

EARLY STAGE WATER CAP OXYGEN CONSUMPTION TRENDS WITHIN THE
FIRST COMMERCIAL SCALE OIL SANDS PIT LAKE, BASE MINE LAKE.

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A Thesis Submitted to the School of Geography and Earth Sciences in Partial Fulfilment
of the Requirements for the Degree Master of Science in Earth and Environmental
Sciences

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Descriptive note:

McMaster university, School of Geography and Earth Sciences,

MASTER OF SCIENCE IN EARTH AND ENVIRONMENTAL SCIENCES

(2017) Hamilton, Ontario

TITLE: Early Stage Water Cap Oxygen Consumption Trends within the first Commercial Scale Oil Sands Pit Lake, Base Mine Lake.

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NUMBER OF PAGES: xi; 65

Lay abstract:

Bitumen extraction in Athabasca's oil sand region generates substantial amounts of waste including tailings that needs reclamation. Pit Lakes have been proposed as a reclamation strategy, where tailings are deposited into a mined-out pit and covered with a water cap. To achieve the reclamation goal, the lake must be able to sustain life and must therefore maintain an oxic water cap. The underlying tailings poses a threat to the oxygenation of the lake because of the constant release of compounds that have the potential to consume oxygen. Additional seasonal effects due to temperature change may further affect oxygen consumption by isolating parts of the water cap. In this thesis the results of two years of field sampling and analyses show that despite active oxygen consumption from tailings-released compounds, oxic status is achieved in the upper layer of the lake during summer and under ice.

Abstract:

Bitumen exploitation in Athabasca's oil sand region generates considerable amounts of waste including tailings and process-affected water that needs reclamation. Water capped tailings technology (WCTT) is currently being assessed as a potential wet reclamation strategy in the oil sand by the commission of Base Mine Lake (BML), the first commercial scale Pit Lake. BML consist of ~40m of fluid fine tailings (FFT) deposited in old mine pit covered with a ~10m water cap. In order to be successful, pit lakes must achieve the ecological roles of a natural lake, which includes colonization of the water by macrofauna therefore necessitating the water cap to be oxic. Due to the reductive nature of the tailings, oxygen consuming constituents (OCC) such as methane, sulfide and ammonia are released from the FFT into the water cap potentially posing a threat to the success of the reclamation. Additional seasonal effects such as stratification and ice cover may further affect oxygen consumption by isolating parts of the water cap therefore allowing accumulation of OCC. Results shows that BML thermally stratifies during the summer and winter and that oxygen persist throughout the water cap despite reaching low level at the FFT-water interface (FWI) during summer. Consistent with the FFT acting as a source of OCC, aqueous CH_4 and NH_4^+ concentrations were highest closer to the FWI, decreasing upwards into the water cap. Using linear regression CH_4 was shown to be an important OCC during the summer of 2015 while NH_4^+ and CH_4 were both important for the summer of 2016 highlighting the emergence of nitrification in BML. Detailed analysis of seasonal data revealed that accumulation of OCC below the hypolimnion depletes oxygen and favors methanotrophic activity. Results from both studies suggest that methanotrophs have a competitive advantage at low oxygen levels against nitrifiers.

Acknowledgments:

This thesis is the result of two years of research that was only made possible with the tremendous help from wonderful individuals at McMaster and at Syncrude Canada Ltd. First and foremost, I owe my deepest gratitude to Dr. Lesley A. Warren who helped me grow as a scientist by giving me unwavering guidance and encouragement all throughout the completion of my degree.

My deepest appreciation goes to the Aquatic Microbial Geochemistry lab members at McMaster including Patrick Morris, Daniel Arriaga, Sean Winland-Gaetz, David Camacho, Gerhard Jessen and Jiro Mori for their advice and moral support throughout this project. Special thanks to Tara Colenbrander Nelson who gave me valuable knowledge in the field and much needed life advice. I would also like to recognize the immense participation to the project from the Organic Geochemistry lab members Cory Goad and Dr. Greg Slater as well as their help revising manuscripts and Sian Ford for listening to my rants all the time.

I would like to express my sincere gratitude to Reclamation and Closure Research Group, Syncrude Canada Limited, for field sampling support and especially Tara Penner for her valuable advice in the development of this research and this manuscript. I would also like to offer my special thanks to the boat operators Christopher Beierlin and Richard Kao, the BML coordinator Janna Lutz, the field laboratory manager Mohamed Salem and the field leads Wendy Kline, John Arnold and Mike Arsenault for the immense help and support they provided all along this project. These people made the two summers of field work in Fort McMurray one of the greatest work experience of my life and I always felt at home within this amazing community.

My deepest heartfelt appreciation goes to my family for the unconditional love that supported throughout these two years of my thesis. Their support allowed me to carry out my project despite the difficult challenges that I encountered in 2015 and 2016. Thank you for helping me keeping my head up and pushing forward relentlessly.

Lastly I would like to acknowledge Syncrude Canada Ltd, COSIA, NSERC (CRDPJ 488301-15) and CREATE Mine of Knowledge for funding this research.

