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Characterization of suspended solids in a stream receiving acid mine effluents, Bersbo, Sweden

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Abstract—Suspended particulate matter was recovered by filtration (0.40 μm) of water from a stream receiving acidic effluents from a mine tailings deposit. This solid phase formed rapidly as pH increased from 3.5 at the release point to 6.5, approximately 2 km downstream. The suspended solid was present in concentrations that ranged from 10–20 mg/l for anoxic conditions (winter) to 30–120 mg/l for oxic conditions (early spring). The solid consisted of FeOOH + $Fe(OH)_3$(am) and AlOOH + $Al(OH)_3$(am), as well as silicates. The organic content (of natural origin) was up to 30% (dry wt). Most of the Fe and Al from the leachate was precipitated in the particulate phase, approximately 98% of total metal content in the aqueous phase, as well as ~50% of Mn, Cu, Zn, Cd and Pb. These elements were predominantly adsorbed on the hydrous oxide precipitate, or to some extent (Mn and Pb) coprecipitated, as indicated from a sequential leaching procedure and powder X-ray diffractometry. All the elements, particularly Cu, were to a significant degree associated with organic matter.

INTRODUCTION

IN RECENT years the chemical properties of suspended solids in surface waters as well as stationary solid phases in aquifers have gained interest because of their hydrochemical significance in controlling the distribution and transport of trace constituents in the water. Naturally occurring particulate matter can be an efficient scavenger of metals such as Al, Cd, Cu, Fe, Mn, Pb and Zn (TESSIER *et al.*, 1979; LION *et al.*, 1982; FÖRSTNER and SALOMONS, 1983; MAHER, 1984; SALOMONS and FÖRSTNER, 1984; JOHNSON, 1986). Important inorganic sorbents in natural surface waters include the hydrous oxides of Al, Fe, Mn and Si. Their chemical structure may vary from amorphous compounds to more crystalline solids, and are often found in association with natural organic matter (SHOLKOWITZ and COPLAND, 1981; HART, 1982; SINGH and SUBRAMANIAN, 1984). The ability of hydroxides to bind trace metals, either by adsorption to surface sites or coprecipitation, has been utilized for water purification purposes (BENJAMIN *et al.*, 1982; MERRILL *et al.*, 1984).

The most important parameter governing the transfer of a trace metal from solution to solid phases appears to be the pH of the aqueous phase (BENES and MAJER, 1980; HART, 1982; SALOMONS and FÖRSTNER, 1984). Changes in chemical speciation due to variations in the hydrochemical conditions (e.g. pH, Eh) will have great impacts on solubilities, sorption phenomena, transport properties and distribution of dissolved metals within a watershed. The speciation will also have implications on the hazards related to the biological toxicity of these elements (BABICH and STOTZKY, 1980; SALOMONS and FÖRSTNER, 1984).

Theoretical estimations concerning the partitioning of trace metals between aqueous phase and solids generally have low levels of confidence because of the limited accuracy of thermodynamic data concerning these species and processes. Analytical procedures for speciation of metals in natural waters typically include a physical separation of operationally defined solids from the solute but the subsequent characterization mainly focuses upon soluble entities (FLORENCE and BATLEY, 1980; STUMM and MORGAN, 1981; BATLEY, 1983).

Characterization of the solids is typically obtained by dissolving elements bound to the solid phase either using concentrated mineral acids, for complete dissolution, or by applying a sequential leaching procedure to estimate operationally defined associations between the metals and the solid (TESSIER *et al.*, 1979; SALOMONS and FÖRSTNER, 1980; TESSIER *et al.*, 1980; LION *et al.*, 1982; MAHER, 1984; TESSIER *et al.*, 1985).

The present study is focused upon the transfer of Al, Cd, Cu, Fe, Mn, Pb and Zn from solution to suspended solids when acid leachates from a mine tailings deposit are mixed with, and neutralized by, near surface groundwater in a small stream (c.f. ALLARD *et al.*, 1987a). A combination of solubility estimates, powder X-ray diffractometry and sequential leaching has been used to obtain information on the metal-solid associations. The elements originating from the leachates, operationally defined as dissolved (0.40 μm), appear in association with suspended solids within a distance of 2–3 km from the deposit (up to 98% of the total contents in the aqueous phase for some of the elements; KARLSSON *et al.*, 1987a).

DESCRIPTION OF THE AREA

The mine tailings deposit is located at Bersbo, in the municipality of Åtvidaberg, some 250 km SW of Stockholm (Fig. 1). Mining began in the area in the

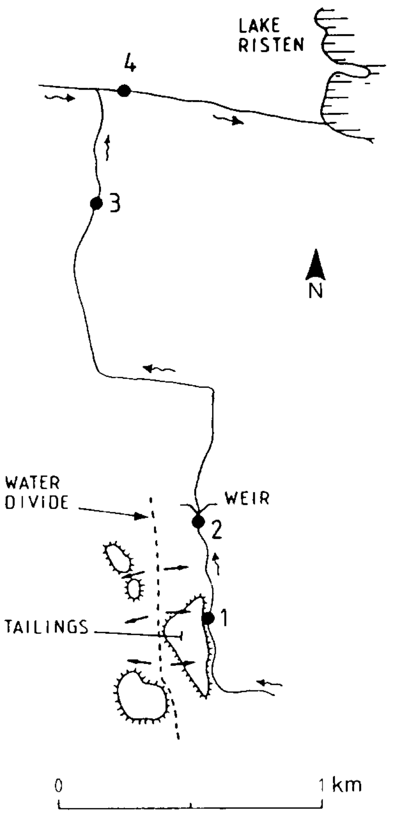

FIG. 1. Map of the Bersbo area (ALLARD *et al.*, 1987a).

medieval period and ceased in 1902. The deposit under study originates from a period of extensive mining operations during the last part of the 19th century. The principal ore was chalcopyrite with associated pyrite and minor quantities of sphaelerite and galena. The leptitic host rock is separated from the ore by a layer of amphiboles. Tailings from this mining period cover an area of approximately 0.055 km^2, with some 300,000 m^3 of waste material consisting of grain sizes from silt to rock, with the last fraction in predominance. The hydraulic conductivity of the tailings is estimated by hydrological modelling procedures to be 10^{-3} m/s. Thus, the tailings are readily exposed to conditions which enhance oxidation of the sulphide minerals.

Very acidic (pH down to 3) and metal-rich leachates flow into the stream east of the deposit, which is investigated in this work, by at least two adjacent influxes (location 1; Fig. 1). Groundwater in the area is rich in carbonate (total $CO_2 \sim 6$ meq/l) and has a $pH > 7$. The till soil has largely been protected from metal contamination by a dense clay layer below the tailings deposit. Upstream of the deposit there is a small bog area rich in organic material (see Fig. 1). The stream water has an organic content (expressed as humic and fulvic acids) of at least 50 mg/l at location 2 and 5–15 mg/l at the locations further downstream. Annual variations in water flow and in metal transport show that the highest mass fluxes occur during the snow melt in the spring and during rainy periods in the autumn (high flow), although maximum concentrations are found during drought periods in the summer (low flow) (SANDÉN *et al.*, 1987a). A more complete description of the site conditions is given by ALLARD *et al.* (1987a).

