Sulfur Cycling in an Oil Sands Tailings Pond

Sebastian Stasik, Katrin Wendt-Potthoff

Helmholtz Centre for Environmental Research - UFZ, Department of Lake Research, Brückstraße 3a, 39114 Magdeburg, Germany, sebastian.stasik@uniklinikum-dresden.de, katrin.wendt-potthoff@ufz.de

Abstract

Oil sands tailings ponds are used as the primary storage and settling basins for toxic tailings produced during oil sands processing in northern Alberta (Canada). As a result of microbial metabolism, methane production contributes to greenhouse gas emissions and was shown to affect tailings densification. In particular, sulfur cycling is supposed to play a key role both for the turnover of organic matter and the regulation of methane emissions. Adversely, the activity of sulfate-reducing bacteria (SRB) is likely to generate huge quantities of toxic H_2S, which pose a strong concern for both gas- and water-phase environments in the vicinity of the ponds.

In order to identify reactive zones of sulfur cycling and to assess the impact of microbial sulfate reduction on organic matter transformation and CH_4 emissions, biogeochemical analyses of original tailings from two vicinal pond profiles were combined with a number of laboratory experiments performed under well-defined conditions.

In conclusion, results give evidence that H_2S outgassing from the pond is effectively prevented by the biochemical re-oxidation and primary incorporation of H_2S into iron sulfide minerals. As demonstrated by the long-term incubation of original tailings in anoxic microcosms, considerable volumes of CH_4 emissions may be prevented by the activity of SRB in sulfidic tailings between 3.5–7.5 m in situ. In addition, results show that microbial sulfate reduction is essential for the anaerobic mineralisation of labile organic matter with significance for tailings ponds carbon cycle and gas production.

Key words: Oil sands tailings ponds, sulfur cycling, CH_4 emissions, carbon transformation

Introduction

The Athabasca basin in northern Alberta (Canada) harbors one of the world's largest oil sands deposits, holding an estimated amount of 170 billion barrels of recoverable oil (Alberta Environment and Research Development 2013). Despite short-term economic benefits, oil sands industry is controversially discussed due to considerable environmental impacts, like the large-scale disturbance of landscape, the high operational water demand and the generation of toxic tailings during oil extraction (BGC Engineering 2010). For storage and passive bioremediation tailings composed of sand, clay, metals, unrecovered bitumen and toxic process chemicals are pumped into huge anaerobic settling basis on site. As of 2014, these oil sands tailings ponds already cover an area of 182 km^2 (Alberta Environment and Research Development 2013), representing a large and unique mine water problem. In the ponds, tailings settle to the bottom reaching a density of about 30% solids referred to as mature fine tailings. During densification pore water is released to the surface of the ponds, forming a shallow water layer on top (~ 3 m) which is used to recycle water to the extraction plants (McKinnon 1989). Depending on the initial toxicity and rate of bioremediation, tailings ponds can be integrated into the surrounding environment as prospective aquatic habitats (Westcott 2007).

In oil sands tailings ponds, sulfur cycling is promoted by the presence of sulfate which is added to the ponds in form of gypsum ($CaSO_4 \cdot 2H_2O$) in order to enhance the densification of fine tailings (Ramos-Padrón et al. 2011). Consequently, microbial sulfate reduction is supposed to represent the quantitatively most important electron-accepting processes for the anaerobic transformation of organic matter and may therefore be substantial for tailings detoxification and reclamation (Figure 1) (Holowenko et al. 2000). However, the contribution of sulfate reduction to organic matter decomposition in tailings ponds has not been quantified yet.

