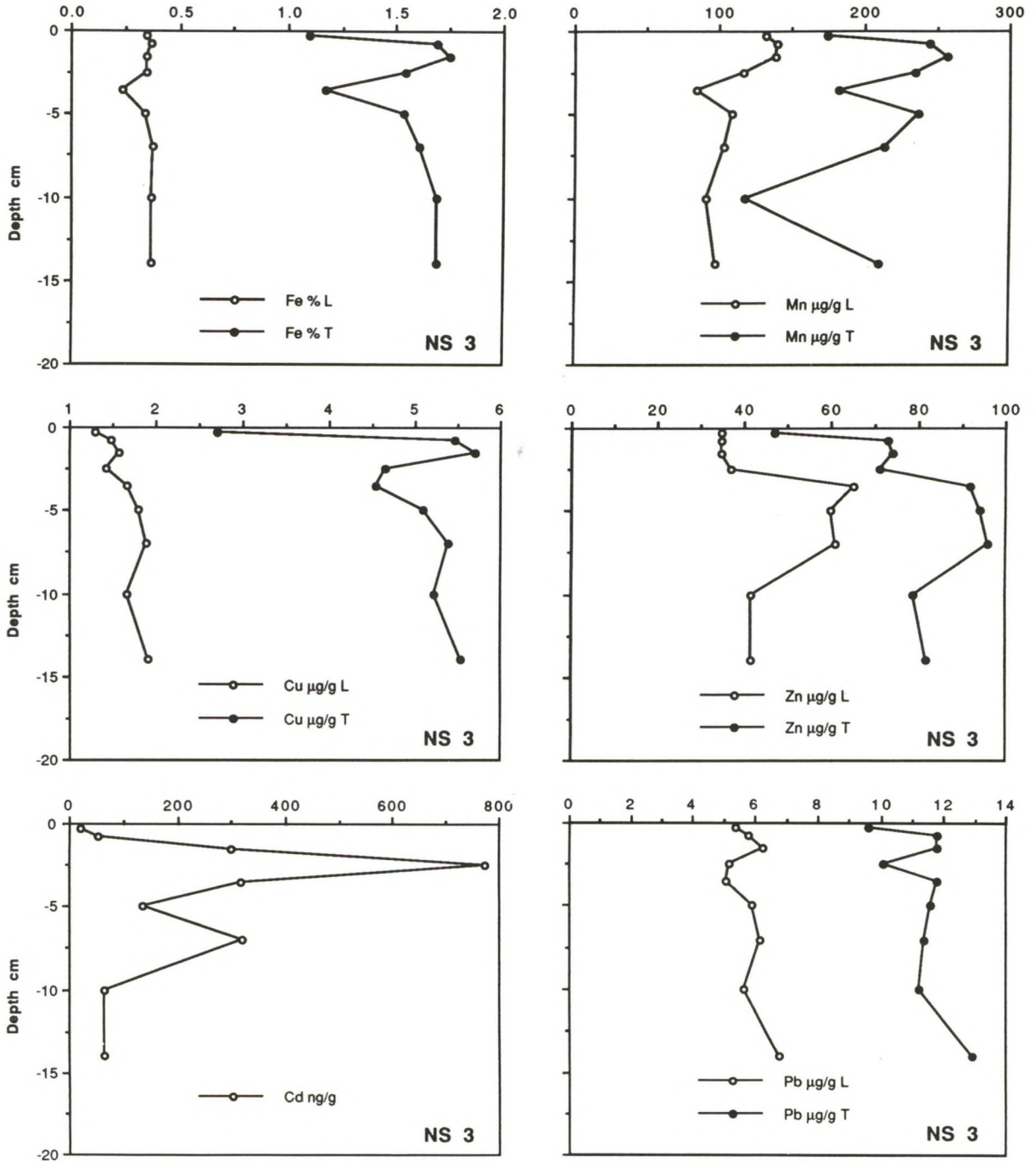


Fig. 6 continued

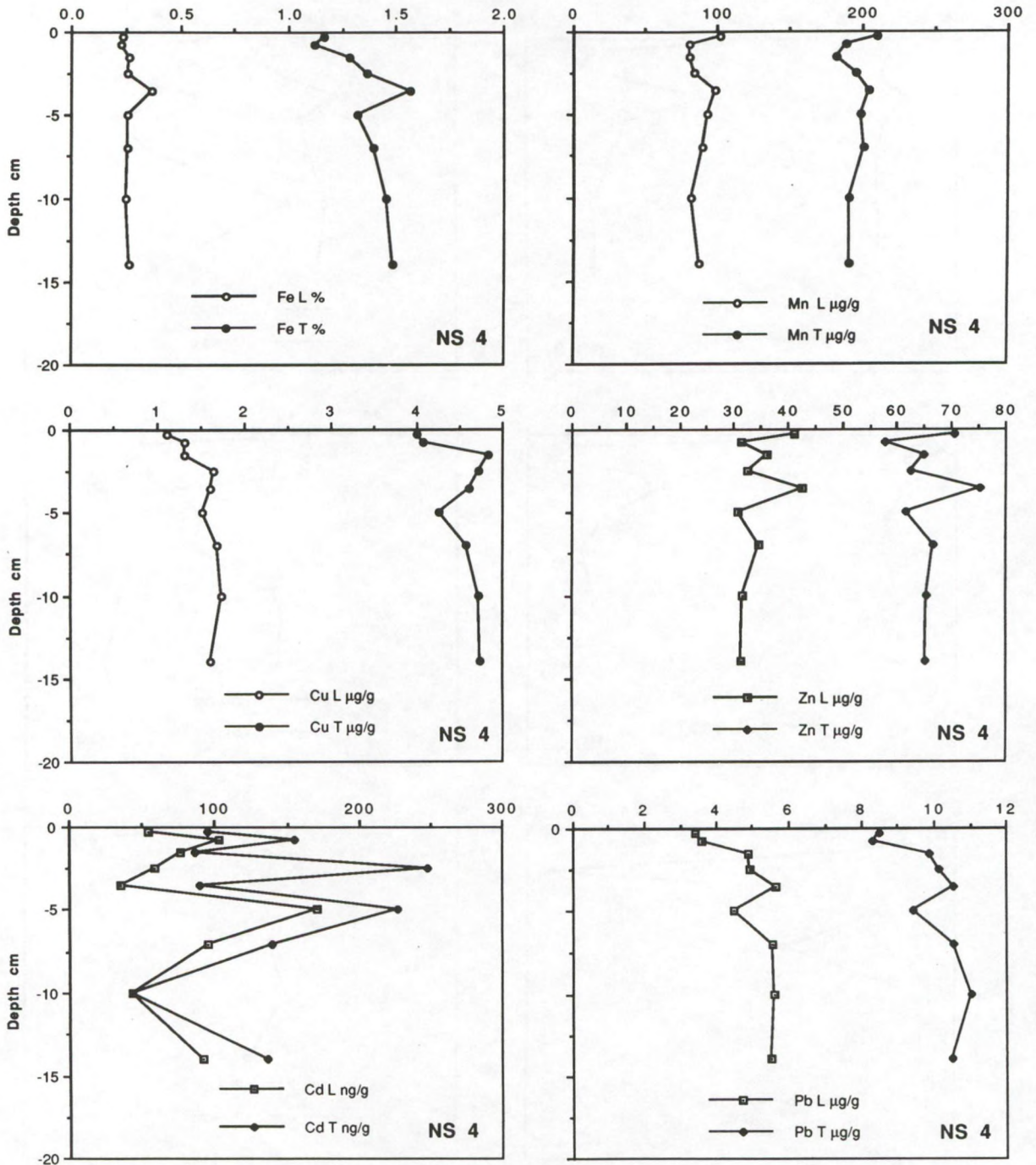


Fig. 6 continued

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

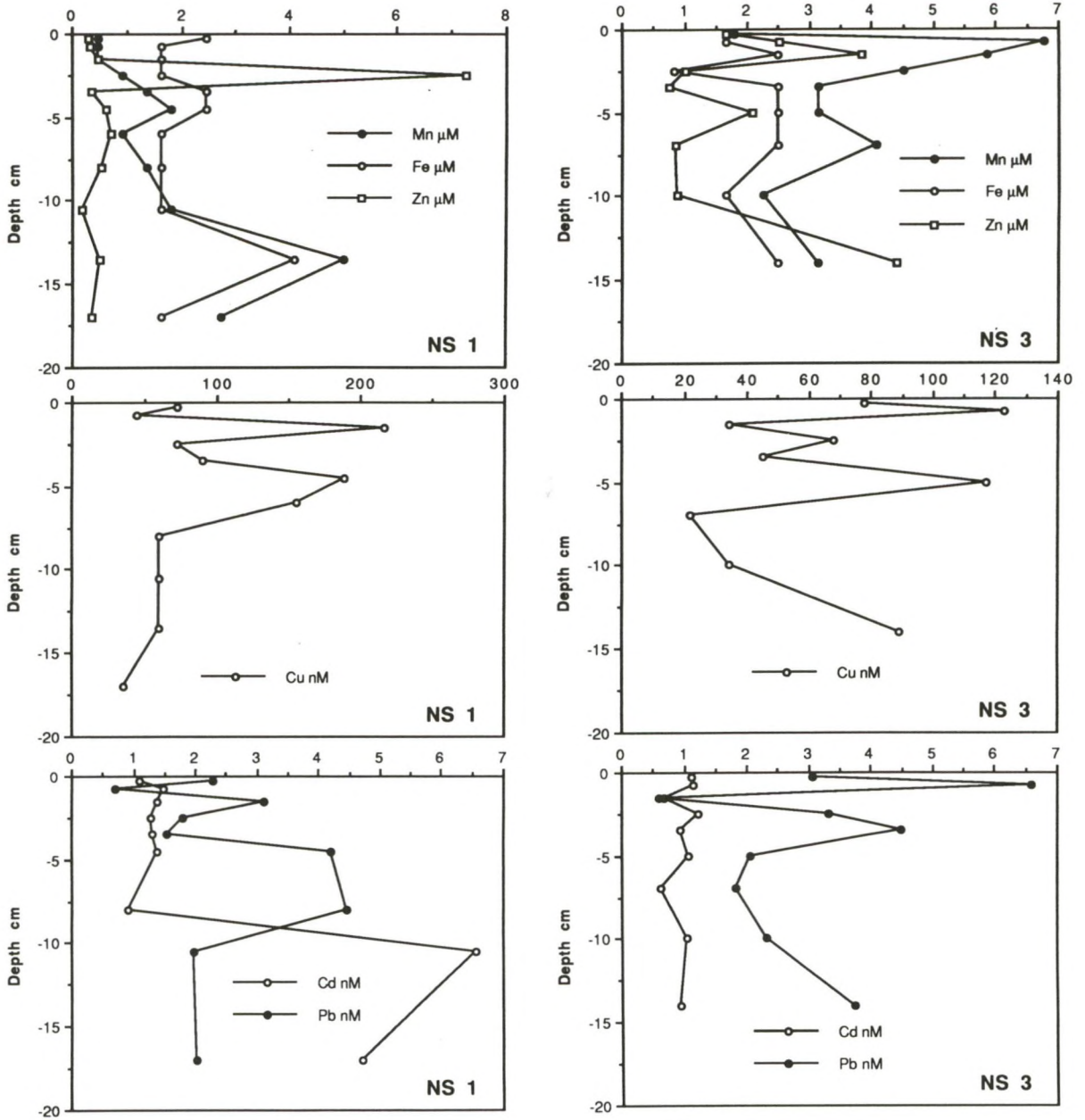


Fig. 7. Pore water profiles of Mn, Fe, Cu, Zn, Cd and Pb in NS1, NS3 and NS4 stations (PW= pore water).

