Natural isotope tracers for assessing the mechanisms of heavy metal mobilization in copper ore tailings

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ABSTRACT

The hydrodynamic mechanism of heavy metal mobilization from slag heaps in a former copper mining region of Saxony-Anhalt / Germany has been investigated by means of natural isotope tracers.

The heap is considered to be a black box, with no indication given, if the heavy metals in the spring water flowing out from the heap are leached from the processing residues by percolating rain water, by groundwater entering the heap's base, or by groundwater recharged in the heap itself. While percolating rain water can be excluded for heavy metal leaching, hydrochemical and isotopic evidence do not allow for a clear assignment of one of the two remaining components to the contaminant mobilization. However, it seems very likely that the mobilization takes place during the transit of the heap groundwater from the recharge zone to the base of the heap. According to our findings, the application of a non-permeable cover on top of the heap would inhibit the mobilization by newly recharged heap groundwater. However, the first effects would be visible two to three decades from now at the earliest so that the chemical treatment of the water is still necessary.

INTRODUCTION

The weathering and erosion of mining and ore processing residues may have a negative impact on local surface waters, which again is likely to be detrimental to groundwater quality. Assessing the environmental response and the dimension of the impacts requires understanding of the interaction between the contaminant source and the involved flow systems.

The Mansfeld region of Saxony-Anhalt / Germany is known for the mining and processing of marine black shale of Permian age, the "Kupferschiefer" or "copper shale". Mining and ore processing lasted for more than 800 years and played a key role for the local economy in the late 20th century. However, due to economical and ecological reasons all pyrometallurgical activities came to an end in 1990.

Nevertheless, even today fifteen years after the termination of mining and ore processing local surface waters still suffer continuing heavy metal immissions which are closely linked to the former ore processing activities. The heavy metals have their sources in the various by-products left behind by the former mining and ore processing. Three major by-products can be distinguished. Today, two of them form typical features of the local landscape - waste rock and slag, which have been piled up in huge heaps during the 20th century. The third by-product, the so-called "Theisen Sludge", is found in rather small volumes compared to waste rock and slag. In spite of that, heavy metal emissions which originate in the weathering of the sludge play a key role for the local groundwater and surface water quality (Schreck *et al.*, 2005). This sludge, which has been produced by scrubbing the hot process gases during the ore processing in order to wash out flue dust, was deposited in hollows or "ponds" on top of the highly porous slag and waste rock heaps. Since the bases of these ponds had not been sealed, it has to be assumed that large amounts of sludge have infiltrated the heap bodies uncontrollably. The sludge contains considerable amounts of heavy metal sulphides that can easily be oxidized by dissolved oxygen in a wet environment releasing heavy metal ions to the surrounding water. Besides the actual sludge deposits, particularly the sludge which infiltrated the slag and waste rock heaps and which is diffusely scattered there represents a serious source for heavy metal emission to percolating water (Schubert *et al.*, 2003).

This paper presents results of a research on the potential of environmental isotope signatures (^{3}H, ^{18}O, and ^{2}H) to trace heavy metal emissions from a heap of processing residues via a spring situated at the foot of the heap.

The main goal of the investigation was to localize the source of contamination. The examined heap is considered to be a black box, with no indication given, if the heavy metals in the spring water, with concentrations of up to 2.000 mg/l, are predominantly leached from the processing residues by percolating rain water, by groundwater entering the heap's base, or by groundwater recharged in the heap itself. Knowledge of these processes is essential for the remediation of the site. Thus, the aim of the investigation was to correlate the waters of different origin to the heavy metal contents of the spring water. High contaminant concentrations in the spring water did not allow for distinguishing the waters by their chemical composition. In consequence, isotope signatures were used for differentiation.

REGIONAL SETTING AND ANALYTICAL METHODS

The area of investigation is situated in the Mansfeld Mining District in Saxony-Anhalt, Germany, about 30 km west of the city of Halle. For this study, an exemplary slag heap - deposited between 1900 and 1990 and located close to the small town of Helbra - was chosen (Figure 1). The slag heap is about 40 m high and covers an area of ca. 100 000 m². During deposition of the slag material a spring producing groundwater from the carbonatic

"Rogenstein" aquifer was covered. Forced to move on a new flow path, the water is now exiting the slag heap at its western foot rim at the so called "Stadtborn" spring. In contrast to the low mineralized water discharged from the former natural Stadtborn spring, the water exiting the new Stadtborn is heavily contaminated with heavy metals and has to be considered as the major local point source of heavy metals.