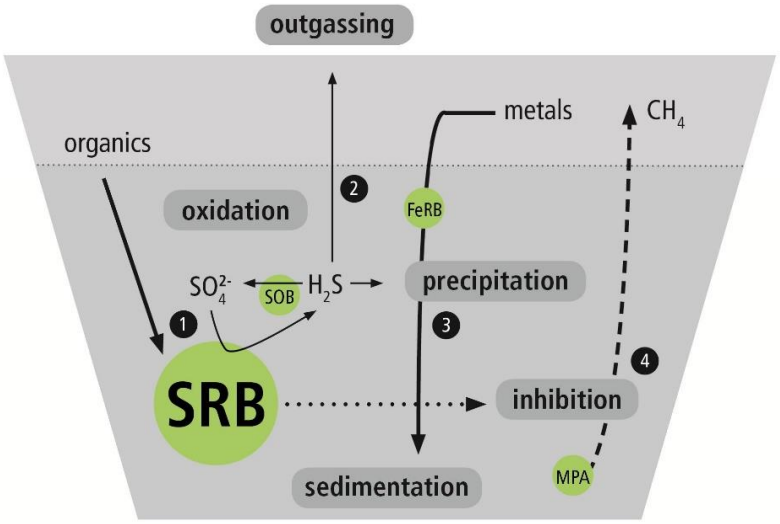

Figure 1 *Sulfur cycling in oil sands tailings ponds (adapted from M. Koschorreck). 1) Transformation of organic matter; 2) H_2S outgassing/re-oxidation; 3) Precipitation; 4) Effect on CH_4 emissions. SRB – sulfate-reducing bacteria; SOB – sulfur-oxidizing bacteria; FeRB – iron-reducing bacteria; MPA – methane producing archaea*

As a result of microbial metabolism, a distinct sulfidic zone evolved in many ponds, potentially generating huge amounts of hydrogen sulfide (H_2S) or HS^- (Ramos-Padrón et al. 2011). Beside operational challenges regarding eventual adverse impacts of H_2S ebullition on tailings sedimentation (BGC Engineering 2010), H_2S exhibits a high chemical demand for oxygen (COD) and is toxic to many organisms (Reis et al. 2004). In addition, biogenic sulfur gases (e.g. H_2S or dimethyl sulfide) can degas to the atmosphere, eventually contributing to air pollution and acid rainfall in the surrounding environment after re-oxidation to SO_2 and SO_4^{2-} (Howarth et al. 1992). Beside re-oxidation upon contact with oxygen or by sulfur-oxidizing bacteria, H_2S is likely to react with dissolved metal(loid)s (Rickard and Morse 2005) in anaerobic pond layers to form insoluble precipitates like iron sulfides (FeS) (Salloum et al. 2002). With respect to water quality, the formation of sulfide minerals may contribute to the immobilization of both toxic H_2S and heavy metals during disposal of reactive mine tailings. Until now, quantitative measurements examining potential H_2S outgassing and the composition and distribution of total reduced inorganic sulfur in tailings ponds are still lacking. In addition to H_2S, methane contributes to 60–80% of gas flux over oil sands tailings ponds. Beside its contribution to greenhouse gas emissions, methanogenesis was shown to increase tailings densification (Siddique et al. 2014), which is relevant for operational water re-use. In laboratory incubations, methane production significantly decreased in tailings supplemented with sulfate, suggesting an inhibition of methanogenesis by sulfate reduction due to the competition for methanogenic substrates (Holowenko et al. 2000; Ramos-Padrón et al. 2011). However, not much is known about the impact of microbial sulfate reduction on methanogenesis in tailings of different depths, which is essential to predict overall CH_4 emissions from the ponds.

From the previous findings and theoretical considerations outlined above, sulfur cycling in oil sands tailings ponds represents a central elemental cycle with relevance for pond management and eco-toxicological assessment. Therefore the aims of the present study were to assess information on possible factors of sulfur biogeochemistry controlling (i) H_2S outgassing and metal sulfide formation, (ii) methane emissions and (iii) the transformation of labile organic matter. To achieve this, microbial numbers and activities were integrated with wet geochemical analysis and stable isotope geochemistry in material from two vicinal sites of an active oil sands tailings pond. In order to determine the impact of microbial sulfate reduction on carbon transformation and CH_4 emissions, original tailings were subsequently incubated with/without a set of relevant organic acids (lactate, acetate, formate, propionate and butyrate) in anoxic microcosms with/without molybdate as selective inhibitor for microbial sulfate reduction. Over a period of 180 days, we monitored methane production and organic acid transformation.

Methods

2.1. Sampling, geochemical and isotope analysis

Samples were collected on September 2011 from two vicinal (~ 100 m) sites of an active tailings pond. Samples were obtained from the water cap (1, 2, 3 m) and from the tailings zone (4.5, 5.5, 7.5, 13.5 m) using a piston sampler (Penner and Foght 2010). Samples for geochemical analysis, most probable numbers (MPN) and microbial activity were transferred into sterile 500 mL plastic Nalgene® bottles. Subsamples for analysis of sulfur isotopes were transferred into 125 mL Nalgene® flasks containing Zn-acetate. Bottles were shipped within two weeks, cooled and darkened without any headspace. Wet geochemical analysis were performed using standard procedures as described in Koschorreck et al. (2007). Total reduced inorganic sulfur (TRIS) was analyzed according to a sequential extraction after Canfield (1989) and Fossing and Jørgensen (1989).The extracted fractions of acid volatile sulfide (AVS), chromium reducible sulfide (CRS) and elemental sulfur (S^0 extracted as dimethylformamide-extractable sulfur (DMFS)) were measured polarographically. Stable isotopes of sulfur were analyzed according to Knöller and Schubert (2010).

