Chemical Geology 382 (2014) 44–53

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Understanding biogeochemical gradients of sulfur, iron and carbon in an oil sands tailings pond

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ARTICLE INFO

Article history:
Received 24 January 2014
Received in revised form 9 May 2014
Accepted 14 May 2014
Available online 29 May 2014

Editor: David R. Hilton

Keywords:
Oil sands tailings ponds
Sulfur cycle
Iron reduction
Methanogenesis
Microbial community
Stable isotopes

ABSTRACT

Oil sands tailings ponds in Alberta (Canada) are strongly stratified ecosystems structured in an upper water layer and underlying mud layers that harbour a diversity of microorganisms, contributing to hydrocarbon degradation and elemental cycling. Until now not much is known about the biogeochemistry of the ponds and their spatial structure is not well explored yet. An understanding of microbial activity and community composition is important, in particular, in order to determine potential effects on pond properties and long term development. Therefore, the purpose of the present study was to identify reactive zones of iron, carbon and sulfur cycling in an active tailings pond, by comparing biogeochemical data along two depth profiles. For both profiles a zone of intense sulfur cycling was substantiated by maxima of: (a) dissolved and solid sulfides; (b) sulfate reduction rates and thiosulfate oxidation potentials; and (c) viable counts of sulfate reducers and relative abundances of functional genes. In addition, methanogenesis and microbial iron reduction were shown to be important electron accepting processes in the ponds. All processes coexisted in a zone of intense elemental cycling at a depth of 1–4 m below the water–mud interface, where fresh tailings are likely to accumulate. Microbial activity and biomass decreased with depth, where tailings had higher age and density. While the upper mud layers were influenced by the presence of different archaea, the microbial communities showed an increased presence of bacterial species at depth. Insights from qPCR, ^{35}S radiotracer technique and stable isotope analysis mirrored some differences between the profiles, regarding sulfur and carbon cycling. Despite this, both profiles showed remarkably similar patterns of microbial community composition and activity, revealing a good reproducibility of biogeochemical cycling within a few metres.

1. Introduction

The Athabasca basin is the largest out of three designated oil sands areas in Alberta (Canada), with a number of bitumen-bearing deposits (Alberta Energy and Utilities Board, 2005). During the extraction and upgrading process of bitumen massive volumes of tailings, composed of water, mineral solids, unrecovered bitumen and other organic compounds, are produced and pumped into huge settling basins on site (Allen, 2008; Giesy et al., 2010). During deposition fine tailings slowly settle and consolidate over time, creating a stratified system with an overlying water layer, a narrow water–mud interface and a tailings zone. With depth solids content increases up to a mud composition of 30–40% solids, referred to as mature fine tailings (MFT) (MacKinnon, 1989). Due to the acute toxicity of certain substances (e.g. naphthenic acids) to aquatic organisms (Headley et al., 2011) and the slow densification rate of fine tailings (Eckert et al., 1996), the oil sands industry faces environmental and operational challenges for a sustainable pond management and safe containment of tailings (BGC Engineering Inc., 2010). Since reclamation plans include a wet landscape option that considers tailings ponds as a permanent storage and remediation opportunity (Westcott, 2007), the success of this approach strongly relies on natural processes of microbial biodegradation and detoxification over time (Nix and Martin, 1992).

A highly diverse microbial community (Fedorak et al., 2002; Salloum et al., 2002; Penner and Foght, 2010) has been shown to be involved in the anaerobic degradation of organic compounds and elemental cycling in the ponds (Siddique et al., 2007, 2011). As a result of microbial metabolism, the generation of methane accelerates the densification of finer particles in the ponds and can thereby enhance the recovery of water that can be recycled for the running oil extraction processes (Holowenko et al., 2000; Fedorak et al., 2003). In terms of MFT long time storage under a water cap, microbial gas production can also have adverse effects, causing a remixing of fluid fine tailings with the overlying water (BGC Engineering Inc., 2010). Furthermore, the biogenic production of toxic H_2S gas may determine in part the suitability of a self-sustaining end pit lake. Several studies reported the presence of a

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http://dx.doi.org/10.1016/j.chemgeo.2014.05.026
0009-2541/

distinct sulfidic zone below the water–mud interface (Penner and Foght, 2010; Ramos-Padrón et al., 2011) potentially emitting considerable amounts of H_2S gas. In this respect, the linkage of bacterial sulfate reduction to microbial sulfur oxidation and iron reduction is important, since H_2S can be oxidised both chemically and microbially (Luther et al., 2011) or precipitate to metal sulfides under anaerobic conditions (Jong and Parry, 2003), each time leading to an immobilisation of toxic H_2S. However, oil sands tailings ponds are highly dynamic and heterogeneous environments, frequently releasing (water recycling) and receiving (fresh tailings) material. Accordingly, the microbial community patterns and the corresponding activities underlie temporal (Fru et al., 2012) and spatial variations (Ramos-Padrón et al., 2011). Except for microbial sulfate reduction and methanogenesis not much is published about the rates of microbial processes and their vertical and horizontal distribution in the ponds.

The main goal of the present study was to identify reactive zones of biogeochemical cycling and quantify microbial numbers and activities related to sulfur, iron and carbon cycling, as a function of depth. A second important purpose was to evaluate the reproducibility of depth profiles taken in close vicinity at the same time. To achieve this, wet geochemical analyses were combined with stable isotope geochemistry, incubation experiments, microbial selective cultivation and DNA-based analyses of original samples from two profiles.

