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*Studierapport no. 8*

SEQUENTIAL EXTRACTION OF  
HEAVY METALS FROM  
A SALT MARSH SOIL PROFILE  
(Western Scheldt)

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Sequential analyses of heavy metals in a salt marsh soil (Western Scheldt).

### Preface

In the years 1984 and 1985 the intertidal soils of the Western Scheldt estuarium have been investigated.

It was evident that these soils have been contaminated by heavy metals. It was also clear that the amounts of heavy metals were more or less proportional to the clay content in the sediments, but that within the soil profile chemical reactions took place.

The present study of the sequential analyses of heavy metals was set up in order to investigate the various binding components in these soils and to obtain indications about the mobility and the availability. This availability for plants and animals passes various thresholds that vary from species to species and depend on the different elements. This subject will be the study of the Soil Department in the coming years.

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### ABSTRACT

In spring, 1986, samples were taken from a salt marsh soil (Verdronken land van Saeflinge) and from estuary suspended matter (Western-Scheldt water). The samples were treated with an eight-step extraction scheme after CALMAND & FOERSTNER (1983) and TESSIER et al. (1979). The samples were analysed for trace metals Fe, Mn, Zn, Ni, Pb, Cd, Co, Cu and Cr.

The purposes of this study were to establish the speciation of particulate matter bound trace metals, to study the influence of changing physicochemical conditions on the speciation upon deposition of suspended matter, to study the influence of soil development on metal speciation and to study possible artifacts as a result of sample treatment and resulting from different ways of sampling.

Fe-Mn-oxyhydroxides were found to be the most important sinks for trace metals. Carbonates and organic matter/sulphides are important sinks too. A negative correlation between total metal content and the metal content of the residual fraction has been observed.

It was found that deposition most likely alters the speciation of Mn, Ni, Cu, Zn and Pb. Fe and Cr were hardly affected.

Soil development influenced the speciation of Mn, Fe, Zn, Pb and Ni. Cr was hardly affected.

It was found out that oxidation of reduced samples dramatically changes the metal distribution. Storage of the samples caused changing physicochemical conditions which influenced the speciation. The speciation for samples obtained with a continuous-flow centrifuge and by filtration are different, probably as a result of oxidation.

## 1. Introduction

In the last two years a thorough investigation of the Western-Scheldt estuary has been performed. In 1984 (REIJNDERS et al., 1985) vegetation, (soil)fauna and soils have been studied. The soils were analysed for texture, pedogenesis together with the main physicochemical properties like Eh, pH, Cl<sup>-</sup>-concentration, CaCO<sub>3</sub>-content, S-, N-, P-budget. Maps were constructed with some important soil-characteristics, like texture. Besides many surface samples were analysed for trace metals viz. Pb, Cd, Cr, Co, Cu, Ni, Zn, Fe, Mn. Fe and Mn are usually not referred to as trace metals but will continued to be mentioned so for sake of simplicity. After this it was concluded that various parts are heavily contaminated with trace metals. This study became a starting-point for a follow-up-case. Points of interest were:

- Soil profiles, their genesis and morphology.
- How is the vertical distribution of trace metals? This means what is the influence of soilgenesis and -development on trace metal distribution?
- Are there significant relationships between total clay percentage and trace metals; between lime content and trace metals; total organic matter content and trace metals; trace metal content per percent clay (concentration index)?
- Mutual relationship between trace metals.

These relationships have been studied in the year 1985 (GIESBERTS et al., 1986). In the former studies trace metals have been analysed by

- a soil extraction at pH=1, after Sørensen (19..)
- total destruction by HF/HNO<sub>3</sub>/HClO<sub>4</sub>.

The latest point of interest was: how is the general model for the Western-Scheldt?

- How are these metals chemically bound in estuary suspended matter?
- What is the influence of (anaerobic) sedimentation on trace metal speciation?
- What is the influence of soil development on trace metal speciation?

Other points of interest were:

- How does oxidation of a formerly reduced sediment affect metal speciation, or what are the effects of careless samplereatment with regard to oxygen, biologic activity?
- Is there a difference between the upper water layer and the lower near-bottom water layer?

All these questions shall be dealt with in this study.



### 1.1 SAMPLING

In March 1986, after a relatively cold winter a soil-profile on the salt marsh the "Konijnenschor", on the "Verdronken land van Saeftinge", was sampled (figure 1.1). It concerned a "gorsvaaggrond" (Hydraquent, Soil Taxonomy) with the following horizons:



- 1 0-20 cm. G<sub>0</sub>-horizon, brownish heavy clay containing many roots and plantparts.
- 2 20-40 cm. G<sub>suI</sub>-horizon, dark grayish heavy clay with sulphides.
- 3 40-50 cm. G<sub>suII</sub>-horizon, greyish-black heavy clay with even more sulphides.
- 4 50-60 cm. G<sub>r</sub>-horizon, hardly altered sandy soil containing only few sulphides.

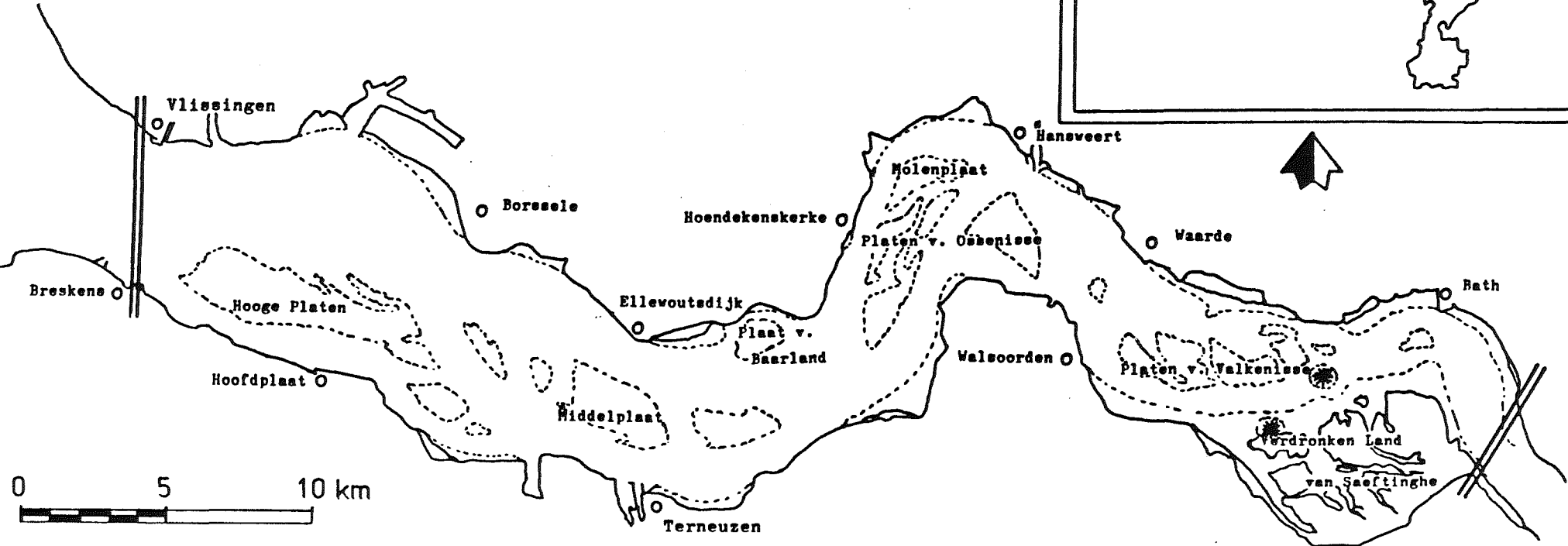
In order to have cross-checks samples 1 and 2 were taken in four-fold, samples 3 and 4 were taken in duplo. Further a peatlump was sampled, belonging to the "Hollandveen" peat formation, present at the surface in the contaminated watersystem.

All samples were stored in polyethylene jars, completely filled to avoid air-inclusion, subsequently sealed with screw caps and put in a cool-box until sample preparation in the laboratory. These samples will be called S (Saeftinge)1a, S1b, S1c, S1d, S2a, S2b, S2c, S2d, S3a, S3b, S4a, S4b and SV. In the laboratory one part was quickly prepared and treated (see section 1.4) in a sealed nitrogen glove-box to prevent oxygen contamination. Another part was allowed to oxidize, so as to study differences in metal speciation due to O<sub>2</sub>-influence. These samples have a subscript o, S<sub>o</sub>1a etc.

At the end of spring (May) samples were taken from estuary water. First water was filtered over a cellulose-nitrate 0.45 µm pore filter (Schleicher & Schuell), with nitrogen pressure. The filtrate was kept in polyethylene tubes together with distilled, oxygen-free water. Besides water was centrifuged at 500 l min<sup>-1</sup> with a continuous flow centrifuge. The centrifuge residue was split into two parts, a lower part being more coarsely grained than the upper part. Six filter samples were taken, a triplo from 13 meters depth, another from 1 meter depth. For the centrifuge sample triplos were taken from each part of the tube and from both depths. The samples were stored in small polyethylene jars with screw cap under distilled water. All samples were stored in a refrigerator until further treatment. These samples will be called W (Western Scheldt) R (reduced)1a, WR1b, WR1c, WR2a, WR2b, WR2c. One stands for 13 meters depth, 2 for 1 meter depth, respectively, WC (centrifuge)1o, WC2o, WC3o, WC4o, WC5o, WC6o, WC1b, WC2b, WC3b, WC4b, WC5b and WC6b. Here subscript o stands for lower part of the centrifuge, subscript b denotes upper part. Number 1-3 are from 13 meters depth, number 4-6 are from 1 meter depth.

Figure 1.1 Sample location

 gebieden boven GLW  
 samples



### Sample key

Saeftinge (Konijnenschor), reduced.  
S1 a, b, c, d  
S2 a, b, c, d  
S3 a, b  
S4 a, b  
peat lump SV.  
Saeftinge, idem after oxidation.  
So1 a, b, c, d  
So2 a, b, c, d  
So3 a, b  
So4 a, b  
Western-Scheldt suspended matter, centrifuge.  
WC 4o, 5o, 6o (lower part)  
1m. 4b, 5b, 6b (upper part)  
WC 1o, 2o, 3o (lower part)  
13m. 1b, 2b, 3b (upper part)  
Western-Scheldt suspended matter, filtration.  
WR 1a, 1b, 1c filter 1m depth  
WR 2a, 2b, 2c filter 13m depth

Due to lack of time only WC1o, -3o, -5o, -6o, -1b, -2b, -5b and -6b have been analysed. WR-samples were quickly treated in a nitrogen glove box.

### 1.2 Methods

TESSIER et al. (1979) were the first to lay a basis for sequential metal extraction by means of step-wise shaking with ever stronger leaching agents. Hereafter several authors suggested modifications (e.g CALMAND & FOERSTNER, 1983). The first batch was treated according to GOUD et al. (1985). After it was found out this method leads to severe errors (see 1.3) Foerstners method was almost completely followed (CALMAND & FOERSTNER, 1983). First a brief discussion of the various steps will be given.

### 1.3 LITERATURE REVIEW

Little can be said about trace metal contamination when measuring only total metal content. Therefore sequential extraction techniques were invented to study the effects of changing physicochemical conditions on metal speciation. In this way something can be said about the availability of metals to the environment, thus leading to an understanding with regard to the toxicity of a soil when it is polluted with trace metals. This leads to a distinction in (TESSIER et al., 1979; SALOMONS & FOERSTNER, 1984)

- changing ion strength/composition, affecting metals bound by electrostatical forces (clays, Fe, Mn-oxyhydroxides, organic matter).
- changes in pH, reflected by e.g. carbonate dissolution/precipitation.
- changes in Eh, reduction-oxidation processes, leading to dissolution/precipitation of Fe- and Mn-oxyhydroxides.
- decomposition of organic matter and oxidation of sulphides.

Many scientists have used sequential extraction methods. Some use 4, others 5, 6 or even 7 steps. TESSIER et al. (1979) were the first to introduce a generally applicable concept for a five steps extraction. They distinguished:

- exchangeable ions. Leaching for 1 hour with 1M MgCl<sub>2</sub>, pH 7 under continuous agitation.
- carbonate bound metals. 5 hours shaking with 1M NaOAc-HAc, adjusted to pH 5, under continuous agitation.
- Fe, Mn-oxyhydroxides. 6 hours shaking with 0.04M NH<sub>2</sub>OH-HCl-HAc, pH 2, 96°C.
- organic-matter-bound metals. 5 hours 30% H<sub>2</sub>O<sub>2</sub>, 85°C, shaking with 1M NH<sub>4</sub>OAc to prevent readsorption of trace metals.
- residual fraction, digestion with 5:1 HF/HClO<sub>4</sub>-mixture.

However they warn that the results should not be interpreted as distinct geochemically defined phases but rather as method defined fractions.

The most widely used scheme is the one proposed by CALMAND and FOERSTNER (1983) after modifying Tessier's scheme:

- exchangeable- 1M NH<sub>4</sub>OAc, pH 7, solid/solution ratio (R) 1:20, two hours shaking time (t).
- carbonate- 1M NaOAc, pH 5, R= 1:20, t= 5 hours.
- easily reducible phases (mainly Mn-oxides and partly amorphous Fe-hydroxides), 0.1M NH<sub>2</sub>OH.HCl + 0.1M HNO<sub>3</sub>, pH 2, R= 1:100, t= 12 hours.
- moderately reducible phases (amorphous and poorly crystalline Fe-hydroxides), 0.2M ammoniumoxalate + 0.2M oxalic acid, pH 3, R= 1:100, t= 24 hours.
- organic matter, sulphides, 30% H<sub>2</sub>O<sub>2</sub>, pH 2, 85 °C; 1M NH<sub>4</sub>OAc, pH 2.5, R= 1:100, t= 24 hours.
- residual fraction as with Tessier.

For solid/solution ratio the symbol "R" will be used.

Other schemes are in use (e.g. KITANO et al., 1980), but this scheme seems to meet most of the demands for selectivity. In addition a first step to determine water soluble metals was introduced in the present study although DUINKER (1980) shows that this fraction hardly contributes to the overall metal content.

GOUD et al. (1985) use a scheme which has also been used in this study for S-samples (fraction 3, 4 and 5) but did not satisfy. This is because they do not shake long enough (only 1 hour which is probably too short for complete equilibrium).

FOERSTNER et al. (1979) state it is still impossible to distinguish between organic material and acid volatile- and bisulphides (AVS). Besides RAPIN et al. (1985) conclude that the selectivity for steps 3 and 4 is doubtful as it also dissolved 90% of the AVS, even under a nitrogen atmosphere. RAPIN and FOERSTNER (1983) observed partial attack of  $\text{CaCO}_3$  during step 1 (see also TESSIER et al., 1979). Besides they observed partial attack of AVS during step 2, attack of smectites in step 3 and a far from complete dissolution of goethite during step 3. Finally, (like RAPIN et al., (1985)) they observed that over 50% of AVS were attacked during step 1 up to and including 3 under nitrogen atmosphere, for reduced fresh water sediments.

Care should be taken not to shake too long during step 2 as this also leads to attack of Mn-oxides (TESSIER et al., 1979). It is very important that all samples are shaken equally long because otherwise the results are not comparable. FOERSTNER et al. (1979) point out that the solid/solution ratio must not be too great, as this causes the system to overload, leading to changing pH-conditions.

Only recently it has been recognized that it is very important to prevent contact with the air when dealing with reducing samples (RECKE & FOERSTNER, 1985; RAPIN et al., 1986). This leads to dissolution of AVS in steps 1, -2 and -3. Besides it oxidizes Fe- and Mn-oxyhydroxides which scavenge metals thus brought into solution. Cadmium and Zinc were found to change from sulphides and easily reducible phases to exchangeable- and carbonate phases (RAPIN & FOERSTNER, 1983). FOERSTNER et al. (1979) found a sharp decrease in fraction 5 (organic matter/sulphides) after step 4 (ammoniumoxalate/ oxalic acid).

From the above discussion it is clear that the main problem involving selective extraction techniques is selectivity. Factors influencing selectivity are:

- Preextraction sample treatment. Samples are best stored in a refrigerator under water, when the samples are reduced. This should not be done when the samples are fully oxidized.
- Reducing samples must be treated under argon or nitrogen, to prevent oxidation of AVS.
- Shaking times, R, t and leachate concentrations must remain constant during the experiment in order to obtain comparable results. Centrifuging preferably under a nitrogen atmosphere.

Even with all these precautions selectivity is sometimes poor. It should be stressed that the results are not to be considered as distinct phases. This is not surprising as the present phases are no distinct endmembers. For instance ironoxides pass through an entire range going from amorphous to poorly cristalline to well cristalline compounds. The same holds good for sulphides. Organic matter is poorly defined as well, part being soluble, part hardly destructable (lignin, parafins, cellulose).

It can be concluded that only a semiquantitatively trend is indicated. Measure errors are probably about 10% relatively.

#### 1.4 SAMPLE TREATMENT

Samples from S<sup>o</sup> and WC were treated without precautions to prevent contact with oxygen. Samples S and WR were treated in a nitrogen glove box until the oxidation step with H<sub>2</sub>O<sub>2</sub>. Centrifugation was not performed under a nitrogen atmosphere so this introduces a first uncertainty with regard to selectivity. Before the first extraction and before the fourth extraction moisture content was measured. All samples were centrifuged for 30 minutes at a speed of 3000 rpm. All supernatant liquids were filtered over a 0.45 um cellulose-nitrate filter (Sartorius). Except for sample S all samples were acidified to pH 0-1 and stored in polyethylene jars. All glass work and plastics were thoroughly rinsed in 14% HNO<sub>3</sub>. All reagents are of pro analysi grade. Sample S can only be considered semiquantitatively because the liquid was stored in glass jars and was not acidified. Acidifying of the samples is necessary to prevent readsorption of the metals on the sides. Slight contamination of zinc can be expected because this metal is used as a weakmaker in plastics. This effect is considered to be negligible. All samples were stored at 2° C to prevent algal growth. However samples WS and S<sup>o</sup>, step one still showed algae, probably because these samples are merely diluted estuarine waters and contain large amounts of nutrients.

Step 1: "interstitial water"

R= 1:20. One hour shaking with distilled (oxygen-free) water.

Step 2: "exchangeable metals"

R= 1:20, t=1 hour. Shaking with 1M  $\text{NH}_4\text{OAc}$ , pH 7.0.

Step 3: "carbonate bound metals"

R= 1:20, t= 5 hours (1 hour for sample S and WR). Shaking with 1M  $\text{NaOAc}$ , pH 5.0 adjusted with acetic acid.

Step 4: "easily reducible fraction"

R= 1:100, t= 12 hours (3 hours for WR, 1 hour for S). Shaking with 0.2M  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , pH 2.0, adjusted with  $\text{HNO}_3$ .

Step 5: "moderately reducible fraction"

R= 1:100, t= 24 hours (6 hours for WR, 1 hour for S). Shaking with 0.2 M ammonium oxalate + 0.2 M oxalic acid.

Step 6: "organic matter/sulphides"

R= 1:100, 5 hours  $80^\circ\text{C}$  with 30%  $\text{H}_2\text{O}_2$ . Afterwards shaking with 1M  $\text{NH}_4\text{OAc}$ , pH 2.5.

Step 7/8: "residual fraction/total metal content"

Digestion with  $\text{HF}/\text{HNO}_3/\text{HClO}_4$  (as TESSIER et al., 1979).

The results of these extraction will be called "fraction" or "F" which will be used intervariably.

### 1.5 Bottle necks

The sequential extraction procedure might seem easy to perform but proved to be very tedious and tricky.

1. Weight determination: It is very important that the R-index be known. Therefore the weight of the sample must be known. For reduced samples oxygen contact must be avoided, so a balance should be present in the glove-box.

2. Homogeneity: Various authors stress the importance of a homogeneous sample which is difficult to obtain for wet claylumps containing all sorts of plantparts. The results of fraction 8 compared with the sum of fractions 1 to 7 shows the importance of a homogeneous sample (TESSIER et al., 1979; FOERSTNER et al., 1979; RECKE & FOERSTNER, 1986).

3. Carbonate extraction: Upon addition of sodium acetate carbon dioxide gas arises. After 5 hours of shaking it is sure the tubes will explode. Three samples were lost in this way. It is recommended to shake the samples in the glove-box under gentle release of CO<sub>2</sub>.

4. After centrifugation it is hard to shake loose the residue without glasspearls. These must be rinsed in a 14% HNO<sub>3</sub> solution.

5. Shaking under a nitrogen atmosphere is difficult. So well sealed centrifuge tubes with nitrogen above the liquid should do (e.g. parafilm combined with screw caps).

6. After each step the residue was rinsed with 10 ml. distilled water. This volume should be kept low in order to prevent extensive solution of organic matter or AVS.

7. Pipetting the supernatant liquid in a glove-box poses problems. When taking the centrifuge tubes in the vacuum-lock the tubes will burst when vacuum is attained. Maybe strong screw caps could offer a solution.

8. Analysis.

8.1 Analysis by atomic absorption spectrometry (AAS).

Because of the strong salt contents of the various matrices frequent clogging of the burner occurred. This was especially the case for sodium acetate (see also TESSIER et al., 1979) and ammonium oxalate/oxalic acid buffer. Besides severe matrix effects occurred so an internal standard must be included to correct for this effect. This is to be preferred over making different standards for all the matrices.

8.2 Inductively coupled (argon) plasma (optical emission spectrometry) (ICP).

Because the ICP pumps instead of sucks the sample no clogging arised. Rinsing between each three samples in case of NaOAc is recommended. An internal standard is necessary.

8.3 Graphite furnace with Zeeman effect.

Because of the low detection limits this method is well suited for Pb- and Cd-measurements. Pb has a very high detection limit on both AAS and ICP and is very unstable. Cd is usually below detection limit because of the small amounts of Cd in the samples. One is dissuaded to use a graphite furnace because of the amount of time necessary for analysis.

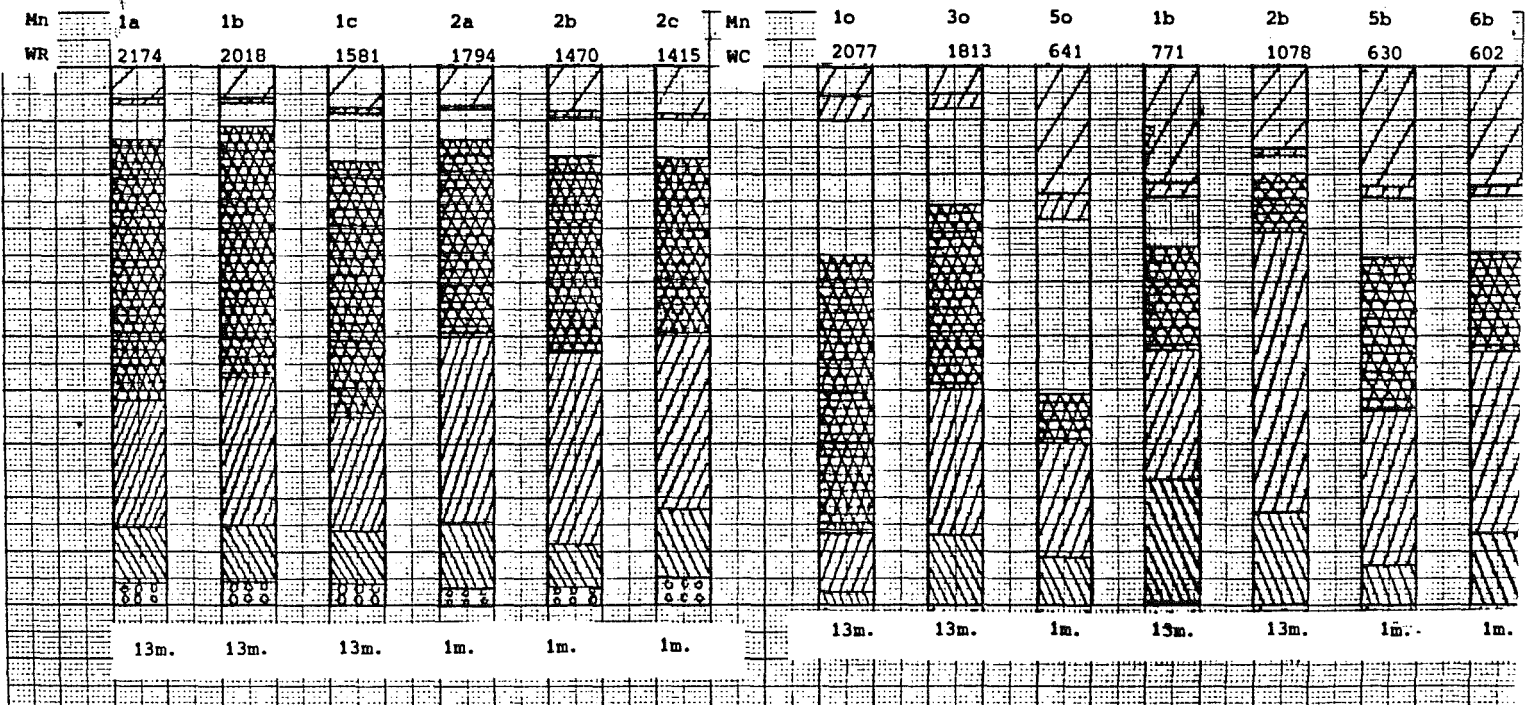


## 2. RESULTS and DISCUSSION

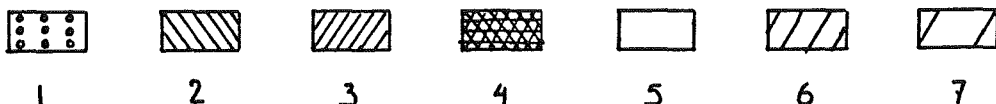
The concentrations for all elements are in tables 1, 2 and 3. Tables 1.1, 1.1a and 1.1b show textural analyses and pyrite content, sulphate content and carbonate content. Some authors recalculate the metal concentrations based on 1% clay (fraction smaller than 2  $\mu\text{m}$ .). This has not been performed for two reasons. The first reason is that the textural difference between various samples is too small. The second reason and the more important is that there is always a background concentration independent of clay content. So for samples low in their metal contents this ratio would yield wrong information with regard to possible pollution effects.

