Applied Geochemistry 93 (2018) 49–59

Contents lists available at ScienceDirect

Applied Geochemistry

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

The interplay of methane and ammonia as key oxygen consuming constituents in early stage development of Base Mine Lake, the first demonstration oil sands pit lake

Florent F. Risacher[a], Patrick K. Morris[a], Daniel Arriaga[a], Corey Goad[a], Tara Colenbrander Nelson[a], Gregory F. Slater[a], Lesley A. Warren[a,b,*]

[a] School of Geography and Earth Sciences, McMaster University, 1280 Main St W., Hamilton, ON, L8S 4L8, Canada
[b] Department of Civil & Mineral Engineering, University of Toronto, 35 St. George St. Toronto, ON, M5S 1A4, Canada

ARTICLE INFO

Editorial handling by Khalil Hanna

Keywords:
Oil sands pit lake
Water cap biogeochemistry
Methane
Ammonia
Fluid fine tailings (FFT)
Nitrification

ABSTRACT

The efficacy of oil sands water capped tailings technology is currently being assessed in the first pilot pit lake in the Athabasca Oil Sands region (AOSR). Base Mine Lake (BML, Syncrude Canada Mildred Lake mine, Fort McMurray AB Canada) was commissioned in December of 2012 and consists of circa 40 m depth of fluid fine tailings (FFT) overlain by circa 10 m of a freshwater cap. As this is the first oil sands pit lake, it is unknown to what extent known oxygen consuming constituents (OCC) such as methane, hydrogen sulfide and ammonia will mobilize from the underlying FFT layer in BML and impact oxygen concentrations within the water cap. Thus, the field objectives here were to characterize the physico-chemistry and geochemistry of the BML water cap from the FFT water interface (FWI) to the surface over two summers (2015 and 2016). Results identify that the ~10 m water cap thermally stratifies and that oxygen persists, albeit at low levels (i.e. < 5% saturation) to the FWI during the summer season for both years. Consistent with the FFT acting as an OCC source, aqueous CH_4, ΣH_2S and NH_4^+ concentrations were highest closer to the FWI, decreasing upwards into the water cap. As O_2 persists to the FWI, ΣH_2S was rapidly removed within this region, with little mobilized to the overlying water as evidenced by nondetectable ΣH_2S within 1 m of the FWI. In contrast, CH_4 and NH_4^+ concentrations were detectable higher up into the water cap, indicating incomplete oxidation at the FWI most likely due to oxygen limitation. In 2015, CH_4 was the only identified variable significantly negatively related to BML water cap oxygen concentrations. However in 2016, NH_4^+ emerged as an important OCC negatively related to water cap oxygen concentrations in addition to CH_4. Mass balance of nitrogen redox species throughout the water column are consistent with active nitrification occurring in 2016; which was not evident in 2015 results. Thus, within 4 years of commissioning, nitrification has become an active and important process affecting water column oxygen concentrations within this pit lake. This is in contrast to an absence of detectable microbial nitrification in active oil sands tailing ponds, despite high levels of ammonia. While the absence of nitrification occurring in oil sands tailings ponds has previously been suggested to reflect naphthenic acids toxicity, results here identify that some lower limit of oxygen may also be required for this metabolism to flourish and that at very low oxygen levels (i.e. < 5% saturation), nitrifying microbes appear to be outcompeted by methanotrophs, at least during early establishment stages within a pit lake.

1. Introduction

The Athabasca Oil Sands region (AOSR) covers over 140,200 km^2 of land in the western Canadian sedimentary basin in northern Alberta, and has one of the largest oil deposits in the world (Alberta Energy, 2013). The waste slurry produced during the extraction of bitumen from surface mined oil sand contains residual bitumen (0.5–5% by mass), fine particles of silt and clay, sand, naphtha and a large volume of oil sands process water (OSPW; Chalaturnyk et al., 2002). This slurry is transferred to holding ponds, until the sand has settled out during gravity densification, resulting in a fluid-like, brackish (~1/15 seawater salinity) material known as fluid fine tailings (FFT) (Penner and Foght, 2010). Clay particles in FFT remain in suspension and settle slowly over decades (MacKinnon, 1989). The large volume of oil sands