2.2. Most probable numbers (MPN)

MPN to enumerate viable cells of SRB and SOB were performed as serial dilutions in deep-well plates (Wendt-Potthoff and Koschorreck 2002). Selective media were used with modified concentrations of [g L^{-1}] NaCl (1.0), $MgCl{\cdot}6H_2O$ (3.0), NH_4Cl (0.3), KH_2PO_4 (0.2), KCl (0.3), $CaCl_2{\cdot}2H_2O$ (0.15) (Widdel and Bak 1992). All media were adjusted to pH 7.5 and incubated in the dark at 20°C for 6 weeks. MPN and their confidence intervals were calculated using the program of Klee (1993).

2.3. Activity rates

All assays were conducted in duplicate in the dark at 20 °C. For the measurement of microbial gas production, 1 mL of sample was filled into a 10 mL sterile glass vial, sealed with a butyl rubber stopper and immediately gassed with nitrogen. Methane and carbon dioxide production in the headspace was monitored for 30 days, using a gas chromatograph (SRI 8610C, Schambeck) equipped with a flame ionization detector (FID) and a methanizer (SRI instruments, Torrance, U.S.A.). Rates were calculated from the linear regression of CH_4 and CO_2 partial pressure in the headspace. Thiosulfate oxidation potentials were measured in batch slurries containing a 1:1 (v/v) ratio of sample to added liquids. Liquids consisted of a mineral media containing [mg L^{-1}] NaCl (1.0), $MgCl{\cdot}6H_2O$ (3.0), NH_4Cl (0.3), KH_2PO_4 (0.2), KCl (0.3), $CaCl_2{\cdot}2H_2O$ (0.15), a trace element solution SL12 (Widdel and Bak 1992) and $Na_2S_2O_3{\cdot}5H_2O$ with a final concentration of 7.5 mmol L^{-1}. Assays (70 mL) were incubated under aerobic conditions in 125 mL Erlenmeyer flasks on a shaker (100 rpm) with autoclaved controls. Thiosulfate concentrations were measured by ion chromatography (Dionex ICS-3000). Rates were calculated as linear regression of thiosulfate decrease over time. Microbial sulfate reduction was determined by adding 20 µL of a 1.33 mmol L^{-1} $^{35}SO_4^{2-}$ solution to 5 mL of sample. Assays were incubated in 150 mL serum bottles under N_2 for 22 h. Subsequently, 5 mL of a Zn-acetate solution was added to stop the reaction. Extraction of radioactive sulfide was done by passive diffusion (Meier et al. 2000). Radioactivity was measured in a scintillation counter (TRI-CARB 2300TR, Perkin Elmer). Statistical tests were carried out using SigmaPlot version 12.0.

2.4. Microcosm studies

Microcosms were set up as batch slurries in 125 mL serum bottles with an equal ratio of original samples to added liquids (35 mL each). The liquids consisted of an anoxic mineral media containing [g L^{-1}] NaCl (1.0), $MgCl{\bullet}6H_2O$ (3.0), NH_4Cl (0.3), KH_2PO_4 (0.2), KCl (0.3), $CaCl_2{\bullet}2H_2O$ (0.15) and Na_2SO_4 (4.0). After autoclaving and gassing with nitrogen, 1 mL L^{-1} each of a sterile selenite solution, a vitamin solution (DSMZ 148 medium, www.dsmz.de) and a trace element solution (SL10), 30 mL L^{-1} of a 1 M $NaHCO_3$ solution and 1 mL L^{-1} of 1M Na_2S solution were added aseptically (Widdel and Bak 1992). A mixture of carbon sources containing 2.5 mM each of Na-lactate, Na-acetate, formate, propionate and butyrate was added from sterile concentrates to half of the microcosms. The final pH of the media was adjusted to 7.5. Na-molybdate at a final concentration of 10 mM was added to part of the microcosms as specific inhibitor of microbial sulfate reduction. Serum bottles were sealed with butyl rubber stoppers and flushed aseptically with N_2 gas. Autoclaved controls served to account for

