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The simultaneous influence of pH and Acid Volatile Sulphide on the speciation of heavy metals in calcareous sediments.

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CONTENTS

SUMMARY

The influence of the pH on the release of Acid Volatile Sulphide (AVS) and Simultaneously Extracted Metals (SEM) in various freshwater sediments was studied to gain information with respect to the speciation of heavy metals in these natural systems. Various concentrations of hydrochloric acid were added to a sediment suspension to cover a final pH range from approximately 0 to about 5. These experiments were performed with three different sediments. The released H_2S was trapped in a NaOH solution by flushing the sediment suspension with nitrogen gas. Then, sulphide was measured after a colourimetric reaction by spectrophotometry. Parallel, metals were measured in the resulting sediment extract by flame-AAS or ICP-AES depending on the metal. Beforehand, for the present experimental set-up the influence of the amount of weighed sediment on resulting AVS and SEM concentrations was studied over a range of 2 to 10 grams of wet sediment at a pH of circa 0.

AVS and SEM concentrations appeared to be independent of the amount of sediment taken into consideration, whereas AVS and SEM concentrations decreased linearly with decreasing acidity. Furthermore, SEM-to-AVS ratios decreased linearly with increasing pH as well. This observation is of great practical importance, since the SEM-to-AVS ratio might be used for the derivation of sediment quality criteria for heavy metals. In addition, the carbonate content of the sediment seemed to influence metal sulphide dissolution, probably due to its acid buffering capacity. This resulted in steeper slopes for AVS versus pH plots for sediments with low carbonate content. Slopes were found to be -7.16; -3.09 and -1.99 μmol AVS g^{-1} d.w. per pH unit, for sediments with 4.4; 8.7 and 16.0 % $CaCO_3$, respectively.

In the sediment suspensions, the dissolution of metal due to acid conditions has been described by a simplified exchange model. For the present set of samples, the model could be applied for the metal zinc only due to limitations in the determination of the concentrations of the other metals. Nevertheless, the model was able to predict the speciation of zinc in the sediments quite well. From this model a proton exchange coefficient can be obtained which appeared to be in line with literature data.

Regarding the comparable physico-chemical behaviour of zinc in the three sediments, the proposed model for zinc dissolution in calcareous sediments might be extended to other metals and other type of sediments. Since the results are of practical importance for ecotoxicity studies and, hence, the setting of environmental quality objectives, further experimental validation of this hypothesis is highly recommended.

SAMENVATTING

De invloed van de zuurgraad op het vrijmaken van extraheerbaar sulfide (AVS) en simultaan geëxtraheerde metalen (SEM, totaal van Cd, Cu, Pb, Ni en Zn) is onderzocht in een aantal verschillende zoetwatersedimenten om meer inzicht te verkrijgen in de speciatie van zware metalen in sedimenten. Voor de bepaling van AVS bij verschillende zuursterkten, werden verschillende concentraties HCl aan een sediment suspensie toegevoegd. Hier werd vervolgens stikstof doorgeleid, waardoor sulfide als H_2S werd vrijgemaakt. Dit gas werd met de stikstofstroom meegevoerd en opgevangen in een NaOH-oplossing, waarin het sulfide uiteindelijk coulorimetrisch wordt bepaald. Het sediment extract werd gefiltreerd, waarna hierin Cd, Cu, Pb, Ni, Zn, Fe, Mn en Ca werden gemeten met vlam AAS en ICP-AES, afhankelijk van het element. Als onderdeel van dit onderzoek werd vooraf de invloed van de in behandeling genomen massa sediment op de AVS en SEM concentratie bepaald.

Variabele ingewogen massa's nat sediment (2 tot 10 gram) bleken constante waarden te geven voor AVS en SEM. Echter, AVS en SEM concentraties en de SEM/AVS ratio namen lineair af met afnemende zuurgraad. Dit resultaat is van groot praktisch belang, aangezien de SEM/AVS ratio gebruikt zou kunnen worden bij de normstelling van zware metalen in het compartiment sediment. Het carbonaatgehalte van het sediment bleek van invloed op het oplosgedrag van de verschillende metalen. Hierbij speelt waarschijnlijk de buffercapaciteit voor protonen van carbonaat een rol. Sediment met een laag carbonaatgehalte vertoonde een steilere helling voor het verband tussen AVS versus pH, dan sediment met een hoog carbonaatgehalte. Voor sedimenten met carbonaatgehalten van 4.4; 8.7 en 16.0 % waren de hellingen respectievelijk -7.16; -3.09 en -1.99 µmol AVS g^{-1} droog sediment per pH eenheid.

Het oplosgedrag van de metalen in de sedimenten is beschreven met een vereenvoudigd uitwisselingsmodel. Dit model kon alleen toegepast worden voor zink, omdat door analytische beperkingen niet voldoende gegevens voor de andere metalen voorhanden waren. Het model was in staat om de speciatie van zink in de sedimenten redelijk goed te beschrijven. Uit het model kan een protonuitwisselcoëfficiënt bepaald worden, die in vergelijking met de literatuurwaarden bevredigend was .

Omdat de resultaten van belang zijn voor een goede interpretatie van ecotoxiciteitsexperimenten in sedimentsystemen en, dus direct van belang voor de afleiding van milieukwaliteitsdoelstellingen voor het compartiment, zou de geldigheid van het gepresenteerde uitwisselingsmodel verder getoetst moeten worden voor andere metalen en andere sedimenten.

1. INTRODUCTION

Knowledge with respect to the distribution of heavy metals over the solid phase and porewater and within these phases in sediments is important in predicting the toxicity of these metals. Metals that are irreversibly bound to the solid phase are not expected to be bioavailable and, thus, will not to lead to toxic effects for organisms. It is now well known that toxic effects can hardly be described on the basis of total metal concentrations in the natural system. Toxicity is assumed to be mostly caused by free metals or metal complexes. Hence, it is important to know the speciation of metals in these systems to be able to predict the toxicity.

Under anaerobic conditions sulphide plays an important role in the speciation of metals [1-3]. In anaerobic sediments sulphate reduction takes place by bacteria in the presence of organic matter. The sulphide formed in this process reacts with iron- and manganese to form iron- or manganese sulphides (see Figure 1).

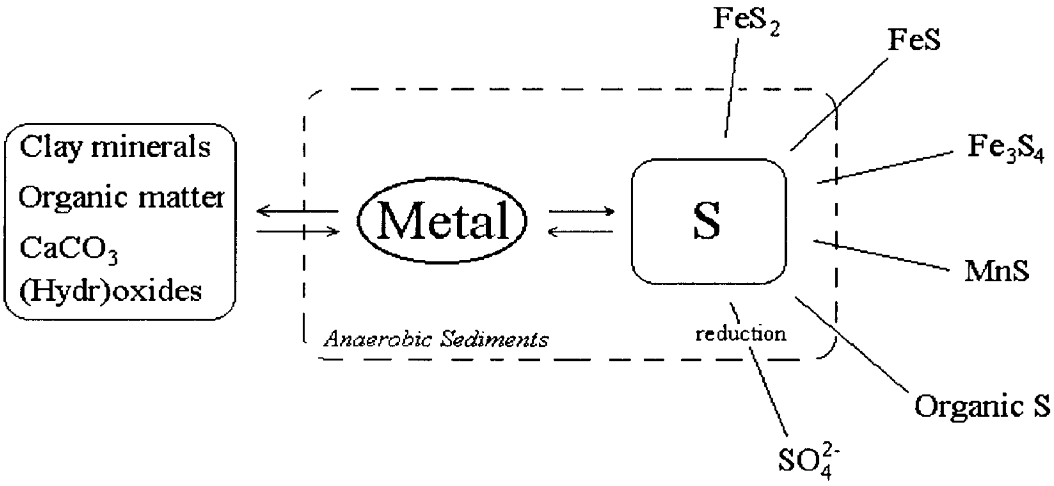

Figure 1. Simplified metal and sulphur speciation scheme for sediments

Due to pollution of the surface water heavy metals, like cadmium and copper, may enter the sediment. These metal sulphides are less soluble than iron- and manganese sulphides, which is expressed in their lower solubility constants (see Table 1). From a purely thermodynamic point of view this will cause heavy metals to react with the iron and manganese sulphides to form heavy metal sulphides. Taking cadmium as an example, one can derive the following overall exchange reaction.

$$FeS\ (s) + Cd^{2+}\ (aq) \rightarrow CdS\ (s) + Fe^{2+}\ (aq) \qquad (1)$$

Based on thermodynamics, it is thus expected that when sulphide is in excess over metals, the heavy metals will be present mainly as metal sulphide precipitates. This should lead to very low concentrations of free metal ions in the porewater (10^{-12}-10^{-18}

mol l^{-1}). Furthermore, if one assumes that toxicity is mainly caused by free metal ion concentrations, toxic effects on benthic organisms in this compartment will be negligible. This hypothesis is confirmed in several experimental studies in which the influence of the molar metal-to-sulphide ratio on the toxicity of Ni, Cd, Cu and Zn for various organisms in marine, freshwater and estuarine sediments was studied [2-5].

Table 1. Metal sulphide solubility products [6]

Metal sulphide	log K_{sp}
MnS	-11.7
FeS	-18.1
ZnS	-24.7
NiS	-26.6
CdS	-27.1
PbS	-27.5
CuS	-36.1

In anaerobic sediments one of the sulphide pools that can bind trace metals through sorption and coprecipitation is pyrite [7]. A more reactive sulphide pool is Acid Volatile Sulphide (AVS), which is according to Huerta-Diaz et al. [8] equal to the sommation of amorphous FeS, mackinawite (FeS) and greigite (Fe_3S_4). Although pyrite concentrations in sediment are found to be present in much larger concentrations than AVS (80-150 μmol g^{-1} d.w. vs. 5-20 μmol g^{-1}, respectively [8-10]), AVS has a larger storage capacity for trace metals than pyrite. In experiments with artificial pyrite, pyrite was found to absorb metals with a maximum concentration of circa 0.25 - 1.40 μmol mol^{-1} FeS_2 [11, 12]. For a natural sediment system, approximately 0.3 μmol metals g^{-1} dry sediment were found to be associated with pyrite [8]. This corresponds to approximately 2.0-3.8 mmol metals mol^{-1} FeS_2, using the pyrite concentrations mentioned above. Although this is a very large range, the binding capacity of pyrite is still a factor 250 smaller than of AVS, which can bind an equivalent amount of metals (i.e. 1 mol metals mol^{-1} AVS) if sulphide ions precipitate according equation (1). Hence, AVS appears to be more important in the binding of metals in sediment than pyrite.

To complete the possible interaction patterns of heavy metals in sediment systems, we should add that trace metals can also bind to organic material and under aerobic conditions to iron and manganese oxides and oxyhydroxides [11]. In addition surface precipitation with $CaCO_3$ and binding to clay minerals may take place too in these systems (Figure 1).

With the extraction of AVS in laboratory analysis various metals like Cd, Zn, Ni, Pb and Cu are extracted as well, the so-called Simultaneously Extracted Metals (SEM). From ecotoxicity experiments, it was found that for SEM/AVS ratios smaller than 1 toxicity effects were absent, whereas with SEM/AVS > 1 toxic effects were observed [2, 3]. The results were explained by considering reaction (1). However, direct confirmation of the thermodynamic model under natural conditions hasn't been given yet in literature. One of the reasons is that metal concentrations in the anaerobic porewater are well below detection limit. In addition, it is difficult to prevent disturbance of the anaerobic conditions during experiments. This may easily result in measurable but erroneous metal concentrations.

In the present study, which is described in research plan 96/LAC/502501/AVS/00, the effect of HCl concentration on AVS and metal release was investigated, in order to increase the knowledge on the relationship between AVS and SEM. The equivalent release of sulphide (AVS) and heavy metal does not necessarily mean that the metal is bound by sulphide in the sediment. The sulphide could originate from FeS whereas the metal could be liberated from $CaCO_3$ or organic matter (Figure 1). However, if no metal is liberated by an acid addition that liberates sulphide from the sediment, it is highly unlikely that the metal was bound by sulphide [1]. Beside determination of Cd, Zn, Ni, Pb and Cu, we determined Fe and Mn concentrations as well since these elements play an important role in the speciation of sulphide in anaerobic sediments [7, 13].

As part of the present study, the influence of the amount of sediment used in the experimental set-up was investigated. Brouwer and Murphy [14] used an extraction method, which was based on diffusion of hydrogen sulphide after addition of acid to unstirred sediment, and found an increase in AVS content by using smaller amounts of sediment. In the present experimental set-up however, the hydrogen sulphide is transported by a nitrogen flow and the sediment suspension is contineously stirred. Hence, it is expected that the amount of sediment will not influence the AVS or SEM concentrations measured in the sediment. This is checked by performing AVS and SEM extractions using different amounts of wet sediment at the same acid strength.

2. MATERIALS AND METHODS

2.1 Sediments

Freshwater sediments were obtained from various Dutch sample sets present at RIVM and the University of Utrecht. The wet samples originate from the Kromme Rijn at Odijk, Biesbosch and Botlek. The Biesbosch sample is chosen from four different Biesbosch samples, which were screened for AVS and SEM contents. The Kromme Rijn and Botlek samples had been analysed before [10]. LIMS codes for Biesbosch, Kromme Rijn and Botlek samples were 41874, 42417 and 43083, respectively. In order to check the efficiency of the sediment digestion procedure for total metal analysis, two dry reference sediments were applied as quality control samples: (1) PACS-1, NRC Canada, marine sediment, and (2) CRM-280, BCR, lake sediment.

2.2 Chemicals

Calcium carbonate (precipitated, p.a.), N,N-diethyl-1,4-phenylammonium-sulfate (DPD, p.a.), sodium hydroxide (pellets p.a.), potassium dichromate (p.a.), hydrochloric acid solutions (37 %, p.a.; 30 % s.p.), nitric acid (65 %, s.p.), cadmium, copper, lead, nickel, zinc, iron, manganese, calcium, gallium and indium standard solutions (all 1000 mg l^{-1}, s.p.) were all obtained from Merck. Sodium sulphide (anhydrous powder) was manufactured by Johnson Matthey. All solutions were prepared using demineralised tap water, produced by a Millipore-Q Reagent-Grade water system (further referred to as milli-Q).

2.3 Sediment characterisation

In order to characterise the sediment, total carbon, nitrogen and sulphur were measured as well as carbonate content and total metal concentrations.

2.3.1 Calcium carbonate

Calcium carbonate was measured with the Scheibler method according to a former Standard Operating Procedure (SOP) of the Laboratory for Soil and Groundwater (LBG) [15]. Some slight changes were made in the calibration procedure. First, the carbonate content was classified by the extent of foaming when adding 4 mol l^{-1} HCl to dry, ground sediment. Dry sediment (1-10 g, depending on the estimated carbonate content) was weighed into a conical flask. Three standards of 100, 200 and 300 mg $CaCO_3$ and a blank were used for calibration. To all flasks 20 ml milli-Q and a stirring bar were added. Reagent-tubes were filled with 7 ml 4 mol l^{-1} HCl and placed in the conical flasks which were then connected to the Scheibler apparatus. When the fluid level in the Scheibler burettes was stable, the reagent tubes were tipped over to start the reaction. The flasks were stirred for an hour, after which the volume of formed gas was read from the Scheibler apparatus. $CaCO_3$ in the samples was calculated using a calibration curve of the $CaCO_3$ standards. Samples were analysed in duplicate.