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List of Abbreviations and Symbols:

$\Sigma\text{H}_2\text{S}$: Sum of sulfides (H_2S , HS^- and S^{2-})

AOSR: Athabasca's oil sand region

BML: Base Mine Lake

CH_4 : Methane

Chl-a: Chlorophyll a

DOC: Dissolved organic carbon

Fe^{2+} : Iron (II)

Fe^{3+} : Iron (III)

FFT: Fluid fine tailings

FWI: FFT-water interface (see FFT)

IOB: Iron oxidizing bacteria

IRB: Iron reducing bacteria

NA: Naphthenic acid

NH_4^+ : Ammonia

NO_2^- : Nitrite

NO_3^- : Nitrate

O_2 : Oxygen

OCC: Oxygen consuming constituent

OSPW: Oil sand process-affected water

SO_4^{2-} : Sulfate

SOB: Sulfur oxidizing bacteria

SRB: Sulfate reducing bacteria

TOC: Total organic carbon

Declaration of Academic Achievements:

This thesis is the work of Florent Frédéric Risacher for the partial fulfilment of the requirements for the degree Master of Science in Earth and Environmental Sciences. Chapter 3 is a manuscript that has been submitted to a peer review journal while chapter 4 is currently being review to undergo the same process. Therefore, parts of this thesis was accomplished thanks to the following contributors and their contributions:

Lesley A. Warren: Conceived the original project goals, contributed to results generation and greatly helped with the writing and reviewing process for the manuscripts (chapter 3 and 4).

Patrick K. Morris: Participated in the gathering of data during the field work season of 2015 and 2016.

Daniel Arriaga: Participated in the gathering of data during the field work season of 2015 and 2016.

Corey Goad: Performed all methane analysis.

Tara Colenbrander Nelson: Helped with the planning and execution of the fields season especially during the winter of 2017.

Gregory F. Slater: Reviewed the chapter 3 manuscript before submission.

Tara Penner: Reviewed chapter 3 manuscript before submission and reviewed this thesis.

Chapter 1: Introduction

1.1 Oil sands bitumen extraction and tailings generation

Athabasca's oil sand region (AOSR) located in northern Alberta is the third largest oil reservoir in the world with a total of 1.7 trillion barrels of bitumen over an area of 142 000 km² (Alberta Energy, 2013). The mining operations consist of surface mining the oil sands ore and then extracting the bitumen using a warm water extraction process. This process generates large volumes of mine tailings that are discharged in large reservoirs called tailings ponds. These tailings consist of a mixture of sand, silt, clay particles, residual bitumen (0.5-5%) and oil sand process-affected water (OSPW) (Chalaturnyk et al, 2002). The tailings ponds allow some of the larger particles in the tailings to settle so the water can be recovered for further extraction. Fluid fine tailings (FFT) are a slightly saline (1/15 sea water) fluid mixture made up of the slowly settling clay particles left after the coarse sand particles have settled out, with a solids content of 25-35 wt% solids (Penner & Foght, 2010). The small particle size of the clays, and the chemistry of the FFT porewater makes the settling of particles minimal even over decades (MacKinnon, 1989). Currently, Athabasca's oil sand region holds the largest tailings facilities in the world with volumes exceeding 700 million m³ which creates an important need for safe storage and isolation of the fluid fine tailings (FFT) for the reclamation of the landscape.

1.2 Water capped tailings technology

Water capped tailings technology is currently being assessed as a reclamation strategy for the oil sands with the commission in 2012 of Base Mine Lake (BML), the first commercial scale pit lake in the industry. BML consist of an old mined-out pit filled with 30 to 60m of fluid fine tailings (FFT) transferred from out-of-pit settling basins after densification over the past decades (Figure 1-1). The FFT was then covered with a water cap of about 7m composed of a mixture of fresh and oil sand process-affected water (OSPW). (Westcott, 2007). As the FFT continued to slowly densify, the FWI became lower, and the water cap reached 9-10m in 2016. The goal is to separate the tailings from the environment by isolating them under the water cap with no further discharge of FFT (Boerger et al. 1992, Westcott & Watson, 2007). In the long run, sedimentation associated with natural lake processes would further isolate the FFT by slowly burying them. Ultimately, the goal of a pit lake is to assume the role and function of a natural lake and to become integrated into the local watershed (Charette et al., 2012). In order to behave as such, BML must assume the same ecological functions as a natural lake such as allowing the establishment of a basic food chain in the water cap i.e. colonization of invertebrates

and zooplankton. In 2007, approximately 27 pit lakes were planned in the AOSR and as the development of mining operations extends, more are in underway (Westcott, 2007).

