

Assessing Natural Attenuation in AMD Contaminated Aquifers – “The Integrative Dual Isotope Approach”

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Summary

An artificial dump aquifer in an abandoned lignite mine contaminated with acid mine drainage was investigated for its overall natural attenuation potential. Due to its capability of producing alkalinity and of facilitating a sustainable fixation of sulfur in the sediment, bacterial sulfate reduction is the key natural attenuation process for such type of contamination.

The joint investigation of sulfur and oxygen isotope signatures (dual isotope approach) of different dissolved and sedimentary sulfur compounds was used to prove the occurrence of sulfate reduction and to estimate its hydrochemical relevance on an integrative field scale.

Especially the oxygen isotope composition of dissolved sulfate provided sound evidence for the occurrence of sulfate reduction throughout the examined aquifer section. However, differences between field based and experimental isotopic fractionation parameters indicated the influence of secondary sulfur transformations such as the re-oxidation of precipitated or dissolved sulfide.

Completely separated sulfur isotope signature frequency distributions for sedimentary sulfide and coexisting inorganic sulfate proved the field scale hydrochemical dominance of bacterial sulfate reduction and thus a strong overall natural attenuation potential of the aquifer section. Consequently, a significant improvement of the water quality and an eventually complete attenuation of the acid mine drainage contamination can be expected from a long term perspective.

Introduction

Bacterial reduction of dissolved sulfate (BSR) is a key process determining the natural attenuation in many contaminated aquifers. For example, in groundwater bodies affected by acid mine drainage (AMD) BSR reduces the contaminant load by producing alkalinity and facilitating a sustainable fixation of sulfur in the sediment.

Due to the isotope selectivity of sulfate reducing bacteria, BSR shows the most pronounced isotope fractionation within the sulfur cycle. While sulfur displays a straightforward kinetic enrichment in the residual sulfate described by the enrichment factor epsilon ($^{34}\epsilon$), the mechanism of oxygen isotope fractionation is still being discussed controversially. Nevertheless, it is agreed on that oxygen isotope exchange between ambient water and residual sulfate occurs during BSR in natural environments. With respect to this potential isotope exchange, the fractionation parameter theta ($^{18}\theta$) is introduced instead of the kinetic enrichment factor epsilon ($^{34}\epsilon$). The dual isotope system considering both sulfate-sulfur and sulfate-oxygen isotope fractionation and the respective fractionation parameters $^{34}\epsilon$ and $^{18}\theta$ provides an excellent tool for the recognition and quantification of BSR. Beyond that, the dual isotope approach may help identify and estimate interfering sulfur transformations such as re-oxidation and

disproportionation processes which is especially vital for the understanding of the overall natural attenuation potential of the investigated aquifers.

In contrast to the severe isotope fractionation occurring in the course bacterial sulfate reduction, only minor sulfur isotope fractionation is observed during the oxidation of sedimentary sulfides. Consequently, sulfate from sulfide oxidation will show a very similar isotope signature as the precursor sulfide. On the other hand, sedimentary sulfide precipitated from dissolved hydrogen sulfide formed by sulfate reducing bacteria is generally depleted in ^{34}S relative to the precursor sulfate.

The isotopic difference between coexisting sulfate and sedimentary sulfide may help assess the extent of bacterial sulfate reduction in a contaminated aquifer. This is especially valid for an integrative combination of the point scale information of a sufficiently high number of sampling points covering the investigated aquifer in a statistical distribution pattern.

If the $\delta^{34}\text{S}$ frequency distributions of sulfate and sedimentary sulfide significantly overlap BSR is of minor importance and the relictic primary sedimentary sulfide is subject to further oxidation. In case of a partly overlapping of the frequency distributions, a local or temporal dominance of BSR is indicated. The sedimentary sulfide pool represents a mixture of relictic primary sulfides and of secondary sulfide formed as a result of BSR. Completely separated frequency distributions of sulfide and coexisting sulfate suggest a major field scale impact of BSR on the natural attenuation in the contaminated aquifer.

Site of investigation and methods

The investigated artificial dump aquifer is situated in the Lusatian lignite district on the site of an abandoned lignite mine that was operated until 1956. The aquifer material mainly consists of fine grained sand with inclusions of sedimentary pyrite. Due to the lack of carbonate minerals the buffer capacity is very low. The aquifer is flanked by two pit lakes on the southern and northern part and by a stream in the eastern part. It has thickness of ca. 15 m; the average groundwater table is 2 m below surface. 18 small sampling wells were installed covering an area of ca. 180 by 100 m. The pH and sulfate concentrations in the groundwater range from 2.5 to 4.8 and from 600 to 1900 mg/L, respectively.