chemical reactions. All incubations were done in duplicate and incubated at 15°C in the dark. Concentrations of methane, CO_2, sulfate and organic acids were measured every 2–6 weeks. Gas production was monitored by gas chromatography (Section 2.3) after removing 0.2 mL of headspace gas aseptically with a syringe. Concentrations of carbon sources were measured using HPLC (Thermo Separation Products). Sulfate concentrations were measured by ion chromatography (Dionex ICS-3000). Microcosms were replenished with sulfate to 2000 mg L^{-1}, when concentrations dropped below 500 mg L^{-1}.

Results

3.1. Major biogeochemical characteristics and sulfur isotopes of original samples

Both sites contained tailings under a water cap of about 3.6 m. Solids content increased from nearly zero (water layer) up to 40% solids (w/w) at 13.5 m. No oxygen was detected below the water-tailings interface at both sites. Sulfate concentrations dropped sharply from 4 mM in the water to less than 0.5 mM below the water-tailings interface (Figure 2). No sulfide was detected in the water cap. Fractions of AVS, CRS and DMFS increased below the water-tailings interface with highest concentrations (~ 9 mM) between 4.5–7.5 m. Generally, sulfides were dominated by AVS (~ 4 mM), the primary product of microbial sulfate reduction. At 4.5 m, DMFS represented the dominant sulfur species, indicating partial oxidation of sulfides. Beside the concentration, the isotopic composition of sulfur varied with depth (Table 1). In particular, $\delta^{34}S$ of sulfide at 4.5 m was 1‰, which is 6‰ lower than the sulfur isotope signature of sulfate in the water cap, most likely reflecting fractionation during microbial sulfate reduction.

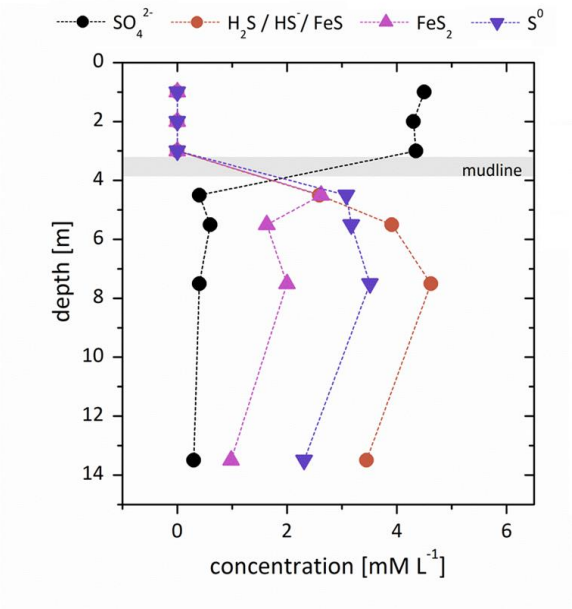

Table 1 *Sulfur isotopic composition*

depth	$\delta^{34}S$–S ‰	sulfur species
1 m	7.37	SO_4^{2-}
2 m	7.31	SO_4^{2-}
3 m	7.43	SO_4^{2-}
4.5 m	**0.91**	**H_2S, HS^-, FeS**
5.5 m	4.41	H_2S, HS^-, FeS
7.5 m	3.72	H_2S, HS^-, FeS
13.5 m	3.91	H_2S, HS^-, FeS

Figure 2 *Concentrations of sulfide and sulfate along the pond profile. The different fractions represent: (●) sulfate, (●) AVS (acid volatile sulfur), (▲) CRS (chromium reducible sulfur) and (▼) DMFS (dimethylformamide extractable sulfur).* (*Data are from Stasik et al. 2014)*

3.2. Cell counts and microbial activity

Highest numbers of SRB (10^4–10^6 cells mL^{-1}) were detected at 5.5–7.5 m (Figure 3a). Accordingly, sulfate reduction rates (SRR) increased below the water-tailings interface, with a maxima at 7.5 m (~ 100 nmol mL^{-1} d^{-1}), before decreasing to 10 nmol mL^{-1} d^{-1} at 13.5 m. Throughout the pond high numbers of viable cells were also detected for aerobic SOB, ranging between 10^4–10^8 cells mL^{-1} (Figure 3b). Thiosulfate oxidation potentials increased below the mudline, with a maximum around

600 nmol mL^{-1} d^{-1} at a depth of 5.5 m. No methanogenesis or CO_2 production was observed in the water cap. Below the mudline CH_4 production fluctuated between 54–76 nmol mL^{-1} d^{-1} (not shown).

