

Environmental Impacts of an Old Mine Tailings Deposit – Metal Adsorption by Particulate Matter

S. Karlsson, P. Sandén and B. Allard

Department of Water in Environment and Society,
Linköping University, Sweden

The distribution of metals (aluminum, manganese, iron, copper, zinc, cadmium and lead) between suspended particles and solution phase has been studied by analysis of time series data in a stream receiving leachates from a mine tailings deposit. A precipitation of aluminum and iron takes place when the acidic effluents are neutralized by unpolluted groundwater, while the other dissolved elements never reach saturation. The particulate fraction is largely amorphous. A transfer of dissolved elements from the solution phase to the particle phase, increasing in the order zinc < cadmium < copper < lead with increasing pH, is observed. This removal of metals from the aqueous phase appears to be due to sorption processes rather than to coprecipitation. The formation of a particulate metal fraction could be the means for long-range transportation and redistribution of metals in environmental water systems.

Introduction

The occurrence and mobility of »heavy metals« (copper, zinc, cadmium, lead etc.) have been studied in various natural environments, since many of these metals are considered toxic and are expected to have a negative impact on the ecosystem at concentrations above natural background levels. Important knowledge has been obtained from studies in unpolluted watersheds as well as in polluted waters (Florence and Batley 1980; Förstner and Wittman 1979; Hart 1982; Salomons and Förstner 1984).

Observations under »natural« conditions can not generally be transferred to heavily polluted systems, since different processes could be of importance for the

control of metal solubility, transport and distribution (Chapman *et al.* 1983). A better understanding of extreme situations is needed, e.g. for the quantitative description of the transport of metals from a point source or the release and spreading of metals due to acidification.

Severe pollution of heavy metals can often be found in the vicinity of old mining areas. Valuable information can be obtained from such point sources concerning the processes controlling transport and redistribution of heavy metals. The present study focuses on the role of particulate matter for the speciation and occurrence of metals from a mining area along a water pathway. Effluents from a deposit of mine tailings are analysed and the subsequent distribution of metals (Al, Mn, Fe, Cu, Zn, Cd and Pb) between solution phase and particulate suspended matter has been studied under various hydrological conditions (from September 1983 to December 1985).

All data presented in this study originate from field observations. Laboratory experiments (precipitation-coprecipitation, sequential leaching) will be presented elsewhere. A general description of the mine area (local geology, hydrology, hydrochemistry etc.) is previously given (Allard *et al.* 1987). Since sorption of elements onto solids in the bottom sediments would have a large effect on the metal distribution these processes are discussed separately (Sandén *et al.* 1987a).

Collection of Field Data

Sampling

Water was sampled and analyzed at various distances from the tailings, representing different degree of dilution of leachates with uncontaminated waters at locations presented in Allard *et al.* (1987).

Manual sampling was made weekly at all sites. Automatic samplers were used as both at sites 3 and 4 for more frequent collection of samples e.g. in case of rapid events such as heavy rainfalls. No data obtained from the automatic sampling are considered in the present analysis due to storage effects. Samples were collected in the centre of the stream and great care was taken to avoid discrimination of particle sizes in the sampling procedures and contamination from the bottom sediments.

Contamination of samples by trace metals as well as sorption to the container vessels used for collection and sample preparation can create serious errors. Precautions were taken to minimize these effects by only using containers made of polyethylene and polypropylene which were acid washed prior to use (cleaning in 6 M HNO₃ followed by soaking for 24 h in 2 M HNO₃ + 1 M HCl; rinsing in MilliQ water and storage in polyethylene bags).

Separation

Separation of solids from solution was made by pressure filtration using filters with a pore diameter of 0.40 µm. Only particles retained by this pore size are considered

in the following discussion. Typically, the amount of solid matter corresponded to 5-20 mg/l. Filters with a pore size of 0.20 μm were also tested. However, the amount of particulate matter retained by these filters was only some 3-5 % larger in comparison with the filtrations using 0.40 μm filters. No significant differences could be detected when comparing samples filtered in the field with samples treated identically in the laboratory. Polycarbonate filters (Nuclepore Corp.) were used, since the sorption reactions or release of trace metals were negligible with these filters under the present conditions (concentration ranges and filtering times). Before use the filters were rinsed with deionized water (Milli-Q quality, Millipore Corp).