In order to monitor short term variations in the chemical and isotopic composition of the spring water especially related to heavy precipitation events, an automatic refrigerated sampling system ISCO 6712ER was installed at the site allowing sequential and composite sampling. Composite water samples were taken continuously on a diurnal basis. Triggered by heavy rain events, a second sampling sequence started collecting a total of 24 samples in intervals of 30 minutes. The spring discharge was monitored on a 30 minutes schedule using an ISCO 730 Bubbler Flow Module. Rain fall has been monitored with the ISCO 674 Rain Gauge also on a 30 minutes schedule. Both discharge and precipitation data were continuously stored in the computer system controlling the ISCO 6712ER. Composite rain water samples were collected during each heavy rain event to determine the stable isotopic composition of the precipitation. To hydrochemically and isotopically characterize the groundwater feeding the old slag covered Stadtborn spring, groundwater samples from three wells in the Rogenstein aquifer were taken.

Groundwater and spring water samples were analyzed for their heavy metal contents using ICP-AES. A standard ion chromatography procedure was applied for determining sulfate concentrations. The stable isotopic composition of spring water, groundwater, and precipitation samples was determined by the H_2O-H_2 equilibration method (^2H) with an analytical precision of ±1.0 ‰ and the H_2O-CO_2 equilibration method (^{18}O) with an analytical precision of ±0.1‰. The results of the hydrogen and oxygen isotope measurements are expressed as delta notations (^{18}O, ^2H), relative to the Vienna Standard Mean Ocean Water (VSMOW). The tritium content of spring water and groundwater samples was measured by LSC after electrolytic enrichment. The detection limit is 0.5 TU (tritium units), the relative standard error of the method for higher tritium concentrations is ≤10 %. For tritium data in precipitation, the data set of the sampling station Leipzig was considered as representative for the study area that is situated about 60 km west of Leipzig.
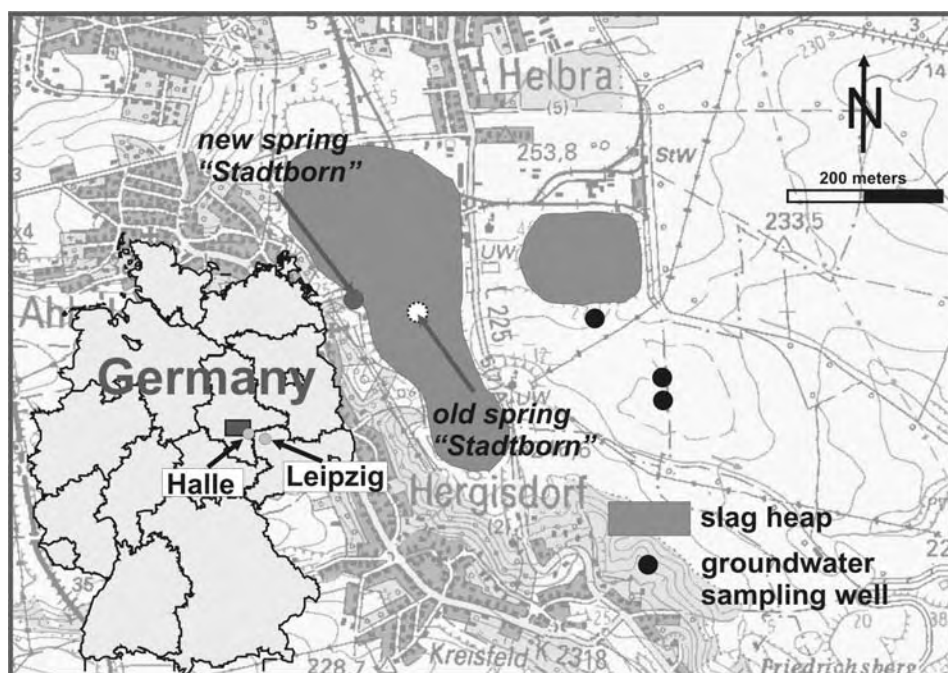

Figure 1: Overview of the study area

RESULTS AND DISCUSSION

During rain free periods, the hydrochemical and stable isotopic composition of the spring water showed only minor temporal variation. No correlation between long term fluctuations of the discharge rate and the concentrations of major components or the isotope data was observed. The spring water shows a constant pH of about 5.7 and a temperature of 7°C. Average zinc and sulphate concentration are 1400 mg/L and 4000 mg/L, respectively. While the mean ^{18}O values of the spring water were around -9.1 ‰ (VSMOW), rather constant hydrogen isotope values of ca. -64 ‰ were measured. In contrast to the homogeneous hydrochemical and isotopic composition in dry periods, the concentrations and isotope values of the spring water showed a very different behaviour during and after heavy rainfalls. The normal discharge rate at the Stadtborn Spring amounts to about 1.2 L/s.