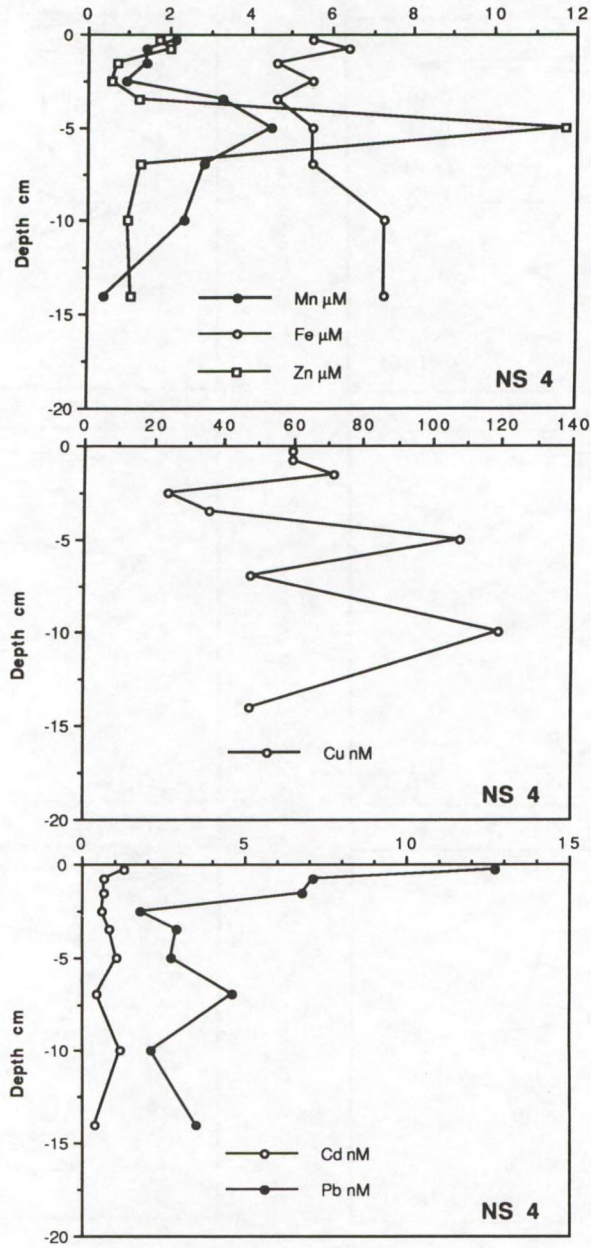


Fig. 7 continued

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

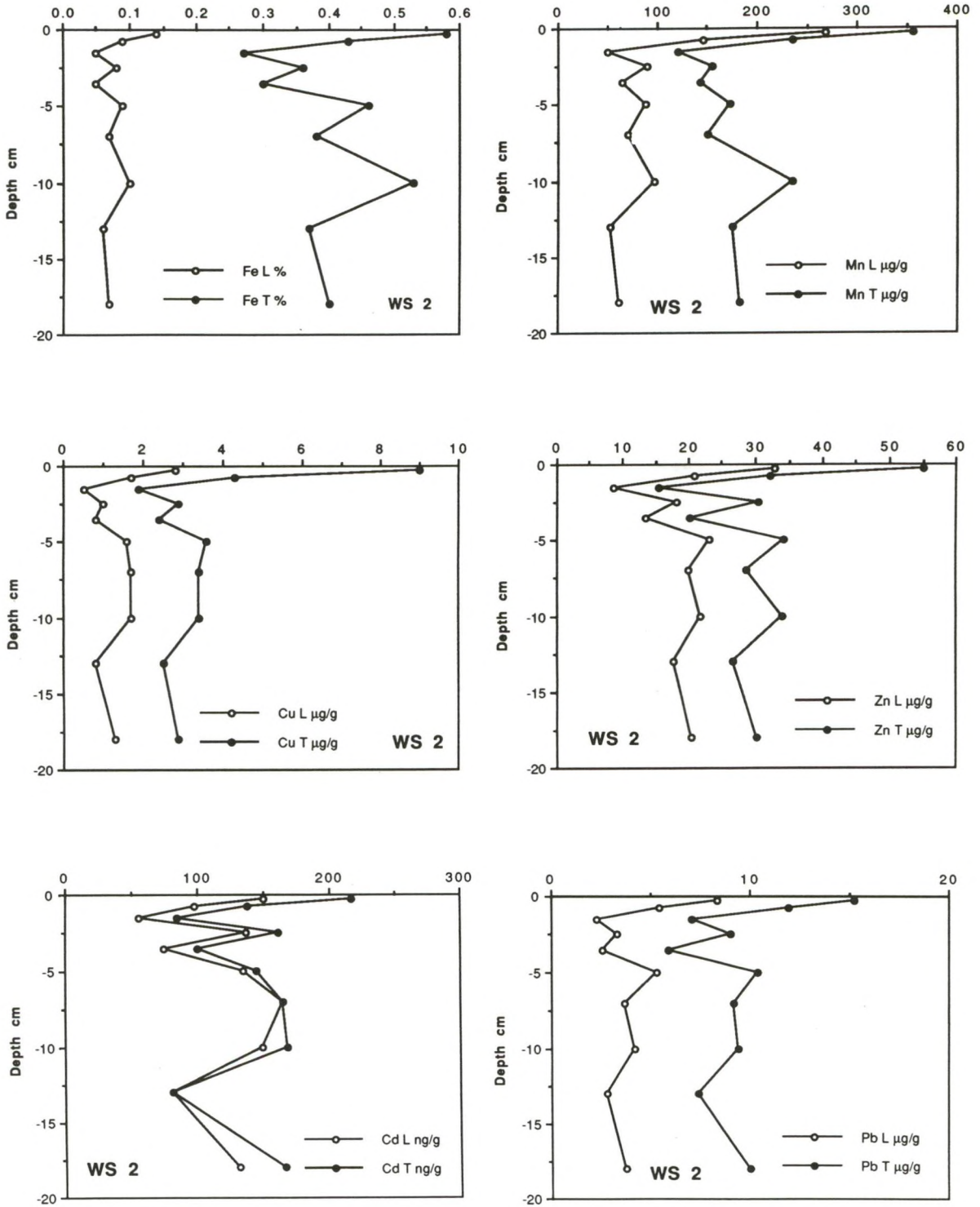


Fig. 8. Solid phase profiles of Mn, Fe, Cu, Cr, Zn, Cd and Pb in the WS2, WS3 and WS5 Stations (L= leachable, T= total).

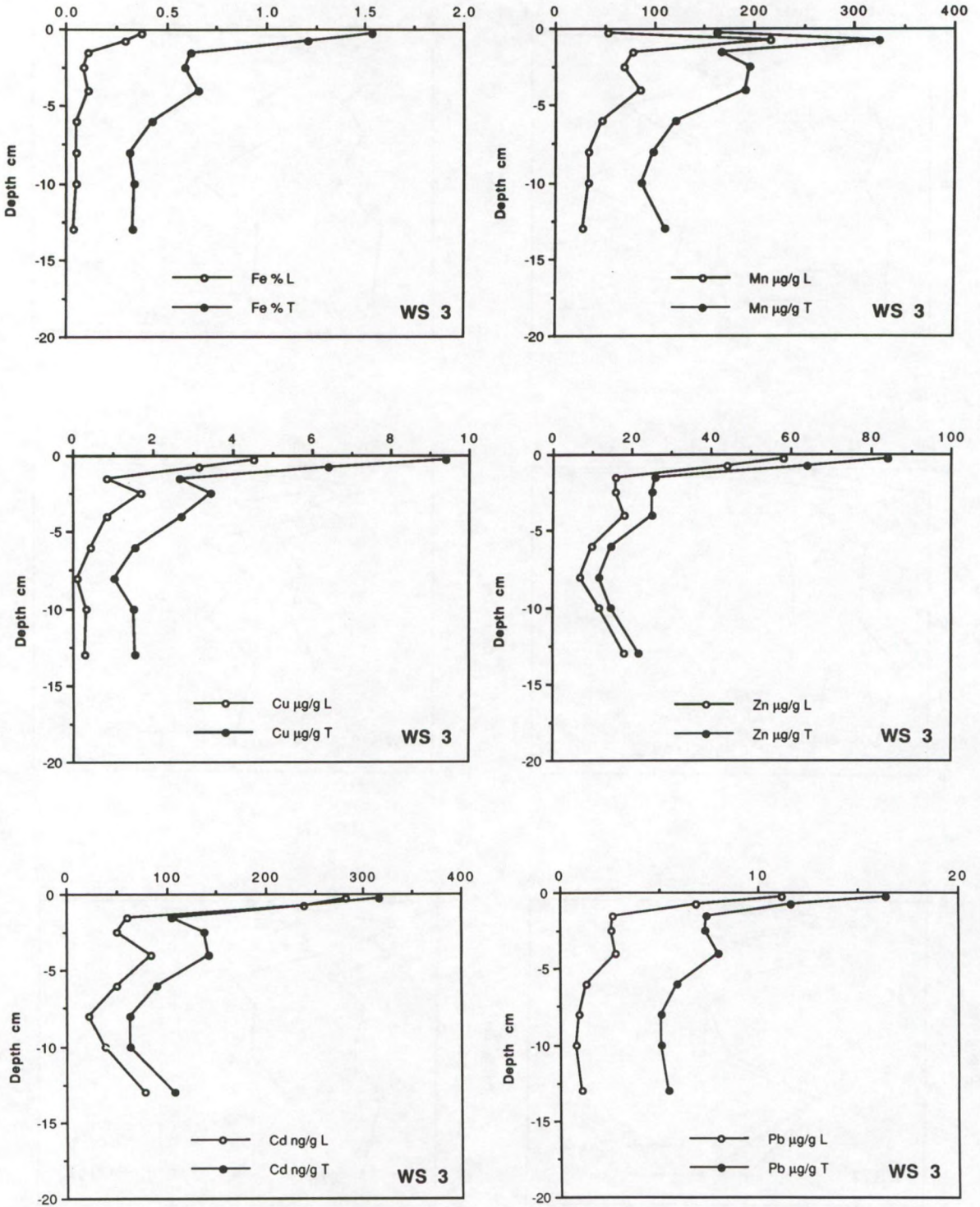


Fig. 8 continued

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

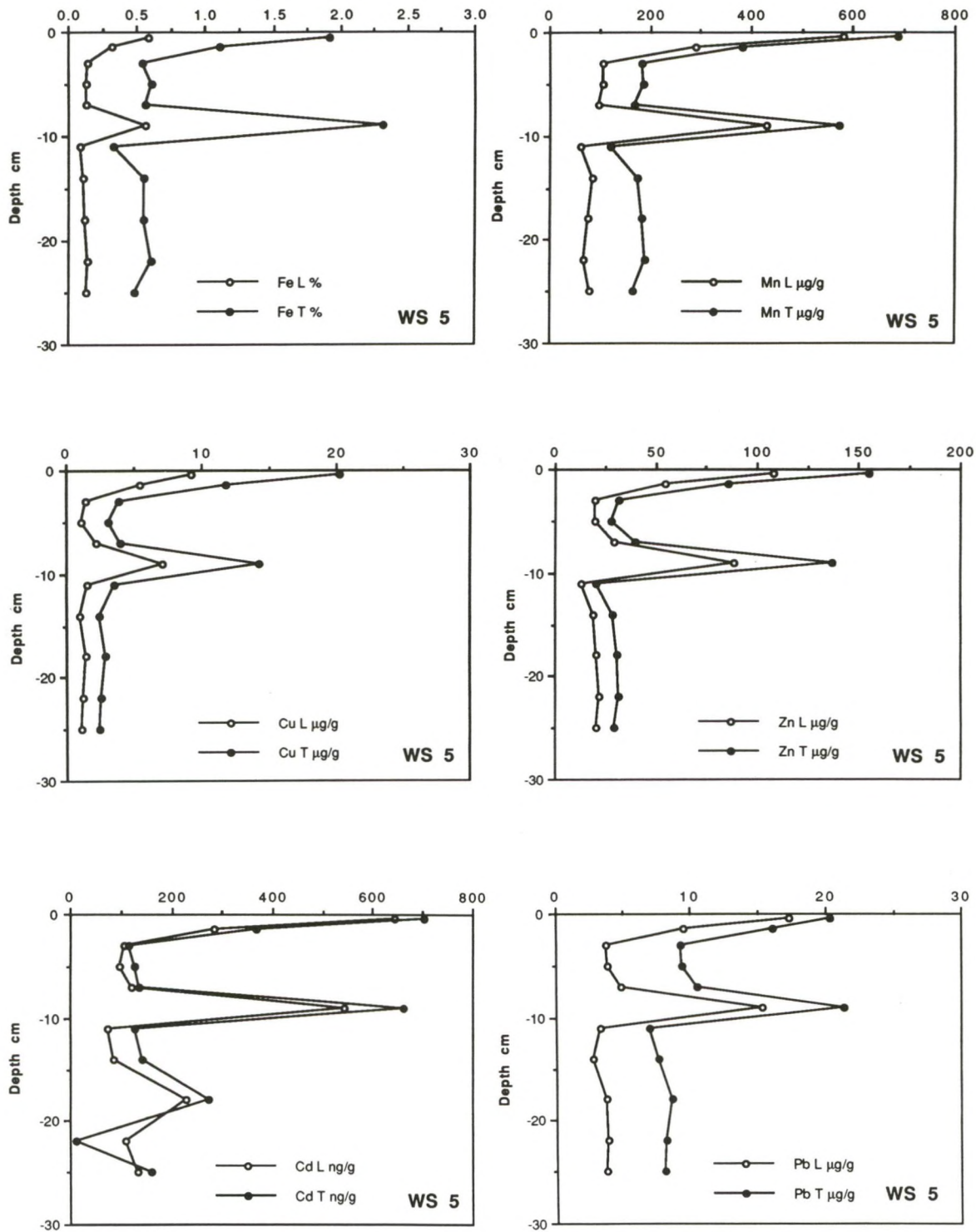


Fig. 8 continued

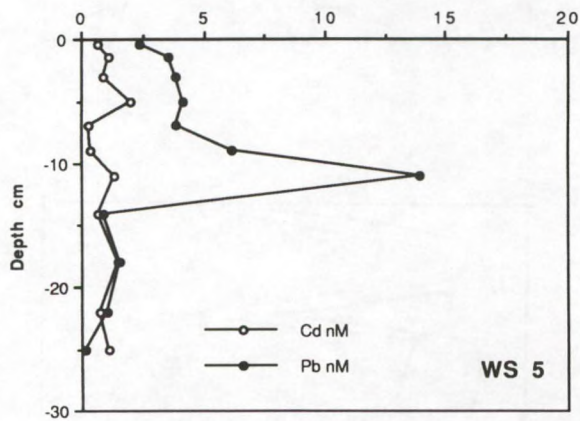
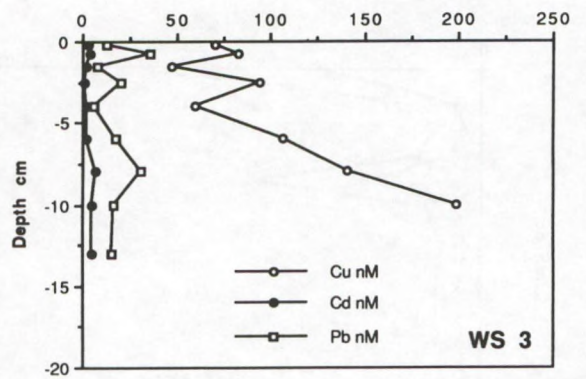
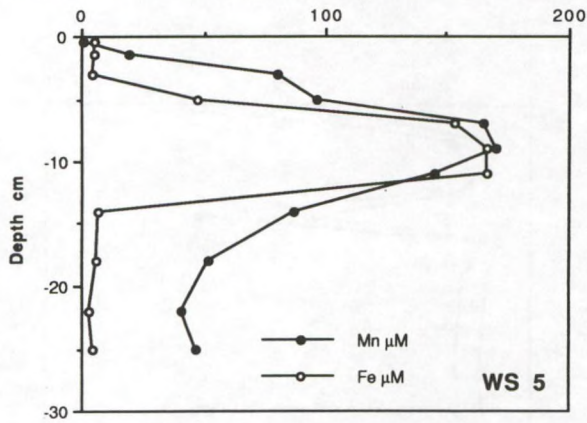
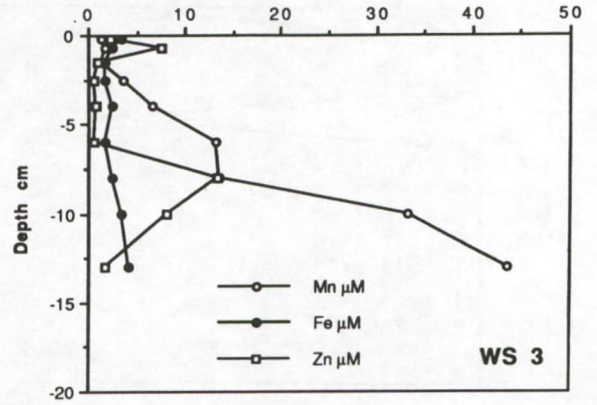
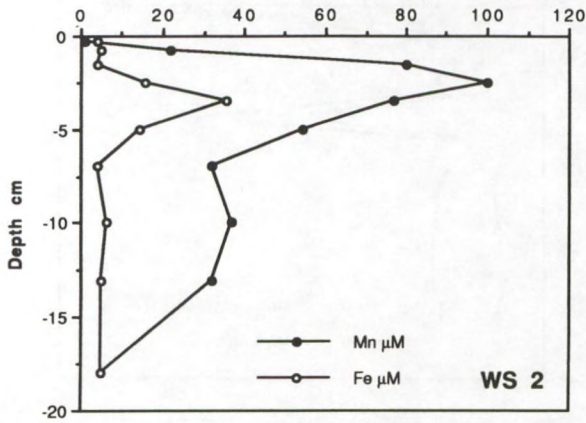


Fig. 9. Pore water profiles of Mn, Fe, Cu, Zn, Cd and Pb in the Wadden Sea (PW= pore water) stations (WS2, WS3, WS5).