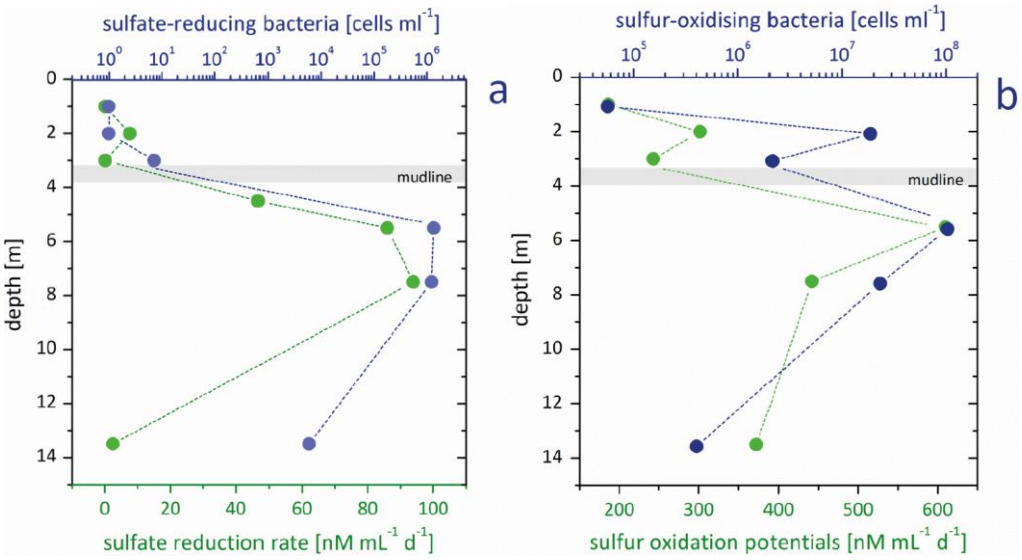

Figure 3 *Microbial cell numbers and activity as a function of depth. a) Sulfate reduction rates and cell numbers of SRB, b) Thiosulfate oxidation potential and cell numbers of SOB* (*Data are from Stasik et al. 2014)*

3.3. Impact of sulfate reduction on CH_4 production

During the long-term incubation of pond material in anoxic microcosms, methane was produced with rates ranging between 2–13 µmol L^{-1} d^{-1} in tailings at 5.5–13.5 m (not shown). No methane was generated in samples of the water cap (1–3 m). The inhibition of bacterial sulfate reduction by molybdate increased methane production in tailings (5.5–13.5 m) by a factor of 2–6.

3.4. Impact of sulfate reduction on the transformation of labile organic matter

In microcosms without molybdate concentrations of lactate, formate, propionate, acetate and butyrate decreased in water (~210 µmol L^{-1} d^{-1}**)** and tailings (~370 µmol L^{-1} d^{-1}). The transformation of organic acids and the production of CO_2 (not shown) generally decreased in microcosms with molybdate (Table 2), indicating the significance of microbial sulfate reduction for the mineralisation of labile organic matter in the pond material. When sulfate reduction was inhibited, transformation rates of acetate and butyrate decreased to <5% in the water cap and to 4–16% in tailings. SRB also dominated propionate turnover in tailings, but were not essential for formate and lactate metabolism.

Table 2 *Effect of molybdate addition on the transformation of organic acids, expressed as % of transformation rates measured in microcosms without molybdate*

	depth	lactate	formate	acetate	propionate	butyrate
water	1 m	73	71	2*	96	1*
	2 m	74	85	3*	94	2*
	3 m	78	80	5*	93	3*
tailings	5.5 m	101	100	4*	9*	4*
	7.5 m	102	105	4*	5*	7*
	13.5 m	101	109	16*	2*	15*

* significant ($p < 0.05$) difference to rates measured in microcosms without molybdate. (n=4) Differences were analyzed by two-tailed Student‘s t-test and a p-value of <0.05 was considered significant.