Figure 2 displays the monitored data of spring discharge, precipitation rate, ^{18}O, D, sulfate, and zinc concentration during a selected observation period in June 2004. The discharge of the spring showed an immediate response to heavy precipitation. At its peak the discharge was almost twice as high as before the event. During the rain event, the isotopic composition of the spring water showed a significant shift towards the measured isotopic composition of the composite rain water sample (^{18}O: -7.5 ‰, D: -48.2 ‰). Using the simple

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isotope mixing equation *(1)*, the share of rain water in the spring water was calculated. In this equation δ_m, δ_R, δ_{BG} are the oxygen or hydrogen isotope values of the spring water at the time of the event, of the rain water, and of the spring water before the event, respectively. X_{QF} stands for the share of rain water in the spring discharge.

$$\delta_m = X_{QF}\delta_R + (1 - X_{QF})\delta_{BG} \qquad (1)$$

The share of rain water represents the so called quickflow, a hydrological component referring to the surface runoff plus the shallow interflow contributing to the spring immediately after the rain event started. The calculated shares of rain water indicate that only part of the additional discharge directly results from quickflow. A considerable part of the additional discharge seems to derive from an elevated baseflow. The highest percentage of the quickflow component in the additional discharge is observed ca. 30 minutes after the start of the rain event (ca. 60%). In the further course, the percentage of quickflow decreases dramatically even though the discharge stays way above its background level.

During the displayed heavy rain event the lowest metal and sulfate concentrations are reached 30 minutes after the first increase of the discharge, i.e. when the influence of percolating rainwater is most pronounced. At the peak of the spring discharge, however, the concentrations begin to rise again. That indicates that as soon as the share of percolating rain water in the spring water decreases and the spring water is dominated by baseflow, dilution becomes less relevant.

Tritium measurements of the groundwater in the Rogenstein aquifer feeding the old Stadtborn spring showed no or only a small content of tritium (0…2 TU). Hence, the water entering the slag heap at its base should also show a minor tritium content only. Due to the existing morphology, this water definitely flows to the new Stadtborn spring. However, the tritium content of the water at the new Stadtborn spring is between 10 and 11 TU. This clearly indicates that the water at the new spring does not only consist of the water emerging from the old spring but rather represents a mixture of old groundwater from the Rogenstein aquifer and younger groundwater with a higher tritium content that had been recharged in the heap itself.
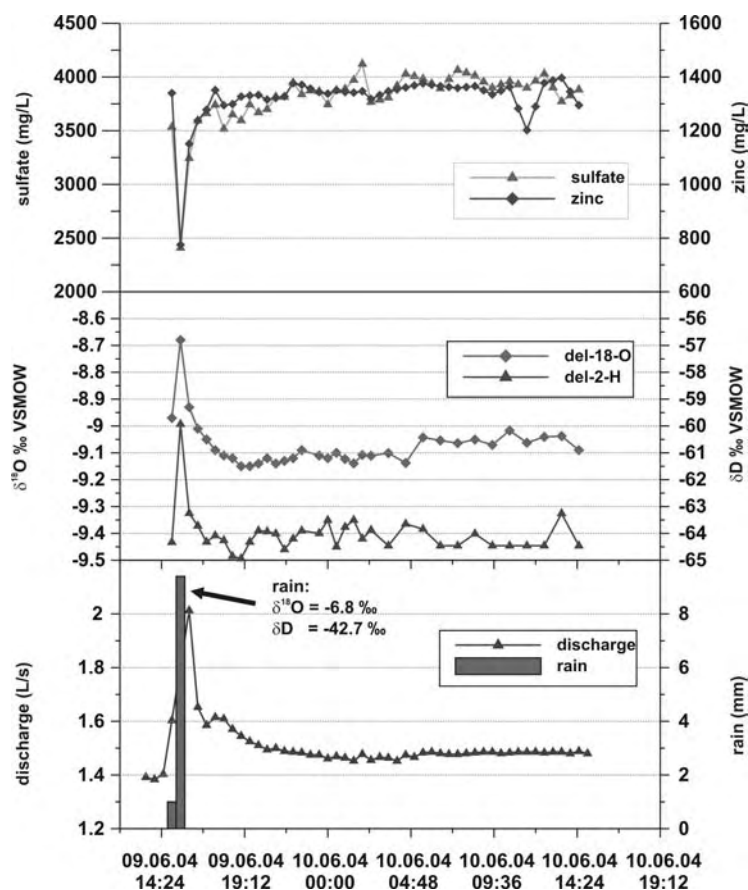