Sampling was performed on 10 February and 24 March, 1986, at locations indicated in Fig. 1. The sampling dates correspond to two periods with different chemical and hydrological conditions. The first period (10 February) represented winter conditions when an ice layer prevented influx of leachate to the stream and reduced diffusion of gases across the air/water interface. The concentrations of dissolved oxygen were low. The metals present in the aqueous phase of the stream obviously originated from the metal-rich sediments. The chemical conditions also reflected an in-flow of deep goundwater into the stream.

The second period (24 March) represented conditions just after snow melt and was associated with a large influx of leachate and near surface groundwater. The stream water was well oxygenated as a result of rapid and turbulent flow.

EXPERIMENTAL

Sampling and phase separation

Water was collected in 1 l polyethylene bottles. Five replicate bottles, each consisting of five subsamples, were collected at every site. The samples were taken from the center of the stream (1 m wide and 0.5 m deep) to avoid intrusion of bottom sediments and in such a way as to minimize contact with the air. All equipment in contact with the samples was made of polypropylene or polyethylene which was acid washed before use. Great care was taken to minimize potential metal contamination and losses during phase separation and analytical procedures.

Pressure filtration was applied to separate the suspended solids from the solution in each 1 l sample. In samples from the February period nitrogen was preferred in order to minimize possible redox changes during the filtration while compressed air was used for the March samples. Polycarbonate filters (Nuclepore Corp.) with a diameter of 47 mm and a defined pore size of 0.40 μm were used. Metals passing through this pore size were considered as "dissolved". Before use, the filters were soaked in HCl (10% v/v, analytical grade), thoroughly rinsed with water (Milli-Q quality: Milli-Q Corp.), dried in an evacuated desiccator at 60°C, cooled to room temperature and weighed. The filtration was carried out under constant stirring with a Teflon coated magnetic bar to reduce size dependent accumulation of solids on the filter surface which might alter the effective pore size. The filters containing the solids were purged with an excess of the gas used for filtration and immediately transferred to acid washed polyethylene vials and dried in an evacuated desiccator (60°C).

The solid contents were 18 ± 14 mg/l and 12 ± 6 mg/l at locations 3 and 4 in the February samples, and 33 ± 1 mg/l, 122 ± 5 mg/l and 76 ± 23 mg/l at locations 2, 3 and 4, respectively, in the March samples (average of 5 samples, 95% confidence intervals).

A distribution of trace elements between colloidal matter and an aqueous phase that could be related to the particle

Table 1. Composition of the water (five samples, 95% confidence intervals)

Component*	Site† 1	2	3		4	
	Anox	Ox	Anox	Ox	Anox	Ox
Al	940 ± 13	150 ± 10	58 ± 4	180 ± 11	24 ± 1	220 ± 8
Ca	190 ± 6	190 ± 13	430 ± 18	280 ± 6	520 ± 9	370 ± 14
Cd	1.7 ± 0.003	0.89 ± 0.002	0.067 ± 0.001	0.59 ± 0.002	0.089 ± 0.001	0.18 ± 0.003
Cu	150 ± 1	24 ± 0.4	5.0 ± 0.1	14 ± 0.1	0.5 ± 0.01	1.4 ± 0.01
Fe	120 ± 6	40 ± 2	33 ± 1	46 ± 2	36 ± 1	64 ± 1
K	3.70 ± 0.06	2.81 ± 0.03	2.42 ± 0.10	3.21 ± 0.05	4.60 ± 0.01	6.79 ± 0.03
Mg	670 ± 14	210 ± 16	240 ± 8	210 ± 7	260 ± 9	220 ± 9
Mn	42	8.9	5.2	5.5	10	4.9
Na	15 ± 12	272 ± 9	368 ± 14	596 ± 8	363 ± 18	425 ± 11
Pb	0.27 ± 0.002	0.017 ± 0.002	<0.003	0.004	<0.003	<0.003
Zn	590 ± 14	95 ± 3	43.6 ± 6	97 ± 3	10 ± 1	15 ± 1
HCO_3^-	0	1.0 ± 0.1	360 ± 10	44 ± 7	1 070 ± 32	700 ± 19
SO_4^{2-}	3 400 ± 62	750 ± 18	480 ± 16	540 ± 19	220 ± 9	150 ± 11
Cl^-	53 ± 0.3	161 ± 0	240 ± 1	279 ± 3	290 ± 2	279 ± 2
O_2‡	n.d.	63 ± 3	4 ± 2	76 ± 2	1 ± 1	40 ± 5
pH	3.58 ± 0.01	4.46 ± 0.01	6.50 ± 0.01	5.41 ± 0.01	6.62 ± 0.01	6.51 ± 0.01

* Concentrations in μmoles/l.
† See Fig. 1; Anox = anoxic conditions (10 February), Ox = oxic conditions (24 March).
‡ Concentrations in percent of saturation.

size has been reported by Hoffman *et al.* (1981). However, in this study only minor and not always statistically significant differences in the efficiency of removal were indicated when a complementary filtration of some samples was performed, using polycarbonate filters (Nuclepore Corp). with a pore size of 0.05 μm. The composition of the water and the distribution between the operationally defined suspended and dissolved species are given in Tables 1 and 2, respectively.

Leaching procedures

Several choices of chemical treatments for sequential leaching or dissolution of solid materials are described in the literature (Tessier *et al.*, 1979, 1980; Salomons and Förstner, 1980; Förstner and Salomons, 1983; Maher, 1984; Slavek and Pickering, 1986). A procedure similar to the one used by Tessier *et al.* (1980) was selected for this study, with a complementary treatment to extract humic and fulvic acids. The following extractions were performed to distinguish between metals having operationally defined associations with the suspended material.

Ion exchangeable, carbonates and hydroxides (*fraction* 1). Leaching with sodium acetate (1.0 M) at pH 5.0 (90°C for 5 h).

Hydrous oxides (*fraction* 2). The hydroxylamine hydrochloride/acetic acid reagent (0.04 M NH_2OH–HCl in 25% HAc, 90°C for 5 h) was chosen to dissolve amorphous oxides because the commonly applied dithionite/citrate reagent sometimes results in the precipitation of insoluble sulphides, and frequently suffers from severe contamination by Zn (Tessier *et al.*, 1980). The ability of the applied reagent to dissolve freshly precipitated amorphous (hydrous) oxides has been supported by Slavek and Pickering (1986), who found ~85% dissolution of FeOOH(am) while 10% of goethite was dissolved.

Labile organics and amorphous metal sulphides (*fraction* 3). Organics and amorphous metal sulphides were oxidized by hydrogen peroxide in acidic solution (0.02 M HNO_3 + 30% H_2O_2 (3:5 v/v) at pH 2, 3h at 85°C and addition of 3.2 M NH_4Ac in HNO_3 (20%) + double distilled water), as adopted from Tessier *et al.* (1980). This treatment has been

Table 2. Distribution of metals betwen suspended (>0.40 μm) and dissolved species under oxic conditions (five samples, 95% confidence intervals)

Component*	Site† 1	2	3	4
Al	0	0.05 ± 0.01	0.94 ± 0.06	0.99 ± 0.08
Ca	0	0.15 ± 0.06	0.09 ± 0.02	0.13 ± 0.01
Cd	0	0.33 ± 0.05	0.41 ± 0.04	0.50 ± 0.02
Cu	0	0.23 ± 0.03	0.62 ± 0.03	0.42 ± 0.04
Fe	0	0.78 ± 0.06	0.94 ± 0.07	0.98 ± 0.03
Mg	0	0.08 ± 0.02	0.21 ± 0.03	0.03 ± 0.02
Mn	0	0.08 ± 0.03	0.29 ± 0.03	0.71 ± 0.02
Pb	0	n.d.	n.d.	n.d.
Zn	0	0.17 ± 0.03	0.26 ± 0.01	0.41 ± 0.01

* Fraction in particulate phase.
† See Fig. 1; oxic conditions (24 March).

reported to break down organic coatings and detrital material effectively (c.f. Karlsson *et al.*, 1987b).