2.3.2 *Total carbon, nitrogen and sulphur*

The total carbon, nitrogen and sulphur content of the sediment were determined with a Fisons EA 1108 CHNS analyser, according to LAC-SOP M369 [16]. Dry sediment is used for the analysis. Sulfanylamide was used as a standard. Samples were measured in duplicate.

2.3.3 *Sediment digestion*

The digestion of sediment is carried out with a HNO_3/HCl mixture under pressure in a CEM MDS-2000 microwave [17], according to NVN 5770 [18]. Approximately 0.5 gram wet sediment is weighed in duplicate into digestion vessels and a mixture of 4 ml concentrated HNO_3, 12 ml HCl (30 %) and 10 ml milli-Q is added. Wet sediment is used to prevent losses of volatile components during drying. In addition two reference sediments (PACS-1 and BCR) are digested. Milli-Q water is used as a blank. The digestion vessels are weighed before and after digestion to check for losses due to leakage. The microwave is programmed as follows: 1 min. 30 % power, 4 min. 80 % power, 60 min. 100 % power and 30 min. cooling down. After depressurisation of the vessels the content is transferred quantitatively into a 100 ml volumetric flask to which 1 ml indium- and 1 ml gallium-solution (both 1000 mg l^{-1}) are added as internal standards. The flasks are filled up with water and stored for a few hours. After settling of some final particles the solution is transferred to poly-ethylene bottles. In the resulting solution the elements Cd, Ni, Zn, Pb, Cu, Fe, Mn and Ca are analysed by ICP-AES.

2.3.4 *Dry weight*

AVS and metal concentration are expressed per gram dry sediment.To determine the dry weight content of the sediment approximately 10-30 gram of wet sediment was weighed in triplicate, dried for 24 hours at 105 °C and weighed again. The dry weight content is calculated as the mass of dry sediment divided by the mass of wet sediment and expressed as a percentage.

2.4 Acid volatile sulphide and extracted metals

2.4.1 *Titration of sediment*

To gain information on the amount of acid needed in the AVS-analysis to obtain a certain pH in the extract (see 2.4.2), first the sediment samples were titrated with HCl. To that end a titration vessel with 50 ml milli-Q was flushed with nitrogen for 15 minutes to remove oxygen. Approximately 2 grams of wet sediment were added to the titration vessel which was again flushed with nitrogen for 15 minutes. Then the pH of the suspension was measured. This set-up is comparable to the set-up used for carrying out the AVS-extraction (the amounts of milli-Q and used sediment are halved due to titration vessel size). The sediment was titrated with 20-1000 µl aliquots of 6 mol l^{-1} HCl to a total amount of 3 ml (i.e., 18 mmol HCl). The pH was measured after 5 and 10 minutes. The vessel was contineously flushed with nitrogen to prevent oxidation of the sediment sample.

2.4.2 *Extraction procedure*

For the determination of acid volatile sulphide (AVS) a procedure was developed at the RIVM which is analogous to the one described by Allen et al. [1] and is described in detail in RIVM-report no. 719101017 [9].

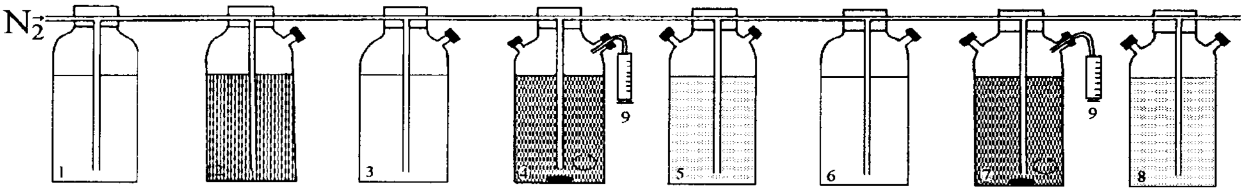

Figure 2. Experimental set-up for the analysis of AVS in sediment. For explanantion see text.

In short, the experimental set-up consists of 8 bottles which are connected serially with Argyle tubing (Fig. 2). The first 3 bottles are used to wet the gas and to eliminate oxygen and other impurities from the nitrogen flow. Bottles 4 and 7 are filled with 100 ml milli-Q, and bottles 5, 6 and 8 with 100 ml 0.5 N NaOH. The 6th bottle is used to trap any sulphide which is not trapped in the bottle 5, to prevent carry-over to bottle 7. However, in this extra bottle sulphide was never detected [9]. Approximately 4 grams of wet sediment are added to each milli-Q bottle (4 and 7) and with a syringe (connected with Argyle tubing to the bottle) 10 ml of a HCl solution of varying acid strength is added. These syringes (10 ml, Fortuna) have no rubber cap on the plunger to prevent contamination of the HCl with sulphur and metals from this rubber. The suspension is stirred contineously and flushed with nitrogen for 45 minutes. During this time, sulphide from the sediment is dissolved and transferred to the NaOH-bottle as H_2S by the nitrogen flow, where it is fixed as sulphide again. The sulphide in the NaOH bottles is measured after a colourimetric reaction (see 2.5.1). The experimental set-up is checked daily for leakage by extracting a freshly prepared Na_2S-solution by adding 10 ml 12 mol l^{-1} HCl. From the sulphide concentration in the NaOH bottles the recovery of the set-up can be calculated. Recovery was 89 % on average. Data were rejected when the recovery was lower than 80 %.

2.4.3 Extracted metals

The sediment suspension resulting from the AVS extraction is filtered immediately at the end of the extraction procedure, first through a folded paper filter (Schleicher & Schuell, 595 ½) and then through a 0.45 μm filter (Millipore, Millex HA) using a syringe. The extracted metals Cd, Ni, Pb, Cu, Zn, Fe, Mn and Ca are analysed in this filtered extract by flame-AAS and ICP (see below).

2.5 Analysis of sulphide and metals

2.5.1 Sulphide

Sulphide is measured colourimetric. A blue coloured solution is formed after reaction of sulphide with N,N-diethyl-1,4-phenylammonium-sulphate (DPD) and potassium dichromate. The extinction of this solution is measured at a wavelength of 670 nm on a Pharmacia spectrophotometer (Biochrom 4060). A calibration curve is made with the sodium sulphide standard which is also used for the recovery test. The concentration of this standard solution is determined by a titration procedure with thiosulphate [9].

2.5.2 Metals

For practical reasons different methods were used for the measurement of metals in different matrices:

sediment extracts

Cd, Ni, Pb, Cu are analysed on a Perkin Elmer 2100 Atomic Absorption Spectrometer [19] according to SOP LAC/M154/02 [20]. Samples are measured undiluted and standards are prepared according to the SOP. Detection limits were 0.003, 0.013, 0.034 and 0.007 μmol g^{-1} d.w. for Cd, Ni, Pb and Cu, respectively.

Zn, Fe, Mn and Ca are analysed on a Spectro Spectroflame M5 Inductively Coupled Plasma (ICP) [21] according to SOP LAC/M259/03 [22]. Samples were diluted 1-50 times with 0.1 mol l^{-1} HCl. Standards were prepared according to the SOP. Detection limits were 0.004, 0.008, 0.002 and 0.125 μmol g^{-1} d.w. for Zn, Fe, Mn and Ca, respectively.

digests

Cd, Ni, Pb, Cu, Zn, Fe, Mn and Ca are analysed on an Perkin Elmer Optima 3000 XL ICP, according to research plan 94/LAC/502501/milestone/01 [23]. Samples were diluted 1 and 10 times with a blank solution containing 10 mg l^{-1} gallium, 10 mg l^{-1} indium, 12 % HCl (v/v) and 4 % HNO_3 (v/v). Standards were prepared in the same matrix. Detection limits were 0.002, 0.07, 0.38, 0.05, 1.48, 0.17, 0.18 and 0.60 μmol g^{-1} d.w. for Cd, Ni, Pb, Cu, Zn, Fe, Mn and Ca, respectively.

2.5.3 *Influence of sediment mass*

As mentioned in the introduction, the amount of wet sediment used for the AVS-analysis might influence the measured AVS concentration and, thus, the SEM-to-AVS ratio. To check whether this is the case for the presently applied experimental set-up, AVS and SEM were analysed in sample 41874 for different amounts of sediment. Sulphide and extracted metals were analysed as described before.

2.5.4 *Influence of pH on AVS and SEM concentrations*

The influence of the acidity of the sample solution on AVS and SEM concentrations was studied by adding different amounts of HCl. The volume of the added HCl was kept at 10 ml but its concentration varied between 12 and 0.084 mol l^{-1}. After filtration of the sediment suspension the pH was measured in the extract. AVS and metal concentrations are plotted against this pH. Finally, the metals were analysed in these extracts as described in section 2.5.2.

3. RESULTS AND DISCUSSION

3.1 Sediment characterisation

3.1.1 Calcium carbonate, total carbon, nitrogen, sulphur and dry weight

For the characterisation of the sediments $CaCO_3$ content, dry weight content, total carbon, nitrogen and sulphur were determined. In table 2 the results of these measurements are given in weight percentages. Sediments are given in order of increasing $CaCO_3$ content, which is an important parameter, as will be shown later. Sediment 42417 has the highest total C, N and S content, sediment 41874 the lowest. Total sulphur content for sediment 43083 was just below the detection limit of 0.5 % as given in the SOP [16], whereas for sediment 41874, the total sulphur content was well below the detection limit. Duplicates and triplicates were in good agreement, relative standard deviations were less than 5 %.

Table 2. $CaCO_3$, dry weight content (d.w.), total carbon, nitrogen and sulphur (in weight percentages)

sediment	$CaCO_3$ (%)	std. dev.	d.w. (%)	std. dev.	total C (%)	std. dev.	total N (%)	std. dev.	total S (%)	std. dev.
42417	4.4	0.05	33.4	0.41	6.24	0.30	0.51	0.01	0.56	0.01
41874	8.7	0.04	55.7	1.31	4.40	0.01	0.24	0.00	<DL	-
43083	16.0	0.12	31.5	0.02	5.79	0.08	0.36	0.01	0.49	0.01
		n=2		n=3		n=2		n=2		n=2

DL = detection limit

3.1.2 Total metals

Total metals were measured after microwave digestion of the sediment with an acid mixture of HCl and HNO_3. In table 3 the average results of duplicates are given. Duplicates were in good agreement with relative standard deviations less than 3.2 %. Fe and Mn concentrations are highest for all sediments. From the metals that make up SEM in AVS analysis, Zn is present at the highest concentration. Cu, Ni and Pb have similar concentrations, whereas Cd is present in only very small amounts.

Table 3. Average total metal and sulfur concentrations after sediment digestion by microwave (n=2)

sediment	Cd μmol g^{-1}	Cu μmol g^{-1}	Ni μmol g^{-1}	Zn μmol g^{-1}	Pb μmol g^{-1}	Total μmol g^{-1}	Fe μmol g^{-1}	Mn μmol g^{-1}	Ca μmol g^{-1}	S μmol g^{-1}
42417	0.05	1.47	0.80	12.75	0.71	15.78	627.8	23.42	0.45	167.5
41874	0.09	0.85	0.58	12.64	0.71	14.88	460.8	15.87	0.82	77.0
43083	0.07	1.71	0.82	9.44	0.73	12.76	590.8	28.38	1.49	163.7

Calcium was measured to compare its concentration with the concentration measured indirectly with the Scheibler method (described in section 3.1.3). Total sulphur measured by elemental analysis is in good agreement with total sulphur measured after digestion (0.56 % S is 173 μmol g^{-1}, as compared to 168 μmol g^{-1}; 0.49 % S is 153 μmol g^{-1}, as compared to 164 μmol g^{-1}).

3.1.3 Comparison of Ca data obtained by different methods

Calcium was measured with three different methods: (i) with the Scheibler method, assuming equivalent amounts of released calcium and carbonate; (ii) in the AVS extracts, where calcium is released by using 1 mol l^{-1} HCl; and (iii) total calcium, measured after microwave digestion of the sediment with acid. In table 4 the results of these very different methods are compared.

Table 4. Ca concentrations in sediment determined with different methods

	Scheibler	digest	extracts		
sediment	Ca mmol g^{-1}	Ca mmol g^{-1}	Ca mmol g^{-1}	avg. Ca mmol g^{-1}	std. dev.
42417	0.44	0.45	0.53	0.47	0.05
41874	0.87	0.82	0.98	0.89	0.08
43083	1.60	1.49	1.55	1.55	0.06

Calcium concentrations obtained by the three methods are in good agreement, with relative standard deviations between 4 and 11 %. This means that the carbonate measured with the Scheibler method is mainly present as calcium carbonate and that most calcium measured in the extracts and digests originates from calcium carbonate.

3.2 Titration of sediment

In figure 3, acid titration curves of the various sediments are presented as pH versus the amount of HCl added. The sediment with the lowest carbonate content has the highest decrease in pH per added equivalent acid, the sediment with the highest carbonate content the lowest. As expected, the acid-buffering capacity increases with carbonate content.

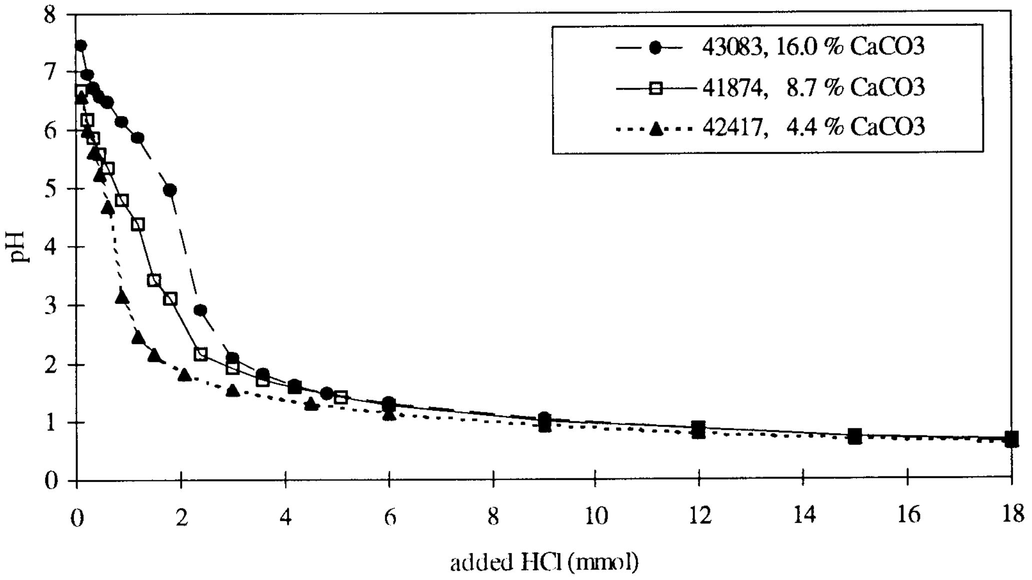

Figure 3. pH vs. added HCl

Unfortunately, it was not possible to use the information from the titration curves in figure 3 for estimating the amount of acid to get a certain final pH in the AVS extraction. In general, the final pH in the sediment extract turned out to be higher than expected from the titration curves. Several reasons can be given for this observation. Most likely, the observed discrepancy is due to the longer stabilisation time before measuring pH in the AVS extraction (45 minutes), as compared to 10 minutes in the titration. After addition of the first few aliquots of acid in the titration experiments it could be observed that the pH first dropped and, then increased again by about 0.2 pH units in 5 minutes. Thus, after 45 minutes, the pH in the sediment extract would be higher than if it would be measured after 10 minutes.