### The peat lump

All metal concentrations were below detection limit except for iron. Therefore the results are not published in this study. Probably only the outer layer of the peat lump was contaminated with trace metals and not the inner parts which were sampled in this study. More careful sampling is necessary to gain information about the scavenging capacities of peat and bog.



Legend



2174 ; F. 1.7 (ppm)

Figure 2.1 Percentual distribution of manganese for WR and WC samples

## 2.1 Manganese

WR: The percental distributions are in figure 2.1. The distribution of Mn is essentially the same at 1m. as at 13m., although there is a slight difference between fractions 2, -3 and -4. The most important fractions are F3 and F4, which means Mn is mainly present as amorphous Mn-oxides or adsorbed/coprecipitated with amorphous Fe-oxyhydroxides and carbonates. Mn is present in unstable compounds as shown by the amounts in F1, F2 and less unstable fractions F3 and F4. About 40% at 13m. and 50% at 1m. is present in fractions F1-3, which means Mn in the divalent state (HONG & FDERSTNER, 1983). Mn can be incorporated in calcite because of their similar ionic radii (Mn(ii)= 0.80 Å; Ca= 0.99 Å). Only a very small amount of manganese is present in F6. F7 is small. Total Mn is consistent with values given by MARTIN & MEYBECK, (1979). Samples from 1m contain less Mn than samples from 13m.

WC: The homogeneity between dupli is absent in the WC-samples. There are no significant differences between 1m- and 13m-samples. There is some difference between the coarser part and the finer fraction, further called "coarse" and "fine". As can be calculated from table 1.1 and 1.1a more than 92% of the fine sample is smaller than 17 µm, whereas some 83% of the coarse sample is smaller than 20(!) µm. F4 and F5 are greater in the coarse part than in the fine part. In the fine part F2 and F3 are greater. As can be seen F7 is twice as big as in WR-samples on an average. No Mn was found in fraction 1. F6 is very small, although somewhat greater for the coarse part. Samples from 1m contain less Mn than samples from 13m. Samples in the coarse part contain only little more Mn than samples from the fine part.

So: The results of WR and WC differ considerably from the soil-profile of Saeftinge's. The reproducibility of four-folds and dupli is good so they will be dealt with as an average for each horizon (G<sub>0</sub>, G<sub>su(i)</sub>, G<sub>su(ii)</sub> and G<sub>r</sub>).

G<sub>0</sub>: F4 is the most important fraction accounting for more than 65% of total Mn. F3 and F5 are of minor importance although they cannot be neglected. F6 is again very small. No Mn is found in F1 and F2. F7 is small. It can be seen that more than 75% of total Mn is present as Mn(iv). This is much more than for WR and WC. It must be noted that Mn-oxidation is very slow in absence of bacteria (MURRAY et al., 1983).

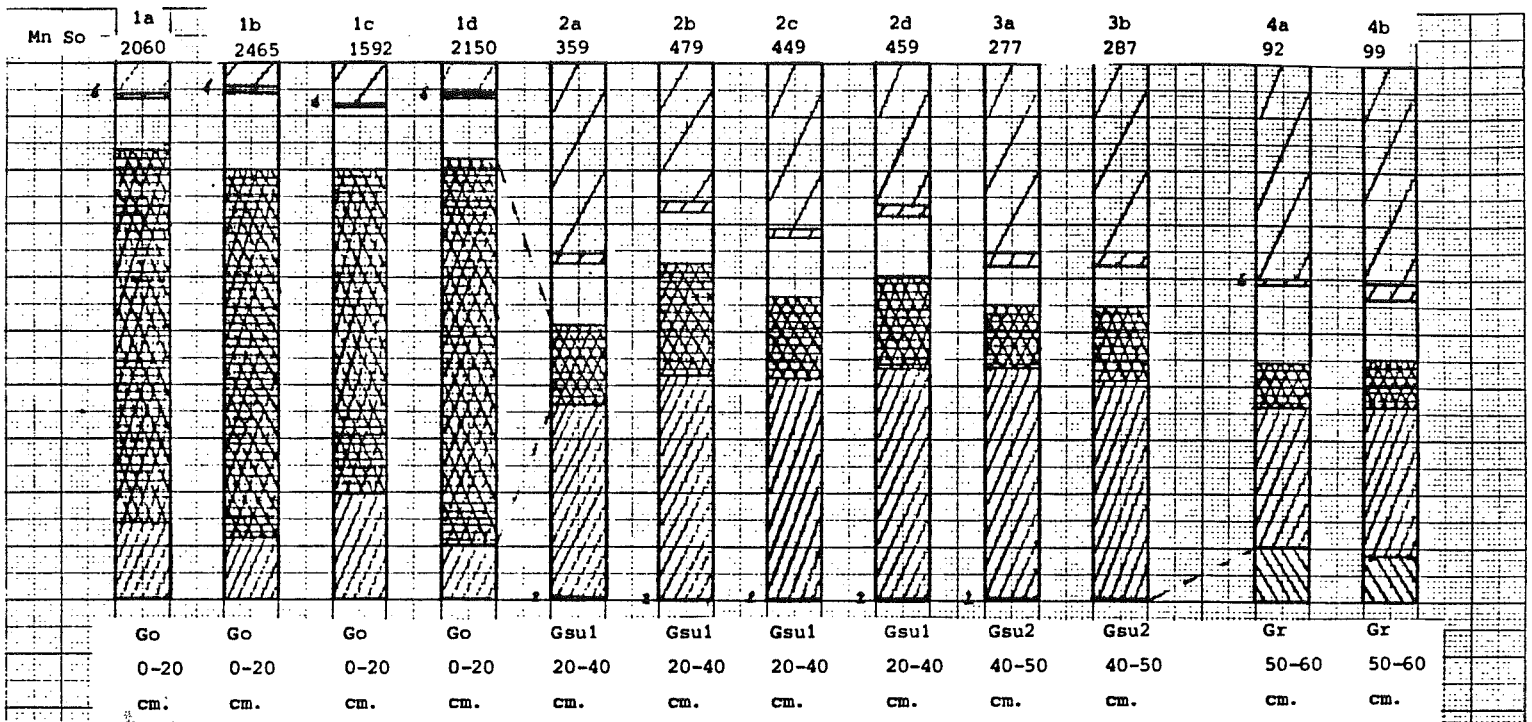


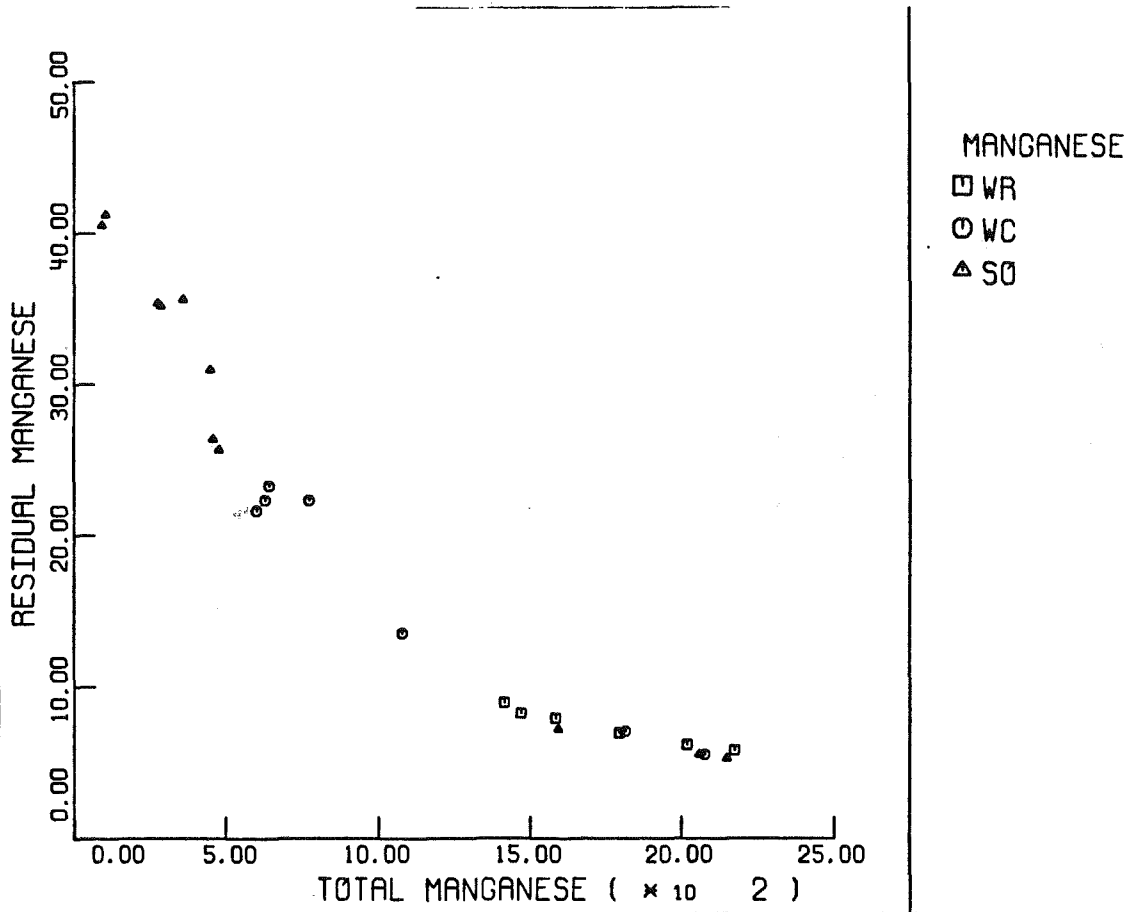
Figure 2.1 Percentual distribution of manganese for So samples

Gsu(i): A dramatic decrease of  $Mn_c$  is observed, having great consequences for the Mn-distribution. F7 increased about four-fold. As can be seen in figure (2.2) Mn7 is reversely proportional with total Mn-content with a very high negative correlation ( $r = -0.954$ ). No change occurred in F5 and F6. The main change was a shift from F4 to F3 now accounting for more than 40% of total Mn. This implies Mn was reduced in this horizon. As the underlying horizons contain less Mn than Gsu(i), Mn must have diffused upward to Go. A very small amount is present in F2.

Gsu(ii): The distribution is essentially the same as in Gsu(i). F7 is greater in accordance with figure (2.2) Gsu(ii) is still small although somewhat greater than Go.

Gr: F7 is greater than the above horizons (see figure (2.2)). Total Mn is very low as compared with literature (SALMONS & FDERSTNER, 1984). There is a remarkable increase in F2 probably at the cost of F3. As both samples show this behaviour analytical artifacts are not likely.

Figure 2.2 Scattergram of Mn<sub>7</sub> - Mn<sub>t</sub>, y-axis in percent of total metal content, x-axis in ppm



Summarizing there is a sharp decrease in Mn<sub>t</sub> from G<sub>0</sub> to the underlying horizons, coupled with a shift from F<sub>4</sub> to F<sub>3</sub>. Mn<sub>7</sub> increases as total Mn decreases as supported by figure (2.2). As no increase in Mn is found in the horizons beneath G<sub>su(i)</sub> diffusion of dissolved Mn must have proceeded towards G<sub>0</sub>. As Mn(ii) is much more soluble than Mn(iv) porewater concentrations in G<sub>su(i)</sub> and G<sub>su(ii)</sub> are higher than G<sub>0</sub> resulting in a concentration-gradient from G<sub>su</sub> to G<sub>0</sub>.

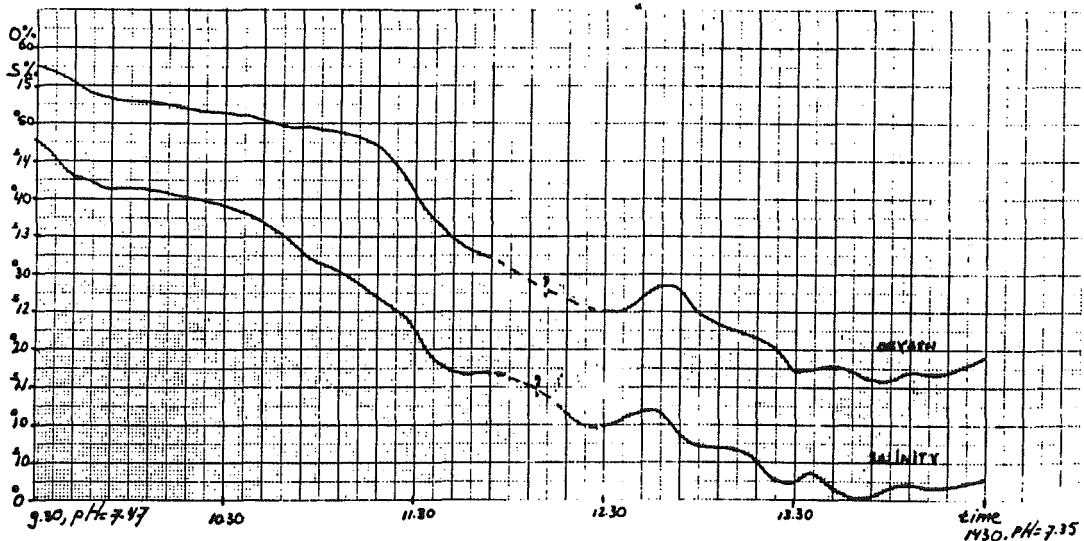


Figure 2a Traject of the O<sub>2</sub>-content, the salinity and the pH at the start and the end, of the Western-Scheldt samples. Recorded at M.V DELTA during sampling. Results not published.

## 2.1a Discussion

As Mn-compounds are famous for their trace-metal scavenging capacities (KRAUSKOPF,1956; MURRAY et al.,1973,1975; MC KENZIE,1980; STUMM & MORGAN,1981; SALOMONS & FOERSTNER,1984; FEELEY et al.,1983 and many others) a study of the behaviour of Mn is very important when dealing with trace metal distributions, as trace-metals display a different affinity for Mn. Cr and Mn show contrasting behaviour (MURRAY et al.,1983) whereas Co goes often with Mn and Fe (JACOBS et al.,1985; KREMLING,1983). Three processes will be discussed. The changes that occur when suspended matter is deposited, the changes in distribution in a soil profile and the processes coupled with careless sample-treatment with regard to oxidation (WR-WC). Besides each sample is treated separately. When possible S-samples will be used for comparison. This scheme will be used for the other elements as well.

WR: As was mentioned samples from 1m have more Mn in F3 than samples from 13m at the cost of F4. Water from 13m has a higher salinity and a higher pH and oxygen-content (figure 2.a). Mn in F3 is thought to be present as Mn(ii) so maybe some Mn(iv) has formed in the water table at 13m depth were there is more oxygen. The results show that much manganese is unstably bound as shown by the amounts present in F1 and F2. Mn in F1 is either in solution or has passed the filter in colloidal form. F2 is thought to be Mn bound electrostatically to clay-particles.

So: The soil-profile shows what happens to manganese when it is deposited in a partially reduced sediment. The absence of F1 is due to oxidation during storage (on purpose) because S-samples show Mn in F1. When the upper layer of the sediment is oxidizing Mn(ii) will be converted to Mn(iv) and precipitated as Mn-oxides. When the upper layer is reducing more Mn will reduce and diffuse back to the water-column. This is a commonly observed phenomenon as Mn-reduction is extremely rapid contrary to Mn-oxidation (TRAMONTANO et al.,1984; KEENEY-KENNICUTT et al.,1986; HIRST & ASTON,1983). When precipitated in an oxidizing environment the freshly precipitated Mn-oxides can adsorb huge amounts of trace metals (see also results for other elements). The small amount of Mn in F6 is consistent with literature. Mn does not form insoluble sulphides and has a low affinity for organic matter (KERNDORFF & SCHNITZER,1980).

The soil-profile: The soil becomes reduced at a certain depth as shown by black sulphides present in Gsu and deeper. At the time the samples were taken the sulphides were seated deeper than 20 cm, but in summer they are thought to be present just below the surface. In winter bacterial activity stops and oxygen can enter the soil through cracks and rootcanals. This has been observed in february 1986 at Rilland-Bath where the black sulphidic horizon was deeper than 40 cm. As stated before Mn-reduction is rapid and complete and Mn ions will go into solution. Part is coprecipitated with carbonates and part loosely bound on clay-particles due to competition of free  $Mn^{2+}$ -ions as shown by the increase in F2 and F3 and the decrease in F4. Mn which is still present in F4 is thought to be adsorbed or bound by amorphous Fe-oxyhydroxides and not as amorphous Mn-oxides as Mn-reduction was probably complete. Besides LUOMA & DAVIS (1983) show that the total manganese content in these samples cannot account for 100% of the metal scavenging capacity. They took the apparent binding capacity (abc) as appr.  $2.5 \cdot 10^{-3} Mg^{-1}$ . The total binding capacity (i.e.  $abc \cdot Mn_c$ ) is less than the amount of metals bound by F4. So part of this fraction must consist of amorphous iron-oxyhydroxides.

Most of the Mn will diffuse away to the G<sub>0</sub>-horizon where part is precipitated again as Mn-oxides. However a considerable amount will diffuse into the water-column as Mn-oxidation is slow. It must be noted that the absence of sulphides in G<sub>0</sub> does not mean oxidizing conditions for Mn.  $SO_4^{2-} = S^{2-}$ ; Eh = -500 - -600 mV, Mn(IV) = Mn(II), Eh = 100-800mV, (from SALOMONS & FOERSTNER, 1984, figure (2.3)).

WR-WC: The results show that care should be taken to prevent oxygen contact during sample treatment. As Mn-oxidation is a rather slow process -chemical iron oxidation occurs up to 500 times as fast as chemical manganese oxidation- this could explain the heterogeneous distribution and the poor reproducibility of dupli in WC. There are some differences between coarse and fine. More Mn is found in F5 in the coarser part, which implies adsorption onto poorly cristalline Fe-oxyhydroxides. F6 is slightly greater which will be explained with nickel (2.3)

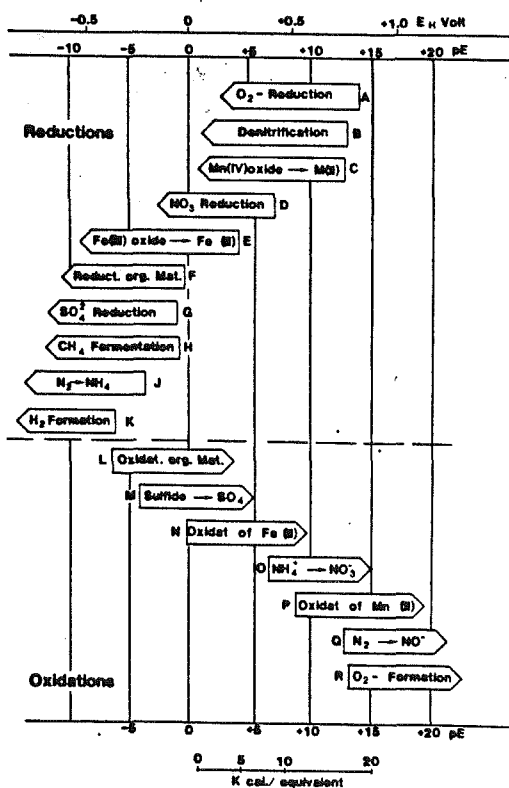


Figure 2.3 Redox couples for some species

(from SALOMONS & FOERSTNER, 1984)

## 2.2 Iron

The percental distributions are in table 2 and figure 2.4.

WR: Comparison between three-folds is good. Most Fe is present in F7 and F5 followed by a smaller portion in F4. This implies most Fe is present in a trivalent state in oxyhydroxides, ranging from amorphous to well-crystalline. It was found that well-crystalline Fe-oxyhydroxides are poorly leached by ammonium-oxalate/oxalic acid-buffer (TESSIER et al., 1979). F6 is small but obviously present and consists of sulphides and organically bound iron. The results are consistent with literature which frequently report high Fe-content in F7 (TESSIER et al., 1979 and many others). As with Mn there is a subtle shift in 1m-samples and 13m-samples. At 1m more Fe is found in F3 and F4 at the cost of F5. Total iron concentrations are consistent with values reported by MARTIN and MEYBECK (1979). F1 and F2 are practically absent. However table 3 shows some Fe in unfiltered Western-Scheldt samples, values are between  $0.79 \mu\text{M l}^{-1}$  and  $6.4 \mu\text{M l}^{-1}$ . With the present pH and Eh only very little Fe is thought to be in true solution.

WC: As for Mn the results are heterogeneous and poorly comparable. In essence the same distribution as for WR-samples is observed. F7 is high. Figure (2.5) shows the relation between Fe7 and Fe<sub>t</sub>. There is a negative correlation which was also found for Mn ( $r = -0.487$ ). F1-3 are negligible. F5 and F6 are somewhat greater in the coarse samples. F4 is smaller than in the Fine samples. Total Fe is consistent with literature, (MARTIN & MEYBECK, 1979). No difference between 1m- and 13m-samples is observed. The differences between coarse and fine more obvious.

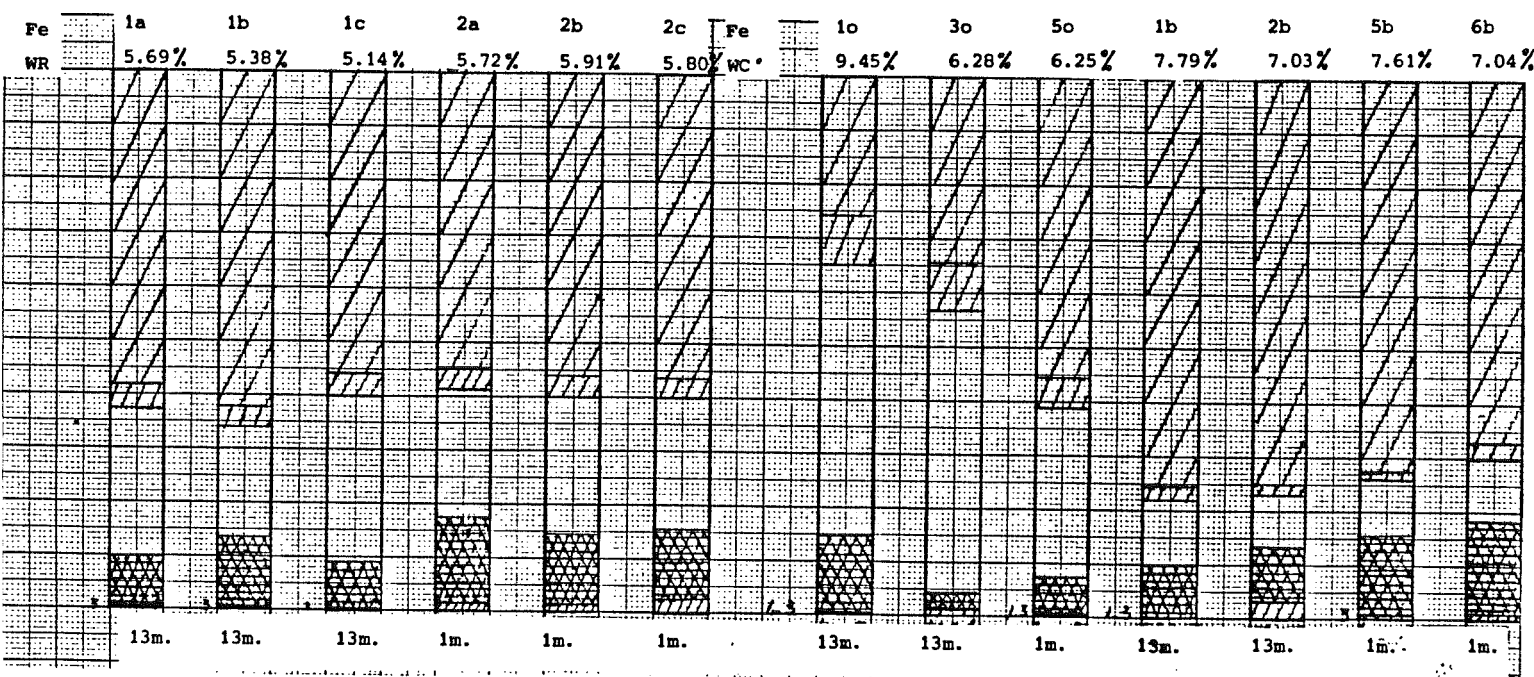
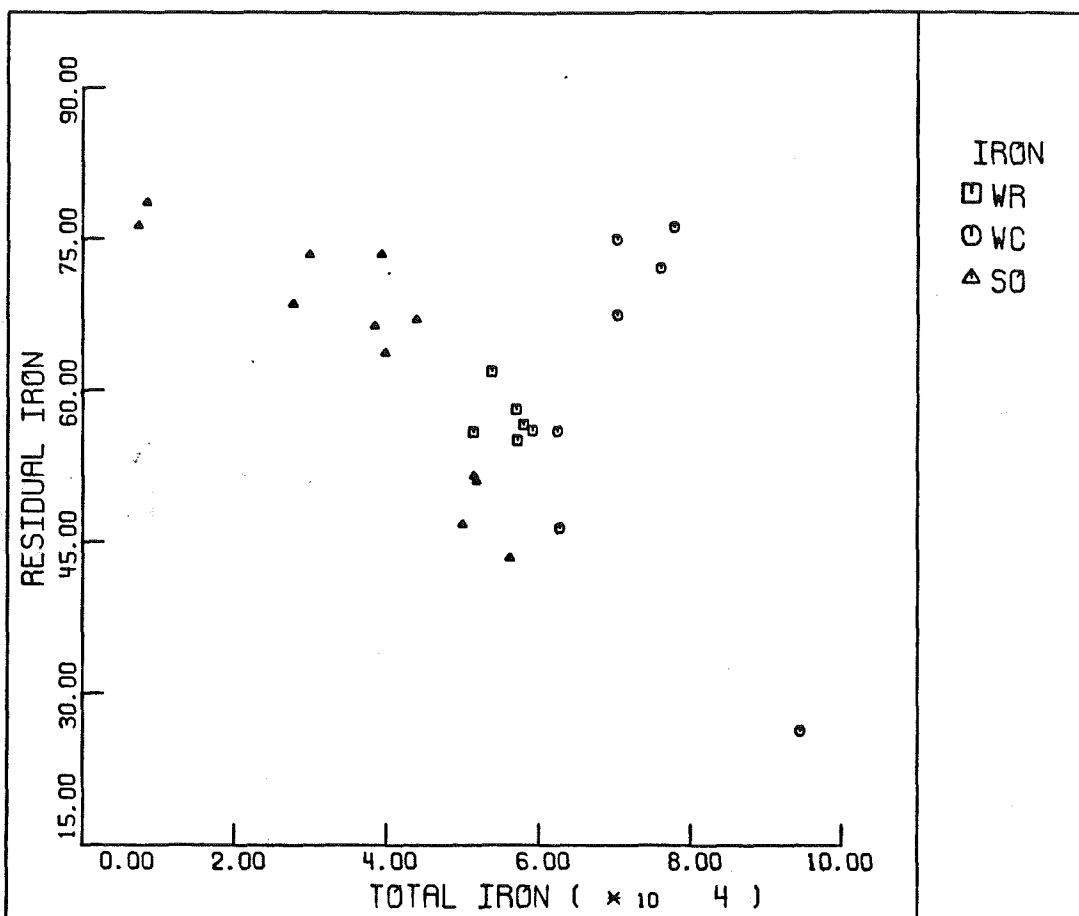


Figure 2.4 Percental distribution of iron for WR and WC samples

Figure 2.5 Scattergram of Fe7 - Fe<sub>t</sub>, y-axis in percent of total metal content, x-axis in ppm



So: Generally the same distribution as for WR and WC is observed. Most of the Fe-sulphides will have oxidized as can be seen from table 1.1.b, which shows the amount of pyrite and mackinawite originally present. However this accounts for only 10-20 % of Fe<sub>t</sub>. Oxidation of reduced iron-compounds is rapid so all sulphides are thought to have oxidized (VAN BREEMEN,1976). Fe-sulphides are important for coprecipitation of trace metals (SALDMONS & FOERSTNER,1984 and many others). There is a decrease in total Fe-concentration in the soil-profile leading to a slight increase of F7 at the cost of F5. The decrease is not as sharp as for Mn. F1-3 are almost absent although there is a slight increase in F3 when going from G<sub>0</sub> to G<sub>su</sub>. S-samples show considerable amounts of Fe in F1 but this is precipitated upon oxidation. Diffusion of Fe must have proceeded upwards (see Mn) where most Fe is precipitated.