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

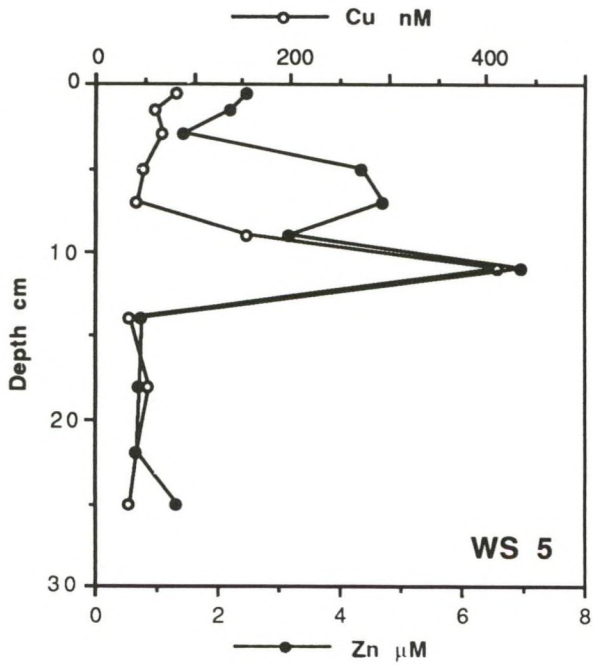
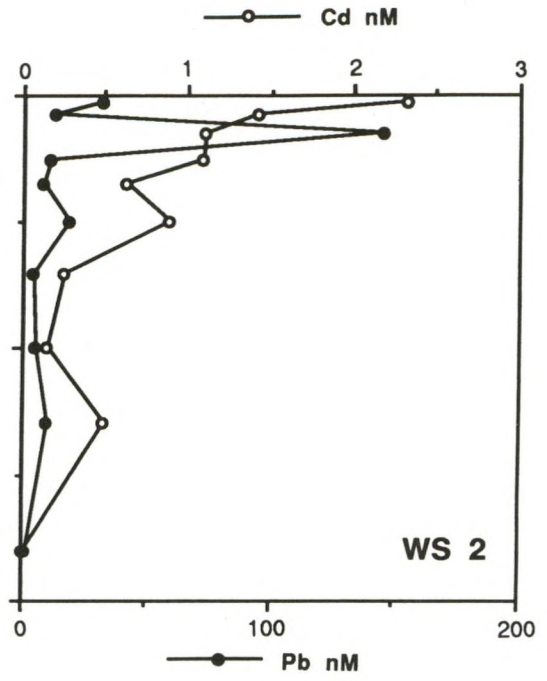
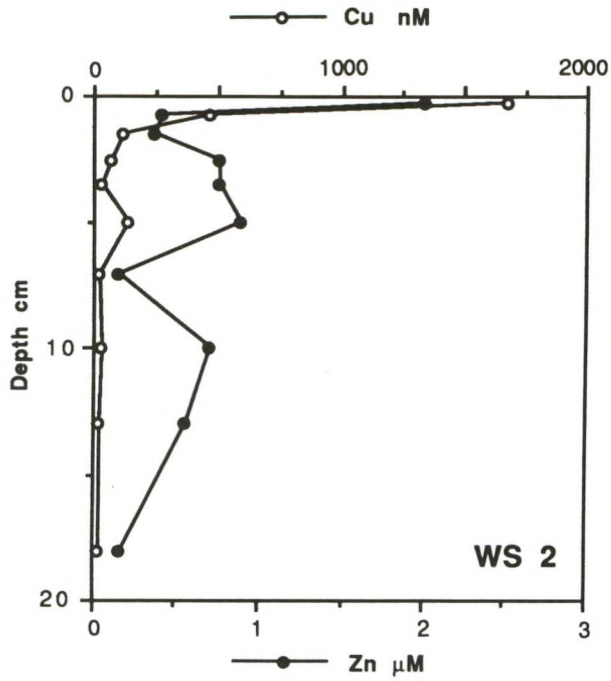


Fig. 9 continued

5. DISCUSSION

5.1. ANALYTICAL ACCURACY

The analytical procedures for sediment and pore water analysis were repeatedly validated by analyzing standard reference materials. In this work, two reference standards, BCR 142, a sandy soil and BCR 277, an estuarine sediment, both having almost similar major element composition, were analyzed for major and trace elements. The obtained agreement (Appendix 1) between the measured and the certified values assures the reliability of the analytical procedures.

The analytical blanks were found negligible compared to the sample values for Mn, Fe and Cr in HCl-extracted sediments. The residual fractions had relatively higher blank values because of the filter digested in the teflon bomb. For Ni, Cu, Zn, Cd and Pb, these were 0.62, 1.25, 15.0, 0.05 and 1.48 $\mu\text{g.l}^{-1}$ respectively. For Cr, Mn and Fe in residual fractions, the blanks were negligible compared to the sample values.

For Mn and Fe in pore water, standards in 0.1 M HCl were used for calibration. For Cu and Zn, the standard addition method was used after diluting the samples with Milli-Q water. For Cd and Pb, external calibration with standards in 0.1 M HNO_3 (Suprapure, E. Merck) was applied. The procedural blank for Mn in pore water was negligible relative to the sample concentrations. For Fe, Cu, Zn, Cd and Pb, the blanks were 30, 0.40, 0.08, 0.02 and 0.30 $\mu\text{g.l}^{-1}$, respectively.

TABLE 8

The estimated analytical accuracy of trace elements measured in pore waters from NS 4. The concentrations are given in μM for Mn, Fe and Zn and nM for Cu, Cd and Pb. CV = coefficient of variation (%). Cu and Zn were measured with GFAAS directly after dilution with Milli-Q water

Element	Conc \pm SD	CV
Mn	2.36 \pm 0.14	6.0
Fe	7.29 \pm 0.43	6.0
Zn	1.07 \pm 0.05	5.0
Cu	119 \pm 5.95	5.0
Cd	1.27 \pm 0.05	4.0
Pb	12.7 \pm 0.8	6.5

The precision of the analytical procedures was estimated for the pore water concentrations of Mn, Fe, Cu, Zn, Cd and Pb. The precision of absorbance measurements, variation in the calibration during

measurements, errors in blank correction, dilutions (for Cu and Zn) and solvent extraction procedures (for Cd and Pb) was taken into account. All these errors are concentration dependent. The overall uncertainties estimated at a measured concentration level of NS4 are given in Table 8 for example. The estimated precision of FAAS measurements was \pm 0.0005 absorbance unit.

5.2. SPATIAL DISTRIBUTION OF TRACE AND MAJOR ELEMENTS

The spatial distribution of trace and major elements partly represent their sources of terrigenous materials. To evaluate this aspect of the sediments, the average contents in the top 2 cm layer of the elements was calculated on the basis of calcium carbonate free sediments to eliminate the dilution effect. The leachable and the residual fractions were summed. Results are summarized in Fig. 10.

The CaCO_3 corrected surface distributions of the trace metals show considerable variations between the stations. Particularly WS5 has large contents of Ni (18.2 $\mu\text{g.g}^{-1}$), Cu (18.3 $\mu\text{g.g}^{-1}$), Pb (21.0 $\mu\text{g.g}^{-1}$), Cr (61.0 $\mu\text{g.g}^{-1}$), Cd (609 $\mu\text{g.g}^{-1}$) and Mn (615 $\mu\text{g.g}^{-1}$) compared to the other stations. Differences between North Sea and Wadden Sea stations were not very pronounced. Only for Zn, Cr and Fe, slightly lower contents were measured in the Wadden Sea. Cd contents were higher in the Wadden Sea than in the North Sea.

In a recent study SAAGER *et al.* (1989) found similar values for Pb and Cd in the Doggerbank area. Also the study of KRAMER *et al.* (1989) indicates contents comparable to our values, particularly at NS3, WS3, WS5.

From the stations in the Wadden Sea, distinct distribution patterns were observed in WS3 and WS5, where all the elemental contents are higher than in the other three WS stations. The inputs to these stations probably have sources of pollution of Cr, Ni, Cu, Cd, Pb and possibly of Zn. The highest content (13.2%) of CaCO_3 was found in WS5 (Table 6); the Mn content (615 $\mu\text{g.g}^{-1}$) was also highest in this station. This apparent relationship between CaCO_3 and Mn can be explained by the fact that calcite minerals provide zones of higher pH as well as nucleation centres for precipitation of Mn on the surface of carbonates (PRUYERS *et al.*, 1991).

The content of the redox elements Mn and Fe was highest on the surface sediments of WS5, the next being WS3. This may indicate that the oxidation of Mn and Fe is very pronounced in these stations resulting in the precipitation of iron and manganese oxyhydroxides in the surface sediments.

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

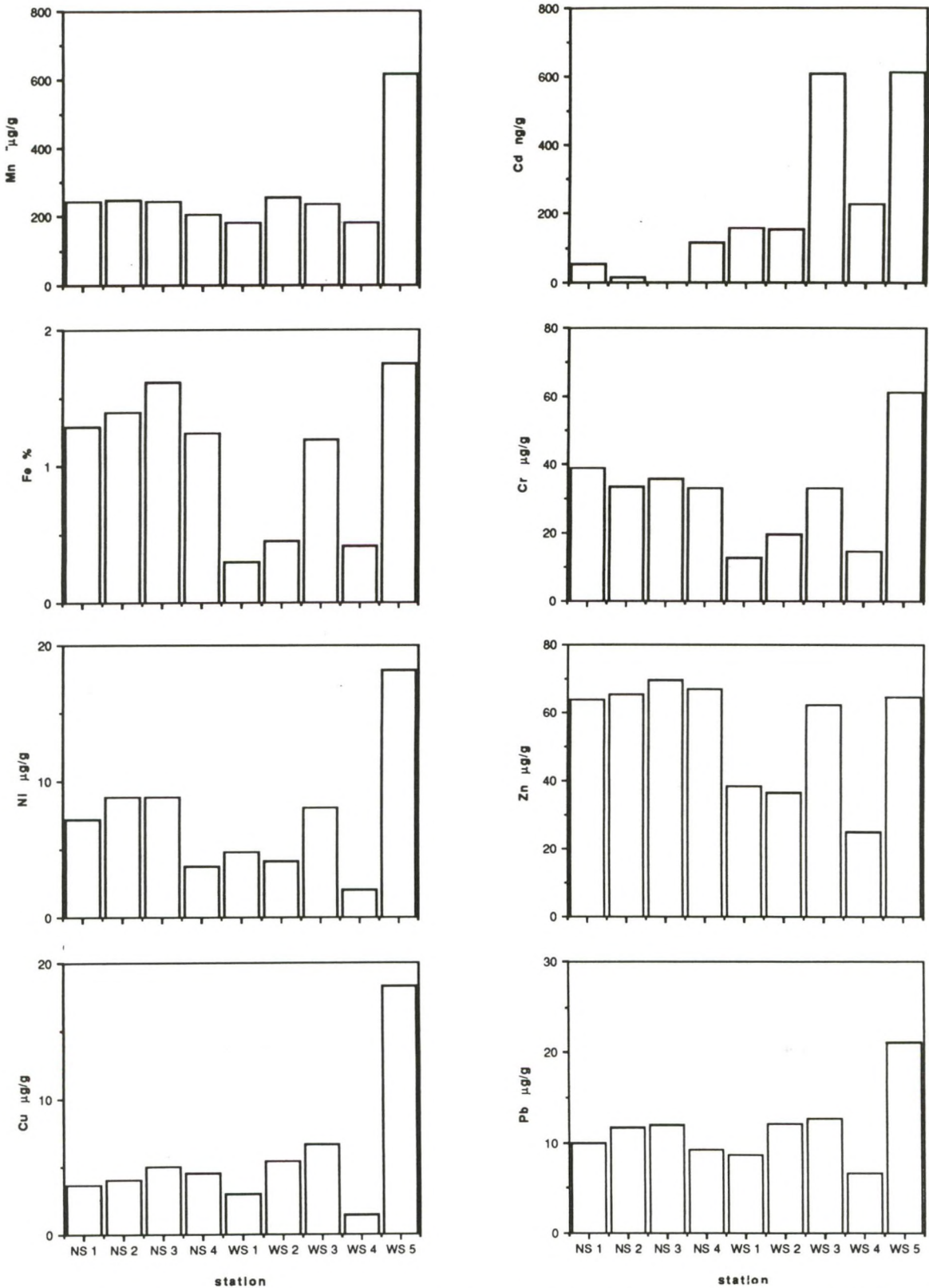


Fig. 10. Spatial distribution of trace elements in the surface sediments (top 2 cm layer) of North Sea and Wadden Sea. The contents are calculated on the basis of CaCO_3 free sediments.

5.3. TRACE ELEMENTS OF THE 0.1 M HCL LEACHABLE FRACTION

One of the ways to evaluate the impact of accumulation of heavy metals on marine sediments is to distinguish between the extractable and the residual fractions of the total content. The extractable fraction is loosely bound to the sediment matrix and reflects partly upon the contribution of the anthropogenic sources. In addition, the mobilization of trace elements from the 'labile' fraction of the surface sediment can be different from that of the relatively older and deeper sediment layers. To evaluate this, the percentage of leachable fractions from the top layer (0-1 cm) and the depth interval of 11-15 cm were determined for all the stations. The relative contributions of the two fractions for Mn, Fe, Cr, Ni, Cu, Zn, Cd and Pb are illustrated in Fig. 11.

The leachable fractions (as percentage of the total) from the surface sediments were generally larger than those from the deeper layers. One exception is Cd for which some surface layers had relatively smaller leachable fractions than the deeper layers.

Also, the exchangeable Pb content is lower in the surface sediment than in deeper layers of the North Sea stations and at WS4. In the other Wadden Sea stations, the opposite was observed. For example, the total Pb content in the surface layer of WS5 consists for 85% of 0.1 N HCl-extractable Pb. In the deeper layer this percentage is 44%.

The percentage of leachable Mn is higher in the surface layers of all stations except WS4 and NS4. This indicates that the deeper layers may have undergone some degree of Mn depletion. The high values in the oxic upper layers point at MnO₂ precipitation which is a normal feature in surface layers (SHAW *et al.*, 1990). Extractable Cr was found to follow the same pattern as the redox element Mn. Similar observations for Cr have been reported earlier for coastal sediments (GAILLARD *et al.*, 1991).

5.4. ELEMENT/AL RATIOS

Aluminium in marine sediments mostly originates from chemical weathering of crustal rocks. Anthropogenic inputs may, however, be considerable. In the present investigation, Al contents, expressed as Al₂O₃ were found to be in

the range of 6.56-12.0% (Table 6). In view of the crustal content of approximately 31% (Al₂O₃) (GUOHUI *et al.*, 1988), this may be considered as the background level related to the mixing clay minerals with sands. It has been observed that if trace element contents are expressed as ratios between the trace elements and crustal elements such as Al or Ti, more revealing information can be obtained (Zuo *et al.*, 1989). Trace element:Al ratios in the top 0-2 cm layer of the sediments are presented in Fig. 12.

The Zn:Al, Ni:Al and Pb:Al ratios are nearly equal in the surface sediments of all the stations. This indicates that deposition of Zn, Ni and Pb is most likely of natural origin. Accumulation of Fe is relatively higher in the North Sea than in the Wadden Sea. Fe:Al ratios in the NS ranges from 0.44 to 0.55 whereas in the WS it is 0.17 to 0.48. The opposite trend holds for Cd:Al being lower in the North Sea. Cu:Al ratios are highest in the WS. Station WS4, however, has the lowest (0.09) value of all the calculated ratios. Copper is highly complexed by organic ligands. In the surface sediments of WS4, the carbon content is low (Tables 2, 6). The high Cu:Al ratios at WS5 (Org. C -0.05%) are not easily explained. Maybe precipitation of sulphides are responsible for the observed ratio at this station.

It is clearly observable that the surface sediments of WS3 and particularly WS5 are enriched with all the trace elements as compared to the other stations. This is well correlated with the higher Fe:Al ratio in these stations. This can probably be explained by the flocculation-deposition process of FeOOH-organic matter which controls the transport of Pb, Cu, Ni and Zn to the sediment (ZURICH, 1991; GERRINGA, 1990).

Largest variations were observed in the Cd:Al ratios, by an order of magnitude in the NS and a factor of 2 to 3 in the WS. The Cd:Al ratio at NS3 is not included in Fig. 12 because of potential contamination during analysis. The Cd:Al ratios in all the stations in WS are significantly higher than those of the North Sea: 0.63-2.20 in the WS, compared to 0.04-0.41 in the NS. These deviations may indicate anthropogenic sources of Cd in the Wadden Sea. The higher deposition rate in the Wadden Sea is another factor to be considered for comparison of results from these two regions.