Discussion

4.1. Sulfur cycling, H_2S outgassing and metal sulfide formation

Both microbial activities and viable counts of sulfur-related bacteria demonstrated the presence of a distinct sulfidic zone within the first 4 m below the water-tailings interface (Figure 3) that was also evident by a sharp drop of sulfate and a pronounced increase of sulfides (Figure 2). In addition, sulfur isotope signatures of sulfide showed that the sulfidic zone might have persisted for a long time at the respective depths (Table 1). Interestingly, the sum of sulfate (4 mM) and dissolved sulfide (H_2S/HS^-) (<0.1 mM) measured in the water cap was below an expected sum of 7.3 mM that would result from an average dose of 1 kg m^{-3} gypsum ($CaSO_4$) typically added to tailings in order to enhance their consolidation. Similar observations in another pond (Ramos-Padrón et al. 2011) suggest that this difference might be due to the precipitation of H_2S/HS^- into sulfide minerals that prevents H_2S outgassing. Indeed, while dissolved sulfides were absent in the water cap, considerable amounts of AVS (>4 mM) were found below the water-tailings interface in our profiles. Beside H_2S/HS^-, AVS comprises iron monosulfides (FeS) that are generally quickly formed in presence of reactive (HCl-soluble and hydroxylamine reducible) iron (Rickard and Morse 2005). Tailings ponds contain huge quantities (50 mM) of total reactive iron (Fe(II)+Fe(III); Stasik et al. 2014) that enables the precipitation of iron monosulfides. Throughout the pond, FeS_2 (CRS) was a minor fraction of reduced sulfur compounds indicating limitation of pyrite formation (Gagnon et al. 1995) presumptively due to the abundance of reactive iron that reduced the availability of free sulfides. Nevertheless, an average AVS:FeS_2 ratio of ~2 is in the typical range of natural coastal sediments (0.02–7.2) (Gagnon et al. 1995). In addition to FeS and pyrite, the presence of DMFS at the water-tailings interface suggested a partial re-oxidation of sulfides to elemental sulfur (S^0). The re-oxidation of sulfides in the pond can be estimated by comparing rates of sulfate reduction with the accumulation of TRIS. The investigated pond has been in operation since 1995, suggesting that oldest tailings deposited at the bottom (~ 40 m) correspond to an age of about 20 years. However, tailings investigated in our study were obtained between depths of 5.5–13.5 m, representing a zone where initial sedimentation of tailings occurs during the first 2–3 years after deposition (McKinnon 1989). Assuming a tailings age of 2.5 years, integrated TRIS accumulation between 5.5– 13.5 m would correspond to a rate of 3.6 mmol sulfide L^{-1} y^{-1}. Thus, based on a SRR of 18.25 mmol SO_4^{2-} L^{-1} y^{-1} (calculated from an average SRR of ~ 50 µmol L^{-1} d^{-1} between 5.5–13.5 m) approximately 81 % of sulfide is re-oxidized in the pond. This is in the range of sulfide re-oxidation typically estimated for natural aquatic sediments (72–94 %) (Boesen and Postma 1988). However, as no oxygen was detected in situ and reactive iron was mainly Fe(II), it is likely that sulfides were re-oxidised by crystalline iron oxides and (oxy) hydroxides that are typically abundant and associated with clay minerals in oil sands tailings (Kaminsky et al. 2008). Apart from the chemical oxidation of H_2S/HS^-, high numbers of viable SOB and their potential activity also indicated biologically mediated sulfide oxidation throughout the pond. Interestingly, pools of total reduced sulfur (>9 mM) even exceeded concentrations assumed from theoretical considerations (>7.3 mM) in tailings below the water cap, suggesting a gradual accumulation of sedimentary sulfides. With respect to the development of a future lake ecosystem, the permanent precipitation of metals and sulfides in anoxic sediments below the water body may prevent the dispersion of toxic dissolved sulfide into the overlying water. However, FeS_2 may oxidize upon contact with oxic lake water, resulting in the dissolution of SO_4^{2-}, Fe^{2+} and H^+ and consequently the generation of acid mine drainage (Singer and Stumm 1970; Kuznetsov et al. 2015).

