Environmental Impacts of an Old Mine Tailings Deposit –
Metal Concentrations and Water Pathways

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Variations in metal concentrations in a heavily polluted stream receiving acidic
leachates from an old mine tailings deposit are analysed from a hydrological
perspective. From an extensive data material, collected during three years, the
variations in concentrations of four metals (copper, zinc, cadmium and lead)
are discussed. The deposit is the principal source for these metals in the
watershed. The variation in metal concentrations in the vicinity of the deposit
can to a large extent be explained by simple dilution of contaminated water
with uncontaminated water from the surrounding area. Further downstream
the deposit, other processes become increasingly important for the metal con-
centrations in the water bodies.

Introduction

Metal concentrations in polluted waters depend on hydrological, chemical and
biological processes in the entire watershed in a complex manner. This multifaced
problem calls for simplification in order to enable a balanced control strategy. It is
therefore important to identify general pattern and major operating mechanisms in
relevant time and space dimensions, to be able to reshape the knowledge for use in
management applications. The aim of this paper is to evaluate the influence of
hydrological processes, particulary dilution of contaminated water with uncontami-
nated water, on the variation in metal concentrations at various sites along a
stream, heavily polluted with acidic leachate from a mine tailings deposit.

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The hydrological concept used to evaluate effects of dilution in the present work has been developed over the last 20 years for humid areas (Ward 1984). In this concept the groundwater is of major importance for the generation of stream flow at flood events (e.g. Pinder and Jones 1969; Sklash and Farvolden 1979; Sklash, Stewart and Pearce 1986; and Rodhe 1984). Hortonian overland flow (Horton 1933) is considered to be of minor importance, while saturated overland flow might occur.

The mixing of contaminated water with uncontaminated water is determined by the proportion of water from the deposit to that from the surrounding area. The variation in this distribution is governed by the difference in hydraulic properties of the deposit and the rest of the watershed. The lack of vegetation and the low field capacity of the deposit, depending on the course size of the material, results in very low evaporation. The tailings also provide little resistance to water flow and consequently a high hydraulic conductivity (possibly over 10^{-3} m/s). Till soils, on the other hand, have normally a fairly low hydraulic conductivity (10^{-6}-10^{-8} m/s), but might be as high as 10^{-3} m/s in the top centimeters of the soil (Lundin 1982), due to biological activity, draught cracks and so forth. This is probably valid for the till soils in this watershed. Evaporation is also considerable on vegetated soils. In this area it is estimated to 65% of the precipitation, on a yearly basis (Allard *et al.* 1987).

The watershed, with the mine tailings deposit, is situated in southeastern Sweden (Fig. 1, Allard *et al.* 1987). The deposit, which originates from copper mining in the area between 1750 and 1902, lacks vegetation and the tailings have an average size of about 0.1 m. The main part of the watershed is vegetated with coniferous forest on till soil. In the lower part there is also some agricultural fields.

Weekly samples have been collected and analysed for major constituents and trace metals at 5 sites (Allard *et al.* 1987). The first site (1) is located in a bog area upstream the deposit, and is considered to represent background concentrations in the area. Sampling site 2 represents drainage from the deposit, covering an area of 0.055 km². Water flow is continuously recorded at a weir downstream the deposit at site 3, with a drainage area of 0.87 km². Two more sampling sites (4 and 5) are located downstream the weir, with drainage areas of 2.7 and 28 km² respectively. Automatic samples have also been collected daily, when possible, at sites 3 and 4. The sampling and analysis of metals started in September 1983, and the weir has been in operation since January 1984.