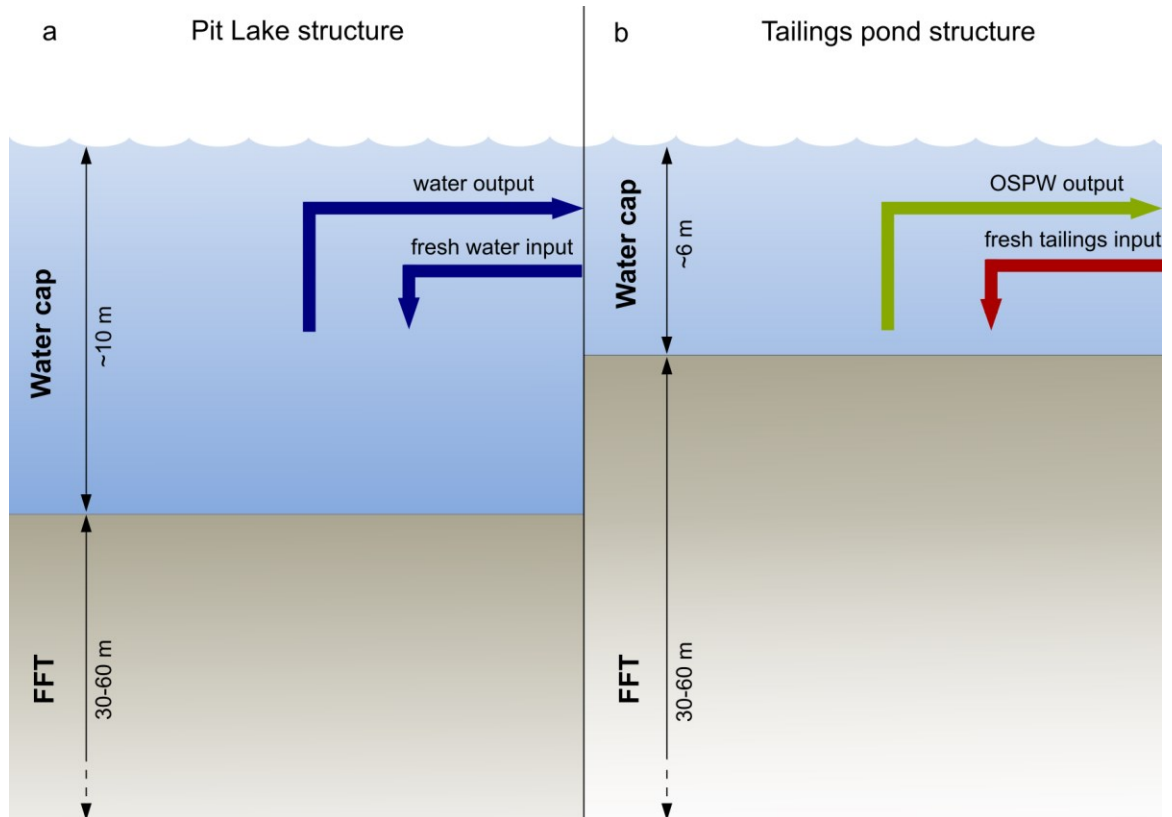


Figure 1-1: Pit lake structure comparison to tailings ponds.

1.3 Water capped tailings technology in metal mining

Water capped tailings technology has been widely used in the metal mining industries for almost a century (Castro and Moore, 2000). Similar to WCTT in the oil sands, abandoned mine pits are filled with overburden rocks and tailings from the mining operations and are then capped with fresh water to act as a natural lake (Castro and Moore, 2000). Despite the similarities in the practices, the distinct nature of the tailings in metal mining create problems that are specific to the industry. One of these is the concern for acid mine drainage (AMD) which is the acidification of the water cap by the oxidation of sulfides present in the tailings (Gammons et al., 2009; Fisher and Lawrence, 2006; Neil et al., 2009). Other problems such as metal release and metal contamination has also been associated with coal and metal mining pit lakes (Miguel-Chinchilla et al., 2014; Levy et al., 1997). However, because of the extensive use of pit lakes in the last century these concerns have been extensively addressed (Frömmichen et al., 2004; Costa et al., 2005;

Christensen et al., 1996) and improvements made such as isolation of the tailings from the oxic water cap to avoid sulfide oxidation (Castendyk et al., 2015). The success of pit lakes and WCTT has driven the oil sands industries to investigate this solution for the application to reclamation of oil sands tailings.

1.4 End-Pit Lakes challenges

In comparison to metal and coal mining, WCTT presents new complex challenges mainly associated to the composition and nature of the tailings. As mentioned above, the settling of particles in the FFT is very slow thus hindering the separation and isolation of the tailings from the water cap (MacKinnon, 1989). In order for BML to be successfully reclaimed, an oxic water cap must develop to support the establishment of full aquatic ecosystem. However, there are many problems that could prevent the oxygen input (i.e. diffusion from atmosphere, rain, etc.) to be greater than the oxygen consumption in BML. These concerns are due to the reductive nature of the FFT which releases reduced compounds in the overlying water cap that could in turn consume oxygen either abiotically or by microbial consumptive processes (Holowenko et al., 2000; Stasik et al., 2014; Chen et al., 2013; Ramos-Padrón et al., 2010). Studies of geochemical cycling of oil sands tailings ponds have identified two main constituents that are of high importance for oxygen consumption: CH_4 and $\Sigma\text{H}_2\text{S}$ (Chen et al., 2013; Holowenko et al., 2000; Penner and Foght, 2010). Moreover, high concentrations of NH_4^+ have also been found but have had no proven contribution to the oxygen consumption, potentially because of naphthenic acid toxicity (Misiti et al., 2013). It is therefore expected that these three compounds could be significant oxygen consuming constituent (OCC) in BML. Microbial studies also identified a diverse array of microbial communities that play a large role in the geochemical cycling in tailings ponds, some of which are methanogens, methanotrophs, sulfate reducing bacteria and sulfur oxidizing bacteria (Foght et al., 2017; Penner and Foght, 2010; Foght et al., 1985). Moreover, the physical limnology of the lake could play an important role in limiting or enhancing the oxygen consumption from the oxidation of reduced compounds. Indeed, the dewatering of the FFT releases latent heat stored in the FFT to the overlying water as well as salt from the extraction process that could potentially disturb or help the stratification of the system (Dompierre and Barbour, 2016; Westcott, 2007). A stratified system would limit the consumption of oxygen by further isolating the upper part of the water cap from the FFT and the release of reduced compounds. Lastly, the seasonal effect of freeze/thaw and wind induced mixing will further influence potential consumptive processes by either limiting oxygen supply (ice on during winter) or enhancing exchange between the FFT and the water cap (mixing events).

1.5 Methane

Methane is a simple organic compound composed of one carbon atom and four hydrogen atoms. Under ambient conditions methane is a gas but it can dissolve in water with a saturation in aqueous solution of 1.4 mM. The processes associated with methane cycling are all controlled by microbial pathways. In natural environments and tailings ponds, methane is formed by organisms called methanogens and its consumption is carried out by methanotrophs.