Stable organics (*humic and fulvic material*) (*fraction* 4). Humic and fulvic material was extracted with sodium hydroxide (0.1 M NaOH, 3 h at 85°C) and enriched on DEAE (diethylaminoethyl cellulose) according to the method of Allard *et al.* (1987b). The combined oxidation/ extraction of organics was chosen because Maher (1984) reported Fe and Mn being retrieved in the hydrogen peroxide step in samples with high organic content. Those results could indicate formation of a complex between the metals and the organics, e.g. as organic coatings on the particle surface, preventing attack by the reagent applied to dissolve amorphous oxides.

Remaining organics, oxides and sulphides (*fraction* 5). Concentrated nitric acid (90°C for 3 h) was used to dissolve the remaining organics, oxides and sulphides although a slight attack on silicate lattices cannot be avoided.

Solid residuals. The final dissolution of residual solids was made in condensed H_3PO_4 (290°C) (Hannaker and Quing-Lie, 1984).

The leaching was carried out in acid-washed polyethylene vials with the ratio of 1:100 (solid to reagent). Great precautions were taken to minimize contamination and transfer of elements between the different treatments. In each step separation of solids from the leaching solution was made by centrifugation at 3000 rpm for a minimum of 1 h. The solution was transferred to an acid-washed and evacuated polypropylene vial through a Teflon tubing, acidified and stored until the determination of its metal composition. The solids were rinsed several times with reagent solution before addition of the following extractant to avoid transfer of dissolved elements between different fractions. All chemicals were of analytical grade or better.

Chemical analysis

The metal contents were determined by atomic absorption spectrometry (Perkin–Elmer 5000/Zeeman instrument). Standard solutions used for calibration of the instrument were prepared so as to match the sample composition as closely as possible. Metal impurities were determined in each batch of reagents.

Flame technique was applied when concentrations of the metals were sufficiently high. The accuracy of the applied instrumental settings was checked by dilution and standard addition procedures. For elements present at low concentrations the flame determinations were compared with determinations using graphite furnace, after sufficient dilution.

Analytical difficulties were experienced in the analysis of fraction 1 and to some extent fraction 2 due to high salt concentrations or complex formation during atomization in the graphite furnace. The analytical accuracy was improved by dilution and elevation of the charring temperatures. The graphite furnace equipped with Zeeman background corrector seemed, however, to compensate for matrix effects in fractions 4 and 5. The furnace technique was used for the determinations of Cd and Pb in most fractions. The accuracy was generally improved for these elements by applying maximum power heating and addition of a matrix modifier ($Mg(NO_3)_2$ (250 mg/l) and $NH_4H_2PO_4$ (5000 mg/l)) to reach high charring temperature and thus reduce non-specific absorption during atomization. Addition of the modifier was made directly in the graphite tube in a volume of 1–5 times that of the sample.

All solids (dried at 60°C) were characterized by X-ray powder diffractometry.

The concentration of humics in fraction 4 was determined spectrophotometrically on the enriched DEAE fraction by measurements at 250 and 365 nm with well-characterized humic materials as calibration standards, previously isolated from the stream (Allard *et al.*, 1987b).

Analysis of HCO_3^- was made by end-point titration (pH 5.4) with 0.02 M HCl under continuous purging with CO_2-free N_2. Chloride was determined by precipitation with Ag^+, and indicating the inflexion point with the Ag/AgCl/ $HgSO_4$ electrode pair. Titrations were made in a HNO_3/ KNO_3 (1.0 M) buffer to avoid effects of ion-strength on the inflexion point. Analysis of SO_4 was carried out by flow injection analysis (FIA) based on the Ba-methylethylethymole blue method where decolouration of the Ba-complex occurs as the $BaSO_4$-complex is formed. Precipitation is avoided by performing the reaction in ethanol. The Winkler method was used for determinations of dissolved oxygen.

RESULTS AND DISCUSSION

Total concentrations of dissolved constituents in the stream water for both oxic and anoxic conditions are given in Table 1, and the quantitative distribution between suspended matter and aqueous phase for the oxic sampling period are shown in Table 2. Mixing with uncontaminated groundwater results in a progressively increasing pH downstream of the outlet (from pH 3.6 in the leachate to pH 6.5 at location 4 under oxic conditions). These pH changes result in a transfer of metals from the solution phase to the suspended solids in the stream (cf. Table 2). Certain size fractions of the suspended matter will most likely settle on the bottom of the stream as the water velocity decreases downstream (Karlsson *et al.*, 1987c), making quantitative estimates rather uncertain when comparing different sampling locations.

Besides sorption to suspended particles, as well as to the bottom sediments (Sandén *et al.*, 1987b), the total concentrations of dissolved metals in the stream will be affected by dilution. The input of SO_4 in great excess from the leachate to the stream can be used to estimate, roughly, the dilution with groundwater of low SO_4 content. Thus, the change in SO_4 concentrations (Table 1) indicates that the leachate is diluted approximately 5, 8 and 190 times, respectively, at locations 2, 3 and 4 during the sampling in March. By comparing concentrations of metal constituents (Table 1) in a similar way, it can be concluded that there is a net removal of Al, Cd, Cu, Pb and Zn from the stream between location 1 and location 2, while the other elements are added, possibly via the groundwater. Further downstream there appears to be addition of all the analysed constituents, with the exception of Mn, from inputs via external sources.

Suspended matter

Measured metal concentrations in the aqueous phase (before and after filtration) are given as a function of pH in Fig. 2. In the calculations of solubilities the following solid species have been considered:

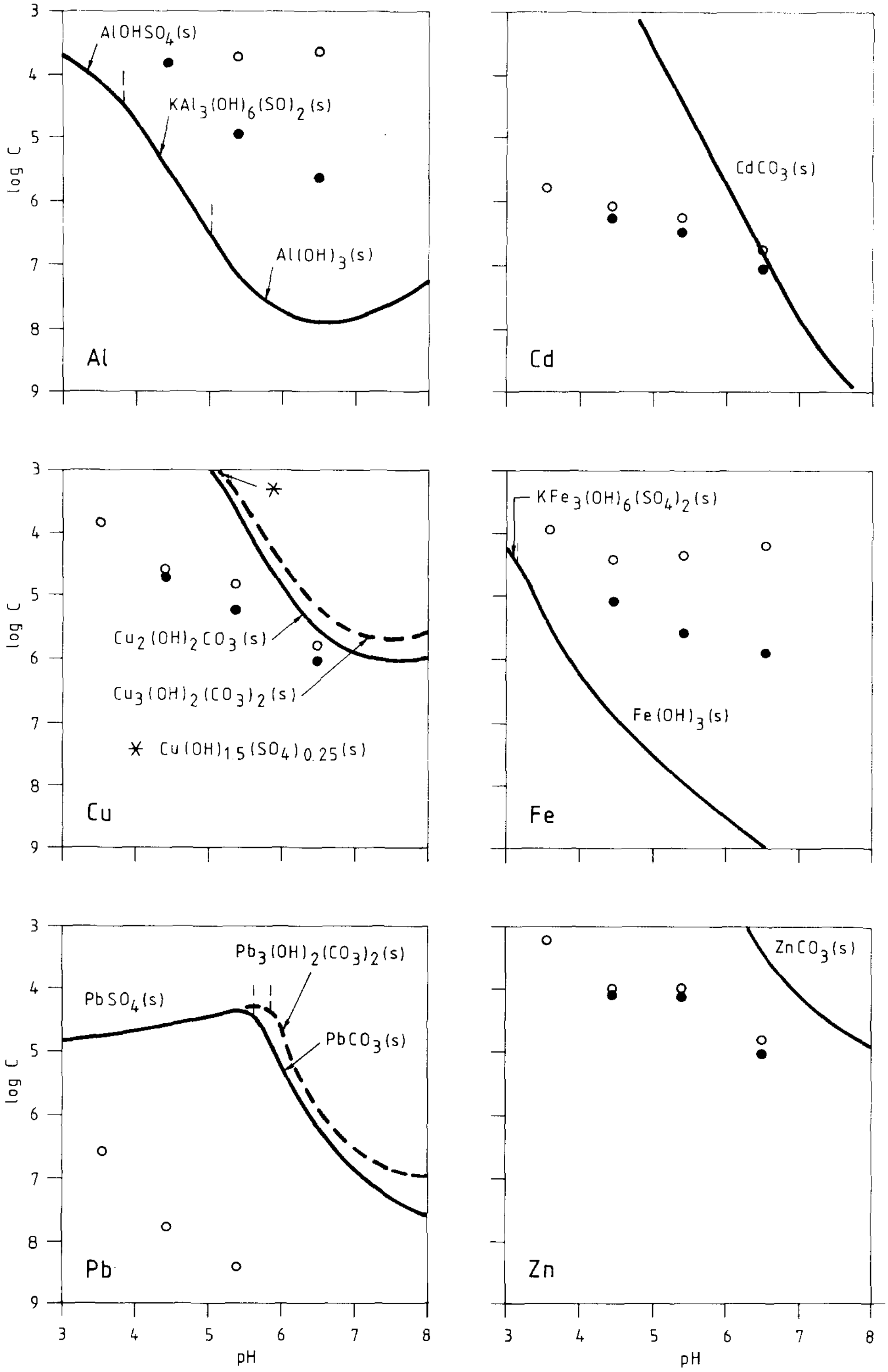

FIG. 2. Metal concentrations (C, moles/l) at sampling sites. 1–4 (from 24 March) and calculated total solubilities. ○ Unfiltered samples. ● Filtered samples (0.40 μm).

$Al(OH)_3$, $Al_2(SO_4)_3$, $AlOHSO_4$, $Al_4(OH)_{10}SO_4$, $KAl_3(OH)_6(SO_4)_2$; $Cd(OH)_2$, $Cd(OH)_{1.5}(SO_4)_{0.25}$, $CdCO_3$; $Cu(OH)_2$, $Cu(OH)_{1.5}(SO_4)_{0.25}$, $CuCO_3$, $Cu_2(OH)_2CO_3$, $Cu_3(OH)_2(CO_3)_2$, $Fe(OH)_3$, $NaFe_3(OH)_6(SO_4)_2$, $KFe_3(OH)_6(SO_4)$, $Pb(OH)_2$, $PbCO_3$, $PbSO_4$, $Pb_3(OH)_2(CO_3)_2$, $NaPb_2(OH)(CO_3)_2$, $PbOH(SO_4)_{0.5}$, $Pb(OH)_{1.5}(SO_4)_{0.25}$; $Zn(OH)_2$, $ZnCO_3$, $Zn(OH)_{1.28}(CO_3)_{0.36}$, $Zn(OH)_{1.5}(SO_4)_{0.25}$.

Also the soluble species MOH^+, $M(OH)_2$, MCO_3 and MSO_4 for Cd, Cu, Pb and Zn as well as MOH^{2+}, $M(OH)_2^+$, $M(OH)_3$, $M(OH)_4^-$, MSO_4^+ for Al and Fe are considered.

Formation constants for probable solubility-limiting solids are provided in Table 3. Carbonate and SO_4 concentrations are estimated from their respective pH relations obtained from time series of approximately 600 observations, giving $\log(CO_3) = 2.32\,pH - 21.92$ and $\log(SO_4) = -0.45\,pH - 0.87$.

Solid phases were identified or inferred from X-ray powder diffraction data for the dried (60°C) particulate phase (prior to the leaching). The results are summarized in Table 4. Generally, the background is high and the resolution poor in the diffractograms, particularly for the material from site 2. The solids appear to be largely amorphous, not unexpectedly. Possibly the poor crystallinity reflects the high contents of organic materials in the particulate fraction (see below) or the speed of formation.

The hydroxides $Al(OH)_3(s)$ (gibbsite) or $Al(OH)_3(am)$, and possibly $Al_2O_3(s)$ have been assumed to be solubility-limiting solid Al phases in natural waters (FLORENCE and BATLEY, 1980). Under slightly acidic conditions, however, and in the presence of SO_4, various sulphates or hydroxy sulphates could be the solubility controlling species (NORDSTROM, 1982; CHAPMAN *et al.*, 1983). Total concentrations of Al in the stream under oxic condition indicate oversaturation with respect to $Al(OH)_3(s)$ at all sampling locations and also with respect to hydroxosulphates (alunite and jurbanite) except at site 4, where the pH is too high. The hydroxides $Al(OH)_3(s)$ and β-$AlOOH(s)$ are positively identified from the X-ray powder diffraction data, and both $Al(OH)(SO_4)\cdot 5H_2O(s)$ as well as

Table 3a. Formation constants used in calculations of total solubility and species distribution

Species	Log K	Species	Log K
$AlOH^{2+}$	8.5	$PbOH^+$	6.3
$Al(OH)_2^+$	17.7	$Pb(OH)_2$	10.9
$Al(OH)_3$	25.9	$Pb(OH)_3^-$	13.9
$Al(OH)_4^-$	32.5	$PbCO_3$	5.4
$AlSO_4^+$	3.0	$Pb(CO_3)_2^{2-}$	6.5
		$PbSO_4$	2.8
$CdOH^+$	3.9		
$Cd(OH)_2$	7.7	$ZnOH^-$	5.0
$Cd(OH)_3^-$	10.2	$Zn(OH)_2$	11.1
$CdCO_3$	4.5	$Zn(OH)_3^-$	13.6
$Cd(CO_3)_2^{2-}$	5.6	$ZnCO_3$	5.1
$CdSO_4$	2.5	$Zn(CO_3)_2^{2-}$	7.3
		$ZnSO_4$	2.8
$CuOH^+$	6.3		
$Cu(OH)_2$	12.8		
$Cu(OH)_3^-$	14.5		
$CuCO_3$	6.8		
$Cu(CO_3)_2^{2}$	9.9		
$CuSO_4$	2.4		
$FeOH^+$	11.8		
$Fe(OH)_2^+$	22.3		
$Fe(OH)_3$	28.4		
$Fe(OH)_4^-$	34.4		
$FeCO_3^+$	9.7		
$FeSO_4^+$	4.0		

