



Effect of naphtha diluent on greenhouse gases and reduced sulfur compounds emissions from oil sands tailings



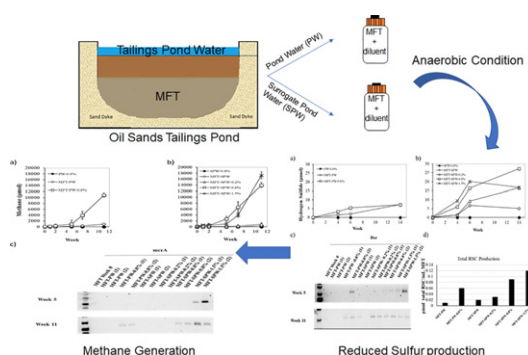
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HIGHLIGHTS

- Indigenous microbes degraded residual diluent in tailings thus producing emissions.
- Reduced sulfur compounds were produced first at a max. of $0.12 \mu\text{mol}$ RSCs/mL MFT.
- H_2S and 2-methylthiophene contributed 81% of the RSCs gas produced.
- CH_4 and CO_2 production occurred after week 5.
- A max. of $40.7 \mu\text{mol}$ CH_4 /mL MFT and $5.9 \mu\text{mol}$ CO_2 /mL MFT was produced.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 12 January 2017

Received in revised form 14 April 2017

Accepted 14 April 2017

Available online 28 April 2017

Editor: D. Barcelo

Keywords:

Greenhouse gases
Reduced sulfur compounds
Methanogens
Sulfate reducing bacteria
Oil sands tailings
Diluent

ABSTRACT

The long-term storage of oil sands tailings has resulted in the evolution of greenhouse gases (CH_4 and CO_2) as a result of residual organics biodegradation. Recent studies have identified black, sulfidic zones below the tailings-water interface, which may be producing toxic sulfur-containing gases. An anaerobic mesocosm study was conducted over an 11-week period to characterize the evolution of CH_4 , CO_2 and reduced sulfur compounds (RSCs) (including H_2S) in tailings as it relates to naphtha-containing diluent concentrations (0.2, 0.8, and 1.5% w/v) and microbial activity. Our results showed that RSCs were produced first at $0.12 \mu\text{mol}$ RSCs/mL MFT (1.5% w/v diluent treatment). RSCs contribution (from highest to lowest) was H_2S and 2-methylthiophene > 2,5-dimethylthiophene > 3-methylthiophene > thiofuran > butyl mercaptan > carbonyl sulfide, where H_2S and 2-methylthiophene contributed 81% of the gas produced. CH_4 and CO_2 production occurred after week 5 at $40.7 \mu\text{mol}$ CH_4 /mL MFT and $5.9 \mu\text{mol}$ CO_2 /mL MFT (1.5% w/v diluent treatment). The amount of H_2S and CH_4 generated is correlated to the amount of diluent present and to microbial activity as shown by corresponding increases in sulfate-reducers' Dissimilatory sulfite reductase (DsrAB) gene and methanogens' methyl-coenzyme M reductase (MCR) gene.

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1. Introduction

The oil sands deposits in Alberta are the third largest in the world after Saudi Arabia and Venezuela, with an estimated oil reserve of 166 billion barrels of oil (Government of Alberta DoE, 2014). Bitumen is commonly extracted from surface-mined oil sands ore using the Clark

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Hot Water Extraction Process, which, in turn, has generated enormous quantities of fluid tailings waste (Arkell et al., 2015). These fluid tailings, an alkaline slurry mixture of process water, sand, silt, clays, organics, inorganics, and unrecovered bitumen and diluent (Small et al., 2015) are deposited in large tailings ponds under a zero discharge policy (Government of Alberta DoE, 2013). Following the initial settling of coarse solids (>44 μm) (Chalaturnyk et al., 2002), the suspended fines in the fluid fine tailings (FFT, ~10 wt% solids) gradually settle over 2–4 years to become mature fine tailings (MFT, ~30 wt% solids) (Arkell et al., 2015). Due to their poor consolidation properties, it may require several decades or more in situ before tailings sufficiently consolidate for reclamation (BGC Engineering Inc., 2010). Currently, the surface area of these ponds is approximately 182 km² and contains an estimated 976 million m³ of accumulated tailings (Government of Alberta DoE, 2013; Government of Alberta DoE, 2014).

