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TRACE ELEMENT GEOCHEMISTRY OF SANDY SEDIMENTS AND OVERLYING WATERS AT THE DOGGERBANK, NORTH SEA

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SUMMARY

The trace element composition of the sediments, the water column and suspended particulate matter in the area near the Doggerbank does not yield evidence for large scale anthropogenic inputs. It is as yet not possible to distinguish between natural (i.e. background) concentrations and man-made influence. Interstitial water trace element concentrations are high in comparison with the very low concentrations for Mn, Fe (and Si, P) found in the poor sandy Doggerbank sediments and are of the same order of magnitude as those found for east Pacific sediments consisting mainly of fine clays (SHAW, 1987). The large concentration gradients near the sediment water interface may result in substantial fluxes to the overlying North Sea waters. Mixing of the shallow North Sea waters would quickly erode the elevated concentrations resulted from these fluxes a few meters away from the seafloor. It is however likely that very near the seafloor dissolved trace element concentrations in the water column are much higher than in overlying waters.

1. Introduction

This project is part of the BEWON (Beleidsgericht Wetenschappelijk Onderzoek NIOZ) research programme which focuses on the ecology and trace chemical pollutants in the North Sea. In the summer of 1988 the WINDOW expedition on board RV TYRO investigated the Doggerbank (Fig. 1). Our objective was a first study of the trace metal diagenesis in coarse sandy sediments. Almost all previous studies investigating trace metal diagenesis have dealt with fine grained sediments, which are far easier to sample and to process than sandy sediments. During the past ten years the North Sea watercolumn has been extensively studied for its dissolved and suspended particulate trace element composition (DUINKER and NOLTING, 1978; 1982; BALLS, 1985a; 1985b; KREMLING and HYDES, 1988).

The combination of specially designed watertight boxcores with a novel pore water centrifuge tube allowed us to sample large volume interstitial water from coarse sandy sediments. Furthermore the sediment itself and the immediately overlying waters and suspended particulate matter were sampled.

The water overlying the Doggerbank and the area in the immediate vicinity is very shallow and nowhere stations were deeper than 90 meters. The sediments in this region consist of coarse sands with very low concentrations of organic matter and have low biological activity. Because of the near-by presence of highly industrialized countries elevated concentrations of some trace elements are expected.

2. Materials and methods

2.1 Sediments

North Sea sediments were collected with new stainless steel boxcores (50 cm i.d.). However, the use of steel boxcores must be avoided in future studies since they probably are a significant source of contamination. Upon recovery subsamples were taken with acid-washed acrylic tubes (50 mm i.d.). The sediment cores were cut into 0.5 or 1 cm slices and the sediments were dried at 105 °C for 24 hours. In order to minimize contamination the sediments were not ground, except samples 67 and 75 which were provided by Van Raaphorst and Kloosterhuis. These samples had been ground in an agate mill. The acrylic liners had been beveled several times on board ship in case they had broken. The lubricant used for beveling is also a likely source of contamination. Ample supply of acid washed acrylic liners is recommended and broken liners must be replaced by clean new liners.

Sediment texture analyses were made by LASER-spectrometry at the University of Utrecht. Sediment porosity was determined by weight loss of the sample after drying at 105 °C for several hours. The organic carbon content and total nitrogen content were determined by CHN-analyzer at the Limnological Institute. The aluminum concentration was determined after total digestion of the sediment and measured by flame AAS (Perkin Elemer 403 atomic absorption spectrophotometer), see below for total digestion procedure. Data on sediment porosity, organic carbon content, total nitrogen concentration and aluminum concentration were provided by Van Raaphorst and Kloosterhuis.

For the determination of the total metal content about 0.5 gram of homogenized sediment was digested using a mixture of HF/HNO₃/HCl (5 ml HF, 1 ml Aqua Regia, ultrapure quality) in a teflon bomb at 120 °C for 6 hours. After digestion 30 ml

supersaturated ultra pure boric acid were added and the volume was adjusted to 100 ml with double distilled water. Six procedural blanks consisting of reagents only were treated accordingly.

Many elaborate schemes exist to determine the reactive fraction of the trace metal content in the sediment. The reactive trace metal fraction is the amount of trace metal that can go into solution under changing physico-chemical conditions in the sediment pore waters, e.g. changing redox potential or pH. In this study a one step acid-leach with 1 N HCl was used to assess the total amount of exchangeable metal, without attempting or claiming any subtle distinction between the various chemical solid phases in the sediment. It is thought that most of the reactive metal fraction is present in ferromanganese oxides and organic coatings, which will largely dissolve by this method (DE BAAR et al., 1988). It is however important to remember that the metal content thus determined is operationally defined and not necessarily related to certain in situ chemical phases in the sediment. The residual fraction is thought to be incorporated within the crystal structure of silicate lattices and is believed to be inert under low temperature geochemical conditions.

For the determination of the acid-leachable fraction 0.5 gram of homogenized sediment was leached in 50 ml ultra pure 1 N HCl for 24 hours. Three procedural blanks consisting of reagents only were treated accordingly.

Mn, Fe and Ti were measured by Flame AAS (Perkin Elmer 403 atomic absorption spectrophotometer) using the method of standard addition. Cd, Co, Cu, Ni, Pb and Zn were measured by Graphite Furnace AAS (Perkin Elmer 5000 atomic absorption spectrophotometer, HGA-500 heated graphite furnace and AS-40 autosampler) also using standard addition. Precision of the method is 10 percent. Blank concentrations were always below the detection limit.

The acid-leached sediment was not treated by the total digestion procedure afterwards. To justify this decision a sediment (sample 98, 20-30 cm) was split into two parts in a separate experiment. One part was completely digested as described above, the other part

was first leached in 1 N HCl and then digested like the other half. The result is shown in table 1.

2.2 Interstitial water

For the collection of interstitial waters sediment boxcores were subsampled using acid-washed acrylic liners (5 cm i.d.). The sediment cores were immediately transported to a nitrogen glove-box situated in a cold van and subsampled in 0.5 or 1 cm slices at in situ temperature under an inert atmosphere. The sediments were centrifuged under nitrogen at 1500 g for five minutes (MSE-200 centrifuge). The centrifuge tubes had been specially designed for the extraction of coarse sandy sediment (SAAGER et al., 1989). Precautions were taken to avoid trace metal contamination during sampling and processing. The filtrate was immediately discarded into hot-acid cleaned polyethylene bottles and acidified to pH 2 with triple quartz distilled HNO_3 to prevent oxidation of redox sensitive elements, algal growth and adsorption of trace metals to the wall of the vials.

For the analysis of trace elements the samples were preconcentrated with APDC-DDDC solvent extraction (DANIELSSON, 1979) modified after GERRINGA (Pers. Comm.) as follows. Ten milliliter of the sample was buffered to pH 4-4.5 with 0.1 ml of a mixture containing ammonium acetate/acetic acid and APDC/DDDC. After vigorous shaking the metal-APDC/DDDC-complexes were extracted into 10 ml of FREON and then backextracted into 0.1 ml triple quartz distilled concentrated HNO_3 . Lastly 1 ml quartz distilled H_2O was added to obtain a preconcentration of a factor 10. Fe and Mn were directly measured either by Flame AAS or direct injection Graphite Furnace AAS using standard addition. The preconcentrated samples analyzed for Cd, Co, Cu, Ni, Pb and Zn by Graphite Furnace AAS using standard addition. Overall procedural blanks were made by extracting reagents only and concentrations were corrected for blank concentrations. Precision of the measurements is 3% for Fe and Mn and 5% for the other elements.

For measuring interstitial water nutrient profiles separate sediment slices were squeezed with Reeburgh type squeezers (REEBURGH,

1967). Nutrient concentrations were determined by autoanalyzer according to the method of STRICKLAND and PARSONS, 1968.

2.3 Suspended Particulate Matter

Suspended particulate matter was collected on acid-rinsed pre-weighed 0.4 μm Nuclepore filters mounted in an acid-cleaned all Teflon filtration unit. In the shore laboratory the filters were weighed and then leached in about 30 ml triple quartz-distilled 1N HCl for 24 hours. Unused, pre-cleaned filters were also leached to assess blank concentrations. The metal concentration was measured by Graphite Furnace AAS with standard addition. Blanks were always below detection limit.

2.4 Dissolved trace elements

Seawater samples were collected using a CTD-Rosette sampler with pre-cleaned, modified (BRULAND et al., 1979) 12-litre GoFlo bottles (General Oceanics). The rosette sampler was first sent down in order to obtain real time hydrographic data and to flush the GoFlo bottles. Upon recovery, the bottles which were sampled during the upcast, were hooked onto the outside of a clean air lab container. The water was pressure filtered through acid-washed 0.4 μm Nuclepore filters, using in-line pre-cleaned all Teflon filtration units and stored in 1 litre hot acid cleaned polyethylene bottles. The samples were acidified to pH 2 with triple quartz distilled HNO_3 .

Surface water samples were collected with a rubber boat about 200 meters upwind from the main vessel. Samples were collected in hot acid cleaned 1 litre polyethylene bottles and immediately acidified on board ship. The samples were not filtered.

In the shore laboratory the samples were preconcentrated using Chelex-100 ion exchange chromatography modified after DE BAAR (1983). Only acid-washed Teflon labware was used for the Chelex columns. Quartz distilled reagents and ultrapure Milli-Q water were used after blank concentrations were assessed and found negligible or below detection limit. All handling was performed inside a class-100 laminar flow bench situated in a clean air laboratory. Overall

procedural blanks were assessed by extracting reagents according to the procedure used for sea water.

The extracts were measured by Graphite Furnace AAS against a standard calibration curve made in 0.1 N HNO₃ (Perkin Elmer 5000 atomic absorption spectrometer, HGA-500 heated graphite furnace, AS-40 autosampler). Procedural blanks were mostly low and concentrations were corrected for blanks. Precision of the method is 5% for most elements and 10% for Pb.

3. Results

3.1 Sediment characteristics

The sediments of the Doggerbank area and vicinity have a coarse sandy texture and concomitant low porosity (table 2). On the Doggerbank proper the grain size averages 200 μm (stas. 21, 56, 67, 75), the texture becoming slightly more fine grained away from the Doggerbank (sta. 15 = 160 μm , stas. 8 and 98 average grain size is about 100-130 μm). At stations 21, 56, 67 and 75 the amount of particles smaller than 20 μm (siltsize) is less than 1 %, whereas the amount of particles smaller than 2 μm (clay fraction) was below the detection limit. At station 15 about 3% of the particles was smaller than 20 μm , while no particles smaller than 2 μm were measured. At stations 8 and 98 about 5-10 % of the particles was smaller than 20 μm , the amount of particles smaller than 2 μm being less than 1 %. The porosity of the sediments ranges from 35% to 45% at stations 21, 56, 67 and 75. Porosity was not measured for station 15, At station 16a, located near station 15 it averages 45% while at stations 8 and 98 the porosity is about 45-55% (table 3).

The organic carbon content (table 3) is less than 0.5 % at stations 21, 56, 67 and 75. At stations 8 and 98 the organic carbon content is about 0.5-0.7%. No data are available for station 15. At station 16a the organic carbon content is less than 0.5%. At stations 21, 56, 67 and 75 the Al-content (table 3) is about 1% while at stations 8 and 98 the Al-content is about 2%.

According to above characteristics the sediments can be divided into two distinct groups with only station 15 taking an intermediate position. Stations 21, 56, 67 and 75 have coarse sediment texture and low porosity, with also low organic carbon and Al-content. At stations 8 and 98 sediment texture is less coarse with a modestly higher porosity than at the other stations. Also the organic carbon and the Al-content are higher at these stations.

3.1.1 Ti, Fe, Mn

The Ti-content (table 4, Fig. 2a) does not exhibit significant differences between stations. The concentration varies between 0.1 and 0.4 % wt. while no clear trends can be discerned. Interpretation is difficult without information on the mineralogical composition of the sediment.

The Fe content (table 4, Fig. 2b) exhibits interesting differences between the two groups of sediments. At stations 21, 56, 67 and 75 the total Fe-content is lower than at stations 8, 15 and 98 by a factor of about 1.5. The relative percentage of acid-leachable Fe is however lower by a factor 2. This implies that at stations 8, 15 and 98 a greater part of the Fe is present as Fe(Mn)oxyhydroxides having implications for the interstitial water Fe concentrations, since under reducing conditions Fe-oxyhydroxides go into solution. None of the sediments show Fe enrichment at the top of the sediment column. Upward migration of dissolved Fe followed by oxidative precipitation in the oxic zone was not observed. The Fe-concentrations found in these sediments fall in the range of Fe-levels generally encountered in sandy sediments (DREVER, 1982) and are about a factor of 5-7 lower than estuarine clays and open ocean sediments (GRAYBEAL and HEATH, 1984; SALOMONS and FOERSTNER, 1984).

Mn concentrations range from 80 to 300 mg/kg (table 4, Fig. 2c) and also fall in the range normally found for sandy sediments (DREVER, 1982). As for Fe the clearest trends are displayed by the relative amount of acid-leachable Mn. In the sediments on the Doggerbank less than 10% of the Mn is acid-leachable. This implies that the amount of reactive Mn which can go into solution under reducing conditions is also very low. At station 21 about 25% is leachable and at the stations away from the Doggerbank about 35% (stas. 8 and 98) to 60% (sta. 15) of the Mn is acid-leachable. At stations 15, 75 and 98 there is clear evidence of diagenetic Mn enrichment in the top layer of the sediment, resulting from the upward migration of reduced Mn and precipitation in the oxic upper centimeters of the sediment. This enrichment is best displayed by the acid-leachable fraction since the precipitated Mn consists of Mn(Fe)-oxyhydroxides.

3.1.2 Trace elements

For a few elements the leachable metal content is larger than the total metal content, although the difference is mostly small. For Ni this is always the case, for Co and Cu at a few stations and for Zn at one station. It suggests that a major amount of the metal content is present in the leachable fraction.

Poor homogenization of the samples especially of samples which were not ground (i.e. all except stations 67 and 75) probably partly explains this observation. Precipitates, formed in the matrix used for total destruction of the sediment, which coprecipitate trace metals is possible, though not very likely. The low concentrations in these sediments, often near the detection limit possibly prevent a good reproducibility as well.

Cd: Total Cd-concentrations (table 4, Fig. 2d) show considerable scatter and do not exhibit significant differences between stations. The relative amount of acid-leachable Cd is slightly higher at the stations off the Doggerbank (stas. 8, 15, 98, about 20% leachable Cd) than at the stations on the Doggerbank (stas. 21, 56, 67 and 75, with

about 10% leachable Cd). At stations 21, 67, 75 and 98 there is some enrichment in the upper centimeters of the sediment. Both diagenetic processes and anthropogenic input sources may yield such enrichments, but further there is no evidence for large scale anthropogenic influence in these sediments. Concentrations are characteristic for sandy sediments (DREVER, 1982).

Co: At most stations the amount of acid-leachable Co (table 4, Fig. 2e) is larger than the total Co-content. For this reason only leachable Co-profiles are displayed in Fig. 2e for stations 8, 21, 56, 67, 75. The data must be considered merely as an indication of the concentration levels. Only for stations 15 and 98 both total and acid-leachable Co are displayed. Most Co is present in the leachable fraction (80%). Since Co has its own oxidation-reduction chemistry part of this leachable Co could go into solution under reducing conditions at about the same redox-potential as for Mn (HEGGIE and LEWIS, 1984). The amount of leachable Co is much higher at the stations off the Doggerbank than at the stations on the Doggerbank. No evidence of either diagenetic enrichment or anthropogenic inputs can be inferred from the data. Concentrations fall in the range reported for sandy sediments (DREVER, 1982)

Cu: Concentrations (table 4, Fig. 2f) fall in the range typical of sandy sediments (DREVER, 1982). Concentrations of leachable Cu are lowest on the Doggerbank (stas. 67, 75, about 50 % Cu is leachable), the difference being less obvious for total Cu-concentrations. At station 98 about 70% of the total Cu content is present in the leachable fraction. There is no evidence for diagenetic or anthropogenic enrichment in the sediment.

Ni: At all stations the leachable Ni fraction was higher than the total Ni content (table 4, Fig. 2g). The data must thus be regarded as an indication of the concentration levels at best. Concentrations are typical for sandy sediments (DREVER, 1982). As for the other metals, also leachable Ni concentrations are highest at the stations off the Doggerbank.

Pb: Only total Pb data are available (table 4, Fig. 2h). Since Pb-chloride is very insoluble the acid-leach method cannot be used for Pb. Based on results for sandy sediments in the Western Scheldt (SAAGER, 1986) it is reasonable to assume about 30-50% of the Pb-content will be present in the leachable fraction. As for the other metals highest concentrations are found at the stations off the Doggerbank without any evidence for diagenetic or anthropogenic input sources. Pb levels are characteristic for sandy sediments (DREVER, 1982).

Zn: Concentrations (Table 4, Fig. 2i) are highest off the Doggerbank (stas. 8 , 15 and 98) and a large part (about 70%) is found in the leachable fraction, whereas at stations 56, 67 and 75 only 40-50% is present as leachable Zn, the total Zn content showing considerable scatter. Zn concentrations fall in the range reported for sandy sediments (DREVER, 1982). There is no evidence for either diagenetic or anthropogenic input sources.

