Application of stable isotopes to assess reducing processes in lignite mining dumps

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ABSTRACT

After the end of lignite exploitation in Eastern Germany mining areas, the abandoned pits were flooded by groundwater or river water inflow. The associated dump sites consist of heterogeneous material of Quaternary and Tertiary age, which contain sulfide minerals. Oxidation of these minerals leads to acidification, influencing the development of water quality in the lakes and the groundwater. An aggressive process is bacterial sulfate reduction. By means of sulfur and oxygen isotope analyses it is possible to verify the occurrence of this process, which proceeds only locally due to the inhomogeneity of the sediment distribution.

INTRODUCTION

Until 1992 Tertiary lignite in Eastern Germany was predominantly extracted from open pit mines. Around 470 km^2 of the surface area were affected by material displacement and 1100 km^2 from the drawdown of the groundwater level (Häfner *et al.* 2004). Thereafter the hydrogeological recovery in these areas started with groundwater rise. Later on the mining pits were flooded by river water and drainage water from other open pit mines. The outcomes were long term changes in the water quality. Different mining lakes were formed, partly with pH values lower than 4.

Oxidation of pyrite and marcasite of Tertiary sediments in the aerated zones of the dumps produces sulfuric acid. Acid mine drainage means not only output of acidity and lowering the pH value, but also mobilisation of iron, aluminium and different trace metals, which might reach the groundwater and the lake. Pyrite oxidation is known as the strongest naturally occurring acidification reaction, i.e. 2 mol H$^+$ for each mol FeS$_2$ (Singer & Stumm 1970). Neutralisation, and also support of the pollutants, are only possible by bacterial sulfate reduction and the fixing of generated H$_2$S in sedimentary sulfide minerals (Schindler *et al.* 1980, Brown 1985, Rudd *et al.* 1986, Spratt *et al.* 1987, Spratt & Morgan 1990, Vile & Wieder 1993, Blodau *et al.* 1998, Knöller *et al.* 2003).

The reduction of sulfate is accompanied by considerable isotope fractionation of the sulfur, based on kinetic isotopic effects. These effects result from variations in the reaction rates of the different isotope species, particularly caused by selective microbial isotope effects. The heavier sulfur isotope (^{34}S) is enriched in the residual sulfate. Also ^{18}O is enriched in the residual sulfate, but fractionation is smaller than in the sulfur.

COSPUDEN AREA

The mining area Cospuden is situated on the southern border of Leipzig within the Central German Lignite District (figure 1). It covers an area of about 4 km^2. Mining of the Tertiary lignite occurred from 1980 to 1990.

Figure 1: Location of the study area in Central Germany (after Schreck 1998)

With the rise of the groundwater level, different lake parts were formed in the Cospuden mining pit. These small lakes varied especially in their pH values, ranging from pH 2.5 to 8.5 (Schreck 1998). Flooding with water from other mining pits and from a nearby river changed the hydrochemical milieu to neutral because of the higher

carbonate buffering capacity of these waters and also owing to the prevention of further pyrite oxidation within the lake. However, there are still no stable hydrogeological conditions in the mining dumps.

The mining dumps are divided in two genetically different sections, the spreader dump (SD), mainly consisting of Tertiary sediment material and the conveyor bridge dump (CBD) dominated by Quaternary matter (figure 2). Both are separated by a weathering zone resulting from long time exposure of the CBD sediments to the atmosphere before they were covered by SD material. The weathering zone contains large amounts of weathering products that can be mobilised easily and transported into the deeper sediments. While there are no major differences in the pyrite content (0.6 to 1.2 wt.%) between the two dumps, a clear distinction is possible from the isotope ratios of sedimentary sulfur species.
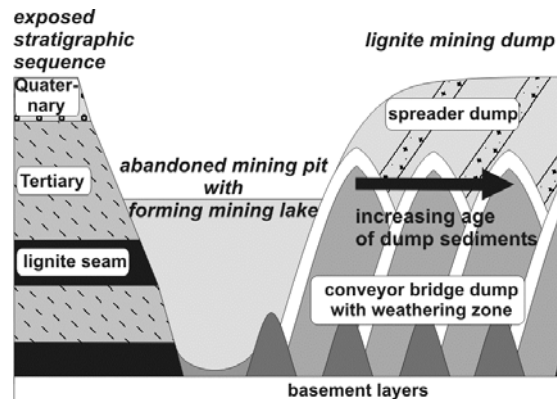

Figure 2: schematic cross section of Cospuden mining area (Knöller *et al.* 2003)

The pyrite δ^{34}S values of the conveyor bridge dump lie within a narrow range of -27 to -25 ‰ CDT (Knöller 2000) and are isotopically very light. In contrast, the isotope values in the spreader dump vary between -15 and +7 ‰ CDT, which is attributed to the heterogeneity of the overburden with a locally very high content of low-grade coal. Dohrmann (1999) shows local maxima up to 26 wt.% C_{org} and a positive correlation between the pyrite content and C_{org}, and emphasises the influence of this coal on the sediments in the spreader dump.

SULFATE REDUCTION

Sulfate reduction processes play a specific role in the degradation of sulfate and also in the dump waters. With isotope analyses it is possible to characterise these processes. The basis for the explanation of the isotopic fractioning during the sulfate reduction is the 4-step model of Harrison & Thode (1958), which is specified by Rees (1973):

    (1)   sulfate reception by microorganisms
    (2)   reaction of sulfate and Adenosintriphosphate (ATP) to Adenosin-5-Phosphosulfate APS
    (3)   reduction of APS to sulfite
    (4)   reduction of sulfite to hydrogen sulfide

Steps (1), (2), and (3) are reversible, but step (4) is irreversible due to the assumptions of Rees (1973).