For the purpose of the present analysis data for copper, zinc, cadmium and lead were selected from the extensive data material. The principal source of these metals within the watershed is the deposit. Weekly samples, as well as automatically collected samples when at hand, have been used. The metal analysis were performed on samples, which were adjusted to a pH below 2 with HNO_3, using atomic adsorption spectrophotometry. A full description of the area, mining history, sampling and chemical analysis is given in Allard *et al.* (1987).
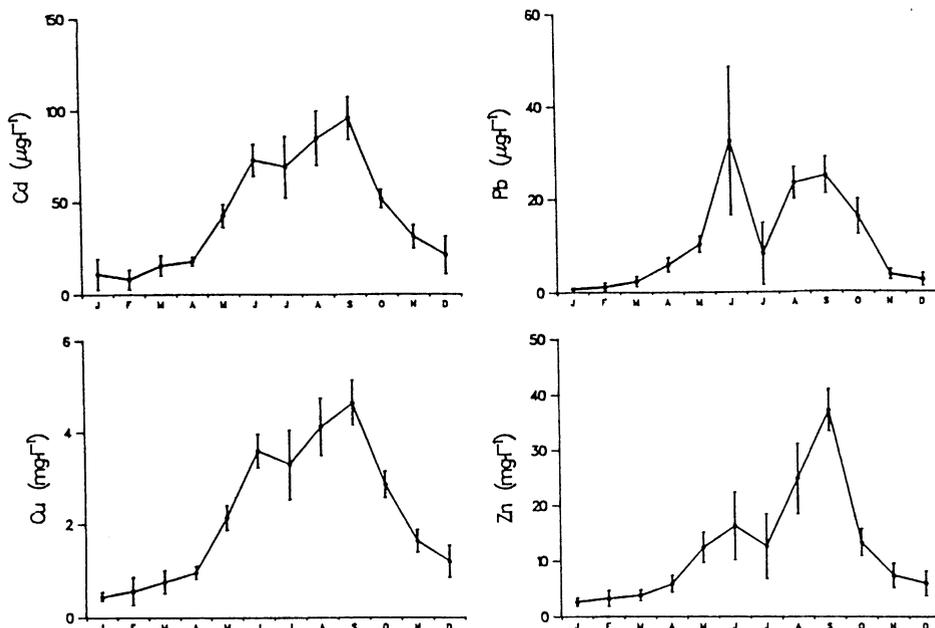
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Fig. 1. Mean metal concentrations per month, with 95 % confidence interval, for copper (mg/l), zinc (mg/l), cadmium (mg/l) and lead (mg/l) for the period January 1984 to June 1986, at site 3.

Results and Statistical Analysis

The seasonal variations in metal concentrations at site 3 is illustrated as monthly mean values, using data from the period September 1983 to June 1986 (Fig. 1). The lowest concentrations occur in the beginning of the year (January or February). A rapid increase takes places during April and May. The maximum concentrations are obtained in September, with the exception of lead which exhibits the highest value in June. In October and November there is a rapid decline in concentrations. For copper, zinc and cadmium the maximum value is between 10 and 15 times the minimum, while lead shows a difference of almost 50 times. The pH follows a reversed pattern compared to the metals, with a maximum of 5.2 during the winter, and a minimum of 3.8 in September, at the same site.

In the rest of this paper only one metal is selected for the figures. The other metals exhibits similar pattern.

The relationship between metal concentrations and water flow is inverse (Fig. 2). A regression model was fitted to the observed metal concentrations, using above described seasonal variations, as independent variables. The general form of the model is
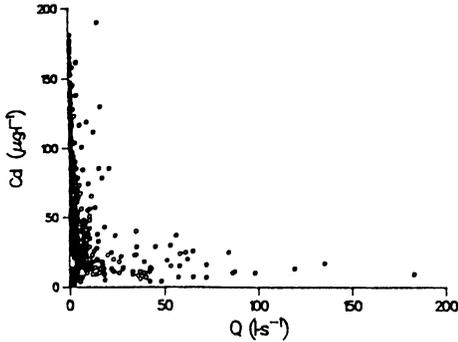
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Fig. 2.
Scatter-plot of cadmium versus water flow (Q), for the period January 1984 to June 1986, at site 3.

$$[M] = k_0 + k_1 \frac{1}{Q} + k_2 \sin(\pi \frac{month-3}{12})$$

where

[M] – the predicted metal concentration
Q – the water flow
k_0, k_1 and k_2 – constants.

The r^2 values indicate that around 60% of the variation in metal concentrations could be explained by this model (Table 1), for copper, zinc and cadmium. The variation in lead concentrations is only explained to 30%.

Examination of the time series of predicted values and observed values reveals some important deviations (Fig. 3). The model fails to reproduce much of the short-term variations in metal concentrations, while the long-term variations are fairly well described.