Methanogens are anaerobic microorganisms responsible for the production of methane. They are mainly composed of archaea that present two distinct pathways for the production of methane. The acetoclastic methanogens are using acetate as an electron donor and are splitting it into methane and CO₂. The hydrogenotrophs, on the other hand, are using H₂ as an electron donor to reduce CO₂ to CH₄ (Liu and Whitman, 2008). Other pathways such as methylotrophy, the splitting of methylated C1 compounds into methane and other products (H₂O, CO₂, NH₃, ...), exist to a minor extent or occur in specific environments such as hypersaline conditions (Potter et al., 2009). A common feature of methanogens is their need for simple substrate, either acetate or H₂, which are not usually abundant because of their rapid uptake by different microbes. Methanogens, therefore, rely on syntrophic associations, and more specifically on fermenting bacteria to degrade complex organic carbons such as sugars and lipids into simple two carbon molecules and hydrogen (Schink, 1997). The reduction of the partial pressure of hydrogen by the methanogens' consumption allows the fermentation metabolism to stay favorable. This is especially important in wet lands where a large portion of the methane produced comes from syntrophic hydrogenotrophs and fermenting microbes (Bridgeham et al., 2012). In the oil sand regions, methanogens have had a lot of attention, especially because of the sudden increase of activity and methane generation in tailings ponds years after their creation (Penner and Foght, 2010). Bioreactor studies show that methanogenesis becomes the dominant metabolism in tailings pond sediments after 300 days (Chi Fru et al., 2013). This delay is possibly due to the slow rise of syntrophic association between methanogens and fermentative bacteria that cannot use as efficiently simple organic carbon where other anaerobic metabolisms can. This factor is important because methanogens/fermenters associations would have an advantage in consuming complex carbon that cannot be degraded by other anaerobic organism. In older tailings, labile organic carbon is likely to have already been consumed, leaving only complex compounds such as BTEX (benzene, toluene, ethylbenzene, and xylenes) and naphthenic acids. Syntrophic associations of methanogens and fermenters have been shown to degrade BTEX, alkanes and naphtha compounds in oil sands tailings ponds (Siddique et al., 2012). It is therefore expected that with age, tailings pond sediments would become methanogenic, enhancing the production of methane in the FFT (Figure 1-2).

The methane produced in the sediments can move up and reach the oxic sediment-water interface. The presence of methane and oxygen can induce the activity of methanotrophs, which oxidize CH_4 into CO_2 . Their presence has been shown in surface waters of tailings ponds (Saidi-Mehrabad et al., 2013) which make them potentially active throughout the whole water cap when oxygen is present. This could be a problem for pit lakes since methanotrophs could quickly deplete the oxygen (Figure 1-2). Fortunately, anaerobic methanotrophs could prevent this by consuming most of the methane before it reaches the oxic water-sediment interface (Figure 1-2). In wetlands, up to 90% of the methane produced can be reduced by anaerobic methane oxidation (Bridgham, 2013). A variety of terminal electron acceptors could be used, but sulfate is a good candidate in this case, not only because this mechanism has been shown to occur in a variety of environment (marine, hydrothermal, terrestrial, etc...) (Knittel and Boetius, 2009), but also because sulfate is abundant in oil sands process-affected water.

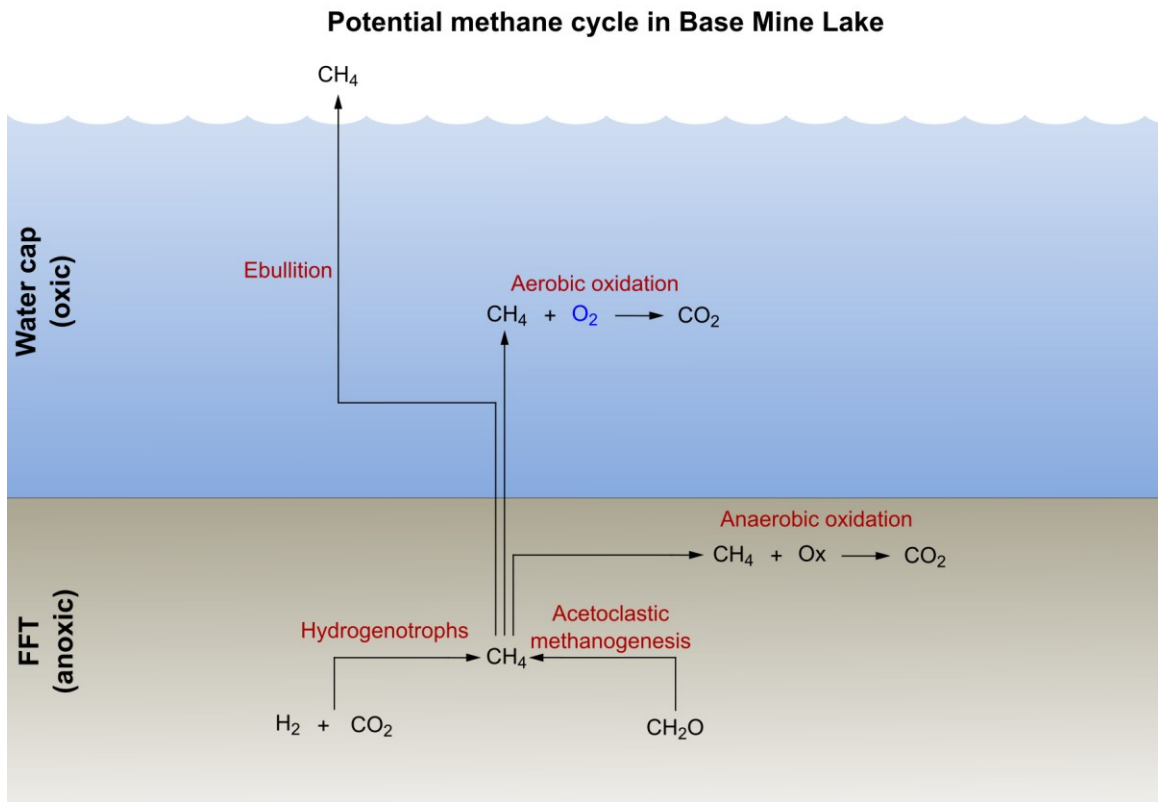


Figure 1-2: Potential pathways for methane cycling in BML.