Groundwater samples were collected twice (October 2006 and February 2007) from each well and analyzed for hydrochemical field parameters and major ion concentrations. Furthermore, samples were taken for isotope analyses of water ($\delta^{18}\text{O}$, $\delta^2\text{H}$) and sulfate ($\delta^{34}\text{S}$, $\delta^{18}\text{O}$) as well as for sulfur isotope analyses of dissolved hydrogen sulfide. During the installation of the sampling wells a total number of 70 sediment samples were taken for sulfur isotope analyses of inorganic sedimentary sulfate, acid volatile sulfur (AVS), and chromium reducible sulfur (CRS).

Results and discussion

Prior to the interpretation of hydro(geo)chemical data it was necessary to reveal the details of the flow dynamics of the investigated aquifer section especially with respect to the groundwater flow direction and to a potential interaction with the flanking pit lakes. Due to evaporation, the two pit lakes show a significantly higher $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values compared to the local groundwater background. The meteoric background isotope signature related to local groundwater recharge was detected in most of the sampling wells throughout the investigated aquifer section. A mixture of meteoric and evaporation influenced water was found in a few sampling well in the eastern part of the aquifer section indication a local infiltration of lake water. The large scale model suggests a general groundwater flow direction of W-E. However, the local flow direction is subject to significant seasonal fluctuations so no distinct flow paths can be postulated. As a consequence, all sampling wells have to be considered as single batch reactors with very similar environmental conditions.

The integrative approach combines the point scale information from the single wells to derive general information on the overall hydrochemical status quo of the investigated aquifer section.

For a field based assessment of BSR, valid isotope fractionation parameters have to be known. In batch and columns experiments using local sediment and local groundwater $^{34}\epsilon$ values for sulfur isotope fractionation ($^{34}\epsilon = -21\text{‰}$) and $^{18}\vartheta$ values for oxygen isotope fractionation ($^{18}\vartheta = 1.7$) were determined. The obtained values fit very well in the experimentally determined range for different environmental conditions (Knöller et al. 2006, 2008).

As seen in Fig. 1, no clear correlation between sulfate concentrations and $\delta^{34}\text{S}$ values was found. The observed significant data scattering might in part be due to heterogeneous initial conditions during sulfide oxidation especially with respect to the sulfur isotopic variability of the oxidized sulfide. Trying to fit a logarithmic equation to the data set yields an enrichment factor for sulfur of -5‰ which seems unrealistic compared to the experimental value of -21‰ . The observed straightforward correlation between normalized oxygen isotope data (Brunner et al. 2005) and sulfate concentrations is a clear indication for a widespread occurrence of BSR. However, the low $^{18}\vartheta$ value of 0.2 suggests the local influence of secondary sulfur transformations especially re-oxidation of secondary sulfides.

Fig. 2 shows the $\delta^{34}\text{S}$ frequency distributions for sedimentary sulfide and coexisting inorganic sulfate from all sediment samples. The isotopic difference between the frequency maxima for sulfide and sulfate is ca. 23‰ corresponding with the experimental $^{34}\epsilon$ value. As stated above in the introduction section, the observed lacking overlap of the frequency distribution clearly indicates an overall domination of bacterial sulfate reduction.