Table 3b. Solubility products used in calculations of total solubilities and species distribution [$M_xA_yB_z(s) \rightarrow xM + yA + zB, \log K$]

Species	Log K	Species	Log K
$Al(OH)_3(s)$	−33.9	$Pb(OH)_2(s)$	−14.9
$Al_2(SO)_4(s)$	−7.0	$Pb(CO_3)(s)$	−13.9
$AlOHSO_4(s)$	−17.8	$Pb_3(OH)_2(CO_3)_2(s)$	−14.5
$Al_4(OH)_{10}SO_4(s)$	−116.0	$NaPb_2(OH)(CO_3)_2(s)$	−31.0
$KAl_3(OH)_6(SO_4)_2(s)$	−85.4	$PbSO_4(s)$	−7.7
		$PbOH(SO_4)_{0.5}(s)$	−13.6
$Cd(OH)_2(s)$	−14.4	$Pb(OH)_{1.5}(SO_4)_{0.25}(s)$	−15.7
$Cd(CO_3)(s)$	−13.7		
$Cd(OH)_{1.5}(SO_4)_{0.25}(s)$	−12.5	$Zn(OH)_2(s)$	−16.2
		$ZnCO_3(s)$	−10.0
$Cu(OH)_2(s)$	−19.3	$Zn(OH)_{1.28}(CO_3)_{0.36}(s)$	−14.4
$CuCO_3(s)$	−9.6	$Zn(OH)_{1.5}(SO_4)_{0.25}(s)$	−14.3
$Cu_2(OH)_2CO_3(s)$	−34.0		
$Cu_3(OH)_2(CO_3)_2(s)$	−46.0		
$Cu(OH)_{1.5}(SO_4)_{0.25}(s)$	−17.2		
$Fe(OH)_3(s)$	−38.8		
$FeOOH(s)$	−41.5		
$NaFe_3(OH)_6(SO_4)_2(s)$	−89.3		
$KFe_3(OH)_6(SO_4)_2(s)$	−75.4		

Table 4. Solid phases in the particulate fractions as indicated from X-ray diffraction data (site 4)

Compound	Comment*	
$Al(OH)_3$	2	M
β-AlOOH	2	
$Al(OH)(SO_4)\cdot 5H_2O$	1	
$KAl(SO_4)_2\cdot aq$	1	
$Cu_3(OH)_2(CO_3)_2$	1	
$Fe(OH)_3$	2	M
FeOOH	1	
$Pb_3(OH)_2(CO_3)_2$	2	
$Pb_4(OH)_2(CO_3)_2SO_4$	1	
$ZnSiO_3$	1	
SiO_2	2	
$K_2Al_2Si_4O_{12}\cdot aq$	1	

* 2—positively identified, 1—possible.
M = major component.

$KAl(SO_4)_2)(s)$ are possible solid constituents in the suspended fraction.

The existence of a particulate Al fraction some 300 m downstream from the deposit, possibly $Al(OH)_3(am)$, is also indicated from the leaching results (c.f. Fig. 2). Another solid phase is also present and appears in fraction 5 (Table 4). At sites 3 and 4 only 6% and 1%, respectively, of the total Al remains as soluble species (Table 2). The solid fractions corresponding to organic species (steps 3 and 4) are quite significant and do not change from site 3 to site 4. As the system becomes anoxic Al appears to form more easily degraded solids.

As expected, Ca largely remains in the solution phase, even at site 4. The fraction in the particulate phase (up to 13% of total amounts at site 4) is almost entirely encountered as exchangeable species (fraction 1) under both oxic and anoxic conditions.

Saturation with respect to $CdCO_3(s)$ could possibly be achieved at site 5 (Fig. 2), but the presence of this carbonate is not indicated from the X-ray data. A large fraction of the total Cd appears in the particulate phase (up to 50% at site 4). Most of this Cd is exchangeable (Fig. 3) or, to a minor extent, associated with the hydrous oxide phase (fraction 2). A small but significant amount is retrieved in fraction 3, corresponding to an organic form. Variations in oxygen saturation does not appear to influence the stability of the solid speciation of Cd.

Possible solubility limiting Cu Species are CuO(s), $Cu(OH)_2(s)$ as well as various hydroxy carbonates. The oxide is not a likely solubility limiting phase because of the slow kinetics of its formation. The observed Cu concentrations indicate undersaturation with respect to $Cu(OH)_2(s)$ but possibly close to saturation with respect to hydroxy carbonates at high pH. The presence of $Cu_3(OH)_2(CO_3)_2(s)$ is possible as indicated by the X-ray diffraction data. Under anoxic conditions the leaching results suggest solid Cu species to be more easily dissolved.

The distribution of leachable Ca over the five fractions is similar to the Cd distribution. However, the exchangeable solid species (fraction 1) is much less, and particularly the organic part (fraction 3) is much larger than for Cd. Also, there is a large amount of Cu dissolved in fraction 5, as well as fraction 2 (hydrous oxides). This could be an indication of a coprecipitation/adsorption with solid Al and/or Fe hydrous oxides formed in the stream.

Table 5. Composition of the suspended solids (five leachings. step 1–5; 95% confidence intervals)

	Site†				
	2	3		4	
Component*	Ox	Anox	Ox	Anox	Ox
Al	1.02 ± 0.08	1.30 ± 0.8	1.32 ± 0.05	0.90 ± 0.21	1.19 ± 0.06
Ca	0.23 ± 0.03	80 ± 21	15 ± 3	253 ± 27	123 ± 8
Cd	0.084 ± 0.009	0.35 ± 0.16	0.084 ± 0.013	0.19 ± 0.012	0.091 ± 0.006
Cu	42 ± 3	42 ± 28	34 ± 3	16 ± 11	7.9 ± 0.6
Fe	1.06 ± 0.05	0.83 ± 0.41	9.5 ± 1.9	1.5 ± 0.1	0.70 ± 0.01
Mg	0.021 ± 0.003	0.20 ± 0.07	0.15 ± 0.01	0.21 ± 0.04	0.44 ± 0.02
Mn	1.3 ± 0.1	16 ± 13	4.6 ± 0.2	67 ± 37	8.2 ± 0.4
Pb	0.99 ± 0.10	0.22 ± 0.03	0.24 ± 0.04	0.16 ± 0.10	0.17 ± 0.05
Si	0.46 ± 0.06	n.d.	0.36 ± 0.12	n.d.	0.50 ± 0.08
Zn	6.6 ± 0.7	110 ± 43	43 ± 7	81 ± 26	62 ± 8
Tot.‡	90	95	576	179	92
§	174	175	948	203	155
Solids‖	33 ± 1	18 ± 14	122 ± 5	12 ± 6	76 ± 23

* Concentrations in mmoles/g for Al, Fe, Mg and Si; in μmoles/g for Ca, Cd, Cu, Mn, Pb and Zn.
† See Fig. 1; Anox = anoxic conditions (10 February), Ox = oxic conditions (24 March).
‡ Sum of all metals, mg/g.
§ Sum of $Al(OH)_3$ + FeOOH + SiO_2, mg/g.
‖ Total particulate fraction > 0.40 μm, mg/l.
Note: Na and K not determined.