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

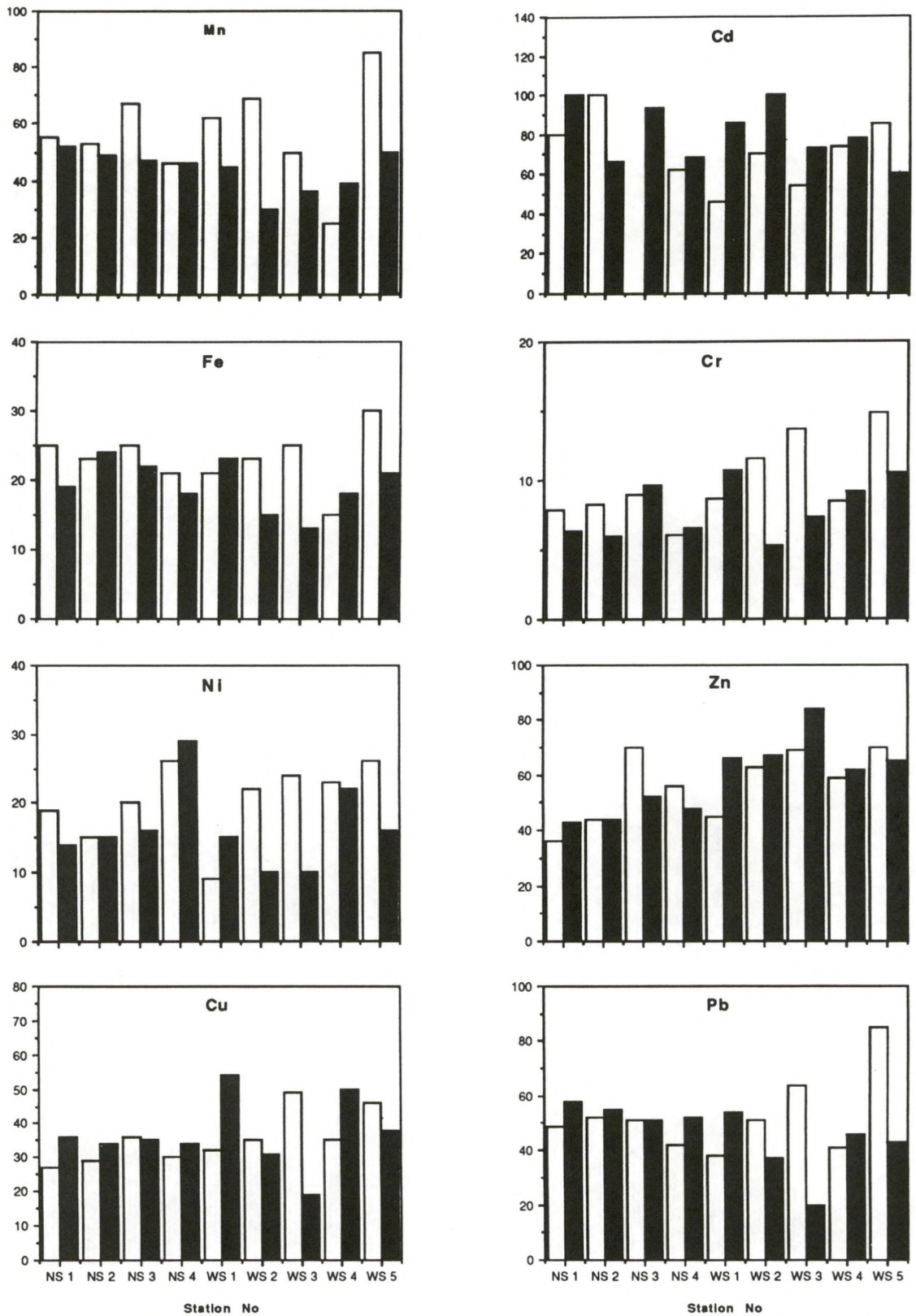


Fig. 11. Distribution of trace elements in the leachable fraction of the surface (0-1 cm) and the deep layer (11-15 cm) of sediment cores (□= top layer and ■= bottom layer).

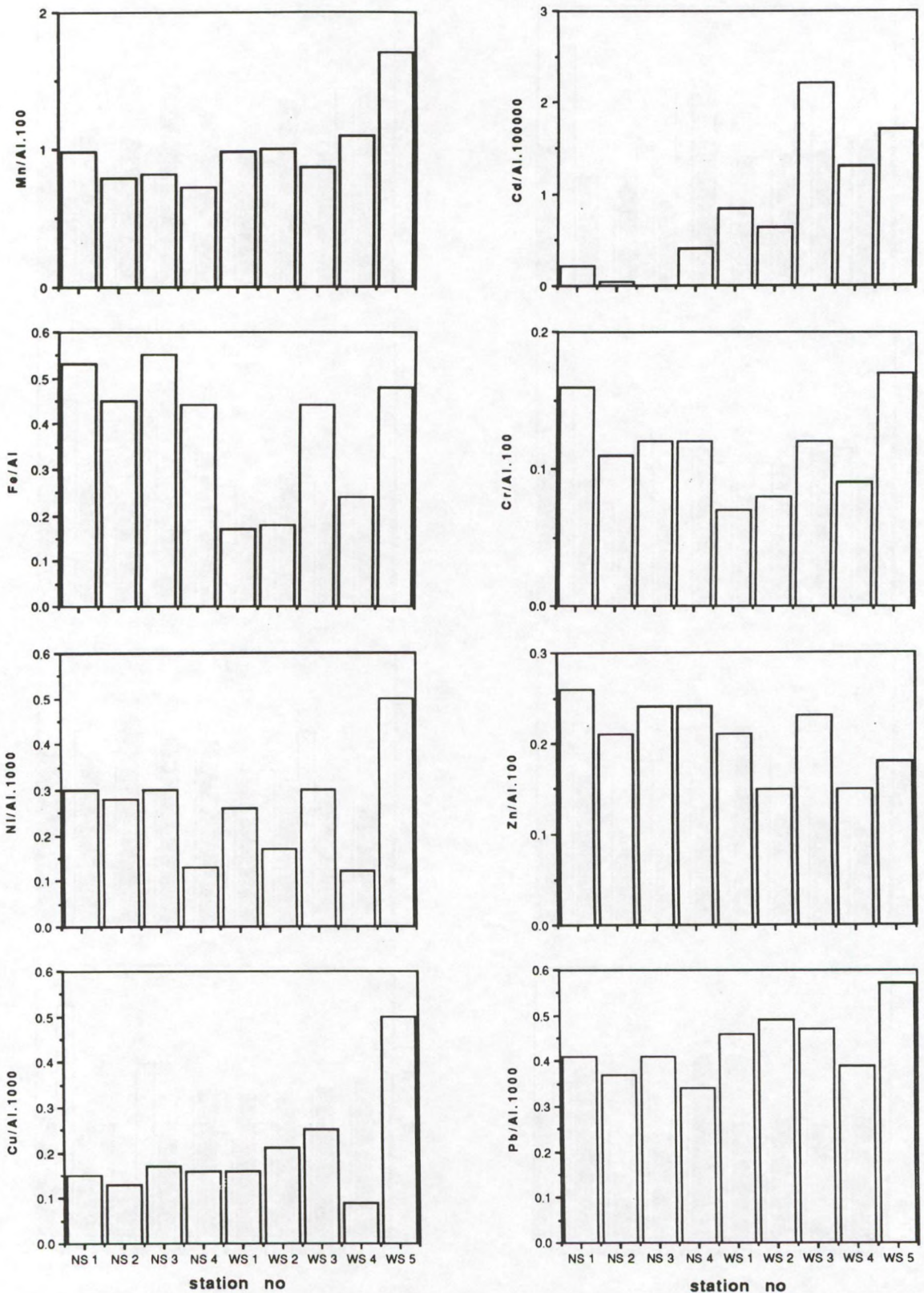


Fig. 12. Trace element:Al ratios for the top layer (0-2 cm) sediments in the North Sea and the Wadden Sea.

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

5.5. VERTICLE PROFILES OF TRACE ELEMENTS IN SEDIMENTS AND INTERSTITIAL WATERS

5.5.1. SEDIMENT PROFILES NORTH SEA (FIG. 6)

Mn and Fe

The investigated North Sea sediments are very sandy with low organic carbon contents. The profiles are very homogenous indicating steady state conditions. The percentage of the acid-leachable fraction is ca 50% for Mn. For Fe, this fraction is lower by a factor of ca. 2.5. This implies that Fe is present in the sediments in the form of Fe-Mn-oxyhydroxides, a general feature of oxic sediments. Similar findings have been reported previously for the Oyster Grounds (SAAGER *et al.*, 1989). Relatively higher contents of Mn and Fe were observed below 10-15 cm depth.

Cu and Zn

The total content of Cu varies between 3 and 6 $\mu\text{g.g}^{-1}$. The leachable fraction was between 25 and 35%. The distributions are fairly homogeneous with depth. The present results of Cu appear to be higher compared to previous studies of similar sediments (SAAGER *et al.*, 1989). Spatial inhomogeneity may be the cause for this difference. The higher concentrations of Zn obtained in the present study may have similar reasons. The fraction of leachable Zn was 40-50% with the exception of station NS3, where it is 50-70%. The total content (70-95 $\mu\text{g.g}^{-1}$) of Zn was also significantly higher in this station than at the other North Sea stations. This may indicate higher contributions of anthropogenic inputs at NS3.

Cd and Pb

All lead profiles of the examined North Sea sediments were very stable. The leachable content was almost constant between 5 to 7 $\mu\text{g.g}^{-1}$, the lowest values being observed at NS4. During hydrochloric acid extraction, the solubility of PbCl_2 can become important. The lowest value of leachable Pb coincides with the low total Pb content at NS4. Probably dilute nitric acid extraction may provide better results for Pb than HCl extraction.

Below the surface, deposition of Pb appears to be uniformly increasing with depth. This may imply a gradual decrease of the anthropogenic inputs of Pb to the marine environment. The total lead content is similar to the values reported earlier for sandy North Sea sediments (SAAGER *et al.*, 1989). In recently contaminated sediments Pb profiles generally show an opposite feature (KRAMER *et al.*, 1989).

Excluding contamination in the laboratory (Appendix 1) the Cd profiles indicate some 'hot

spots' of Cd pollution at a depth of about 6-8 cm at NS1 and 1-2 cm at NS3. The total contents of Cd at these depths were 1.5 and 2.6 $\mu\text{g.g}^{-1}$, respectively. The upper and lower layers, have contents of the order of 50 to 100 ng.g^{-1} . The origin of the high subsurface Cd contents is unclear, but it may be related to recent deposits of organics and fine grained sediments.

5.5.2. SEDIMENT PROFILES WADDEN SEA (FIG. 8)

Mn, Fe and Cd profiles

From the Mn and Fe profiles, clear evidences of redox reactions are observable at a depth of about 3 cm at WS2, WS3 and WS5. No compression of the redox boundary towards the surface is observed. In general such a moving front would be observable at decreasing bottom water oxygen concentration. In the Cd profiles, the minimum in the leachable Cd content is within the aerobic zone of the sediment. This indicates that the gradual removal of Cd from the solid phase is correlated with oxygen penetration depth. This observation is very similar to those reported by GOBEIL *et al.* (1987) for much deeper coastal marine environments.

At WS4 (not shown), the solid phase profile of Mn and Fe appeared to be homogeneous with depth, however, with a mild sub-surface perturbation at a depth of about 1-2 cm. The Cd distribution in this core has a minimum at a depth of ≈ 1 cm and there seems a diffusion barrier at about 2 cm. This may be due to the Cd sulphide precipitation. The range of total contents in the surface layer (169-702 ng.g^{-1}) is very similar to those reported previously but they are distinctly higher than the values in the North Sea. 'Hot spots' of Cd accumulation at WS3 (1-27 $\mu\text{g.g}^{-1}$) probably indicate the presence local sources. Similar observations have been reported elsewhere (KRAMER *et al.*, 1989).

Cu and Zn profiles

In all the examined sediment cores, distinct enrichment of both Cu and Zn was observed in the surface sediments, except at station WS4 where the enrichment of Zn seemed less significant. Similar profiles of Cu and Zn have been reported by others (MACDONALD *et al.*, 1991). This type of enrichment on the surface is mostly due to anthropogenic sources of contamination.

In some stations in the Wadden Sea, enrichment of Cu below the Mn-oxide zone is observed. For example at WS5 the total content is 14.2 $\mu\text{g.g}^{-1}$ at 9.0 cm, whereas it is 3.86 $\mu\text{g.g}^{-1}$ at 3.0 cm. This trapping enrichment can be explained in terms of carbon diagenesis which in some circumstances can

control the distribution of Cu, Zn and Pb. The organic carbon content was also highest (0.37%) at about this depth at WS5.

Cr and Pb

A sharp depletion of Cr contents is observed at the redox boundary of Mn, except at WS5 where a gradual depletion occurs with depth. At this station, however, sharp fluctuations (16.5, 63.1 and 7.48 $\mu\text{g.g}^{-1}$) are observed between 7 and 11 cm depth.

The distribution of lead has similar trends as those of Cu and Zn, which is in agreement with findings of SHAW *et al.* (1990). The leachable fraction and the total content profile at WS2 have patchy distributions with a significant enrichment of the residual fraction at a depth of 6 cm. At WS3, both the leachable and the total contents decrease with depth.

The highest contents of Pb (16.1-20.4 $\mu\text{g.g}^{-1}$) are observed in the surface layers. However, some strong perturbation is observed in deeper layers of WS5. Apart from this, the general decrease with depth, both of the leachable fraction and of the total content, indicates recent inputs from anthropogenic sources.

5.5.3. PORE WATER PROFILES

REDOX ELEMENTS (Mn, Fe)

WS2: The Mn profile sharply rises up to a value of 99.7 μM at a depth of 2-3 cm, then gradually decreases to a value of 5.12 μM at 18 cm. The rise of Fe is more gradual with the maximum concentration (35.4 μM) at a depth of 3-4 cm. From this depth, a gradual decrease to 4.73 μM with a minor fluctuation at about 10 cm is evident. These trends in the profiles of the redox elements are reflections of common redox processes in marine sediments.

WS3: the Mn concentration profile gradually increases up to 43.7 μM . The iron profile on the other hand, initially decreases and then remains fairly constant below 2-3 cm depth. The same constancy is observed in the percentage of the leachable fraction of the solid phase.

WS5: In the top layers the Fe concentration remains constant at a level of ca. 5 μM down to a depth of 3 cm and then sharply increases with a maximum of 167 μM at about 9-11 cm, again decreasing to a value of 4.19 μM below. The Mn profile steeply rises with a maximum at 7-9 cm just above the Fe maximum. Similar redox profiles were recently reported by SHAW *et al.* (1990) in nearshore sediments under different depositional conditions.

Near the sediment-water interface, 0.1 N HCl leachable Fe is high due to high oxygen concentrations. Depletion of dissolved Fe due to oxalic precipitation is clearly evident at this station.

NS1, 3, 4: In all the North Sea sediments weak but similar trends of dissolved Mn were observed. The general trend indicates initial constancy and then a slow rise to an almost constant level. At NS3, the sharp rise is from 1.8 μM to ca. 6.8 μM at 1 cm depth. This type of Mn pore water profiles is related to well oxidized sandy sediments with low carbon contents. The Fe profile at NS3 shows an almost constant pattern (5.8 μM) with depth. In the other cores, a slow initial decrease to a minimum and then a rise to a constant level occurs, indicating the presence of oxic/sub-oxic conditions. The constant pattern of the extractable fractions of the solid phase with depth, however, indicates equal amounts of Fe-oxides at all depths studied.

TRACE ELEMENTS

Cu and Cd

The Cu profiles distribution peaks at 3 depths at NS stations. In general, a significant enrichment in the top layer (0-0.5 cm) is observed. The subsequent removal and regeneration of Cu may partly point at oxic/sub-oxic transitions. Similar observations have been reported for transition elements (SHAW *et al.*, 1990). The remobilization of Cu below the oxic/sub-oxic zones may be explained by non-steady state conditions and resulting transient peaks. The peak concentration may also be explained by alteration of the solid phase carrier such as Mn-oxides or metal sulphides.