After filtration the filtrates were immediately preserved by addition of HNO_3 (Suprapur, Merck Co.) to $\text{pH} < 2$ in order to reduce any reactions before the analysis of the samples.

Filtration as a means of separating particles with different diameters is generally difficult to control since the successive accumulation of solids on the surface can alter the effective pore size (Danielsson 1982). These potential errors cannot fully be avoided. However, the total volumes in the filtrations were restricted to less than 100 ml, in order to minimize these effects.

Analysis

Metals (Na, K, Mg, Ca, Al, Mn, Fe, Cu, Zn, Cd, Pb) were determined by atomic absorption spectrophotometry (Perkin-Elmer 5000/Zeeman) with the use of flame or graphite furnace technique depending on the concentrations present in each sample. Determinations were made by direct calibration of the instrument since there were no significant errors caused by matrix or background interferences. Metal analyses were generally completed within 24 hours after the sample collection.

Anions (Cl^- , HCO_3^- , SO_4^{2-}) were determined in aliquots taken from the original sample. Alkalinity was determined by titration with HCl. Dissolved oxygen was determined by the Winkler method and sulphate by spectrophotometry (FIA technique; formation of BaSO_4 from a Ba-methyltymole complex). A complete description of analytical procedures is given by Allard *et al.* (1987).

General Hydrochemistry

Waterflow in the stream was continuously monitored at site 3 and precipitation data for the area was supplied by the Swedish Meteorological and Hydrological Institute having a precipitation gauge in the vicinity of the deposit.

The contribution of leachates coming from the tailings varies somewhat in the stream as a result of variations in precipitation and is absent under the frozen period, usually January and February.

The concentrations of major components in the stream are given in Table 1

Table 1 – Water composition (major components) at the sampling sites. Average values (in mol/l) with standard errors (within parenthesis) for the time period Sept. 1983 – Dec. 1985 (weekly sampling). (Sites are described in Allard et al, 1987).

	Site				
	1	2	3	4	5
Na	0.25(0.01)	0.26(0.02)	0.28(0.01)	0.41(0.03)	0.33(0.02)
K	0.041(0.007)	0.10(0.007)	0.18(0.18)	0.096(0.012)	0.098(0.006)
Mg	0.32(0.17)	1.35(0.18)	0.75(0.25)	0.81(0.26)	0.29(0.10)
Ca	0.20(0.03)	0.47(0.05)	0.37(0.04)	0.57(0.09)	0.51(0.04)
Cl ⁻	0.21(0.02)	0.062(0.005)	0.24(0.01)	0.39(0.03)	0.34(0.02)
HCO ₃ ⁻	0.25(0.12)	0	0.11(0.37)	0.42(0.10)	0.92(0.08)
SO ₄ ²⁻	0.38(0.08)	6.49(0.02)	2.05(0.37)	1.27(0.20)	0.36(0.05)
pH	5.32(0.43)	3.36(0.19)	4.47(0.62)	5.83(0.72)	6.70(0.22)

(average values). Since the groundwater is rich in bicarbonate and has a pH of ca. 7.3, the mixing with this water will lead to a neutralization of the acid leachate. The inflow of groundwater into the stream shows large variations related to precipitation and seasonal differences (Sandén *et al.* 1987b). These fluctuations result in large deviations from the averages in chemical compositions for sites 3 and 4. The dilution due to mixing with groundwater downstream site 2 can be estimated from the sulphate concentration (Sandén *et al.* 1987a).