4.2. Impact of sulfate reduction on the organic acid transformation and CH_4 emissions

In tailings of all depths, rates of carbon turnover and CO_2 production significantly decreased when sulfate reduction was inhibited, demonstrating the role of bacterial sulfate reduction as the most important terminal oxidative process in anoxic tailings. As a general trend, the relative contribution of SRB to the turnover of butyrate and acetate decreased with depth (Table 2). Contrarily, SRB were responsible for the turnover of propionate in deeper tailings, but not essential for its consumption in the water cap. Interestingly, SRB were not predominantly involved in lactate and formate turnover, demonstrating the presence of other microbial metabolisms. The particular importance of

methanogenic biodegradation for hydrocarbon transformation in tailings was recently demonstrated (Siddique et al. 2012). Accordingly, enormous amounts of CH_4 contribute to greenhouse gas emissions and may have both adverse and beneficial effects in oil sands tailing ponds (Fedorak et al. 2003). When competing for the major fermentation products H_2 and acetate, sulfate-reducing bacteria have a thermodynamic advantage over methanogens (Holland et al. 1987). This is in line with slightly increased methanogenesis in molybdate-amended sulfate-rich microcosms, demonstrating a partial inhibition of methanogenesis by microbial sulfate reduction. An inhibition of methanogenesis by SRB was previously shown in laboratory incubations with mature fine tailings from other ponds (Holowenko et al. 2000; Salloum et al. 2002). However, in order to estimate the inhibition of CH_4 emissions by sulfate reduction in situ, the microbial activity in original tailings has to be considered. Based on our measurements, microbial sulfate reduction and methanogenesis coexisted in situ exclusively in sulfate-rich tailings between 3.5–7.5 m, with methane production rates increasing by a factor of 2–3 (~ 10 μmol L^{-1} d^{-1}) after inhibition of sulfate reduction. Taking an estimated pond surface area of about 6 km^2 and a sulfidic layer of 4 m, the activity of SRB would prevent at least ~ 5.37 million litres of CH_4 emissions from the pond per day.

Conclusions

In conclusion, results give evidence that H_2S outgassing from the pond is effectively prevented by the biochemical re-oxidation of H_2S and formation of iron sulfide minerals that may contribute to the permanent burial of sulfide in anoxic tailings. Throughout the pond, rates of carbon transformation and CO_2 production significantly decreased when sulfate reduction was inhibited, demonstrating the role of bacterial sulfate reduction as the most important terminal oxidative process in anoxic tailings with significance for tailings ponds carbon cycle and gas production. As demonstrated by the selective inhibition of SRB, microbial sulfate reduction may have prevented considerable volumes of CH_4 emissions from the pond due to the competition with methanogens. Moreover, findings on sulfur cycling can be regarded as the actual state of an active oil sands tailings pond prior to the conversion to an end pit lake. In combination with ongoing monitoring programs this will help to understand the development of key elemental cycles and geochemical gradients during subaqueous deposition of tailings and ultimately to evaluate the success of a wet-landscape reclamation.

Acknowledgements

This research was funded primarily by the Helmholtz-Alberta Initiative. We thank Juliane Schmidt, Corinna Völkner, and Martin Wieprecht for excellent help in the laboratory. Dr. Matthias Koschorreck is acknowledged for manifold suggestions in the process of planning and setting up the microcosms. We finally acknowledge Dr. Christopher Weisener, Dr. Gillian Walshe, Tara Penner and Robert Donohue, who substantially contributed to the organisation of the sampling campaign.

References

Alberta Environment and Research Development (2013) Oil sands landcover status 2011. Edmonton, AB AERSD 1995

BGC Engineering Inc (2010) Oil Sands Tailings Technology Review. Oil Sands Research and Information Network, OSRIN Report TR-1, 136 pp

Boesen C, Postma D (1988) Pyrite formation in anoxic environments of the Baltic. Amer J Sci 288:575-603

Canfield DE (1989) Reactive iron in marine sediments. Geochim Cosmochim Acta 53:619–632

Fedorak PM, Coy DL, Dudas MJ, Simpson MJ, Renneberg AJ, MacKinnon MD (2003) Microbially-mediated fugitive gas production from oil sands tailings and increased tailings densification rates. J Environ Eng Sci 2:199–211

Fossing H, Jørgensen BB (1989) Measurement of bacterial sulfate reduction in sediments: evaluation of a single-step chromium reduction method. Biogeochem 8:205–222

Gagnon C, Mucci A, Pelletier E (1995) Anomalous accumulation of acid-volatile sulphides (AVS) in a coastal marine sediment, Saguenay Fjord, Canada. Geochim Cosmochim Acta 59:2663- 2675

Holland KT, Knapp JS, Shoesmith JG (1987) Anaerobic bacteria. Chapman and Hall, New York, 130–133