General: A major part of the trace element content is found in the acid-leachable fraction. This fraction represents the reactive part of the metals in the sediment. At the stations off the Doggerbank the amount of reactive metal in the sediment is higher than on the Doggerbank itself. Part of this can be explained by the difference in textural composition. The amount of fine grained particles is higher in the sediments off the Doggerbank. Smaller particles have a greater affinity to adsorb trace metals because of their higher specific surface area (the total surface area of one cubic centimeter of particles). Generally the major part of reactive metals is thought to be present in the fraction smaller than 63 μm (SALOMONS and FOERSTNER, 1984).

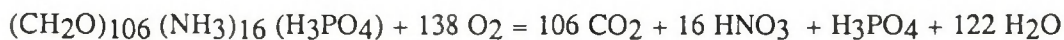
3.2 Interstitial water characteristics

General: Nutrient results are shown in Table 5. No final oxygen data and only preliminary profiles were available at the time this report was made. The oxygen characteristics are summarized briefly

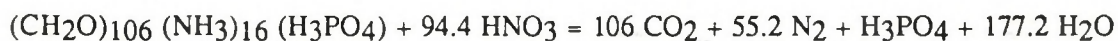
below. The results for Mn and Fe as well as of the other trace elements are shown in table 6 and figures 3-8.

At all stations the sediments are anoxic below 4-6 mm depth. At station 75 anoxic conditions set in at 1 cm depth. In the upper one centimeter nitrate concentrations reach a maximum ranging from 10 μM (sta. 56) to 45 μM (sta.8). At station 75 the nitrate maximum is reached at 3 cm depth. Below this maximum concentrations drop exponentially as a result of nitrate reduction and reach levels between 0.5-5 μM , the low levels possibly resulting from filter blanks. Just at or below the onset of nitrate reduction Mn reduction starts, resulting in elevated Mn concentrations in the interstitial waters. At the same depth or at some stations just below, Fe reduction sets in as well, also leading to elevated dissolved Fe concentrations in the interstitial waters. Below the oxidation sequence for the break down of organic matter is given, assuming reactive Mn and Fe are present in the sediment as MnO_2 and FeOOH respectively. Average organic matter is represented by the formula $(\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} (\text{H}_3\text{PO}_4)$ (from FROELICH et al., 1979):

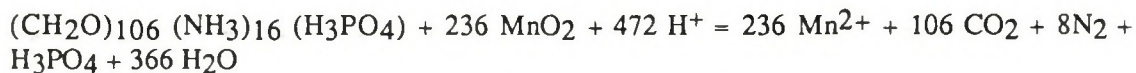
oxidant is oxygen:



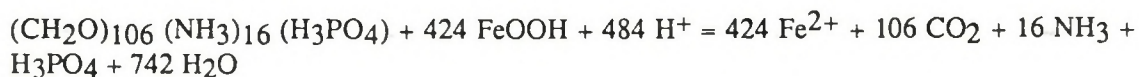
oxidant is nitrate:



oxidant is manganese:



oxidant is iron:



Sulfide was not measured but grey-black Fe-sulfides were observed from 3-4 cm downwards. Ammonia concentrations also increase downwards reaching levels ranging from 15-70 μM . Ammonia is a product of iron- and sulphate reduction (FROELICH et al., 1979). Ammonia concentrations are at the (very) low end of the range reported for open ocean pore water studies. The cycli of silicate and phosphate also appear to be influenced to a considerable degree by the redox cycle of Fe but discussion of these elements is beyond the scope of this report. Also for silicate and phosphate the concentrations are at the low end of the range normally encountered in open ocean sediments.

Mn and Fe: Because of anoxic conditions prevailing at all stations interstitial water Mn and Fe concentrations increase downwards in the sediment (Fig. 3,4). The maximum concentrations reached are however largely determined by the amount of MnFe-oxyhydroxides in the solid state, this is the amount of potentially reducible Mn and Fe. As with solid state sediment characteristics the same two distinct groups can be identified on basis of the interstitial Mn and Fe concentrations, station 15 being intermediate. At the stations on the Doggerbank Mn values start increasing at a depth of 1 cm and reach maximum concentrations of only 1-2 μM ! These concentrations are amongst the lowest reported for anoxic sediments thus far. At station 15 just off the Doggerbank maximum Mn concentrations are reached in the upper few millimeters (4 μM) and decrease sharply to constant values around 1.5 μM at 3-7 cm depth. At the stations off the Doggerbank Mn concentrations are below detection limit near the surface and increase from 0.2 to 0.7 cm depth reaching maximum concentrations of about 28 and 41 μM at 1-3 cm depth at stations 8 and 98 respectively. These values are still at the low end of interstitial water Mn concentrations normally found for reducing (fine grained) sediments. Below these maxima Mn levels drop sharply to about 10-15 μM at 4-6 cm depth. Concentrations decreasing below the Mn maximum could be the result of the formation of Mn-carbonates or possibly Mn incorporated in Fe-sulfides.

Fe concentrations also increase down in the sediment. There is however considerable scatter obscuring detailed structures. At the stations on the Doggerbank maximum Fe concentrations are only 2-10 μM . As for Mn highest Fe concentrations are found at station 98 off the Doggerbank. At a depth of 2 cm dissolved Fe levels reach 85 μM which is in the range of interstitial water Fe concentrations reported for anoxic sediments. Fe concentrations drop below this depth as a result of Fe-sulfide formation.

3.2.1 Trace elements

Co: Co is the only trace element in this study which has its own redox chemistry: $\text{Co}^{3+} + e^- = \text{Co}^{2+}$, where like for Mn and Fe the reduced form is the better soluble. Coupling between Mn and Co in interstitial waters has been reported for reducing open ocean sediments (HEGGIE and LEWIS, 1984). At stations 8 and 98 Co goes into solution at the same depth as Mn (Fig. 5), clearly exhibiting the same features as Mn. Maximum concentrations are about 17-23 nM which is two orders of magnitude higher than in overlying North Sea waters (KREMLING and HYDES, 1988). The decrease deeper down the sediment column can result from incorporation in Mn-carbonates as well as from coprecipitation in Fe-sulfides. At stations 67 and more clearly station 75, Co concentrations increase together with Mn (and Fe) but the maximum concentrations are much lower than at the stations off the Doggerbank (4-7 nM at stations 75 and 67 respectively).

Cd: Reliable interstitial water Cd profiles have only been measured from stations 75 and 98, fortunately representing one Doggerbank sediment and one sediment located off the doggerbank. Cd regeneration starts in the upper layer of the sediment (Fig. 6) resulting in Cd maxima of 35 nM at a depth of 2.8 cm at station 75, which is more than two orders of magnitude higher than overlying North Sea water concentrations (KREMLING and HYDES, 1988; also this study). Immediately below this maximum Cd levels decrease sharply to values of 2-5 nM, probably as a result of the formation of insoluble Cd-sulfides or incorporation in Fe-sulfides. The same

feature is observed at station 98, where maximum Cd concentrations (22 nM) are reached at 7.5 mm depth, also two orders of magnitude higher than overlying North Sea waters. At station 98 concentrations increase again as from 4 cm depth. In contrast to the redox type elements highest maximum concentrations are reached at the Doggerbank station. It is not clear why Cd behaves differently from the redox type elements in this respect. It is clear that the Cd cycle in the interstitial water column is not governed by the redox cycle of Mn and Fe. More likely the regeneration of Cd is related to that of organic matter.

Nitrate production as a result of the break down of organic matter continues to about the same depth as for Cd at both stations. The strong concentration gradients drive the transport of dissolved Cd both in an upward and in a downward direction, possibly leading to large fluxes across the sediment-water interface.

The Cd-profiles bear a striking resemblance with the profiles measured for the Laurentian Trough by GOBEIL et al. (1987). They report dissolved Cd maxima in the very top of the sediment followed by a sharp decrease in concentration further down in the sediment. At two stations they too find increasing concentrations at the bottom of their sediment cores. Maximum Cd concentrations in the Laurentian Trough sediments (2-5 nM) are an order of magnitude lower than at our stations. They attribute the Cd maxima to break down of organic matter, thereby releasing adsorbed Cd to the interstitial waters. Precipitation as sulfides probably caused the sharp concentration decrease, while the increasing concentrations at the base of the sediment would be caused by the formation of stable polysulfide complexes (also JACOBS et al., 1985).

Cu: The only reliable interstitial water Cu profile was measured at station 8 (Fig. 7). The profile shows evidence of rapid Cu regeneration in the upper few millimeters of the sediment leading to concentrations of 75 nM, about 30 times higher than overlying North Sea waters (BALLS, 1985a; also this study). Down the sediment column interstitial water concentrations drop sharply. Coprecipitation with Mn carbonates or, deeper in the sediment Fe-sulfides could result in this decrease. As for Cd the Cu cycle appears to be governed by the degradation of organic matter.

Ni: Two reliable pore water profiles have been measured for Ni (stas. 8 and 75, Fig. 7) representing the Doggerbank area and the area off the Doggerbank. The profiles bear a striking resemblance with the Cd profiles. At the station off the Doggerbank Ni regeneration proceeds in the upper cm of the sediment column with maximum Ni concentrations of 200 nM, two orders of magnitude higher than the overlying North Sea waters (KREMLING and HYDES, 1988; also this study). Deeper down the sediment concentrations decrease again, probably as a result of incorporation in several mineral phases like Mn-carbonates and Fe-sulfides. As for Cd and Cu the interstitial water Ni cycle seems to be largely determined by the regeneration of organic matter. The strong concentration gradients especially at station 8, where the largest concentration gradient is located at the surface, large Ni fluxes into the overlying waters may be expected. The concentration levels are of the same order of magnitude as those reported for open ocean interstitial waters.

Zn: At all stations the profiles show Zn regeneration and concomitant increased concentrations near or at the top of the sediment followed by a decrease in Zn levels deeper down the sediment (Fig. 8). At stations 21 and 56 concentrations start to increase immediately below a Zn minimum located at 1-2 cm depth. Formation of stable Zn-sulfide complexes which are better soluble has been invoked to explain a comparable concentration increase in anoxic basins like Framvaren Fjord (JACOBS et al., 1985). It is not clear, however, why this concentration increase is not observed at the other two stations. It is possible that at these stations Zn concentrations still increase deeper down the sediment, since at all stations the presence of sulfides was observed. Interstitial water Zn concentrations are two orders of magnitude higher than overlying North Sea waters and are comparable with values found for the east Pacific (SHAW, 1987). There is no significant difference in concentration levels between stations on and stations off the Doggerbank. Concentration gradients are steep near the sediment water interface probably giving rise to large Zn fluxes to the overlying waters. It is however possible that a significant amount of dissolved Zn is coprecipitated

in freshly precipitated MnFe-oxyhydroxides in the upper few millimeters of the sediment.

4. Suspended Particulate Matter

Suspended Particulate Matter (SPM) has only been analysed for the trace element composition and for Mn and Fe (Table 7). Concentrations fall in the range reported for SPM in the same area by NOLTING and EISMA (1989). The time section at station 75 will not be discussed in detail here. Also, Co data are too scanty to allow for an extensive discussion. It immediately appears from Table 7 that the SPM concentration levels of all elements are much higher than solid state sediment concentrations. SPM consists to a large degree of authigenic particles like organic matter, organically coated particles and MnFe-oxyhydroxides which have a high affinity for trace metals. In the sediment a large part of the particles is regenerated through break down of organic matter or dissolution of MnFe-oxyhydroxides thus releasing the adsorbed trace elements back into solution. This is evidenced by the order of magnitude higher trace element concentrations in the interstitial waters of the sediments compared to overlying seawater concentrations.

Both Mn and Fe concentrations in SPM and the actual particulate Mn and Fe concentrations in the water column (expressed as the concentration of particulate Mn or Fe in nanomoles per liter) increase towards the seafloor for all stations. This suggests regenerative fluxes from the sediment are important where dissolved Mn and Fe reprecipitate as authigenic oxyhydroxides upon entering the oxygenated overlying water column. These freshly precipitated MnFe-oxyhydroxides may then scavenge trace elements from the water column (BALISTRERI et al., 1981). After deposition on the seafloor the particles can be partly dissolved again in the interstitial waters of the sediment column thereby releasing the adsorbed trace elements.

The SPM trace metal concentration does not systematically increase towards the seafloor suggesting adsorption on MnFe-oxyhydroxides is not the only factor determining their SPM distribution.

Adsorption on organic particles or organically coated mineral phases is likely to play an important role as well.

SPM trace element concentrations in the area near the Doggerbank are among the lowest reported for the entire North Sea (NOLTING and EISMA, 1989).

5. Dissolved trace elements

The results for dissolved trace element concentrations are shown in Table 8. Because of its low dissolved concentration Mn also belongs to the category of trace elements in seawater. For Mn, Cu, Cd and Zn concentrations are comparable with previously reported results for the North Sea (KREMLING and HYDES, 1988; BALLS, 1985a; 1985b; NOLTING, 1986; DUINKER and NOLTING, 1982). The results for Ni must be regarded with caution since a large reagent blank concentration had to be subtracted and the concentrations are probably somewhat too low. Results for Fe and Co were not reliable due to contamination and are not included in the Table. A comparison with the SPM trace element concentrations shows that on an average 50-90% of the trace element concentration is present in the dissolved state. Surface water concentrations of Mn, Pb and Zn are about a factor of 2 (Pb) to 20 (Zn) higher than in the open ocean, while surface water Cu and Ni concentrations are of the same order as open ocean surface water concentrations. Surface water Cd concentrations in the open ocean depend largely on the nutrient concentration in the water column and vary greatly. In the North Sea cadmium concentrations vary only very little. There is no apparent relationship with either nitrate or phosphate (Table 9).

Atmospheric deposition of trace elements is an important source especially for Pb, Cd and Zn in the ocean. A land enclosed basin like the North Sea thus receives large inputs from atmospheric deposition both from natural and man-made sources. It is not possible to distinguish between the relative importance of either natural or man-made inputs. River inputs further supply another important source of trace elements to the oceans.

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Table 1. Acid-leach experiment. Explanation is given in the text. The difference between the total metal content (total destruction only) of the sediment, shown in the last column, and the sum of the acid-leachable fraction plus refractory metal fraction is only 5% for Mn, Fe, Ni, Zn, Cd. For Cu the difference is very large. Concentrations are in mg/kg, for Fe in % wt.

	HCl-leach (L)	Refractory (R)	Sum (L+R)	Total
Cd	0.34	0.61	0.95	1.02
Cu	1.1	2.3	3.4	2.3
Fe	0.08	0.65	0.73	0.69
Mn	35	99	134	131
Ni	1.6	9.9	11.5	11.3
Zn	6.7	14.8	21.5	21.9

Table 2. Sediment Texture, mean grain size per depth interval is given in μm .

Station 08		Station 15		Station 21	
depth (mm)	grain size	depth (mm)	grain size	depth (mm)	grain size
2.5	128	2.5	161	2.5	203
7.5	134	7.5	159	7.5	199
12.5	125	15.0	161	15.0	204
17.5	128	25.0	163	25.0	202
22.5	113	35.0	156	35.0	195
27.5	113	45.0	159	35.0	192
32.5	109	55.0	157	55.0	194
37.5	106	65.0	156	65.0	194

Station 56		Station 67		Station 75		Station 98	
depth (mm)	grain size	depth (mm)	grain size	depth (mm)	grain size	depth (mm)	grain size
5.0	191	2.5	213	2.5	189	2.5	96
15.0	193	7.5	201	7.5	197	7.5	100
25.0	189	15.0	201	15.0	193	15.0	99
35.0	196	30.0	208	30.0	194	25.0	100
45.0	187	50.0	203	50.0	197	35.0	102
55.0	187	80.0	190	80.0	182	45.0	90
						55.0	98
						65.0	98

Table 3.
Sediment Characteristics
(elements in % weight[†]).

Station 08

Depth (mm)	Porosity (l/l)	Al	C-tot	N-tot	C:N
2.5	0.72	2.3	0.55	0.05	12.8
7.5	0.50	1.7	0.46	0.05	10.7
15.0	0.45	2.0	0.45	0.04	13.1
30.0	0.39	2.1	0.63	0.06	12.3
50.0	0.46	2.2	0.62	0.03	24.1
80.0	0.48	2.2	0.82	0.06	15.9

Station 16a

Depth (mm)	Porosity (l/l)	Al	C-tot	N-tot	C:N
2.5	0.45	1.3	0.26	0.05	6.1
7.5	0.45	1.4	0.28	0.04	8.2
15.0	0.43	1.4	0.34	0.05	7.9
30.0	0.44	1.3	0.44	0.06	8.6
50.0	0.41	1.3	0.37	0.04	10.8
80.0	0.41	1.5	0.48	0.06	9.3

Station 21

Depth (mm)	Porosity (l/l)	Al	C-tot	N-tot	C:N
2.5	0.41	1.0	0.46	0.05	10.7
7.5	0.41	1.0	0.51	0.02	29.8
15.0	0.38	0.9	0.16	0.02	9.3
30.0	0.38	1.1	0.12	0.05	2.8
50.0	0.38	1.0	0.16	0.06	3.1
80.0	0.37	1.2	0.41	0.07	6.8

Table 3, continued.
Sediment Characteristics
(elements in % weight).