Another reason could be that during the titration first the carbonate was dissolved, whereas in the AVS-extraction procedure various "dissolution" processes occurred simultaneously. Apart from carbonate, organic matter and sulphide react in the presence of H^+ as shown in equations 2-4, in which c = cation; OM = organic matter; Me = metal:

$$CaCO_3 + 2\,H^+ \rightarrow Ca^{2+} + CO_2\uparrow + H_2O \qquad (2)$$

$$OM\text{-}c + H^+ \leftrightarrow OM\text{-}H + c^+ \qquad (3)$$

$$MeS + 2H^+ \rightarrow H_2S\uparrow + Me^{2+} \qquad (4)$$

For the dissolution of $CaCO_3$ and metal sulphides under acidic conditions into carbon dioxide and hydrogen sulphide respectively, 2 moles of protons are required per mol of initial reagent. When estimating that organic matter is well represented by fulvic acid, its proton binding capacity is assumed to be about 5.5 mmol g^{-1} organic matter [24]. From the organic carbon content of the sediment, the organic matter content can be calculated by multiplication with a factor of 1.7 [25]. From these data the proton binding capacity of the OM can be expressed in mmol H^+ g^{-1} d.w.

A third reason for the difference in pH in the titration curves versus AVS extracts could be the difference in pH measurement due to a suspension effect. In the titration experiment, pH was measured in a suspension whereas the AVS extracts were filtered solutions.

3.3 Influence of sediment mass on AVS and SEM concentrations

In figure 5, AVS and SEM concentrations and the SEM-to-AVS-ratio versus wet sediment mass are presented. Average values for AVS and SEM are 15.3 and 12.2 µmol g^{-1} d.w., with standard deviations of 1.0 and 0.8 µmol g^{-1} d.w., respectively. For the SEM-to-AVS-ratio the average is 0.8 with a standard deviation of 0.06. As shown in figure 5, there is no influence of the amount of sediment used in AVS analyses on the AVS or SEM concentration and, thus, not on the SEM/AVS ratio. In the experiments with varying acid strengths, between 3.9 and 4.9 gram wet sediment is used. Based on the results presented in figure 5, the variation in mass of the weighed sediment will not influence the resulting AVS and SEM values.

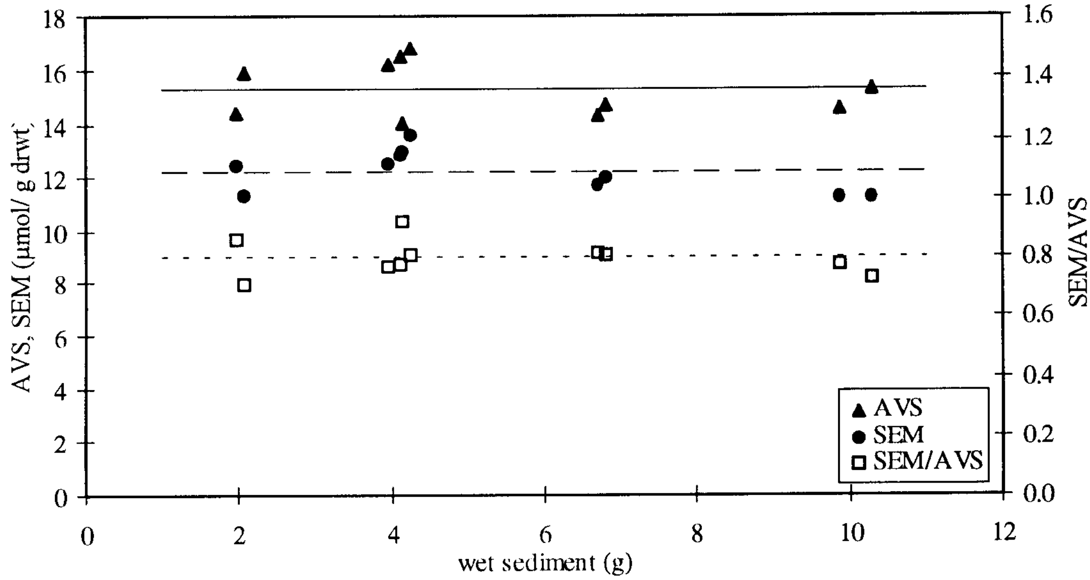

Figure 5. AVS, SEM and SEM/AVS vs. wet sediment mass (sample 41874).

3.4 Influence of pH on AVS and metal concentrations

3.4.1 AVS and SEM

In figures 6-8, the AVS and SEM concentrations and SEM/AVS ratio measured at various acid strengths are presented versus pH for sediment sample 41874. With decreasing acidity both AVS and SEM concentrations decrease. This can be expected as less acid will most likely dissolve less carbonate, organic matter and metal sulphides. The decrease of AVS and SEM with increasing pH appears to be linear with quite good correlation (see table 5). This result seems to be typical for the present set of sediments since a similar observation is found for sample 42417 and 43083 (appendix, figures 1-4). The SEM/AVS ratio also decreases with increasing pH. This means either that at high acid strength, metals from other phases than sulphide (see Figure 1) are released, or that at low acid strength metals can reabsorb onto other phases, so SEM/AVS is low at high pH.

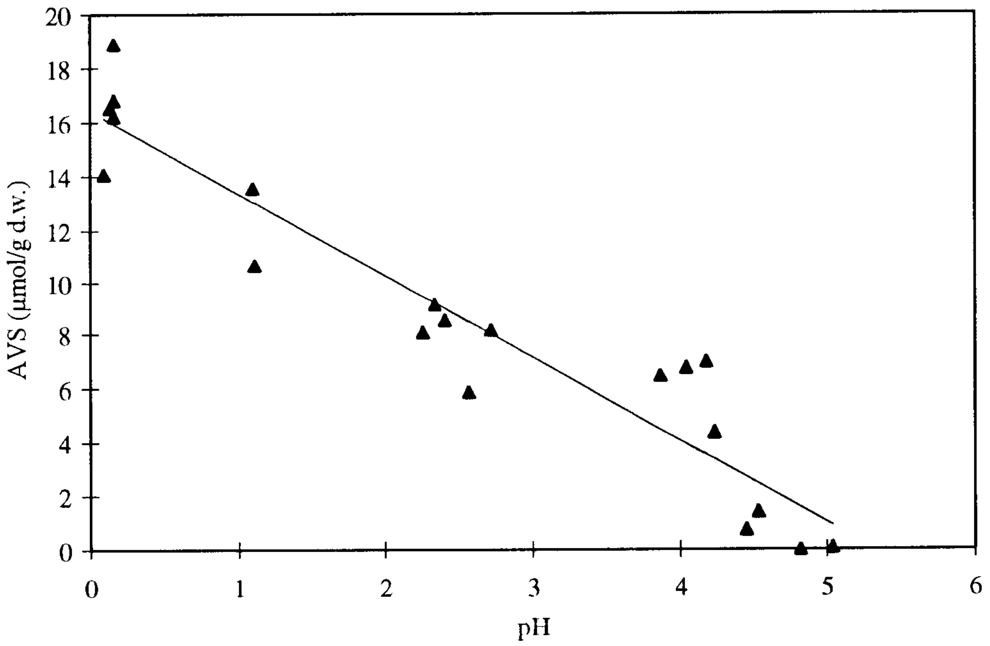

Figure 6. AVS vs. pH, sample 41874

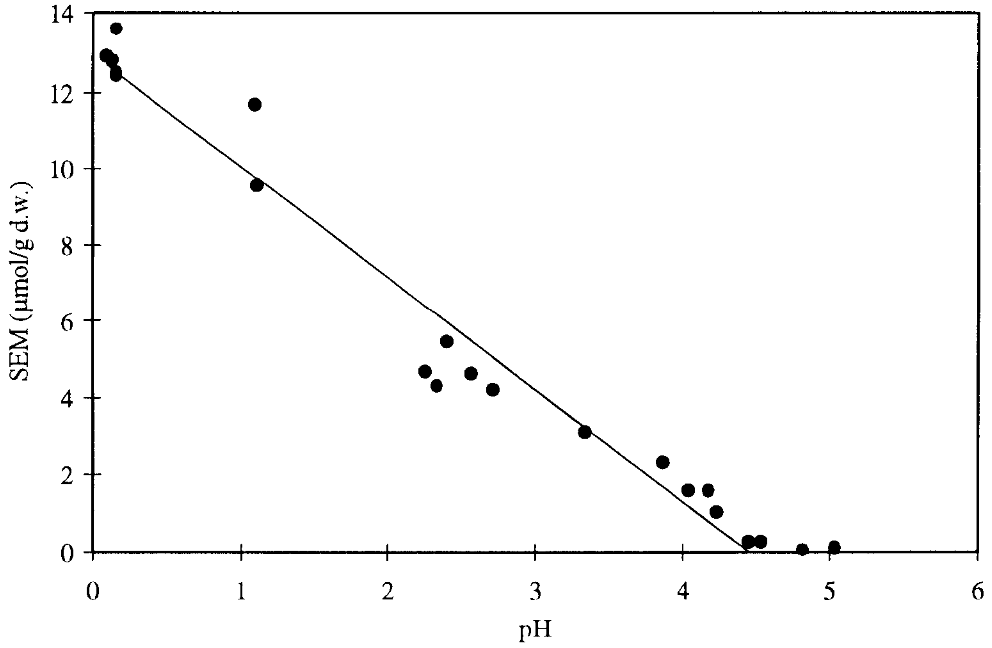

Figure 7. SEM vs. pH, sample 41874

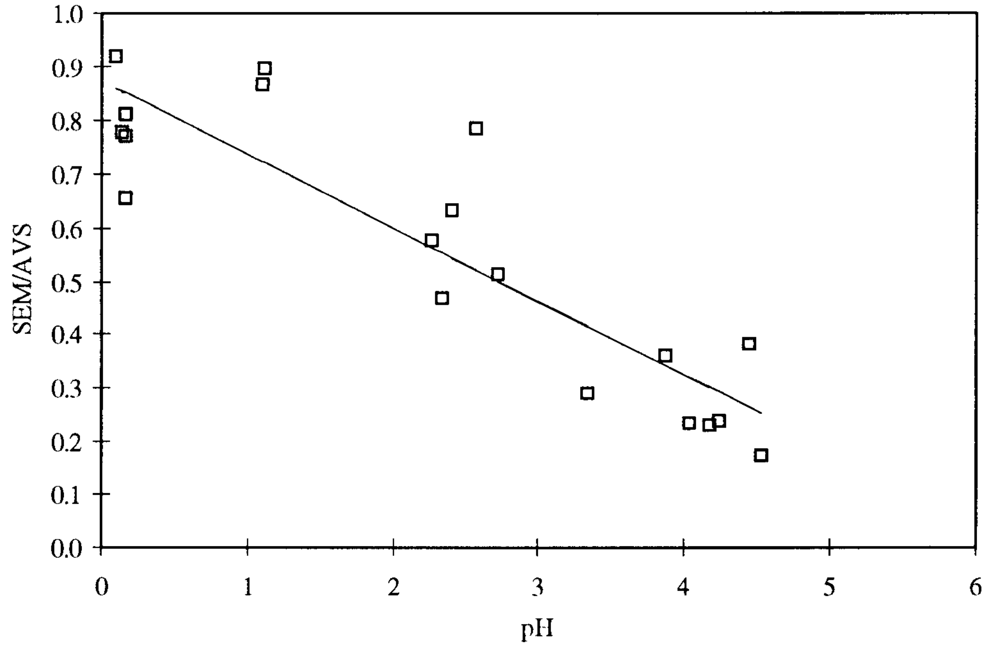

Figure 8. SEM/AVS vs. pH, sample 41874

Slopes, intercepts and correlation coefficients for the above mentioned plots are given in table 5. The highest slope for AVS corresponds with the highest slope for SEM. For AVS and SEM the slope decreases with increasing $CaCO_3$ content. A large slope implies that more protons per pH unit are available for the dissolution of metal sulphides compared to a small slope. Thus, for a sediment with low carbonate content it can be expected that more protons are available for sulphide dissolution, resulting in a steeper slope for the plot of AVS and SEM versus pH.

Table 5. Slopes, intercepts and correlation coefficients for AVS, SEM and SEM-to-AVS ratio vs. pH (given units are only valid for SEM and AVS)

	slope (μmol g^{-1} d.w. pH^{-1})			intercept (μmol g^{-1} d.w.)			correlation coefficient		
sediment	AVS	SEM	SEM/AVS	AVS	SEM	SEM/AVS	AVS	SEM	SEM/AVS
42417	-7.16	-3.01	-0.08	33.88	12.43	0.40	0.92	0.97	0.95
41874	-3.09	-2.92	-0.14	16.44	12.98	0.87	0.95	0.98	0.89
43083	-1.99	-2.07	-0.15	12.55	9.51	0.87	0.85	0.99	0.89

Figure 7 shows that metal concentrations decrease with increasing pH in a similar way as AVS. At this point it seems useful to reconsider the dissolution reaction (4) of metal sulphides in the presence of protons. We will focus on zinc, because zinc is the only metal which was detected over the whole range of acid strengths used in this experiment, due to its high concentration. The other metals (Cd, Pb, Cu and Ni) are found to be present in much lower concentrations and below detection limit at low acid strengths (pH > 2). Starting point in this procedure is the liberation of zinc associated by the solid phase in an anaerobic sediment system by acid, which can be written by the simplified exchange reaction:

$$\mathrm{ZnSolid} + \mathrm{nH^+} \leftrightarrow \mathrm{Zn^{2+}} + \mathrm{H_nSolid^{n-2}} \qquad (5)$$

where ZnSolid is the amount of exchangeable zinc bound by the solid phase, including sulphides, organic matter, carbonate and clay minerals, and n is the proton exchange coefficient. The corresponding exchange constant K for this reaction is:

$$K = \frac{\left[Zn^{2+}\right]\cdot\left[H_nSolid^{(n-2)}\right]}{\left[ZnSolid\right]\cdot\left[H^+\right]^n} \qquad (6)$$

Rearranging this equation yields:

$$\frac{\left[Zn^{2+}\right]}{\left[ZnSolid\right]} = \frac{K\cdot\left[H^+\right]^n}{\left[H_nSolid^{(n-2)}\right]} \qquad (7)$$

Taking the logarithm:

$$\log\frac{\left[Zn^{2+}\right]}{\left[ZnSolid\right]} = \log K' - n\cdot\left(pH + \log\gamma\right) \qquad (8)$$

in which $K' = K / \left[H_nSolid^{(n-2)}\right]$ and γ is the activity coefficient. The activity coefficient will be of influence at high ionic strength, which exists at pH 0 in this experiment (log $\gamma \approx -0.26$ at an ionic strength of 1 mol l^{-1}, [26]). At lower acid strengths γ will become negligible (log $\gamma \approx -0.039$ at ionic strength of 0.01 mol l^{-1}, [26]). In order to plot log $[Zn^{2+}]/[ZnSolid]$ versus pH, $[Zn^{2+}]$ and $[ZnSolid]$ were calculated as follows: for $[ZnSolid]_{total}$ the Zn concentration at pH 0 is taken. The [ZnSolid] at a certain pH is calculated as the difference of $[ZnSolid]_{total}$ and [Zn] as measured in the AVS-extract. A plot of log $[Zn^{2+}]/[ZnSolid]$ versus pH is shown in figure 9 for sample 41874 (for samples 42417 and 43083 see Appendix figure 7 and 8, respectively). This plot shows a straight line, which is in agreement with the above mentioned model (equations 5-8). In that case, plotting log $[Zn^{2+}]/[ZnSolid]$ versus pH should give a straight line with slope n and intercept log *K'*. Slopes, intercepts and correlation coefficients for the three sediment samples are given in table 6. We should note that the data in figure 9 were not corrected for activity influences, because the ionic strength for the individual data are not available. As explained above, this correction is of importance at very low acidity values only, which finally would result, on a qualitative basis, in a slightly smaller slope of the regression line.