1.6 Sulfur cycle

Sulfide (S^{2-}) is a reduced form of the sulfur ion and can be present in aqueous solution under three forms S^{2-} , HS^- and H_2S . The speciation of the ion will depend on the pH of the water, under circumneutral pH (~ 7) half of the sulfide is present as hydrogen sulfide ion (HS^-) while the other half is hydrogen sulfide (H_2S). It is only above pH 11 that sulfide (S^{2-}) starts to form from HS^- . It is also important to note that H_2S is volatile and tends to move from aqueous solution to gas form. Sum of H_2S (ΣH_2S) is used to represent the sum of all three forms of sulfide in solution regardless of the fractionation between species. In natural lakes, sulfide is only found in anoxic environments because of the rapid abiotic oxidation in presence of oxygen. Sulfide is produced by chemoheterotrophic microbes called sulfate reducing bacteria (SRB), or sulfate reducers (Figure 1-3).

Sulfate reducers are microbes that are using sulfate as a terminal electron acceptor coupled with oxidation of simple organic carbon molecule (I.e. Acetate, lactate, butyrate, etc.) or oxidation of hydrogen (H_2) to produce energy in anaerobic environments (Muyzer and Stams, 2008). Similarly to methanogens, sulfate reducers rely on the presence of other microorganisms to provide some substrates such as hydrogen and acetate. However, they do not seem to create syntrophic relationships. This may be due to their capability to use electron acceptors other than sulfate, and their possible fermentative metabolism (Muyzer and Stams, 2008). Depending on the pH, S^{2-} , HS^- or H_2S will form as an end-product of sulfate reduction. Nonetheless, in most systems (circumneutral) the main speciation would be HS^- . Unlike H_2S , which is gaseous and escape from the water, HS^- dissolves in the water. This can be problematic as it is very reactive and spontaneously reacts with oxygen to abiotically oxidize and form sulfate. This has been observed in tailings ponds and microcosm experiments where the depletion of oxygen has been attributed to the production of reduced sulfur compounds from anoxic sediments (Chen et al., 2013). Similarly to tailings ponds, the risk for rapid oxygen depletion in pit lakes is important because of the potential production of reduced sulfur compounds from the high sulfate concentration derived from process-affected water (Stasik et al., 2014). However, it is important to note that the reduced sulfur compounds will not always reach the aerobic layer of the sediments to react with oxygen (Figure 1-3). An experiment by Salloum et al. (2002) showed that tailings ponds amended with sulfate were also producing acid volatile sulfide (AVS) in the sediments which encompasses sulfur bound to different metals such as iron that precipitate and prevent the release of HS^- . This reduced speciation of sulfur has been proven to be an important sink of sulfide in marine water (Rickard and Morse, 2005) and could prove as important in tailings ponds and pit lakes.

Sulfur oxidizers are microbes that oxidize inorganic reduced sulfur species such as sulfur (S^0), thiosulfate ($S_2O_3^{2-}$) or sulfide (S^{2-}) to sulfate (Friedrich, 1998). This reaction is mostly coupled with oxygen reduction, but other terminal electron acceptors such as nitrate can be used (Burgin et al., 2012). Since reduced sulfur species are easily abiotically

oxidized in the presence of oxygen, sulfur reducers must be present in a micro-oxic or anoxic environment depending on the electron acceptor. In tailings ponds, sulfur oxidizing bacteria (SOB) and sulfate reducing bacteria (SRB) abundances were strongly correlated where the zone of highest SOB corresponded to the zone of highest SRB (Stasik et al., 2014). This region of production/consumption was in the sediments where oxygen was present in trace amounts or completely absent. This shows that sulfur oxidizers have the potential of consuming the sulfide produced by the sulfate reducers, potentially mitigating the diffusion from the sediments in the water cap and thus limiting the oxygen depletion from abiotic $\Sigma\text{H}_2\text{S}$ oxidation (Figure 1-3).