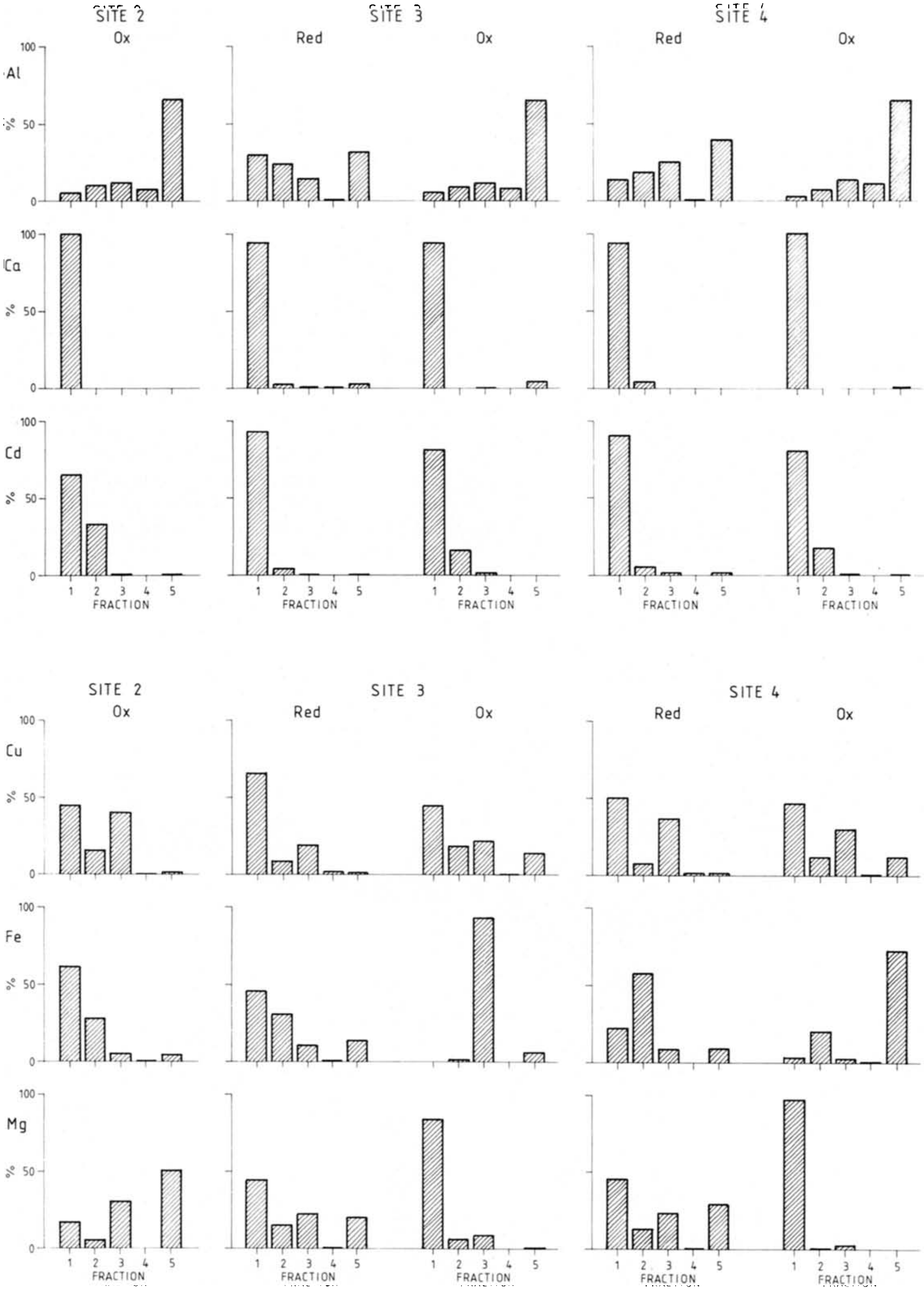

FIG. 3. Metal distribution between leaching steps 1–5 (Table 3). Red = reducing conditions (19 February). Ox = oxic conditions (24 March).

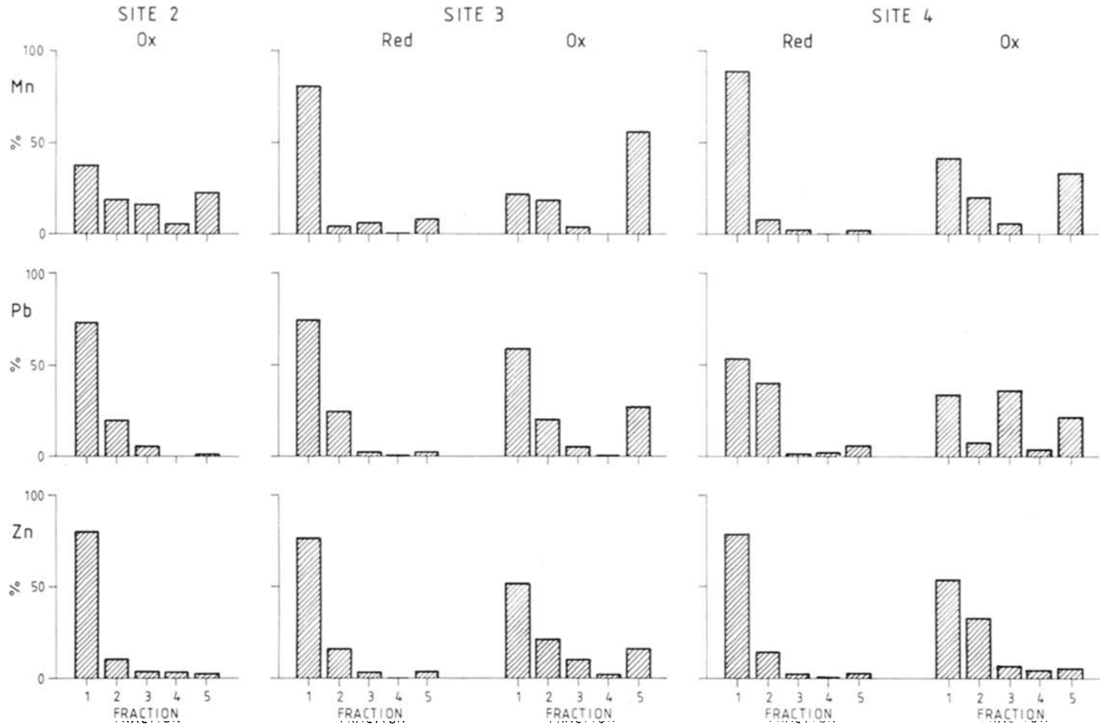

FIG. 3. *Continued.*

The oxidation of divalent Fe in the stream and subsequent precipitation of the hydroxide removes almost 80% of the total Fe already at site 2, and approximately 98% at site 4, under oxic conditions.