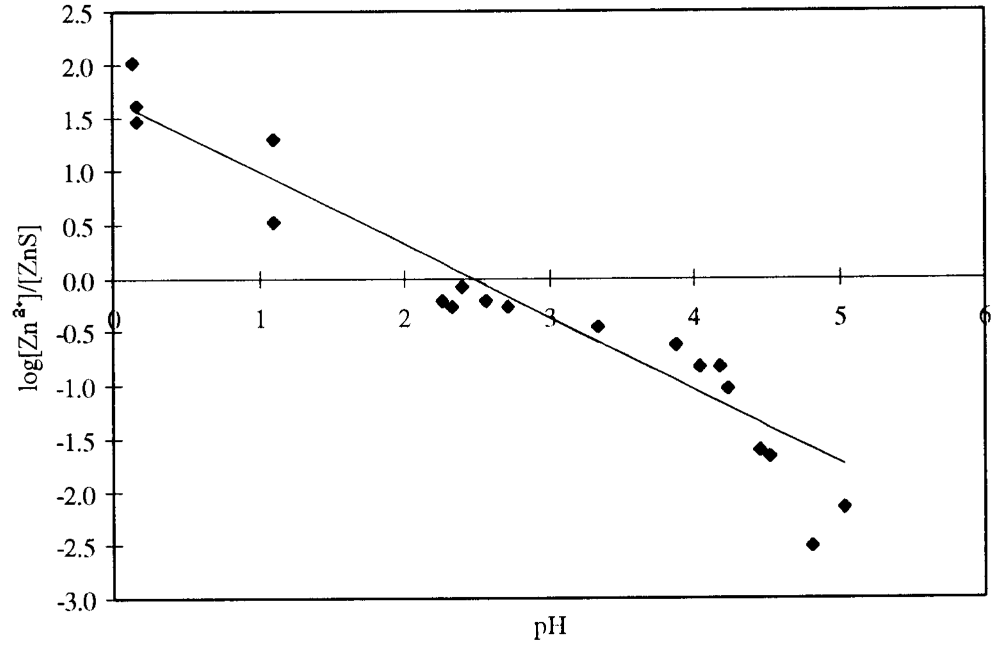

Figure 9. log $[Zn^{2+}]/[ZnSolid]$ vs. pH, sample 41874

The slope for the plot of log $[Zn^{2+}]/[ZnSolid]$ versus pH is 0.7 on average and appears to be comparable for the three sediment samples. Theoretically this would mean that 0.7 mol H^+ is needed in the exchange of 1 mol zinc from the solid phase into the aqueous solution. From the present set of data, it is not possible to distinguish from which solid pool zinc liberates and, hence, the underlying dissolution process remains uncertain. Furthermore, for the other metals (Ni, Cd, Cu and Pb) the concentrations appear to be below the limit of detection, which makes the determination of proton exchange coefficients for these metals impossible. Nevertheless, the present approach seems to be in line with Freundlich-like binding models modified for the competition with protons. For example, for cadmium proton exchange coefficients reported in the literature vary from 0.46 to 0.64 [27-30]. For other metals, literature data on proton exchange coefficients are scarce. Based on batch adsorption experiments with 38 Danish soils, Anderson and Christensen [29] found a proton coefficient of 0.89±0.05 for the metal zinc, which appears somewhat higher than the one obtained in the present study. On the other hand, in a recent study of Janssen et al. [30], for zinc a proton exchange of 0.61 was found, which was based on the determination of metal concentrations in pore water and solid phase in 20 Dutch soils. In conclusion, although the proposed exchange model is to some extent oversimplified, the resulting proton coefficient appears to be realistic.

Table 6. Slopes, intercepts and correlation coefficients for log $[Zn^{2+}]/[ZnSolid]$ vs. pH

sediment	slope	intercept	corr. coeff.
42417	-0.70	1.34	0.992
41874	-0.68	1.67	0.966
43083	-0.70	1.91	0.950
average	-0.69	1.64	0.969
RSD (%)	1.9	17.3	2.2

3.4.2 Proton consumption

To obtain varying acidity in the resulting extraction solution, different amounts of HCl were added to the sediment suspension for the analysis of AVS. From the amount of added HCl the initial pH can be calculated, which is plotted against the pH as measured in the AVS extract after 45 minutes of reaction time.

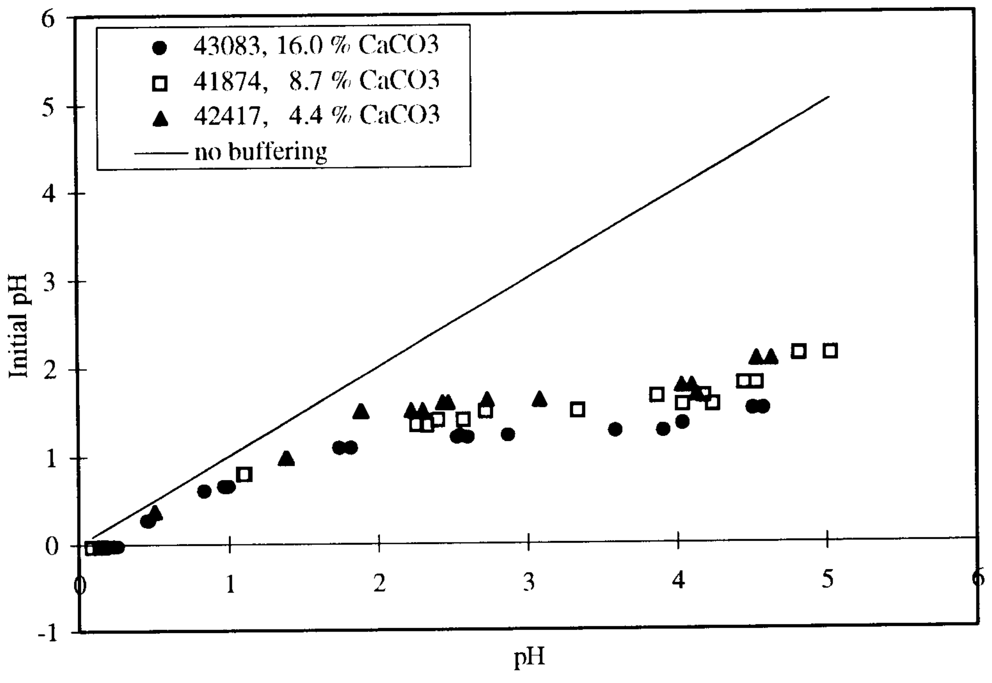

Figure 10. Initial pH vs. "final" pH

From figure 10, it can be seen that the final pH is not the same as the initial pH, which is expected for the case of non-buffering conditions. However, the pH increases during the extraction. This is due to proton consumption by carbonate, organic matter and sulphide, as explained in section 3.2. Figure 10 also shows that the pH increase is largest for the sediment with the highest carbonate content (closed dots, sediment 43083) due to its large buffering capacity for protons.

3.4.3 Calcium and calcium carbonate

In line with the heavy metals, calcium extracted during the AVS analysis also shows a decrease with pH, although not linear (see figure 11 for sample 43083, and figures 9 and 10 in the appendix for samples 42417 and 41874, respectively). From the amount of added acid it can be calculated how much $CaCO_3$ can dissolve, assuming that first all carbonate dissolves before organic matter is fully protonated or sulphides are dissolved (see also discussion in section 3.2). The computed calcium concentrations are presented in figure 11 as a dotted line. The observed decrease in calcium concentration starts at a lower pH than calculated. This is probably due to the fact that at higher pH, competition for protons by organic matter starts playing a role, which is not accounted for in the calculations. Another reason is that the measured pH is not an equilibrium pH due to the separation of the solid phase and the supernatant after the extraction procedure. Kinetic aspects may play a crucial role in this aspect and need primary attention in future research activities.

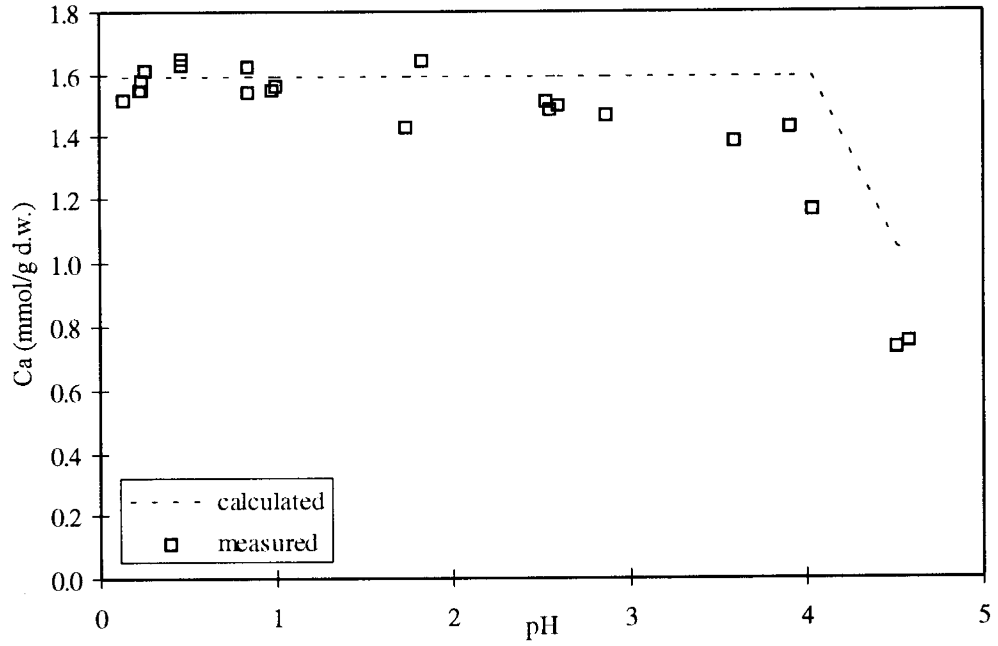

Figure 11. Ca vs. pH, sample 43083

3.4.4 Iron and manganese

In the AVS-extracts iron and manganese were measured as well. Fe and Mn concentrations versus pH are plotted in figure 12 for sediment sample 41874 (for samples 42417 and 43083 see figures 11 and 12, respectively, in the appendix). This plot shows a non-linear decrease of Fe and Mn concentrations with increasing pH in contradiction with the observed physico-chemical behaviour of SEM. For sample 41874, in figures 13-16, SEM, Fe, Mn and AVS concentrations are plotted against the initial HCl concentration (as described in 3.4.2; not the whole acid range is shown). From figures 13 and 16, it can be seen from the S-shaped curve that SEM and AVS do not dissolve immediately after addition of the smallest amount of acid. However, Fe and Mn concentrations increase already at the smallest acid addition (figures 14 and 15). This could explain the shape of the iron and manganese plot in figure 12. At high pH, acid is consumed by Fe and Mn compounds. When more acid is added, heavy metal sulphides start to dissolve and compete for protons with Fe and Mn compounds. This causes a decrease in dissolution of Fe and Mn, which can be seen in figure 12 as the slope decreases at low pH.

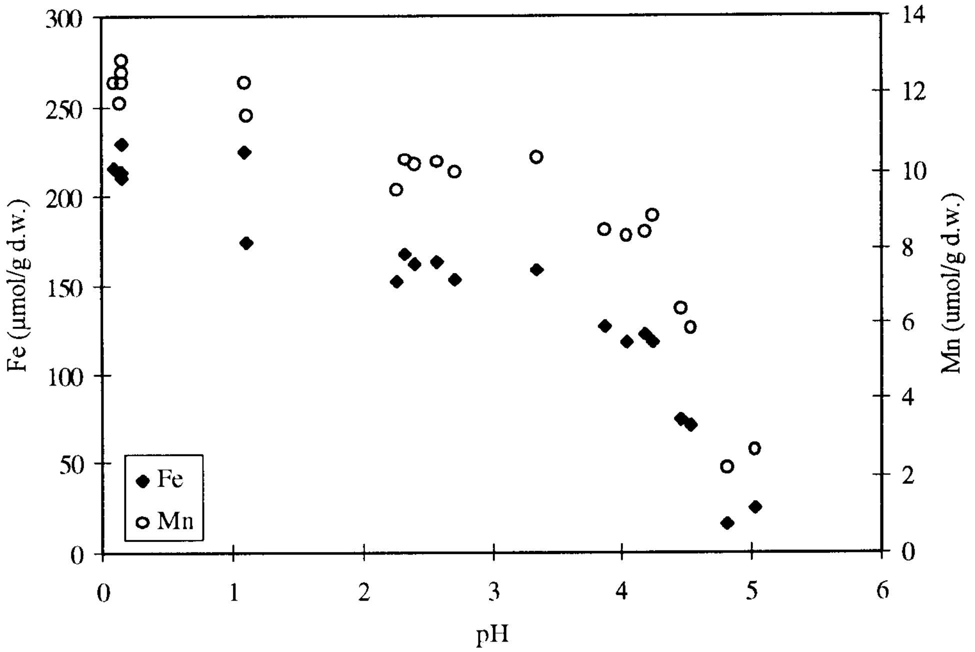

Figure 12. Fe and Mn vs. pH, sample 41874

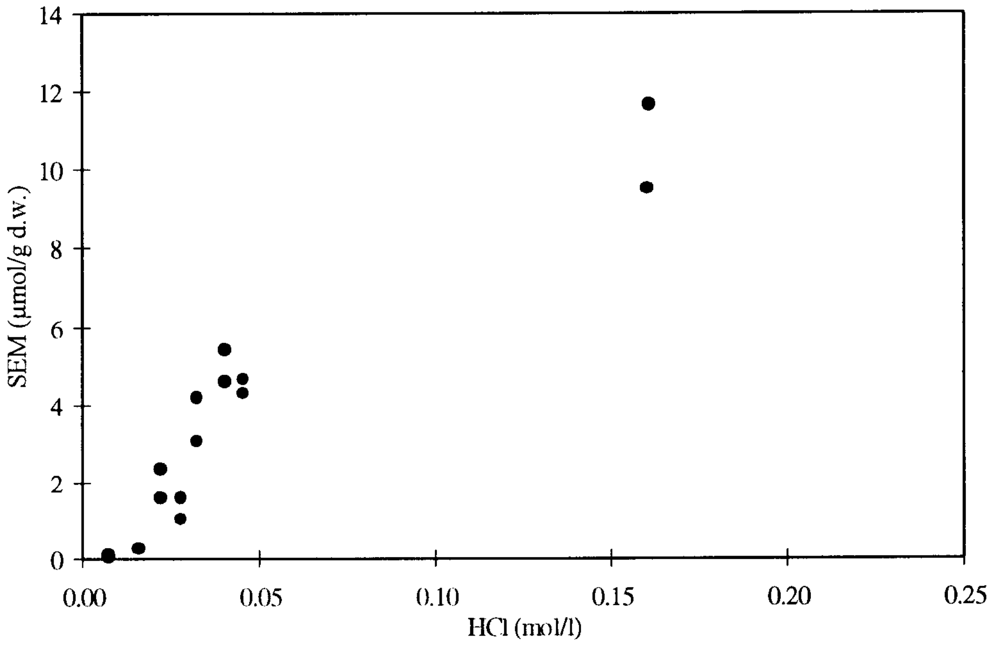

Figure 13. SEM vs. initial HCl concentration, sample 41874 (at 1.07 mol HCl l^{-1} [SEM] is 12.8 µmol g^{-1} d.w.).