The peaks in metal concentrations, not explained by the regression model, are related to flood events (Fig. 4). During snow melt in the spring there is a time lag of 3 to 7 days between these concentration peaks and the corresponding flow peaks. At the spring flood maximum the metal concentrations decrease to the winter levels. This pattern is clearly visible during the three consecutive springs 1984-1986,

Table 1 – Regression model for the metals of the form.

$$[M] = k_0 + k_1 \frac{1}{Q} + k_2 \sin(\pi \frac{month-3}{12})$$

where [M] ≡ metal concentrations, Q ≡ water flow.

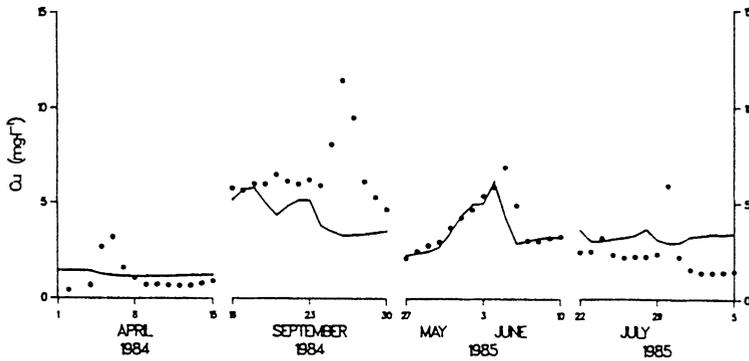|	k_0	k_1	k_2	r^2
Cu	.378	1.26	2.80	.59
Zn	.261	10.4	15.4	.63
Cd	2.13	33.8	51.7	.63
Pb	2.53	3.14	14.8	.28

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Fig. 3. Observed (●) and predicted (—) copper concentrations at site 3, during some selected periods. Predicted values according to the regression model

$$[Cu] = 0.378 + 1.26\frac{1}{Q} + 2.8\sin(\pi\frac{month-3}{12})$$

where [Cu] ≡ predicted copper concentration and Q ≡ water flow.
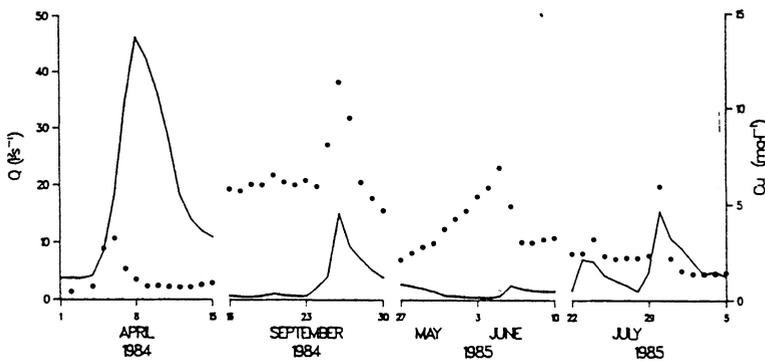

Fig. 4. Water flow (l/s, —) and copper concentration (mg/l, ●) at site 3, for some selected periods.

although the absolute values vary between the years. The lag between concentration peaks and flood at storm events is obvious in April and May. In July the lag effect is gone and the concentration peak coincides with the flood. This pattern is prevailing during the autumn.

The variations in metal concentrations at the discharge from the deposit are not reflected in the variation at site 3 (Fig. 5). Although the concentrations at site 3 vary considerably, the concentrations at the discharge from the deposit (site 2) are more or less constant.

