



Reaction time scales for sulphate reduction in sediments of acidic pit lakes and its relation to in-lake acidity neutralisation



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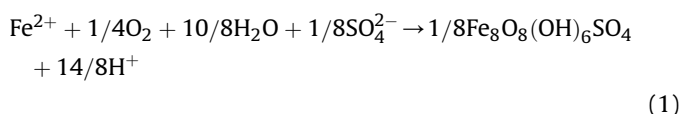
ABSTRACT

Sulphate reduction is a key reaction to remove acidity from water bodies affected by acid mine drainage. In this study, $^{35}\text{S}\text{-SO}_4^{2-}$ reduction rates determined in sediments from a variety of acidic lignite pit lakes have been compiled. The rates decreased with pH and are strongly dependent on carbon substrate. The rates were fitted to a Monod model adapted to the specific conditions of acidic pit lakes (APL) sediments: i) sulphate reduction rate is independent from sulphate concentration due to the high concentration typically observed in APL systems (10–30 mM), ii) the observed pH dependency of sulphate reduction was accounted for by an inhibition function F_{inhibit} which considers the occurrence of low cell numbers of sulphate reducing bacteria at pH values < 4.75. Simulated steady-state sulphate reduction rates are predicting measured rates at carbon substrate concentrations of < 10 μM . Estimated steady-state reaction time scales range between 2.4 h at pH 7 and 41 h at pH 3 at a carbon half-saturation constant of $K_{\text{C-S}} = 100 \mu\text{M}$ and are increasing with increasing $K_{\text{C-S}}$ values. Time scales at low pH are too long to allow for significant generation of alkalinity during the time of residence of groundwater passing through the top and hence most reactive zone of APL sediments which has important implications for the remediation of acidic pit lakes.

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1. Introduction

The occurrence of pit lakes is a global phenomenon at sites where mineral deposits relatively close to the Earth surface are mined (Geller et al., 2013). Pit lakes are frequently subject to strong acidification following inflow of reduced, Fe(II) bearing, weakly buffered groundwater, oxidation of Fe(II) upon contact with air and subsequent hydrolysis to generate a ferric hydroxo sulphate, such as schwertmannite (Regenspurg et al., 2004; Schultze, 2013):



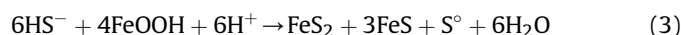
pH values typically observed in acidic pit lakes range between 2 and 4 buffered by schwertmannite (Geller et al., 2013; Regenspurg et al., 2004). Remediation of acidic pit lakes or prevention of acidification is a key task in the environmental management of pit lakes (an excellent review on these topics can be found in Geller and

Schultze, 2013).

Dissimilatory sulphate reduction has long been recognized as the key reaction for internal neutralisation of aqueous systems affected by acid mine drainage (Herlihy and Mills, 1985; Peine and Peiffer, 1996; 1998) because of its supply of alkalinity upon dissimilatory respiration.



Mass balances together with ground water flow modelling have revealed that sulphate reduction in lake sediments has led to an increase in pH to 7 and loss of acidity in a groundwater affected formerly acidic mining lake (Schäfer et al., 2016). Similarly, clear trends in recent recovery from acidity can be observed in pit lakes (Weilner, 2013), where already 20 years ago accumulation of reduced solid-phase sulphur (FeS_2 , FeS , S^0) in the lake sediment was determined (Peine and Peiffer, 1998).



Hence, knowledge about rates of sulphate reduction in sediments of acidic pit lakes is critical to assess internal neutralisation because they can be related to the inflow and internal production of

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acidity (e. g. Blodau, 2006).

The potential for internal neutralisation is limited, though. Reoxidation of sulphide in ferric-iron rich environments as well as interferences with the iron cycle itself under acidic conditions will counteract internal neutralisation (Blodau et al., 1998; Peine et al., 2000; Koschorreck and Tittel, 2007; Wendt-Potthoff, 2013).

The neutralisation process is constrained by organic matter quality and thermodynamic effects, which together control the relative rates of sulphate and iron reduction (Blodau and Peiffer, 2003). Moreover, low pH values appear to even inhibit sulphate reduction rates directly because of protonation of volatile fatty acids, which are a substrate for many sulphate reducing bacterial (Koschorreck, 2008). Protonated fatty acids are inhibitory to microorganisms, because they may pass the cell membrane and act as an decoupler.

The classical approach to measure sulphate reduction rates is the determination of radiolabelled ^{35}S (-II) after a short incubation with $^{35}\text{SO}_4^{2-}$ (e. g. Jørgensen and Cohen, 1977). This technique has been applied in the study of sulphate reduction in pit lakes and has revealed a large variation depending on pH (e. g. Koschorreck and Wendt-Potthoff, 2012) but also organic carbon (e. g. Meier et al., 2004).

In this publication, characteristic reaction time scales for sulphate reduction will be derived from measured sulphate reduction rates in acidic pit lakes (APL) as determined by the $^{35}\text{SO}_4$ incubation technique. The reaction time scale denotes the time that is needed for a certain turnover of substrate (here SO_4^{2-}). It is an important parameter to characterise aquatic systems in regard to their capability to process materials within a certain time of exposure to suitable processing conditions, the exposure time typically being controlled by the hydraulic residence time (Oldham et al., 2013).