2. Material and methods

2.1. Sampling

Samples were collected on August 31st and September 1st 2011 from two sites of an active tailings pond (coordinates: site A: 57°0′46.09″N, 111°36′31.32″W; site B: 57°0′47.00″N, 111°36′24.65″W) containing oil sands tailings under a water cap of about 3.6 m depth. Samples were obtained from several depths within the water cap (1, 2, 3 m) and from the tailings zone (4.5, 5.5, 7.5, 8.5, 10.5, 13.5, 18.5 m) using a piston sampler, as described previously (Penner and Foght, 2010). Samples (4.5–18.5 m) for qPCR and T-RFLP analysis were filled into sterile 50 mL centrifuge tubes, frozen immediately and processed at the University of Windsor (Canada). To perform denaturing gradient gel electrophoresis (DGGE), subsamples were filled into 15 mL conical centrifuge tubes and processed at the University of Alberta (Canada). Samples (1, 2, 3, 4.5, 5.5, 7.5, 13.5 m) for most probable numbers (MPN), biomass and microbial activity were transferred into sterile 500 mL plastic Nalgene® bottles. In addition, 200 mL of sample was filled into appropriate Nalgene® vessels for geochemical analysis. Subsamples for analysis of sulfur isotopes were transferred into 125 mL Nalgene® flasks containing Zn-acetate. All bottles were filled to the top without any headspace. Samples were sealed and shipped to the Helmholtz Centre for Environmental Research in Magdeburg (Germany) within 2 weeks, darkened and cooled to minimize changes in the biochemical properties (Hulecki et al., 2010).

2.2. Chemical and isotope analysis

Analysis of major anions and cations, heavy metals, nutrients and organic/inorganic carbon was performed using standard procedures as described in Koschorreck et al. (2007). Concentrations of organic acids (acetate, lactate, propionate, formate and butyrate) were measured using high performance liquid chromatography (HPLC) (Thermo Seperation Products) (Koschorreck et al., 2002). Pore water was obtained by centrifugation (30 min; 15,000 rpm). Concentrations of HCl soluble reactive ferrous iron ($Fe(II)_R$) and hydroxylamine reducible reactive total iron ($T\text{-}Fe_R$) were measured after total sediment digestion according to Wendt-Potthoff et al. (2010). Total reduced inorganic sulfur (TRIS) was analysed according to a sequential extraction method 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) were measured polarographically (Frömmichen et al., 2004). Stable isotopes of sulfur and oxygen were analysed according to Knöller and Schubert (2010). Briefly, any precipitated ZnS was converted to Ag_2S after filtration (0.45 μm). Reduced inorganic sulfur compounds (AVS and CRS) were recovered by a two step distillation (Fossing and Jørgensen, 1989). Sulfate was precipitated as $BaSO_4$. After conversion to SO_2, the composition of sulfur isotopes was measured using an elemental analyser coupled to an isotope ratio mass spectrometer (ThermoFinnigan). Oxygen isotope analysis on $BaSO_4$ was done by high temperature pyrolysis in a thermal conversion elemental analyser coupled to a delta plus XL mass spectrometer (ThermoFinnigan). Beside the pond samples, a water sample obtained from the Athabasca River near the oil sands facilities was used to analyse the isotopic composition of sulfate for comparative purposes. Sulfur isotope measurements of the prepared $BaSO_4$ or Ag_2S were performed with an analytical error of the measurement of better than ±0.3‰. However, the overall analytical precision of the sulfur isotope determination including sampling, laboratory preparation, and isotope measurement is assumed to be around ±0.6‰. Oxygen isotope analysis on barium sulfate samples was carried out with an analytical error of better than ±0.5‰. The overall uncertainty of the method including sampling and preparation is ±0.9‰.

2.3. Most probable numbers (MPN) and biomass

MPN to enumerate viable cells of iron-reducing bacteria (FeRB), sulfate-reducing bacteria (SRB) and thiosulfate-oxidising bacteria (SOB) were performed as serial dilutions in deep-well plates as described in Wendt-Potthoff and Koschorreck (2002). Selective media (Meier et al., 2004) for SRB and SOB 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). For the FeRB a modified anaerobic *Geobacter* medium (DSMZ No. 579) was used (Meier et al., 2004). All media were adjusted to pH 7.5. Plates were incubated in the dark at 20 °C for 6 weeks. MPN and their confidence intervals were calculated using the programme of Klee (1993). Microbial biomass was determined by phospholipid phosphate extraction (Bligh and Dyer, 1959), modified after Gessner and Neumann (2005). Phosphate was detected after a modified protocol of Findlay et al. (1981) and converted to cell concentrations using the conversion factors given by Balkwill et al. (1988).

2.4. Activity rates

All assays were conducted in duplicate in the dark at 20 °C, which is close to the in situ temperature of the pond (16 °C). Statistical tests were carried out using SigmaPlot version 12.0.

2.4.1. Methane and carbon dioxide production

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. The 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 methaniser (SRI instruments, Torrance, U.S.A.). Rates were calculated from the linear regression of CH_4 and CO_2 partial pressure in the headspace.

2.4.2. Thiosulfate oxidation potentials

Potential oxidation rates of thiosulfate, an important intermediate in the sulfur cycle that may be formed by biological sulfide oxidation or by chemical oxidation of free and iron-bound sulfides (Jørgensen and Bak, 1991), were quantified to obtain information about biotic reactions in sulfur recycling. Thiosulfate oxidation rates 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),