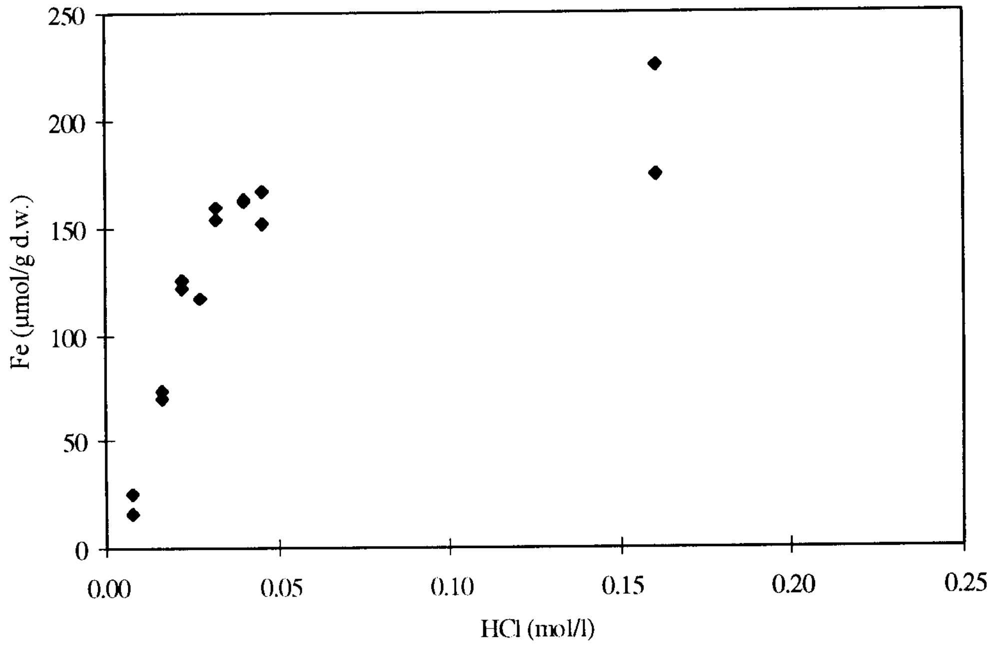

Figure 14. Fe vs. initial HCl concentration, sample 41874 (at 1.07 mol HCl l^{-1} [Fe] is 213 µmol g^{-1} d.w.)

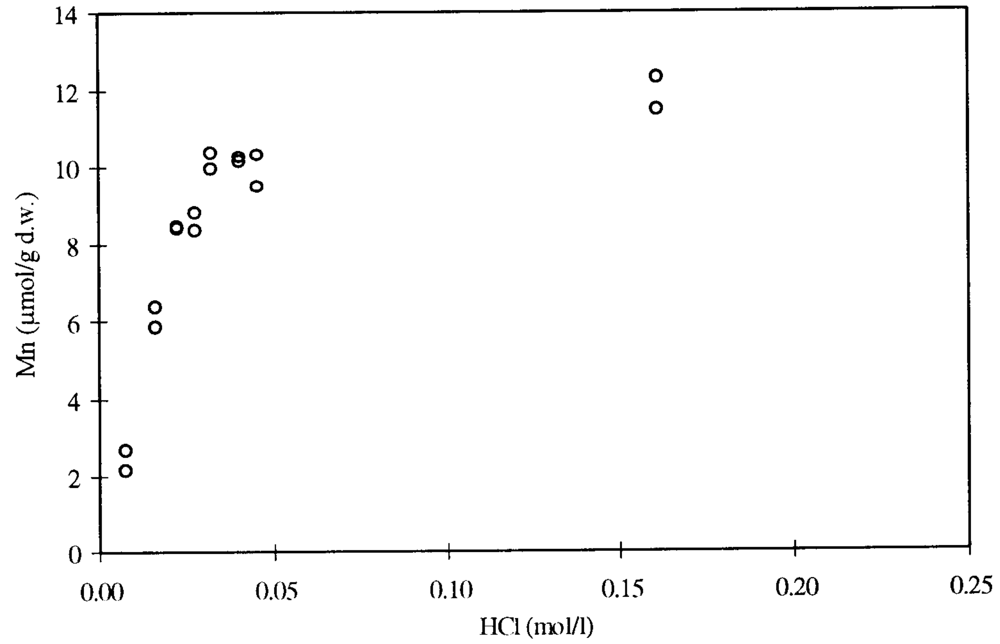

Figure 15. Mn vs. initial HCl concentration, sample 41874 (at 1.07 mol HCl l^{-1} [Mn] is 12.3 µmol g^{-1} d.w.)

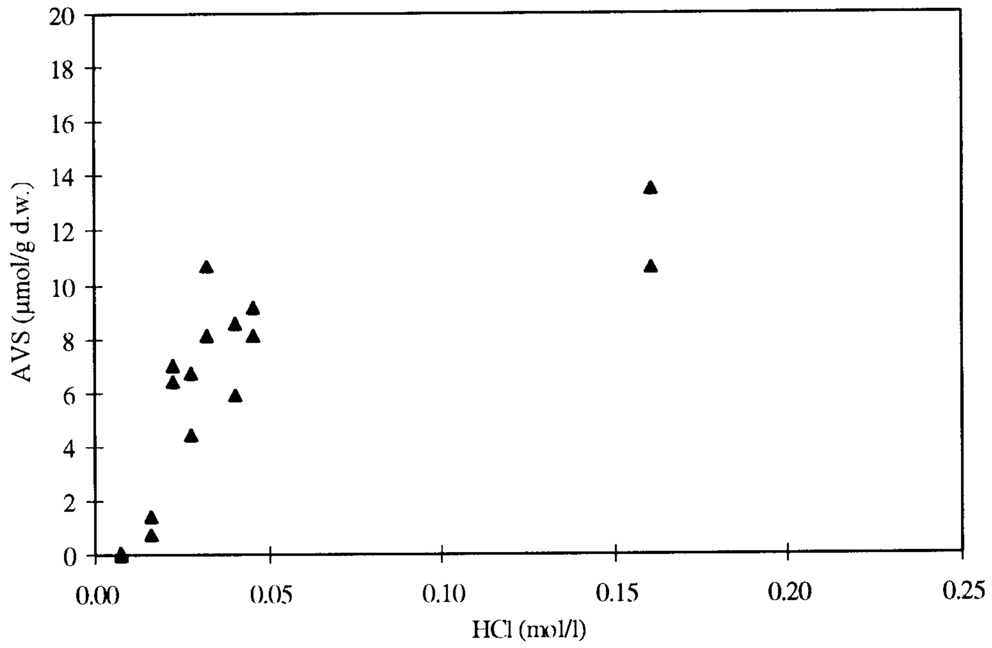

Figure 16. AVS vs. initial HCl concentration, sample 41874 (at 1.07 mol HCl l^{-1} [AVS] is 16.5 µmol g^{-1} d.w.)

3.4.5 Analytical aspects

From figures 6 and 7, it could be expected that the extraction of AVS and metals still increases at negative pH. However, when plotting AVS and metal concentrations against acid concentration instead of pH (figures 11-16), it can be seen that the concentrations reach a maximum value at approximately 1 mol HCl l^{-1} (pH 0, data not shown). This is in good agreement with results from a complementary study by Van den Berg (personal communication), where no significant difference in AVS and SEM concentrations measured at 1 and 6 mol HCl l^{-1} was found. Only copper and nickel concentrations were somewhat increased at the higher acid strength. Brumbaugh and Arms [31] however found significant higher AVS, Cu, Zn and Fe concentrations when extracting with 3 mol HCl l^{-1} instead of 1 mol HCl l^{-1}. In most studies with respect to AVS-ecotoxicoty relationships, an acid strength of 1 mol HCl l^{-1} is used in AVS determinations (see e.g. Allen *et al.* [1]). From the present study, it can be concluded that application of lower acid concentrations will not extract all AVS and metals (see figures 6, 7 and 12).

3.4.6 Comparison of metals data

In table 7, metals analysed in the AVS-extracts are expressed as percentages of total metal concentrations as measured after sediment digestion. These results show that the simultaneously extracted metals Cd, Cu, Ni, Zn and Pb make up for 70-86 % of the total content of these metals in the sediment as obtained after microwave digestion. Zn, Pb and Cd represent the largest fraction of the total content of the respective metals; Cu and Ni are found in much smaller quantities. The reason for this is that Cu is most likely bound to organic matter whereas Ni is probably built into clay minerals.

Table 7. Metals in AVS-extracts as percentages of their total concentrations in sediment digests

sediment	Cd %	Cu %	Ni %	Zn %	Pb %	SEM %	AVS %	Fe %	Mn %
42417	70.5	20.5	4.4	94.6	86.2	82.6	21.9	68.9	88.6
41874	81.2	37.6	31.1	92.1	86.4	86.3	21.4	46.3	77.8
43083	67.3	38.4	23.0	79.5	88.6	70.8	14.1	35.1	74.6

In tables 8 and 9 the fraction of "SEM" (total of Cd, Cu, Ni, Zn and Pb) that each of these metals represent, is given for the extracts and the digests respectively. These fractions are quite comparable. The Zn fraction is somewhat larger in the AVS-extracts and Cu and Ni fractions are somewhat smaller. These two metals are also the metals that have the lowest recovery in the AVS extracts as compared to total metal concentrations. Apparently at the lower acid strength used in AVS extraction as compared to microwave digestion, the binding strength of Zn with complexing compounds is weaker than in case of Cu and Ni. This leads to an increase in dissolution. As mentioned in section 3.4.5 at 6 mol HCl l^{-1} Van den Berg found higher Cu and Ni concentrations. At these high acid strengths Cu and Ni are probably released from other sources than sulphides (see figure 1). Most likely clay minerals are dissolved at this acid strength and Cu may desorb from organic matter.

Table 8. Metals, percentages of SEM in AVS-extracts

sediment	Cd %	Cu %	Ni %	Zn %	Pb %	SEM %
42417	0.2	2.3	0.3	92.5	4.7	100
41874	0.6	2.5	1.4	90.7	4.8	100
43083	0.5	7.3	2.1	83.0	7.1	100

Table 9. Metals, percentages of "SEM" in digests

sediment	Cd %	Cu %	Ni %	Zn %	Pb %	SEM %
42417	0.3	9.3	5.1	80.8	4.5	100
41874	0.6	5.7	3.9	85.0	4.8	100
43083	0.5	13.4	6.4	74.0	5.7	100

4. CONCLUSIONS AND RECOMMENDATIONS

The acid strength at which AVS and SEM are analysed in sediment, strongly influences the resulting AVS and SEM concentrations. Over the studied range of pH 0-5, AVS and SEM are maximum extracted at pH 0 (1 mol l^{-1} HCl). AVS analyses at acid concentrations lower than 1 mol l^{-1} result in lower SEM-to-AVS ratios which might lead to incorrect assessments of toxicity.

The amount of wet sediment used in the analysis of AVS does not influence the resulting AVS and SEM concentration in the range of 2-10 gram wet sediment, corresponding with 1-6 gram dry sediment. For the studied sediment the AVS concentration was 15.3 µmol g^{-1} dry sediment with a standard deviation of 1.0 µmol g^{-1} d.w. The SEM concentration was 12.2 µmol g^{-1} dry sediment with a standard deviation of 0.8 µmol g^{-1} d.w.

For the present sediment samples with a carbonate content ranging from 4.4 to 16.0 %, carbonate appears to be an important parameter, influencing the effect of acidity on the speciation of the metals. This most likely is due to its acid buffering capacity. To get more insight into the effect of carbonate, it might be useful to study the influence of acidity on AVS and SEM in a sediment without carbonate. Parallel to this aspect, it might be interesting to study the effect of acidity in a sediment without sulphide. This could probably be achieved by aeration of the sediment and consecutive extraction of metals.

Using a simplyfied model for the exchange of zinc sorbed onto the solid phase with acid, the influence of pH on the speciation of Zn can be assessed. For other metal sulphide precipitates (Cd, Ni, Pb and Cu) this is not yet possible because not enough data points were available. This was due to the relatively high detection limit of the AAS. Therefore it will be useful to develop a different technique for the analysis of metals in AVS-extracts with a lower detection limit (e.g. ICP-MS).

Based on the analysis of total metals in sediments, it was found that for the case of 1 mol HCl l^{-1}, Zn, Pb and Cd were extracted for 70-95 %, whereas Cu and Ni were released in much smaller amounts. For Cu this is probably caused by binding to organic matter and Ni might be built into clay minerals.

For Fe and Mn, the influence of acidity on their release was found to be different from the other metals. Although it is expected that the sediments are anaerobic, since sulphide is detected, Fe and Mn may be present as (hydr)oxides in sediment, which might be a cause for their different behaviour. Thus, it will be interesting to analyse (hydr)oxides, simultaneously with sulphides in the sediment.

REFERENCES

[1] **Allen, H.E., G. Fu and B. Deng** (1993) Analysis of acid volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments. *Environ. Toxicol. Chem.* **12** : 1441-1453.

[2] **Di Toro, D.M., J.D. Mahony, D.J. Hansen, K.J. Scott, M.B. Hicks, S.M. Mayr and M.S. Redmond** (1990) Toxicity of cadmium in sediments : the role of acid volatile sulfide. *Environ. Toxicol. Chem.* **9** : 1487-1502.

[3] **Di Toro, D.M., J.D. Mahony, D.J. Hansen, K.J. Scott, A.R. Carison and G.T. Ankley** (1992) Acid Volatile Sulfide predicts the acute toxicity of cadmium and nickel in sediments. *Environ. Sci. Technol.* **26** : 96-101.

[4] **Smith, R.M. and A.E. Martell** (1976) Critical Stability Constants, vol. 4, Inorganic Complexes, Plenum, New York, NY.