From the pore water profiles it is evident that Cu is released to the pore water phase in the oxic surface layers, possibly due to the oxidative degradation of organic matter (GOBEIL *et al.*, 1987). This is in contrast to Mn as discussed earlier. In the anoxic sub-surface layers Cd concentrations increase again. For example, the concentration is 1.27 nM at 0-0.5 cm of NS4, decreasing to a minimum of 0.6 nM at 2.5 cm depth and then increasing to 1.05 nM at 5 cm. Similar fluctuations were observed in the Wadden Sea.

Pb

Examination of the Pb profiles of WS2 together with the total content in the solid phase indicates a direct correlation between the two phases. At this station, the concentration is 32.2 nM in the top 5 mm increasing to 145 nM at 1-2 cm. Less pronounced, fluctuations were observed down the core. The higher concentrations in the top layer point at

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anthropogenic sources. Two regeneration zones were observed at a depth of 1.5 cm and at 5 cm.

The subsurface increase in Pb concentration is known to be sulphide dependent. The observed increase in pore water concentrations may thus be related to the mineralisation of organic matter by sulphate reduction.

5.5.4. ASSOCIATION OF TRACE ELEMENTS WITH CLAY MINERALS

The extraction characteristics (Table 7) of the elements, Mn, Fe, Cr, Ni and Cu were studied in the fraction < 10 µm of the sediment. From the results it is apparent that a high proportion of the elements is associated with the fine fraction, although the percentage < 10 µm is only between 2 to 6% of the bulk sediment in the study areas.

The extraction results of Cr and Ni, which are mainly associated with illite/mica, indicate that ca. 85% of Ni and 95% of the total extractable fraction of Cr is mobilized by oxalic acid at pH = 2. For Mn, Fe and Cu, this percentage was 94, 97 and 75%, respectively. The extraction results of Mn, Cu and Cr may be explained by association with FeOOH and with chlorite in the fine sediment fraction. Similar influences of the chemical composition of the clay minerals on the extraction of trace elements has been reported by other researchers (PROHIC & KNIEWALD, 1987; PANDARINATH & NARAYANA, 1991).

Further physico-chemical investigation of the sediments may provide insight in the possible mechanism of trace element association with clay minerals, adsorption on the surface or inclusion in the crystal lattice. The proportions of the crystalline and the poorly crystalline materials would indicate how much of the fine fraction originates from detrital particles and the authigenic deposits carrying the trace elements.

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APPENDICES

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APPENDIX 1

Trace and major element composition of some standard reference materials (BCR 142 and BCR 277) used in this study for quality assurance of analytical results.

Element	BCR 142		BCR 277	
	This work	Certified	This work	Certified
Al ₂ O ₃ *	9.48±0.56	(9.32)	9.70	8.81
CaO	3.82±0.28	(4.94)	6.70	8.75
Fe ₂ O ₃	2.79±0.13	(2.80)	6.24	6.53
SiO ₂	69.4±6.9	(68.2)	51.2	50.9
Cd	0.24±0.06	0.27±0.09	-	-
Cu	27.3±0.7	27.6±1.9	-	-
Cr	73.6±4.4	(74.9)	-	-
Mn	566±2.8	(569)	1310	(700)**
Ni	28.7±1.3	29.2±2.5	-	-
Pb	34.2±0.6	37.8±1.9	-	-
Zn	92.2±5.5	92.4±4.4	568±34	547±4.4

* For Fe, Ca, Al and Si, the concentrations are in % as oxide while for the others, these are in µg/g of the dry sediment. The values in the parenthesis are tentative.

** The manganese content of the standard, BCR 277, is not certified. It is the concentration found after separation, while in the present analysis it is the total concentration.

APPENDIX 2

Mn in North Sea sediments. D = mean depth; L = leachable; R = residual; T = total; L' = leachable percent; P = pore water.

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L' (%)	P(μM)
NS 1	0.25	113	100	213	53.1	0.46
53°42.52'N	0.75	124	96	220	56.3	0.46
4°29.45'E	1.50	123	116	239	51.4	0.46
	2.50	122	68	190	64.2	0.91
	3.50	119	119	238	50.0	1.37
	4.50	124	124	248	50.0	1.82
	6.00	130	109	239	54.4	0.91
	8.00	125	131	256	48.8	1.37
	10.50	116	115	231	50.2	1.82
	13.50	122	115	237	51.5	5.01
	17.00	128	114	242	52.9	2.73
NS 2	0.25	130	103	233	55.8	1.29
53°41.80'N	0.75	112	105	217	51.6	0.86
4°30.20'E	1.50	125	118	243	51.4	-
	2.50	125	118	243	51.4	1.29
	3.50	119	111	230	51.7	1.29
	4.50	111	118	229	48.5	-
	6.00	112	119	231	48.5	2.14
	8.00	108	95	203	53.2	1.29
	10.50	118	117	235	50.2	2.57
	14.00	111	117	228	48.7	3.00
NS 3	0.25	132	42	174	75.9	1.80
53°57.39'N	0.75	140	105	245	57.1	6.76
4°58.01'E	1.50	139	118	257	54.1	5.86
	2.50	117	117	234	50.0	4.51
	3.50	84	98	182	46.1	3.15
	5.00	109	128	237	46.0	3.15
	7.00	103	110	213	48.3	4.06
	10.00	91	97	118	48.4	2.25
	14.00	98	112	210	46.7	3.15
NS 4	0.25	102	108	210	48.6	4.24
54°59.98'N	0.75	81	108	189	42.9	1.41
6°26.22'E	1.50	81	101	182	44.5	1.41
	2.50	84	112	196	42.9	0.94
	3.50	99	106	205	48.3	3.30
	5.00	93	106	199	46.7	4.51
	7.00	90	111	201	44.8	2.83
	10.00	82	109	191	42.9	2.36
	14.00	88	107	191	46.1	1.41

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APPENDIX 3

Fe in North Sea sediments. D = mean depth; L = leachable; R = residual; T = total; L' = leachable percent; P = pore water.

Station	D(cm)	L($\mu\text{g/g}$)	R(%)	T(%)	L' (%)	P(μM)
NS 1	0.25	0.30	0.98	1.28	23.4	2.45
53 ⁰ 42.52'N	0.75	0.29	0.79	1.08	26.8	1.64
4 ⁰ 29.45'E	1.50	0.25	0.98	1.23	20.3	1.64
	2.50	0.32	0.76	1.08	29.6	1.64
	3.50	0.33	1.23	1.56	21.1	2.45
	4.50	0.33	1.34	1.67	19.7	2.45
	6.00	0.36	1.37	1.73	20.8	1.64
	8.00	0.31	1.34	1.65	18.7	1.64
	10.50	0.34	1.35	1.69	20.1	1.64
	13.50	0.32	1.41	1.73	18.5	4.08
	17.00	0.34	12.37	1.71	19.9	1.64
NS 2	0.25	0.33	1.14	1.47	22.4	1.64
53 ⁰ 41.80'N	0.75	0.30	1.01	1.31	22.9	2.45
4 ⁰ 30.20'E	1.50	0.31	1.16	1.47	21.0	-
	2.50	0.33	1.26	1.59	20.7	3.27
	3.50	0.35	1.29	1.64	21.3	1.64
	4.50	0.35	1.33	1.68	20.8	2.45
	6.00	0.32	1.32	1.64	19.5	-
	8.00	0.34	1.13	1.47	23.9	2.45
	10.50	0.35	1.37	1.72	20.3	2.45
	14.00	0.33	1.37	1.40	23.5	2.45
NS 3	0.25	0.35	0.75	1.10	31.8	1.66
53 ⁰ 57.39'N	0.75	0.37	1.32	1.69	21.9	1.66
4 ⁰ 58.01'E	1.50	0.35	1.40	1.75	20.0	2.49
	2.50	0.35	1.19	1.54	22.7	0.83
	3.50	0.24	0.93	1.17	20.5	2.49
	5.00	0.34	1.19	1.53	22.2	2.49
	7.00	0.38	1.23	1.61	23.6	2.49
	10.00	0.37	1.32	1.69	21.9	1.66
	14.00	0.37	1.32	1.69	21.9	2.49
NS 4	0.25	0.24	0.92	1.16	20.7	2.52
54 ⁰ 59.98'N	0.75	0.23	0.89	1.12	20.5	1.68
6 ⁰ 26.22'E	1.50	0.27	1.01	1.28	21.1	2.52
	2.50	0.26	1.10	1.36	19.1	2.52
	3.50	0.37	1.19	1.56	23.7	5.04
	5.00	0.26	1.06	1.32	19.7	3.36
	7.00	0.26	1.13	1.39	18.7	2.52
	10.00	0.25	1.20	1.45	17.2	2.52
	14.00	0.27	1.21	1.48	18.2	2.52

APPENDIX 4

Cr in North Sea sediments. D = mean depth; L = leachable; R = residual; T = total; L' = leachable percent.

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L' (%)
NS 1	0.25	3.14	31.4	34.5	9.1
53 ⁰ 42.52'N	0.75	2.37	32.2	34.6	6.8
4 ⁰ 29.45'E	1.50	1.78	38.1	39.9	4.5
	2.50	2.37	23.2	25.6	9.3
	3.50	2.45	37.6	40.1	6.1
	4.50	2.64	40.0	42.6	6.2
	6.00	2.66	40.3	43.0	6.2
	8.00	2.61	36.3	38.9	6.7
	10.50	2.80	39.9	42.7	6.6
	13.50	2.76	41.0	43.8	6.3
	17.00	3.10	35.3	38.4	8.1
NS 2	0.25	2.40	27.8	30.2	7.9
53 ⁰ 41.80'N	0.75	2.18	21.1	23.3	9.4
4 ⁰ 30.20'E	1.50	2.28	38.2	40.5	5.6
	2.50	2.32	39.0	41.3	5.6
	3.50	2.71	35.9	38.6	7.0
	4.50	2.48	36.9	39.5	6.5
	6.00	2.50	37.2	39.7	6.3
	8.00	2.50	32.6	35.1	7.1
	10.50	2.65	35.6	38.3	6.9
	14.00	2.62	41.0	43.6	6.0
NS 3	0.25	2.57	17.2	19.6	13.1
53 ⁰ 57.39'N	0.75	2.80	36.9	39.7	7.1
4 ⁰ 58.01'E	1.50	2.90	37.5	40.4	7.2
	2.50	2.71	34.4	37.1	7.3
	3.50	2.34	28.6	30.9	7.5
	5.00	3.08	32.4	35.5	8.6
	7.00	3.18	40.1	43.3	7.3
	10.00	3.22	40.7	43.9	7.3
	14.00	3.35	31.4	34.8	9.6
NS 4	0.25	1.85	27.9	29.8	6.2
54 ⁰ 59.98'N	0.75	1.84	29.1	30.9	5.9
6 ⁰ 26.22'E	1.50	2.26	32.5	34.8	6.5
	2.50	2.24	34.4	36.6	6.1
	3.50	2.93	28.4	31.3	9.3
	5.00	2.31	26.4	28.7	8.0
	7.00	2.41	29.2	31.6	7.6
	10.00	2.64	37.4	40.0	6.6
	14.00	2.48	35.6	38.1	6.5

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

APPENDIX 5

Ni in North Sea sediments. D = mean depth; L = leachable; R = residual; T = total; L' = leachable percent.

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L' (%)
NS 1	0.25	1.13	6.07	7.20	15.7
53 ⁰ 42.52'N	0.75	1.14	4.19	5.33	21.4
4 ⁰ 29.45'E	1.50	1.44	6.23	7.67	18.8
	2.50	1.12	2.62	3.74	29.9
	3.50	1.85	8.13	9.98	18.5
	4.50	1.52	9.15	10.67	14.2
	6.00	1.42	9.07	10.49	13.5
	8.00	1.53	9.17	10.70	14.3
	10.50	1.60	9.59	11.19	14.3
	13.50	1.60	9.69	11.56	13.8
	17.00	1.76	9.85	11.61	15.1
NS 2	0.25	1.20	7.58	8.78	13.7
53 ⁰ 41.80'N	0.75	1.22	6.39	7.61	16.0
4 ⁰ 30.20'E	1.50	1.31	6.93	8.24	15.9
	2.50	1.40	8.07	9.47	14.8
	3.50	1.78	8.88	10.66	16.7
	4.50	1.58	8.25	9.83	16.1
	6.00	1.70	8.75	10.45	16.3
	8.00	1.45	7.18	8.63	16.8
	10.50	1.86	10.10	11.96	15.6
	14.00	1.68	9.38	11.06	15.2
NS 3	0.25	1.18	3.18	4.36	27.1
53 ⁰ 57.39'N	0.75	1.36	8.80	10.16	13.3
4 ⁰ 58.01'E	1.50	1.43	8.74	10.17	14.1
	2.50	1.25	7.30	10.55	11.8
	3.50	1.44	5.89	7.33	19.6
	5.00	1.99	8.35	10.34	19.2
	7.00	1.75	7.97	9.72	18.0
	10.00	1.60	8.39	9.99	16.0
	14.00	1.78	9.27	11.05	16.1
NS 4	0.25	1.03	2.54	3.57	28.9
54 ⁰ 59.98'N	0.75	0.74	2.55	3.29	22.5
6 ⁰ 26.22'E	1.50	1.14	2.84	3.98	28.6
	2.50	1.28	2.97	4.25	30.1
	3.50	1.54	3.23	4.77	32.2
	5.00	1.25	2.57	3.82	32.7
	7.00	1.26	2.76	4.02	31.3
	10.00	1.32	2.96	4.28	30.8
	14.00	1.45	3.50	4.95	29.3

APPENDIX 6

Cu in North Sea sediments. D = mean depth; L = leachable; R = residual; T = total; L' = leachable percent; P = pore water.

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L' (%)	P(μM)
NS 1 53°42.52'N 4°29.45'E	0.25	0.92	3.62	4.54	20.3	72.1
	0.75	1.01	1.94	2.95	34.2	45.0
	1.50	0.64	2.11	2.75	23.3	217
	2.50	0.99	2.95	3.94	25.1	72.1
	3.50	1.49	3.45	4.94	30.2	90.3
	4.50	1.70	4.07	5.77	29.5	189
	6.00	1.64	3.60	5.24	31.3	155
	8.00	1.70	3.89	5.59	30.4	59.9
	10.50	1.90	3.83	5.73	33.2	59.9
	13.50	2.08	3.78	5.86	35.5	59.9
17.00	2.01	4.16	6.17	32.6	36.0	
NS 2 53°41.80'N 4°30.20'E	0.25	1.28	2.94	4.22	30.3	60.7
	0.75	1.02	2.56	3.58	28.5	45.5
	1.50	1.25	3.43	4.68	26.7	250
	2.50	1.62	5.18	6.80	23.8	53.0
	3.50	2.46	3.78	6.24	39.4	45.2
	4.50	1.75	3.41	5.16	33.9	30.4
	6.00	1.78	3.41	5.19	34.3	30.4
	8.00	1.69	2.94	4.63	36.5	30.4
	10.50	1.89	3.55	5.44	34.7	30.4
	14.00	1.99	3.94	5.93	33.6	30.4
NS 3 53°57.39'N 4°58.01'E	0.25	1.29	1.42	2.71	47.6	78.2
	0.75	1.49	3.98	5.47	27.2	123
	1.50	1.58	4.12	5.70	27.7	33.5
	2.50	1.42	3.22	4.64	30.6	67.5
	3.50	1.67	2.86	4.53	36.9	44.5
	5.00	1.79	3.30	5.09	35.2	117
	7.00	1.88	3.51	5.39	34.9	22.2
	10.00	1.67	3.55	5.22	32.0	33.5
	14.00	1.91	3.63	5.54	34.5	89.4
NS 4 54°59.98'N 6°26.22'E	0.25	1.11	2.90	4.01	27.7	59.6
	0.75	1.32	2.75	4.07	32.4	59.6
	1.50	1.31	3.52	4.83	27.1	71.5
	2.50	1.65	3.08	4.73	34.9	23.9
	3.50	1.61	3.01	4.62	34.8	35.7
	5.00	1.52	2.74	4.26	35.7	108
	7.00	1.68	2.89	4.57	36.8	47.8
	10.00	1.74	2.98	4.72	36.9	119
	14.00	1.61	3.13	4.74	34.0	47.8

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

APPENDIX 7

Zn in North Sea sediments. D = mean depth; L = leachable; R = residual; T = total; L' = leachable percent; P = pore water.