The titrimetric alkalinity data appear merely to reflect the equilibrium with carbon dioxide from the atmosphere (Sandén *et al.* 1987a). In analogy with this system dissolved oxygen appears to be in equilibrium with the atmosphere. The concentration of dissolved oxygen is usually greater than 90 % of equilibrium concentrations expected from the atmospheric partial pressure. Anomalies were observed in January and February when the ice layer reduced diffusion of gases across the air/water interface.

Total concentrations of trace metals show a similar pattern to sulphate with decreasing concentrations downstream, Fig. 1. The largest variations are observed at the sites 3 and 4. The decline in metal concentrations cannot fully be accounted for by dilution effects, based on sulphate mass balances as a reference. There is obviously a transfer of elements from solution e.g. to exposed solid surfaces as pH increases (Sandén *et al.* 1987a).

Metal Distribution

Metal Concentrations and Dilution Effects

It is evident from Figs. 1 and 2, that a large fraction of the heavy metals is associated with the suspended particulate phase. In a system responding only to dilution the total metal concentration and metals associated to suspended solids would be

Mine Tailings – Metal Adsorption

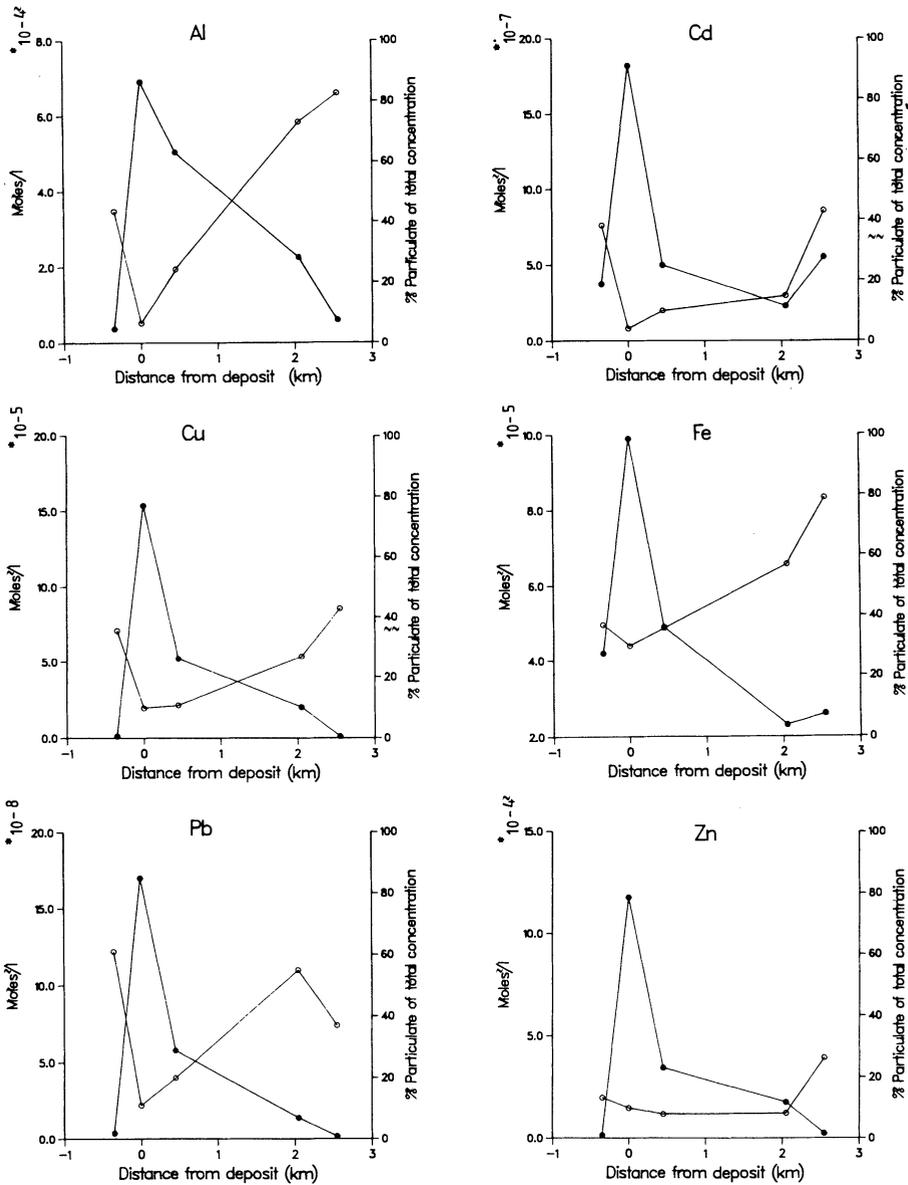


Fig. 1. Trace elements (unfiltered samples) at the sampling sites (●) and corresponding particulate fractions (○) for the time period Sep. 1983-Dec. 1985 (weekly sampling, average values).

represented by a straight line having a slope of 1.0. This ideal behaviour is not found. Fig. 2 rather indicates a transfer of elements from the solution phase to the suspended particle phase.