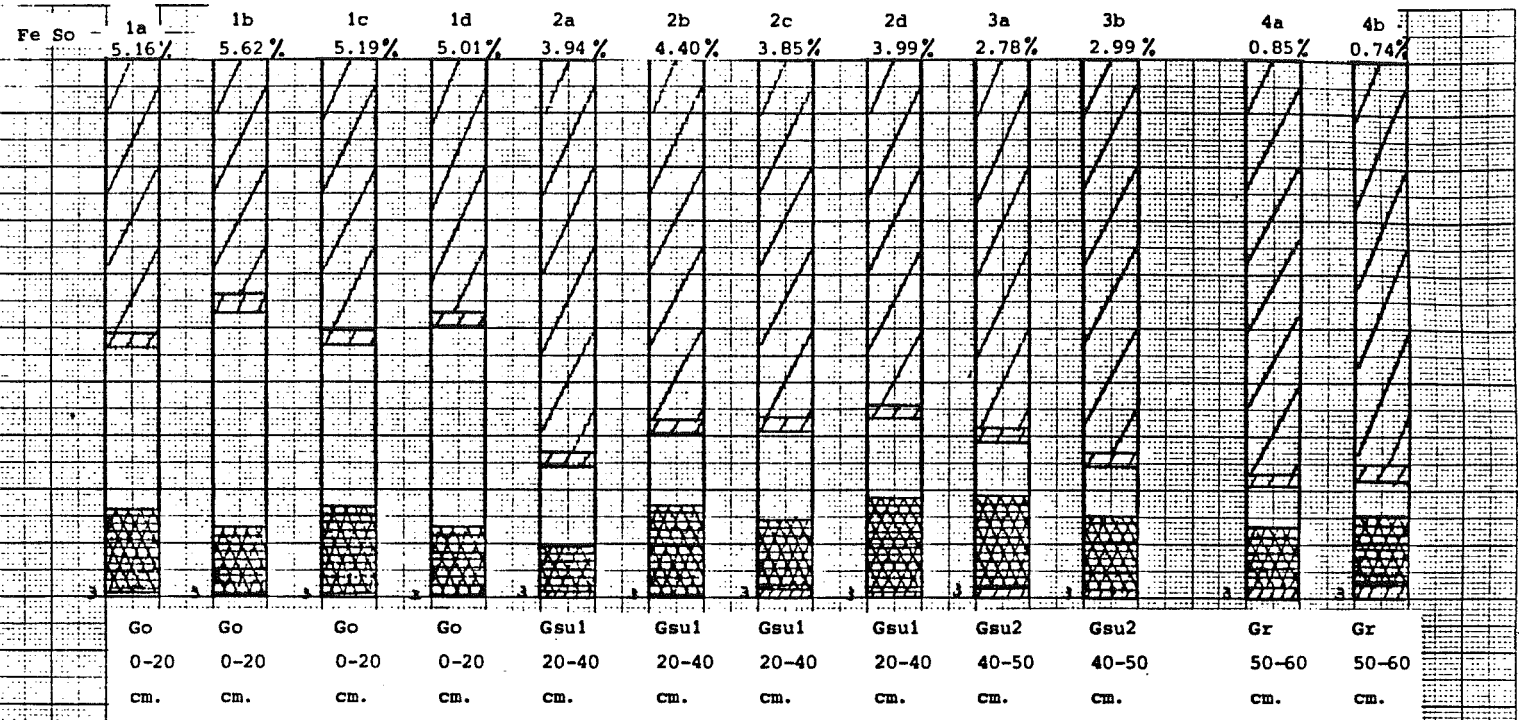


Figure 2.4 Percentual distribution of iron or So samples

### 2.2a Discussion

Fe-oxyhydroxides have a high capacity to scavenge trace metals (BALISTRERI et al.,1982; STUMM & MORGAN,1981; FLETCHER & HOLMES,1983; LUDMA & DAVIS,1983 and many others). As with manganese an understanding of the distribution of Fe-species is important in understanding the behaviour of the other trace metals.

WR-So: Most iron is present as Fe<sup>3+</sup> as can be seen from the importance of F4, F5 and F7, accounting for more than 90% of Fe<sub>t</sub>. Fe is easily oxidized chemically, although slowly reduced in absence of bacteria. The reverse holds good for manganese (NEALSON,1982). Fe<sup>3+</sup> is the stable iron species in the Western Scheldt area, thermodynamically. It is shown that kinetics are fast enough to convert all iron to its trivalent state whereas most Mn was seen to be present as Mn(ii). It is a well recognized fact that Fe-humates enhance the solubility of Fe<sup>3+</sup> by several orders of magnitude (SHOLKOVITZ,1976 and many others). Fe forms stable organo-iron complexes (KERNDORFF & SCHNITZER,1980). Fe-sulphides are very insoluble. This can account for the presence of iron in F6.

Still the Fe(iii)-compounds are more important. The presence of freshly precipitated Fe-Mn-oxyhydroxides is very important as they easily form stable coatings on inert particles like quartz and feldspars, thus giving them a much higher adsorption capacity than can be explained by the adsorption capacity of these species themselves. Besides these oxides might act as a glue for clay-humus-flocs (EISMA, 1986).

There is a slight increase in F3 and F4 at the cost of F5 at 1m-samples compared to 13m-samples. The difference is probably too small to be significant so an explanation will not be given.

Fe-species can coprecipitate with calcite because of their similar ionic radii ( $Fe^{2+} = 0.74 \text{ \AA}$ ;  $Fe^{3+} = 0.64 \text{ \AA}$ ;  $Ca^{2+} = 0.99 \text{ \AA}$ ).

When iron-oxyhydroxides are deposited in an oxidizing environment no great changes will occur as can be seen from G<sub>0</sub>. In a reducing environment sulphate is reduced to sulphide together with the reduction of Fe(iii) to Fe(ii). Iron-sulphide precipitation will be the result. There is a vast amount of literature concerning sulphate reduction and pyrite formation so this will not be dealt with in this study (GOLDHABER & KAPLAN, 1974; RICKARD, 1973; V. BREEMEN, 1976 and many others). In the Western-Scheldt estuary Fe will not be the limiting constituent so most iron will not be precipitated as iron-sulphides. This can be seen from the amount of pyrite in table 1.1.b. Upon deposition most organic matter will be consumed which releases the iron bound by the organic matter.

G<sub>0</sub>: Total iron decreases from G<sub>0</sub> to the underlying horizons together with an increase in F7 (cf. FOERSTNER et al., 1979). Part of the iron will have precipitated in sulphides upon reduction in the G<sub>su</sub>-horizons. Another part is thought to be bound by carbonates as can be seen from the increase in F3. Some 0.5 percent will have diffused to the G<sub>0</sub>-horizon - as the G<sub>0</sub>-horizon contains about 5% Fe<sub>e</sub> and the G<sub>su</sub>(i)-horizon about 4%, about 0.5% Fe must have diffused upwards assuming a constant Fe-supply by sedimentation which is a valid assumption - where it is rapidly oxidized and precipitated as Fe-hydroxides (lepidocrocite or an amorphous form). In contrast with Mn only very little Fe is thought to be released to the water column. The diffusion of Fe towards G<sub>0</sub> can be explained by a concentration gradient as Fe-sulphides - although they are considered to be insoluble - are more soluble than Fe-oxides. The decrease is less dramatic than for Mn reflecting the kinetic barrier for Fe-reduction and the much lower solubility of Fe-sulphides compared with Mn-sulphides. Comparison with S-samples shows the importance of working in an inert atmosphere.

WC: The results are influenced by oxidation which mediates incontrollable processes. The dupli are poorly comparable. It is likely that most amorphous hydroxides have aged towards their more crystalline forms.

### 2.3 Nickel

The percental distributions are in table 2 and figure 2.6.

WR: Comparison between threefolds is good. The samples from 13m are mainly determined by F2, F3 and F4. F5 is of minor importance. F7 is remarkably small. F1 and F6 are absent. Because of the similarity in ionic radius Ni can be incorporated in calcite ( $Ni^{2+} = 0.69 \text{ \AA}$ ). Total nickel concentrations are much higher than average for rivers (MARTIN & MEYBECK, 1979). Samples from 1m depth are above average as for Ni. F2 is smaller while F7 is greater than at 13m depth. F3, F4 and F5 are about the same. F1 and F6 are absent. Ni is found to display a low affinity for organo-metal complexation (KERNDORFF & SCHNITZER, 1980). On the other hand NRIAGU & COKER (1980) found association of Ni with organic matter in Lake Ontario. Ni is readily incorporated in Fe-sulphides besides forming sulphides of its own. The official formula of pyrite is  $Fe_{0.7}Ni_{0.1}S_2$ .

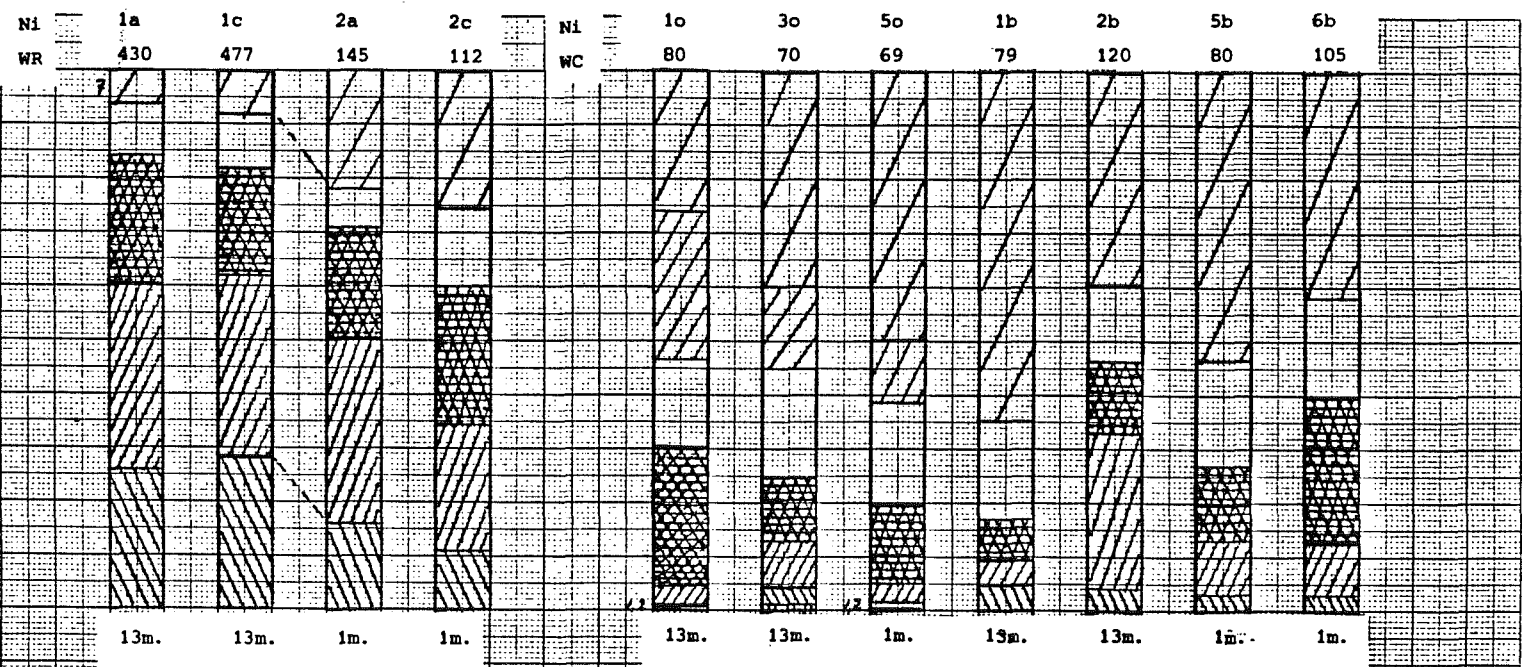


Figure 2.6 Percental distribution of nickel for WR and WC samples

WC: Comparison between dupli is moderate. Total Ni is about average as for world rivers (MARTIN & MEYBECK,1979). In the coarse samples F7 is the biggest. F4, F5 and F6 are equal while F1-3 constitute a very small rest. In contrast with WR and WC-fine there is a considerable amount in F6. In the fine samples, sample WC2b shows a distribution more like WR2a and WR2c with relatively much Ni in F3. The other fine samples have a high F5 and F7. F3 and F4 are also clearly present. F2 is small. F1 and F6 are absent. As for Fe and Mn there is an inverse relation between Ni7 and Ni<sub>e</sub> (see figure (2.7)). For WR and WC the relation is clear.

sample	Ni <sub>e</sub>	Ni7
WR13m	454	6.9 %
WR1m,WC2b	125	28.9 %
WC	80	48.3

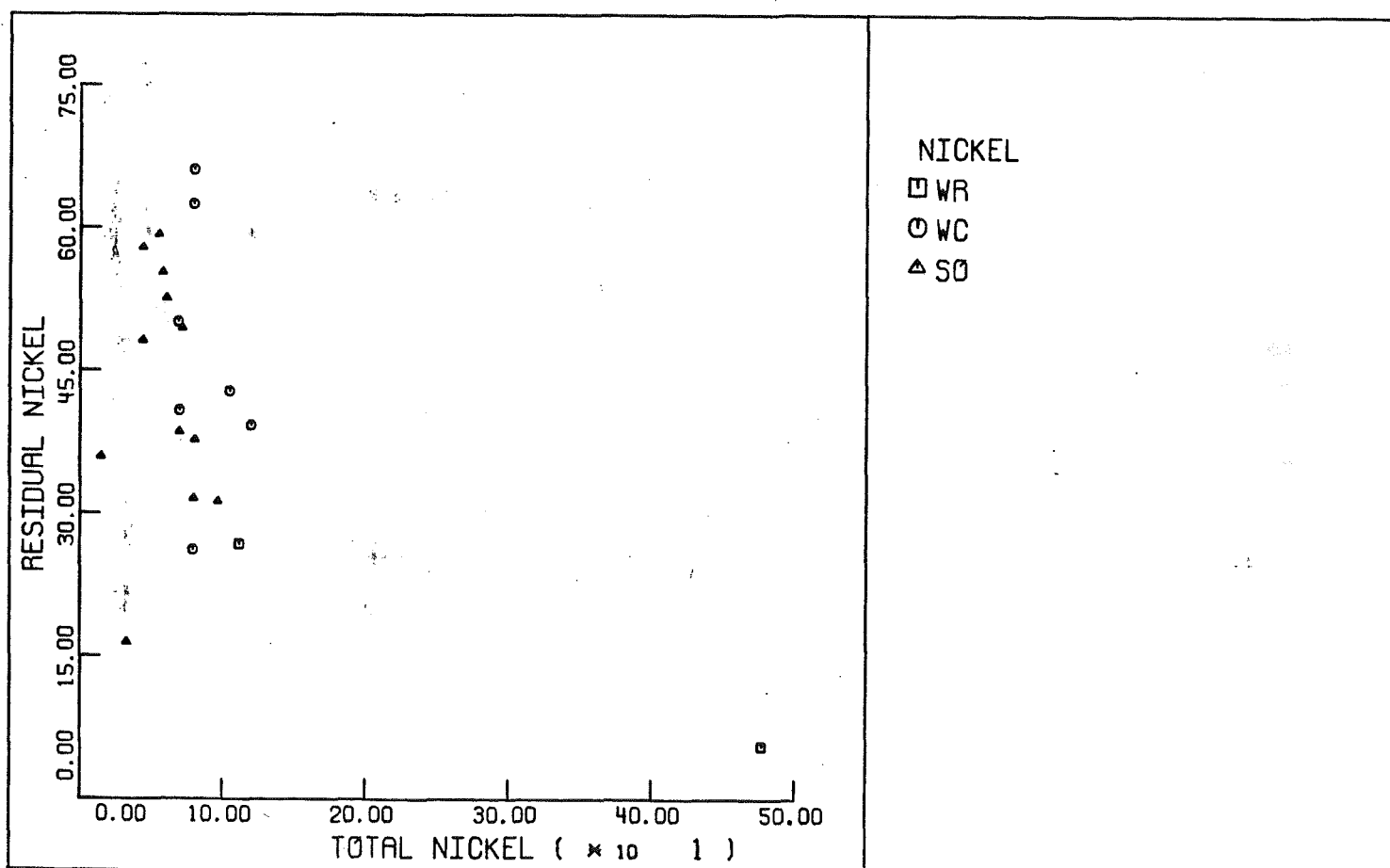


Figure 2.7 Scattergram of Ni7 - Ni<sub>e</sub>, y-axis in percent of total metal content, x-axis in ppm

So: Comparison between four-folds and dupli is reasonable. Samples from Gr cannot be trusted as because of the low solid/solution-ratios (R) for F4, F5 and F6 these fractions were often below detection limit. The R for F3 was much higher so F3 is probably overrepresented. As can be seen from S-samples F3 constituted about 10%.

Go: F7 and F4 are most important accounting for more than 65% of Ni<sub>e</sub> in equal amounts. F5 and F6 account for some 12-20 % of Ni<sub>e</sub>. F3 is small, F1 and F2 are absent.

Gsu(i)/Gsu(ii): A sharp increase in F7 at the cost of F4 and F5 is observed. F5 disappeared save for So2a and F4 about halved. F3 and F6 show an almost insignificant increase. No Ni is found in F1 and F2.

Total Ni is about twice the background values reported for freshly deposited sediments, i.e 35 ppm (WEDEPOHL,1978).

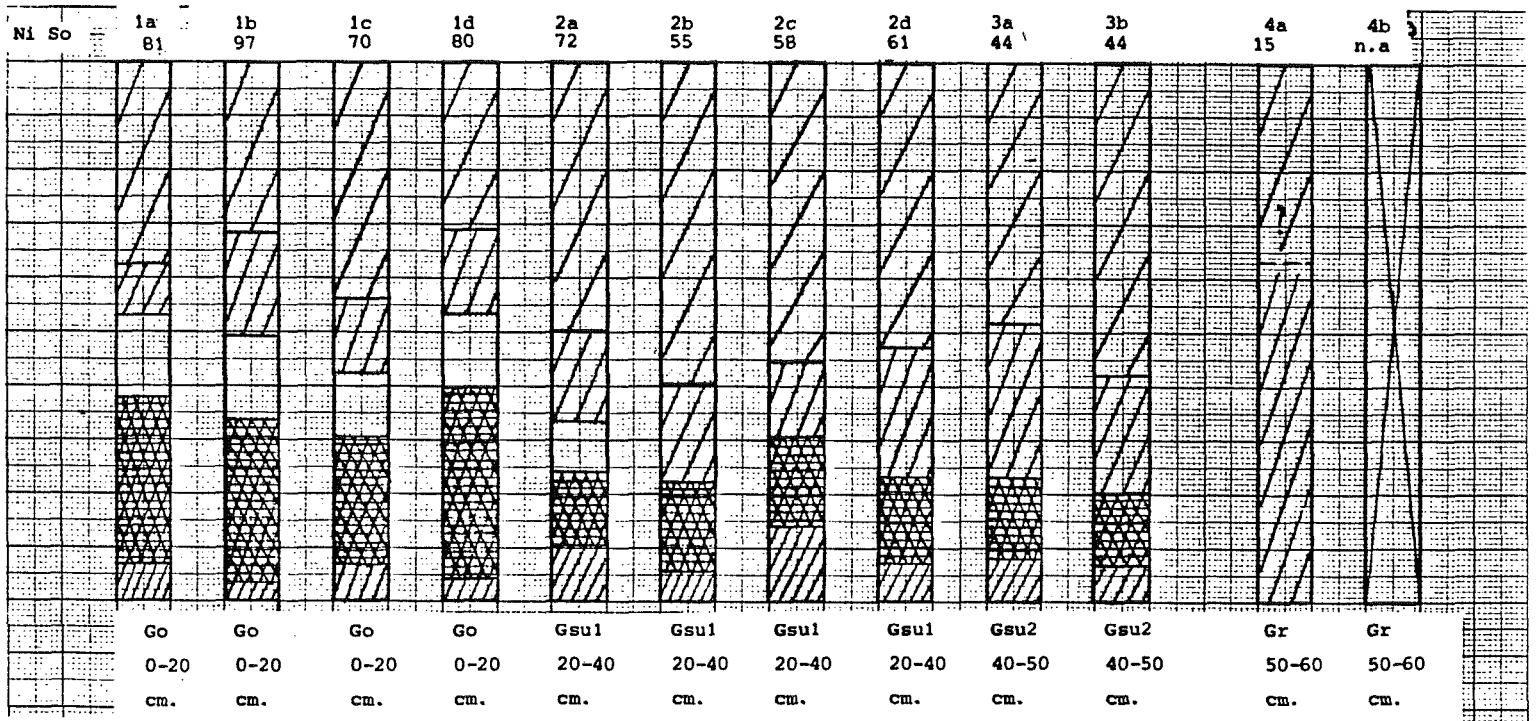


Figure 2.6 Percentual distribution of nickel for So samples

### 2.3a Discussion

In contrast with Fe and Mn, Ni is only present as  $Ni^{2+}$ . This means that Ni is hardly affected by oxidation/reduction-processes but that its distribution is dependent on Fe-Mn-oxyhydroxides. WR: Even when selectivity is poor the amount in F2 and F3 is remarkable. Between 40-60% is associated with these fractions. Together with the high concentrations of total nickel anthropogenic influence is evident (SALOMONS & FOERSTNER, 1984). Ni in F2 and F3 is unstably bound as exchangeable ions and incorporated in carbonates. Partial leaching of F4 may have occurred. Ni is not often studied in selective extraction studies. The literature values for Ni-distribution contradict each other and vary widely but a high F2 has not been reported before. Ni appears to be bound by (amorphous) Fe-Mn-oxyhydroxides. Together with the amount in F2 and F3 more than 80% is present in labile compounds. Although oxyhydroxides display a pH-dependent charge the difference in pH at 1m and 13m is too small to account for the decrease in F2 and a subsequent increase in F7. As Ni is not redox sensitive no shift in F4, F5 and F6 is observed.

WC: Again the difference between 1m and 13m is overshadowed by the centrifuge-fractions "coarse" and "fine". F6 is much greater for the coarse part than for the fine part and accounts for 10-25% of Ni. EISMA states (1986) that organo-mineral flocs are mostly present in the silt/fine-sand fraction which might explain the difference. It does not explain why no Ni is found in F6 in WR samples. Total nickel is less than for WR. This is coupled with a smaller F1-3 and a greater F7. When Ni is brought into the watersystem by sewage most Ni will be bound by all sorts of unstable fractions.

Another reason for the amount of Ni in F6 is the next: After wet storage of the samples for some weeks in the refrigerator the coarse samples showed black spots and -domains indicating the presence of Fe-sulphides. These were not present in the original sample. Apparently cold storage could not prevent bacterial activity. The same feature is found for all other metals (Mn, Fe, Pb, Zn, Cu, Cr). This clearly reveals the importance of sulphides as a sink for trace metals. No black parts were present in the fine samples. The distribution for the fine samples is essentially the same as for the coarse ones save for the absence of F6. Upon reduction Ni is released from oxides as shown by the presence of F1 in the coarse samples.

So: The disappearance of F5 in Gsu(i) is puzzling. Upon reduction of Fe- and Mn-oxyhydroxides most nickel will be bound by sulphides. This cannot explain the absence of F5 as a big part of F4 in Gsu(i) and Gsu(ii) will consist of Fe-oxyhydroxides and not of Mn-oxyhydroxides (see manganese). The inverse relation between Ni7 and Ni<sub>e</sub> is too vague to be significant.

sample	Ni <sub>e</sub>	Ni7
Go	82	34.8 %
Gsu	55	53.9

For the remainder no dramatic changes occurred. As nickel has only one valency state it mostly behaves passively with Fe and Mn, as shown by the decrease in both F4 and F5. Part of the Ni will precipitate with sulphides, part will diffuse towards the Go-horizon.

WR-So: There is a shift in the distribution of Ni upon deposition. Upon sedimentation Ni moves from exchange sites and carbonates to sulphides and Fe-Mn-oxyhydroxides. This will be caused by diagenetic reactions like decomposition of organic matter, sulphate reduction and a subsequent release of CO<sub>2</sub>. Changing redox conditions indirectly influence the distribution of Ni. This shows the importance of a thorough understanding of the behaviour of Fe and Mn as Ni itself is not affected by redox reactions. The release of Ni from exchange sites down the soil-profile may be caused by an increase of competing ions as Mg and Ca as the total electrolyte concentration increases in the soil profile.