Station 56

Depth (mm)	Porosity (l/l)	Al	C-tot	N-tot	C:N
2.5	0.39	1.1	0.28	0.08	4.1
7.5	0.38	1.3	0.50	0.03	19.4
15.0	0.37	1.1	0.40	0.03	15.6
30.0	0.38	1.1	0.26	0.04	7.6
50.0	0.36	1.1	0.43	0.05	10.0
80.0	0.36	1.2	0.19	0.03	7.4

Station 67

Depth (mm)	Porosity (l/l)	Al	C-tot	N-tot	C:N
2.5	0.41	0.8	0.17	0.08	2.5
7.5	0.46	0.8	0.29	0.03	11.3
15.0	0.37	0.7	0.31	0.00	
30.0	0.41	0.9	0.78	0.06	15.2
50.0	0.38	1.0	0.28	0.05	6.5
80.0	0.33	1.1	0.76	0.05	17.7

Station 75

Depth (mm)	Porosity (l/l)	Al	C-tot	N-tot	C:N
2.5	0.38	0.9	0.22	0.07	3.7
7.5	0.41	1.0	0.24	0.04	7.0
15.0	0.41	1.1	0.20	0.09	2.6
30.0	0.39	1.0	0.19	0.07	3.2
50.0	0.37	1.0	0.19	0.03	7.4
80.0	0.39	1.0	0.29	0.06	5.6

Table 3, continued.
Sediment Characteristics
(elements in % weight).

Station 98

Depth (mm)	Porosity (l/l)	Al	C-tot	N-tot	C:N
2.5	0.56	2.0	0.64	0.10	7.5
7.5	0.56	2.0	0.77	0.10	9.0
15.0	0.55	2.1	0.76	0.09	9.9
30.0	0.52	2.2	0.77	0.09	10.0
50.0	0.49	2.1	0.71	0.08	10.4
80.0	0.45	2.1	0.75	0.07	12.5

Table 4.
Sediment Metal Concentrations
(Ti, Fe in %, other elements in mg/kg).
T= total, L = leachable

Station 8

Depth (mm)	Ti-T	Mn-T	Mn-L	Fe-T	Fe-L	Co-T	Co-L	Cd-T	Cd-L
2.5	0.3	130	47	0.66	0.36	1.8	1.6	0.13	0.03
7.5	0.31	110	37	0.62	0.33	1.5	1.4	0.08	0.05
12.5	0.30	114	37	0.65	0.35	1.4	1.5	0.52	0.02
17.5	0.28	119	39	0.64	0.38	1.7	1.5	0.06	0.02
22.5	0.29	118	50	0.79	0.42	1.2	1.8	0.05	0.02
27.5	0.28	107	52	0.71	0.45	1.0	2.0	0.23	0.01
32.5	0.31	105	47	0.76	0.42	2.2	1.8	0.05	0.03
37.5	0.34	121	54	0.86	0.47	1.2	2.0	0.13	0.05

Depth (mm)	Zn-T	Zn-L	Pb-T	Pb-L	Ni-T	Ni-L	Cu-T	Cu-L
2.5	13.2	9.9	12.6	0.5	4.0	4.0	1.8	1.2
7.5	12.1	9.2	10.9	0.7	3.1	3.7	2.0	1.3
12.5	13.2	9.2	9.8	0.5	3.0	3.8	1.5	1.2
17.5	12.1	9.3	11.5	0.6	3.2	4.5	1.6	1.2
22.5	15.4	10.6	9.3	0.6	3.0	5.2	1.6	2.1
27.5	14.3	11.1	7.7	0.5	2.3	5.5	1.2	1.7
32.5	16.5	10.6	13.7	0.8	4.7	5.3	2.5	1.6
37.5	18.7	11.3	8.0	0.6	3.1	5.7	1.6	1.8

Table 4, continued.
 Sediment Metal Concentrations
 (Ti, Fe in %, other elements in mg/kg).
 T= total, L = leachable

Station 15

Depth (mm)	Ti-T	Mn-T	Mn-L	Fe-T	Fe-L	Co-T	Co-L	Cd-T	Cd-L
2.5	0.09	100	90	0.59	0.34	1.6	1.5	0.24	0.02
7.5	0.13	96	68	0.60	0.36	1.9	1.4	0.48	0.02
15.0	0.15	81	56	0.58	0.32	1.7	1.4	0.07	0.04
25.0	0.16	89	55	0.57	0.30	1.8	1.3	0.18	0.06
35.0	0.14	81	52	0.61	0.33	1.8	1.4	0.16	0.04
45.0			56		0.33		1.5		0.03
55.0	0.15	89	59	0.65	0.36	1.8	1.4	0.74	0.04
65.0	0.19	106	66	0.78	0.43	2.1	1.8	0.09	0.03

Depth (mm)	Zn-T	Zn-L	Pb-T	Pb-L	Ni-T	Ni-L	Cu-T	Cu-L
2.5	9.9	6.8	10.6	0.6	2.8	4.2	1.7	1.3
7.5	10.7	7.2	11.4	0.4	3.4	4.1	1.8	1.3
15.0	10.5	6.7	10.9	0.9	3.2	4.1	2.1	1.6
25.0	10.5	6.6	12.3	0.6	3.9	3.7	1.8	1.1
35.0	11.2	7.1	11.0	0.3	3.6	3.8	2.0	1.2
45.0		8.0	8.0	0.4		4.1		1.5
55.0	13.7	7.6	10.9	1.0	3.2	4.6	1.8	3.5
65.0	15.2	8.4	12.2	0.3	4.7	5.3	2.2	2.5

Table 4, continued.
 Sediment Metal Concentrations
 (Ti, Fe in %, other elements in mg/kg).
 T= total, L = leachable

Station 21

Depth (mm)	Ti-T	Mn-T	Mn-L	Fe-T	Fe-L	Co-T	Co-L	Cd-T	Cd-L
2.5	0.14	110	33	0.44	0.16	1.0	0.7	0.10	0.05
7.5	0.12	96	33	0.42	0.17	0.7	0.7	0.44	0.02
15.0	0.14	111	34	0.46	0.15	0.5	0.6	0.20	0.01
25.0	0.12	99	35	0.46	0.18	0.7	0.7	0.57	0.02
35.0	0.17	134	35	0.57	0.19	1.1	0.8	0.19	0.01
45.0	0.16	120	29	0.50	0.17	0.9	0.6	0.14	0.01
55.0	0.31	173	27	0.63	0.15	1.4	0.6	0.10	0.01
65.0	0.15	119	25		0.16		0.7		0.01

Depth (mm)	Zn-T	Zn-L	Pb-T	Pb-L	Ni-T	Ni-L	Cu-T	Cu-L
2.5	5.5	4.1	5.6	0.4	1.4	2.1	0.7	0.6
7.5	3.4	4.1	4.8	0.4	1.2	1.9	0.9	0.7
15.0	4.7	3.3	4.5	0.2	1.0	2.1	0.8	0.5
25.0	4.8	4.8	5.0	0.2	1.3	2.6	0.9	1.0
35.0	6.3	4.3	6.0	0.4	2.5	2.0	2.1	0.6
45.0	6.2	3.6	5.6	0.3	1.6	1.9	1.0	0.6
55.0	5.0	3.2	6.2	0.2	1.4	1.6	0.9	0.5
65.0		3.7		0.3		1.8		0.6

Table 4, continued.
 Sediment Metal Concentrations
 (Ti, Fe in %, other elements in mg/kg).
 T= total, L = leachable

Station 56

Depth (mm)	Ti-T	Mn-T	Mn-L	Fe-T	Fe-L	Co-T	Co-L	Cd-T	Cd-L
5.0	0.34	275	20	0.62	0.11	0.4	0.4	0.12	0.02
15.0	0.29	208	20	0.56	0.13	0.4	0.5	0.40	0.01
25.0	0.21	155	13	0.44	0.10	0.5	0.4	0.10	0.05
35.0	0.32	239	17	0.57	0.11	1.1	0.4	0.20	0.02
45.0	0.44	329	14	0.76	0.10	1.0	0.5	0.27	0.01
55.0	0.30	238	11	0.58	0.07	1.1	0.3	0.34	0.12

Depth (mm)	Zn-T	Zn-L	Pb-T	Pb-L	Ni-T	Ni-L	Cu-T	Cu-L
5.0	4.8	1.0	4.4	0.2	0.4	0.9	0.4	0.9
15.0	4.2	1.5	4.7	0.2	0.5	1.3	0.4	1.0
25.0	2.8	0.9	6.9	0.7	0.7	1.4	0.6	(5.2)
35.0	3.9	1.8	10.0	0.2	1.3	1.3	0.9	1.5
45.0	4.8	2.1	6.8	0.5	0.8	2.2	0.6	1.5
55.0	4.3	1.0	8.4	0.4	1.1	0.9	0.9	0.6

Table 4, continued.
 Sediment Metal Concentrations
 (Ti, Fe in %, other elements in mg/kg).
 T= total, L = leachable

Station 67

Depth (mm)	Ti-T	Mn-T	Mn-L	Fe-T	Fe-L	Co-T	Co-L	Cd-T	Cd-L
2.5	0.32	182	11	0.4	0.08	0.2	0.2	0.11	0.05
7.5	0.24	131	6	0.4	0.09	0.5	0.3	0.10	0.06
15.0	0.15	80	8	0.3	0.08	0.5	0.2	(0.93)	0.01
30.0	0.23	134	11	0.3	0.08	0.2	0.2	0.08	0.01
50.0	0.27	146	11	0.4	0.08	0.5	0.2	0.09	0.01
70.0	0.41	207	10	0.5	0.07	0.6	0.2	0.02	
Depth (mm)	Zn-T	Zn-L	Pb-T	Pb-L	Ni-T	Ni-L	Cu-T	Cu-L	
2.5	0.7	1.5	0.8	0.4	0.8	1.0	1.3	0.7	
7.5	(14.8)	1.0	3.2	0.3	0.6	1.2	2.2	0.8	
15.0	1.5	1.3	4.2	0.5		1.5	2.5	0.6	
30.0	(8.2)	0.6	1.2	0.3	0.3	0.9	2.0	1.1	
50.0	2.9	0.9	3.5	0.3	0.2	0.9	1.8	0.8	
70.0	(5.5)	1.0	3.1	0.3	0.6	0.9	2.4	1.2	

Table 4, continued.
 Sediment Metal Concentrations
 (Ti, Fe in %, other elements in mg/kg).
 T= total, L = leachable

Station 75

Depth (mm)	Ti-T	Mn-T	Mn-L	Fe-T	Fe-L	Co-T	Co-L	Cd-T	Cd-L
2.5	0.22	149	52	0.32	0.12	0.1	0.4	(1.0)	0.02
7.5	0.27	162	29	0.38	0.13	0.2	0.4	(5.0)	0.01
15.0	0.31	174	18	0.44	0.12	0.2	0.4	0.4	0.01
30.0	0.42	211	13	0.51	0.10	0.7	0.4		0.01
50.0	0.34	201	16	0.48	0.11	0.5	0.4	(4.3)	0.02
70.0	0.23	117	20	0.40	0.13	0.1	0.7	(1.4)	0.03
Depth (mm)	Zn-T	Zn-L	Pb-T	Pb-L	Ni-T	Ni-L	Cu-T	Cu-L	
2.5	3.3	3.3	1.9	1.7	0.0	1.2	1.7	0.8	
7.5	4.9	2.8	3.9	1.2	0.5	1.1	1.9	0.9	
15.0	5.4	3.1	3.8	1.0	0.8	1.1	2.3	0.6	
30.0	6.8	3.7	5.9	0.9	1.1	1.4	2.6	0.8	
50.0	5.8	2.8	5.5	0.9	1.6	1.4	2.3	1.7	
70.0	(2.1)	4.3	1.4	1.3		2.5	2.6	1.7	

Table 4, continued.
 Sediment Metal Concentrations
 (Ti, Fe in %, other elements in mg/kg).
 T= total, L = leachable

Station 98

Depth (mm)	Ti-T	Mn-T	Mn-L	Fe-T	Fe-L	Co-T	Co-L	Cd-T	Cd-L
2.5	0.24	179	123	0.72	0.39	2.1	1.7	0.22	0.05
7.5	0.22	150	81	0.69	0.37	1.8	1.6	0.17	0.07
15.0	0.28	141	59	0.72	0.37	1.9	1.6		0.02
25.0	0.30	136	54	0.73	0.37	1.9	1.7	0.10	0.03
35.0	0.24	130	57	0.69	0.36	1.9	1.7	0.20	0.03
45.0	0.28	136	52	0.71	0.37	2.1	1.7	0.60	0.04
55.0	0.29	137	53	0.75	0.37	2.1	1.7	0.10	0.02
65.0	0.26	126	54	0.75	0.38	2.1	1.8	0.20	0.02

Depth (mm)	Zn-T	Zn-L	Pb-T	Pb-L	Ni-T	Ni-L	Cu-T	Cu-L
2.5	16.9	10.7	17.2	1.0	7.4	6.1	3.1	2.0
7.5	16.0	11.4	15.6	0.7	7.9	5.9	2.7	1.8
15.0	17.1	11.5	19.6	1.1	7.1	5.8	5.1	2.0
25.0	15.1	11.9	14.2	0.9	6.8	5.9	2.7	2.1
35.0	17.4	12.0	13.6	0.9	7.9	5.9	2.7	1.9
45.0	15.0	13.1	11.2	0.7	6.8	6.3	2.5	1.9
55.0	18.0	11.9	14.9	0.7	4.8	6.2	3.1	1.9
65.0	21.6	19.0			7.7	6.5	2.9	2.2

Table 5.
Pore Water Nutrient Concentrations
(all concentrations are in μM).

Station 08

Depth	PO ₄	Si	NH ₄	NO ₂	NO ₃
0	0.62	10.0	1.5	0.06	0.38
2.5	0.99	66.1	6.1	2.59	45.4
7.5	1.20	96.8	16.4	2.50	39.5
15.0	0.65	111.5	26.8	1.82	34.73
30.0	1.70	117.4	61.9	1.42	19.4
50.0	3.44	81.4	71.8	1.05	20.0
70.0	4.71	109.0	48.4	1.24	4.9
90.0	2.58	77.6	5.3	1.10	4.6
110.0	3.55	62.9	34.7	2.60	7.8

Station 16a

Depth	PO ₄	Si	NH ₄	NO ₂	NO ₃
0	1.07	0.0	1.22	0.03	0.2
2.5	8.63	178.6	13.1	1.39	21.4
7.5	16.21	259.9	27.4	1.45	20.9
15.0	4.58	81.4	22.2	1.31	31.3
30.0	12.70	74.6	40.6	0.86	18.2
50.0	5.60	66.9	46.0	0.68	4.8
70.0	2.64	64.1	46.8	0.40	1.5

Station 21

Depth	PO ₄	Si	NH ₄	NO ₂	NO ₃
0	0.08	0.9	1.2	0.00	0.0
2.5	2.75	13.7	16.6	0.57	15.6
7.5	5.18	18.9	14.0	0.46	10.5
15.0	2.33	28.5	16.2	0.32	7.5
30.0	2.24	25.2	14.8	0.43	7.6
50.0	2.20	30.3	16.0	0.35	6.5
70.0	2.07	26.5	17.2	0.32	4.2

Table 5, continued.
 Pore Water Nutrient Concentrations
 (all concentrations are in μM).

Station 56

Depth	PO ₄	Si	NH ₄	NO ₂	NO ₃
0	1.95	0.8	0.6	0.04	0.1
2.5	0.97	8.5	9.8	0.87	9.5
7.5	0.72	11.8	9.5	0.51	9.7
15.0	0.28	24.5	6.2	0.38	1.2
30.0	2.45	27.9	11.3	0.38	2.9
50.0	2.17	32.1	8.3	0.33	0.5
70.0	3.30	39.5	30.5	0.34	0.0
90.0	2.46	33.4	47.6	0.45	2.0

Station 67

Depth	PO ₄	Si	NH ₄	NO ₂	NO ₃
0	0.21	0.4	1.0	0.11	0.4
2.5	1.15	15.9	6.7	0.73	16.1
7.5	2.18	22.1	4.2	0.93	20.8
15.0	3.81	27.3	11.7	0.36	13.6
30.0	3.84	31.6	17.1	0.48	11.5
50.0	1.61	31.0	24.4	0.29	9.2
70.0	14.36	29.5	80.8	1.03	6.4
90.0	2.01	48.2	39.7	0.52	4.4

Table 5, continued.
 Pore Water Nutrient Concentrations
 (all concentrations are in μM).