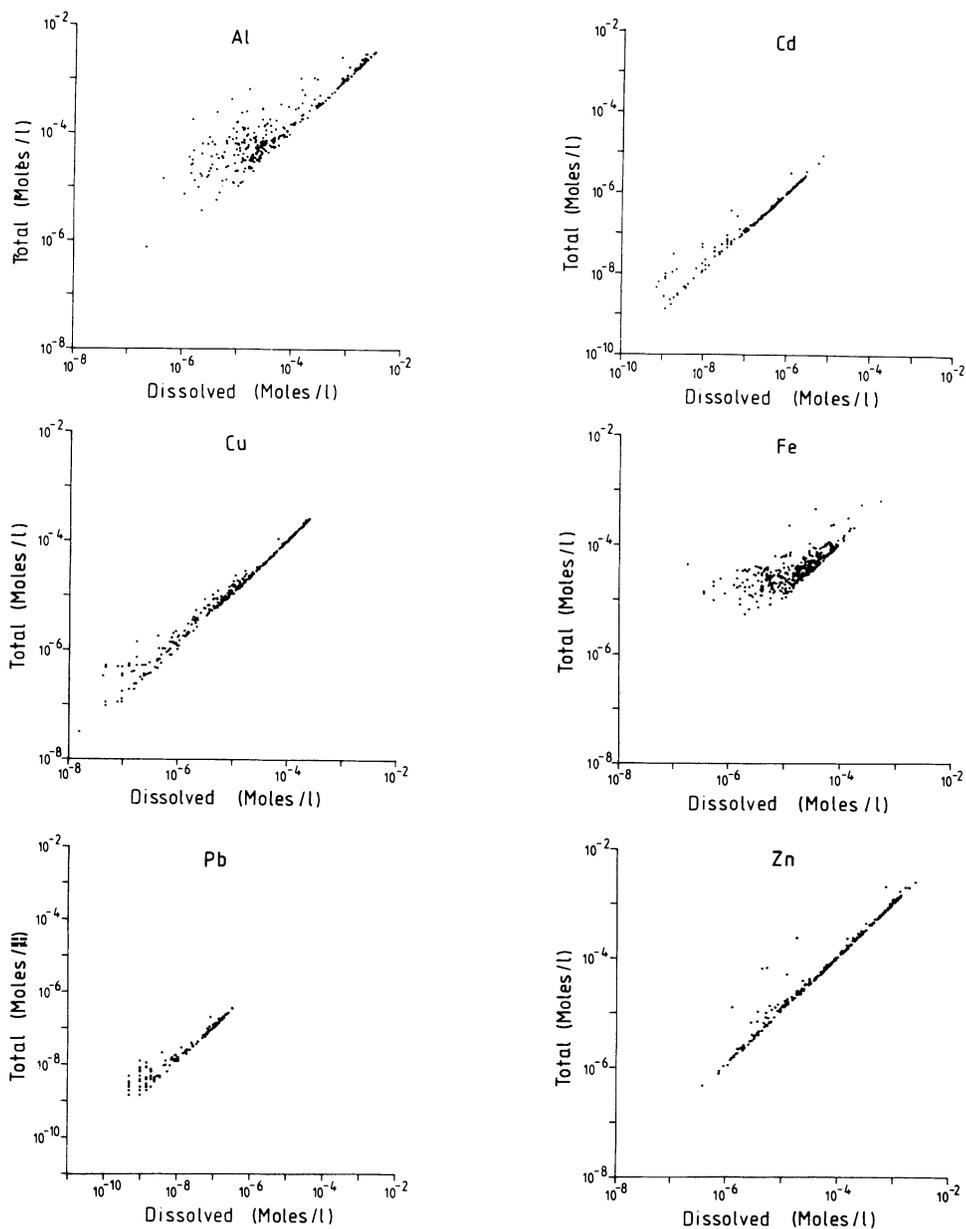


Fig. 2. Distribution of metals between suspended ($0.40 \mu\text{m}$) and dissolved metal species.

Effects of pH on the Metal Distribution

It is well known that pH has a large influence on the distribution of trace elements between solid and aqueous phases (see e.g. Benes and Majer 1980; Salomons and Förstner 1984). This is in fact true regardless of the mechanism leading to the

Mine Tailings – Metal Adsorption

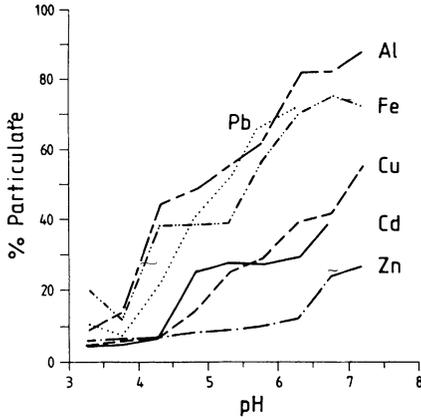


Fig. 3. Distribution of metals between suspended phase (0.40 μm) and solution as a function of pH. Average values calculated for pH-intervals of 0.5.

removal of the dissolved element from the aqueous phase (physical adsorption, chemisorption or electrostatic interaction; precipitation – coprecipitation).

The field data presented in Fig. 1 show a very strong effect of pH on the transfer of metals from the solution phase to the suspended particle phase. This transfer becomes significant at different pH-levels for the various