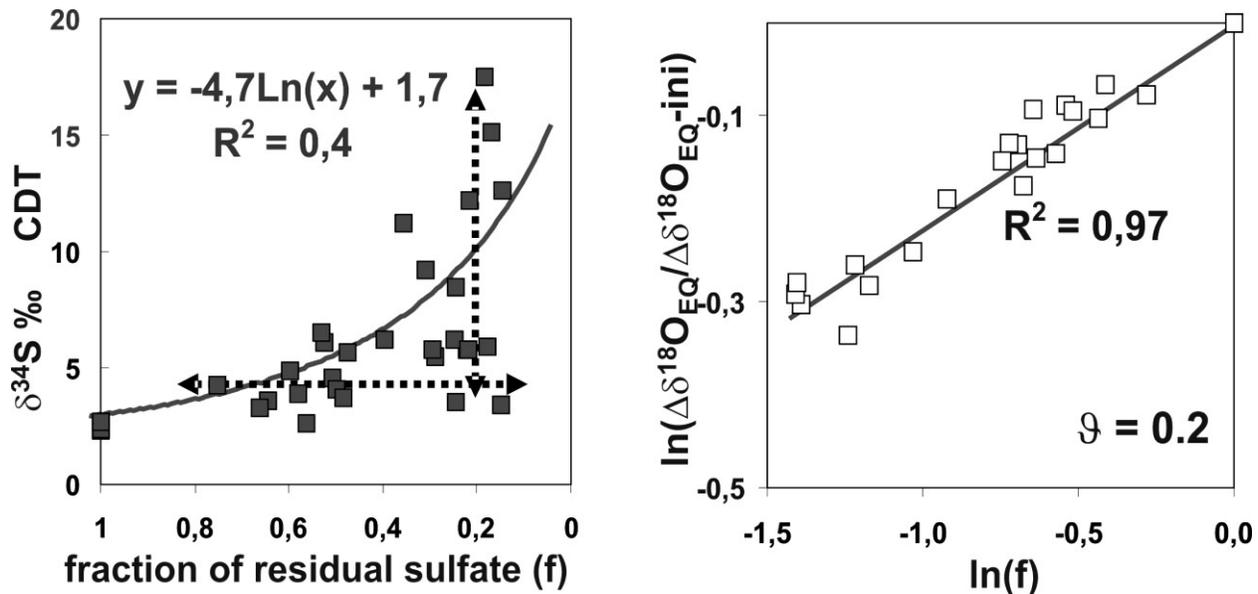


Fig. 1: Correlation between sulfate concentration and sulfate-sulfur values as well as normalized sulfate-oxygen isotope data (normalization after Brunner et al. 2005)

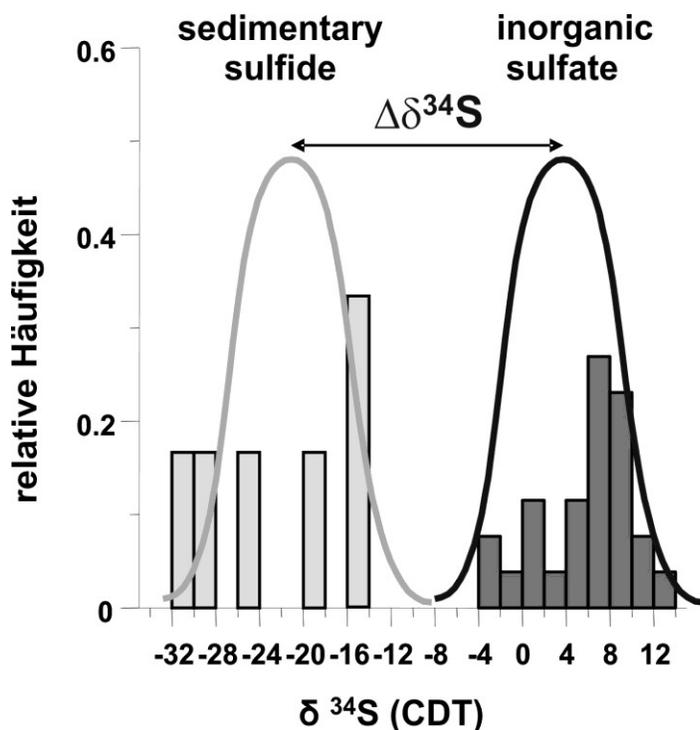


Fig. 2: $\delta^{34}\text{S}$ frequency distributions for sedimentary sulfide and coexisting inorganic sulfate from aquifer sediment samples

Conclusions

The isotopic investigation of dissolved groundwater sulfate and of different sedimentary sulfur species in an AMD contaminated artificial aquifer revealed the widespread occurrence and the hydrochemical dominance of bacterial sulfate reduction. Even though a local or temporal interference of BSR with secondary sulfur transformations such as re-oxidation of precipitated or dissolved sulfides cannot be excluded, the domination of the reduction processes suggests a strong overall natural attenuation potential of the investigated aquifer section. Despite the unfavorable environmental conditions such as low pH, stable or growing microbial communities seem to be capable of maintaining BSR on a dominating level so that a significant improvement of the water quality and an eventually complete attenuation of the AMD contamination can be expected from a long term perspective.

References

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