Figure 2: Temporal variation of the zinc and sulphate concentrations, of the stable isotopic composition, and the discharge at the new Stadtborn spring during an exemplary heavy rain event

Assuming a two component mixture and one tritium free component (input from the Rogenstein aquifer via the old Stadtborn spring), the tritium content of the second component (heap groundwater), which cannot be measured directly and has therefore to be calculated, depends on the relative proportions of the two components in the water of the new Stadtborn spring. The theoretical tritium content of the heap groundwater calculated for a relative share of Rogenstein aquifer water in the new Stadtborn spring water of 20, 40, 60, and 80% would be 13, 17, 25,

and 49 TU, respectively. However, the actual share of old spring water remains quite speculative because no reliable data exist for the discharge rate of the old Stadtborn spring. Due to the fact that in the 18th and 19th century the old spring was used as water supply for downstream developments ("Stadtborn" means "spring of the town"), we assume a discharge rate that results in a minimum contribution of at least 40% to the present discharge of the new Stadtborn spring. Considering the tritium output functions calculated from the input function at the tritium sampling station Leipzig and two different model assumptions (dispersion model, piston flow model), the heap groundwater component has an apparent age of more than 20 years (Figure 3).
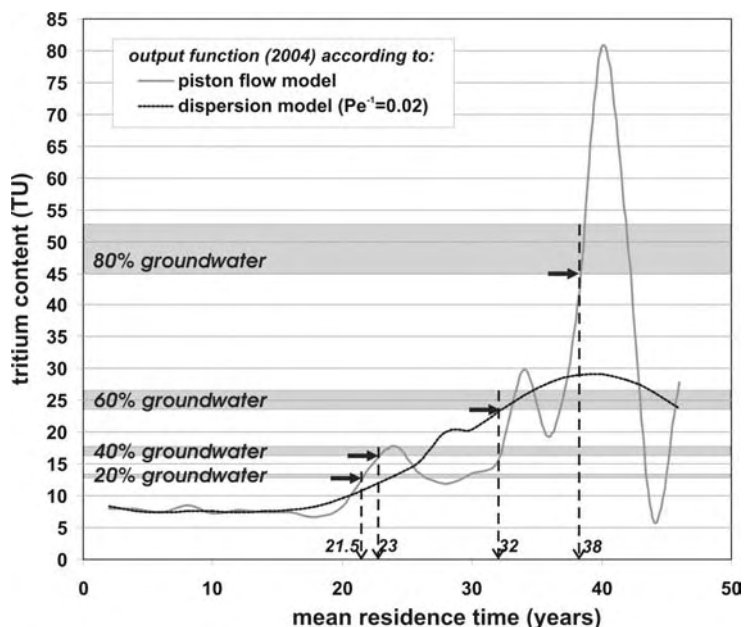

Figure 3: Apparent age of the heap water component calculated from a theoretical tritium content depending on the share of groundwater from the Rogenstein aquifer in the discharge of the new Stadtborn spring

CONCLUSIONS

The investigation revealed the occurrence of three different water components influencing the hydrodynamics in the slag heap, i.e. percolating rain water (quickflow), aquifer groundwater, and heap ground water. Stable isotope results showed that percolating rain water does not contribute significantly to the mobilization of the heavy metals. The spring water predominantly represents a mixture of two different groundwater components. Hydrochemical and isotopic evidence do not allow for a clear assignment of one of the two components to the contaminant mobilization. However, it seems very likely that the mobilization takes place during the transit of the heap groundwater from the recharge zone to the base of the heap. Nevertheless, heavy metal mobilization by entering aquifer groundwater cannot be excluded.

In the investigated case, the most discussed remediation strategy is the application of a non-permeable cover on top of the slag heap. According to our findings, this measure would inhibit the mobilization by newly recharged heap groundwater. However, no short term improvement of the water quality at the spring can be expected. Due to the long transit time of the heap groundwater from the recharge area to the new Stadtborn spring, the first effects of this measure would be visible two to three decades from now at the earliest so that the chemical treatment of the water would still be necessary.

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