trace metals, at increasing pH in the order $\text{Fe} \approx \text{Al} \approx \text{Pb} < \text{Cu} \approx \text{Cd} < \text{Zn} < \text{Ca} \approx \text{Mn}$, Fig. 3. Evidently, the preference for the suspended phase is rather related to the increase in pH than to any specific location along the stream.

Table 2 – Formation constants for metal complex.

Ligand (L)	Complex (x,y)	$\log K_{xy}^a$					
		Fe(III)	Al(III)	Cu(II)	Zn(II)	Cd(II)	Pb(II)
OH^-	1,1	11.8	8.5	6.3	5.0	3.9	6.3
	1,2	22.3	17.7	(12.8)	(11.1)	7.7	10.9
	1,3	28.4	25.9	(14.5)	13.6	(10.2)	13.9
	1,4	34.4	32.5				
CO_3^{2-}	1,1	9.7		6.8	(5.1) ^b	(4.5) ^b	(5.4) ^b
	1,2			9.9	(7.3) ^b	(5.6) ^b	(6.5) ^b
SO_4^{2-}	1,1	4.0	3.0	2.4	2.4	2.5	2.8
Fulvic acid ^c	1,1			4.0	3.7	3.0	4.1

^a For $x\text{M} + y\text{L} + \text{M}_x\text{L}_y$, 25°C, ionic strength 0; extrapolated values within parenthesis; from Smith and Martell (1976).

^b Estimated from formation constants for oxalates with the assumption that $\log K(\text{CO}_3^{2-}) / \log K(\text{oxalate})$ is constant.