Station 75

Depth	PO ₄	Si	NH ₄	NO ₂	NO ₃
0	1.01	2.6	3.6	0.17	1.5
2.5	3.58	79.2	11.1	0.62	16.9
7.5	3.58	82.5	17.7	0.44	21.8
15.0	5.53	93.6	19.3	0.34	21.0
30.0	2.72	75.7	7.5	0.33	31.9
50.0	3.76	81.6	7.8	0.41	25.0
70.0	5.66	90.5	19.6	0.33	21.0
90.0	3.07	77.8	21.9	0.54	19.5
110.0	3.03	69.5	33.9	0.67	11.5

Station 98

Depth	PO ₄	Si	NH ₄	NO ₂	NO ₃
0					
2.5	1.58	102.7	0.9	0.84	19.0
7.5	2.80	148.4	1.1	0.96	6.9
15.0	10.85	192.9	23.0	0.45	1.1
30.0	16.79	199.6	54.5	0.69	2.1
50.0	12.87	205.3	51.6	0.42	0.7
70.0	9.09	239.6	52.8	0.36	0.5

Table 6.
 Pore Water Metal Concentrations
 (Mn, Fe in μM , other elements in nM).

Station 08

Depth	Mn	Fe	Co	Cd	Zn	Pb	Ni	Cu
2.5	23.6	3.1	16.6	2.9	357	34.9	185	75
7.5	27.4	7.3	23.4	4.2	505	38.2	208	63
12.5	11.3	1.4	9.7	1.5	50	19.8	146	45
17.5	8.0	3.4	7.8	4.3	295	8.9	83	26
22.5	7.7	0.6	6.6	1.8	540	15.5	129	47
27.5	9.7	0.6	12.4	1.3	215	21.7	127	51
32.5	11.2	(13.6)	14.2	3.8		34.3		
37.5	11.1	1.9	15.9	1.4	172	10.6	125	35

Table 6, continued.
 Pore Water Metal Concentrations
 (Mn, Fe in μM , other elements in nM).

Station 15

Depth	Mn	Fe	Co	Cd	Zn	Pb	Ni	Cu
2.5	4.0	4.9	5.8	19.1	2800	15.0	59	129
7.5	3.2	10.8	3.9	1.9	20	18.3	41	25
12.5	3.4	14.2	7.8	6.1	290	3.9	40	13
17.5	2.3	5.6	3.5	28.0	2820	13.0	48	33
22.5	1.9	21.6	11.2	3.2	863	15.0	116	60
27.5	1.7	11.4	2.6	10.3	1840	10.9	42	25
32.5	1.6	9.5	3.4	6.1	597	11.7	44	13
37.5	1.8	16.4	6.8	5.0	1500	20.5	60	33
42.5	2.0	21.9	2.4	8.9	205	2.3	33	71
47.5	1.7	12.2	1.4	4.2	641	5.2	28	8
52.5	2.3	9.8	3.8	6.4	1060	18.4	50	89
57.5	2.2	14.6	4.9	13.7	1322	20.3	58	34
62.5	2.0	14.2	1.4	3.2	120	8.0	24	16
67.5	1.4	8.4	0.5	6.0	640	14.3	29	30

Table 6, continued.
 Pore Water Metal Concentrations
 (Mn, Fe in μM , other elements in nM).

Station 21

Depth	Mn	Fe	Co	Cd	Zn	Pb	Ni	Cu
2.5	0.20	1.8	17.7	47.2	422	18	94	57
7.5	4.40	13.8	6.4	22.2	502	71	127	136
12.5	1.15	3.5	13.6	21.4	646	23	107	52
17.5	0.61	5.1	6.0	35.6	755	63	151	193
22.5	0.74	3.3	2.4	17.2	132	14	59	32
27.5	1.11	4.5	3.9	17.2	5	19	98	59
32.5	0.65	2.4	3.6	30.7	186	26	84	149
37.5	0.81	7.8	3.1	19.9	360	25	87	73
42.5	1.38	8.7	5.8	42.1	265	33	136	55
47.5	0.97	8.1	5.7	22.4	164	18	125	33
52.5	1.04	10.5	7.3	20.7	529	60	121	107
57.5	0.56	5.1	4.2	17.7	351	24	106	48
62.5	1.42		10.0	7.4	210	38	200	
67.5	0.48	3.9	6.9	27.9	443	34	193	113

Table 6, continued.
 Pore Water Metal Concentrations
 (Mn, Fe in μM , other elements in nM).

Station 56

Depth	Mn	Fe	Co	Cd	Zn	Pb	Ni	Cu
2.5	0.25	0.60	1.4	26.3	138		66	54
7.5	0.26	0.48	5.5	9.2	115		133	74
12.5	0.23	0.56	4.6	12.5	48		57	32
17.5	0.35	1.42	7.1	29.9	85		88	32
22.5	0.51	0.90	4.5	18.4	108		55	37
30.0	0.78	(8.60)	(10.1)	15.4	89		91	(150)
40.0	1.03	1.70	4.6	14.9	115		70	49
50.0	2.48	5.00	5.8	26.7	138		102	44
60.0	1.28	1.68	3.8	22.0	131		55	133

Table 6, continued.
 Pore Water Metal Concentrations
 (Mn, Fe in μM , other elements in nM).

Station 67

Depth	Mn	Fe	Co	Cd	Zn	Pb	Ni	Cu
2.5	0.10	0.0	2.1	6.7	145	6.4	37	34.0
7.5	0.11	0.1	3.2	7.8	214	18.6	74	27.6
12.5	0.31	0.4	5.4	6.8	257	24.6	53	35.9
17.5	0.46	3.1	4.6	10.3	442	33.3	60	79.3
22.5	0.72	2.4	2.5	7.6	242	15.9	44	42.0
27.5	1.04	5.5	3.6	8.2	408	34.7	83	83.3
32.5	1.43	7.3	3.3	7.9	345	27.9	80	52.9
37.5	1.31	5.6	3.4	8.5	362	22.5	79	40.6
42.5	0.75	1.9	5.3	9.9	350	27.5	62	54.4
47.5	1.15	11.2	7.1	11.4	175	42.3	54	40.2
55.0	2.06	11.9	6.5	3.3	142	40.7	58	60.3
65.0	1.47	6.3	4.7	3.9	226	32.4	89	40.8
75.0	1.29	6.3	6.8	30.8		36.7	85	71.4
85.0	1.33	10.1		3.3	222		58	86.2

Table 6, continued.
 Pore Water Metal Concentrations
 (Mn, Fe in μM , other elements in nM).

Station 75

Depth	Mn	Fe	Co	Cd	Zn	Pb	Ni	Cu
2.5	0.31	0.2	1.2	16.4	182	3.2	30.5	22.8
7.5	0.50	1.8	2.2	13.6	129	6.0	27.5	19.6
12.5	0.76	1.8	2.0	13.3	100	3.1	30.4	18.0
17.5	1.18	7.9	2.5	23.2	126	12.3	28.2	19.5
22.5	1.63	3.0	2.3	26.1	129	5.9	58.5	11.8
27.5	1.51	6.0	2.8	34.9	223	20.3	40.7	24.7
32.5	1.76	8.0	3.0	14.4	79	6.6	37.3	16.8
37.5	1.08	4.1	2.4	5.6	147	20.0	35.2	27.0
42.5	2.00	4.5	2.7	6.1	117	18.2	34.2	23.2
47.5	1.96	4.5	4.2	7.4	55	18.0	27.2	75.0
52.5	2.00	2.1	3.2	1.6	42	5.6	31.1	15.9
57.5	2.00	3.5	4.6	4.9	131	7.1	22.7	(320)
62.5	1.91	4.2	2.7	5.2	173	9.3	31.0	(168)
67.5	1.69	4.4	2.4	4.6	80	18.1		24.5

Table 6, continued.
Pore Water Metal Concentrations
(Mn, Fe in μM , other elements in nM).

Station 98

Depth	Mn	Fe	Co	Cd	Zn	Pb	Ni	Cu
2.5	0.0	0.0	3.0	14.0	155	18.3	75	26.7
7.5	6.7	0.0	4.7	22.0	295	16.8	135	25.3
12.5	29.2	9.1	9.7	18.4	490	18.1	150	44.5
17.5	41.3	34.4	17.5	8.8	154	17.0	98	28.1
22.5	27.4	86.2	11.8	3.6	66	20.0	118	23.2
30.0	27.2	74.6	13.3	11.2	223	34.6	182	39.7
40.0	23.1	80.1	12.2	6.2	110	6.0	191	57.4
50.0	16.1	43.4	5.0	6.7	56	15.5	94	22.4
60.0	13.1	60.0	7.4	12.6	67	24.3	189	25.6

Table 7. Suspended Particulate Metal Concentrations.

Sample	Ni ($\mu\text{g/g}$)	Ni (nM)	Zn ($\mu\text{g/g}$)	Zn (nM)	Cd ($\mu\text{g/g}$)	Cd (pM)	Cu ($\mu\text{g/g}$)	Cu (nM)
08-30	15	0.33	54	1.07	0.8	9	43	0.88
08-45	7	0.12	135	2.06	2.1	19	49	0.77
15-15	9	0.07	84	0.58	2.8	11	159	1.13
15-36	9	0.08	73	0.56			48	0.38
17-10	6	0.10	85	1.30	1.7	15	48	0.76
21-15	32	0.22	100	0.61	1.5	5	76	0.48
21-24	121	0.82	24	0.15	5.4	19	56	0.35
56-15	12	0.16	84	1.03	2.5	18	66	0.83
56-24			103	1.32	2.0	15	36	0.48
67-15	14	0.10	270	1.65	78	280	167	1.05
67-30	11	0.21	77	1.30	0.4	4	25	0.43
68-30	4	0.14	66	2.12	1.7	32	14	0.46

Table 7, continued. Suspended Particulate Metal Concentrations.

Sample	Ni ($\mu\text{g/g}$)	Ni (nM)	Zn ($\mu\text{g/g}$)	Zn (nM)	Cd ($\mu\text{g/g}$)	Cd (pM)	Cu ($\mu\text{g/g}$)	Cu (nM)
75-00-05	186	0.95					605	2.90
75-06-05	27	0.11	119	0.45	18.4	41	56	0.22
75-12-05			75	0.29	25.4	56	101	0.40
75-17-05			87	0.27	17.0	30	108	0.34
75-22-05			21	0.14			80	0.57
75-00-31	17	0.35	72	1.32	2.4	26	59	1.10
75-06-33	26	0.19	106	0.70	12.5	48	114	0.77
75-12-33	13	0.16	178	1.99	144	935	20	0.23
75-17-33	26	0.22	99	0.76	4.1	18	5	0.04
75-22-32	46	0.39	109	0.83	1.5	7	90	0.71

Table 7, continued. Suspended Particulate Metal Concentrations.

Sample	Ni ($\mu\text{g/g}$)	Ni (nM)	Zn ($\mu\text{g/g}$)	Zn (nM)	Cd ($\mu\text{g/g}$)	Cd (pM)	Cu ($\mu\text{g/g}$)	Cu (nM)
88-25	24	0.20	57	0.44			20	0.16
88-30			50	0.76	3.8	33	34	0.54
91-15			88	1.08	0.3	2	16	0.20
93-15	30	0.20	163	1.00	1.6	6	19	0.12
93-34	5	0.06	64	0.73			12	0.14
95-20	21	0.18	44	0.34	10.2	45	274	2.16
95-46	15	0.11	77	0.53			23	0.17
98-18	11	0.06	39	0.18			18	0.09
98-32			152	0.93	3.4	12	87	0.55
98-50			96	0.44			91	0.43

Table 7, continued. Suspended Particulate Metal Concentrations.

Sample	Mn ($\mu\text{g/g}$)	Mn (nM)	Fe ($\mu\text{g/g}$)	Fe (nM)	Pb ($\mu\text{g/g}$)	Pb (pM)	Co ($\mu\text{g/g}$)	Co (nM)
08-30	725	17.1	10300	239	38	183	8	154
08-45	1268	23.1	23495	420	102	492	13	224
15-15	737	6.0	8887	71	268	582		
15-36	848	7.7	12037	107	106	256	14	121
17-10	368	6.7	15256	272	30	145	14	239
21-15	62	0.5	1987	14	102	197	15	101
21-24	82	0.6	5198	37	50	96	40	269
56-15	347	5.0	15470	221	50	193		
56-24	408	6.2	17623	264	158	641		
67-15	56	0.4	4685	34	88	170		
67-30	362	7.2	13660	268	59	314		
68-30	414	15.8	21082	791	56	565	6	214

Table 7, continued. Suspended Particulate Metal Concentrations.

Sample	Mn ($\mu\text{g/g}$)	Mn (nM)	Fe ($\mu\text{g/g}$)	Fe (nM)	Pb ($\mu\text{g/g}$)	Pb (pM)	Co ($\mu\text{g/g}$)	Co (pM)
75-00-05	436	2.4	1618	8.7	55	80		
75-06-05	15	0.07	332	1.5	193	223		
75-12-05	21	0.10	129	0.6	6	7	15	65
75-17-05	20	0.07	447	1.6	27	26		
75-22-05	33	0.27			5	10		
75-00-31	11	0.24	299	6.4	11	63		
75-06-33	363	2.8	1408	10.8	24	50		
75-12-33	51	0.68	944	12.3	24	86	11	134
75-17-33	382	3.47	4068	36.3	38	91		
75-22-32	197	1.79	5177	46.2	174	420		

Table 7, continued. Suspended Particulate Metal Concentrations.

Sample	Mn ($\mu\text{g/g}$)	Mn (nM)	Fe ($\mu\text{g/g}$)	Fe (nM)	Pb ($\mu\text{g/g}$)	Pb (pM)	Co ($\mu\text{g/g}$)	Co (pM)
88-25	516	4.7	15094	135	49	118		
88-30	329	6.0	11138	199	31	150		
91-15	296	4.3	11113	159	43	167	6	84
93-15	32	0.23			43	84		
93-34	203	2.77	8908	119	29	105	14	185
95-20	28	0.25	1447	12.9	385	930		
95-46	270	2.21	7523	61	481	1040		
98-18	19	0.1	323	1.7	25	35	22	112
98-32	275	2.0	1987	14.2	78	151	13	91
98-50	499	2.70	6392	34.2	181	262		

Table 8. Dissolved Trace Element Concentrations.

Sample	Cu (nM)	Pb (pM)	Zn (nM)	Cd (nM)	Ni (nM)	Mn (nM)
08-0	2.18	263	3.1	0.36		19.1
08-30	2.65	480	5.0	0.19		10.5
08-45	2.5	204	6.1	0.24		17.3
15-0	2.24	299	5.4	0.29		16.0
15-0a	1.9	204	2.9	0.26		16.3
15-15	2.11	261	4.1	0.26		8.6
15-36	2.15	87	1.2	0.22	1.31	8.1
17-10		115	1.78	0.15		10.6
21-0	1.75	403	2.75	0.24	2.08	14.2
21-15	1.66		3.1	0.15		9.7
21-24		245		0.29		8.9
56-15	1.59	71	1.32	0.19	0.7	10.2
56-24						7.4
67-0	0.76	114	2.15	0.34		
67-15		10	1.21	0.14	6.1	
67-30	2.52	127	2.73		0.77	12.0
68-30	1.92	151	3.98	0.22	1.45	7.7
75-00-05	2.77		7.6	0.37	1.69	9.7
75-06-05	3.39	687	1.35	0.4	1.0	2.8
75-12-05		197	2.36	0.24		4.25
75-17-05		115	1.96	0.15		3.78
75-22-05			3.27	0.22		4.7
75-00-31	1.49				2.17	7.8
75-06-33	1.89	156	4.78	0.34	0.7	4.2
75-12-33	2.15	228	3.43	0.28	0.91	5.7
75-22-32		163	2.9	0.22		4.75
88-25		586		0.25		10.3
88-30		264	2.78	0.16		9.5
91-15	1.54	116	3.0	0.21		10.3
93-15	2.04		9.5	0.16		6.6
93-34	2.05	271		0.32	1.53	12.5
95-46	4.21	342	3.11	0.39	1.47	13.1
98-0	2.05	271		0.32	1.31	3.7
98-18	1.47	244	2.0	0.16		3.5
98-32	1.84	233	3.2	0.21		3.9
98-50	1.65		11.3	0.27		5.8
98-84	2.34	428	4.84	0.27	1.44	4.0

Table 9. Dissolved Nutrient Concentrations, Salinity and Temperature.