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L' (%)	P(μM)
NS 1	0.25	22.4	62.4	84.8	26.4	0.30
53°42.52'N	0.75	19.6	24.4	44.0	44.5	0.34
4°29.45'E	1.50	17.1	33.9	51.0	33.5	0.47
	2.50	26.6	21.7	48.3	55.1	7.26
	3.50	27.5	37.3	64.8	42.4	0.36
	4.50	27.1	51.4	78.5	34.5	0.62
	6.00	31.7	46.1	77.8	40.7	0.70
	8.00	29.6	36.8	66.4	44.5	0.52
	10.50	31.5	36.2	67.7	46.5	0.18
	13.50	29.1	38.6	67.7	42.9	0.51
	17.00	31.2	47.7	78.9	39.5	0.37
NS 2	0.25	26.9	31.6	58.5	45.9	0.43
53°41.80'N	0.75	22.5	29.9	52.4	42.9	0.25
4°30.20'E	1.50	24.8	47.0	71.8	34.5	2.17
	2.50	24.8	37.0	61.8	40.1	0.35
	3.50	29.9	37.2	67.1	44.5	0.76
	4.50	29.7	34.5	64.2	46.2	0.19
	6.00	27.6	37.4	65.0	42.5	-
	8.00	29.3	29.3	58.6	50.0	0.31
	10.50	29.6	36.8	66.4	44.5	0.08
	14.00	26.6	34.4	61.0	43.6	0.24
NS 3	0.25	34.7	12.3	47.0	72.3	1.67
53°57.39'N	0.75	35.1	37.4	72.5	48.4	2.51
4°58.01'E	1.50	34.8	39.6	74.4	46.8	3.84
	2.50	36.9	34.2	71.1	51.9	1.00
	3.50	64.7	27.3	92.0	70.3	0.76
	5.00	59.5	34.2	93.7	63.5	2.08
	7.00	61.4	34.2	95.6	64.2	0.86
	10.00	42.2	37.1	79.3	53.2	0.87
	14.00	42.4	39.7	82.1	51.6	4.41
NS 4	0.25	41.4	29.5	70.6	58.2	1.73
54°59.98'N	0.75	31.4	26.4	57.8	54.3	2.00
6°26.22'E	1.50	36.1	28.7	64.8	55.7	0.72
	2.50	32.6	30.0	62.6	52.1	0.59
	3.50	42.8	32.6	75.4	57.8	1.23
	5.00	30.9	30.7	61.6	50.1	11.72
	7.00	34.7	32.1	66.8	51.9	1.27
	10.00	31.6	33.9	65.5	48.2	0.97
	14.00	31.5	33.6	65.1	48.3	1.07

APPENDIX 8

Cd in North Sea sediments. D = mean depth; L = leachable; R = residual; T = total; L' = leachable percent; P = pore water.

Station	D(cm)	L(ng/g)	R(ng/g)	T(ng/g)	L' (%)	P(μM)
NS 1	0.25	26	18	44	59.1	1.09
53 ⁰ 42.52'N	0.75	49	nd	49	~100	1.48
4 ⁰ 29.45'E	1.50	34	20	54	62.9	1.37
	2.50	43	259	302	14.2	1.27
	3.50	49	194	243	20.1	1.30
	4.50	54	34	88	61.3	1.37
	6.00	15	1.23*	1.45*	6.8	-
	8.00	53	1.04*	1.09*	48.6	0.90
	10.50	40	na	40	~100	6.56
	13.50	19	na	19	~100	-
	17.00	38	43	81	46.9	4.71
NS 2	0.25	15	nd	15	~100	-
53 ⁰ 41.80'N	0.75	10	nd	10	~100	-
4 ⁰ 30.20'E	1.50	19	103	122	18.4	-
	2.50	10	44	54	18.5	-
	3.50	29	49	78	37.2	-
	4.50	25	54	79	31.6	-
	6.00	25	nd	25	~100	-
	8.00	22	10	32	68.7	-
	10.50	29	nd	29	~100	-
	14.00	19	10	29	65.5	-
NS 3	0.25	20	6.06*	6.08*	3.28	1.12
53 ⁰ 57.39'N	0.75	54	na	-	-	1.14
4 ⁰ 58.01'E	1.50	29	2.59*	2.62*	1.10	0.68
	2.50	772	na	-	-	1.23
	3.50	317	137	490	64.7	0.93
	5.00	137	nd	137	~100	1.05
	7.00	320	24	344	93.0	0.61
	10.00	64	na	-	-	1.04
	14.00	64	na	-	-	0.94
NS 4	0.25	54	41	95	56.8	1.27
54 ⁰ 59.98'N	0.75	103	52	155	66.4	0.65
6 ⁰ 26.22'E	1.50	76	10	86	88.3	0.67
	2.50	59	189	248	23.7	0.63
	3.50	35	55	90	38.6	0.84
	5.00	170	57	227	74.8	1.05
	7.00	95	44	139	68.3	0.44
	10.00	43	nd	43	~100	1.19
	14.00	92	44	136	67.6	0.37

* concentration in μg/g

na = not analyzed because of contamination

nd = not detected

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

APPENDIX 9

Pb in North Sea sediments. D = mean depth; L = leachable; R = residual; T = total; L' = leachable percent; P = pore water.

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L' (%)	P (nM)
NS 1	0.25	4.29	5.17	9.36	45.8	2.27
53°42.52'N	0.75	4.71	4.50	9.21	51.1	0.69
4°29.45'E	1.50	4.49	4.76	9.25	48.5	3.12
	2.50	5.00	3.43	8.43	59.3	1.78
	3.50	6.32	5.17	11.49	55.0	1.53
	4.50	7.17	5.24	12.41	57.7	4.21
	6.00	6.55	4.91	11.56	56.7	-
	8.00	7.18	5.69	12.87	55.7	4.46
	10.50	7.07	5.31	12.38	57.1	1.97
	13.50	7.63	5.60	12.23	57.7	-
	17.00	6.46	5.25	11.71	55.1	2.02
NS 2	0.25	6.00	5.60	11.60	51.7	-
53°41.80'N	0.75	5.17	4.84	10.01	51.6	-
4°30.20'E	1.50	5.52	5.68	11.20	49.3	-
	2.50	6.08	6.11	12.19	49.9	-
	3.50	6.87	5.84	12.71	54.1	-
	4.50	6.83	5.52	12.35	55.3	-
	6.00	6.58	5.74	12.32	53.4	-
	8.00	6.42	4.24	10.66	60.2	-
	10.50	7.00	5.00	12.00	58.3	-
	14.00	7.01	5.65	12.66	55.4	-
NS 3	0.25	5.38	4.21	9.59	56.1	3.05
53°57.39'N	0.75	5.78	6.02	11.80	49.0	6.58
4°58.01'E	1.50	6.25	5.54	11.79	53.0	0.59
	2.50	5.17	4.90	10.07	51.3	3.32
	3.50	5.07	6.72	11.79	43.0	4.49
	5.00	5.91	5.64	11.55	51.1	2.06
	7.00	6.17	5.19	11.36	54.3	1.81
	10.00	5.65	5.54	11.19	50.5	2.32
	14.00	6.77	6.15	12.92	52.3	3.74
NS 4	0.25	3.41	5.07	8.48	40.2	12.7
54°59.98'N	0.75	3.61	4.71	8.32	43.3	7.12
6°26.22'E	1.50	4.90	4.95	9.85	49.7	6.75
	2.50	4.95	5.17	10.12	48.9	1.78
	3.50	5.64	4.91	10.55	53.4	2.91
	5.00	4.51	4.89	9.40	47.9	2.66
	7.00	5.55	4.97	10.52	52.7	4.61
	10.00	5.61	5.40	11.01	50.9	2.11
	14.00	5.50	5.00	10.50	52.3	3.46

APPENDIX 10

Ca contents of North Sea sediments. D = mean depth; L = leachable.
(Residual fraction is negligible; T = L).

Station	D(cm)	L(%)	Station	D(cm)	L(%)
NS 1	0.25	26.3	NS 2	0.25	29.6
53°42.52'N	0.75	26.6	53°41.80'N	0.75	27.3
4°29.45'E	1.50	27.2	4°30.20'E	1.50	28.9
	2.50	28.4		2.50	30.8
	3.50	29.8		3.50	31.8
	4.50	30.8		4.50	30.5
	6.00	31.3		6.00	30.9
	8.00	30.4		8.00	30.5
	10.50	31.4		10.50	31.7
	13.50	31.3		14.00	31.5
	17.00	32.9			
NS 3	0.25	24.9	NS 4	0.25	17.2
53°57.39'N	0.75	26.9	54°59.98'N	0.75	16.6
4°58.01'E	1.50	28.2	6°26.22'E	1.50	18.2
	2.50	24.5		2.50	19.0
	3.50	18.8		3.50	23.7
	5.00	23.0		5.00	18.3
	7.00	24.9		7.00	19.7
	10.00	26.6		10.00	20.0
	14.00	25.5		14.00	19.6

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

APPENDIX 11

Al and Si contents of North Sea sediments. D = mean depth;
R = residual. For Al and Si, the leachable fraction is negligible
($R \approx T$).

Station	<u>Aluminium</u>		<u>Silicon</u>	
	D(cm)	R(%)	D(cm)	R(%)
NS 1	0.25	2.47	0.25	37.9
53°42.52'N	0.75	1.96	0.75	31.3
4°29.45'E	1.50	2.42	1.50	38.8
	2.50	2.36	2.50	nd
	3.50	2.85	3.50	36.6
	4.50	3.01	4.50	36.0
	6.00	3.08	6.00	36.6
	8.00	3.01	8.00	35.2
	10.50	3.11	10.50	35.6
	13.50	3.28	13.50	36.1
	17.00	3.22	17.00	32.1
NS 2	0.25	2.79	0.25	36.8
53°41.80'N	0.75	3.18	0.75	36.0
4°30.20'E	1.50	2.79	1.50	35.1
	2.50	2.96	2.50	36.0
	3.50	3.00	3.50	35.5
	4.50	3.05	4.50	34.4
	6.00	3.12	6.00	35.5
	8.00	2.81	8.00	nd
	10.50	3.25	10.50	34.3
	14.00	3.28	14.00	33.7
NS 3	0.25	1.93	0.25	nd
53°57.39'N	0.75	3.08	0.75	33.8
4°58.01'E	1.50	3.20	1.50	33.2
	2.50	2.76	2.50	34.7
	3.50	2.86	3.50	nd
	5.00	2.90	5.00	33.6
	7.00	3.00	7.00	35.4
	10.00	3.03	10.00	33.9
	14.00	3.16	14.00	35.0
NS 4	0.25	2.72	0.25	35.5
54°59.98'N	0.75	2.53	0.75	37.2
6°26.22'E	1.50	2.85	1.50	34.3
	2.50	2.91	2.50	33.0
	3.50	2.80	3.50	33.6
	5.00	2.92	5.00	34.2
	7.00	3.03	7.00	34.4
	10.00	3.19	10.00	34.6
	14.00	3.18	14.00	33.3

nd = not detectable

APPENDIX 12

Mn in Wadden Sea sediments. D = mean depth; L = leachable; R = residual; T = total; L' = leachable percent; P = pore water.

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L' (%)	P(μM)
WS 1	0.50	101	62.7	164	61.5	0.42
53°00.50'N	1.50	126	49.4	175	72.0	4.24
5°04.67'E	2.50	104	90.1	194	53.6	14.84
	4.00	88.2	98.0	186	47.3	99.25
	6.00	100	130	230	43.4	86.95
	8.00	129	109	238	54.2	39.87
	11.00	115	120	235	48.4	28.42
	15.00	83.3	102	185	44.8	7.63
	19.00	104	99.1	203	51.2	6.79
	23.00	98.5*	131*	230	43.0	12.30
		99.2	104			
WS 2	0.25	268	87.7	356	75.2	0.85
53°01.12'N	0.75	146	88.7	235	62.1	21.74
5°04.51'E	1.50	51.0	69.5	121	42.1	80.13
	2.50	89.9	65.9	156	57.6	99.74
	3.50	64.6	77.5	143	45.5	77.15
	5.00	89.3	84.3	173	51.4	53.70
	7.00	70.6	89.0	151	47.0	31.97
	10.00	97.5	139	235	41.7	37.51
	13.00	52.5	124	177	29.9	32.39
	18.00	69.9*	114	184	38.0	5.12
		61.6				
WS 3	0.25	54.4	109	163	33.1	1.30
53°18.24'N	0.75	216	108	324	66.6	1.75
5°31.51'E	1.50	79.0	87.8	167	47.3	1.30
	2.50	69.1	127	196	35.2	3.50
	4.00	85.6	105	191	45.0	6.55
	6.00	47.6	73.6	122	39.3	13.11
	8.00	34.4	64.9	99	34.3	13.55
	10.00	34.4	54.0	88	36.6	33.21
	13.00	28.8*	83.1	371	77.6	43.69
		27.5				

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

Appendix 12 continued

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L (%)	P(μM)
WS 4	0.25	38.6	96.6	136	28.6	7.47
53°19.20'N	0.75	44.2	172	216	20.3	3.07
5°34.17'E	1.25	55.3	111	166	33.1	1.76
	1.75	52.6	134	187	28.3	1.76
	2.50	36.9	161	198	22.9	1.32
	4.00	38.5	144	183	27.0	7.03
	6.00	33.0	141	174	18.9	3.95
	8.00	34.0	128	162	20.9	2.20
	13.00	32.9	123	156	21.1	1.76
	13.00	33.5	158	192	17.7	3.07
	17.00	48.7	133	182	26.9	5.27
	21.00	67.8	125	202	38.1	15.37
WS 5	0.50	582	106	688	84.5	0.89
52°58.08'N	1.50	290	90.6	381	76.1	19.59
4°55.67'E	3.00	106	78.3	184	57.6	79.68
	5.00	108	79.5	188	57.4	96.55
	7.00	97.2	72.9	170	57.0	165.2
	9.00	429	143	572	75.0	170.0
	11.00	61.2	61.2	122	50.0	145.2
	14.00	86.8	86.8	174	50.0	86.36
	18.00	77.7	107	185	42.0	52.09
	22.00	69.2	120	189	36.5	40.95
	25.00	79.8*	84.8	165	48.4	46.30
		84.3				

* Duplicate measurements

APPENDIX 13

Fe in Wadden Sea sediments. D = mean depth; L = leachable; R = residual; T = total; L' = leachable percent; P = pore water.