#### 2.4 Chromium

The percental distributions are in table 2 and figure 2.8

WR: There is a reverse relationship for Cr7 and Cr<sub>e</sub> (see figure 2.9). However there is much scatter. F5 and F7 constitute the main part of Cr<sub>e</sub>. F4 and F6 are present in smaller amounts. F1-3 play an inferior role. The samples from 1m have more Cr in F5 than the samples from 13m. The results coincide with literature values for selective extraction procedures (see later). Total Cr-concentrations are two to six times the values reported for average river suspended matter (MARTIN & MEYBECK, 1979). Samples from 1m contain slightly more Cr<sub>e</sub> than samples from 13m.

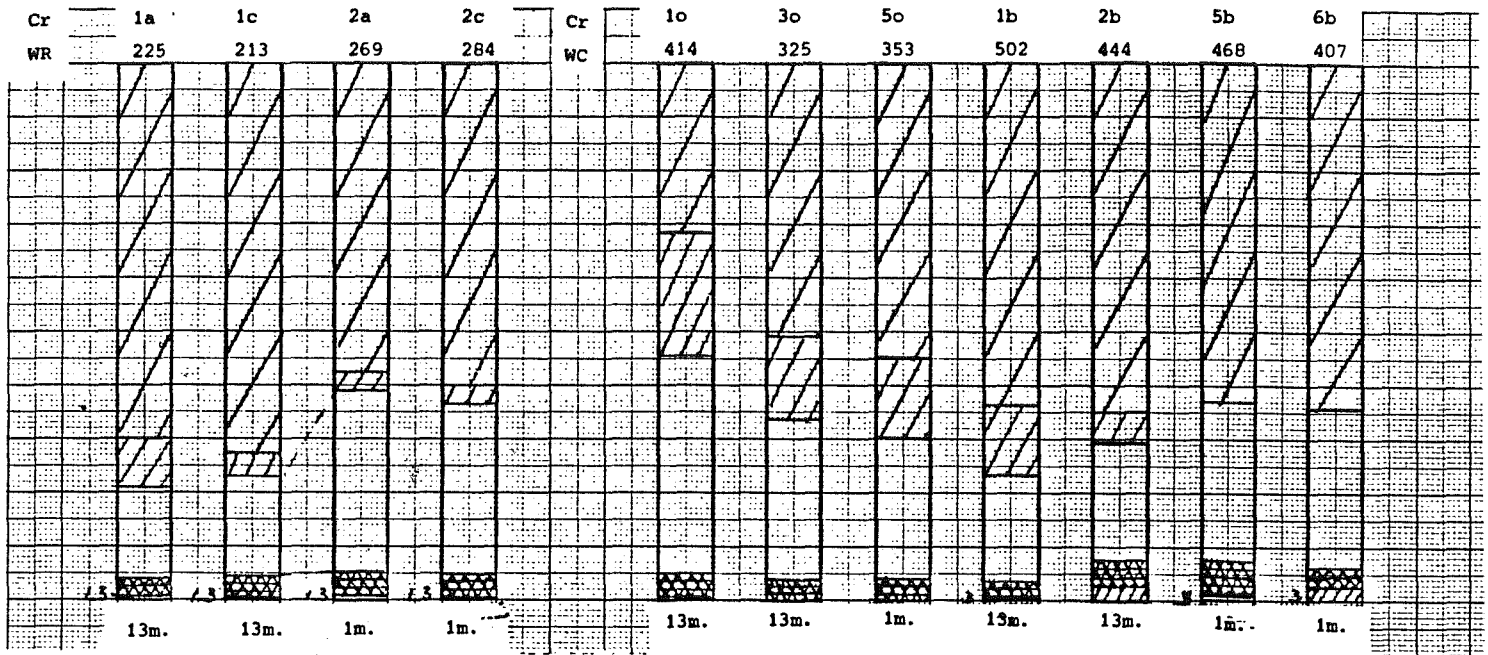


Figure 2.8 Percentual distribution of chromium or WR and WC samples

WC: The coarse samples have more Cr in F6 than the fine samples. F5 and F7 are greatest. F4 is small. F1-3 are absent. For the fine samples there is a difference between 1m- and 13-samples. Samples from 1m have no Cr in F6. F5 and F7 are greatest, F4 is small. Very little Cr is present in F3. The distributions of WR and WC are essentially the same although WC samples contain twice as much total Cr as WR samples.

So: Total Cr-concentrations decrease downwards in the soil-profile. Gr have Cr-concentrations which are background for sandy sediments (WEDEPDL,1978). On an average Gsu(i) contains slightly more Cr than Go, viz. 20 ppm. The distribution is essentially the same in Go, Gsu(i) and Gsu(ii). F7 is greatest followed by F5. F6 is clearly present. F4 is small, F1-3 are practically absent. The inverse relationship for Cr7 and Cr<sub>e</sub> is only vague, see table.

sample	Cr <sub>e</sub>	Cr7
WR,WC:200-250 ppm	219	71.0
250-300 ppm	276	58.5
300-500 ppm	416	56.1
So :200-300 ppm	258	57.7
100-200 ppm	180	64.2

Total Cr-concentrations are twice to four times background for fresh sediments (WEDEPDL,1978).



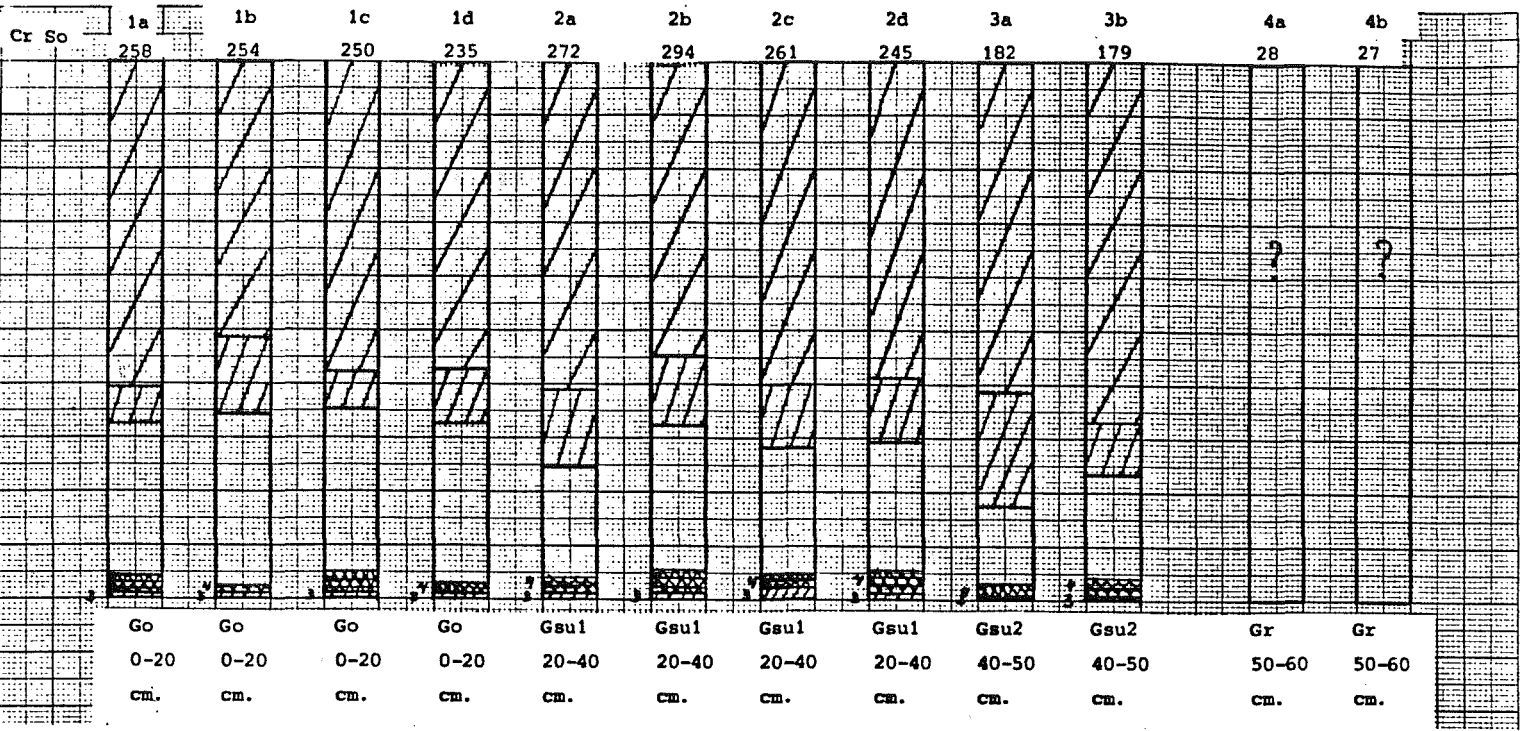


Figure 2.8 Percental distribution of chromium for So samples

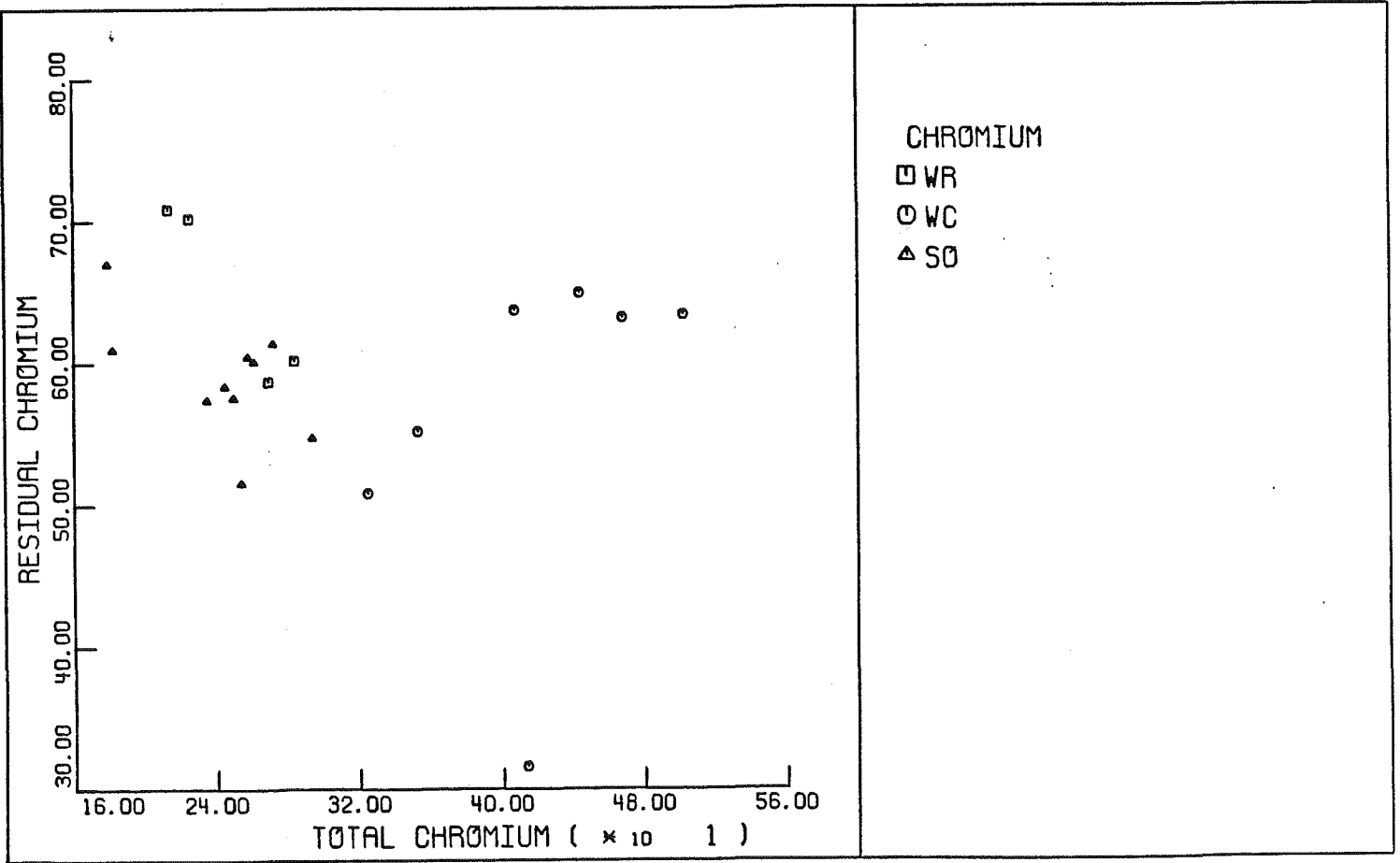


Figure 2.9 Scattergram of Cr7 - Cr6, y-axis in percent of total metal content, x-axis in ppm

## 2.4a Discussion

WR: Cr is mainly present in the residual fraction and F5. This is a frequently reported distribution for Cr ( e.g REUTHER et al.,1983; HONG & FOERSTNER,1983). As only little Cr is found in less stable fractions most Cr will be present as Cr(iii) which is very insoluble. Cr(iii) is easily scavenged by Fe-oxyhydroxides or is precipitated as Cr(OH)<sub>3</sub>. This compound is not leached by steps 4 and -5 as Cr(ii) is also insoluble. Besides Cr(OH)<sub>2</sub> dissociates because it is unstable. Cr has a high affinity for Fe-oxyhydroxides but is seldom found together with Mn. Its concentration in Mn-nodules is low compared to the concentrations for the other transition elements, e.g Co, Ni (CRONAN,1976). Mn and Cr behave differently as Mn(ii) -Mn in its reduced form- is soluble whereas Mn(iv) is not and Cr(iii) -Cr in its reduced form- is insoluble and Cr(vi) is soluble (MURRAY et al.,1983). Cr is not known to form insoluble sulphides. On the other hand Cr forms stable complexes with organic matter (KERNDORFF & SCHNITZER,1983; DOUGLAS et al.,1986). So Cr in F6 is readily explained by its association with organic matter. REUTHER et al. (1983) and HONG & FOERSTNER (1983) observed up to 20 % of Cr<sub>e</sub> in F6.

The ionic radius of Cr(iii) allows partial incorporation in carbonates but not much because of its trivalent state (Cr(iii)= 0.63 Å). Cr(vi) will not incorporate (Cr(vi)= 0.52 Å). The high amount of total Cr points to pollution, see also WC.

WC: Again F6 is very great. As Cr does not easily form insoluble sulphides most of the Cr present in this fraction is thought to be bound by organic matter produced by bacterial/algal activity. Part of it will be incorporated in Fe-sulphides. For the remainder the distribution is essentially the same as WR. The fine samples contain some Cr in F3 which might be associated with carbonates or amorphous Fe-Mn-oxyhydroxides due to lack of selectivity (TESSIER et al.,1979). The absence of F6 in the 1m-samples is striking. As yet no explanation is found. Some Cr was found in F6 but as the amount was less than five times the background signal the results were considered unreliable and assigned D.L, this is below detection limit.

So: The distribution of Cr remains unaffected throughout the soil-profile, also when S-samples are considered (qualitatively). Cr was already present as Cr(iii) so reduction processes did not affect the distribution of Cr. Moreover Cr is associated with relatively stable compounds with regard to redox-processes. Gsu(i) contains slightly more Cr<sub>e</sub> than Go. As the results of WR show that pollution has not yet come to an end two explanations remain. First the difference is probably not significant. Second, maybe Cr(vi) diffused towards Gsu(i) and was precipitated or adsorbed upon reduction to Cr(iii). Note the contrast with Mn-distribution (see also MURRAY et al.,1983).

WR-So: The distribution of Cr appears to be unaffected by deposition and subsequent change in physicochemical conditions. When Cr is added to the environment only part of it will enter unstable compounds like F3-6 depending mainly upon Eh (Cr(iii)-Cr(vi)). Because of its immobility in reducing systems (cf. U(iv)-U(vi) and V) Cr(iii) will be present as Cr(OH)<sub>3</sub> and be adsorbed onto Fe-oxyhydroxides.

### 2.5 Lead

The results of lead must be regarded with caution as lead is highly unreliable on both ICP and AAS and has a very high detection limit. The percental distributions are in table 2 and figure 2.10.

WR: There is hardly any difference between 1m- and 13m-samples. F4 is little greater at 1m. There is a remarkable amount of Pb in F7, accounting for some 60-70% of  $Pb_e$ . This does not coincide with most literature values for lead-distribution (SALOMONS & FOERSTNER, 1984; REUTHER et al., 1983; HONG & FOERSTNER, 1983). The inverse relation between  $Pb_7$  and  $Pb_e$  is vague (see figure (2.11)). F4 and F5 are about equal accounting for 8-18% of  $Pb_e$  each. F6 amounts to 4-7% of  $Pb_e$ , F1-3 are negligible. Total lead is higher than average background values for rivers (MARTIN & MEYBECK, 1979) although considerable scatter exists among these values. Total Pb is comparable with other polluted water systems like the Garonne and the Elbe.

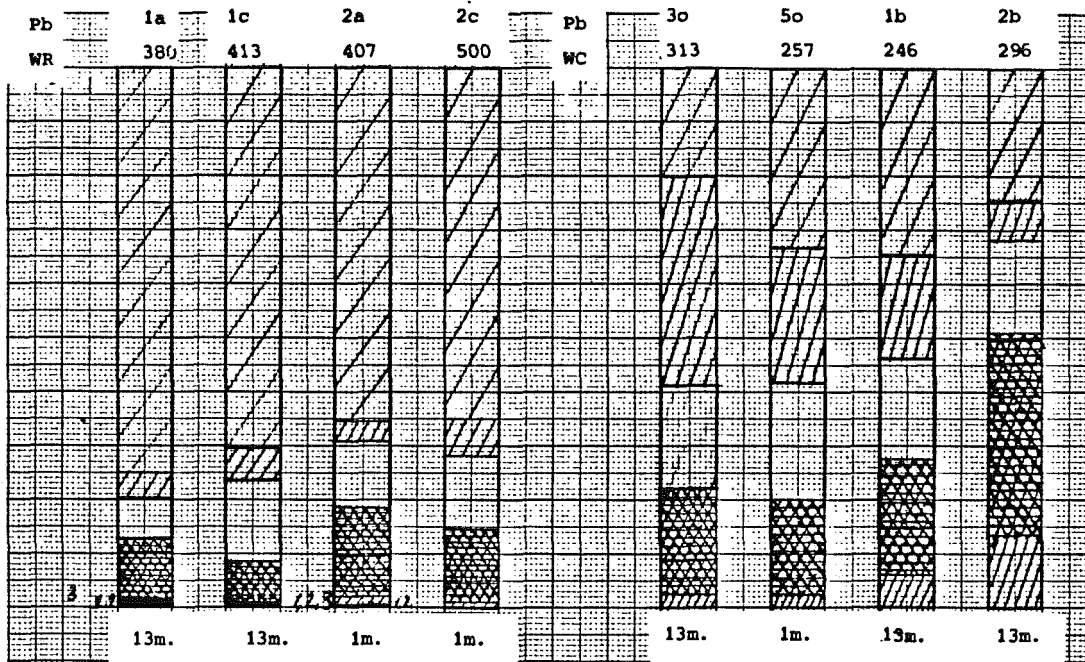


Figure 2.10 Percental distribution of lead or WR and WC samples

WC: The difference with WR is striking. F7 is much smaller. F6 is great for the coarse fraction as was seen for the other metals. F4-6 are about equal. F3 is smaller containing 3-12%  $Pb_e$ . F1 and F2 are absent. Total lead is above the average background value for rivers (MARTIN & MEYBECK, 1979).

So: Comparison between fourfolds and dupli is good. There is a very pronounced change in lead-distribution throughout the soil-profile.

Go: Most lead is present in F7 and F5, accounting for 25-30% of  $Pb_e$  each, followed by F4 (20%). F3 is small, 3-4% of  $Pb_e$ , F1 and F2 are absent. Total Pb content is above background values for sediments (WEDEPOHL, 1978).

Gsu(i): A very pronounced shift is observed. There is a dramatic increase in F3 at the cost of F5 and F6. F7 is somewhat smaller. F1 and F2 are absent.

Gsu(ii): F3 is greater than Gsu(i), so is F4. F5 decreases, F6 has disappeared!

Gr: Total lead is consistent with background values for sandy sediments (WEDEPOHL, 1978). Most lead is present in F7. This is consistent with the reverse relation between  $Pb_7$  and  $Pb_e$  and various literature values (e.g. TESSIER et al., 1979)

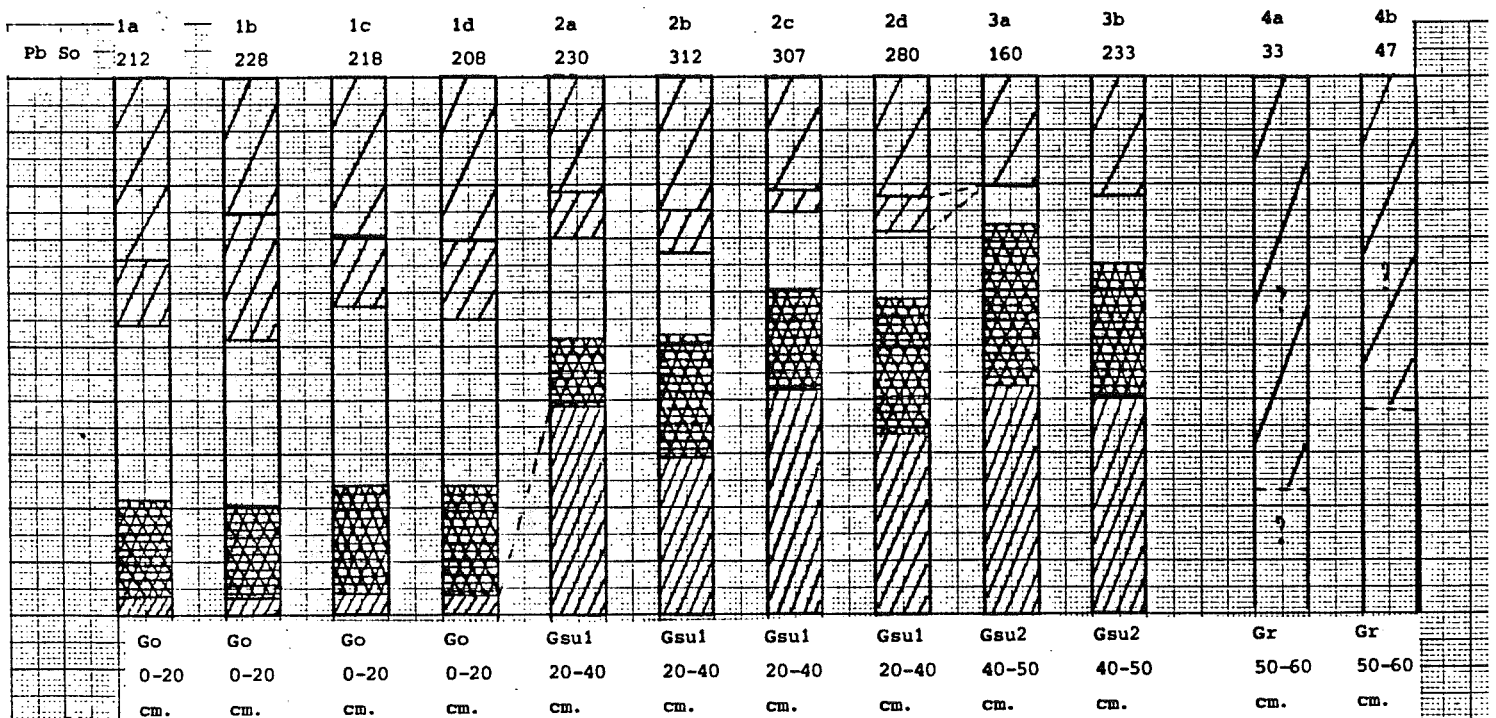


Figure 2.10 Percentual distribution of lead for So samples

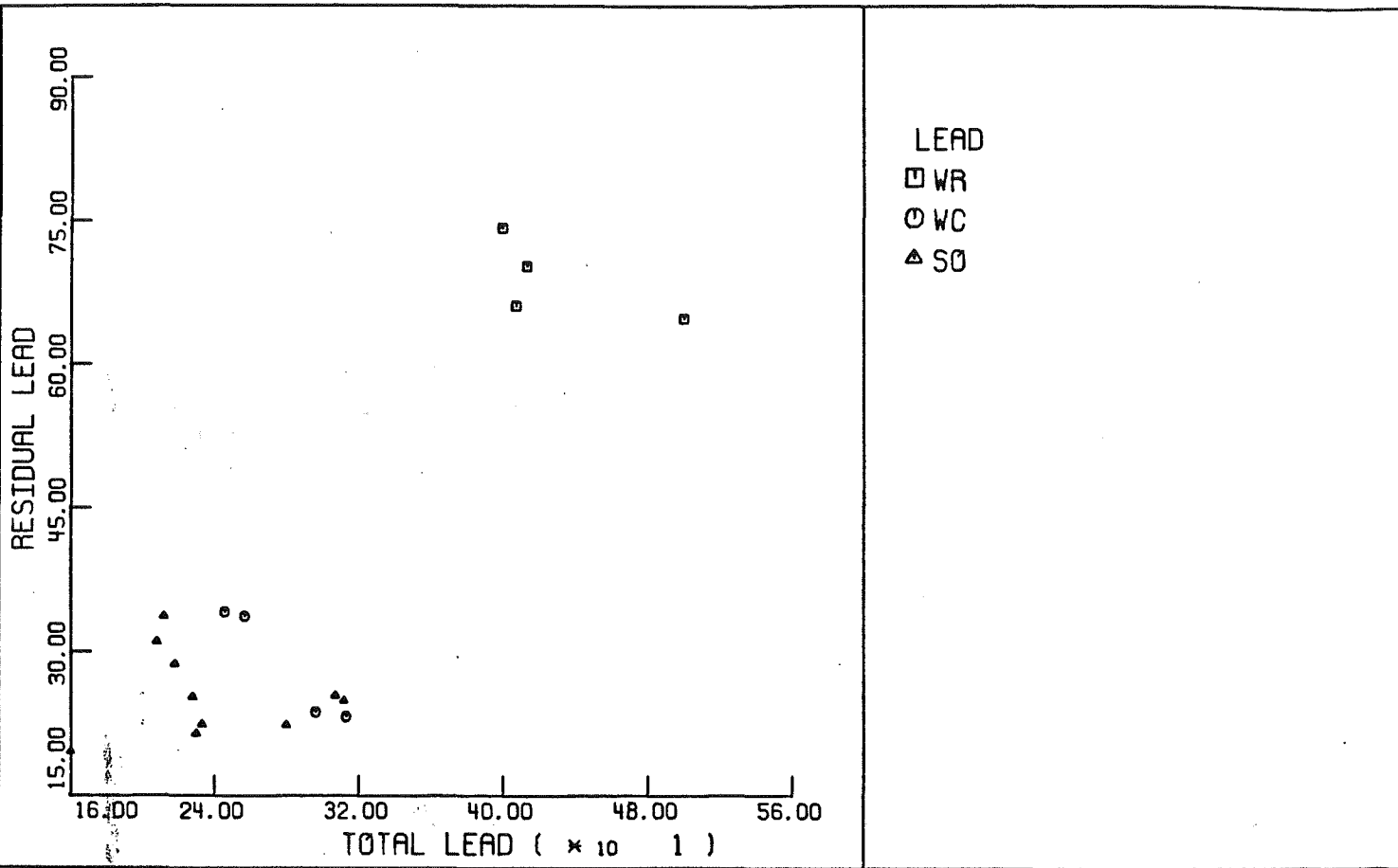


Figure 2.11 Scattergram of Pb<sub>7</sub> - Pb<sub>c</sub>, y-axis in percent of total metal content, x-axis in ppm

### 2.5a Discussion

WR: The great amount of Pb in F7 is striking when total lead content is considered. SALOMONS & FOERSTNER (1984) explain that dry fallout of atmospheric lead is mainly associated with F7 as it consists of (relatively inert) lead-oxides and -sulphates. However upon wet fallout most lead is thought to be bound by unstable compounds like F2, F3, F4 and F6. The remainder is adsorbed onto Fe-Mn-oxyhydroxides and a small part is present as sulphides or stable organo-lead complexes (KERNDORFF & SCHNITZER, 1980).