Sample	P (μM)	Si (μM)	NO_3 (μM)	NO_2 (μM)	Sal. (psu)	Temp. ($^\circ\text{C}$)
08-27	0.67	2.08	0.41	0.05	34.65	12.00
08-43	0.44	6.09	0.59	0.08	34.66	8.88
21-0	0.01	0.58	0.07	0.00		
21-15	0.13	0.62	0.63	0.04	34.80	14.34
21-24	0.03	1.41	0.83	0.03	34.80	14.25
56-10	0.20	1.97	0.07	0.03	34.82	13.85
56-20	0.27	0.00	0.11	0.05	34.81	13.85
56-24	0.68	0.60	0.10	0.02	34.82	13.85
68-30	0.4	2.0	0.13	0.03	34.87	13.1
75-00-05	0.11	0.34	0.07	0.00	34.87	14.63
75-06-05	0.17	0.23	0.00	0.01	34.88	14.61
75-12-05	0.51	0.58	0.22	0.04	34.88	14.62
75-17-05	0.41	0.05	0.01	0.02	34.87	17.73
75-00-31	0.25	0.58	0.03	0.01	34.95	7.33
75-06-33	0.39	1.84	0.04	0.05	34.91	7.60
75-12-33	0.49	1.47	0.09	0.05	34.94	7.56
88-25	0.22	1.58	0.00	0.03	34.80	15.16
88-30	0.24	2.01	0.08	0.03	34.80	15.14
91-11	0.17	1.02	0.05	0.02	34.82	14.00
93-10	0.08	0.72	0.00	0.00	34.83	13.96
93-34	0.19	0.39	0.04	0.02	34.82	10.72
95-40	0.48	3.06	0.96	0.13	34.00	7.84
95-52	0.52	3.02	1.02	0.13	34.84	7.84
98-18	0.16	0.31	0.00	0.02	34.99	13.63
98-32	0.35	1.34	1.59	0.15	35.00	10.50
98-50	0.76	3.46	6.20	0.53	35.05	6.85
98-80	0.45	1.72	3.03	0.26	35.05	6.84

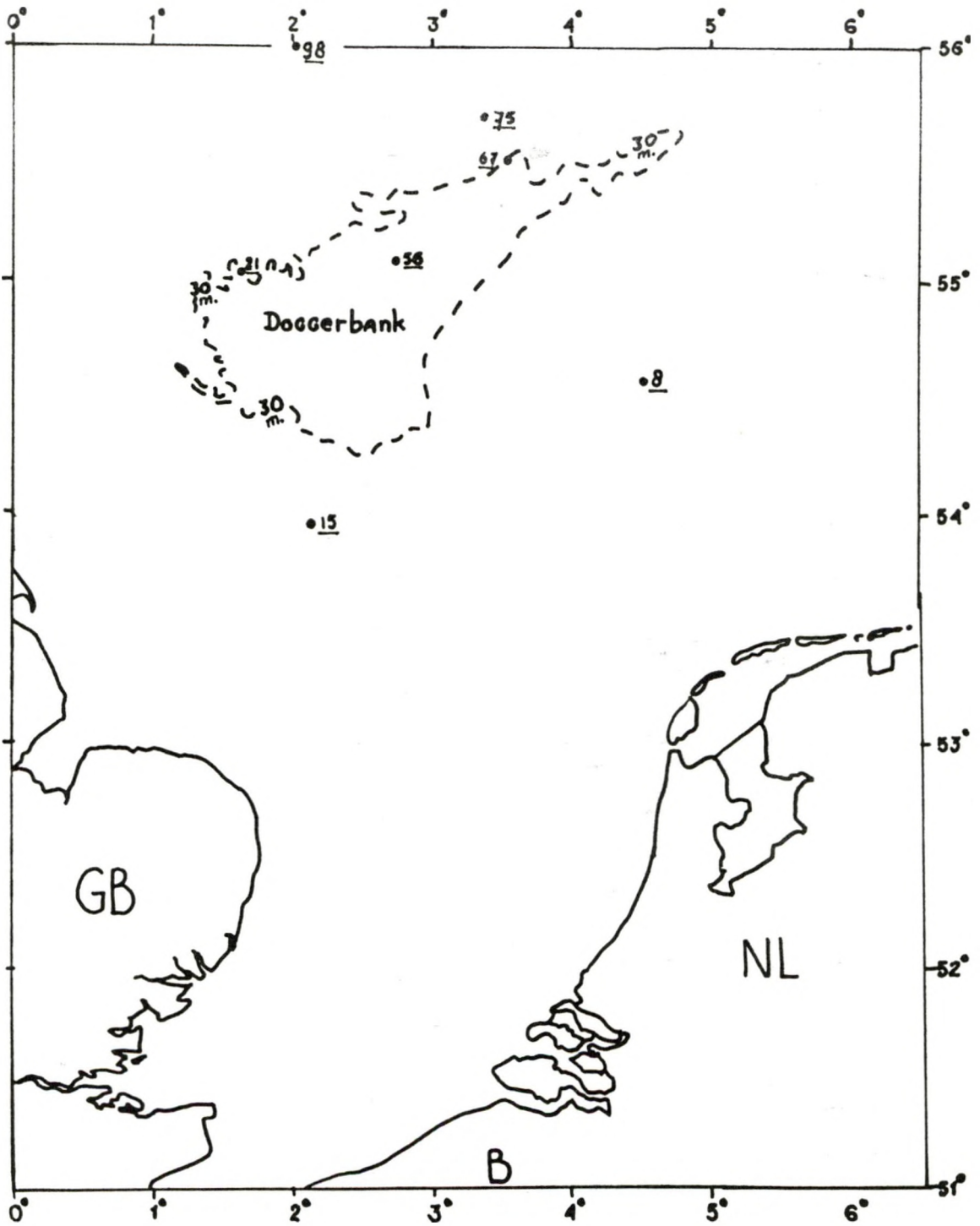


Figure 1. Cruise chart showing sampling stations at the Doggerbank and vicinity.

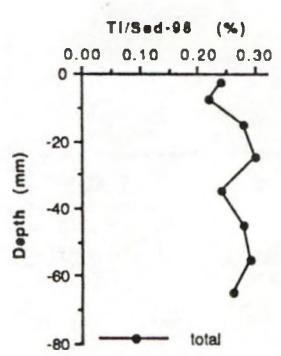
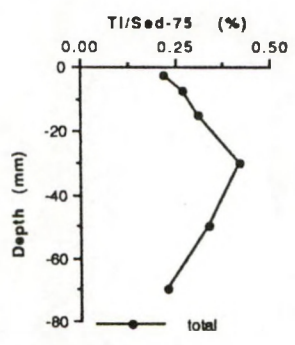
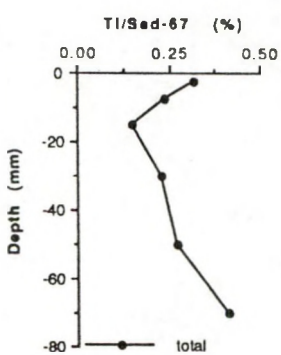
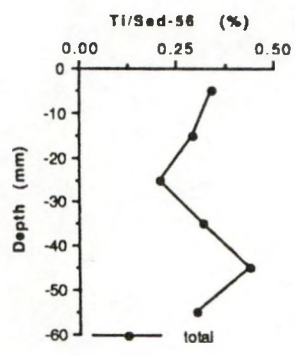
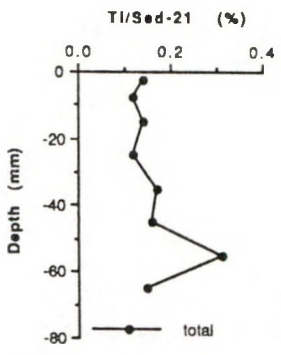
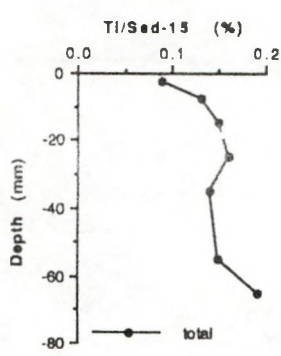
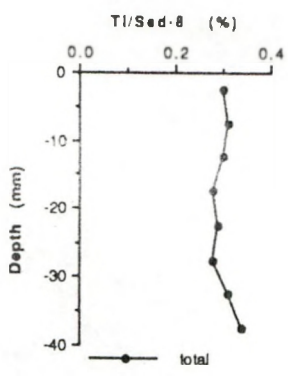


Figure 2a. Sediment Ti-content.

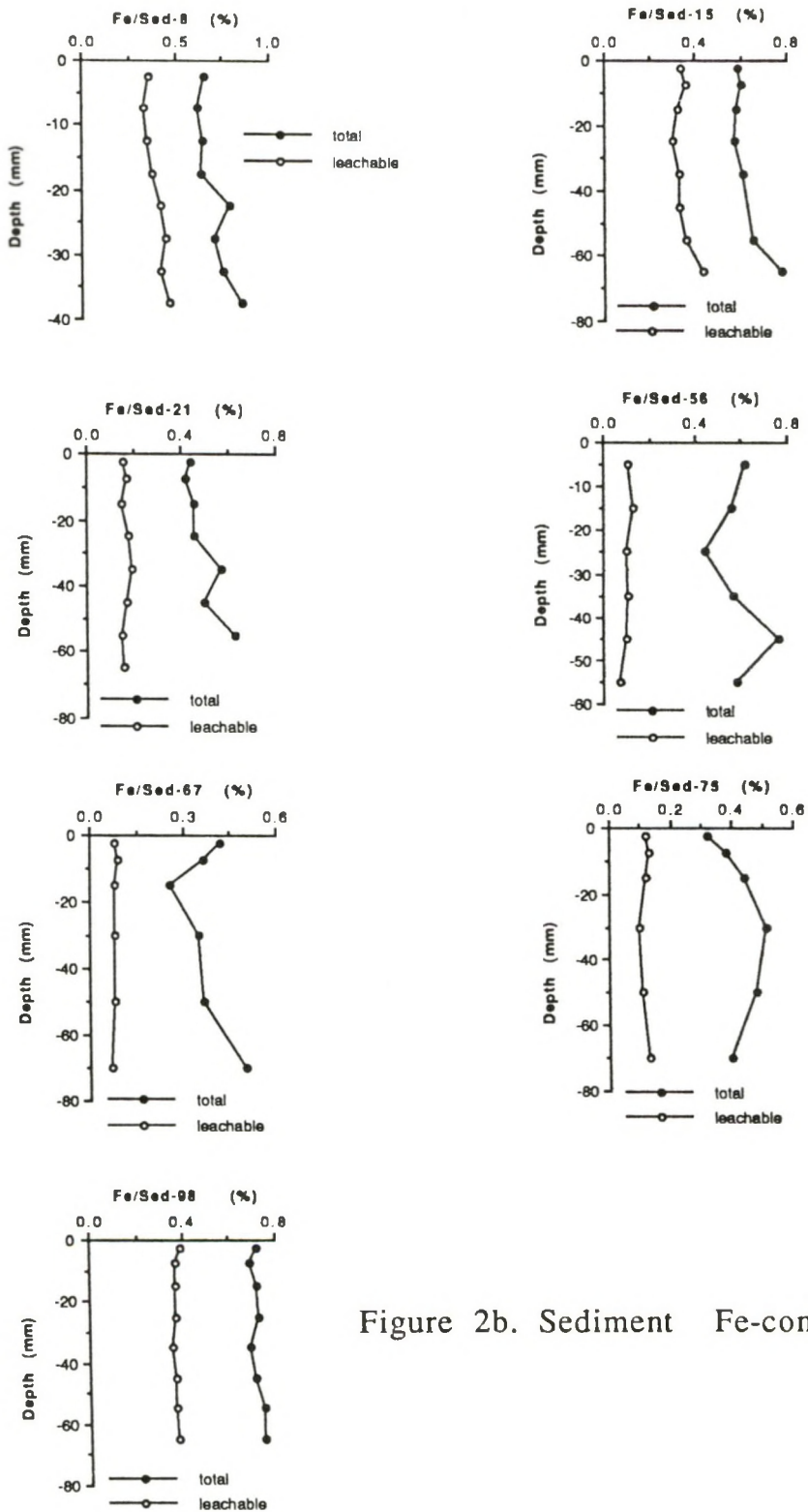


Figure 2b. Sediment Fe-content.

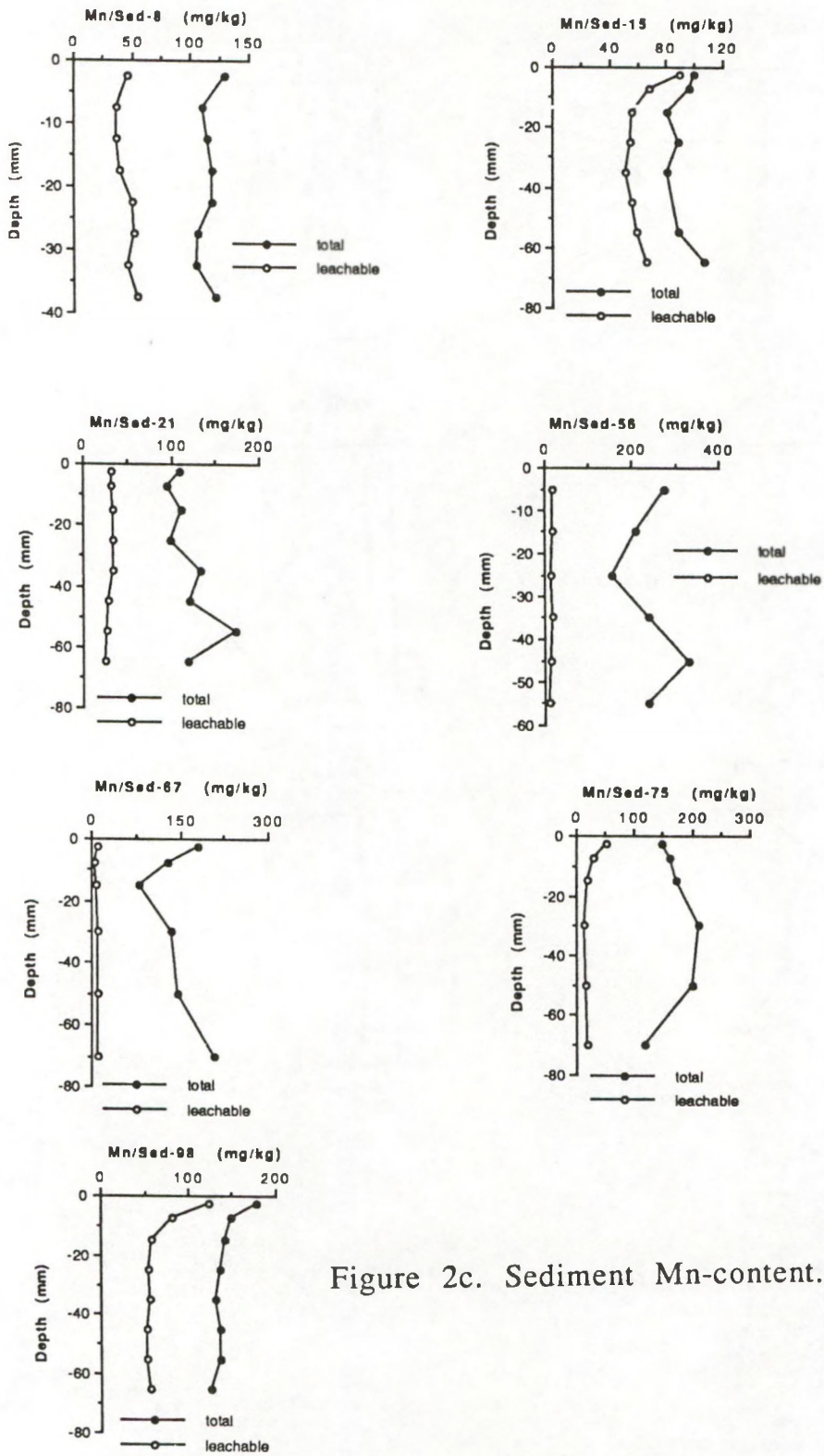


Figure 2c. Sediment Mn-content.