Potential sulfur cycle in Base Mine Lake

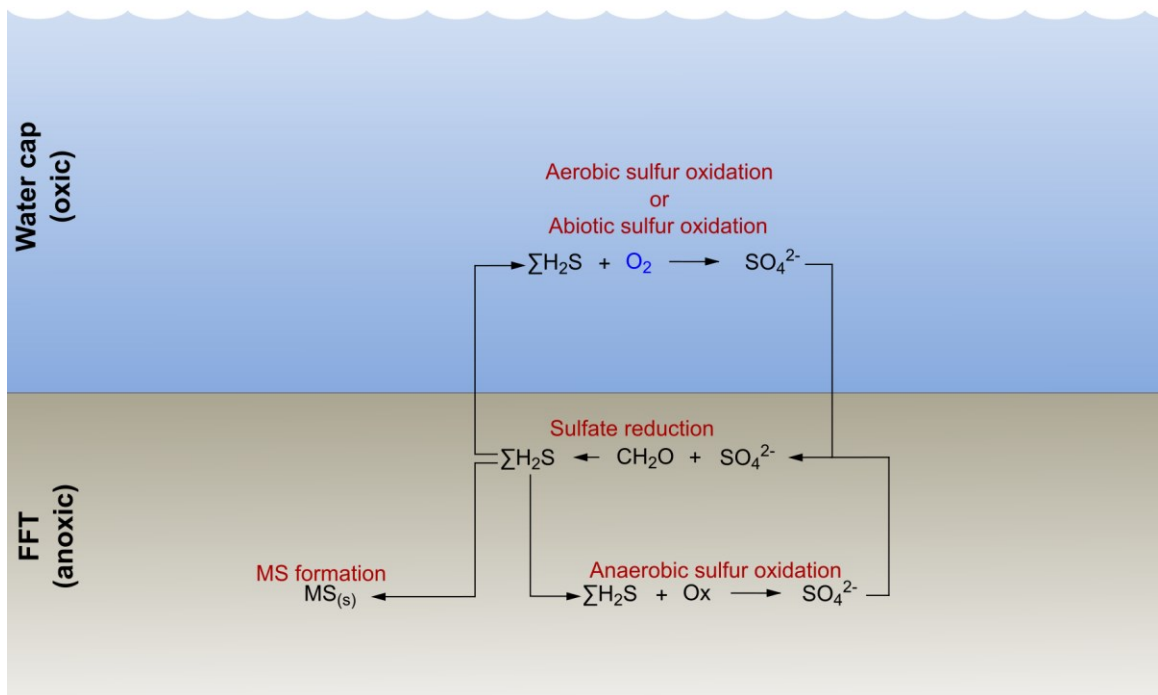


Figure 1-3: Potential pathways for sulfur cycling in BML. $\text{MS}_{(s)}$ stands from metal sulfide compounds.

1.7 Nitrogen cycle

Nitrogen can exist under a redox state from -5 (NO_3^-) to +3 (NH_4^+) with multiple intermediate in between, that can either be oxidized or reduced. In addition to various nitrogen species acting as an electron donor, acceptor or both (I.e. NO_2^-), nitrogen is required as a nutrient in the form of NH_3 which can be fixed from nitrogen gas fixation or

lost through reduction to nitrogen gas. For these reasons it is sometimes complex to understand all the processes affecting nitrogen in a system, however all of these processes are purely microbial which allows to infer some of the potential pathways by looking at some of the nitrogen species present in the water cap (Figure 1-4). The three main nitrogen species present in an aquatic system are ammonia (NH_4^+), nitrite (NO_2^-), and nitrate (NO_3^-). N_2 fixation has been shown to occur in tailings ponds (Collins et al., 2016) while other pathways have not yet been shown to contribute the redox cycling. A study from Misiti et al. (2013) underlines that naphthenic acid toxicity inhibits microbial nitrification which could explain why this pathway did not play an important role in the geochemical cycle of tailings ponds. Nonetheless, high level of NH_4^+ (~500 μM) has been shown to occur in tailings ponds which could partake in oxygen consumption through nitrification in BML since NA levels might not be as high as tailings ponds (Stasik et al., 2014).

Nitrifiers or ammonia oxidizers are chemoautotrophic microbes that use NH_4^+ as an electron donor and oxygen as an electron acceptor (Prosser; 1989). This pathway, called nitrification, is used by nitrifiers to fix inorganic carbon. Since this metabolism needs oxygen to proceed, nitrification can only be carried out in aerobic environments and thus present a risk for oxygen depletion in the BML water cap. However, anaerobic ammonium oxidation (anammox) also has the potential to oxidize ammonia to nitrogen gas using nitrite as an electron acceptor under anoxic conditions (Ding et al., 2013). This metabolism has been shown to account for 50% of nitrogen loss in marine ecosystem (Kuypers et al., 2003) while in fresh water it accounted for up to 20% of nitrogen loss (Zhu et al., 2013). Anammox has therefore the potential to be an important factor in limiting the consumption of oxygen through aerobic oxidation of ammonia in BML.

Microbial reduction of NO_3^- coupled with the oxidation of organic carbon can be carried out through dissimilatory nitrate reduction to ammonium (DNRA) where NH_4^+ is produced or through denitrification where N_2 gas is produced (Canfield et al., 2010). Both these pathways use NO_3^- or NO_2^- as an electron acceptor and thus have to be carried out in anaerobic environments. Assimilatory nitrate reduction is also a metabolism that reduces NO_3^- to NH_4^+ for metabolic assimilation and functions but is mostly carried out when NH_4^+ is limited (Sørensen, 1978). Therefore, only DNRA is a concern for BML since it has the potential to re-cycle the nitrogen back to NH_4^+ which could further drive the depletion of oxygen.