The rate of precipitation as well as the crystallinity of the solid hydrous oxides would be related to the Fe concentration, oxygen saturation, pH as well as the presence of dissolved complexing agents, particularly humic and fulvic acids, and dissolved silica (FLORENCE and BATLEY, 1980; STUMM and MORGAN, 1981; BENJAMIN *et al.* 1982; SINGH and SUBRAMANIAN, 1984; ANDERSON and BENJAMIN, 1985). Formation of FeOOH(am) and $Fe(OH)_3$(am) would be expected, considering the short residence time in the stream.

A recrystallization to more consolidated solids could possibly take place during the sedimentation process. The Fe concentrations in the stream water clearly exceed the solubility limitations determined by $Fe(OH)_3$(s) at all sampling sites. Both $Fe(OH)_3$(s) and FeOOH(s) are identified from X-ray data.

Under oxic conditions most of the Fe at site 2 appears in the exchangeable fraction, which would indicate that some of the Fe remains in the divalent state. At site 3 the organic fraction dominates, while more consolidated structures (fraction 5) dominate at site 4.

However, some of the Fe that appears in fraction 3 is probably the hydrous oxide that is not completely dissolved in fraction 2 due to the presence of organics (KARLSSON *et al.*, 1987b). Possibly, an organic coating on the hydrous oxide, or incorporation in the precipitates, might limit the attack of the reducing agent in the second leaching treatment. If more stable organic forms were present, these species would largely be dissolved in fraction 4, which is not the case. The presence of divalent Fe in the discharging groundwater as well as the successive sedimentation make quantitative comparison between the three sites fairly uncertain.

Under anoxic conditions the first two fractions (exchangeable and hydrous oxides) dominate the leachable Fe at all sites. Only a minor amount of the Fe was present in fraction 5 (oxide) under anoxia. Possible solubility limiting phases are $Fe(OH)_2$(s) and $FeCO_3$(s) as well as hydroxy sulphates (for trivalent Fe).

The behaviour of Mg under oxic condition is, as expected, very similar to Ca in terms of the quantitative distribution between solution and solid phase as well as the dominance of exchangeable species, particularly at site 4. However, at site 2 Mg could be found in both the hydrous oxide and the organic phase (fractions 2 and 3). Under anoxic conditions there is obviously a more even distribution over the five leaching fractions. This does not necessarily reflect the properties of Mg only but could also be related to properties of the solid phases precipitated in the system.

The particulate Mn fraction increases from 8% at site 2 to 71% at site 4. The exchangeable, hydrous oxide bound and organic species (fractions 1–3) are all of importance under oxic conditions, as well as the stable oxide phase (fraction 5). There is a shift towards more easily degraded solids which could reflect the redox-status of the system under anoxic conditions (c.f. the distribution of Fe, Fig. 3). No solid Mn phase could be identified from the X-ray diffraction data.

Solubility limiting Pb species could be $PbSO_4(s)$ (low pH) and $PbCO_3(s)$ or $Pb(OH)_2(s)$ (high pH) (Florence and Batley, 1980). In the present system the formation of hydroxy carbonates would also be feasible, as indicated by the observed Pb concentrations at high pH. The presence of $Pb_3(OH)_2(CO_3)_2(s)$ is indicated from the X-ray data, also $Pb_4(OH)_2(CO_3)_2SO_4(s)$ is a possible solid Pb species. This is somewhat surprising because the concentrations of Pb in the aqueous phase suggest undersaturation with respect to these latter species. The results suggest that further investigation of the chemical conditions at the solid/liquid interfaces is required. Parameters determined in the bulk solution are not always directly applicable at solid interfaces.

The distibution of Pb between the various leaching steps resembles the distribution of Cu. Just as for Cu, there is a resistant fraction (No. 5) that may be attributed to coprecipitation/adsorption with Al and/or Fe under oxic conditions. These observations seem to be confirmed by the shift towards exchangeable solid species as the system becomes anoxic.

The solubility limiting Zn species could be $ZnCO_3(s)$. The measured Zn concentrations are, however, below saturation in all samples and the Zn distribution over the five treatments is similar to that of Cd. The exchangeable and hydrous oxide fractions dominate. The amount designated to the organic fractions is intermediate between Cd and Cu. Although $ZnSiO_3(s)$ is a possible solid phase, according to X-ray data, it is unlikely that this species is formed for kinetic reasons.

Solid residuals

The results from the complete dissolution of solid residuals after the leaching sequence are given in Table 6, showing the major components except carbon and oxygen. The trace elements are omitted because they were not detected. The elemental compositions of the solid residues from the three sites are very similar. Silicon and Al dominate with a mole ratio of ~2.5–3.5. Possibly this corresponds to an allochtonous suspended phase of clayish materials or degradation products that is washed into the stream from the surroundings. A precise mineralogical composition cannot be concluded, however.

Table 6. Composition of the residual fraction (five leachings, step 6; 95% confidence intervals)

	Site†		
Component*	2 Ox	3 Ox	4 Ox
Al	3.4 ± 0.2	2.3 ± 0.3	2.0 ± 0.2
Fe	0.25 ± 0.06	0.24 ± 0.10	0.20 ± 0.06
Mg	0.25 ± 0.09	0.15 ± 0.05	0.13 ± 0.04
Si	8.3 ± 2.4	8.2 ± 1.8	7.1 ± 1.0
Tot.‡	702	717	550

* Concentrations in mmoles/g.
† See Fig. 1; Ox = oxic conditions (24 March).
‡ Sum of Al_2O_3, Fe_2O_3, SiO_2 and MgO, mg/g.

The organic content is approximately 30% (dry wt). It is not possible to obtain an absolute value due to the technique used for drying the samples.

CONCLUSIONS

The acid leachates from the deposit are mixed and gradually neutralized with surface water in the stream and by inflowing groundwater. The formation of a largely amorphous solid phase takes place (totalling 30–120 mg/l under oxic conditions and 10–20 mg/l under anoxic conditions). The major inorganic compounds of this solid fraction are $Al(OH)_3(s)$ plus $AlOOH(s)$ and $Fe(OH)_3(s)$ plus $FeOOH(s)$, although other Al species ($Al(OH)(SO_4)\cdot 5H_2O(s)$, $KAl(SO_4)_2\cdot aq(s)$ may also be formed. An inorganic fraction that does not originate from the leachates is also present [$SiO_2(s)$ and possibly $K_2Al_2Si_4O_{12}(s)$]. The organic content may be as high as 30% (dry wt).

There are significant differences in the nature of the particulate phase depending on the concentrations of dissolved oxygen in the water. Under oxic conditions a largely organic particulate Fe fraction forms rapidly. For Al, a significant fraction of the suspended solids is associated with organics. Under anoxic conditions part of the Fe may remain in the divalent state, which reduces the amount of suspended matter that is formed.

The transition elements Mn, Cu, Zn, Cd and Pb do not reach saturation according to available formation constants, except possibly Cu and Cd at high pH. For both Cu and Pb the presence of solid hydroxy carbonates in the particle phase is indicated by X-ray diffraction analysis. All of the metals Mn, Cu, Zn, Cd and Pb are either coprecipitated with the hydrous oxide phase of Al and Fe or sorbed at available surface sites once the solid has been formed. They are consequently gradually removed from the aqueous phase with increasing pH. The desorption/dissolution behaviour observed in the sequential leaching procedure suggests that all of these elements are largely exchangeable or bound in the hydrous oxide fraction. A large amount of the solid Cu appears, however, to be associated with organics. For Mn and Pb significant fractions are found in the oxide phase of the precipitate, which would indicate a coprecipitation rather than adsorption for these elements.