WC: The amount of lead in F6 was discussed with nickel. Most lead will be present as sulphides or coprecipitated with either amorphous Fe-sulphide or mackinawite. There is an increase in all the other fractions at the cost of F7. It is possible that because of the changing redox-conditions part of F7 was attacked. As with Pb in F3 most lead is present as Pb(ii) because of the present Eh. Whether lead will incorporate in Ca-carbonate or forms carbonates of its own (e.g PbCO<sub>3</sub>, cerrusite) is not known. Pb(ii) has a great ionic radius (1.20 Å) which may inhibit incorporation in Ca-carbonate.

So: Two processes affect the change in lead distribution from G6 to Gsu(i). First Mn is believed to be removed from F4 with as a result release of adsorbed Pb. Most lead will then be bound by sulphides. Probably the bigger part comes from sulphides which were oxidized during storage and are now present in carbonates. Precipitation as hydrous insoluble lead-carbonate is possible (PbCO<sub>3</sub>.nH<sub>2</sub>O)

In Gsu(ii) F6 has completely disappeared. Pb is mainly present in F3-5, this means adsorbed onto Fe-hydroxides and bound by carbonates.

## 2.6 COPPER

The percental distribution is in table 2 and figure 2.12. Figure 2.13 is a scattergram showing the relation between Cu<sub>7</sub> and Cu<sub>6</sub>.

WR: No difference between 1m and 13m is observed. Most Cu is present in F6 and F7. F4 follows with 15% of Cu<sub>6</sub>, F5 contributes another 10%. Compared with the other elements save Mn, F1-3 are big, especially F1. Total Cu is above average for rivers (MARTIN & MEYBECK, 1979).

WC: Again F6 is very big in the coarse samples. F5 and F7 are about equal in the coarse samples. For these samples F1-3 are negligible. In the fine samples Cu is equally distributed over F4, F5 and F7. F6 is small, F1-3 are bigger than for the coarse samples. However comparison between dupli is poor. There is much scatter. Total Cu is twice background for rivers (MARTIN & MEYBECK, 1979).

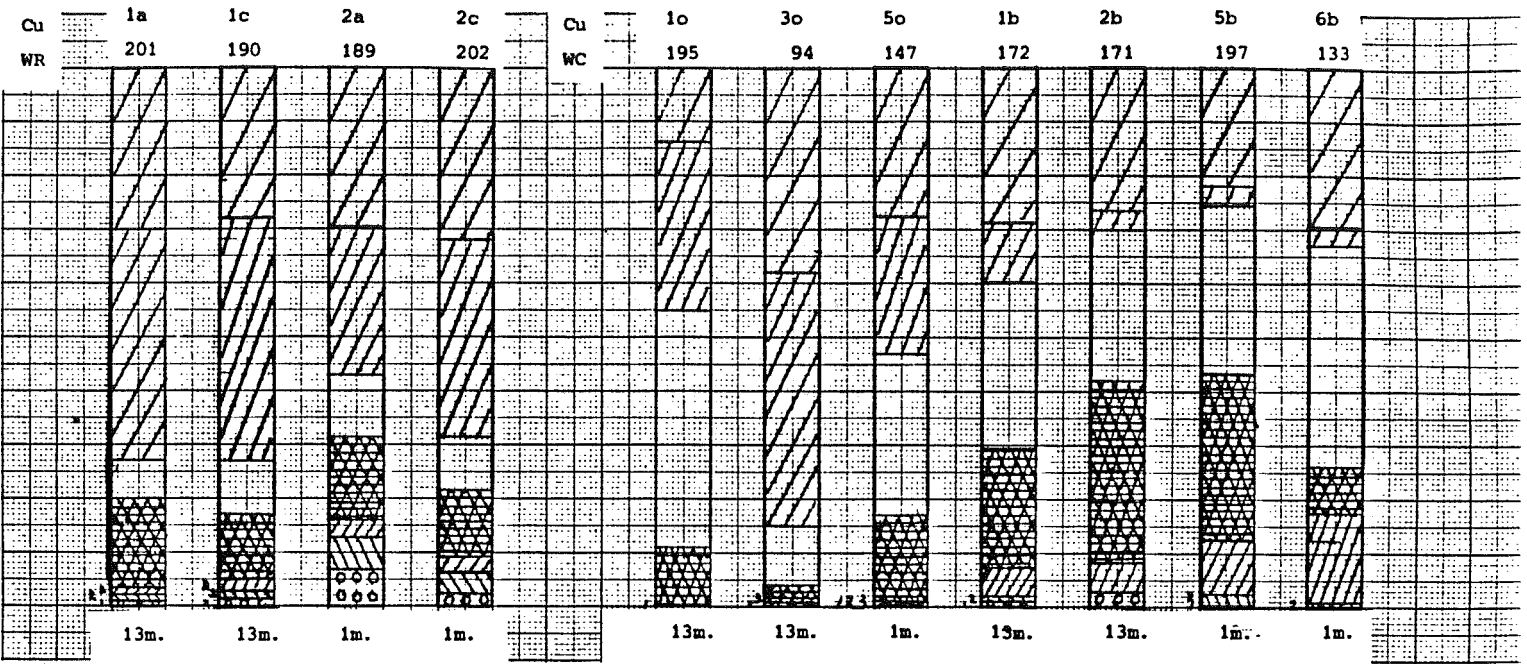


Figure 2.12 Percentual distribution of copper for WR and WC samples

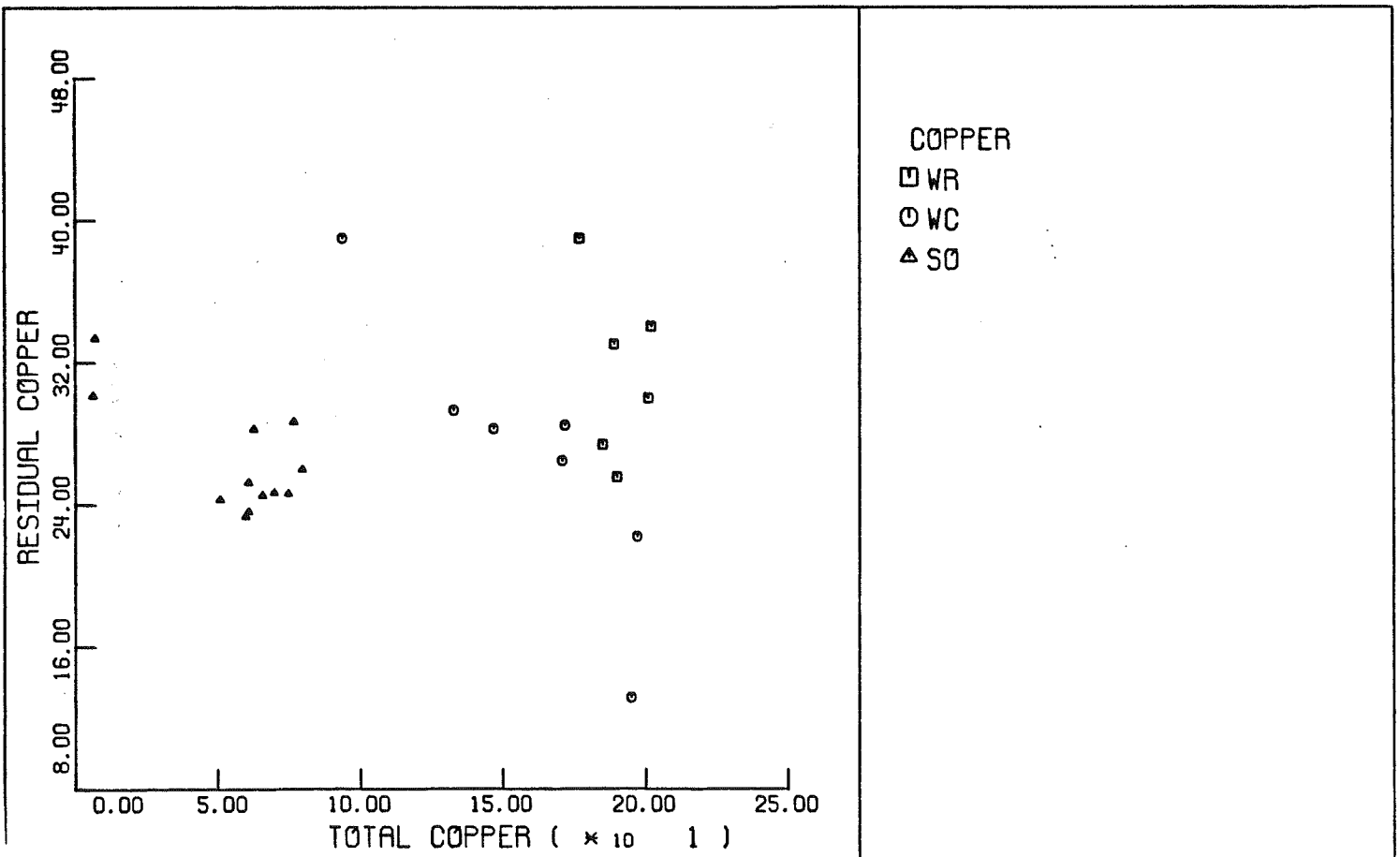


Figure 2.13 Scattergram of Cu7 - Cu6, y-axis in percent of total metal content, x-axis in ppm

S: Much copper is found in F6 in Gsu(i) and Gsu(ii).

So: The distribution is essentially the same for all horizons. F6 has completely disappeared! Cu is known both for its insoluble sulphides and for its high affinity with organic matter (vide infra). Most Cu is present in F5. Various investigators find much Cu in F5 (TESSIER et al., 1982; HONG & FDERSTNER, 1983 and many others). F5 accounts for 40-50% of Cu<sub>t</sub>. F7, F4 and F3 make up the rest, resp. 25%, 20% and 15% of Cu<sub>t</sub>. F2 is present in Gsu(i) for 2%. F1 is absent. Gsu(i) contains slightly more copper than G0. Copper in G0-Gsu(ii) are above average for sediments, Gr is consistent with background values for sandy sediments (WEDEPDHL, 1978). It appears that the suspended matter is more polluted with copper than the sediment. The difference in S and So shows the importance of careful sample treatment. The same was observed for Pb, Fe and Zn (vide infra).

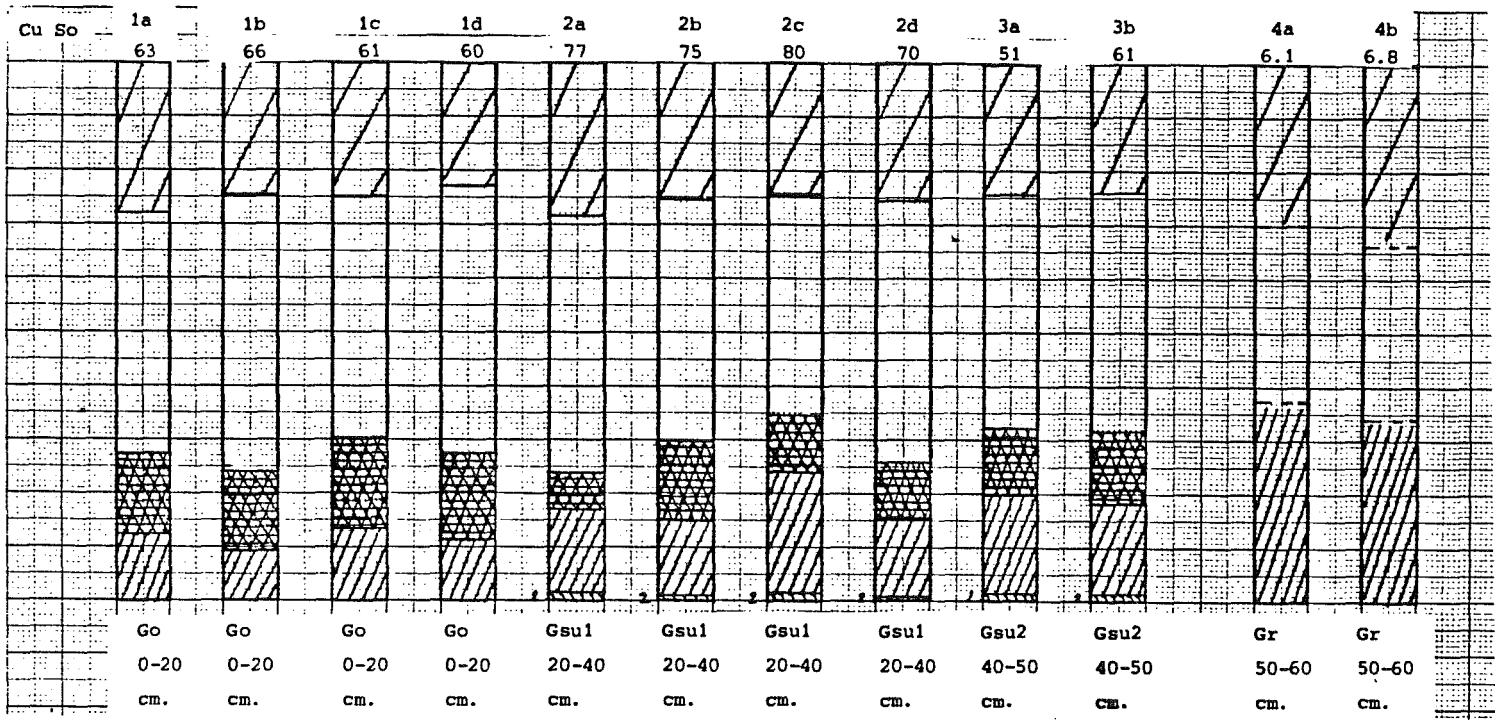


Figure 2.12 Percentual distribution of copper or So samples



## 2.6a Discussion

WR: No difference between 1m and 13m was observed in contrast with e.g. Mn and Fe. Cu is mainly present in F6 which means sulphidic copper and organically bound copper. As the Eh is too high for sulphate-reduction most Cu is present as organo-metal complexes. Some sulphate-reduction might occur in partially reduced suspended matter nodules or -flocs. Cu is well known to form both soluble and stable insoluble organo-copper complexes (KERNDORFF & SCHNITZER, 1980; DAVIS & LECKIE, 1978; DAVIS, 1984; SOHN & HUGHES, 1981 and others). Much copper is loosely bound on exchange sites, carbonates or soluble organic complexes pointing strongly to pollution. The distribution of copper is consistent with literature (HONG & FOERSTNER, 1983; SALOMONS & FOERSTNER, 1984; SCHUMANN et al., 1981 and many others).

WC: F6 can be compared with the other elements (see nickel). Part of the copper will be present in sulphidic form, part as insoluble organo-copper complexes. Probably the amount of copper in F6 keeps F1-3 low which is not the case for the fine samples. Copper sulphide precipitation will determine the solubility of copper.

So: The results clearly show the effect of oxidation. F6 has completely disappeared upon oxidation. As copper is believed to be partially bound by organic matter this fraction must have decomposed during storage. However for all other elements F6 was found so this remains an open question.

F7, F3, F4 and especially F5 are important. There is some copper in F2. This distribution is consistent with literature for copper in oxidizing sediments. Most copper is adsorbed onto Fe-Mn-oxyhydroxides.

In contrast with S-samples no copper was found in F1. Probably all organic matter was decomposed during storage. Upon oxidation Cu-ions came into solution of which part is bound on exchange sites and part is bound by carbonates or adsorbed onto Fe-Mn-oxyhydroxides. Some diffusion of copper towards Gsu(i) might have occurred. It is striking that the suspended matter samples contain much more copper than the sediment samples. It is possible that remobilization from the sediment has occurred as observed by various investigators (e.g. FLETCHER & HOLMES, 1983; WINDOM et al., 1983).

Total copper concentrations are two to three times background which is an indication of pollution, considering the distribution of Cu.

### 2.7 Zinc

The percental distribution s are in table 2 and figure 2.14.

WR: Scatter is too great to show significant differences between 1m and 13m. Total zinc (see also WC) is very high, between 400-1100 ppm. This is much more than the values for rivers as obtained by MARTIN & MEYBECK (1979). The concentrations can be compared with the highly polluted Garonne river: 90-800 ppm. Values are lower than the Rotterdam harbour (up to 3000 ppm). Most Zn is present in F4 (30-40%). F3 and F7 account for some 20% each, followed by F5, F6 and F2. F1 is absent. Most Zn is transported in unstable compounds like Fe-Mn-oxyhydroxides, carbonates and exchange sites.

WC: As for all the other elements F6 is much greater for the coarse samples. There are some differences between fine and coarse samples. In the coarse samples F5 and F6 are greatest with a small F2 and F3. The reverse holds good for the fine samples. F1 is absent. The results bear similarity to the distribution of copper. Comparison of dupli is moderate.

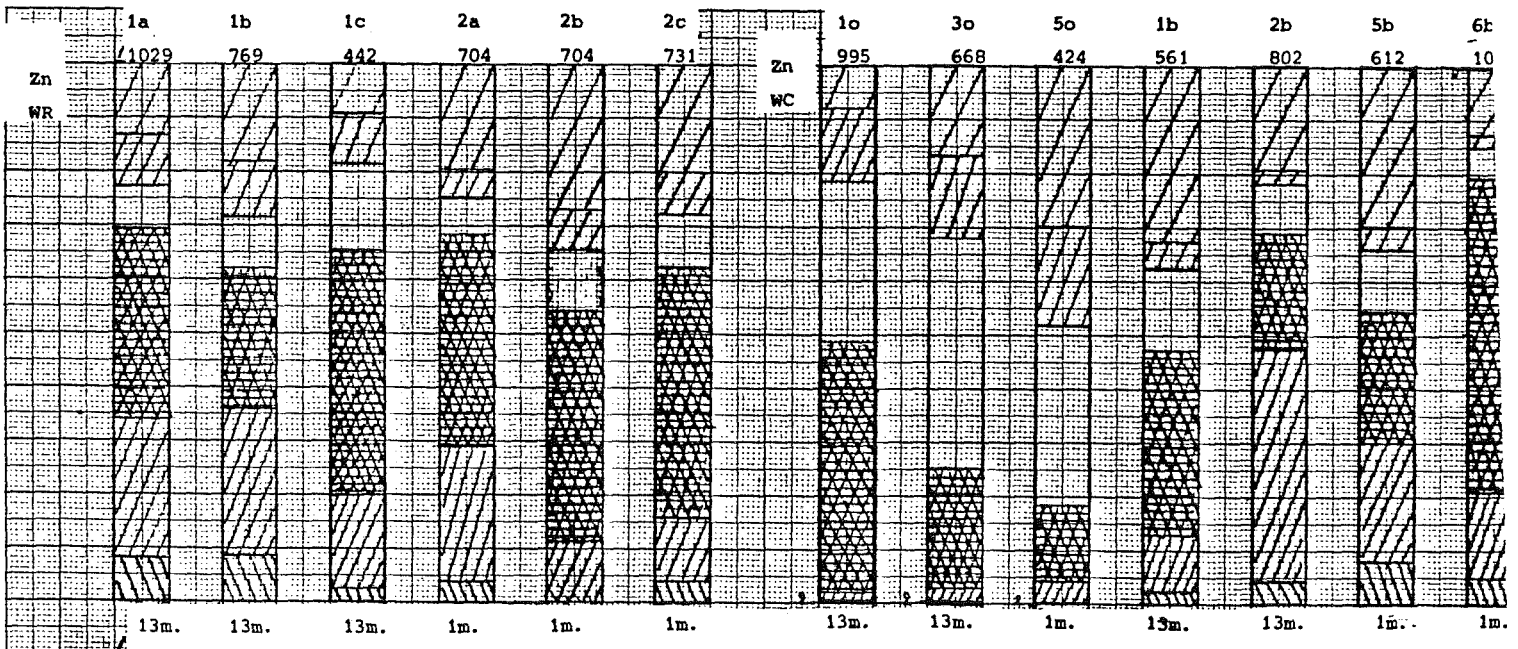


Figure 2.14a Percental distribution of zinc for WR and WC samples

S: When going from G<sub>0</sub> to G<sub>su(i)</sub> F<sub>6</sub> increases at the cost of F<sub>4</sub> and F<sub>3</sub>.

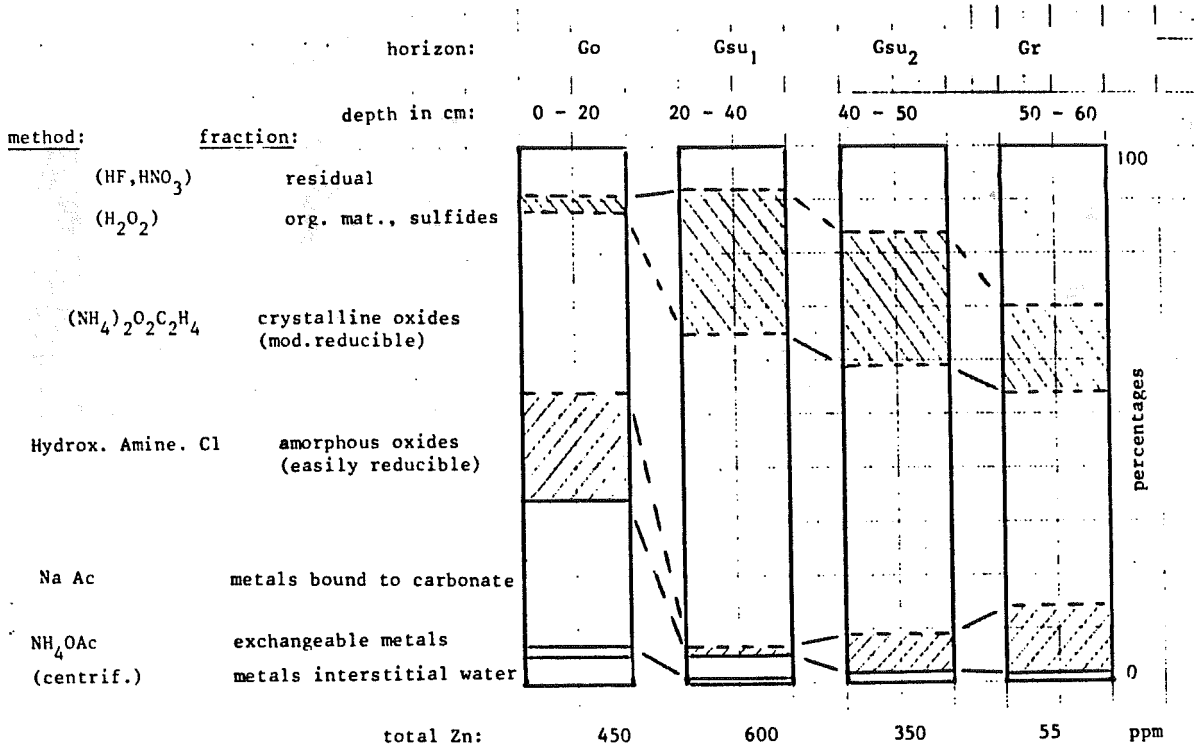


Figure 2.14b Percental distribution of zinc for S-samples

S<sub>0</sub>: The distribution remains almost constant with depth in contrast with the original reduced samples (see S). From G<sub>0</sub> to G<sub>su(i)</sub> there is a slight decrease of F<sub>4</sub> and F<sub>5</sub> with a concomitant increase in F<sub>3</sub>. Zn is evenly distributed over F<sub>3</sub>, F<sub>4</sub>, F<sub>5</sub> and F<sub>7</sub>. The reverse relation between Zn<sub>7</sub> and Zn<sub>e</sub> is very vague if not absent for S<sub>0</sub>-samples (see figure 2.15). This is shown by Gr. F<sub>7</sub> is very small for samples with total Zn only slightly above background values. F<sub>2</sub> is very big. The distribution looks much like the other horizons. Total Zn for the first three horizons is much higher than average (WEDEFOHL, 1978).