The correlation between metal concentrations at site 3 is strong for copper, zinc and cadmium (Table 2). The correlation between these metals and specific electrical conductance is also strong. Lead concentrations differs from the other metals by
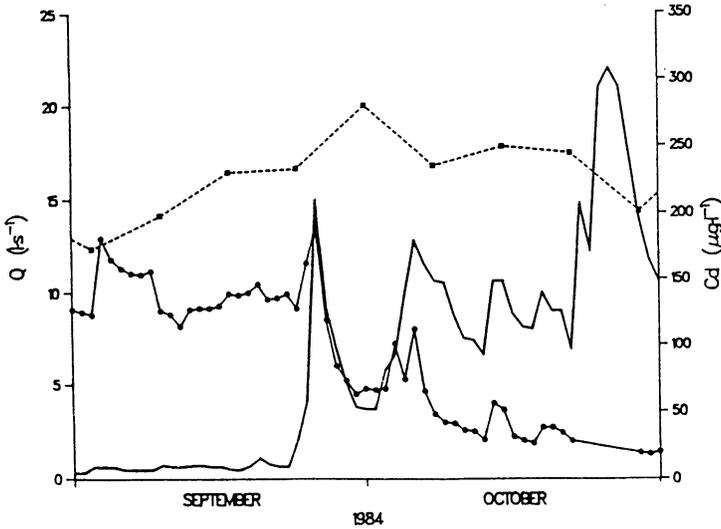
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Fig. 5. Cadmium concentrations (µg/l) at site 2 (-■-), and site 3 (-●-), for the period September 1984 to October 1984, with water flow at site 3 (—).
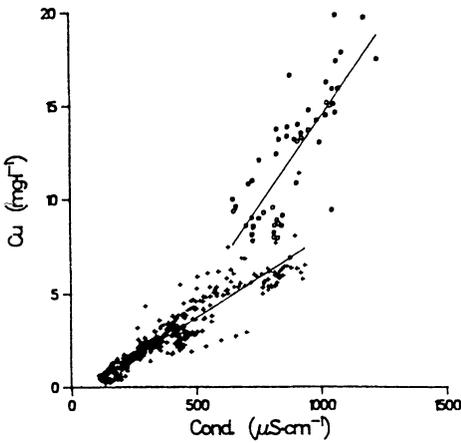

Fig. 6.

Copper concentrations (mg/l) versus specific electrical conductance (µΣ /cm) for the period September 1983 to December 1983 (o), and January 1984 to June 1986 (+), at site 3, with regression lines.

Table 2 – Correlation matrix for metals and conductivity at site 3 for the time period January 1984 to June 1986.

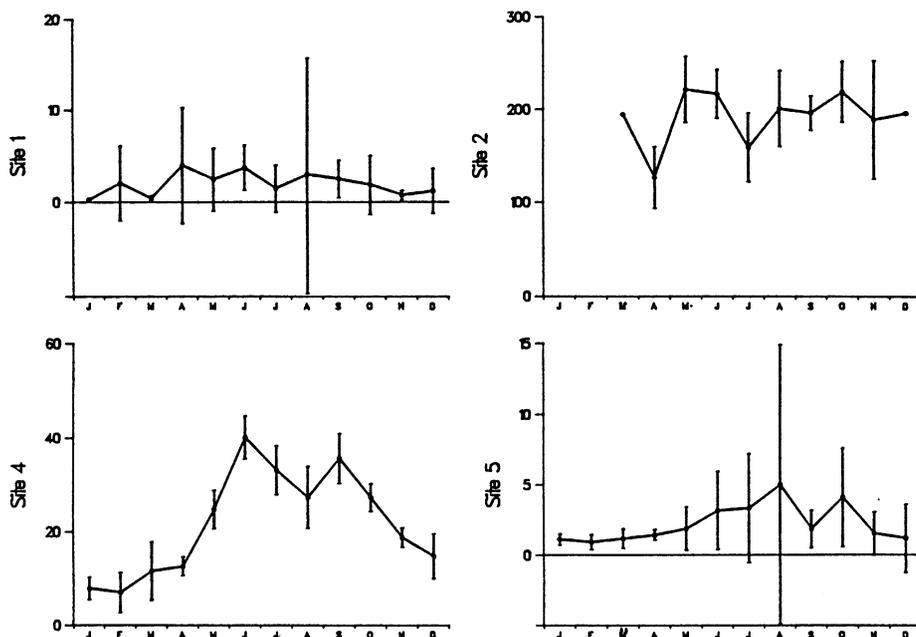|	Zn	Cd	Pb	Cond
Cu	.90	.95	.76	.93
Zn		.80	.63	.94
Cd			.68	.94
Pb				.69

All coefficients statistically significant at the 0.1% level.

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Fig. 7. Mean metal concentration per month, with 95% confidence interval, for cadmium (μg/l) for the period January 1984 to June 1986, at site 1, 2, 4 and 5.

lower correlation coefficients. There is a difference in the relationship of metal concentrations versus specific electrical conductance between the autumn 1983 and the rest of the observed period (Fig. 6). The slope of the regression line is significantly steeper for the autumn 1983 compared with the later period.