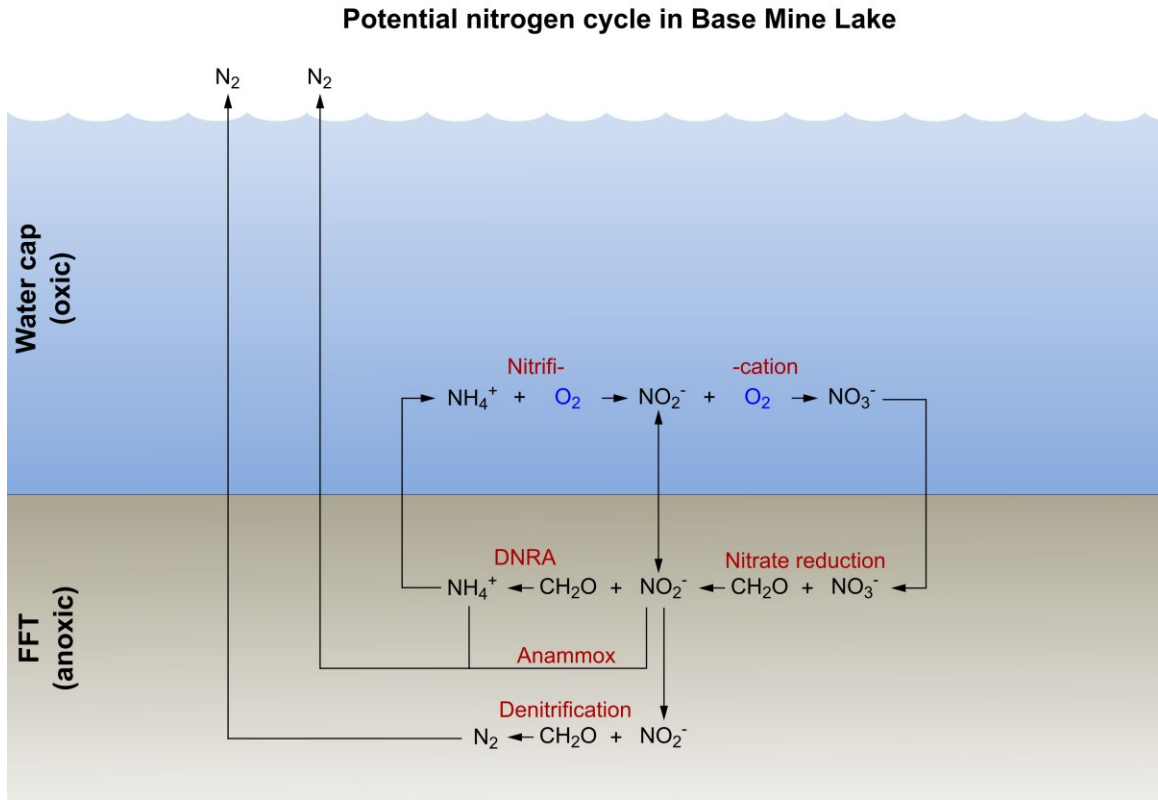


Figure 1-4: Potential pathways for nitrogen cycling in BML.

1.8 Physicochemical properties

Active AOSR tailings ponds are usually less than 6m in depth and therefore do not present a thermal stratification pattern. The constant addition of warm OSPW and tailings also contribute to the lack of stratification by always disturbing any potential thermal profile that could develop (Lawrence and al., 2016). On the other hand, BML now has a deeper (9-10m) water cap that could allow thermal stratification to take place which could in turn affect the oxygen distribution by preventing the distribution of oxygenated water from atmospheric inputs to the full extent water cap. During the summer, the heating of the surface layer of the water cap by solar radiation has the potential to create a thermal stratification by creating a warmer and lighter layer of water called epilimnion. The colder, denser bottom water layer called hypolimnion is thus isolated from the epilimnion. The separation between both is the metalimnion where a sharp drop in temperature can be observed. This stratification pattern has the potential to prevent atmospheric diffusion of oxygen to reach the hypolimnion where we could therefore expect to see most of the OCC accumulate over the summer (Figure 1-5). However, one additional factor could come into play for the stratification patterns of BML: the de-watering of the FFT. Indeed, the water

released by the FFT contains salts from the extraction process (~1/15 of sea water MacKinnon, 1989) and heat coming from the legacy energy stored in the deposited tailings (Dompierre and Barbour, 2016) The salts could create a strong salinity gradient called halocline hence isolating the denser, saltier bottom water layer from the lighter, fresher top water layer. The salinity stratification would have the same effect on oxygen distribution as the thermal stratification, in fact both could co-occur, making the stratification stronger. Heat however would have the opposite effect by warming up the bottom water layer preventing the establishment of a thermal stratification (Figure 1-5).

In winter, BML freezes and the ice layer will reduce or completely prevent the atmospheric input of oxygen with the water. This means that a complete depletion of oxygen is possible, similarly to a winter fish kill that a natural lake could experience (Wetzel, 2001). The difference is that the oxygen would be consumed not because of the decaying organic matter but because of the OCC released by the FFT. Moreover, these compounds could accumulate below ice, further preventing any oxygenation of the water cap (Figure 1-5). Reverse stratification could however limit this accumulation by isolating the FFT below a denser 4°C layer of water that would sink compared to the rest of the water cap that would sit at 0 °C (Figure 1-5).