^c A pH 5, ionic strength 0.1; from Cheam and Gamble (1974), and Schnitzer and Hansen (1970).

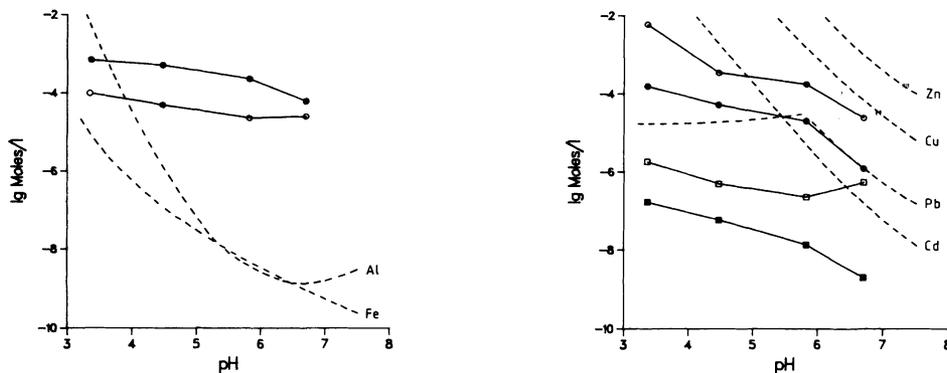


Fig. 4. Observed total metal concentrations (filtered samples) as a function of pH. Average values of pH and metal concentrations at the sampling sites. (Dashed lines represent calculated solubilities).

- a) ● Al, ○ Fe, □ Mn; solubility limiting species $\text{Al(OH)}_3(\text{s})$ and $\text{Fe(OH)}_3(\text{s})$, respectively, are assumed.
- b) □ Cd, ● Cu, ■ Pb, ○ Zn; solubility limiting species $\text{CdCO}_3(\text{s})$, $\text{Cu(OH)}_2(\text{s})$, $\text{PbSO}_4(\text{s})$ (pH 6-7), $\text{PbCO}_3(\text{s})$ (pH 6-7) and $\text{ZnCO}_3(\text{s})$, respectively, are assumed.

Nature of the Suspended Matter

The concentrations and composition of inorganic materials have been calculated for the elements Cu, Zn, Cd and Pb, considering the formation of inorganic complexes, Table 2, and solubility limiting solid phases. In the calculations of the solubilities the following solid species have been considered:

$\text{Cu(OH)}_2(\text{s})$, $\text{Cu(OH)}_{1.5}(\text{SO}_4)_{0.25}(\text{s})$, $\text{CuCO}_3(\text{s})$, $\text{Cu}_2(\text{OH})_2\text{CO}_3(\text{s})$, $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2(\text{s})$, $\text{Zn(OH)}_2(\text{s})$, $\text{ZnCO}_3(\text{s})$, $\text{Zn(OH)}_{1.28}(\text{CO}_3)_{0.36}(\text{s})$, $\text{Zn(OH)}_{1.5}(\text{SO}_4)_{0.25}(\text{s})$, $\text{Cd(OH)}_2(\text{s})$, $\text{Cd(OH)}_{1.5}(\text{SO}_4)_{0.25}(\text{s})$, $\text{CdCO}_3(\text{s})$, $\text{Pb(OH)}_2(\text{s})$, $\text{PbCO}_3(\text{s})$, $\text{PbSO}_4(\text{s})$, $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2(\text{s})$, $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2(\text{s})$, $\text{Pb(OH)}(\text{SO}_4)_{0.5}(\text{s})$, $\text{Pb(OH)}_{1.5}(\text{SO}_4)_{0.25}(\text{s})$.

Probable solubility limiting species are:

$\text{Cu(OH)}_2(\text{s})$, $\text{ZnCO}_3(\text{s})$, $\text{CdCO}_3(\text{s})$ and $\text{PbSO}_4(\text{s})$ (low pH) and $\text{PbCO}_3(\text{s})$ (high pH), respectively. Non of these elements are, however, likely to reach saturation at the present concentration levels (Sandén *et al.* 1987a).