* Corresponding author. Department of Civil & Mineral Engineering, University of Toronto, 35 St. George St. Toronto, ON, M5S 1A4, Canada.
E-mail address: lesley.warren@utoronto.ca (L.A. Warren).

https://doi.org/10.1016/j.apgeochem.2018.03.013
Received 18 August 2017; Received in revised form 13 March 2018; Accepted 21 March 2018
Available online 31 March 2018
0883-2927/

processed from extraction of mined oil sands results in the largest tailings facilities in the world (COSIA, 2014) holding a volume of tailings waste exceeding 700 million m^3 (Dominski, 2007). Current efforts are developing techniques for wet reclamation of FFT (BGC Engineering Inc., 2010) using water capped tailings technology (WCTT), placed within pit lakes. In WCTT, a freshwater cap is placed over a layer of FFT with no further discharge of FFT into the system once commissioned (Boerger et al., 1992; Westcott and Watson, 2007). The goal is to establish a self-sustaining ecosystem with a stable oxic zone occurring within the surface water cap, that provides long-term, stable containment for FFT as part of the closure landscape for a mine. In 2007, ~30 pit lakes were planned in the AOSR with more expected as the development of mining operations extends (Westcott, 2007). The first AOSR demonstration pilot pit lake, Base Mine Lake (BML) was commissioned in December of 2012 to evaluate the potential of WCTT for oil sands FFT reclamation.

Pit lakes have been widely used for reclamation of coal and metal mine sites since the beginning of the 20th century (Castro and Moore, 2000); typically infilling an abandoned open-pit mine with water, tailings and overburden rocks left over from the mining activity (Castro and Moore, 2000). Although the nature of the reclamation solution is the same, i.e. a water cap placed over mining waste, creating a functional ecosystem that can be left as part of a mine closure landscape, the potential challenges affecting the success of metal and coal mining EPLs are different from those likely to occur in an oil sands pit lake. These differences reflect the divergent characteristics of tailings generated by these various extractive industries. The major challenges observed for metal and coal mining pit lakes, reflect oxidation of ΣH_2S rich wastes that can cause acidification as well as metal/metalloid release (Gammons et al., 2009; Fisher and Lawrence, 2006; Neil et al., 2009). As pit lakes have been used for over 100 years in these mining contexts, these challenges have been more extensively studied (Frömmichen et al., 2004; Costa and Duarte, 2005; Christensen et al., 1996) and improvements to the pit lake reclamation strategy have been implemented, namely the burial and isolation of the tailings from the oxic water layer to prevent ΣH_2S oxidation, associated acidity generation, and trace elements release (Castendyk et al., 2015).

Relative to other resource sectors managing tailings (i.e. metals and mineral sector), the reclamation requirement for oil sands tailings is made more challenging by a unique feature; namely their very slow sedimentation and consolidation rates (COSIA, 2014). Thus, how this slow consolidation will affect the development of a pit lake water cap is unclear. Of particular interest, the establishment of an oxygenated zone within the water cap is required for a viable and self-sustaining ecosystem and will ensure success of pit lakes as a reclamation strategy for oil sands FFT. This outcome requires that oxygen inputs from atmospheric diffusion, watershed and rain inputs and any *in situ* photosynthetic production exceed oxygen consumption driven by FFT constituents, enabling some portion of the surface water cap to remain oxygenated.

The concern for the success of WCTT as a FFT reclamation strategy is that mobilization of reductants from the underlying FFT may be sufficiently large to prevent the development of an oxic portion of the water cap. Further, given the saturated concentrations of some reductants like CH_4 or ΣH_2S within FFT pore water (Holowenko et al., 2000; Stasik et al., 2014; Chen et al., 2013; Ramos-Padrón et al., 2011), this source of *oxygen consuming constituents* (OCC) could persist, precluding a positive developmental trajectory over substantial timescales. Indeed, ΣH_2S and CH_4 have been identified as important OCC affecting oxygen concentrations within active oil sands tailings ponds, commonly driving these systems anoxic within a meter of the water surface (Chen et al., 2013; Holowenko et al., 2000; Penner and Foght, 2010). Thus, within a pit lake, they are also likely to be important in determining water cap oxygen status, at least in early development (Fig. 1; Quagraine et al., 2005, Westcott, 2007, Siddique et al., 2012). These compounds may be variably mobilized from the FFT into the overlying watercap through ebullition (i.e. gases), diffusion (aqueous and gaseous) as well as disturbance or mixing (gases, aqueous and particulate).