A general conclusion is that significant fractions of the metals (Mn, Cu, Zn, Cd and Pb, as well as the precipitating Al and Fe) would appear in a particulate phase which forms rapidly (in a matter of hours) as pH increases. At pH values >6.5 more than 98% of the total Al and Fe are present in the operationally defined particulate phase, and ~50% of the other metals are adsorbed/coprecipitated in this phase. Particulate transport is the dominating mechanism for the long range distribution of the metals from the release point.

Further studies are in progress dealing with the sedimentation of particulate matter in the system and the structure and chemistry of the organics present. These studies also include determination of the long-range transport of minute particulate matter and colloidal metal species further downstream into a lake system and eventually into the Baltic Sea (some 40 km).

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REFERENCES

Allard B., Bergström S., Brandt M., Karlsson S., Lohm U. and Sandén P. (1987a) Environmental impacts of an old mine tailings deposit—hydrochemical and hydrological background. *Nordic Hydrol.*, in press.

Allard B., Arsenic I., Borén H., Paxéus N. and Pettersson C. (1987b), in preparation.

Anderson P. R. and Benjamin M. M. (1985) Effects of silicon on the crystallization and adsorption properties of ferric oxides. *Environ. Sci. Technol.* **191**, 1048–1053.

Babich H. and Stotzky G (1980) Environmental factors that influence the toxicity of heavy metal and gaseous pollutants to microorganisms. *Crit. Rev. Microbiol.* **8**, 99–145.

Batley G. E. (1983) The current status of trace element speciation studies in natural waters. In *Trace Elements Speciation in Surface Waters and its Ecological Implications* (ed. G. G. Lippard). Natural Water Research Inst., Burlington, Canada.

Benes P. and Majer V. (1980) *Trace Chemistry of Aqueous Solutions.* Elsevier.

Benjamin M. M., Hayes M. M. and Leckie J. O. (1982) Removal of toxic metals from power-generation waste streams by adsorption and coprecipitation. *J. Water Pollution Control Fed.* **54**. 1472–1481.

Chapman B. M., Jones D. R. and Jung R. F. (1983) Processes controlling metal ion attenuation in acid mine drainage streams. *Geochim. cosmochim. Acta* **47**, 1957–1973.

Florence T. M. and Batley G. E. (1980) Chemical speciation in natural waters. In *Critical Reviews in Analytical Chemistry* (eds B. Campbell and L. Meites), pp. 219–296. CRC Press.

Förstner U. and Salomons W. (1983) Trace elements speciation in surface waters: interactions with particulate matter. In *Trace Elements Speciation in Surface Waters and its Ecological Implications* (ed. G. G. Lippard), pp. 245–273. National Water Research Inst., Burlington, Canada.

Hannaker P. and Qing-Lie H. (1984) Dissolution of geological material with orthophosphoric acid for major element determination by flame atomic-adsorption spectroscopy and inductively-coupled plasma atomic emission spectroscopy. *Talanta* **31**, 1153–1157.

Hart B. T. (1982) Transport of toxic heavy metals and organic contaminants by particulate matter in streams. *Proc. Australian Water Resource Council Conf.*, Vol. 47, pp. 136–149.

Hoffman M. R., Yost E. C., Eisenreich R. J. and Maier W. J. (1981) Characterization of soluble and colloidal-phase metal complexes in river water by ultrafiltration. A mass-balance approach. *Environ. Sci. Technol.* **15**, 655–661.

Johnson C. A. (1986) The regulation of trace element concentrations in river and estuarine water contaminated with acid mine drainage: the adsorption of Cu and Zn on amorphous Fe oxyhydroxides. *Geochim. cosmochim. Acta* **50**, 2433–2438.

Karlsson S., Sandén P. and Allard B. (1987a) Environmental impacts of an old mine tailings deposit—metal adsorption by particulate matter. *Nordic Hydrol.*, in press.

Karlsson S., Håkansson K. and Allard B. (1987b) Simultaneous dissolution of organic acids in sequential leaching of sediment bound trace metals, *J. Environ. Sci. Health*, submitted.

Karlsson D., Håkansson K. and Allard B. (1987c) Chemical characterization of stream bed sediments receiving loadings of metaliferous and acidic mine effluents. *Chem. Geol.*, submitted.

Lion L. W., Altmann R. S. and Leckie J. O. (1982) Trace metal adsorption characteristics of estuarine particulate matter: evaluation of contributions of Fe/Mn oxide and organic surface coatings. *Environ. Sci. Technol.* **16**, 660–666.

Maher W. A. (1984) Evaluation of a sequential extraction scheme to study associations of trace elements in estuarine and oceanic sediments. *Bull. Environ. Contam. Toxicol.* **32**, 339–344.

Merrill D. T., Chow W. and Leckie J. O. (1984) Trace element removal by adsorption/coprecipitation on amorphous iron oxyhydroxide. *Proc. of the 45th Int. Water Conf.*, pp. 279–283.

Nordstrom D. K. (1982) The effect of sulfate on aluminium concentrations in natural waters: some stability relations in the system Al_2O_3–SO_3–H_2O at 298K. *Geochim. cosmochim. Acta* **46**, 681–692.

Salomons W. and Förstner U. (1980) Trace metal analysis of polluted sediments. II. Evaluation of environmental impact. *Environ. Technol. Lett.* **1**, 506–517.

Salomons W. and Förstner U. (1984) *Metals in the Hydrocycle.* Springer.

Sandén P., Karlsson S. and Lohm U. (1987a) Environmental impacts of an old mine tailings deposit—metal concentrations and water pathways. *Nordic Hydrol.*, in press.

Sandén P., Karlsson S. and Allard B. (1987b) Effects of pH and water flow on the transport of metals from mine tailings. *Water Res.*, submitted.

Singh S. K. and Subramanian V. (1984) Hydrous Fe and Mn oxides—scavengers of heavy metals in the aquatic environments. *CRC Crit. Rev. Environ. Control* **14**, 33–90.

Sholkowitz E. R. and Copland D. (1981). The coagulation solubility and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in river water. *Geochim. cosmochim. Acta* **45**, 181–189.

Slavek J. and Pickering W. F. (1986) Extraction of metal ions sorbed on hydrous oxides of Fe(III). *Water Air Soil Pollution* **28**, 151–162.

Stumm W. and Morgan J. J. (1981) *Aquatic Chemistry.* Wiley.

Tessier A., Campbell P. G. C. and Bisson M. (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51**, 844–851.

Tessier A., Campbell P. G. C. and Bisson M. (1980) Trace metal speciation in the Yamaska and St. Francois rivers (Quebec). *Can. J. Earth Sci.* **17**, 90–105.

Tessier A., Rapin F. and Carignan R. (1985) Trace metals in oxic lake sediments: possible adsorption onto iron oxyhydroxides. *Geochim. cosmochim. Acta* **49**, 183–194.