[5] **Ankley, G.T., G .L. Phipps, E.N. Leonard, P.A. Kosian, A.M. Cotter, J.R. Dierkes, D.M. Hansen and J.D. Mahony** (1991) Acid volatile sulfide as a factor mediating cadmium and nickel bioavailability in contaminated sediments. *Environ. Toxicol. Chem.* **10** : 1299-1307.

[6] **Besser, J.M., C.G. Ingersoll and J.P. Giesy** (1996) Effects of spatial and temporal variation of acid-volatile sulfide on the bioavailability of copper and zinc in freshwater sediments. *Environ. Toxicol. Chem.* **15** : 286-293.

[7] **Morse, J.W., F. J. Millero, J.C. Cornwell and D. Rickard** (1987) The chemistry of the hydrogen sulfide and iron sulfide systems in natural waters. *Earth-Science Reviews.* **24** : 1-42.

[8] **Huerta-Diaz, M.A., R. Carignan and A. Tessier** (1993) Measurement of trace metals associated with Acid Volatile Sulfides and pyrite in organic freshwater sediments. *Environ. Sci. Technol.* **27** : 2367-2372.

[9] **Den Hollander, H.A., and M.A.G.T. van den Hoop** (1994) Analysis of Acid Volatile Sulfide and Simultaneously Extracted Metals in sediment and soil (in Dutch). *RIVM report no. 719101017.*

[10] **Van den Hoop, M.A.G.T., H.A. den Hollander and H.N. Kerdijk** (1995) Spatial and seasonal variations of Acid Volatile Sulfide (AVS) and Simultaneously Extracted Metals (SEM) in Dutch marine and freshwater sediments. *RIVM report no. 719101022.*

[11] **Kornicker, W.A. and J.W. Morse** (1991) Interactions of divalent cations with the surface of pyrite. *Geochim. Cosmochim. Acta* **55** : 2159-2171.

[12] **Jean, G.E. and G.M. Bancroft** (1986) Heavy metal adsorption by sulphide mineral surfaces. *Geochim. Cosmochim. Acta* **50** : 1455-1463.

[13] **Boulegue, J., C.J. Lord III and T.M. Church** (1982) Sulfur speciation and associated trace metals (Fe, Cu) in the pore waters of Great Marsh, Delaware. *Geochim. Cosmochim. Acta* **46** : 453-464.

[14] **Brouwer, H. and T.P. Murphy** (1994) Diffusion method for the determination of acid-volatile sulfides (AVS) in sediment. *Environ. Toxicol. Chem.* **13** : 1273-1275.

[15] **SOP LBG/102** Determination of the carbonate content in soil, using a Scheibler apparatus (in Dutch).

[16] **SOP LAC/M369** (concept) Gaschromatographic determination of elemental carbon, nitrogen and sulphur in solid samples (in Dutch).

[17] **SOP LAC/A193** Manual microwave oven CEM MDS-2000 (in Dutch).

[18] **NVN 5770**. Soil and sludge (1993) Sample preparation of soil and sludge for the determination of elements by atomic spectrometry. Digestion with nitric acid and hydrochloric acid in a microwave oven (in Dutch). 1st ed., Dutch Standardization Institute (NNI), Delft.

[19] **SOP LAC/A120** Manual Perkin Elmer 2100 (flame-AAS) (in Dutch).

[20] **SOP LAC/M154** General instruction for the determination of elemental concentrations in aqueous solutions using Flame-AAS (PE 2100) (in Dutch).

[21] **SOP LAC/A257** Manual Spectro Spectroflame M5 (in Dutch).

[22] **SOP LAC/M259** General instruction for the determination of elemental concentrations in aqueous solutions using ICP-AES (Spectroflame model M5) (in Dutch).

[23] **Van der Velde, T.** (1995) Selectivity of the ICP-AES-axial-technique for the element analysis in soil, sludge and sediment (in Dutch). *RIVM report no. 502501038.*

[24] **Sposito, G.** (1989) The chemistry of soils, Oxford University Press, New York, NY.

[25] **Kuipers, S.F.** (1981) Soil Science (in Dutch), Educaboek, Culemborg.

[26] **Bolt, G.H. and M.G.M. Bruggenwert (eds.)** (1978) Soil Chemistry, part A. Basic Elements, Elsevier, Amsterdam.

[27] **Chardon, W.J.** (1984) Mobility of cadmium in the soil (in Dutch), PhD-thesis, Agricultural University Wageningen.

[28] **Van der Zee, S.E.A.T.M. and W.H. van Riemsdijk** (1987) Transport of reactive solute in heterogeneous spatially variable soil systems, *Water Resour. Res.,* **23** : 2059.

[29] **Anderson, P.R. and T.H. Christensen** (1988) Distribution coefficients of Cd, Co, Ni, and Zn in soils *J. Soil Sc.* **39** : 15-22.

[30] **Janssen, R.P.T., P.J. Pretorius, W.J.G.M. Peijnenburg and M.A.G.T. van den Hoop** (1996) Determination of field-based partition coefficients for heavy metals in Dutch soils and the relationships of these coefficients with soil characteristics. *RIVM report no. 71910123.*

[31] **Brumbaugh, W.G. and J.W. Arms** (1996) Quality control considerations for the determination of Acid-Volatile Sulfide and Simultaneously Extracted Metals in sediments. *Environ. Toxicol. Chem.* **15** : 282-285.

APPENDIX

In this appendix the plots of the results for sediments 42417 and 43083 are given, for those experiments performed for all three sediments. For sediment 41874 the plots are given in the text.