Station	D(cm)	L(%)	R(%)	T(%)	L' (%)	P(µM)
WS 1	0.50	0.07	0.27	0.34	25.5	4.06
53°00.50'N	1.50	0.09	0.17	0.26	33.1	4.06
5°04.67'E	2.50	0.10	0.34	0.44	22.5	4.74
	4.00	0.07	0.32	0.39	17.5	4.74
	6.00	0.11	0.38	0.49	22.0	4.74
	8.00	0.17	0.51	0.68	24.6	4.06
	11.00	0.15	0.47	0.62	24.2	5.42
	15.00	0.10	0.35	0.45	22.7	4.06
	19.00	0.14	0.42	0.56	24.9	4.06
	23.00	0.14	0.53	0.67	20.4	4.74
WS 2	0.25	0.14	0.44	0.58	23.8	3.94
53°01.12'N	0.75	0.09	0.33	0.42	21.3	4.73
5°04.51'E	1.50	0.05	0.22	0.27	18.5	3.94
	2.50	0.08	0.28	0.36	21.4	15.7
	3.50	0.05	0.24	0.29	18.2	35.4
	5.00	0.09	0.37	0.46	19.3	14.2
	7.00	0.07	0.31	0.38	17.4	3.94
	10.00	0.10	0.44	0.54	18.1	6.30
	13.00	0.06	0.32	0.38	15.1	4.72
	18.00	0.07	0.33	0.40	17.5	4.73
WS 3	0.25	0.38	1.15	1.53	24.9	3.37
53°18.24'N	0.75	0.30	0.91	1.21	24.6	2.52
5°31.51'E	1.50	0.11	0.51	0.62	17.2	1.68
	2.50	0.09	0.50	0.59	15.4	1.68
	4.00	0.11	0.55	0.66	15.9	2.52
	6.00	0.05	0.38	0.43	11.9	1.68
	8.00	0.05	0.28	0.32	14.1	2.52
	10.00	0.05	0.29	0.34	14.7	3.37
	13.00	0.04	0.28	0.33	12.7	4.21
WS 4	0.25	0.08	0.35	0.43	19.1	3.42
53°19.20'N	0.75	0.05	0.45	0.50	10.1	4.28
5°34.17'E	1.25	0.06	0.29	0.35	17.1	3.42
	1.75	0.06	0.28	0.34	17.0	2.57
	2.50	0.05	0.35	0.40	12.4	2.57
	4.00	0.05	0.35	0.40	12.3	1.71
	6.00	0.06	0.41	0.47	13.3	3.42
	8.00	0.07	0.50	0.57	15.6	0.86
	10.00	0.07	0.42	0.49	14.3	1.71
	13.00	0.12	0.55	0.67	17.6	3.42
	17.00	0.11	0.45	0.56	18.8	1.71
	21.00	0.13	0.56	0.69	19.0	2.57

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

Appendix 13 continued

Station	D(cm)	L(%)	R(%)	T(%)	L' (%)	P(μM)
WS 5	0.50	0.59	1.32	1.91	20.6	0.88
52°58.08'N	1.50	0.32	0.79	1.11	28.8	0.00
4°55.67'E	3.00	0.14	0.40	0.54	25.9	1.76
	5.00	0.14	0.49	0.63	22.1	47.52
	7.00	0.13	0.42	0.55	23.6	173.1
	9.00	0.58	1.73	2.31	24.9	166.6
	11.00	0.09	0.24	0.33	27.3	104.8
	14.00	0.11	0.44	0.55	20.7	2.64
	18.00	0.12	0.42	0.55	22.5	2.64
	22.00	0.14	0.47	0.61	22.9	7.04
	25.00	0.13	0.36	0.49	25.9	2.64

APPENDIX 14

Cr in Wadden Sea sediments. D = mean depth; L = leachable; R = residual; T = total; L' = leachable percent.

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L' (%)
WS 1	0.50	1.22	12.8	14.1	8.7
53 ⁰ 00.50'N	1.50	1.46	8.1	9.59	15.2
5 ⁰ 04.67'E	2.50	1.69	18.3	20.0	8.5
	4.00	1.37	22.6	24.0	5.7
	6.00	2.36	22.2	24.6	9.6
	8.00	3.55	29.6	33.1	10.7
	11.00	3.36	27.0	30.3	11.1
	15.00	2.39	20.0	22.4	10.7
	19.00	3.73	20.0	23.6	15.8
	23.00	4.36	26.4	30.7	14.2
WS 2	0.25	3.78	22.7	26.5	14.3
53 ⁰ 01.12'N	0.75	2.42	18.4	20.8	8.6
5 ⁰ 04.51'E	1.50	1.07	7.2	8.28	12.9
	2.50	1.86	20.9	22.8	8.2
	3.50	1.46	23.2	24.7	5.9
	5.00	2.45	18.0	20.5	11.9
	7.00	1.83	15.5	17.4	10.5
	10.00	2.54	29.4	32.0	7.9
	13.00	1.55	27.4	29.0	5.3
	18.00	2.05	24.0	26.1	7.9
WS 3	0.25	5.86	30.1	36.0	16.3
53 ⁰ 18.24'N	0.75	4.25	33.6	37.9	11.2
5 ⁰ 31.51'E	1.50	1.56	16.5	18.1	8.6
	2.50	1.33	23.0	24.4	5.5
	4.00	1.50	15.3	16.8	8.9
	6.00	0.68	6.93	7.61	8.9
	8.00	0.80	5.95	6.75	11.8
	10.00	0.62	7.86	8.48	7.3
	13.00	0.66	8.38	9.04	7.3
WS 4	0.25	1.51	12.0	13.5	11.2
53 ⁰ 19.20'N	0.75	0.93	14.9	25.9	5.8
5 ⁰ 34.17'E	1.25	0.90	18.1	19.0	4.7
	1.75	0.95	8.27	9.22	10.3
	2.50	0.82	7.98	8.80	9.3
	4.00	0.86	8.51	9.37	9.2
	6.00	1.34	11.7	13.1	10.2
	8.00	1.56	20.7	22.2	7.0
	10.00	1.38	17.7	19.1	7.2
	13.00	2.11	21.0	23.1	9.1
	17.00	2.23	23.0	25.2	8.8
	21.00	2.78	19.3	22.1	12.6

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

Appendix 14 continued

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L' (%)
WS 5	0.50	10.37	58.5	68.9	15.1
52°58.08'N	1.50	5.40	31.8	37.2	14.5
4°55.67'E	3.00	2.18	18.9	21.1	10.3
	5.00	2.16	19.0	21.1	10.2
	7.00	1.94	14.6	16.5	11.8
	9.00	9.06	54.0	63.1	14.3
	11.00	1.30	6.18	7.48	17.4
	14.00	1.78	15.2	17.0	10.5
	18.00	2.05	24.6	26.7	7.7
	22.00	2.70	20.1	22.8	11.8
	25.00	2.45	17.5	20.0	12.3

APPENDIX 15

Ni in Wadden Sea sediments. D = mean depth; L = leachable; R = residual; T = total; L' = leachable percent.

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L' (%)
WS 1	0.50	0.57	5.65	6.12	9.3
53°00.50'N	1.50	0.67	2.34	3.01	22.2
5°04.67'E	2.50	0.67	3.67	4.24	15.8
	4.00	0.29	2.87	3.16	9.2
	6.00	0.74	3.09	3.83	19.3
	8.00	1.03	8.39	9.42	10.9
	11.00	1.19	4.87	6.06	19.6
	15.00	0.69	4.07	4.76	14.5
	19.00	0.88	5.17	6.05	14.5
	23.00	1.12	5.19	6.31	17.7
WS 2	0.25	1.85	4.50	6.35	29.1
53°01.12'N	0.75	0.48	2.91	3.39	14.1
5°04.51'E	1.50	0.30	1.59	1.89	15.8
	2.50	0.59	1.78	2.37	24.8
	3.50	0.32	1.11	1.43	22.4
	5.00	0.48	1.40	1.88	25.5
	7.00	0.31	4.71	5.02	6.2
	10.00	0.45	3.34	3.79	11.9
	13.00	0.47	4.47	4.94	9.5
	18.00	0.85	2.45	3.30	25.7
WS 3	0.25	2.54	7.26	9.80	25.9
53°18.24'N	0.75	1.85	6.74	8.59	21.5
5°31.51'E	1.50	0.40	3.84	4.24	9.4
	2.50	0.40	2.64	3.04	13.2
	4.00	0.16	2.82	3.08	5.2
	6.00	0.30	1.62	1.92	15.6
	8.00	0.12	1.43	1.55	7.7
	10.00	0.08	1.38	1.46	5.5
	13.00	0.15	1.38	1.53	9.8
WS 4	0.25	0.54	1.51	1.95	27.7
53°19.20'N	0.75	0.41	1.80	2.21	18.6
5°34.17'E	1.25	0.38	2.04	2.42	15.7
	1.75	0.26	1.20	1.46	17.8
	2.50	0.16	1.44	1.60	10.0
	4.00	0.24	1.20	1.44	16.7
	6.00	0.58	2.36	2.94	19.7
	8.00	0.65	2.52	3.17	20.5
	10.00	0.51	1.93	2.44	20.9
	13.00	0.92	3.29	4.21	21.8
	17.00	0.82	2.77	3.59	22.8
	21.00	0.98	3.76	4.74	20.7

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

Appendix 15 continued

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L' (%)
WS 5	0.50	4.96	13.97	18.93	26.2
52°58.08'N	1.50	2.48	10.23	12.71	19.5
4°55.67'E	3.00	0.86	3.90	4.76	18.1
	5.00	0.80	1.90	2.70	29.6
	7.00	0.92	4.11	5.03	18.3
	9.00	4.57	15.25	19.82	23.1
	11.00	0.56	2.70	3.26	17.2
	14.00	0.69	3.56	4.25	16.2
	18.00	0.66	3.03	3.69	17.9
	22.00	0.71	3.90	4.61	15.4
	25.00	0.68	5.14	5.82	11.7

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APPENDIX 16

Cu in Wadden Sea sediments. D = mean depth; L = leachable; R = residual; T = total; L' = leachable percent; P = pore water.

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L' (%)	P(nM)
WS 1	0.50	1.10	2.29	3.39	32.4	140
53°00.50'N	1.50	1.09	1.07	2.16	50.4	10.0
5°04.67'E	2.50	0.95	1.29	2.24	42.4	52.2
	4.00	1.27	1.04	2.31	54.9	17.6
	6.00	1.11	1.82	2.93	37.9	17.6
	8.00	2.52	1.94	4.46	56.5	32.5
	11.00	2.19	1.65	3.84	57.0	11.0
	15.00	1.44	1.21	2.65	54.3	nd
	19.00	2.81	1.56	4.37	64.3	11.0
	23.00	2.54	1.71	4.25	59.8	11.0
WS 2	0.25	2.77	6.29	9.06	30.6	1.67*
53°01.12'N	0.75	1.66	2.59	4.25	39.1	459
5°04.51'E	1.50	0.47	1.43	1.90	24.7	115
	2.50	0.97	1.88	2.85	34.0	65.7
	3.50	0.81	1.60	2.41	33.6	32.6
	5.00	1.61	1.96	3.57	45.0	131
	7.00	1.66	1.71	3.37	49.2	16.7
	10.00	1.74	1.68	3.42	50.9	32.6
	13.00	0.79	1.73	2.52	31.3	16.7
	18.00	1.26	1.68	2.94	42.8	16.7
WS 3	0.25	4.51	4.90	9.41	47.9	70.4
53°18.24'N	0.75	3.15	3.27	6.42	49.1	82.2
5°31.51'E	1.50	0.87	1.80	2.67	32.6	47.1
	2.50	1.72	1.71	3.43	50.1	93.7
	4.00	0.87	1.83	2.70	32.2	58.5
	6.00	0.43	1.14	1.57	27.4	106
	8.00	0.12	0.93	1.05	11.4	141
	10.00	0.34	1.19	1.53	22.2	199
			1.09			
	13.00	0.30	1.25	1.55	19.4	2.23*
			1.17			
WS 4	0.25	0.77	1.20	1.97	39.1	39.0
53°19.20'N	0.75	0.50	1.16	1.66	30.1	54.5
5°34.17'E	1.25	0.72	1.43	1.15	62.6	46.9
	1.75	0.31	0.76	1.07	28.9	62.3
	2.50	0.26	1.02	1.28	20.3	93.5
	4.00	0.35	1.23	1.58	22.2	78.1
	6.00	0.72	1.13	1.85	38.9	39.0
	8.00	0.92	1.31	2.23	41.2	7.9
	10.00	1.48	1.08	2.56	57.8	23.2
	13.00	1.42	1.43	2.85	49.8	320
	17.00	1.60	1.56	3.16	50.6	109
	21.00	2.24	2.27	4.51	49.7	39.0

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

Appendix 16 continued

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L' (%)	P(nM)
WS 5	0.50	9.23	10.92	20.15	45.8	81.1
52°58.08'N	1.50	5.37	6.44	11.81	15.5	60.7
4°55.67'E	3.00	1.35	2.51	3.86	35.0	67.7
	5.00	1.13	1.96	3.09	36.6	47.4
	7.00	2.21	1.77	3.98	55.5	40.6
	9.00	7.17	7.04	14.21	50.5	155
	11.00	1.61	1.90	3.51	45.9	412
	14.00	0.95	1.53	2.48	38.3	33.7
	18.00	1.42	1.43	2.85	49.8	54.0
	22.00	1.15	1.40	2.55	45.1	40.6
	25.00	1.07	1.40	2.47	43.3	33.7

* Concentration in $\mu\text{g/g}$

APPENDIX 17

Zn in Wadden Sea sediments. D = mean depth; L = leachable; R = residual; T = total; L' = leachable percent; P = pore water.

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L' (%)	P(μM)
WS 1	0.50	20.3	25.2	45.5	44.6	1.86
53 ⁰ 00.50'N	1.50	23.2	2.32	26.5	86.8	1.17
5 ⁰ 04.67'E	2.50	21.1	8.38	29.5	71.5	0.41
	4.00	16.1	9.12	25.2	63.9	0.41
	6.00	23.4	7.50	30.9	75.7	0.38
	8.00	44.1	33.3	77.4	57.0	0.42
	11.00	39.7	16.7	56.4	70.4	0.60
	15.00	23.9	12.1	36.0	66.4	0.12
	19.00	41.8	9.22	51.0	82.0	0.08
	23.00	46.1	10.5	56.6	81.4	0.24
WS 2	0.25	33.8	21.3	55.1	61.3	2.00
53 ⁰ 01.12'N	0.75	20.7	11.6	32.3	64.1	0.41
5 ⁰ 04.51'E	1.50	8.71	6.95	15.6	55.6	0.36
	2.50	18.2	12.3	30.5	59.7	0.76
	3.50	13.6	7.23	20.3	67.0	0.76
	5.00	23.2	11.1	34.3	67.6	0.88
	7.00	19.9	8.76	28.7	69.3	0.15
	10.00	21.7	12.2	33.9	64.0	0.69
	13.00	17.8	8.87	26.7	66.7	0.55
	18.00	20.5	9.79	30.3	67.7	0.16
WS 3	0.25	58.0	25.9	83.9	69.1	2.20
53 ⁰ 18.24'N	0.75	44.2	20.1	64.3	68.7	7.57
5 ⁰ 31.51'E	1.50	16.4	9.83	26.2	62.6	0.95
	2.50	16.2	8.60	24.8	65.3	0.52
	4.00	17.8	7.14	24.9	71.5	0.79
	6.00	10.1	4.85	15.0	67.3	1.60
	8.00	7.18	4.27	11.5	62.4	13.3
	10.00	11.5	3.63	15.1	76.2	8.17
	13.00	18.3	3.62	21.9	83.6	1.63
WS 4	0.25	15.8	10.8	26.6	59.4	0.99
53 ⁰ 19.20'N	0.75	14.5	9.90	24.4	59.4	0.72
5 ⁰ 34.17'E	1.25	21.2	11.3	32.5	65.2	1.56
	1.75	8.99	5.36	14.4	62.4	1.19
	2.50	6.46	5.17	11.6	55.7	3.12
	4.00	6.73	7.21	13.9	48.4	1.57
	6.00	15.5	8.17	24.3	63.8	0.71
	8.00	13.9	9.52	23.4	59.4	0.16
	10.00	13.5	18.4	31.9	42.3	0.82
	13.00	20.2	12.5	32.7	61.8	0.92
	17.00	26.9	11.6	38.5	69.9	0.57
	21.00	33.8	12.6	46.4	72.8	0.38

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

Appendix 17 continued

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L' (%)	P(μM)
WS 5	0.50	108	46.8	155	69.7	2.47
52°58.08'N	1.50	55.2	30.4	85.6	64.5	2.19
4°55.67'E	3.00	19.5	12.1	31.6	61.7	1.44
	5.00	19.7	8.70	28.4	69.4	4.36
	7.00	29.5	10.9	40.4	73.0	4.68
	9.00	89.3	48.1	137	65.2	3.15
	11.00	13.4	7.59	21.0	63.8	6.95
	14.00	18.8	10.0	25.8	65.3	0.74
	18.00	20.5	10.9	31.4	65.3	0.69
	22.00	21.6	10.3	31.9	67.7	0.64
	25.00	21.1	9.28	30.4	69.4	1.32

APPENDIX 18

Cd in Wadden Sea sediments. D = mean depth; L = leachable; R = residual; T = total; L' = leachable percent; P = pore water.