Further, evidence from Syncrude's tailings pond, Mildred Lake Settling Basin (MLSB) has also identified the occurrence of diverse microbial communities in FFT (Penner and Foght, 2010) with aerobic and anaerobic heterotrophic microbes, as well as autotrophic methanogens present in high numbers (Foght et al., 2017). Anaerobic organisms known to be present, include denitrifying bacteria (NRB), iron reducing bacteria (IRB), substantial communities of sulphate reducing bacteria (SRB) and large methanogenic communities (Holowenko et al., 2000; Penner and Foght, 2010; Siddique et al., 2012; Foght et al., 2017). Over the last three decades, MLSB has developed from a primarily ΣH_2S driven system in terms of oxygen consumption to now include CH_4 generated through microbial activity *in situ* (Foght et al., 2017; Sobolewski, 1992, 1997). Interactions between methanogens and sulfate reducers have since been identified more widely in oil sands tailing ponds throughout the region, indicating these microbial metabolisms are also likely to play a role in determining oxygen concentrations in an FFT containing pit lake (Stasik and Wendt-Potthoff, 2016; Siddique et al., 2012; Holowenko et al., 2000).

It is unclear if BML will evidence similar OCC importance and biogeochemical trajectory compared to current oil sands tailings ponds. BML has a deeper water cap (~10 m) compared to the typical < 5 m water cap associated with tailings ponds, which could support either thermal or chemical stratification and thus lead to biogeochemical zonation and the possibility of isolation of oxygen consumption within the deeper zone from upper waters. However, the dewatering of FFT is an exothermic process that will mix heat and salt into the overlying fresher water cap (Dompierre and Barbour, 2016). Whether these processes will lead to chemical stratification or destabilization of any potential thermal zonation that could occur has yet to be established. However, regardless of physical zonation, microbially active and diverse biogeochemical C, S, N and Fe cycling can be expected to affect net water cap $[O_2]$ through direct consumption and/or transformation of FFT-derived OCC mobilized into the water cap. Thus, the objectives of this study were to establish water cap (defined herein as the region extending from the water cap surface to the FFT-water interface (FWI)) physico-chemistry and geochemistry during early development in the first demonstration pit lake within the AOSR during the summer of 2015 and 2016.

2. Material and methods

2.1. Site description

BML is located on the Syncrude Canada Ltd Mildred lake lease, 40 km north of Fort McMurray, Alberta, Canada (Fig. 2). BML, consists of a mixture of fresh water and oil sands process water (OSPW; ~500 mg/L Cl^-) water cap circa 10 m in depth, covering an up to ~40 m layer of FFT (transferred from a tailings settling basin) in a 7 km^2 manmade lake (Fig. 2; Dompierre et al., 2016). Three permanent platforms, platform 1 (P1), platform 2 (P2) and platform 3 (P3) have been installed on the lake (Fig. 2). The three platforms serve as monitoring stations on BML, housing instruments such as weather stations and CTD and were the sites for all sampling completed in BML during the 2015 field season. Each platform was sampled approximately once per week from June 4 to August 31 in 2015, for a total of 43 sampling campaigns. For each sampling campaign, the physicochemical profile of the water cap (surface to FWI) was used to identify sampling depths, and a minimum of three depth-dependent water samples were subsequently collected from the water cap. As no statistical differences were observed in 2015 results for geochemical analytes from the three platforms (ANOVA, d.f. = 2, p-value > 0.05), in 2016, 35 sampling campaigns were carried out between July 6 and August 30 of 2016 (note the start of the field season was delayed due to wildfires in the Fort McMurray region) focusing on P1, enabling more depths to be