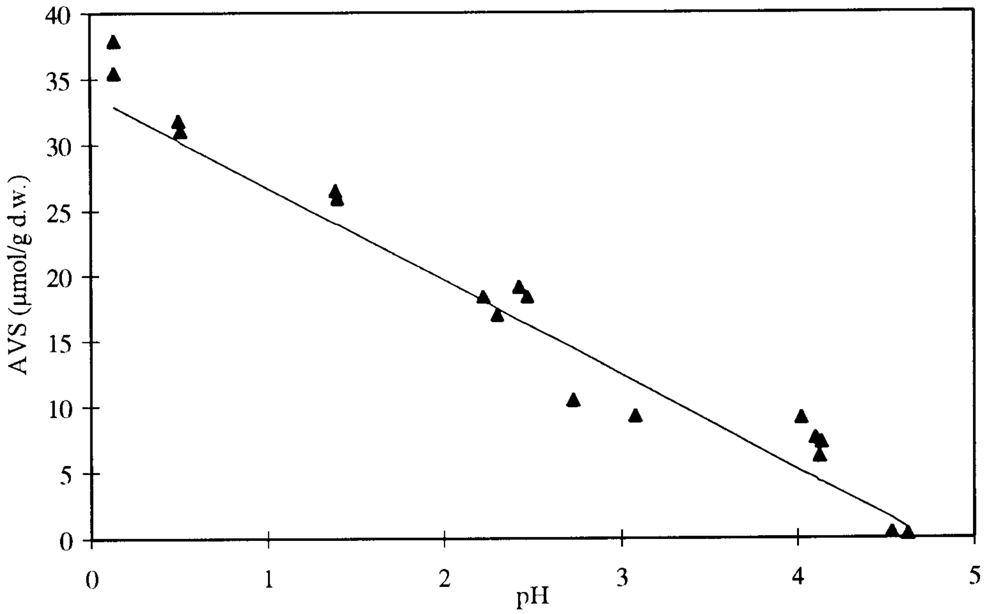

Figure 1. AVS vs. pH, sample 42417

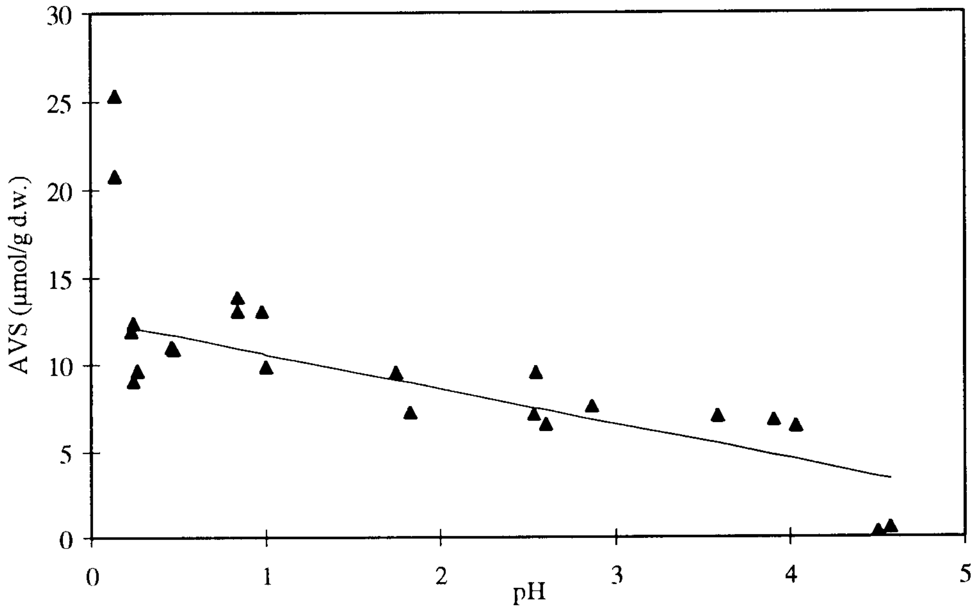

Figure 2. AVS vs. pH, sample 43083

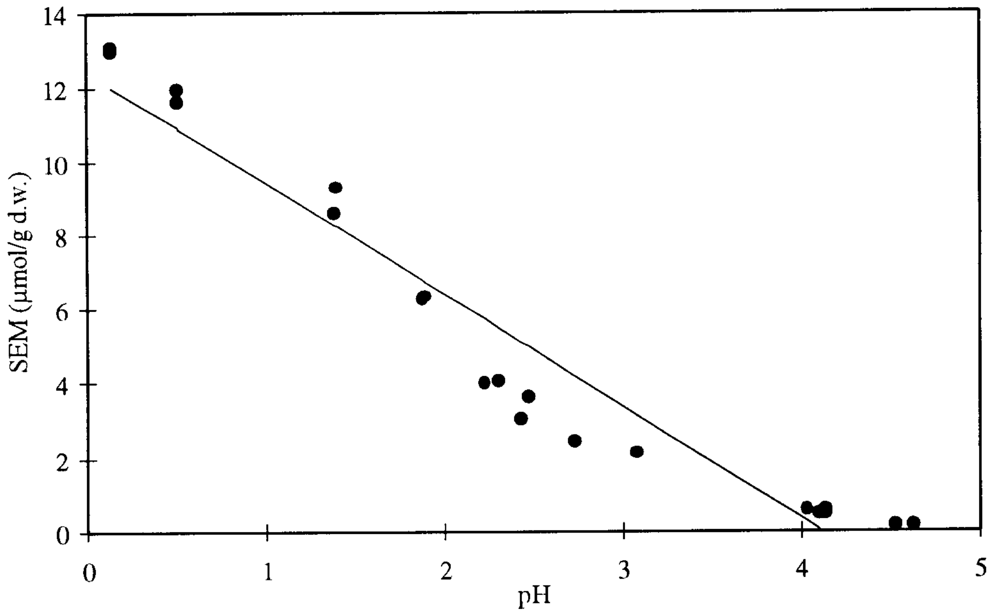

Figure 3. SEM vs. pH, sample 42417

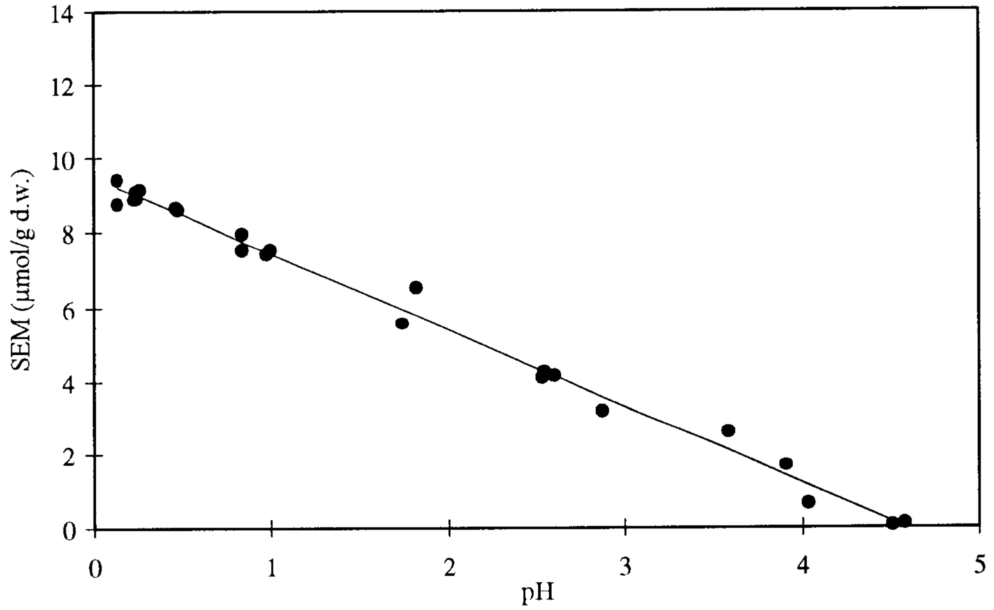

Figure 4. SEM vs. pH, sample 43083

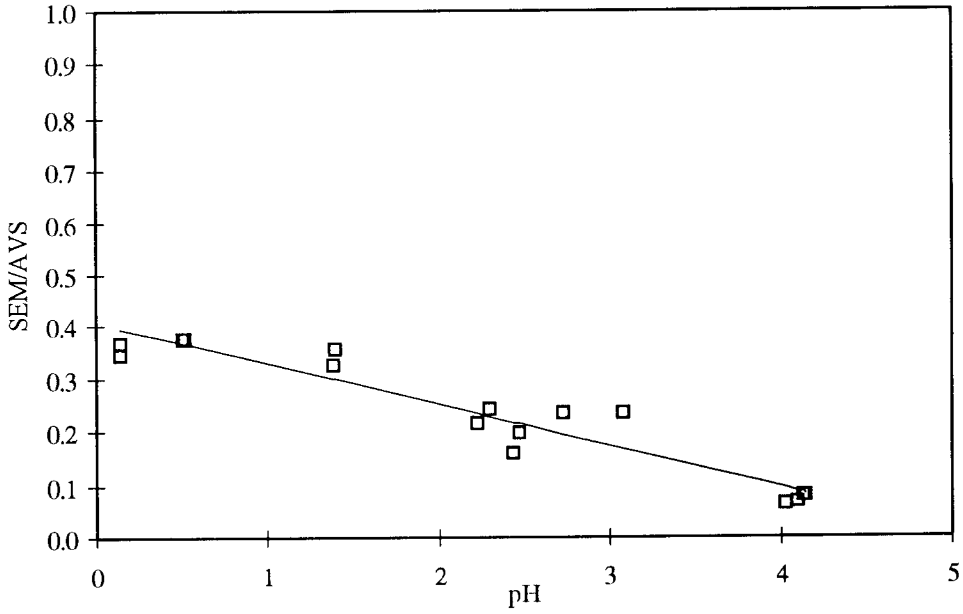

Figure 5. SEM/AVS vs. pH, sample 42417

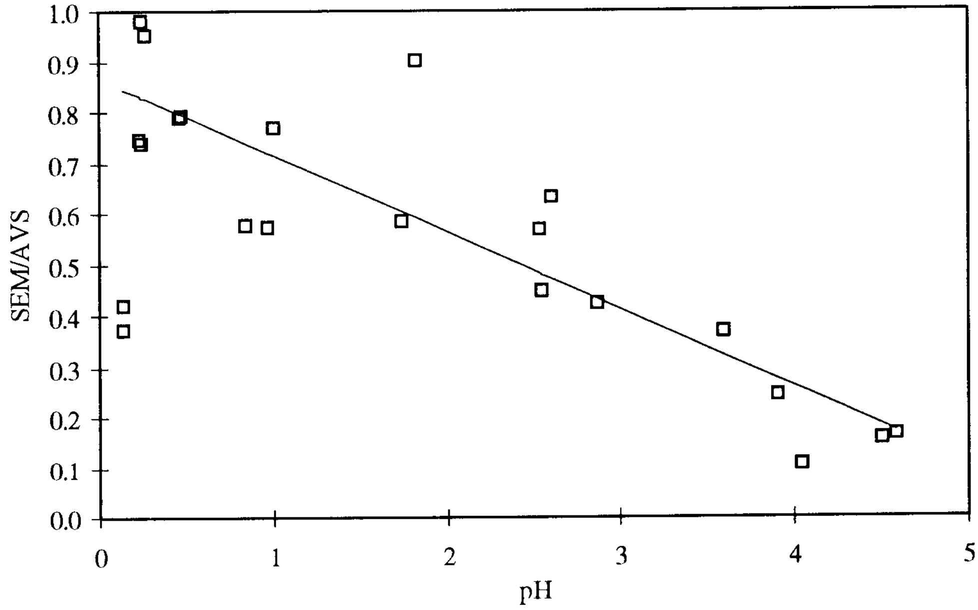

Figure 6. SEM/AVS vs. pH, sample 43083

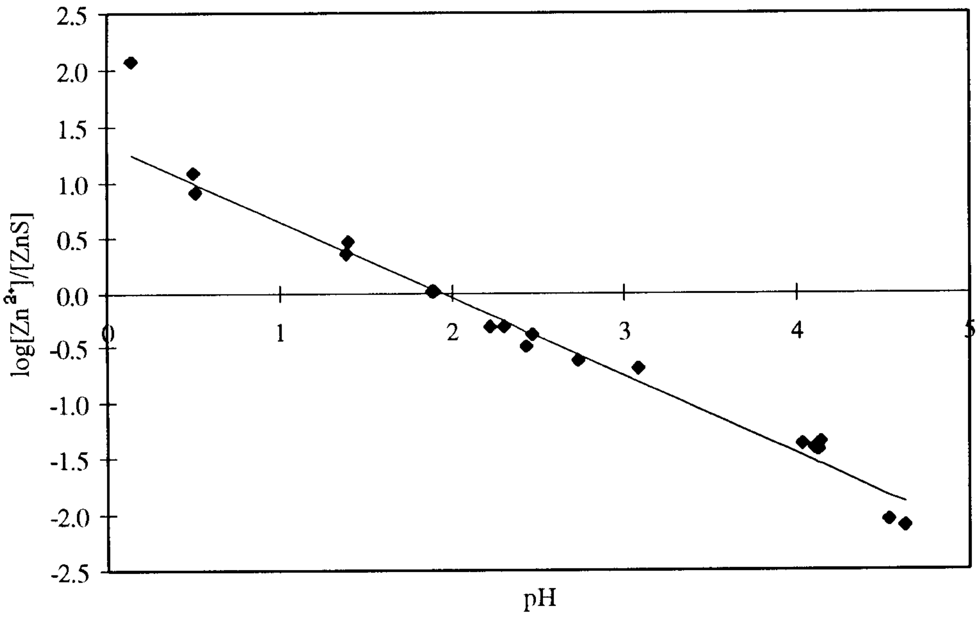

Figure 7. log [Zn2+]/[ZnS] vs. pH, sample 42417

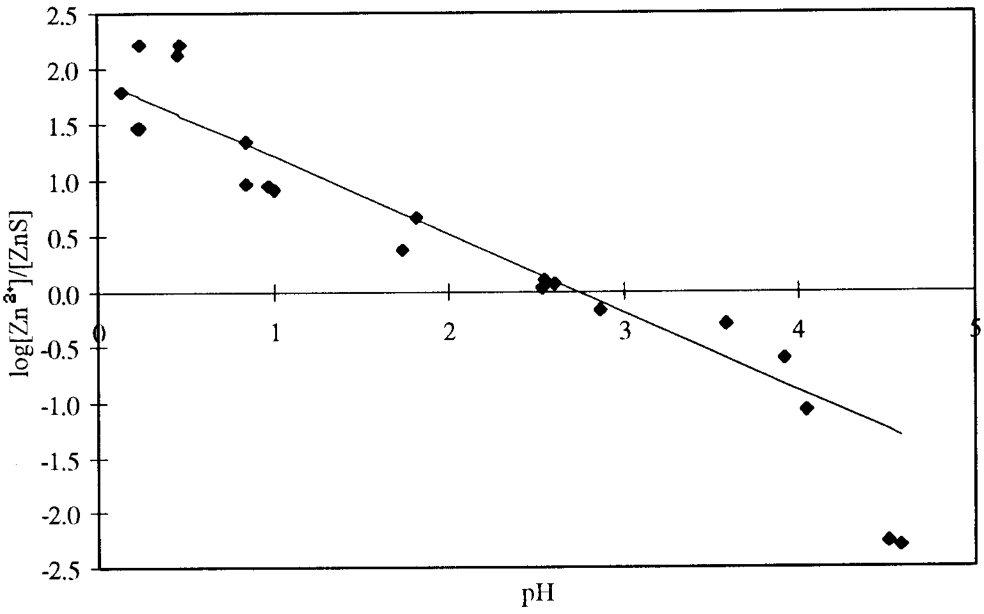

Figure 8. log [Zn2+]/[ZnS] vs. pH, sample 43083

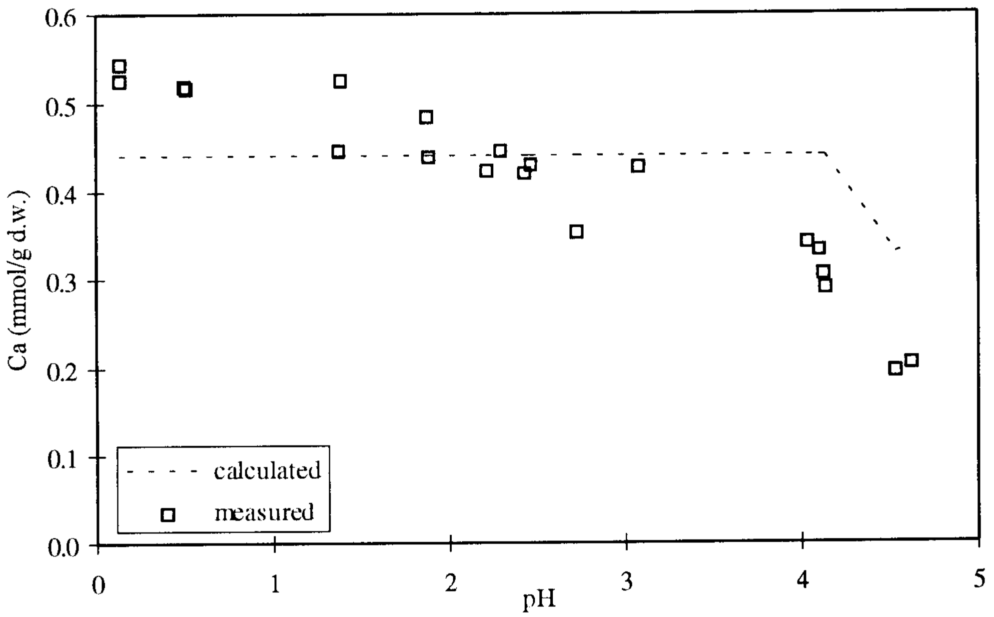

Figure 9. Ca vs. pH, sample 42417

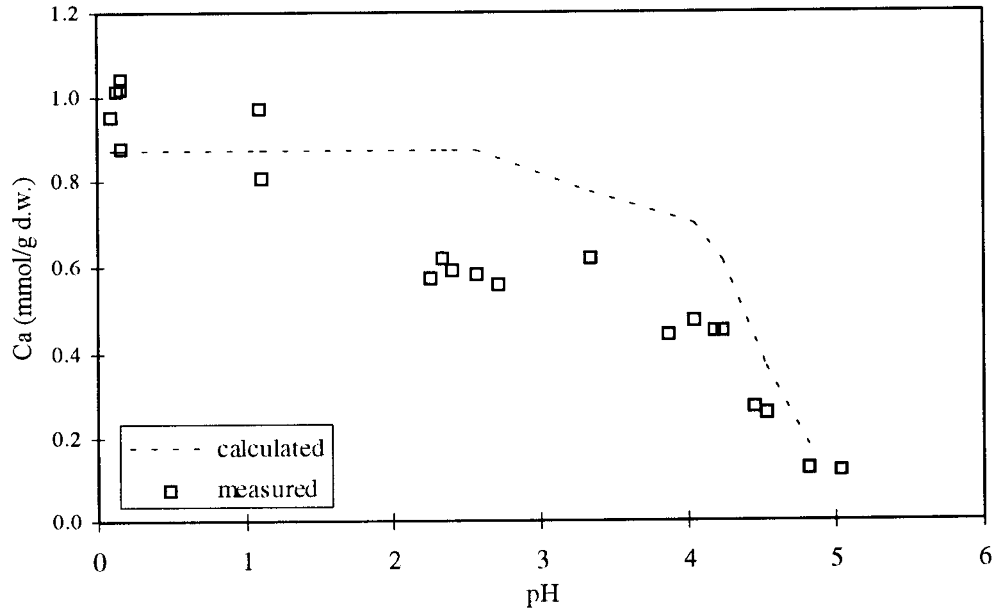

Figure 10. Ca vs. pH, sample 41874

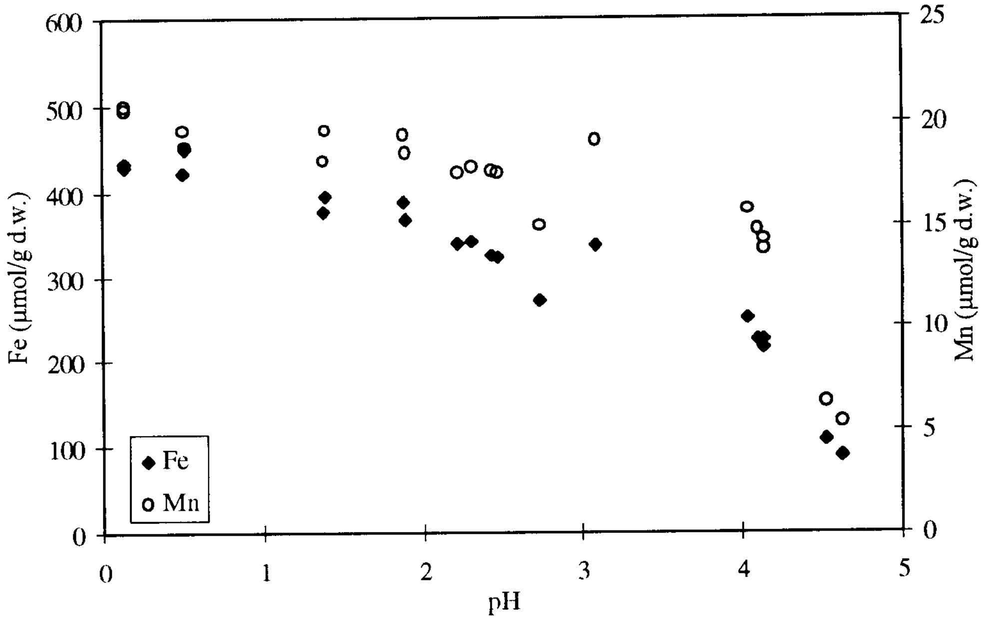

Figure 11. Fe and Mn vs. pH, sample 42417