The speciation and solubility of aluminum and iron were calculated by the use of the chemical equilibrium model PHREEQUE (Parkhurst *et al.* 1984), assuming equilibrium with atmospheric carbon dioxide and oxygen. The model indicates that saturation can be achieved with respect to phases like $\text{Al(OH)}_3(\text{s})$, $\text{Al}_2\text{O}_3(\text{s})$, $\text{Fe(OH)}_3(\text{s})$, $\alpha\text{-FeOOH}(\text{am})$, $\text{FeOOH}(\text{s})$ and $\text{Fe}_2\text{O}_3(\text{s})$, Fig. 4.

From Figs. 1 and 2 it is possible to estimate the concentrations of suspended aluminum and iron from the analyses. Particulate aluminum at a level of 2×10^{-5} – 10^{-4} M corresponds to ca 2–8 mg/l of solid Al(OH)_3 or AlO(OH) , and iron at a level of 10^{-5} – 2×10^{-5} M corresponds to ca 1–4 mg/l of Fe(OH)_3 or FeO(OH) .

Thus, a particulate fraction with an Al/Fe-ratio of ca. 2 and a concentration of around 5-10 mg/l is generally observed, with a maximum around 30 mg/l. This is in reasonable agreement with the mass found by weighing filters containing solid residues (e.g. 10-20 mg/l, average 16 mg/l, at location 4). Organics would also be expected to contribute in this mass balance (see below).

The observed variations in field data have several reasons. Precipitation of $\text{Al}(\text{OH})_3(\text{s})$ is likely to be rapid and merely dependent of pH and of the total aluminum concentration. Recrystallization after formation of the first amorphous compounds could be hindered. The oxidation of Fe(II) to Fe(III) at low pH would be slow, but the velocity of the reaction increases rapidly with increasing pH. Natural organic matter is present in the stream at concentrations usually in the range 5-20 mg/l as humic and fulvic acids at site 1. Organics such as these have a great affinity for all of the present trace elements (cf. Table 2). Concentrations of ca. 4, 8, 40 and 3 mg/l would be required for the metals Cu, Zn, Cd and Pb, respectively, to form an organic dissolved fraction corresponding to 10% of the totally dissolved metal, assuming formation constants according to Table 2.

The presence of organics would affect the sorption of metals to solid surfaces (Benjamin *et al.* 1982; Hart 1982). Low sorbing organic complexes could be formed, but the sorption on the solid might as well be enhanced by interactions between the metal-organic complexes and specific sites on the solid surfaces. Moreover, a precipitation of humic material could be possible, e.g. at site 2 (low pH, high metal concentration) during periods with high inflow of humic material from site 1.

Elementary analysis of the suspended solids were made by digestion in hot concentrated nitric acid followed by determination of totally released and dissolved metals by atomic absorption spectrophotometry. By this treatment all organic materials and amorphous precipitates will be dissolved but the effects are limited on more consolidated solids (Slavek and Pickering 1986). Results discussed here correspond to a sampling period with pH-levels ranging from 4.5 at site 3 to 6.5 at site 5, see Table 3. Major constituents of the suspended solids are aluminum, iron and silicon, but total amounts can not readily be compared between the different sites due to losses of material, e.g. in sedimentation processes. The structure of the solids were investigated by powder X-ray diffractometry. Minor fractions of hy-

Table 3 = Composition of suspended solids from various sampling sites (3, 4 and 5; average pH of 4.5, 5.4 and 6.5).