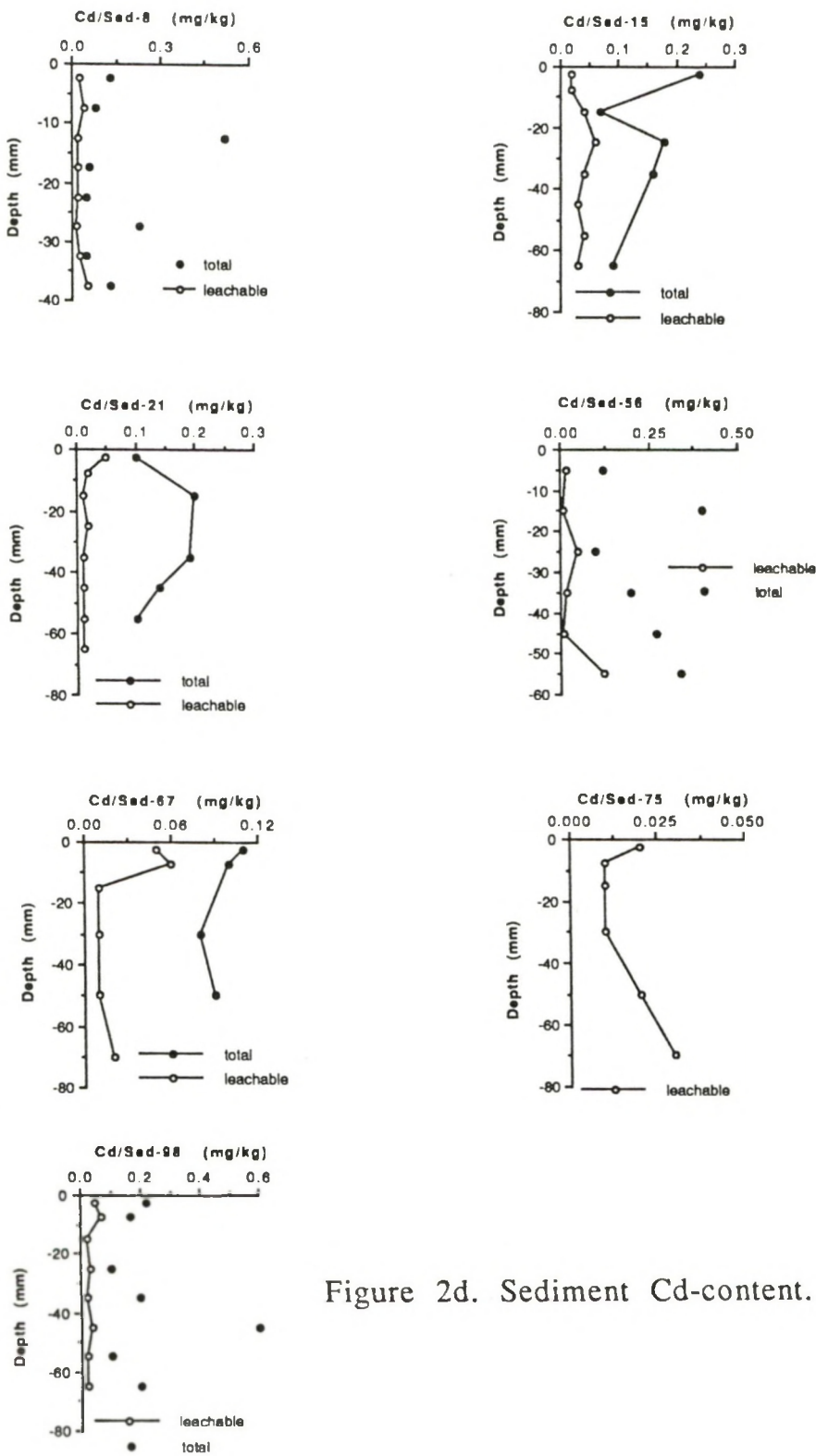


Figure 2d. Sediment Cd-content.

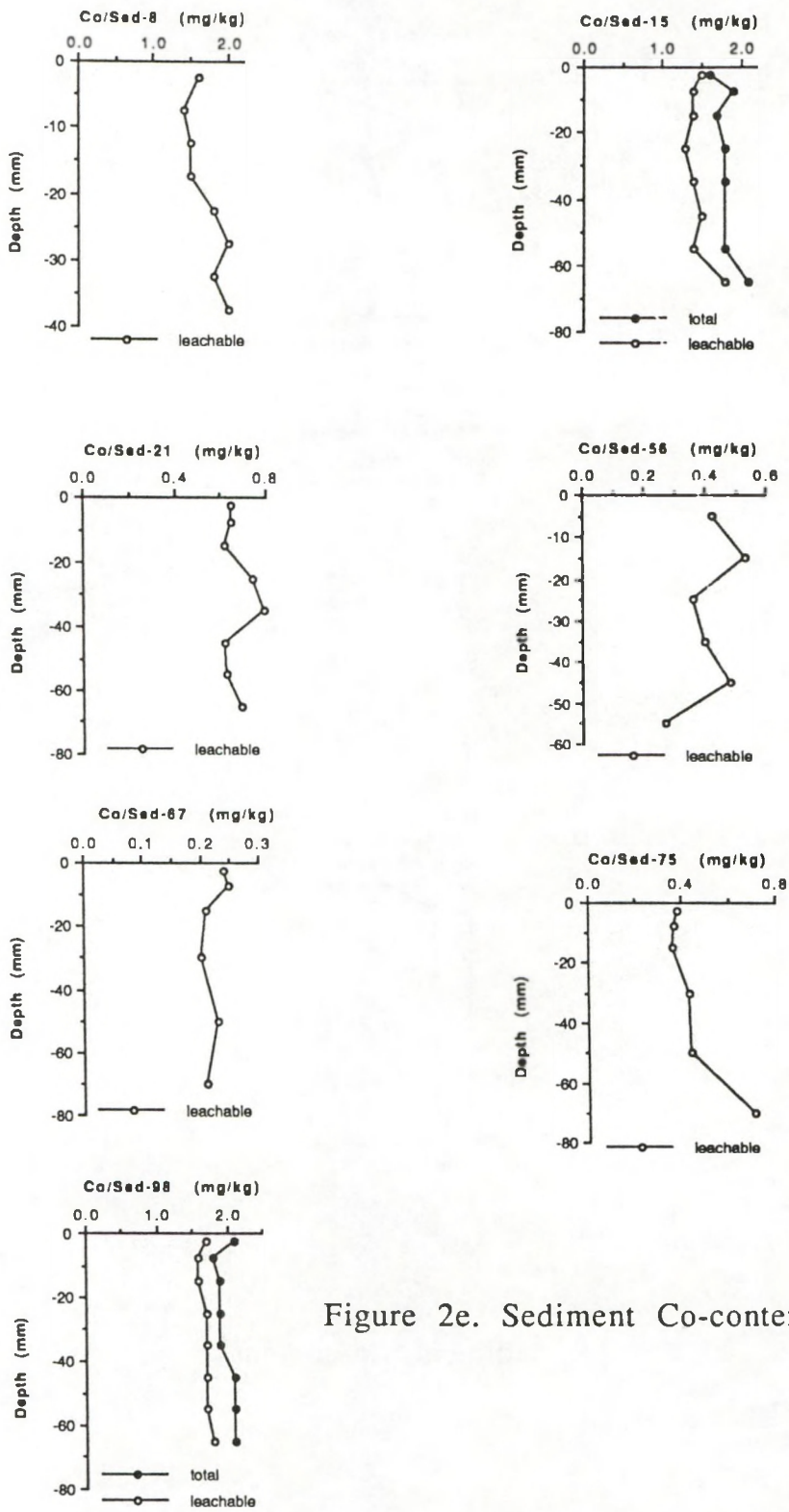


Figure 2e. Sediment Co-content.

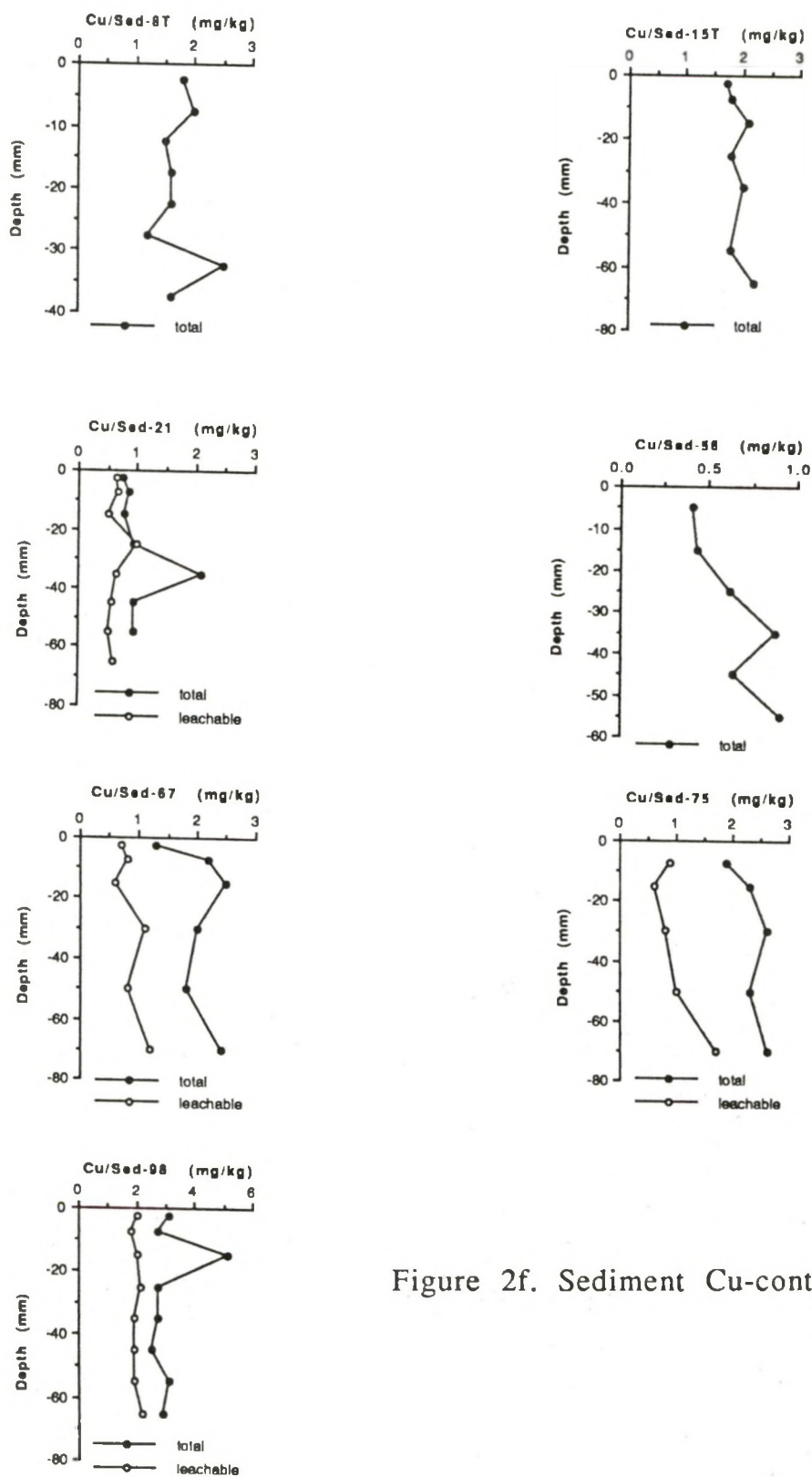


Figure 2f. Sediment Cu-content.

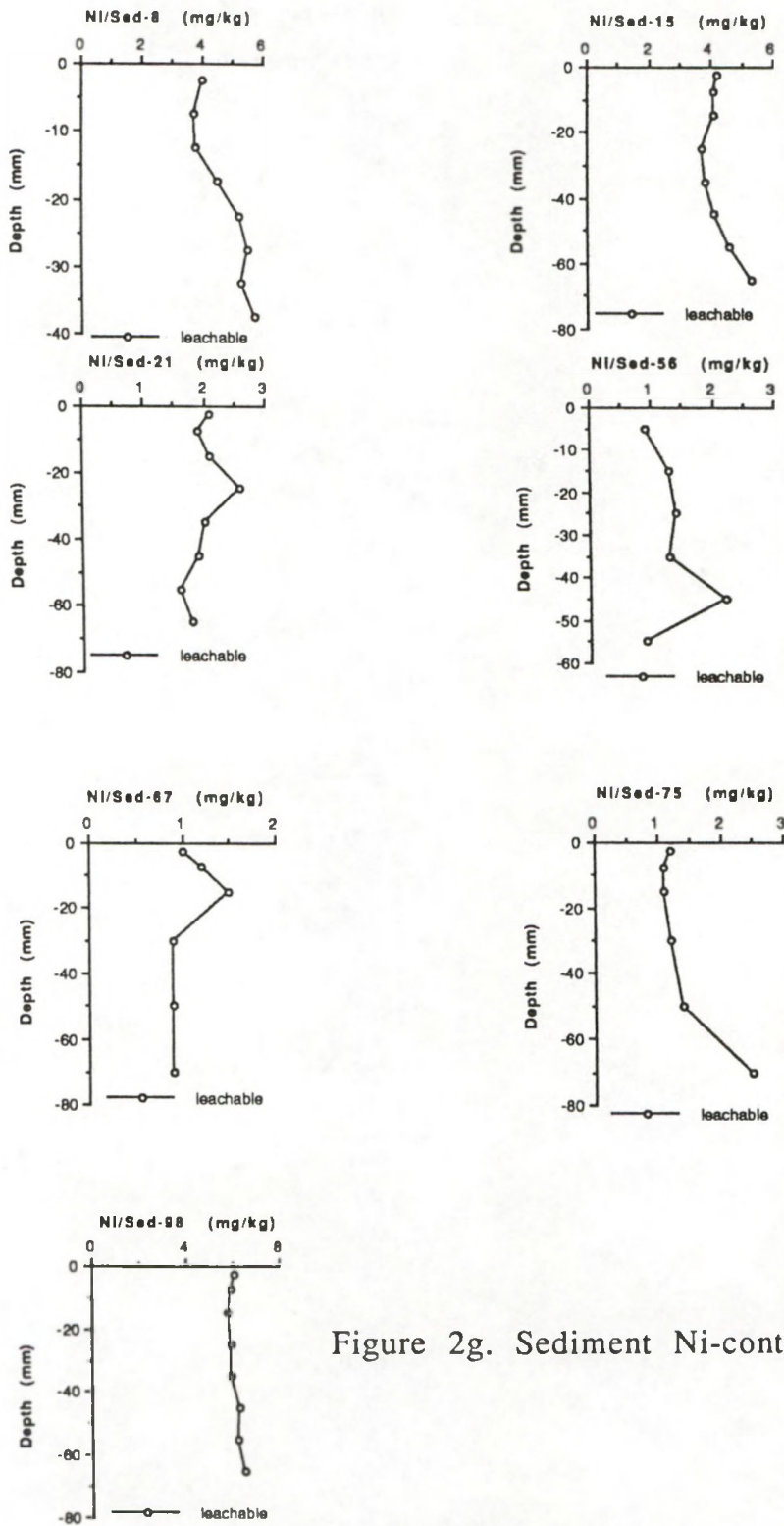


Figure 2g. Sediment Ni-content.

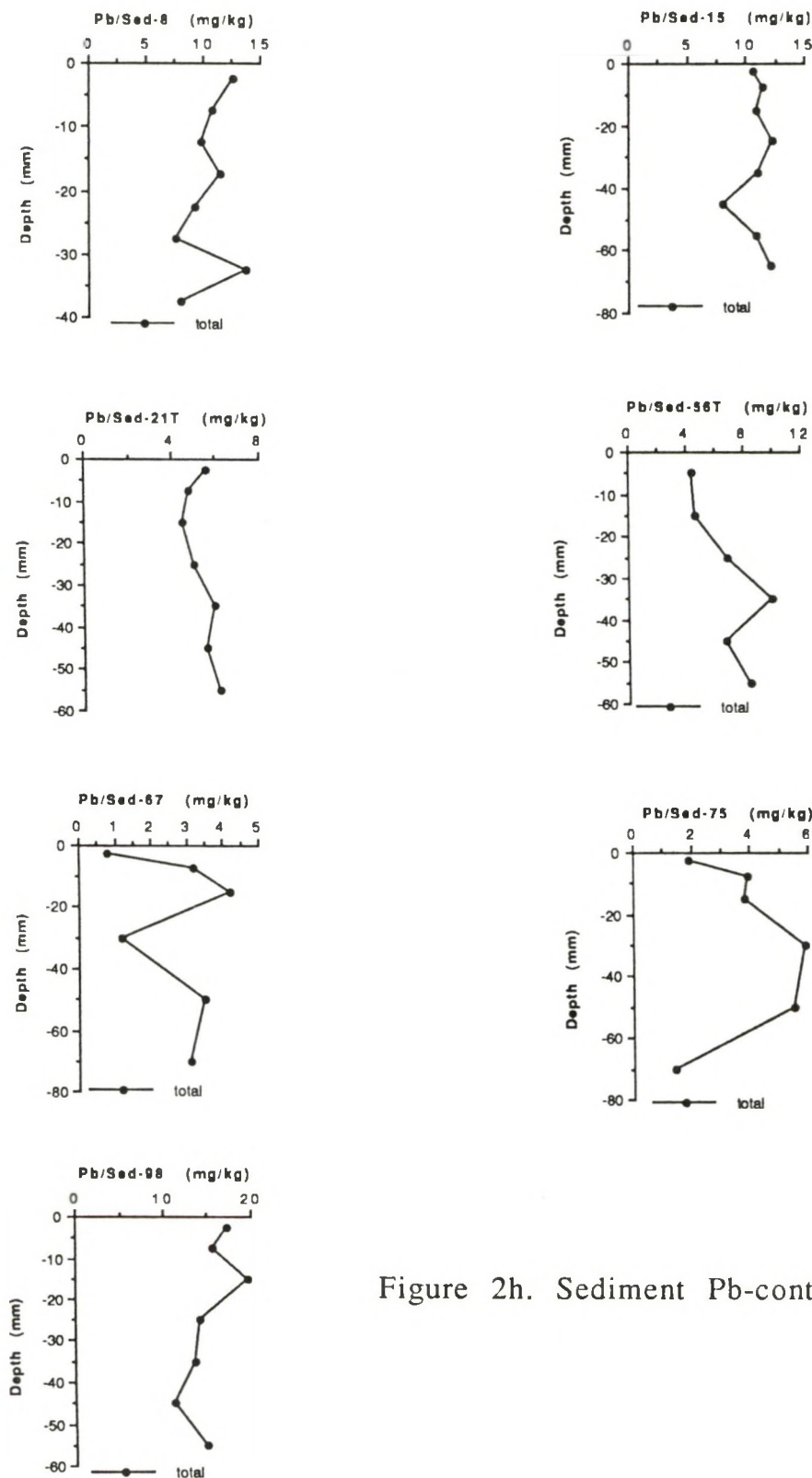


Figure 2h. Sediment Pb-content.