Findings are not as extensive for the other sites, since data on water flow are lacking. The seasonal variations in metal concentrations can, however, be examined (Fig. 7). Site 4 exhibits a similar pattern compared with site 3, with a minimum in metal concentrations during the winter and a maximum in the summer. The difference between the winter and summer values is a factor of five. For the other sites it is difficult to distinguish any clear seasonal pattern.

Correlation analysis was also performed for sites 1, 2, 4 and 5 (Table 3), to compare the variation in metal concentrations. In general the correlation coefficients are less than the corresponding ones at site 3. Copper versus zinc and lead have coefficients above 0.6 at site 1. The correlation between zinc and lead is also statistically significant. At site 2 all coefficients are statistically significant, except for lead versus zinc and cadmium. For site 4 the correlation is fairly strong for all metals (statistically significant at the 0.1% level). The coefficients do, however, not reach the values at site 3. Finally, at site 5 only copper versus zinc and lead are statistically significant.

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Table 3 – Correlation matrix for the metals during the time period January 1984 to June 1986.

	Site 1:				Site 2:		
	Zn	Cd	Pb		Zn	Cd_3	Pb
Cu	.61[3]	.11	.63[3]	Cu	.29[1]	.45[3]	.25[1]
Zn		.13	.25[1]	Zn		.52[3]	−.13
Cd			−.02	Cd			−.07

	Site 4:				Site 5:		
	Zn	Cd	Pb		Zn	Cd	Pb
Cu	.80[3]	.90[3]	.60[3]	Cu	.29[2]	.74[3]	−.05
Zn		.86[3]	.50[3]	Zn		.17	−.05
Cd			.50[3]	Cd			.08

[1] Statistically significant at the 5% level.
[2] Statistically significant at the 1% level.
[3] Statistically significant at the 0.1% level.

Discussion

The seasonal variation in metal concentrations at site 3 could be explained by the difference in water balance between the till soils and the deposit. During summer this results in an increasing proportion of drainage water from the deposit, which would be expected to reach a maximum in the late summer or early autumn. At this time the till soil has its lowest water content, and the groundwater level is at minimum. Consequently the metal concentrations should reach maximum levels at this time. This behaviour is obvious in the graphs of mean monthly metal concentrations (Fig. 1), where the maximum for copper, zinc and cadmium are obtained in September. As the evaporation decreases during the autumn, the soil moisture increases and thereby the proportion of water from the surrounding area to that from the deposit. This results in decreasing metal concentrations in the stream (Fig. 1). Because of the high hydraulic conductivity, discharge from the deposit virtually ceases when it is covered with snow. Thus, the stored water in the deposit is depleted faster than from the surrounding area. The proportion of leachate will then be low during winter, which results in low metal concentrations in the stream (Fig. 1). The seasonal variations in metal concentrations at site 3 can neither be explained by corresponding variations in concentrations of the discharge from the deposit (site 2), nor by the variations at the upstream site 1 (Fig. 7).The regression model can only explain 60 % of the variation in metal concentrations at site 3, taking the water flow and seasonal variations into account (Table 1). If the amount of metals leaving the deposit were constant, the inverse function of water flow would be enough to describe variations in metal concentrations at site 3. Metal

concentrations in the stream are, however, strongly affected by the difference in response to individual flood events between the deposit and the surrounding till soils. The absence of vegetation together with the high hydraulic conductivity of the deposit result in a faster response at snow melt and precipitation events, compared to the other part of the watershed. Hence, the discharge from the deposit will have largest influence on stream flow at the begining of a flood event, resulting in a peak in metal concentrations at this time in the stream. If leachate becomes dominating during flood events the metal concentration peaks and the flow peaks might even coincide. The most important discrepancies between the regression model and the observed concentrations are found at flood events (Figs. 3 and 4). The time lag between the concentration peak and the flow peak is evident during spring flood, while the two peaks coincide in the summer. This indicates that the discharge from the deposit might be dominating during the summer.

In traditional hortonian view on stream flow generation, flood events are dominated by overland flow. As a result the metals in the stream would be diluted by rain water and no peaks in metal concentrations could occur, as the deposit is the metal source. Overland flow is therefore probably not a significant hydrological element in the area.