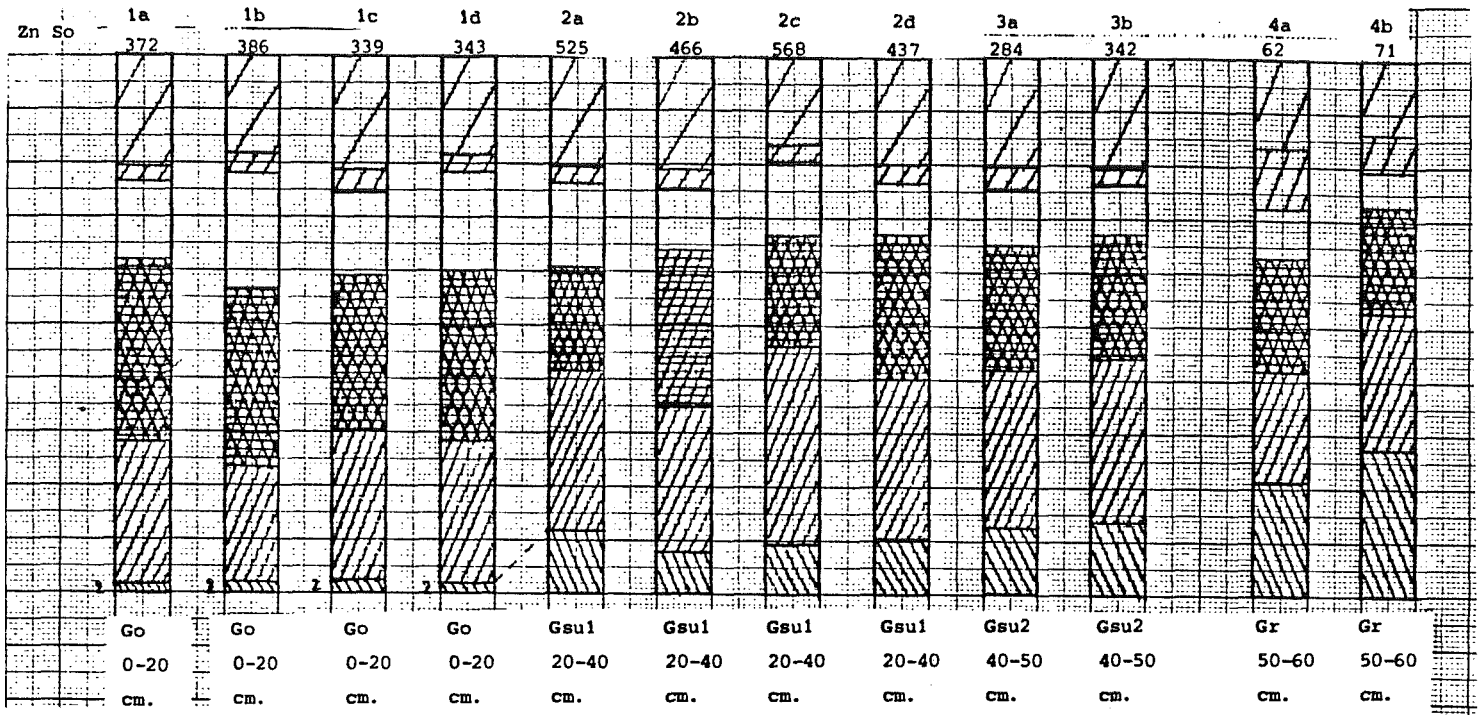


Figure 2.14a Percental distribution of zinc for So samples

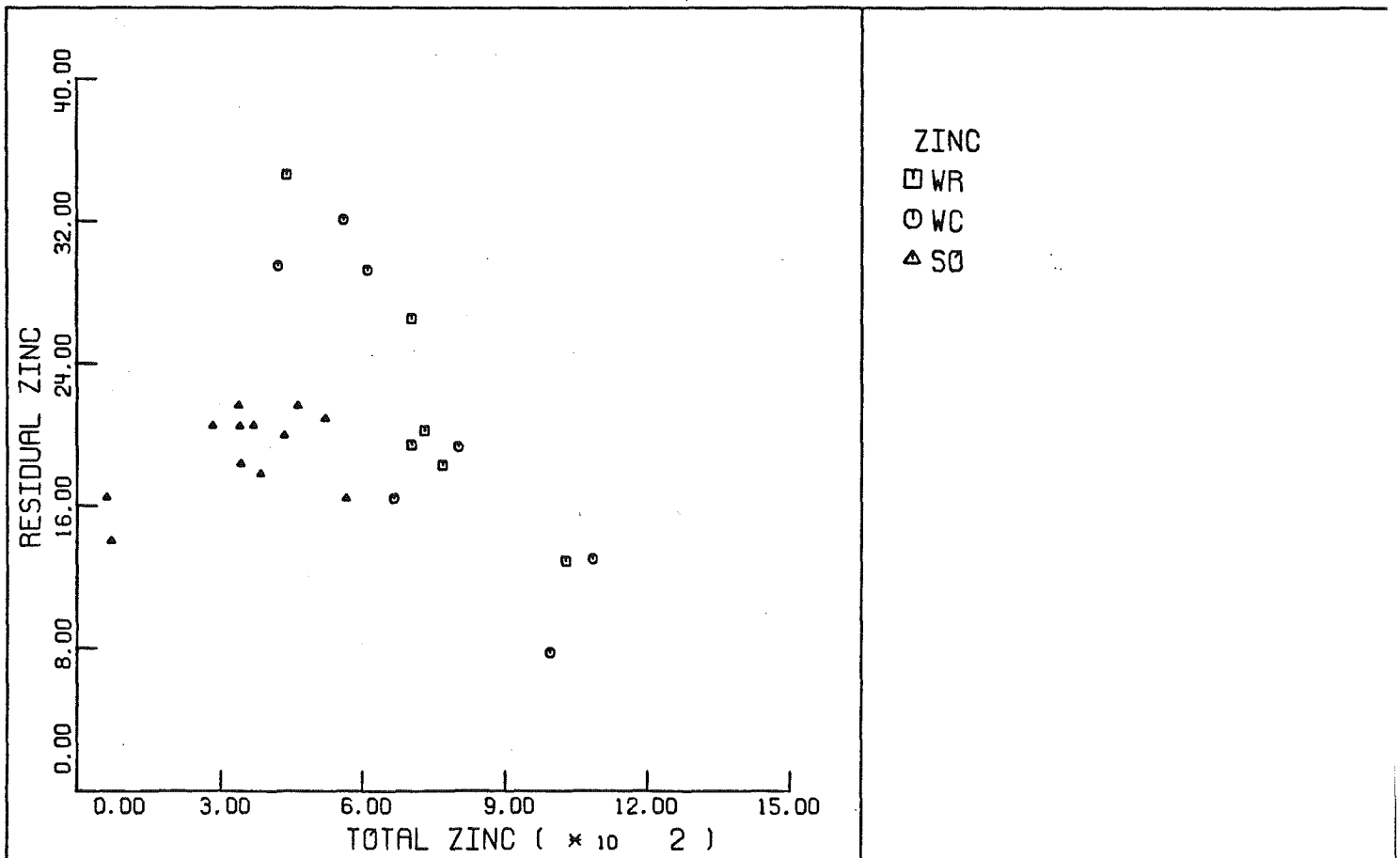


Figure 2.15 Scattergram of Zn7 - Zn<sub>e</sub>, y-axis in percent of total metal content, x-axis in ppm

## 2.7a Discussion

WR: Much Zn is loosely bound. Together with the high total metal concentrations pollution is likely. Zn is known for its adsorption onto Mn-oxyhydroxides and carbonates (FOERSTNER et al., 1979 and any others) so the distribution does not contradict literature.

WC: Upon reduction of sulphates much zinc is incorporated in sulphides resulting in an increase in F6. Like Cu F1-3 are kept low. F5 is rather big. More Zn in F4 was expected. No explanation for this is found.

S-So: Reduction affects the distribution of zinc. Oxides are reduced and much zinc is incorporated in sulphides. When the sediment is oxidized most sulphides were oxidized again resulting in adsorption onto Fe-Mn-oxyhydroxides and (co)precipitation in carbonates. F1 disappears, most Zn adsorbed on F4. When the sulphides are oxidized Zn comes in solution so F2 increases too.  
Gr: The distribution of Gr is puzzling. Background values are lower than Gr but not much. It is not clear why so much Zn is present in unstable fractions. TESSIER et al. 1979 found more zinc in F7 for relatively unpolluted sediments.

Both Cu and Zn show a downward increase in total metal concentration. As pollution probably still continues (WR and WC) another explanation must be sought. Diffusion to  $G_{su}(i)$  by means of a concentration gradient is a possibility as porewater concentrations in  $G_o$  will be higher than in  $G_{su}(i)$ , because Zn-sulphides are very insoluble.

## 2.8 Cadmium and Cobalt

### 2.8a Results and Discussion

The results are in table 2 and table 3. The percental distribution for Cd is in figure 2.16.

Cd: Only very little cadmium data are present because of the method used. The detection limit for ICP and AAS is too high for the samples of this study. Cd appears to be controlled by F3 and F4. It is clear however that both the Western-Scheldt waters and Saeftinge are heavily polluted. WR samples show this pollution has not yet come to an end (some samples contain 20 ppm).

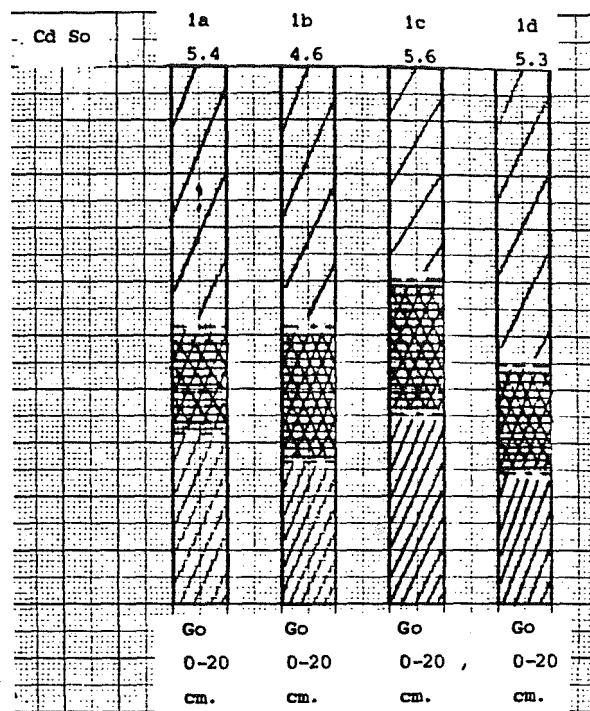
Co: Co mostly goes with manganese. This can be seen from So. Samples 1a-1d have most Co in F4. When Mn is dissolved Co goes to F3 (and F6, but this fraction is oxidized). The results are consistent with literature values for oxidizing sediments. Co has a moderate affinity for organic matter (KERNDORFF & SCHNITZER, 1980). The results indicate anthropogenic influence.

Figure 2.16 Percental distribution of cadmium for So-samples

Table 1.2.

Results for Cobalt, samples from So. All results are in ppm.  
- means d.l., below detection limit.

	Co1	Co2	Co3	Co4	Co5	Co6	Co7	Cot	Co8
1	-	-	-	7.14	-	-	7.58	14.72	16.53
2	-	-	-	6.84	-	-	6.62	13.46	18.95
3	-	-	-	7.26	-	0.9	9.40	17.56	19.37
4	-	-	-	6.48	-	0.9	8.96	16.34	18.60
5	-	-	6.7	4.9	-	-	9.39	20.99	18.23
6	-	-	2.3	-	-	2.7	11.21	16.21	17.12
7	-	-	5.2	-	-	1.8	8.82	15.82	15.20
8	-	-	3.0	-	-	-	11.43	14.43	14.46
9	-	-	3.2	-	-	-	6.90	10.10	6.64
10	-	-	1.9	-	-	-	6.90	8.80	18.10
17	-	-	-	-	-	-	1.7	-	1.7
18	-	-	-	-	-	-	1.1	-	-



### 2.9 Water concentrations

Table 3 shows the results of the unfiltered water concentrations. Most metals are present in very small concentrations. The major elements clearly show the concentration difference of the salt wedge between the samples. Most metals will not be in true solution but be adsorbed on suspended matter.

Table 3. Results of the unacidified watersamples of the Western Scheldt. All values are in ppm.

A.c. stands for after centrifuging, b.c. stands for before centrifuging of the water.

	Sr	Pb	Cd	Co	H3BO3	Mn	Fe	PO4	SO4	Mg	H4SiO4	V	Na	Ca	Zn	Cu	Ni	Cr	K	Li
1m a.c.	1.94	d.l	0.02	0.00	7.03	0.12	0.18	18.83	908.1	292.3	11.67	0.03	2304	150.2	0.02	0.01	0.01	0.04	95.4	0.0
1m b.c.	1.94	0.1	0.01	0.02	7.00	0.04	0.36	20.97	903.5	294.0	11.80	0.03	2299	149.7	0.03	0.01	0.01	0.04	95.9	0.0
13m a.c.	2.26	d.l	0.025	0.01	8.32	0.06	0.04	17.58	1070	354.3	10.69	0.04	2766	163.0	0.01	0.01	0.02	0.05	112.3	0.0
13m b.c.	2.32	d.l	0.025	0.01	8.10	0.055	0.34	20.61	1002	356.6	11.36	0.04	2770	171.0	0.03	0.01	0.01	0.05	114.7	0.0

### 3 Comparison of the results

Most studies deal with many trace elements at the same time. A comparison is not always easy as the elements often show a different behaviour. Most of the elements under investigation are transition elements. As shown by this study most of the elements have different distributions. This can be explained in part by the difference in atomic structure. The transition elements have differently filled outer-shells (the "d"-shell) which causes a difference in stability with regard to chemical compounds (COTTON & WILKINSON, 1976). This is best shown by chromium and manganese. Both are (neighbour) transition elements but have an almost opposite chemical behaviour (MURRAY et al., 1983).

Of the elements under investigation Fe, Mn, Cr and Cu are most sensible to changing redox-conditions, whereas Zn and Ni are not influenced. As Fe and Mn determine to a large extent the distribution of the other trace elements so do changing redox-conditions.

Both Mn and Cr very rarely form insoluble sulphides in nature. Mn has a very low affinity for organic matter whereas Cr can form stable organo-metal complexes (KERNDORFF & SCHNITZER, 1980; DOUGLAS et al., 1986). This can be seen from figures (2.1) and (2.8) for Cr and Mn. Mn is hardly present in F6, Cr is present to some extent. FOERSTNER et al. (1979), REUTHER et al. (1981) and RAPIN & FOERSTNER (1983) observed a similar behaviour. Most elements are found in F6 which has disappeared upon oxidation during storage (cf. S and So).

Mn and Co show similar behaviour as predicted by literature (see Co). However some Co must be bound by sulphides. Most Co is associated with F4, Mn-Fe-oxyhydroxides.

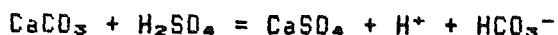
Of the elements under investigation Cr and Cu have the highest affinity for F5. This is consistent with literature, although no explanation is given. An explanation cannot be inferred from the results of this study.

The various elements react in a different way to sulphide oxidation. For Pb, Zn and Ni the increase is mainly found in F2 and F3, i.e. as carbonates or exchange sites (besides partial adsorption onto oxyhydroxides due to lack of selectivity of step 3). Co moves to F3, whereas Cu is mainly enriched in F5. This implies that copper is not fixed by exchange sites or carbonates but rather adsorbs onto Fe-oxyhydroxides.

The course of the various trace metals with depth in the soil profile is different. Cu, Pb, Cr and Zn slightly increase from G<sub>0</sub> to G<sub>su(i)</sub>. After this there is a small decrease from G<sub>su(i)</sub> to G<sub>su(ii)</sub> and a sharp decrease from G<sub>su</sub> to G<sub>r</sub>. Fe and Ni decrease steadily throughout the profile. In more respects Fe and Ni show similar behaviour. Ni has a low affinity for organo metal complexes (KERNDORFF & SCHNITZER, 1980). Mn shows a sharp decrease from G<sub>0</sub> to G<sub>su(i)</sub> followed by a gentle decrease downwards. As for Cr, Cu, Pb and Zn it is not likely that pollution has stopped. This is shown by the results of WR and WC. It is more likely that diffusion plays an important role. For Fe and Mn the diffusion is upwards as their sulphides (especially for Mn) are more soluble than their oxyhydroxides.

It cannot be said that total metal content is a good measure for pollution (e.g FOERSTNER et al., 1979). The speciation of a metal is important. F<sub>7</sub> is inert and not available for flora and fauna. F<sub>1-4</sub> are thought to be easily available upon changing physicochemical conditions. F<sub>6</sub> is only available after oxidation (e.g as a result of reclamation). When these conditions change metals can be released by the fraction which is attacked but often they are scavenged by another fraction. This has happened in this study as the metals do not show a sharp decrease from G<sub>0</sub> to G<sub>su(i)</sub>. Only Mn is practically lost from the G<sub>su(i)</sub> horizon and only partially reprecipitated in G<sub>0</sub>. Most metals show a shift from one fraction to another.

For instance upon oxidation Fe-sulphides will go in solution but the metals will be scavenged by Fe-oxyhydroxides as shown by the difference between S and S<sub>0</sub>. Upon reduction Mn-oxides disappear but most metals readsorb onto Fe-oxyhydroxides or are bound by exchange sites or carbonates. However upon acidification (Cat-clays) when the pH drops to 2-3, F<sub>6</sub> dissolves but also F<sub>4</sub> and F<sub>5</sub> will disappear because of the low pH. This is a situation which might cause danger to the environment. However in this case there is little chance this will happen as the sediment contains too much lime for the formation of catclays. Upon oxidation the released sulfuric acid will react with calcium-carbonate and form gypsum:



It can be concluded that while the system remains reduced no significant amounts of trace metals come in solution. This is supported by a study of BAARS et al. (1986) who showed that sheep from Saeftinge were not infected by trace metals. Sheep are known to be very sensitive to copper.



#### 4 Literature review/comparison with other studies

A comparison of the results with other studies is not easy for several reasons:

- The extraction schemes vary widely.
- The elements under investigation vary widely. Ni and Cr have seldom been studied.
- Only recently the effects of artifacts during sample-treatment as a result of oxidation have been studied.
- There are great differences within one area. It has often been observed that metal speciation changes rapidly within the same water-system.

However some general observations must be mentioned.

F2 is mostly very small. Only for Mn and Cd up to 30% metal content has been observed (HONG & FOERSTNER, 1983; FOERSTNER et al., 1979; REUTHER et al., 1983). Up to 10% Zn was found in F2 for Rhine sediments which are extremely polluted (HONG & FOERSTNER, 1983). In this study Zn (13% in So), Mn (So, WR, S and WC) and Ni (WR) have considerable amounts in F2. Mn and Cu were present in some samples in greater amounts.

F3 plays an important role. This is (of course) dependent on the amount of carbonate present. This step is mostly not included in the extraction schemes. HONG & FOERSTNER (1983) find up to 25% Mn, Cu, Pb, Zn and Cd in F3. FOERSTNER et al (1979) find great amounts of Mn, Cu and Zn in F3 (up to 40%). In this study especially So-samples are important for F3, Zn, Pb and Mn (43% Pb in 6su(i)). Only Cr is hardly present in F3. The amount of Cr in S-samples cannot be explained and is thought to be a result of analytical errors.

F4. The importance of Mn- and amorphous Fe-oxyhydroxides as a scavenger of trace elements is well recognized. Only Cr is scarcely present in F4 in accordance with MURRAY et al (1983).

F5. The same holds good for F5. Zn is usually poorly present in

F5. Cr, Fe Pb and Cu are known for their presence in F5 (FOERSTNER et al., 1979 and many others).

F6. This fraction is most difficult for a good comparison. When no precautions are undertaken to prevent oxidation the importance of this fraction might be gravely underestimated. Furthermore sulphides and organic matter are not separated by this step. Literature values vary widely. Except manganese all metals are found in this fraction although for Fe the percentage is mostly much smaller than F5 and F7.

Ni, Zn, Cu, Co, Pb, Cd and Fe are readily precipitated as sulphide formation or are coprecipitated with Fe-sulphides. This is mostly the only way for Mn to be bound by sulphides (BO et al., 1982 -Cu and Fe-; KREMLING, 1983; JACOBUS et al. CARIGNAN & NRIAGU, 1985; DAVIES-COLLEY et al., 1986).

Cu, Cr, Pb and Fe (Ni and Zn to a much lesser extent) are known to form stable organo-metal complexes (KERNDORFF & SCHNITZER, 1980). Especially copper has been studied intensively (DAVIS, 1984; DAVIS & LECKIE, 1978; SOHN & HUGHES, 1981; RASPOR et al., 1984; MILLS & QUINN, 1984; DOUGLAS et al., 1986).

Only WR will be dealt with as it was the only sample treated under a nitrogen atmosphere. S-samples will be viewed qualitatively. Cu is present up to 45% in accordance with literature. Zn, Pb and Cr had 10-15% in F6. Fe, Mn and Ni were not found in F6. Results from S show that most metals are present in F6, especially Zn and Cu. Up to 0.8% pyrite was present (table 1.1.b). Ni, Mn and Cr are hardly present in F6. The difference between WR and S is that WR is probably determined by organic matter whereas sulphides are the most important part in S.

RAPIN et al. (1986), RECKE & FÖRSTNER (1985) and KERSTEN et al. (1985) studied possible artifacts as a result of oxidation during sample treatment. Their results are unanimously the same, viz. that oxidation severely alters the distribution of the trace metals.

Many studies have been performed to investigate the fate of trace metals both in solution and bound by suspended matter when riverwater comes in contact with seawater. It is stunning how the results differ from each other.

-flocculation as a result of increasing electrolyte concentration (SHOLKOVITZ, 1976; ECKERT & SHOLKOVITZ, 1976; SHOLKOVITZ, 1978 and many others).

-formation of flocs in the silt fraction by glueing action of dissolved organic matter, faecal pellets etc. Little salt flocculation was observed (EISMA, 1986).

-desorption from suspended particulate matter (VAN DER WEYDEN et al., 1977; DUINKER & NOLTING, 1978).

-both processes (?)

For a good understanding of the behaviour of trace metals it is important that these processes be well understood in the area of investment. ZUUR (1954) observed that the fraction 2-20  $\mu\text{m}$  is relatively enriched in estuarine sediments compared to the fraction smaller than 2  $\mu\text{m}$ . Deposition of small particles with a low density as a result of flocculation will not occur as the system is too dynamic in the Western-Scheldt estuary (current- and wave-action). Sedimentation appears to be restricted to salt marshes in the case of fine clays.

Many investigators studied fluxes of metals to the watercolumn from reduced sediments (FLETCHER & HOLMES; WINDOM et al., 1983; TRAMONTANO & BOHLER, 1984; HIRST & ASTON, 1983; HINES, 1984). In this study manganese is thought to be released to the watercolumn by diffusion from the G<sub>su</sub>(i) horizon. Mn-oxidation is too slow to lay down all Mn(ii) in the G<sub>o</sub> horizon. Besides in summer the G<sub>o</sub> horizon will only be a few centimeters thick so also some Fe and Cu will diffuse into the watercolumn. In the oxidated water Fe is rapidly precipitated as Fe(iii)oxyhydroxides or just like Cu and Mn be adsorbed onto suspended matter and taken out of the estuary.

## 5 Conclusions

No conclusion will be drawn regarding the change in speciation upon deposition in an (an)aerobic environment. This is because of the seasonal difference between both samples. As stated before the composition of suspended matter in May is probably not representative for the sedimentation in february. Besides the oxidized layer in the soil moves up and down during the seasons for probably more than 40 cm.

Another reason is that the samples from Saeftinge reduced cannot be regarded quantitatively. The reduced samples and not the oxidized samples are considered representative for the environment of deposition.

Both for the suspended matter samples and for the soil profile it can be concluded that:

Carbonates and especially Fe- and Mn-oxyhydroxides are effective scavengers for trace metals. F1 and F2 are easily available for the flora and fauna but are mostly small. In case of very polluted samples their importance might be greater. The importance of F6 is great save for Mn (and to a lesser extent Cr). However this fraction must not be overestimated. F4 and F5 are mostly far more important save for reduced samples where F6 can compete with F4 and F5.

As stated before F6 is very difficult because of artifacts (This study; RECKE & FOERSTNER,1985; RAPIN et al,1986). Second this fraction is poorly defined as no distinction can be made between organic matter and sulphides (FOERSTNER et al.,1980). Third the method itself is not very selective even when extraction under an inert atmosphere has been performed (This study, RECKE & FOERSTNER,1985).

The influence of soil development is very clear. Both redox processes in general and the strong reduction in Mn-compounds as a result of reducing conditions severely affect metal speciation. Upon disappearance of manganese, sulphides and carbonates appear to take over the role of metal scavengers.

The Gr-horizon probably reflects a relatively unpolluted sediment layer with metal contents only little above natural background values (WEDEPOHL,1978).

There is a slight but probably significant difference between samples from 1m and samples from 13m. The difference between 1m and 13m for WC-samples is overshadowed by the difference between fine and coarse samples, which in itself is probably affected by reduction during storage.

Most metals are enriched because of pollution. This can be inferred from the high amount of total metal concentration combined with a low F7 (see the results). The results indicate that pollution has not yet come to an end. Especially Cd and are still added in great amounts to the Scheldt river.

Speciation is important to say something about the risks for environment. Most metals show a reverse relation of F7 with the metal content.

Oxidation results in a change in trace metal speciation. Reducing samples must be treated under an inert atmosphere like nitrogen or argon.

When the water is reduced samples must be taken by  $N_2$ -filtration or centrifugation under an inert atmosphere. Centrifugation yields much more sample than filtration. The results show that there is a difference between various parts of the centrifuge tube.

The samples must be treated as soon as possible as shown by the coarse samples from WC. One is dissuaded to take too many samples and store them until treatment. When step 1 is included the samples must be quickly analysed even when they are acidified. Samples WRF1, WCF1 and SoF1 contain a lot of nutrients which led to algal growth although the samples were acidified to pH 0.5 and stored at 2 °C.

## 6 Recommendations

The method is tedious and full of bottle-necks. An eight-step extraction procedure must be avoided when dealing with routine analyses as it is very time-consuming. A shorter procedure should be used when dealing with many samples as it does not yield much more information because of the introduction of analytical errors. More information is needed to quantitatively explain the results. Such data include in situ (!) Eh-measurements, pH-measurements (both present at WR and WC), characterization of humic matter, dissolved organic matter content, reliable porewater measurements (obtained by either direct centrifugation at 10,000 rpm under nitrogen or dialysis -CARIGNAN et al., 1985). XRD-measurements for mineral determination and as a check to establish what minerals are attacked by the several extraction steps.