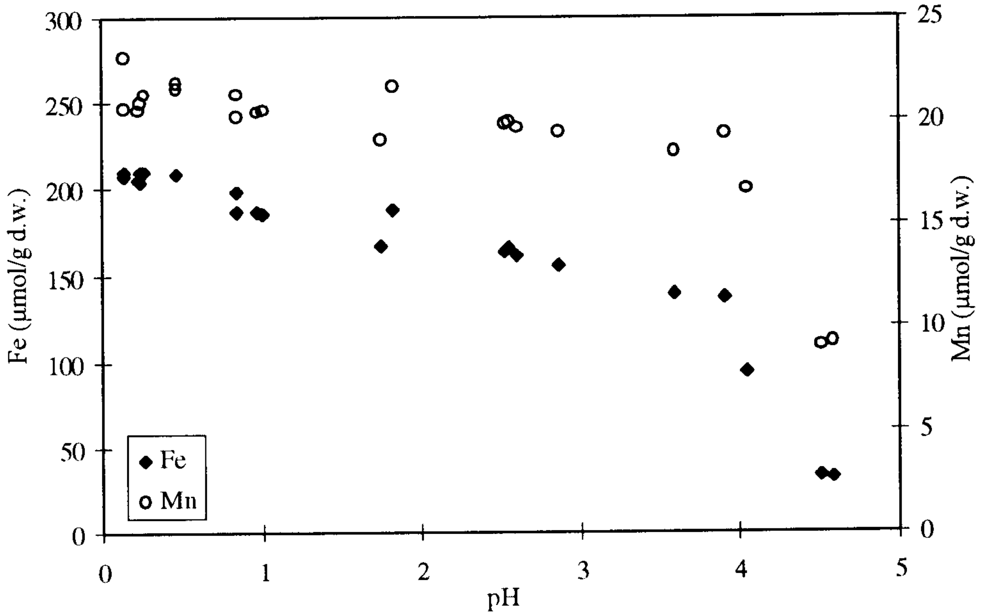

Figure 12. Fe and Mn vs. pH, sample 43083

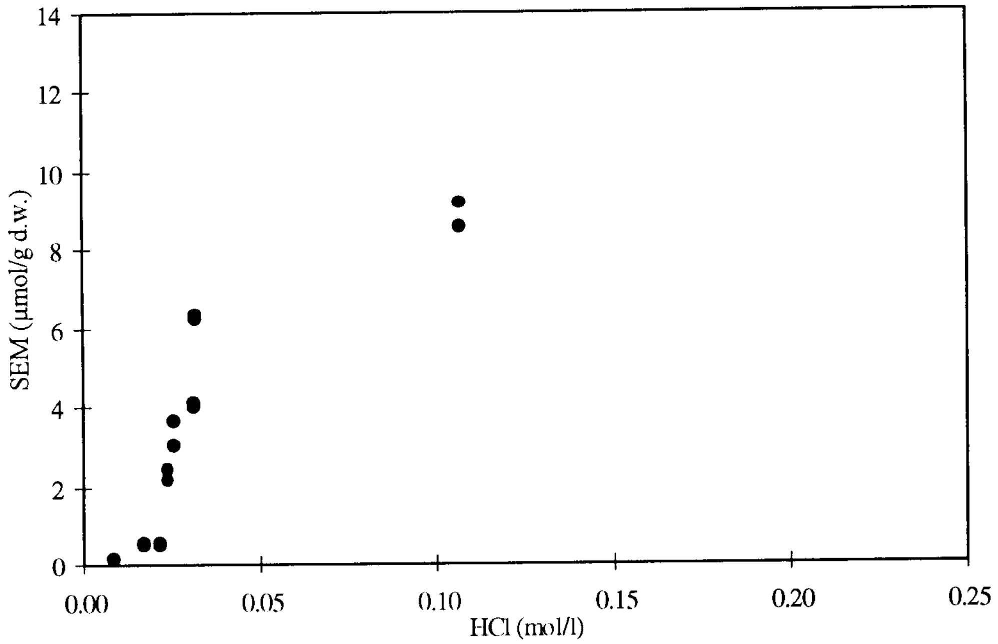

Figure 13. SEM vs. initial HCl concentration, sample 42417

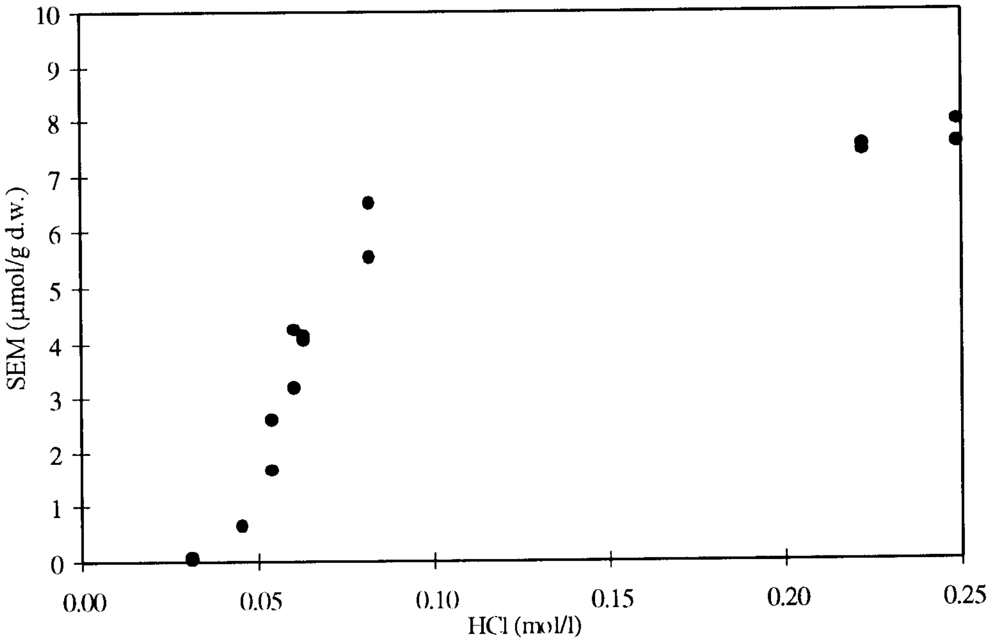

Figure 14. SEM vs. initial HCl concentration, sample 43083

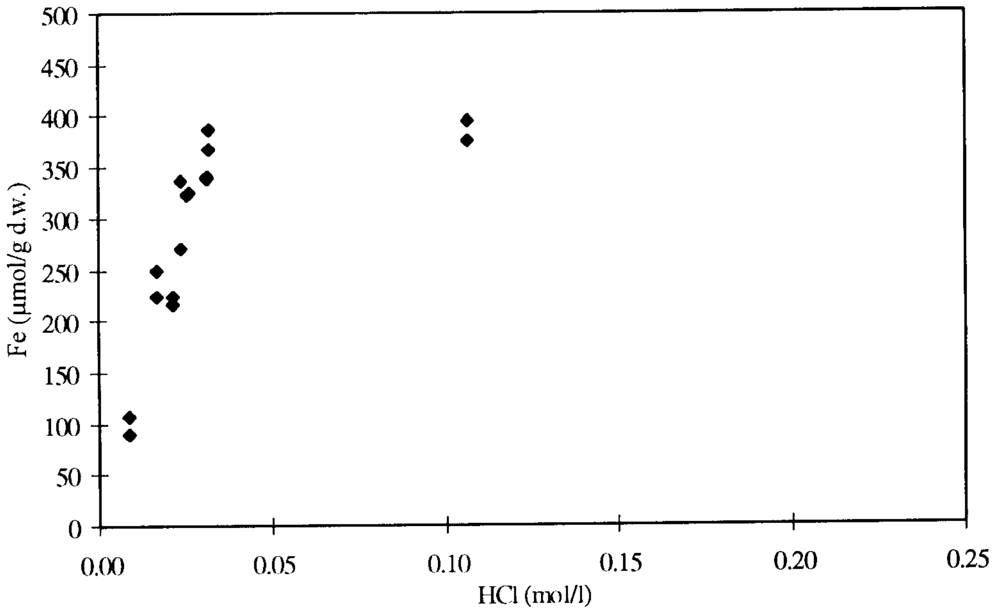

Figure 15. Fe vs. initial HCl concentration, sample 42417

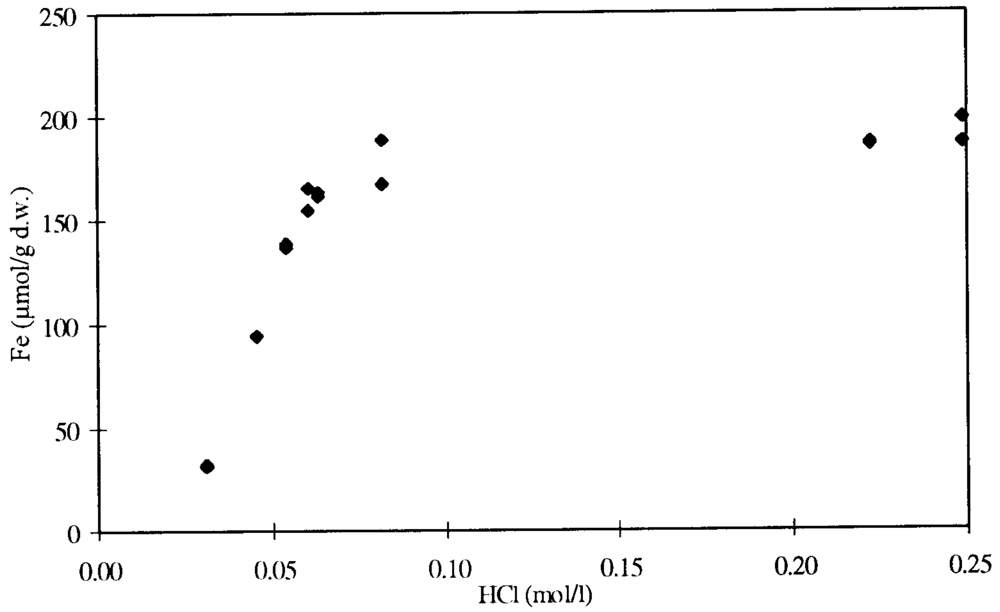

Figure 16. SEM vs. initial HCl concentration, sample 43083

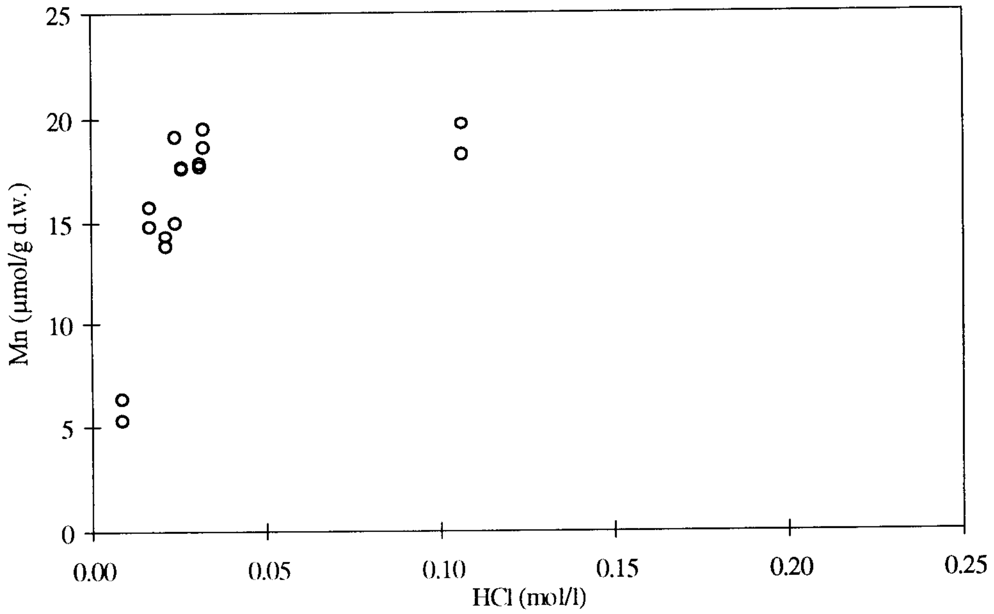

Figure 17. Mn vs. initial HCl concentration, sample 42417

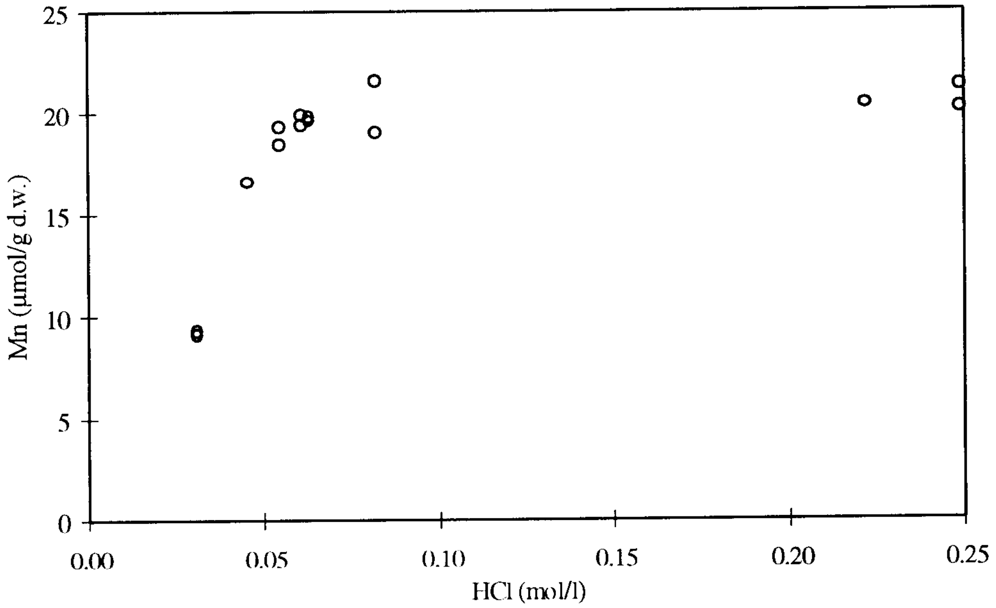

Figure 18. Mn vs. initial HCl concentration, sample 43083

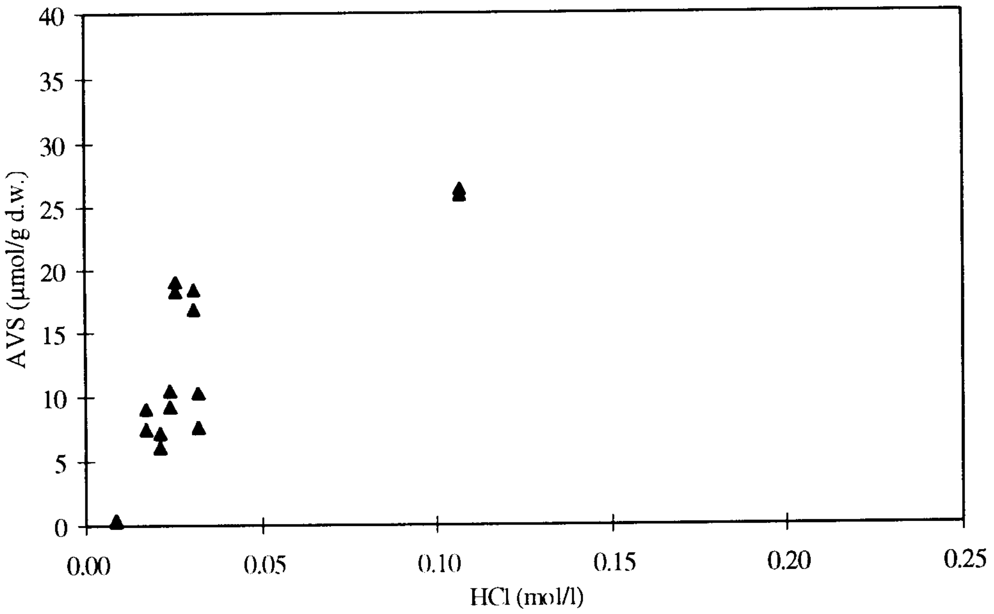

Figure 19. AVS vs. initial HCl concentration, sample 42417

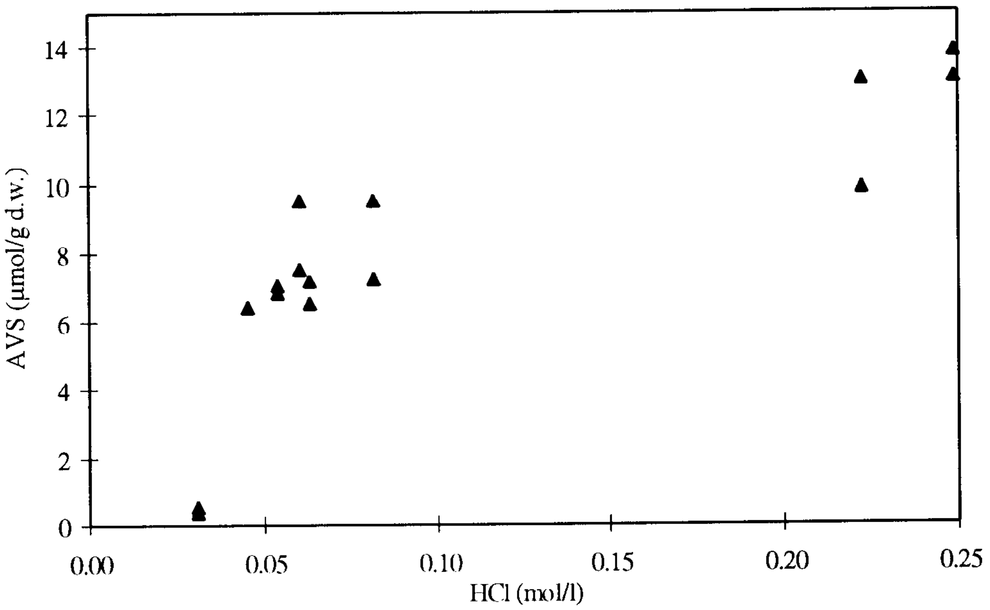

Figure 20. AVS vs. initial HCl concentration, sample 43083