To describe sulfate degradation processes in mining dumps and the linked gradual enrichment of ^{34}S in the residual sulfate Knöller (2000) used a modified Rayleigh equation:

$$\delta^{34}S_t = \left[\left(\delta^{34}S_0 + 1000\right)f_t^{(1-\alpha)}\right] - 1000 \qquad (1)$$

Where
δ^{34}S$_t$:   sulfur isotope value at time t;
δ^{34}S$_0$:   initial sulfur isotope value;
f_t: fraction of residual sulfate at time t;
α: α(SO$_4$-H$_2$S), fractionation factor between sulfate and hydrogen sulfide.

The residual sulfate is determined by

$$f_t = 1 - \frac{C_A}{C_0}t \qquad (2)$$

Where
C_0:   initial sulfate concentration;
C_A: annual sulfate degradation rate;
t: time of sulfate reduction in years.

The application of the Rayleigh equation supposes, after the beginning of sulfate reduction, that a constant degradation rate is in place. Such is only possible in a closed system. In the case of secondary sulfate delivery, isotopic mixing has to be considered in addition to the Rayleigh fractionation. A combination of isotopic effects can be described by

$$\delta^{34}S_t = \frac{m_{(t-1)} - m_A}{m_t}\left[\left(\delta^{34}S_{(t-1)} + 1000\right)\left[\frac{m_{(t-1)} - m_A}{m_{(t-1)}}\right]^{(1-\alpha)} - 1000\right] + \frac{m_i}{m_t}\delta^{34}S_i \qquad (3)$$

Where

t: index, describing the concerning parameter at time t (time of sulfate reduction in years);
(t-1):   index at time t-1 year;
$m_{(t,(t-1))}$: absolute sulfate amount in a defined volume unit in the time interval t to (t-1);
m_A: absolute sulfate amount removed by dissimilatory sulfate reduction from a defined volume unit;
m_i: absolute sulfate amount supplied by secondary delivery to a defined volume unit.

Due to the stability of the hydrogeochemical surroundings in the dump (high sulfate supply, equal DOC contents) relevant for sulfate reduction, it is assumed that the fractionation factor is equally transferable to the entire dump body and exhibits no temporal variability.

Sulfate reduction in the spreader dump

An increasing anaerobic environment already developed in the spreader dump. The age of the mining dump correlates in a characteristic way for sulfate reduction with the $\delta^{34}S$ and the sulfate concentration (figure 3); so sulfate reduction occurs in all mining dump regions but is locally and temporally differentiated depending on the age of the dump sites. Using the initial values for sulfate concentrations of 1,900 mg/L and for $\delta^{34}S$ (SO_4^{2-}) of -13.5 ‰ and the modified Rayleigh equation, Knöller (2000) calculated a sulfate degradation rate by bacterial reduction of 60 (mg/L)/yr.). Also, the $\delta^{18}O$ values follow the sulfate reduction trend. Some exceptions are possibly dependant on isotopic variability of the local sulfur source or on the different extent of the bacterial reduction under varying hydrochemical conditions.
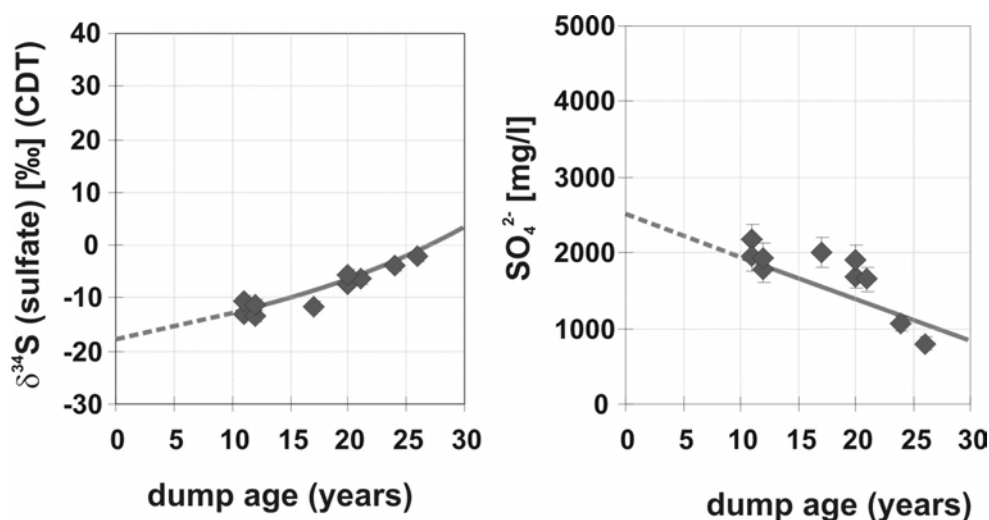

Figure 3: Correlation between dump age and $\delta^{34}S$-sulfate and sulfate concentration respectively.

Sulfate reduction in the conveyor bridge dump

In contrast to the spreader dump the conveyor bridge dump shows no correlation between the dump age and the concentration of dissolved sulfate. The extent of sulfate reduction is much lower and large areas are totally unaffected. Delivery of variable sulfate from the spreader dump and a varying influence of the weathering zone lead to different initial sulfate concentrations, $\delta^{34}S$ values and sulfate reduction rates. However, significant enrichments in ^{18}O and ^{34}S in some places show the local occurrence of bacterial sulfate reduction in this dump.

CONCLUSIONS

Bacterial sulfate reduction is the most important autoregenerative process in the development of dump waters. However, it is strongly controlled by the present environmental conditions. With the isotope ratios of sulfur and oxygen in dissolved sulfate it is possible to prove sulfate reduction in all dump areas of the lake Cospuden, but in different amounts.

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