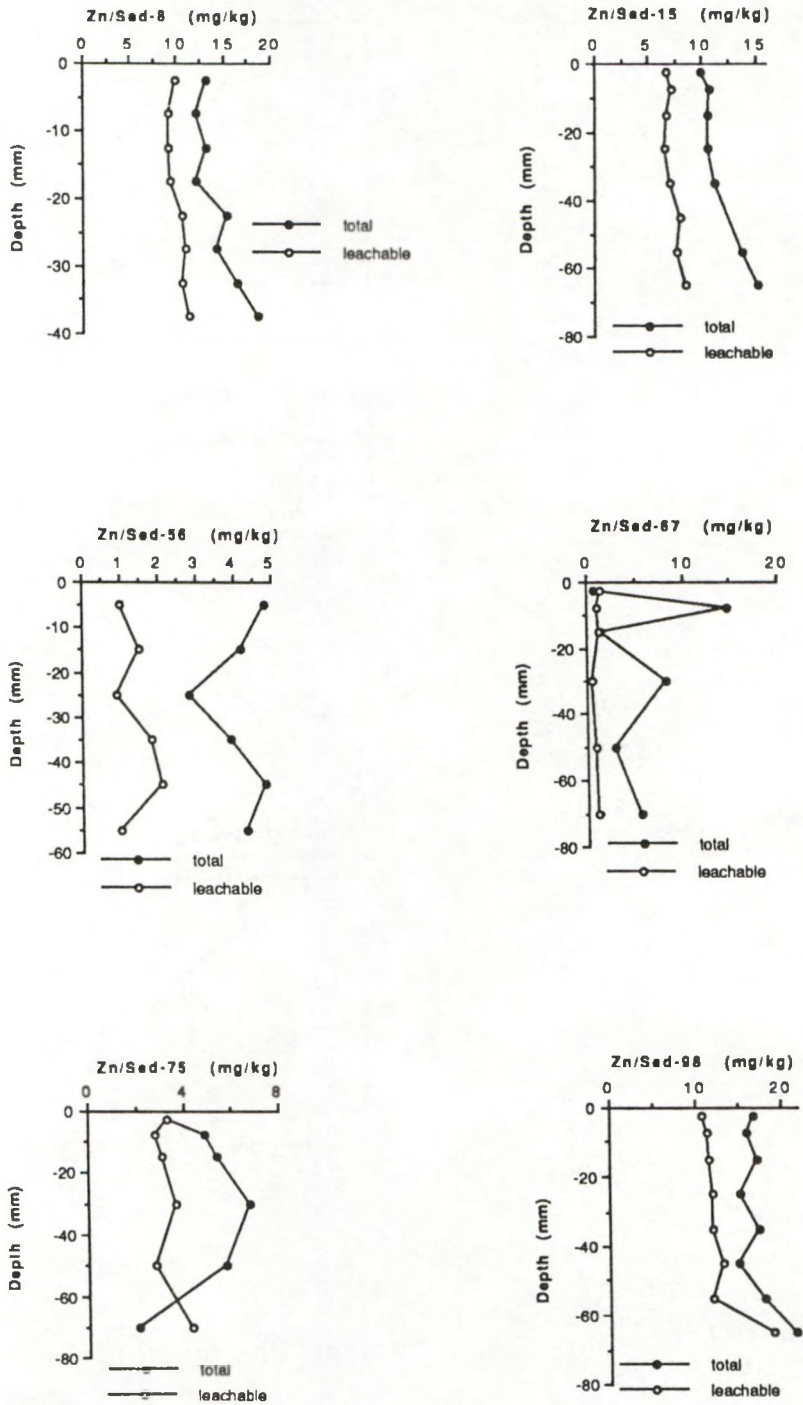


Figure 2i. Sediment Zn-content.

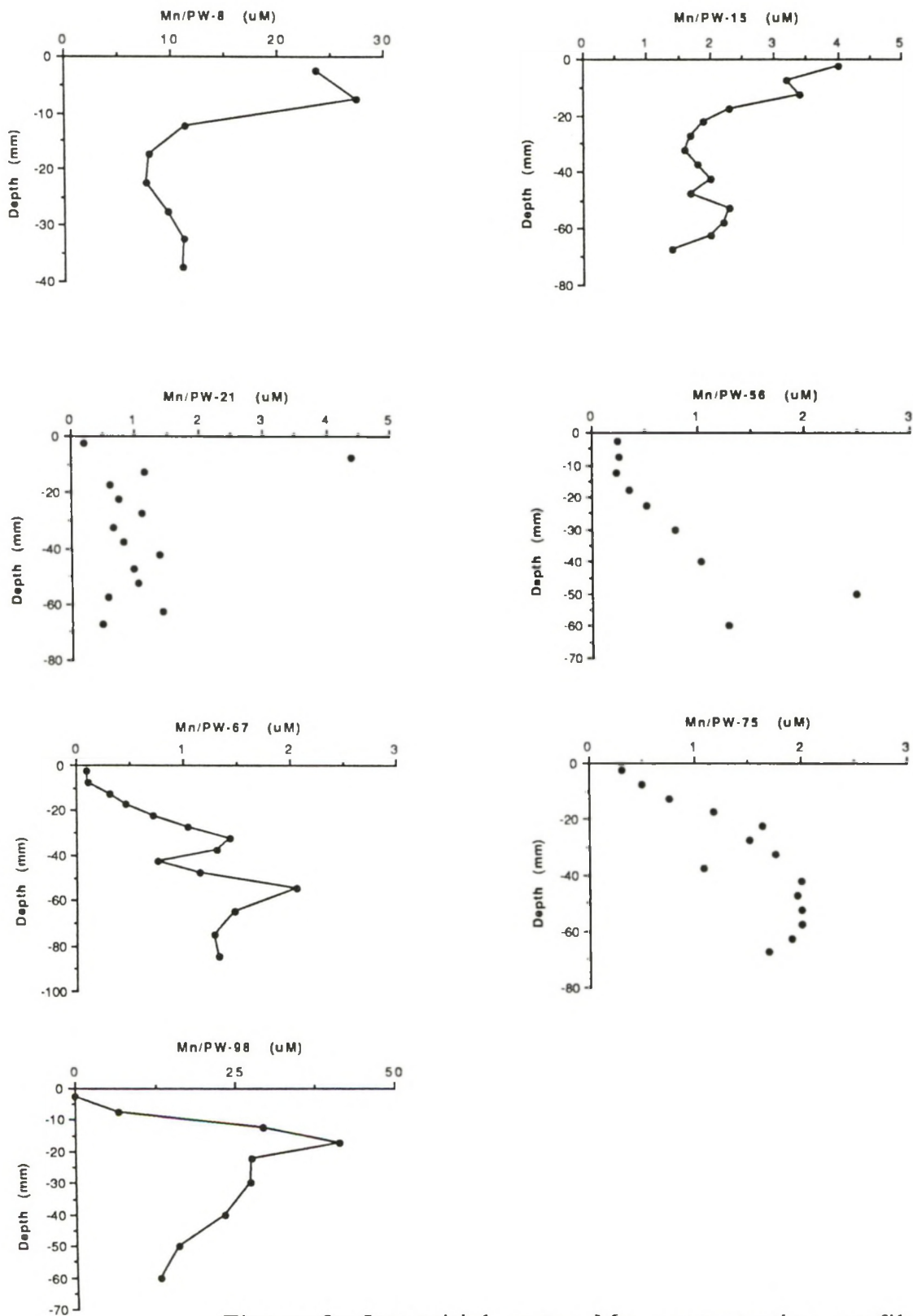


Figure 3. Interstitial water Mn concentration profiles.

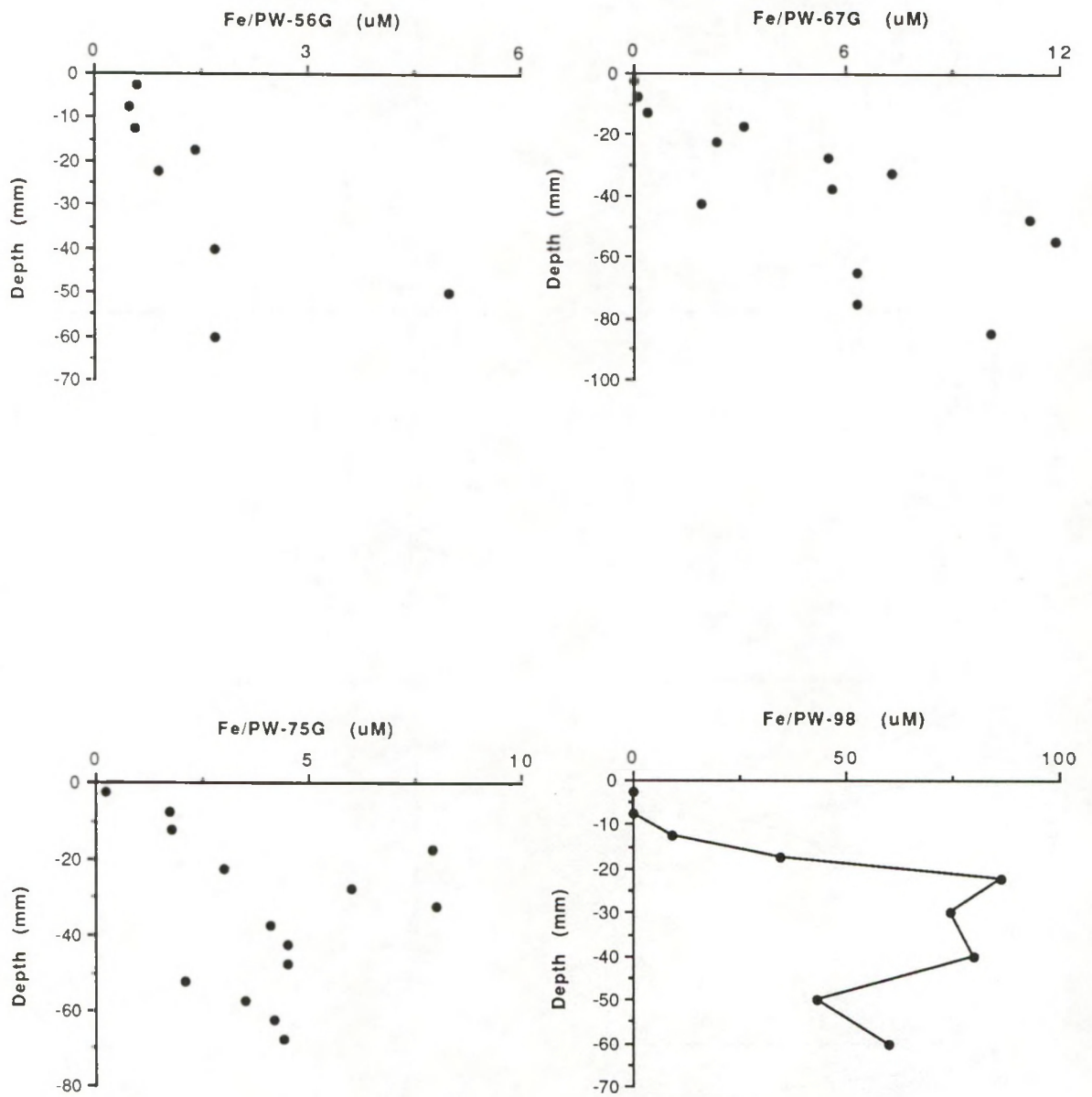


Figure 4. Interstitial water Fe concentration profiles.

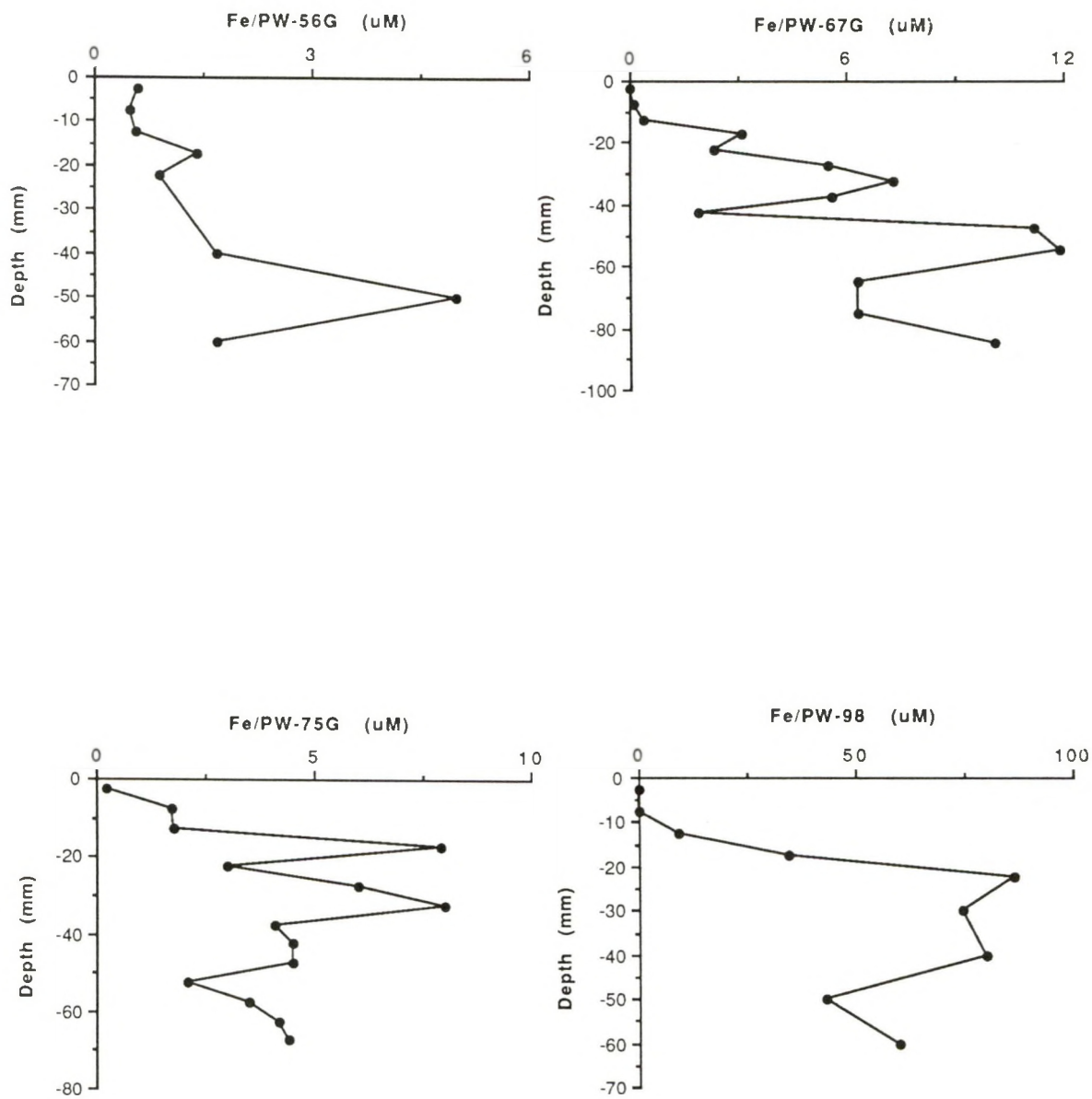


Figure 4. Interstitial water Fe concentration profiles.