Station	D(cm)	L(ng/g)	R(ng/g)	T(ng/g)	L' (%)	P(nM)
WS 1	0.50	77	92	169	45.5	4.17
53°00.50'N	1.50	76	49	125	60.8	1.05
5°04.67'E	2.50	81	27	108	75.0	na
	4.00	123	39	162	75.9	na
	6.00	150	70	220	68.2	na
	8.00	228	203	431	52.9	0.19
	11.00	169	85	254	66.5	-
	15.00	203	32	235	56.3	0.07
	19.00	223	140	363	61.4	0.15
	23.00	356	70	426	83.5	0.22
WS 2	0.25	150	67	217	69.1	2.32
53°01.12'N	0.75	98	40	138	71.0	1.42
5°04.51'E	1.50	56	28	84	66.6	1.10
	2.50	137	24	161	85.0	1.09
	3.50	74	26	100	74.0	0.62
	5.00	134	10	144	93.0	0.88
	7.00	164	nd	164	~100	0.24
	10.00	149	19	168	88.6	0.15
	13.00	81	na	81	~100	0.50
	18.00	131	35	166	78.9	nd
WS 3	0.25	282	34	316	89.2	na
53°18.24'N	0.75	238	1.03*	1.27*	18.7	-
5°31.51'E	1.50	61	44	105	58.1	-
	2.50	50	88	138	36.2	-
	4.00	85	57	142	59.8	-
	6.00	51	39	90	56.6	-
	8.00	22	42	64	34.3	-
	10.00	39	25	64	60.9	-
	13.00	79	29	108	73.1	-
WS 4	0.25	97	29	126	76.9	1.55
53°19.20'N	0.75	53	22	75	70.6	0.71
5°34.17'E	1.25	100	306	406	24.6	3.42
	1.75	182	105	287	63.4	1.53
	2.50	21	46	67	31.3	2.13
	4.00	163	96	262	62.2	1.40
	6.00	263	19	282	83.6	1.29
	8.00	81	55	136	59.5	1.02
	10.00	65	45	110	59.1	0.50
	13.00	86	24	110	78.1	1.83
	17.00	150	80	230	65.2	1.05
	21.00	221	48	269	82.1	0.75

na = not analyzed; nd = not detected

* = concentration in µg/g

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

Appendix 18 continued

Station	D(cm)	L(ng/g)	R(ng/g)	T(ng/g)	L' (%)	P(nM)
WS 5	0.50	644	58	702	91.7	0.67
52°58.08'N	1.50	285	81	366	78.8	1.14
4°55.67'E	3.00	106	10	116	91.4	0.91
	5.00	98	28	126	77.7	2.00
	7.00	121	15	136	88.9	0.28
	9.00	543	119	662	82.0	0.40
	11.00	73	53	126	57.9	1.34
	14.00	86	57	143	60.1	0.70
	18.00	228	44	272	83.3	1.46
	22.00	111	nd	111	~100	0.74
	25.00	134	25	159	84.2	1.09

nd = not detected

APPENDIX 19

Pb in Wadden Sea sediments. D = mean depth; L = leachable; R = residual; T = total; L' = leachable percent; P = pore water.

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L' (%)	P(nM)
WS 1	0.50	3.36	5.60	8.96	37.5	21.7
53°00.50'N	1.50	3.67	3.46	7.13	51.4	9.07
5°04.67'E	2.50	3.14	4.84	7.98	39.3	na
	4.00	2.53	4.45	6.98	36.2	na
	6.00	3.94	3.86	7.80	50.5	na
	8.00	7.51	3.96	11.47	65.5	14.2
	11.00	6.80	3.57	10.37	65.5	na
	15.00	4.07	3.44	7.51	54.2	4.58
	19.00	6.76	3.82	10.58	63.9	5.74
	23.00	7.96	4.01	11.97	66.4	3.40
WS 2	0.25	8.44	6.78	15.22	55.4	32.2
53°01.12'N	0.75	5.51	6.35	11.86	46.4	12.6
5°04.51'E	1.50	2.25	4.84	7.09	31.7	145
	2.50	3.27	5.72	8.99	36.4	10.5
	3.50	2.64	3.28	5.92	44.6	7.84
	5.00	5.26	5.18	10.44	50.3	18.4
	7.00	3.71	5.48	9.19	40.4	4.33
	10.00	4.22	5.23	9.35	45.0	4.89
	13.00	2.75	4.70	7.45	36.9	10.4
	18.00	3.84	6.13	9.97	38.5	0.94
WS 3	0.25	11.20	5.17	16.37	68.4	na
53°18.24'N	0.75	6.91	4.69	11.60	59.6	
5°31.51'E	1.50	2.70	4.72	7.42	36.4	-
	2.50	2.58	4.70	7.28	35.4	
	4.00	2.79	5.25	8.04	34.7	
	6.00	1.33	4.52	5.85	22.7	-
	8.00	0.96	4.10	5.06	19.0	
	10.00	0.82	4.25	5.07	16.2	
	13.00	1.09	4.38	5.47	19.9	-
WS 4	0.25	3.24	3.02	6.26	51.8	12.2
53°19.20'N	0.75	2.10	4.74	6.84	30.7	34.4
5°34.17'E	1.25	2.52	4.64	7.16	35.2	58.4
	1.75	2.14	3.84	5.98	35.8	16.8
	2.50	1.93	2.06	3.99	48.3	13.7
	4.00	2.29	4.86	7.15	32.0	5.23
	6.00	3.16	4.49	7.65	41.3	24.1
	8.00	3.09	4.94	8.03	38.4	5.76
	10.00	2.53	4.53	7.06	35.8	5.66
	13.00	4.28	4.94	9.22	46.4	15.1
	17.00	5.07	5.00	10.07	50.3	49.2
	21.00	6.46	5.30	11.76	54.9	13.2

na = not analyzed

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

Appendix 19 continued

Station	D(cm)	L($\mu\text{g/g}$)	R($\mu\text{g/g}$)	T($\mu\text{g/g}$)	L' (%)	P(nM)
WS 5	0.50	17.36	3.01	20.37	85.2	2.36
52°58.08'N	1.50	9.50	6.60	16.10	59.0	3.59
4°55.67'E	3.00	3.74	5.49	9.28	40.5	3.84
	5.00	3.92	5.57	9.49	41.3	4.12
	7.00	4.97	5.64	10.61	46.8	3.85
	9.00	15.33	5.96	21.29	72.0	6.15
	11.00	3.31	3.64	6.95	47.6	13.9
	14.00	2.80	4.87	7.67	36.5	0.88
	18.00	3.80	4.91	8.71	43.6	1.58
	22.00	3.87	4.39	8.26	46.8	1.07
	25.00	3.77	4.31	8.08	46.6	0.16

APPENDIX 20

Mg in Wadden Sea sediments. D = mean depth; L = leachable; R = residual; T = total; L' = leachable percent.

Station	D(cm)	L(%)	R(%)	T(%)	L' (%)
WS 1	0.50	0.12	0.92	1.04	11.9
53°00.50'N	1.50	0.15	0.06	0.21	70.7
5°04.67'E	2.50	0.15	0.11	0.26	56.1
	4.00	0.14	0.11	0.25	55.1
	6.00	0.18	0.12	0.30	60.4
	8.00	0.26	0.19	0.45	57.3
	11.00	0.25	0.18	0.43	58.8
	15.00	0.18	0.13	0.31	58.9
	19.00	0.19	0.16	0.35	54.0
	23.00	0.24	0.15	0.39	61.6
WS 2	0.25	0.19	0.14	0.33	58.0
53°01.12'N	0.75	0.14	0.08	0.22	63.7
5°04.51'E	1.50	0.09	0.07	0.16	57.1
	2.50	0.15	0.04	0.19	78.2
	3.50	0.12	0.04	0.16	74.4
	5.00	0.15	0.13	0.28	54.9
	7.00	0.15	0.11	0.26	56.7
	10.00	0.19	0.12	0.31	60.2
	13.00	0.14	0.11	0.25	56.2
	18.00	0.17	0.09	0.26	64.8
WS 3	0.25	0.24	0.22	0.46	51.9
53°18.24'N	0.75	0.22	0.19	0.41	53.2
5°31.51'E	1.50	0.10	0.11	0.21	48.3
	2.50	0.11	0.10	0.21	52.8
	4.00	0.11	0.10	0.21	53.0
	6.00	0.06	0.06	0.12	49.4
	8.00	0.04	0.05	0.09	45.4
	10.00	0.06	0.05	0.11	51.2
	13.00	0.05	0.06	0.11	44.1
WS 4	0.25	0.09	0.06	0.15	61.7
53°19.20'N	0.75	0.07	0.04	0.11	65.9
5°34.17'E	1.25	0.06	0.06	0.12	47.3
	1.75	0.04	0.06	0.10	42.4
	2.50	0.05	0.03	0.08	59.5
	4.00	0.05	0.01	0.11	43.4
	6.00	0.08	0.08	0.16	48.7
	8.00	0.11	0.10	0.21	52.1
	10.00	0.08	0.09	0.17	49.2
	13.00	0.15	0.13	0.28	54.1
	17.00	0.12	0.10	0.22	54.9
	21.00	0.13	0.13	0.26	51.0

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

Appendix 20 continued

Station	D(cm)	L(%)	R(%)	T(%)	L' (%)
WS 5	0.50	0.44	0.20	0.64	68.4
52°58.08'N	1.50	0.26	0.13	0.39	65.9
4°55.67'E	3.00	0.14	0.09	0.23	62.7
	5.00	0.17	0.07	0.24	72.0
	7.00	0.13	0.12	0.25	52.1
	9.00	0.48	0.41	0.89	53.9
	11.00	0.07	0.08	0.15	49.4
	14.00	0.18	0.12	0.26	55.5
	18.00	0.16	0.12	0.28	57.1
	22.00	0.16	0.14	0.31	53.3
	25.00	0.15	0.12	0.27	54.9

APPENDIX 21

Ca in Wadden Sea sediments. D = mean depth; L = leachable.

Station	D(cm)	L(%)	Station	D(cm)	L(%)
WS 1	0.50	2.31	WS 2	0.25	3.22
53°00.50'N	1.50	2.63	53°01.12'N	0.75	2.46
5°04.67'E	2.50	2.57	5°04.51'E	1.50	1.65
	4.00	2.45		2.50	2.47
	6.00	2.90		3.50	2.05
	8.00	4.21		5.00	2.38
	11.00	3.99		7.00	2.66
	15.00	2.82		10.00	2.76
	19.00	3.02		13.00	2.22
	23.00	3.59		18.00	2.78
WS 3	0.25	3.44	WS 4	0.25	1.40
53°18.24'N	0.75	3.05	53°19.20'N	0.75	1.04
5°31.51'E	1.50	1.65	5°34.17'E	1.25	0.75
	2.50	1.50		1.75	0.60
	4.00	1.55		2.50	0.62
	6.00	0.97		4.00	0.63
	8.00	0.57		6.00	0.99
	10.00	0.69		8.00	1.62
	13.00	0.78		10.00	1.25
				13.00	2.08
				17.00	1.64
				21.00	1.80
WS 5	0.50	6.40			
52°58.08'N	1.50	4.17			
4°55.67'E	3.00	2.49			
	5.00	3.06			
	7.00	2.50			
	9.00	6.29			
	11.00	1.06			
	14.00	1.77			
	18.00	2.79			
	22.00	3.02			
	25.00	2.84			

TRACE ELEMENT GEOCHEMISTRY IN THE NORTH SEA AND THE WADDEN SEA

APPENDIX 22

Al in Wadden Sea sediments. D = mean depth; R = residual.

Station	D(cm)	R(%)	Station	D(cm)	R(%)
WS 1	0.50	2.15	WS 2	0.25	2.63
53°00.50'N	1.50	1.32	53°01.12'N	0.75	2.42
5°04.67'E	2.50	2.27	5°04.51'E	1.50	1.89
	4.00	2.14		2.50	2.05
	6.00	2.19		3.50	1.72
	8.00	2.15		5.00	2.29
	11.00	2.70		7.00	2.26
	15.00	2.30		10.00	2.30
	19.00	2.29		13.00	2.19
	23.00	2.35		18.00	2.46
WS 3	0.25	2.88	WS 4	0.25	1.54
53°18.24'N	0.75	2.58	53°19.20'N	0.75	1.72
5°31.51'E	1.50	2.06	5°34.17'E	1.25	1.78
	2.50	2.06		1.75	1.61
	4.00	2.13		2.50	1.43
	6.00	1.81		4.00	1.72
	8.00	1.60		6.00	2.02
	10.00	1.66		8.00	2.11
	13.00	1.75		10.00	2.04
				13.00	2.39
				17.00	2.23
				21.00	2.34
WS 5	0.50	3.30			
52°58.08'N	1.50	3.07			
4°55.67'E	3.00	2.37			
	5.00	2.32			
	7.00	2.32			
	9.00	4.03			
	11.00	1.66			
	14.00	2.26			
	18.00	2.21			
	22.00	2.27			
	25.00	2.16			

APPENDIX 23

Si in Wadden Sea sediments. D = mean depth; R = residual.

Station	D(cm)	R(%)	Station	D(cm)	R(%)
WS 1	0.50	35.5	WS 2	0.25	31.8
53°00.50'N	1.50	22.3	53°01.12'N	0.75	38.2
5°04.67'E	2.50	33.3	5°04.51'E	1.50	32.3
	4.00	32.7		2.50	36.4
	6.00	32.4		3.50	24.8
	8.00	32.1		5.00	33.8
	11.00	31.2		7.00	34.2
	15.00	33.9		10.00	34.4
	19.00	32.2		13.00	34.5
	23.00	32.5		18.00	33.5
WS 3	0.25	36.6	WS 4	0.25	32.5
53°18.24'N	0.75	32.5	53°19.20'N	0.75	35.1
5°31.51'E	1.50	39.5	5°34.17'E	1.25	35.8
	2.50	38.9		1.75	36.7
	4.00	37.5		2.50	20.2
	6.00	38.9		4.00	35.2
	8.00	42.5		6.00	35.4
	10.00	39.3		8.00	33.1
	13.00	38.5		10.00	34.5
				13.00	31.2
				17.00	32.7
				21.00	32.1
WS 5	0.50	23.5			
52°58.08'N	1.50	36.9			
4°55.67'E	3.00	44.2			
	5.00	42.6			
	7.00	44.3			
	9.00	27.5			
	11.00	40.0			
	14.00	44.8			
	18.00	45.1			
	22.00	38.8			
	25.00	41.4			

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