Holowenko FM, MacKinnon MD, Fedorak PM (2000) Methanogens and sulfate-reducing bacteria in oil sands fine tailings waste. Can J Microbiol 46:927–937

Howarth RW, Stewart JWB, Ivanov MV (1992) Sulfur cycling on the continents: Wetlands, terrestrial ecosystems and associated water bodies. John Wiley and Sons, New York, N.Y

Kaminsky HAW, Etsell TH, Ivey DG, Omotoso O (2008) Characterization of heavy minerals in the Athabasca oil sands. Miner Eng 21(4):264–271

Klee AJ (1993) A computer program for the determination ofmost probable number and its confidence limits. J Microbiol Meth 18:91–98

Knöller K, Schubert M (2010) Interaction of dissolved and sedimentary sulfur compounds in contaminated aquifers. Chem Geol 276(3–4):284–293

Koschorreck M, Herzsprung P, Wendt-Potthoff K, Lorke A, Geller W, Luther G, Elsner W (2002) An in-lake reactor to treat an acidic lake: the effect of substrate overdosage. Mine Water Environ 21(3):137–149

Koschorreck M, Kleeberg A, Herzsprung P, Wendt-Potthoff K (2007) Effects of benthic filamentous algae on the sediment-water interface in an acidic mining lake. Hydrobiol 592:387–397

Kuznetsov P, Kuznetsova A, Foght JM, Siddique T. (2015) Oil sands thickened froth treatment tailings exhibit acid rock drainage potential during evaporative drying. Sci Total Environ 505:1–10

MacKinnon M (1989) Development of the tailings pond at Syncrude's oil sands plant: 1978–1987. AOSTRA J Res 5:109–133

Meier J, Voigt A, Babenzien HD (2000) A comparison of $^{35}S\text{-}SO_4^{2-}$ radiotracer techniques to determine sulfate reduction rates in laminated sediments. J Microbiol Meth 41:9–18

Penner TJ, Foght JM (2010) Mature fine tailings from oil sands processing harbour diverse methanogenic communities. Can J Microbiol 56:459–470

Ramos-Padrón E, Bordenave S, Lin S, Bhaskar IM, Dong X, Sensen CW, Fournier J, Voordouw G, Gieg LM (2011) Carbon and sulfur cycling by microbial communities in a gypsum-treated oil sands tailings pond. Environ Sci Technol 45(2):439–46

Reis MAM, Almeida JS, Lemos PC, Carrondo MJT (2004) Effect of hydrogen sulfide on growth of sulfate reducing bacteria. Biotechnol Bioeng 40:593–600

Rickard D, Morse JW (2005) Acid volatile sulfide (AVS). Mar Chem 97:141–197

Salloum MJ, Dudas MJ, Fedorak PM (2002) Microbial reduction of amended sulfate in anaerobic mature fine tailings from oil sand. Waste Manage Res 20:162–171

Siddique T, Penner T, Klassen J, Nesbø C, Foght JM (2012) Microbial communities involved in methane production from hydrocarbons in oil sands tailings. Environ Sci Technol 46:9802–9810

Siddique T, Kuznetsov P, Kuznetsova A, Arkell N, Young R, Li C, Guigard S, Underwood E, Foght JM (2014) Microbially-accelerated consolidation of oil sands tailings. Pathway I: changes in porewater chemistry. Front Microbiol 21:5–106

Singer PC, Stumm W (1970) Acid mine drainage: the rate determining step. Science 167:1121-1123

Stasik S, Loick N, Knöller K, Weisener C, Wendt-Potthoff K (2014) Understanding biogeochemical gradients of sulfur, iron and carbon in an oil sands tailings pond. Chem Geol 382:44–53

Widdel F, Bak F (1992) Gram-negative mesophilic sulfate-reducing bacteria. In: Balows A, Trüper HG, Dworkin M, Harder W, Schleifer KH (eds) The Prokaryotes. Springer, Berlin, 3352–3389

Wendt-Potthoff K, Frömmichen R, Herzsprung P, Koschorreck M (2002) Microbial Fe(III) reduction in acidicmining lake sediments after addition of an organic substrate and lime. Water Air Soil Pollut 2:81–96

Westcott F (2007) Oil sands end pit lakes: a review to 2007. The Cumulative Environmental Management Association End Pit Lakes Subgroup. Project 2006-32 (Clearwater Environmental Consultants Inc. 2007), p. 2.