Seasonal influence is very great. The Gsu moves up and down with the seasons. This can influence remobilization and distribution of trace metals (see above).

It is necessary to think about the sample locations especially with regard to the first 5% rise in salinity as flocculation is thought to be complete in this zone (SHOLKOVITZ, 1976 and many others).

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Table 1.1 texture, lime- and organic carboncontent of S<sup>o</sup>

	um: 210-2000	50-210	20-50	2-20	-2	%CaCO3	%Corg.
1	0.13	1.87	13.06	34.83	50.11	13.02	4.96
2	0.17	2.26	13.57	34.29	49.71	13.03	-
3	0.41	1.70	11.45	38.13	48.32	12.51	-
4	0.13	1.64	12.87	35.50	49.85	13.20	-
5	0.05	1.59	10.60	33.01	54.75	10.25	3.79
6	0.04	1.12	8.58	34.74	55.53	11.09	-
7	0.10	2.91	8.98	33.34	54.67	10.11	-
8	0.20	1.91	8.75	33.94	55.20	10.20	-
9	0.19	20.65	12.50	25.63	41.04	7.96	3.59
10	0.30	26.72	13.86	23.10	36.03	8.92	-
17	0.92	89.48	3.69	2.27	3.63	4.75	-
18	1.06	87.48	4.78	2.25	4.43	4.81	0.48

Table 1.1a texture, lime- and organic carboncontent of WC and WR

	um: 2000-50	50-20	20-2	2-0.5	- 0.5	%CaCO3	%Corg.
2-13m.	5.49	11.66	30.13	16.88	35.83	19.66	4.47
4- 1m.	1.43	9.99	32.41	18.63	37.54	18.47	4.94
1-6WR						13.90	

Table 1.1b sulfate-, pyrite- and total Fe-content of S<sup>o</sup> and WC

	ppm SO4	ppm FeS2	%Fet
1	1046	3899	5.13
5	2520	2476	3.87
10	5154	1700	3.12
18	903	1588	1.12
2-13m.	1601	9054	4.41
4- 1m.	642	8020	3.92

	Fe1	Fe2	Fe3	Fe4	Fe5
WR1a	d.1	d.1	345.00	5311.00	15638.00
WR1b	d.1	d.1	361.00	6990.00	11090.00
WR1c	d.1	d.1	378.00	4265.00	15902.00
WR2a	d.1	d.1	898.00	9011.00	13554.00
WR2b	d.1	14.30	1034.00	7588.00	15003.00
WR2c	d.1	64.80	1537.00	7435.00	13972.00

	Fe6	Fe7	FeT	Fe8
WR1a	2528.00	33110.00	56932.00	n.a
WR1b	2059.00	33324.00	53824.00	n.a
WR1c	2130.00	28767.00	51442.00	n.a
WR2a	2189.00	31504.00	57156.00	n.a
WR2b	2368.00	33147.00	59137.00	n.a
WR2c	2171.00	32840.00	57955.00	n.a

	Zn1	Zn2	Zn3	Zn4	Zn5
WR1a	d.1	83.20	266.00	365.00	80.00
WR1b	d.1	66.90	209.00	200.00	140.00
WR1c	d.1	10.60	78.00	201.00	72.00
WR2a	d.1	27.50	176.00	272.00	51.00
WR2b	d.1	d.1	79.00	304.00	84.00
WR2c	d.1	28.40	86.00	339.00	71.00

	Zn6	Zn7	ZnT	Zn8
WR1a	101.00	133.00	1029.00	n.a
WR1b	42.00	141.00	769.00	n.a
WR1c	66.00	153.00	442.00	n.a
WR2a	40.00	137.00	704.00	n.a
WR2b	52.00	167.00	704.00	n.a
WR2c	58.00	148.00	731.00	n.a

Table 1 Metal content of WR; Fe and Zn (ppm)

	Pb1	Pb2	Pb3	Pb4	Pb5
WR1a	.31	1.42	4.40	44.30	31.50
WR1b	d.1	d.1	d.1	62.00	48.00
WR1c	.60	.71	2.94	31.90	61.40
WR2a	.21	1.14	6.48	67.50	48.00
WR2b	d.1	d.1	d.1	45.00	57.00
WR2c	.18	.66	4.17	67.70	69.00
	Pb6	Pb7	PbT	Pb8	
WR1a	d.1	297.00	400.00	n.a	
WR1b	n.a	n.a	n.a	n.a	
WR1c	24.90	290.00	413.00	n.a	
WR2a	13.90	269.00	407.00	n.a	
WR2b	n.a	n.a	n.a	n.a	
WR2c	37.00	324.00	500.00	n.a	
	Cd1	Cd2	Cd3	Cd4	Cd5
WR1a	.09	.29	.70	2.86	d.1
WR1b	n.a	n.a	n.a	n.a	n.a
WR1c	.05	.04	.31	3.99	d.1
WR2a	d.1	.18	.80	4.82	d.1
WR2b	n.a	n.a	n.a	n.a	n.a
WR2c	.04	.02	.05	5.49	d.1
	Cd6	Cd7	CdT	Cd8	
WR1a	d.1	d.1	d.1	n.a	
WR1b	n.a	n.a	n.a	n.a	
WR1c	d.1	d.1	d.1	n.a	
WR2a	d.1	d.1	d.1	n.a	
WR2b	d.1	d.1	d.1	n.a	
WR2c	d.1	d.1	d.1	n.a	
	Mn1	Mn2	Mn3	Mn4	Mn5
WR1a	87.20	227.00	514.00	1055.00	144.00
WR1b	89.60	190.00	555.00	952.00	92.00
WR1c	63.70	157.00	333.00	749.00	141.00
WR2a	65.80	220.00	617.00	656.00	99.00
WR2b	53.50	189.00	449.00	537.00	103.00
WR2c	71.80	180.00	466.00	458.00	97.00
	Mn6	Mn7	MnT	Mn8	
WR1a	18.60	127.00	2174.00	n.a	
WR1b	14.10	125.00	2018.00	n.a	
WR1c	12.00	125.00	1581.00	n.a	
WR2a	11.40	125.00	1794.00	n.a	
WR2b	15.80	122.00	1470.00	n.a	
WR2c	15.10	127.00	1415.00	n.a	

Table 1 Metal content of WR; Pb, Cd and Mn (ppm)

	Cu1	Cu2	Cu3	Cu4	Cu5
WR1a	2.16	2.35	2.82	32.90	14.30
WR1b	d.1	d.1	d.1	40.00	28.00
WR1c	3.15	2.07	4.15	5.30	22.60
WR2a	13.00	11.00	5.54	31.30	21.70
WR2b	d.1	d.1	d.1	26.70	17.20
WR2c	4.49	8.51	4.80	25.50	19.90

	Cu6	Cu7	CuT	Cu8
WR1a	86.20	60.30	201.00	n.a
WR1b	37.60	69.10	177.00	n.a
WR1c	78.00	48.60	190.00	n.a
WR2a	51.30	62.50	189.00	n.a
WR2b	71.70	50.70	185.00	n.a
WR2c	73.40	68.80	202.00	n.a

	Ni1	Ni2	Ni3	Ni4	Ni5
WR1a	d.1	124.00	166.00	114.00	46.00
WR1b	d.1	123.00	144.00	84.00	40.00
WR1c	d.1	16.00	30.60	30.00	d.1
WR2a	d.1	23.10	51.50	30.00	d.1
WR2b	d.1	d.1	21.00	21.00	12.00
WR2c	d.1	12.20	26.20	29.00	d.1

	Ni6	Ni7	NiT	Ni8
WR1a	d.1	27.00	477.00	n.a
WR1b	d.1	d.1	430.00	n.a
WR1c	d.1	38.00	d.1	n.a
WR2a	d.1	d.1	145.00	n.a
WR2b	d.1	31.00	d.1	n.a
WR2c	d.1	30.00	112.00	n.a

	Cr1	Cr2	Cr3	Cr4	Cr5
WR1a	d.1	.17	.86	8.00	38.60
WR1b	d.1	d.1	d.1	8.50	55.00
WR1c	d.1	.13	.86	8.00	40.30
WR2a	d.1	.43	1.76	10.00	48.20
WR2b	d.1	d.1	d.1	12.10	55.40
WR2c	d.1	.23	1.11	8.00	51.20

	Cr6	Cr7	CrT	Cr8
WR1a	16.00	158.00	225.00	n.a
WR1b	24.50	159.00	d.1	n.a
WR1c	18.00	151.00	213.00	n.a
WR2a	8.50	158.00	269.00	n.a
WR2b	8.00	183.00	d.1	n.a
WR2c	6.50	171.00	284.00	n.a

Table 1 Metal content of WR; Cu, Ni and Cr (ppm)

	Pb1	Pb2	Pb3	Pb4	Pb5
WC1o	d.1	d.1	5.80	74.00	108.00
WC3o	d.1	d.1	8.25	d.1	13.00
WC5o	d.1	d.1	5.92	45.00	56.00
WC6o	n.a	n.a	n.a	n.a	n.a
WC1b	d.1	d.1	14.80	55.00	45.00
WC2b	d.1	d.1	94.00	100.00	60.00
WC5b	d.1	d.1	22.10	111.00	50.00
WC6b	d.1	d.1	33.80	d.1	d.1

	Pb6	Pb7	PbT	Pb8
WC1o	d.1	62.50	d.1	200.00
WC3o	122.40	72.80	313.00	150.00
WC5o	63.50	86.70	257.00	166.00
WC6o	n.a	n.a	n.a	194.90
WC1b	47.00	84.10	246.00	156.00
WC2b	d.1	70.20	296.00	358.00
WC5b	d.1	d.1	d.1	247.00
WC6b	30.00	d.1	d.1	227.00

	Cd1	Cd2	Cd3	Cd4	Cd5
WC1o	d.1	d.1	d.1	16.00	d.1
WC3o	d.1	d.1	d.1	d.1	1.98
WC5o	d.1	d.1	d.1	d.1	d.1
WC6o	d.1	d.1	n.a	n.a	n.a
WC1b	d.1	d.1	.73	4.00	d.1
WC2b	d.1	d.1	5.57	d.1	d.1
WC5b	d.1	d.1	1.36	d.1	d.1
WC6b	d.1	d.1	2.00	2.42	d.1

	Cd6	Cd7	CdT	Cd8
WC1o	d.1	1.50	d.1	10.10
WC3o	6.70	2.41	d.1	8.42
WC5o	d.1	2.73	d.1	7.16
WC6o	n.a	n.a	n.a	12.40
WC1b	d.1	4.87	d.1	9.66
WC2b	d.1	4.64	d.1	20.50
WC5b	d.1	4.20	d.1	14.90
WC6b	d.1	3.60	d.1	15.50

Table 1 Metal content of WC; Pb and Cd (ppm)

	Mn1	Mn2	Mn3	Mn4	Mn5
WC1o	.66	48.60	234.70	1071.00	517.00
WC3o	3.78	235.00	489.00	530.00	362.00
WC5o	.27	56.60	135.60	58.40	208.50
WC6o	2.28	45.00	n.a	n.a	n.a
WC1b	3.87	176.00	183.20	146.00	68.40
WC2b	3.47	184.00	555.00	117.00	59.20
WC5b	d.1	47.00	179.70	178.00	71.60
WC6b	d.1	81.30	202.00	110.70	66.60

	Mn6	Mn7	MnT	Mn8
WC1o	89.80	115.10	2077.00	744.00
WC3o	64.40	128.00	1813.00	1603.00
WC5o	32.50	149.00	641.00	573.00
WC6o	n.a	n.a	n.a	n.a
WC1b	20.90	172.00	771.00	1742.00
WC2b	12.20	145.00	1078.00	598.00
WC5b	12.80	140.00	630.00	583.00
WC6b	111.20	130.00	602.00	540.00

	Fe1	Fe2	Fe3	Fe4	Fe5
WC1o	4.74	d.1	199.50	13669.00	47228.00
WC3o	14.80	25.10	838.00	1417.00	26238.00
WC5o	3.88	10.10	258.00	4239.00	19597.00
WC6o	11.10	d.1	n.a	n.a	n.a
WC1b	52.00	42.20	557.00	6755.00	9090.00
WC2b	72.70	d.1	2158.00	7417.00	6577.00
WC5b	31.70	18.70	479.00	11358.00	8051.00
WC6b	d.1	12.80	585.00	12478.00	7804.00

	Fe6	Fe7	FeT	Fe8
WC1o	8518.00	24910.00	9.45	4.24
WC3o	5169.00	29121.00	6.28	3.39
WC5o	3439.00	34998.00	6.25	3.31
WC6o	n.a	n.a	n.a	3.76
WC1b	1988.00	59387.00	7.79	3.53
WC2b	1311.00	52738.00	7.03	6.04
WC5b	1252.00	54911.00	7.61	4.50
WC6b	1946.00	47540.00	7.04	4.58

Table 1 Metal content of WC; Mn and Fe (ppm,

	Zn1	Zn2	Zn3	Zn4	Zn5
WC1o	d.1	2.94	16.20	465.00	295.00
WC3o	d.1	1.69	18.30	148.00	287.00
WC5o	d.1	.63	17.60	61.00	142.00
WC6o	d.1	5.91	n.a	n.a	n.a
WC1b	d.1	13.60	62.00	193.00	84.40
WC2b	d.1	35.50	345.00	171.00	73.60
WC5b	d.1	48.10	135.00	151.00	74.20
WC6b	d.1	52.50	171.00	634.00	63.90

	Zn6	Zn7	ZnT	Zn8
WC1o	136.00	77.50	995.00	470.00
WC3o	102.00	109.00	668.00	367.00
WC5o	77.30	125.00	424.00	378.00
WC6o	n.a	n.a	n.a	480.00
WC1b	27.80	180.00	561.00	374.00
WC2b	20.60	155.00	802.00	820.00
WC5b	23.80	179.00	612.00	700.00
WC6b	22.00	142.00	1086.00	746.00

	Cu1	Cu2	Cu3	Cu4	Cu5
WC1o	.32	d.1	d.1	21.10	87.40
WC3o	.74	d.1	.37	1.70	10.20
WC5o	.23	.49	.14	23.80	44.10
WC6o	.66	d.1	n.a	n.a	n.a
WC1b	1.64	1.40	d.1	37.30	53.90
WC2b	4.94	d.1	9.17	57.50	47.60
WC5b	1.04	3.82	20.20	60.60	60.90
WC6b	d.1	.90	22.00	11.60	54.60

	Cu6	Cu7	CuT	Cu8
WC1o	60.50	25.60	195.00	103.00
WC3o	44.30	36.70	94.00	64.40
WC5o	36.90	41.60	147.00	78.20
WC6o	n.a	n.a	n.a	83.60
WC1b	19.10	49.00	172.00	61.50
WC2b	6.23	45.30	171.00	196.00
WC5b	6.96	43.80	197.00	160.00
WC6b	4.73	39.00	133.00	169.00

Table 1 Metal content of WC; Zn and Cu (ppm)



	Ni1	Ni2	Ni3	Ni4	Ni5
WC1o	.34	.40	2.76	20.70	12.80
WC3o	.81	2.25	6.12	8.30	13.90
WC5o	.42	.59	2.05	d.1	13.00
WC6o	.71	.94	n.a	n.a	n.a
WC1b	d.1	3.76	4.50	5.79	14.70
WC2b	d.1	4.75	35.10	16.50	16.70
WC5b	d.1	2.45	7.99	11.10	15.70
WC6b	d.1	3.08	9.99	28.10	18.80

	Ni6	Ni7	NiT	Ni8
WC1o	22.00	21.00	80.00	57.00
WC3o	10.50	28.60	70.00	47.00
WC5o	8.00	34.60	69.00	52.00
WC6o	n.a	n.a	n.a	n.a
WC1b	d.1	50.00	80.00	69.00
WC2b	d.1	47.10	120.00	83.00
WC5b	d.1	52.90	80.00	69.00
WC6b	9.00	45.00	105.00	69.00

	Cr1	Cr2	Cr3	Cr4	Cr5
WC1o	d.1	d.1	.44	20.20	168.00
WC3o	d.1	d.1	.78	d.1	96.20
WC5o	d.1	d.1	.52	13.10	91.60
WC6o	d.1	d.1	n.a	n.a	n.a
WC1b	d.1	d.1	1.94	15.60	100.00
WC2b	d.1	d.1	12.20	21.50	97.10
WC5b	d.1	d.1	4.13	31.00	136.00
WC6b	d.1	d.1	9.23	15.60	122.00

	Cr6	Cr7	CrT	Cr8
WC1o	94.40	130.00	414.00	312.00
WC3o	50.60	165.00	325.00	182.00
WC5o	53.30	194.00	353.00	233.00
WC6o	n.a	n.a	n.a	227.00
WC1b	65.50	318.00	502.00	190.00
WC2b	20.00	288.00	444.00	497.00
WC5b	d.1	296.00	468.00	556.00
WC6b	d.1	259.00	407.00	402.00

Table 1 Metal content of WC; Ni and Cr (ppm)

	Pb1	Pb2	Pb3	Pb4	Pb5
S1a	n.a	n.a	n.a	n.a	n.a
S1b	n.a	n.a	n.a	n.a	n.a
S1c	n.a	n.a	n.a	n.a	n.a
S1d	n.a	n.a	n.a	n.a	n.a
S2a	n.a	n.a	n.a	n.a	n.a
S2b	n.a	n.a	n.a	n.a	n.a
S2c	n.a	n.a	n.a	n.a	n.a
S2d	n.a	n.a	n.a	n.a	n.a
S3a	n.a	n.a	n.a	n.a	n.a
S4a	n.a	n.a	n.a	n.a	n.a
S4b	n.a	n.a	n.a	n.a	n.a
So1a	d.l	d.l	7.50	38.00	69.00
So1b	d.l	d.l	7.30	39.00	70.80
So1c	d.l	d.l	8.90	45.10	73.80
So1d	d.l	d.l	7.00	36.00	65.20
So2a	d.l	d.l	89.40	28.60	41.90
So2b	d.l	d.l	91.10	71.90	47.90
So2c	d.l	d.l	129.00	56.40	44.40
So2d	d.l	d.l	91.60	70.20	36.10
So3a	d.l	d.l	68.10	48.00	12.00
So3b	d.l	d.l	93.80	57.40	29.80
So4a	d.l	d.l	d.l	d.l	d.l
So4b	d.l	d.l	d.l	d.l	d.l
	Pb6	Pb7	PbT	Pb8	
S1a	n.a	n.a	n.a	n.a	
S1b	n.a	n.a	n.a	n.a	
S1c	n.a	n.a	n.a	n.a	
S1d	n.a	n.a	n.a	n.a	
S2a	n.a	n.a	n.a	n.a	
S2b	n.a	n.a	n.a	n.a	
S2c	n.a	n.a	n.a	n.a	
S2d	n.a	n.a	n.a	n.a	
S3a	n.a	n.a	n.a	n.a	
S4a	n.a	n.a	n.a	n.a	
S4b	n.a	n.a	n.a	n.a	
So1a	25.90	71.40	212.00	182.00	
So1b	52.80	57.70	228.00	200.00	
So1c	28.00	62.70	218.00	214.00	
So1d	30.90	64.70	208.00	206.00	
So2a	20.30	49.50	230.00	250.00	
So2b	23.00	77.90	312.00	264.00	
So2c	15.10	78.30	307.00	227.00	
So2d	193.00	62.70	280.00	229.00	
So3a	d.l	31.40	160.00	123.00	
So3b	d.l	52.30	233.00	232.00	
So4a	d.l	25.60	d.l	33.00	
So4b	d.l	29.00	d.l	47.00	

Table 1 Metal content of S, So; Pb (ppm)

	Cd1	Cd2	Cd3	Cd4	Cd5
S1a	n.a	n.a	n.a	n.a	n.a
S1b	n.a	n.a	n.a	n.a	n.a
S1c	n.a	n.a	n.a	n.a	n.a
S1d	n.a	n.a	n.a	n.a	n.a
S2a	n.a	n.a	n.a	n.a	n.a
S2b	n.a	n.a	n.a	n.a	n.a
S2c	n.a	n.a	n.a	n.a	n.a
S2d	n.a	n.a	n.a	n.a	n.a
S3a	n.a	n.a	n.a	n.a	n.a
S4a	n.a	n.a	n.a	n.a	n.a
S4b	n.a	n.a	n.a	n.a	n.a
So1a	d.1	d.1	1.70	1.00	d.1
So1b	d.1	d.1	1.20	1.10	d.1
So1c	d.1	d.1	1.60	1.10	d.1
So1d	d.1	d.1	1.23	1.10	d.1
So2a	d.1	d.1	d.1	d.1	d.1
So2b	d.1	d.1	d.1	d.1	d.1
So2c	d.1	d.1	d.1	d.1	d.1
So2d	d.1	d.1	d.1	d.1	d.1
So3a	d.1	d.1	d.1	d.1	d.1
So3b	d.1	d.1	d.1	d.1	d.1
So4a	d.1	d.1	d.1	d.1	d.1
So4b	d.1	d.1	d.1	d.1	d.1
	Cd6	Cd7	CdT	Cd8	
S1a	n.a	n.a	n.a	n.a	
S1b	n.a	n.a	n.a	n.a	
S1c	n.a	n.a	n.a	n.a	
S1d	n.a	n.a	n.a	n.a	
S2a	n.a	n.a	n.a	n.a	
S2b	n.a	n.a	n.a	n.a	
S2c	n.a	n.a	n.a	n.a	
S2d	n.a	n.a	n.a	n.a	
S3a	n.a	n.a	n.a	n.a	
S4a	n.a	n.a	n.a	n.a	
S4b	n.a	n.a	n.a	n.a	
So1a	d.1	2.65	5.37	7.35	
So1b	d.1	2.22	4.56	7.49	
So1c	d.1	2.85	5.59	6.95	
So1d	d.1	2.95	5.26	7.17	
So2a	d.1	d.1	d.1	d.1	
So2b	d.1	d.1	d.1	d.1	
So2c	d.1	d.1	d.1	d.1	
So2d	d.1	d.1	d.1	d.1	
So3a	d.1	d.1	d.1	d.1	
So3b	d.1	d.1	d.1	d.1	
So4b	d.1	d.1	d.1	d.1	

Table 1 Metal content of S, So; Cd (ppm)

	Mn1	Mn2	Mn3	Mn4	Mn5
S1a	3.20	5.30	47.70	282.00	n.a
S1b	3.90	8.30	46.70	247.00	n.a
S1c	1.10	1.10	28.90	316.00	n.a
S1d	1.40	1.50	28.90	321.00	n.a
S2a	6.20	26.10	17.90	63.20	n.a
S2b	7.20	20.90	13.90	80.30	n.a
S2c	5.00	28.70	22.90	54.60	n.a
S2d	6.50	38.90	20.70	66.40	n.a
S3a	4.50	28.40	17.20	36.10	n.a
S4a	6.70	1.90	21.30	d.1	n.a
S4b	6.00	3.40	31.40	d.1	n.a
So1a	d.1	d.1	297.00	1416.00	222.00
So1b	d.1	d.1	331.00	948.00	189.00
So1c	d.1	d.1	331.00	948.00	189.00
So1d	d.1	d.1	218.00	1546.00	259.00
So2a	d.1	1.75	129.00	53.30	40.30
So2b	d.1	1.06	202.00	98.50	46.10
So2c	d.1	1.21	185.00	67.00	49.00
So2d	d.1	1.19	197.00	79.70	51.10
So3a	d.1	1.21	119.00	31.40	20.50
So3b	d.1	1.75	116.00	39.70	22.20
So4a	d.1	9.35	23.80	6.90	13.40
So4b	d.1	8.74	28.50	8.70	11.60
	Mn6	Mn7	MnT	Mn8	
S1a	62.10	n.a	n.a	2936.00	
S1b	39.70	n.a	n.a	2520.00	
S1c	98.70	n.a	n.a	2832.00	
S1d	51.80	n.a	n.a	2763.00	
S2a	d.1	n.a	n.a	673.00	
S2b	69.30	n.a	n.a	507.00	
S2c	8.20	n.a	n.a	660.00	
S2d	19.40	n.a	n.a	564.00	
S3a	22.00	n.a	n.a	342.00	
S4a	3.50	n.a	n.a	114.60	
S4b	3.30	n.a	n.a	139.00	
So1a	11.50	114.00	2060.00	1696.00	
So1b	10.60	114.00	1592.00	1571.00	
So1c	10.60	114.00	1592.00	1571.00	
So1d	14.70	113.00	2150.00	1887.00	
So2a	8.00	128.00	359.00	386.00	
So2b	9.10	123.00	479.00	407.00	
So2c	7.70	139.00	449.00	310.00	
So2d	8.60	121.00	459.00	456.00	
So3a	6.40	98.00	277.00	167.00	
So3b	6.10	101.00	287.00	293.00	
So4a	.70	37.30	92.00	92.00	
So4b	3.20	42.90	104.00	99.00	

Table 1 Metal content of S, So; Mn (ppm)

	Fe1	Fe2	Fe3	Fe4	Fe5
S1a	228.00	8.09	79.00	1838.00	1368.00
S1b	116.00	5.40	117.00	1325.00	1078.00
S1c	159.00	2.50	28.00	1085.00	785.00
S1d	176.00	3.74	101.00	1674.00	1404.00
S2a	137.00	346.00	n.a	2213.00	700.00
S2b	181.00	282.00	n.a	4805.00	1006.00
S2c	63.10	317.00	n.a	1794.00	546.00
S2d	52.30	393.00	n.a	2142.00	915.00
S3a	86.10	243.00	n.a	2233.00	247.00
S4a	39.60	9.63	n.a	1346.00	65.00
S4b	44.90	20.90	n.a	387.00	55.10
So1a	7.70	1.21	207.00	8089.00	15505.00
So1b	8.80	d.1	261.00	7087.00	22506.00
So1c	35.30	d.1	346.00	8402.00	15427.00
So1d	36.70	4.00	323.00	6269.00	18702.00
So2a	5.00	d.1	344.00	3321.00	5836.00
So2b	7.40	d.1	360.00	7135.00	5849.00
So2c	3.10	d.1	546.00	5039.00	6394.00
So2d	2.70	d.1	411.00	6925.00	5992.00
So3a	1.70	d.1	512.00	4729.00	2709.00
So3b	7.20	d.1	386.00	4153.00	2743.00
So4a	3.70	d.1	182.00	880.00	602.00
So4b	24.50	d.1	183.00	950.00	457.00
	Fe6	Fe7	FeT	Fe8	
S1a	713.00	n.a	n.a	54120.00	
S1b	662.00	n.a	n.a	54120.00	
S1c	692.00	n.a	n.a	53856.00	
S1d	486.00	n.a	n.a	54571.00	
S2a	d.1	n.a	n.a	50714.00	
S2b	357.00	n.a	n.a	40755.00	
S2c	181.00	n.a	n.a	44440.00	
S2d	391.00	n.a	n.a	40040.00	
S3a	132.00	n.a	n.a	34134.00	
S4a	296.00	n.a	n.a	9244.00	
S4b	145.00	n.a	n.a	11572.00	
So1a	1164.00	26624.00	5.16	4.31	
So1b	1882.00	24411.00	5.62	4.47	
So1c	1366.00	26473.00	5.19	4.54	
So1d	1194.00	23437.00	5.01	4.32	
So2a	917.00	28974.00	3.94	3.46	
So2b	1184.00	29472.00	4.40	3.34	
So2c	943.00	25577.00	3.85	2.92	
So2d	1099.00	25428.00	3.99	3.49	
So3a	745.00	19054.00	2.78	1.81	
So3b	678.00	21972.00	2.99	2.92	
So4a	150.00	6685.00	.85	.91	
So4b	208.00	5649.00	.74	1.00	