2. Compilation of measured sulphate reduction rates from lignite pit lakes

Sulphate reduction has been studied extensively in sediments from lignite pit lakes in Eastern Germany, particularly in the Lusatian mining district (Wendt-Potthoff, 2013). Hence, a large data set is available from aqueous systems of common geochemical background: Lignite pit lakes have formed from refilling of pit holes with groundwater and developed towards a geochemically well-defined environment with sulphate concentrations in the range of ~10 mM and pH values around 3.0, characteristic for the stability window of schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_x\text{SO}_y \cdot n \text{H}_2\text{O}$ where $8-x = y$ and $1.0 < y < 1.75$ (Regenspurg et al., 2004)). Waters are saturated with respect to schwertmannite and a redox equilibrium exists between Fe^{2+} and schwertmannite. Organic geochemistry of the sediments is controlled by lignite-derived OM, which constitutes the major C-fraction, even in the upper sediment layers (Laskov et al., 2002).

Hence, compilation of measured sulphate reduction rates in such geochemically homogenous aquatic systems allows insight into limitations of sulphate reduction and to derive predictive features.

Fig. 1 illustrates rates determined in undisturbed cores using the ^{35}S - SO_4^{2-} incubation technique from five independent studies performed at various APLs from the Lusatian lignite mining district (Blodau et al., 1998; Peine et al., 2000; Meier et al., 2000, 2004; Koschorreck et al., 2007) at a temperature of about 5–10 °C. Rates are highly scattered but increase with pH.

3. Results

3.1. Derivation of Monod parameters for rates in pit lake environments

Sulphate reduction rates R_{SR} can be principally derived from Monod parameters for this process according to

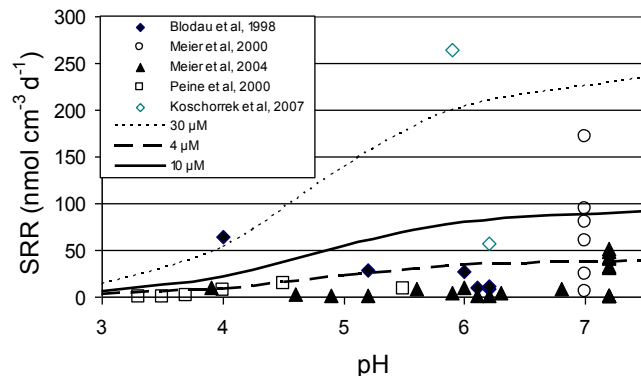


Fig. 1. Measured ^{35}S - SO_4^{2-} reduction rates in sediments from pit lakes from the Lusatian lignite mining area. The continuous lines denote predicted sulphate reduction rates using the inhibition model in Eq. (11) for three different concentrations of carbon substrate.

$$R_{\text{SR}} = \mu_{\text{max}} \frac{c(\text{SO}_4^{2-})}{K_{\text{SO}_4} + c(\text{SO}_4^{2-})} \frac{c(\text{C} - \text{source})}{K_{\text{C-S}} + c(\text{C} - \text{source})} \frac{c(\text{cells})}{Y_{\text{SO}_4^{2-}}} \quad (4)$$

with.

μ_{max} : maximum growth rate [h^{-1}].

$c(\text{cells})$: concentration of cells [g cells L^{-1}].

Y_{SO_4} : specific yield [g cell mol^{-1}].

K_{SO_4} , $K_{\text{C-S}}$: Half saturation constants for sulphate and organic carbon substrate, respectively [M].

$c(\text{SO}_4^{2-})$, $c(\text{C-S})$: concentrations of sulphate and organic carbon substrate, respectively [M].

There is a large diversity of environments where sulphate reduction takes place, such as marine sediments, wetlands, coastal and freshwater sediments and rates vary between $1 \text{ nmol cm}^{-3} \text{ d}^{-1}$ in an acidic lake and almost $10,000 \text{ nmol cm}^{-3} \text{ d}^{-1}$ in sea grass sediments (cf. reviews in Skyring, 1987 and Holmer and Storkholm, 2001). Acidic pit lakes (APL) are particular, since they have high concentrations of sulphate (10–30 mM), are strongly limited in carbon (Blodau et al., 1998; Meier et al., 2004) and heavily enriched in iron (e. g. Regenspurg et al., 2004) with strong competition between iron and sulphate reduction as terminal electron accepting processes (e. g. Küsel et al., 2001). Hence, any attempts to model sulphate reduction in such environments need to account for such effects. In the following we will therefore perform a stepwise analysis of the critical parameters.

There is not a straight forward approach to adapt Monod parameters from the literature, in particular since only very few studies have tried to determine such parameters under field conditions (e. g. Urban et al., 1994; Roychoudhury et al., 1998, 2003; Pallud and van Cappellen, 2006). The latter have estimated the substrate utilisation rate v_{max}

$$v_{\text{max}} = \mu_{\text{max}} \frac{c(\text{cells})}{Y_{\text{SO}_4}} \quad (5)$$

instead of μ_{max} since cell concentrations are typically unknown. In contrast, most of the published Monod parameters μ_{max} , K_{SO_4} , $K_{\text{C-S}}$ and Y_{SO_4} are from biotechnological or (partly chemostat based) fundamental microbial studies in which media were optimised. In the following a critical discussion on adaption of such numbers to our problem will be conducted.

The first simplification of Eq. (4) for the special conditions of APL sediments can be made by elimination of the sulphate Monod term.

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