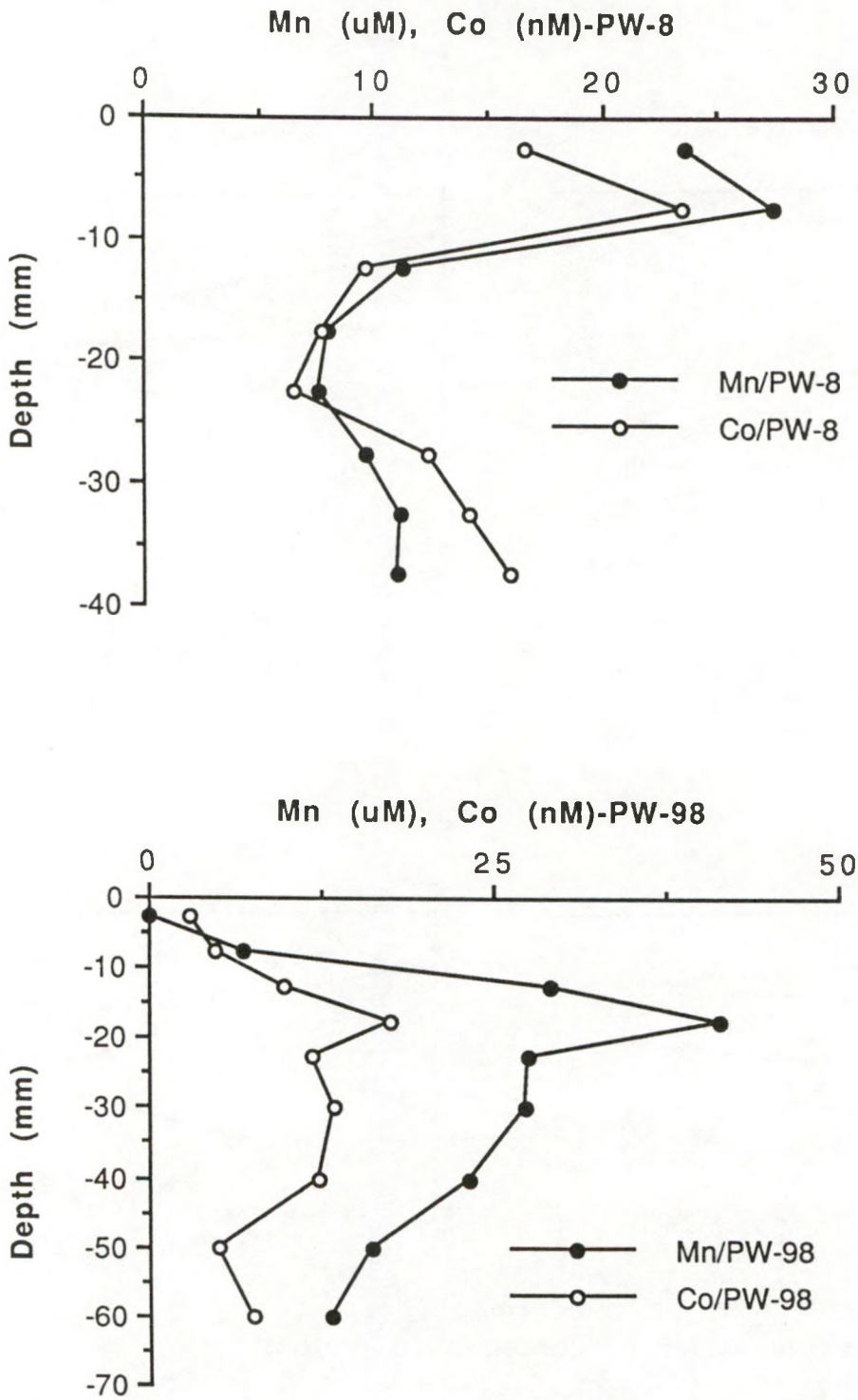


Figure 5. Interstitial water Mn, Fe and Co concentration profiles.

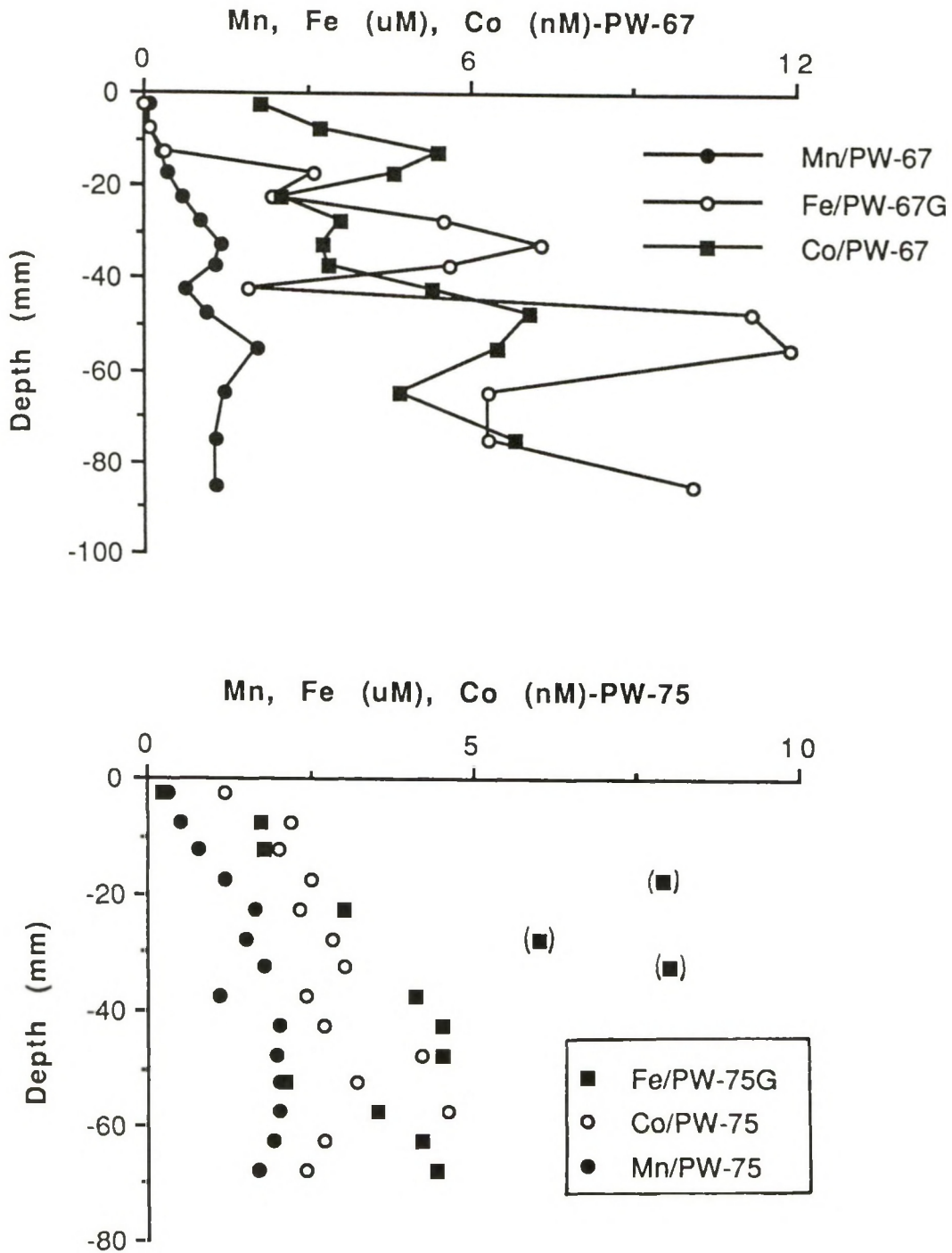


Figure 5. Interstitial water Mn, Fe and Co concentration profiles.

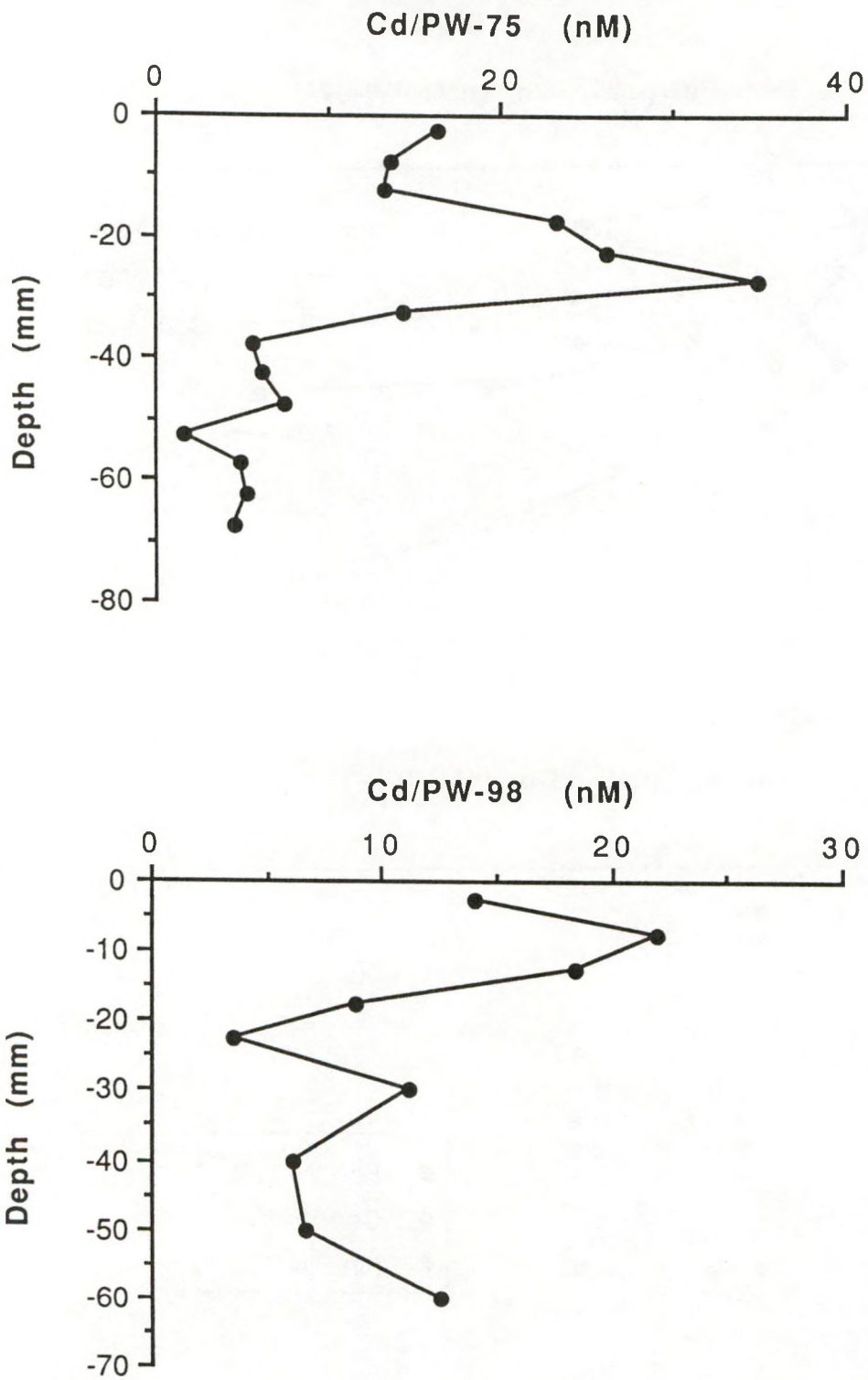


Figure 6. Interstitial water Cd concentration profiles.

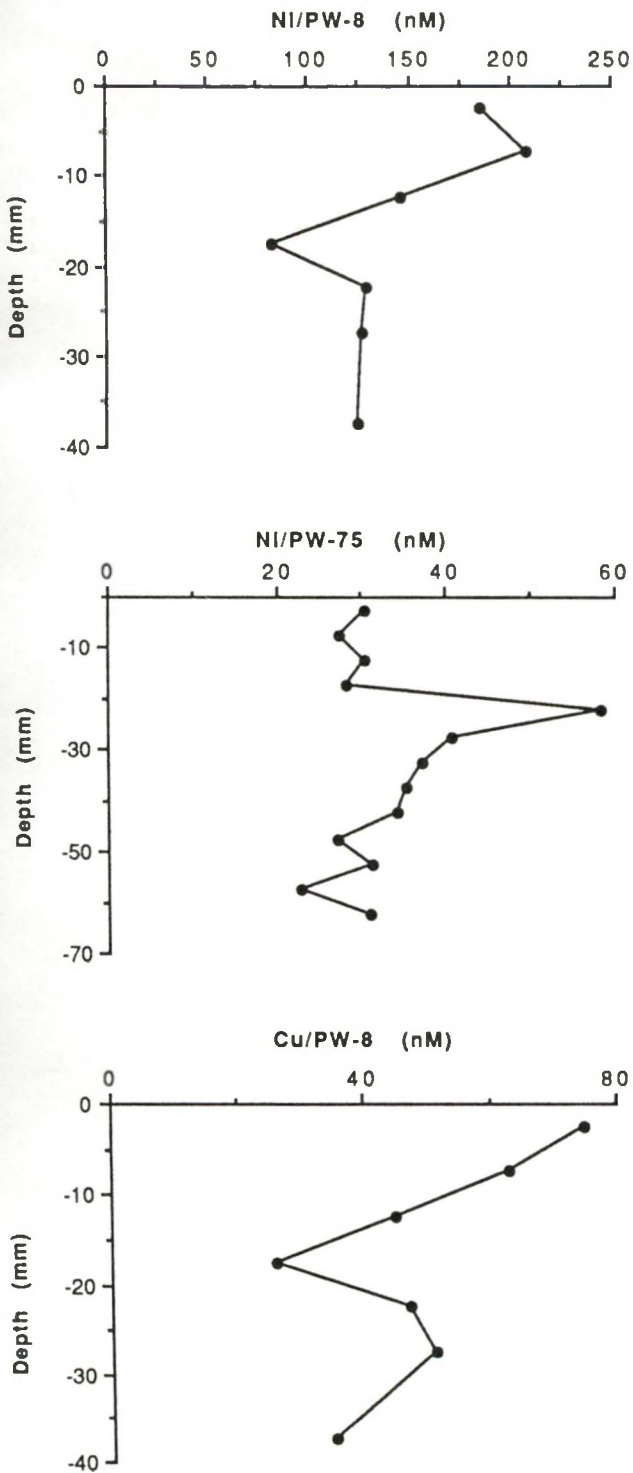


Figure 7. Upper two items: Interstitial water Ni concentration profiles.

Bottom: Interstitial water Cu concentration profiles.

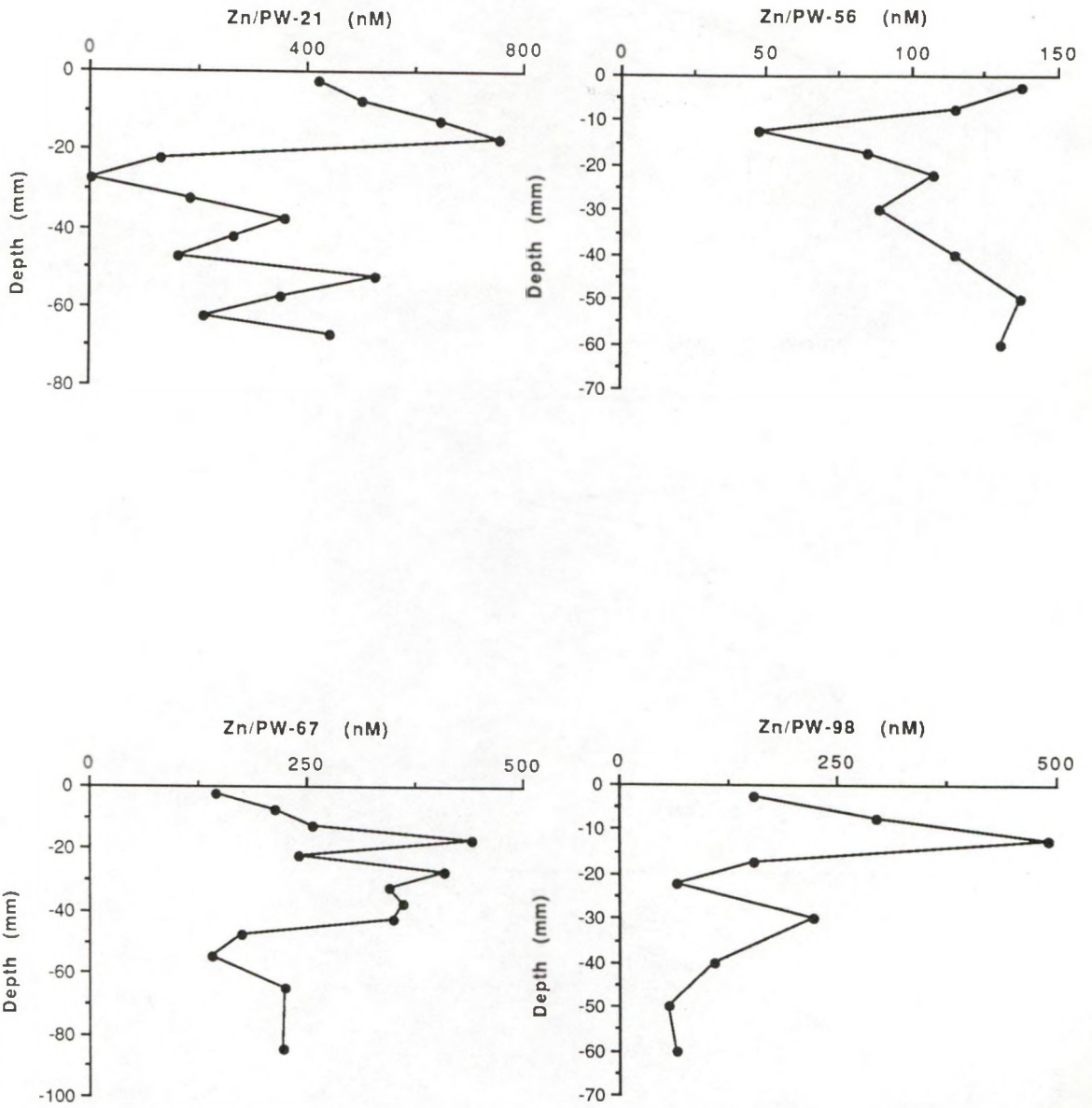


Figure 8. Interstitial water Zn concentration profiles.

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