Table 1 Metal content of S, So; Fe (ppm, FeT and Fe8 So in %)

	Zn1	Zn2	Zn3	Zn4	Zn5
S1a	10.60	4.47	120.00	125.00	125.00
S1b	10.60	5.63	130.00	110.00	115.00
S1c	10.10	2.50	100.00	116.00	125.00
S1d	9.60	4.62	150.00	151.00	92.00
S2a	3.24	d.1	21.90	26.40	180.00
S2b	4.18	d.1	20.80	58.90	248.20
S2c	1.31	d.1	21.40	13.70	104.50
S2d	1.31	d.1	22.00	16.60	221.80
S3a	2.11	5.59	6.02	d.1	45.60
S4a	1.58	d.1	3.17	59.40	21.80
S4b	1.22	d.1	2.18	24.70	23.20
So1a	d.1	5.56	99.30	126.00	54.70
So1b	d.1	6.76	84.10	127.00	83.80
So1c	d.1	8.19	94.10	96.90	52.60
So1d	d.1	6.57	90.20	108.00	62.90
So2a	d.1	62.20	155.00	101.00	81.60
So2b	d.1	36.50	126.00	135.00	52.70
So2c	d.1	53.00	208.00	119.00	77.00
So2d	d.1	45.00	130.00	118.00	41.30
So3a	d.1	35.20	84.00	65.40	29.70
So3b	d.1	46.10	104.00	79.20	31.70
So4a	d.1	13.30	12.90	13.00	5.67
So4b	d.1	19.50	17.80	14.50	4.66
	Zn6	Zn7	ZnT	ZnB	
S1a	9.12	n.a	n.a	456.00	
S1b	6.86	n.a	n.a	432.00	
S1c	10.47	n.a	n.a	453.00	
S1d	9.72	n.a	n.a	459.00	
S2a	d.1	n.a	n.a	518.00	
S2b	183.00	n.a	n.a	585.00	
S2c	43.00	n.a	n.a	540.00	
S2d	81.10	n.a	n.a	1040.00	
S3a	2.70	n.a	n.a	415.00	
S4a	7.26	n.a	n.a	74.00	
S4b	5.80	n.a	n.a	34.00	
So1a	9.50	76.50	372.00	364.00	
So1b	15.10	68.80	386.00	363.00	
So1c	13.40	73.50	339.00	347.00	
So1d	12.50	63.00	343.00	357.00	
So2a	15.40	110.00	525.00	499.00	
So2b	15.80	101.00	466.00	474.00	
So2c	17.50	93.40	568.00	394.00	
So2d	15.20	87.30	437.00	393.00	
So3a	11.60	58.40	284.00	251.00	
So3b	10.90	70.10	342.00	352.00	
So4a	7.10	10.20	62.00	48.00	
So4b	5.00	9.97	71.00	60.00	

Table 1 Metal content of S, So; Zn (ppm)

	Cu1	Cu2	Cu3	Cu4	Cu5
S1a	.16	.19	5.30	d.1	27.40
S1b	.13	.04	5.00	d.1	21.60
S1c	d.1	.02	3.50	d.1	24.70
S1d	d.1	d.1	7.10	d.1	31.30
S2a	.18	d.1	d.1	d.1	d.1
S2b	.18	.16	d.1	d.1	d.1
S2c	d.1	.04	d.1	d.1	d.1
S2d	d.1	d.1	d.1	d.1	d.1
S3a	.19	.11	d.1	d.1	d.1
S4a	.06	.03	d.1	d.1	d.1
S4b	.04	d.1	d.1	d.1	d.1
So1a	d.1	d.1	7.97	9.40	28.20
So1b	d.1	d.1	6.25	9.00	34.10
So1c	d.1	d.1	8.42	10.30	27.30
So1d	d.1	d.1	6.86	9.00	29.80
So2a	d.1	1.31	11.70	5.20	36.40
So2b	d.1	.77	11.00	10.60	34.10
So2c	d.1	1.19	19.30	9.10	35.10
So2d	d.1	.60	9.93	7.70	34.80
So3a	d.1	.70	9.27	6.40	21.80
So3b	d.1	1.00	10.20	8.50	27.20
So4a	d.1	d.1	2.28	d.1	1.95
So4b	d.1	d.1	2.32	d.1	2.24

	Cu6	Cu7	CuT	Cu8
S1a	6.30	n.a	n.a	96.00
S1b	4.90	n.a	n.a	108.00
S1c	6.70	n.a	n.a	114.00
S1d	5.40	n.a	n.a	107.00
S2a	d.1	n.a	n.a	122.00
S2b	40.00	n.a	n.a	121.00
S2c	12.50	n.a	n.a	120.00
S2d	25.10	n.a	n.a	172.00
S3a	9.50	n.a	n.a	85.00
S4a	d.1	n.a	n.a	d.1
S4b	d.1	n.a	n.a	d.1
So1a	d.1	17.00	63.00	59.20
So1b	d.1	16.20	66.00	58.30
So1c	d.1	15.40	61.00	55.20
So1d	d.1	14.00	60.00	56.70
So2a	d.1	22.10	77.00	62.90
So2b	d.1	18.50	75.00	63.30
So2c	d.1	20.80	80.00	52.30
So2d	d.1	17.30	70.00	46.40
So3a	d.1	12.40	51.00	34.30
So3b	d.1	14.40	61.00	48.50
So4a	d.1	1.84	6.10	5.16
So4b	d.1	2.27	6.80	7.10

Table 1 Metal content of S, So; Cu (ppm)



	Ni1	Ni2	Ni3	Ni4	Ni5
S1a	d.1	d.1	8.48	d.1	d.1
S1b	d.1	d.1	9.80	d.1	d.1
S1c	d.1	d.1	5.49	d.1	d.1
S1d	d.1	d.1	7.37	d.1	d.1
S2a	d.1	d.1	d.1	d.1	d.1
S2b	d.1	d.1	d.1	d.1	d.1
S2c	d.1	d.1	d.1	d.1	d.1
S2d	d.1	d.1	d.1	d.1	d.1
S3a	d.1	d.1	d.1	d.1	d.1
S4a	d.1	d.1	d.1	d.1	d.1
S4b	d.1	d.1	d.1	d.1	d.1
So1a	d.1	d.1	5.56	25.30	12.20
So1b	d.1	d.1	3.61	29.20	14.10
So1c	d.1	d.1	4.85	20.10	8.30
So1d	d.1	d.1	3.42	28.10	10.80
So2a	d.1	d.1	7.50	10.00	7.60
So2b	d.1	d.1	3.07	9.10	d.1
So2c	d.1	d.1	8.15	9.70	d.1
So2d	d.1	d.1	4.31	10.00	d.1
So3a	d.1	d.1	3.58	6.20	d.1
So3b	d.1	d.1	2.91	5.90	d.1
So4a	d.1	d.1	d.1	d.1	d.1
So4b	d.1	d.1	d.1	d.1	d.1
	Ni6	Ni7	NiT	Ni8	
S1a	d.1	n.a	n.a	56.00	
S1b	d.1	n.a	n.a	64.00	
S1c	d.1	n.a	n.a	94.00	
S1d	d.1	n.a	n.a	82.00	
S2a	d.1	n.a	n.a	49.00	
S2b	d.1	n.a	n.a	62.00	
S2c	d.1	n.a	n.a	56.00	
S2d	d.1	n.a	n.a	108.00	
S3a	d.1	n.a	n.a	65.00	
S4a	d.1	n.a	n.a	d.1	
S4b	d.1	n.a	n.a	d.1	
So1a	7.70	30.60	81.00	52.70	
So1b	19.10	30.40	97.00	58.80	
So1c	9.70	27.00	70.00	48.60	
So1d	12.30	25.30	80.00	56.20	
So2a	12.20	35.60	72.00	43.80	
So2b	9.80	32.60	55.00	41.70	
So2c	8.10	32.10	58.00	35.10	
So2d	14.80	32.10	61.00	36.40	
So3a	12.80	21.20	44.00	19.20	
So3b	9.20	25.50	44.00	41.30	
So4a	9.20	5.39	15.00	9.66	
So4b	27.60	5.42	32.90	13.40	

Table 1 Metal content of S, So; Ni (ppm)

	Cr1	Cr2	Cr3	Cr4	Cr5
S1a	d.1	d.1	15.40	d.1	14.80
S1b	d.1	d.1	15.10	d.1	18.60
S1c	d.1	d.1	11.00	d.1	13.10
S1d	d.1	d.1	19.10	d.1	23.20
S2a	d.1	d.1	62.30	d.1	8.96
S2b	d.1	d.1	56.80	d.1	21.40
S2c	d.1	d.1	46.30	d.1	8.58
S2d	d.1	d.1	37.70	d.1	14.70
S3a	d.1	d.1	43.30	d.1	3.42
S4a	d.1	d.1	9.20	d.1	d.1
S4b	d.1	d.1	6.70	d.1	d.1
So1a	d.1	d.1	2.45	8.70	73.00
So1b	d.1	d.1	2.42	3.20	80.60
So1c	d.1	d.1	3.06	10.10	75.30
So1d	d.1	d.1	2.34	4.30	69.40
So2a	d.1	d.1	2.97	7.40	55.50
So2b	d.1	d.1	3.50	13.20	78.90
So2c	d.1	d.1	5.36	6.90	61.90
So2d	d.1	d.1	3.22	9.80	58.80
So3a	d.1	d.1	1.00	4.60	26.80
So3b	d.1	d.1	1.50	5.50	35.00
So4a	d.1	d.1	d.1	d.1	d.1
So4b	d.1	d.1	d.1	d.1	d.1
	Cr6	Cr7	CrT	CrB	
S1a	d.1	n.a	n.a	280.00	
S1b	12.70	n.a	n.a	275.00	
S1c	17.60	n.a	n.a	306.00	
S1d	15.10	n.a	n.a	282.00	
S2a	d.1	n.a	n.a	286.00	
S2b	32.00	n.a	n.a	317.00	
S2c	9.36	n.a	n.a	305.00	
S2d	20.90	n.a	n.a	300.00	
S3a	5.30	n.a	n.a	222.00	
S4a	d.1	n.a	n.a	48.00	
S4b	5.50	n.a	n.a	70.00	
So1a	17.70	156.00	258.00	217.00	
So1b	35.90	131.00	254.00	225.00	
So1c	17.70	144.00	250.00	229.00	
So1d	23.60	135.00	235.00	222.00	
So2a	39.10	167.00	272.00	227.00	
So2b	37.40	161.00	294.00	237.00	
So2c	30.20	157.00	261.00	212.00	
So2d	30.70	143.00	245.00	197.00	
So3a	38.30	111.00	182.00	107.00	
So3b	16.60	120.00	179.00	187.00	
So4a	d.1	28.00	28.00	45.00	
So4b	43.30	27.00	60.30	45.00	

Table 1 Metal content of S, So; Cr (ppm)

	Pb1	Pb2	Pb3	Pb4	Pb5	Pb6	Pb7
WR1a	.10	.40	1.10	11.10	8.00	5.00	74.30
WR1b	n.a	n.a	n.a	n.a	n.a	n.a	n.a
WR1c	.10	.20	.70	7.70	4.90	6.00	70.40
WR2a	-.10	.30	1.60	16.60	11.80	3.40	66.30
WR2b	n.a	n.a	n.a	n.a	n.a	n.a	n.a
WR2c	-.10	.10	.80	13.50	13.80	7.00	64.70
WC1o	n.a	n.a	n.a	n.a	n.a	n.a	n.a
WC3o	0.0	0.0	2.60	19.10	19.10	39.00	23.20
WC5o	0.0	0.0	2.30	17.50	21.80	24.70	33.70
WC1b	0.0	0.0	6.00	22.40	18.30	19.10	34.20
WC2b	0.0	0.0	13.50	37.50	16.90	8.40	23.70
WC5b	n.a	n.a	n.a	n.a	n.a	n.a	n.a
WC6b	n.a	n.a	n.a	n.a	n.a	n.a	n.a
So1a	0.0	0.0	3.50	17.90	32.60	12.20	33.70
So1b	0.0	0.0	3.20	17.10	31.10	23.20	25.40
So1c	0.0	0.0	4.10	20.70	33.80	12.80	28.70
So1d	0.0	0.0	3.80	20.20	31.40	14.90	31.10
So2a	0.0	0.0	38.90	12.50	18.30	8.80	21.50
So2b	0.0	0.0	29.20	23.10	15.40	7.40	25.00
So2c	0.0	0.0	41.90	18.40	14.50	4.90	25.50
So2d	0.0	0.0	32.70	25.10	12.90	6.90	22.40
So3a	0.0	0.0	42.70	30.10	7.50	0.0	19.70
So3b	0.0	0.0	40.20	24.60	12.80	0.0	22.40
So4a	n.a	n.a	n.a	n.a	n.a	n.a	n.a
So4b	n.a	n.a	n.a	n.a	n.a	n.a	n.a
	Mn1	Mn2	Mn3	Mn4	Mn5	Mn6	Mn7
WR1a	4.00	10.50	23.70	48.50	6.60	.90	5.80
WR1b	4.40	9.40	27.50	47.20	4.60	.70	6.20
WR1c	4.00	10.00	21.00	47.40	8.90	.80	7.90
WR2a	3.70	12.30	34.40	36.60	5.50	.60	7.00
WR2b	3.60	12.90	30.50	36.50	7.00	1.10	8.30
WR2c	5.10	12.80	32.90	32.40	6.90	1.10	9.00
WC1o	-.10	2.30	11.30	51.60	24.90	4.30	5.50
WC3o	.20	13.00	27.00	34.20	20.00	3.60	7.10
WC5o	-.10	8.80	21.20	9.10	32.50	5.10	23.30
WC1b	.50	22.90	23.80	19.00	8.90	2.70	22.30
WC2b	.30	17.10	51.50	10.90	3.50	1.10	13.50
WC5b	0.0	7.50	28.50	28.30	11.40	2.80	22.40
WC6b	0.0	13.50	33.60	18.40	11.10	1.90	21.60
So1a	0.0	0.0	14.40	68.70	10.80	.60	5.60
So1b	0.0	0.0	11.70	68.30	14.40	1.00	4.60
So1c	0.0	0.0	19.80	59.50	11.90	.70	7.20
So1d	0.0	0.0	10.10	71.90	12.00	.70	5.20
So2a	0.0	.50	36.00	14.90	11.20	2.20	35.70
So2b	0.0	.20	42.20	20.60	9.60	1.90	25.80
So2c	0.0	.30	41.20	14.90	10.90	1.70	31.00
So2d	0.0	.30	42.90	17.40	11.10	1.90	26.40
So3a	0.0	.40	43.00	11.30	7.40	2.30	35.50
So3b	0.0	.60	40.50	13.80	7.70	2.10	35.20
So4a	0.0	10.20	26.00	7.50	14.70	.80	40.80
So4b	0.0	8.40	27.50	8.40	11.20	3.10	41.40

Table 2 Percental distribution; Pb and Mn

	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7
WR1a	0.0	0.0	.60	9.30	27.50	4.40	58.20
WR1b	0.0	0.0	.70	13.00	20.60	3.80	61.90
WR1c	0.0	0.0	.70	8.30	30.90	4.10	55.90
WR2a	0.0	0.0	1.60	15.80	23.70	3.80	55.10
WR2b	0.0	-.10	1.70	12.80	25.40	4.00	56.00
WR2c	0.0	-.10	2.70	12.80	24.10	3.70	56.70
WC1o	-.10	0.0	.20	14.50	50.00	9.00	26.40
WC3o	-.10	-.10	1.30	2.30	41.80	8.20	46.40
WC5o	-.10	-.10	.40	6.80	31.30	5.50	56.00
WC1b	.10	.10	.70	8.70	11.70	2.60	76.30
WC2b	.10	0.0	3.10	10.60	9.40	1.90	75.00
WC5b	-.10	-.10	.60	14.90	10.60	1.60	72.20
WC6b	0.0	-.10	.80	17.70	11.10	2.80	67.60
So1a	-.10	-.10	.40	15.70	30.00	2.30	51.60
So1b	-.10	-.10	.50	12.60	40.10	3.40	43.50
So1c	.10	0.0	.70	16.20	29.70	2.30	51.00
So1d	.10	-.10	.60	12.50	37.30	2.70	46.70
So2a	-.10	0.0	.90	8.40	14.80	2.30	73.50
So2b	-.10	0.0	.80	16.20	13.30	2.70	67.00
So2c	-.10	0.0	1.40	13.10	16.60	2.40	66.40
So2d	-.10	0.0	1.00	17.40	15.00	2.80	63.80
So3a	-.10	0.0	1.80	17.00	9.80	2.70	68.70
So3b	-.10	0.0	1.30	13.90	9.20	2.30	73.40
So4a	.30	0.0	2.10	10.30	7.10	1.80	78.40
So4b	0.0	0.0	2.50	12.80	6.10	2.80	75.90
	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	Zn7
WR1a	0.0	8.10	25.80	35.50	7.80	9.90	13.00
WR1b	0.0	8.70	27.20	26.00	9.70	10.10	18.30
WR1c	0.0	2.40	17.60	45.40	16.20	14.90	14.10
WR2a	0.0	4.00	25.00	38.70	7.80	5.70	19.50
WR2b	0.0	-.10	11.30	43.20	11.90	7.40	26.60
WR2c	0.0	3.90	11.80	46.30	9.80	8.00	20.30
WC1o	0.0	.30	1.60	46.80	29.70	13.70	7.80
WC3o	0.0	.30	2.70	22.20	43.00	15.30	16.50
WC5o	0.0	.10	4.20	14.40	33.50	18.20	29.50
WC1b	0.0	2.40	11.10	34.40	15.00	5.00	32.10
WC2b	0.0	4.40	43.10	21.40	9.20	2.60	19.40
WC5b	0.0	7.90	22.10	24.70	12.10	3.90	29.30
WC6b	0.0	4.80	15.80	58.40	5.90	2.00	13.10
So1a	0.0	1.50	26.70	34.00	14.70	2.60	20.60
So1b	0.0	1.80	21.30	33.00	21.70	3.90	17.80
So1c	0.0	2.40	27.80	28.60	15.60	4.00	21.70
So1d	0.0	1.90	26.30	31.40	18.30	3.60	18.40
So2a	0.0	11.90	29.60	19.20	15.50	2.90	20.90
So2b	0.0	7.80	26.90	28.90	11.30	3.40	21.60
So2c	0.0	9.30	36.70	20.90	13.60	3.10	16.50
So2d	0.0	10.30	29.90	26.90	9.50	3.50	20.00
So3a	0.0	12.40	29.40	23.00	10.50	4.10	20.60
So3b	0.0	13.50	30.50	23.10	9.30	3.20	20.50
So4a	0.0	21.40	20.70	20.90	9.10	11.40	16.40
So4b	0.0	27.30	24.90	20.30	6.50	7.10	13.90

Table 2 Percental distribution; Fe and Zn

	Cu1	Cu2	Cu3	Cu4	Cu5	Cu6	Cu7
WR1a	1.20	1.20	1.40	16.40	7.10	42.90	30.00
WR1b	0.0	0.0	0.0	22.60	15.80	35.60	24.00
WR1c	1.70	1.10	2.20	12.00	9.90	41.10	26.30
WR2a	6.90	5.80	2.90	16.60	11.50	27.20	29.10
WR2b	n.a	n.a	n.a	n.a	n.a	n.a	n.a
WR2c	2.20	4.20	2.40	12.70	9.90	36.40	32.20
WC1o	.20	0.0	0.0	10.80	44.80	31.00	13.10
WC3o	.80	0.0	.40	1.80	10.80	47.10	39.00
WC5o	.20	.30	.10	16.20	29.90	25.10	28.20
WC1b	1.00	.80	5.80	21.60	31.30	11.10	28.40
WC2b	2.90	0.0	5.40	33.70	27.90	3.60	26.50
WC5b	.50	1.90	10.20	30.70	30.90	3.50	22.20
WC6b	0.0	.70	16.60	8.70	41.10	3.60	29.40
So1a	0.0	0.0	12.60	14.80	44.50	0.0	28.10
So1b	0.0	0.0	9.40	14.50	51.60	0.0	24.50
So1c	0.0	0.0	13.70	16.70	44.50	0.0	24.50
So1d	0.0	0.0	11.40	15.90	49.50	0.0	23.20
So2a	0.0	1.70	15.30	6.70	47.40	0.0	28.80
So2b	0.0	1.00	14.70	14.20	45.50	0.0	24.70
So2c	0.0	1.40	22.60	10.60	41.10	0.0	24.30
So2d	0.0	.90	14.10	11.00	49.50	0.0	24.60
So3a	0.0	1.40	18.30	12.70	43.10	0.0	24.50
So3b	0.0	1.60	16.60	13.80	44.40	0.0	23.50
So4a	0.0	0.0	37.60	0.0	32.10	0.0	30.30
So4b	0.0	0.0	34.00	0.0	32.80	0.0	33.20
	Ni1	Ni2	Ni3	Ni4	Ni5	Ni6	Ni7
WR1a	0.0	26.00	34.70	24.00	9.60	0.0	5.70
WR1b	0.0	28.70	33.40	19.80	10.00	0.0	8.10
WR1c	n.a	n.a	n.a	n.a	n.a	n.a	n.a
WR2a	0.0	16.00	35.60	20.70	6.90	0.0	20.70
WR2b	n.a	n.a	n.a	n.a	n.a	n.a	n.a
WR2c	0.0	11.00	23.40	25.80	13.40	0.0	26.70
WC1o	.40	.50	3.50	26.00	16.10	27.60	26.40
WC3o	1.20	3.20	8.70	11.80	19.70	14.90	40.60
WC5o	.60	.90	3.00	14.60	18.90	11.70	50.40
WC1b	0.0	4.80	5.70	7.40	18.70	0.0	63.50
WC2b	0.0	4.00	29.20	13.70	13.90	0.0	39.20
WC5b	0.0	3.10	19.00	13.90	19.60	0.0	66.00
WC6b	0.0	2.90	9.50	26.80	18.00	0.0	43.00
So1a	0.0	0.0	6.80	31.00	15.00	9.50	37.60
So1b	0.0	0.0	3.70	29.90	15.60	19.60	31.20
So1c	0.0	0.0	6.90	28.70	11.90	13.80	38.60
So1d	0.0	0.0	4.30	35.10	13.50	15.40	31.70
So2a	0.0	0.0	10.40	13.80	9.70	16.90	49.30
So2b	0.0	0.0	5.60	16.60	0.0	18.00	59.70
So2c	0.0	0.0	14.00	16.70	0.0	13.90	55.30
So2d	0.0	0.0	7.10	16.30	0.0	24.10	52.50
So3a	0.0	0.0	8.20	14.20	0.0	29.30	48.30
So3b	0.0	0.0	6.70	13.60	0.0	21.20	58.50
So4a	0.0	0.0	0.0	0.0	0.0	63.10	36.90
So4b	n.a	n.a	n.a	n.a	n.a	n.a	n.a

Table 2 Percental distribution; Cu and Ni

	Cr1	Cr2	Cr3	Cr4	Cr5	Cr6	Cr7
WR1a	.10	.10	.40	3.50	17.10	8.90	70.00
WR1b	n.a	n.a	n.a	n.a	n.a	n.a	n.a
WR1c	.10	.10	.40	3.70	18.70	4.70	72.00
WR2a	.10	.20	.70	4.50	33.40	3.70	57.00
WR2b	n.a	n.a	n.a	n.a	n.a	n.a	n.a
WR2c	.10	.10	.40	4.20	31.70	3.50	60.00
WC1a	0.0	0.0	.10	4.90	40.70	22.80	31.60
WC3a	0.0	0.0	.20	3.70	29.60	15.60	50.90
WC5a	0.0	0.0	.10	3.70	25.90	15.10	55.00
WC1b	0.0	0.0	.40	3.10	20.00	13.10	63.40
WC2b	0.0	0.0	2.70	4.80	21.90	5.60	64.90
WC5b	0.0	0.0	.90	6.60	29.20	0.0	63.30
WC6b	0.0	0.0	2.30	3.80	30.20	0.0	63.70
So1a	0.0	0.0	.90	3.40	28.30	6.90	60.50
So1b	0.0	0.0	1.00	1.30	31.80	14.20	51.80
So1c	0.0	0.0	1.20	4.00	30.10	7.10	57.60
So1d	0.0	0.0	1.00	1.80	29.60	10.10	57.50
So2a	0.0	0.0	1.10	2.70	20.40	14.40	61.40
So2b	0.0	0.0	1.20	4.50	26.90	12.70	54.70
So2c	0.0	0.0	2.10	2.60	23.70	11.60	60.10
So2d	0.0	0.0	1.30	4.00	23.90	12.50	58.30
So3a	0.0	0.0	.50	2.50	14.70	21.00	61.10
So3b	0.0	0.0	.80	3.10	19.50	9.30	67.30
So4a	n.a	n.a	n.a	n.a	n.a	n.a	n.a
So4b	n.a	n.a	n.a	n.a	n.a	n.a	n.a

Table 2 Percental distribution; Cr