Walling and Foster (1975) suggested that the concentration peaks in connection with flood events could be accounted for by the flushing of accumulated solutes into the stream by the initial phase of storm runoff. The time lag reported in their paper was much shorter than here (within a day). Furthermore the source of the elements was assumed to be the entire watershed. Concentration peaks in connection to flow peaks have been observed in some other detailed studies (e.g. Grimshaw *et al.* 1976; Hart *et al.* 1982) and similar types of explanation were suggested. In the present study the source of the metals is the deposit, and flushing of accumulated solutes would lead to a concentration peak in the discharge from the deposit corresponding to the peak in the stream. This is not observed (cf. Fig. 5), and consequently this explanation seems less plausible for the present data.

Dilution of contaminated water by uncontaminated water leaves some observations unexplained. Extreme situations, like the very dry summer 1983, need some additional reasoning. The relationship between metal concentrations and specific electrical conductance during the following autumn was completely different to the later period (Fig. 6). A possible reason for this might be a change from normally reducing to oxidizing conditions in the soil. This will result in a different chemical composition of the water passing through the till soils compared with normal conditions (Salomons and Förstner 1984).

The observations on lead are also deviating (concentration maximum in June, maximum 50 times the minimum; the regression model explains only 30 % and the correlation coefficients are less than for the other metals). Some process besides dilution is evidently affecting lead concentrations, possibly precipitation of solids and sorption.

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However, it is evident that a major part of the variations in metal concentrations at site 3 could be explained by dilution with uncontaminated water. This result then opens possibilities for hydrological modelling of the discharge from the tailings. Simple mass balance calculations for the metals could be used to model the discharge from the tailings deposit. A mass balance equation of the form

$$Q_3[M]_3 = Q_2[M]_2 + (Q_3 - Q_2)[M]_1$$

where

Q – water flow
$[M]$ – metal concentration
1,2 & 3 – sampling sites

could be used to obtain an estimate of the discharge. The use of this equation reveals that the fraction of water originating from the deposit is around 10% in spring and autumn. In the summer this fraction increases to about 40%, and occasionally amounts to as high as 70% of the stream flow. These data have been used to calibrate the hydrological model PULSE (Bergström *et al.* 1985) for the deposit area (Brandt *et al.* 1987).

This discussion have so far been based on the data from site 3, as it is the only site where water flow data are available. The seasonal variation in metal concentrations at site 3 is also found at site 4, although the difference between minimum and maximum is smaller. If only dilution took place between site 3 and 4 the magnitude would be more or less the same, despite that the absolute values are lower at site 4. No seasonal pattern can be observed further downstream, at site 5 (Fig. 7). The correlation coefficients (Table 2) also indicate that metals are affected by other processes besides dilution. Hence, hydrological processes could not be used as the only determining variable for the variation in metal concentrations downstream of site 3. Chemical, and maybe even biological, processes have to be taken into account in order to describe the dynamics satisfactorily.

One of the most important factors controlling mobility of metals in natural waters is pH (Salomons and Förstner 1984). The stream water pH varies considerably between the different sampling sites. For sites 2, 3, 4 and 5 pH varies between 2.9-3.9, 3.4-5.9, 4.2-7.2 and 6.2-7.3 respectively. In Sandén *et al.* (1987) it was indicated that a substantial sorption to the sediments of copper, zinc and cadmium takes place when pH exceeds 6.0. The distribution of metals between solution and particulate phase is also strongly pH dependent (Karlsson *et al.* 1987). This could account for some of the differences between site 3 and the sites further downstream. The variation in pH is in turn due to mixing of water with different origin. The highly acidic drainage water from the deposit is diluted with water which has passed through the soil in the other part of the watershed. The pH of the water from the surrounding till soils is related to the residence time in the soil/ground water system (the longer time the higher pH and alkalinity). The proportion of

water from the deposit to water from the surrounding area, as well as the pathway of this water, will then be of major importance for pH in the stream.

The general conclusions of the present study are that the simple dilution of polluted water with unpolluted water can explain the variations in metal concentrations in the vicinity of the deposit, where pH values are low. Further downstream chemical processes, like precipitation, sorption etc., probably have to be taken into account in order to describe the variations satisfactorily . The direct and indirect influence of hydrology on the variations in metal concentrations have to be taken into account when management of the metal pollution from the deposit are considered.

Acknowledgements

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