Element ^a	3	4	5	Element ^a	3	4	5
Al	1.00	1.33	1.19	Cd	0.08	0.08	0.09
Fe	1.06	9.49	0.70	Cu	42	32	7.9
Mn	1.3	4.6	8.2	Pb	1.2	0.24	0.17
Si	0.46	0.24	0.53	Zn	6.1	43	61

^a Concentrations in mmol/g (Al,Fe) and $\mu\text{mol/g}$ (Cd, Cu, Mn, Pb, Si and Zn).

drous oxides of iron as well as Al-silicates could be identified in a largely amorphous matrix. The presence of Al-silicates implies an addition of clay particles to the stream water, probably with the groundwater or washed into the stream from the soil surface under precipitation events. Evidently, a large fraction of the suspended matter can not be accounted for, particularly at sites 3 and 5, Table 3. Possibly, this fraction is of organic origin.

Possible Mechanisms

Only aluminum and iron will be expected to reach saturation as pH increases. Precipitation of e.g. iron hydroxides is known to lead to a coprecipitation of trace elements such as Cd, Cu, Pb and Zn (Benjamin *et al.* 1982). This effect cannot unambiguously be concluded in the present system since the pH required for aluminum and iron to reach saturation clearly deviates from the various pH-ranges when Cd, Cu, Pb and Zn are transferred to the suspended solid phase. This behaviour rather suggests that mechanisms related to sorption processes are controlling the apparent solubilities of these elements.

Coprecipitation could, however, control the solubility of lead since its association with suspended solids seems to be occurring in the same pH-interval as aluminum and iron reach saturation.

These observations invoke the significance of solid speciation for the control of apparent metal solubilities. The solid surfaces are expected to be highly heterogeneous since the suspended matter obviously consists of a complex mixture of amorphous precipitates and clay particles, more or less associated with organic matter. This will cause a wide distribution of surface properties with regard to ZPC (zero point charge) and complexing capacity. In spite of this complex solid system the metals are showing fairly narrow pH-intervals where they become associated to suspended solids, which are in agreement with laboratory studies of metal adsorption to different solids, including FeOOH(am), Fe₂O₃(s), Al₂O₃(s) and sulphide minerals (see e.g. Förstner and Salomons 1983; Gilles and Bancroft 1986).

Implications on Metal Transport

The spreading of trace metals bound to suspended solids would be affected by various mechanisms. The solid aggregates would be immobilized due to sedimentation when their sizes exceed what can be carried with the waterstream. The most superficial parts of the sediments would be carried downstream under events with extreme water flow. As a result, a transport of metal rich superficial sediments could give an important contribution to e.g. the annual transport, although confined to very brief events.

The importance of the colloidal size fraction as a carrier of metals has been demonstrated in other systems (Hoffmann *et al.* 1981). Spreading of metals bound to colloidal matter (pseudo-colloids) can result in transport over longer distances since these solids are less affected by gravitational forces.

Conclusions

In this investigation it has been possible to take advantage of the great variations of the chemical conditions in the system. Precipitation of aluminum and iron in solid phases and the transfer of Mn, Cu, Zn, Cd, and Pb from solution to these suspended solids are evident. In spite of difficulties in defining the solids it seems likely that only aluminum and iron are truly precipitated when acidic leachates are neutralized by unpolluted ground water while the other elements remain in an undersaturated state.

The transfer of heavy metals from solution to suspended solids is increasing in the order $Zn < Cd < Cu < Pb$ with increasing pH. It is not possible to unambiguously define a specific mechanism for this transfer. The observed pH-dependence indicates that a coprecipitation with aluminum and iron is not of major significance. Instead it appears that the mechanism is sorption, related to the chemical speciation of the individual element, rather than the composition of the heterogeneous particulate phase. The apparent solubilities of Cu, Zn, Cd and Pb in an undersaturated state can thus be controlled by sorption reactions. The transport of metals bound to particulate matter would be highly related to the flow conditions governing the sedimentation rates of large aggregates.

Further investigations on the properties of the solids such as the size distribution under natural conditions, mechanisms for the sorption processes, contents of organic matter etc. have been initiated. Efforts to make quantitative descriptions of the total metal fluxes from the deposit are in progress, as well as a further characterization of organic matter, both solid suspended particles and in solution.

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Address:

Department of Water in Environment and
Society, Linköping University,
S-581 83 Linköping, Sweden.