One effect of long-term storage of tailings in the ponds is the evolution of gases. Greenhouse gases (GHG), methane (CH₄) and carbon dioxide (CO₂), are now emitted in most tailings ponds tested to date (Siddique et al., 2012; Small et al., 2015). Tailings ponds that receive froth treatment tailings (FTT), tailings that contain hydrocarbons and diluent, were reported to have higher GHG emissions and were more prone to intensive bubbling compared to using composite tailings and thickened tailings (Burkus et al., 2014). Diluents are added to improve recovery rates of bitumen (Small et al., 2015). The n-alkanes and BTEX (benzene, toluene, ethylbenzene, and xylenes) compounds found in naphtha diluent have been observed to stimulate the biological production of GHG (Siddique et al., 2006; Siddique et al., 2007). Recent research has also revealed the presence of black, sulfidic zones beneath the tailings-water interface (Chen et al., 2013; Chi Fru et al., 2013; Ramos-Padron et al., 2011; Stasik and Wendt-Potthoff, 2014) that are abundant in sulfate reducing bacteria (SRB) (Stasik and Wendt-Potthoff, 2014). Potentially, the SRB in these zones are consuming sulfate and producing considerable amounts of HS⁻ and toxic, hydrogen sulfide (H₂S) gas (Stasik and Wendt-Potthoff, 2014). The addition of gypsum to increase MFT densification increases the sulfate concentration in tailings, which in the presence of organics such as naphtha diluent, provides SRB with substrates for H₂S production. Beside precipitation, H₂S emissions are most likely prevented by the chemical (Ramos-Padron et al., 2011) and microbial re-oxidation (Boudens et al., 2016; Stasik et al., 2014). However, there is a lack of peer-reviewed literature regarding H₂S emissions and other reduced sulfur compounds (RSCs) in tailings. Indeed, H₂S is a well-known toxic gas that impacts human health, and other RSCs (including H₂S) compounds can be transformed into sulfur dioxide and/or sulfuric acid in the atmosphere (Bates et al., 1992). These transformed products can contribute to acidic precipitation and aerosol formation, which further affect human and environmental health (Bates et al., 1992; Small et al., 2015). Additionally, there is little peer-reviewed literature on the temporal relationship between CH₄, CO₂ and RSCs (including H₂S) productions.

As such, the overall objective of this study is to understand the evolution of CH₄, CO₂ and RSCs (including H₂S) in tailings as it relates to: i) diluent concentration and ii) microbial activity. Studying the production of these compounds in tailings will aid in further understanding the emissions currently being released from tailings, and yield further insight on the effect of adding sulfate-containing substrates on gas production that require consideration in current or future tailings remediation plans.

2. Materials and methods

2.1. Mature fine tailings, pond water, and naphtha diluent

MFT and pond water (PW) samples were provided by Canada's Oil Sands Innovation Alliance (COSIA). The samples were taken in June 2012 at a depth of 12 m below the surface and were stored at 4 °C

until use. Due to limited availability of pond water, surrogate pond water (SPW) was also prepared and used in this experiment (see Table S1 for recipe). Naphtha diluent was also provided by COSIA and was determined in our laboratory to have a specific gravity of 0.77 (T = 20 °C and P = 1 atm).

2.2. Mesocosm set-up

Mesocosms were constructed using 1 L Pyrex® glass bottles and modified caps fitted with butyl rubber septa. MFT and pond water samples were oxygen-purged using.

Argon gas (Praxair) prior to use. MFT were amended with typical diluent concentration in the tailings ponds – 0.8% w/v (<1% mass) (Penner and Foght, 2010), whereas a range of diluent concentrations (0.2% w/v, 0.8% w/v, and 1.5% w/v) were studied using the SPW. All experimental mesocosms contained 400 mL MFT and 400 mL pond water (PW or SPW) with diluent. Two types of controls were used in both the PW and SPW groups: no-diluent control (400 mL MFT and 400 mL pond water) as a 0% w/v baseline, and a no-MFT control (800 mL pond water and 0.8% w/v diluent) to account for the presence of MFT in this study. All mesocosms were assembled in an anaerobic chamber (5% CO₂, 5% H₂, N₂ balance) and incubated in the dark at 24 °C. Mesocosms were monitored for 14 weeks (for RSCs production) or 11 weeks (for all other parameters).

2.3. Gas analysis

CH₄ and CO₂ were measured with a 7890A gas chromatograph with a thermal conductivity detector (GC-TCD), and RSCs (hydrogen sulfide, carbonyl sulfide, thiofuran, butyl mercaptan, 2-methylthiophene, 3-methylthiophene, and 2,5-dimethylthiophene) were analyzed using a 7890A GC and an Agilent Technologies 355 sulfur chemiluminescence detector (GC-SCD) (See Supplementary information for detail analysis conditions).

2.4. Chemical analyses

Prior to the experiment the solids, bitumen, and water content of the MFT were characterized using the Dean Stark procedure (Cao et al., 2014). The chemical analyses in this study were conducted on a mixture of released water and pore water but for the purposes of this study will be referred to as oil sands process water (OSPW). Prior to taking a liquid sample, the mesocosms were inverted to ensure complete mixing thus reducing sampling bias. After inversion, the mesocosms were placed upright and allowed to sit for approximately 1 h to minimize solids from clogging the sampling syringe. At each analytical time point, 20 mL of liquid sample was removed from the OSPW layer and measured for redox using an Accumet redox probe (4 M KCl internal solution) in the anaerobic chamber. The OSPW samples were then removed from the chamber, centrifuged at 8000 × g for 5 min at 20 °C, and the supernatant was removed and filtered with 0.45 μm filters. Conductivity and pH were measured using an ExStik®II pH/Conductivity/TDS Meter. Alkalinity was measured using a Mettler Toledo DL53 with 0.02 N H₂SO₄ as a titrant. Dissolved organic carbon samples were analyzed with a Shimadzu TOC-L CPH using the Non-Purgeable Organic Carbon (NPOC) method. OSPW samples for sulfate and nitrate analysis were filtered (0.22 μm) and analyzed using a Dionex ICS-2100 ion chromatography, or by the Department of Biological Sciences at the University of Alberta using a Dionex DX600 ion chromatography and EPA method 300.1 (USEPA 1997). Detailed explanation of the sulfate reduction rate calculation is included in the Supplementary information.

2.5. Microbial analysis

A 1.5 mL MFT and OSPW mixture was withdrawn from each mesocosm under anaerobic conditions in week 5 and 11. In addition,

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