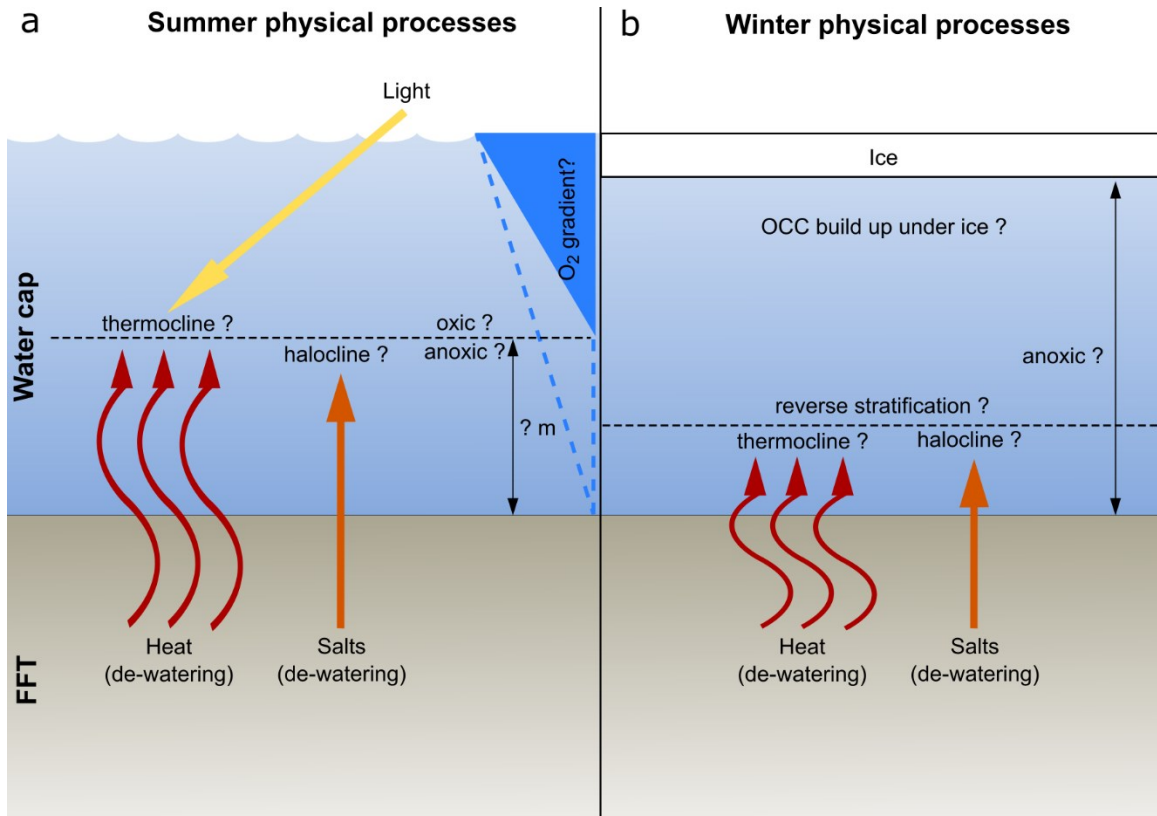


Figure 1-5: Potential stratification pattern and physico-chemical properties of BML.

1.9 Thesis objectives

Syncrude Canada Ltd has commissioned in 2012 the first commercial scale pit lake in the oil sands industry, Base Mine Lake, to assess the efficiency of water capped tailings technology (WCTT) as a reclamation solution. As this new strategy is being tested, it is unknown to what extent the fluid fine tailings (FFT) stored below the water cap can release reduced compounds that could affect the oxygen consumption of the lake. This poses a threat to the future of the reclamation by preventing the establishment of macrofauna and thus the evolution of the pit lake towards a natural ecosystem. Therefore, the research presented in this thesis will focus on the explaining the dynamics of oxygen consumption through two years in the early development of BML. The objectives are as follow:

- 1) Characterization of the physico-chemical and geochemical parameters of the BML water cap.
- 2) Identification of the main oxygen consuming constituent(s) (OCC)
- 3) Assessment of the OCC's effect on oxygen concentration over two years in the early development of the pit lake.
- 4) Characterization of the seasonal effect on the physico-chemical and geochemical parameters of the BML water cap.
- 5) Identification the factors changing the oxygen consumption dynamic between summer and winter in BML.

The first three objectives will be addressed in Chapter 3 while objectives four and five will be addressed in Chapter 4.

Chapter 2: Methods

2.1 Site description

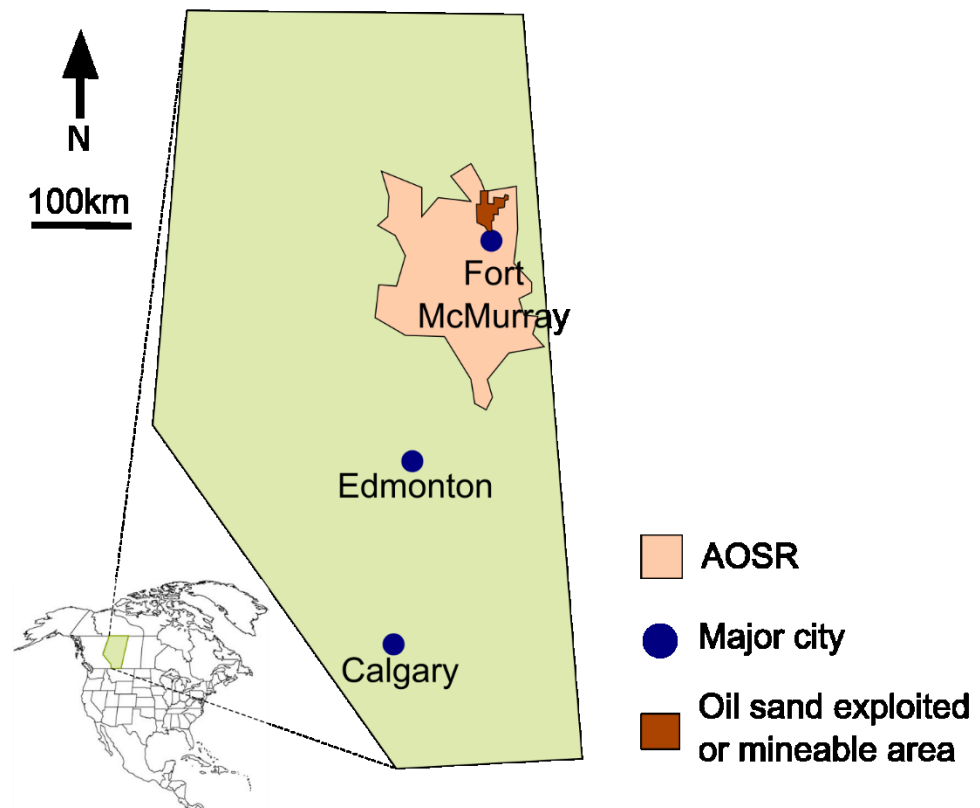


Figure 2-1: Map of Alberta and the AOSR (orange). The major cities in Alberta are represented by blue dots. The current exploitation of the oil sands and mineable area is represented by the brown area, in which BML is located.

The site studied for this thesis is Base Mine Lake (BML), located on Syncrude Canada Ltd. lease about 40 km north of Fort McMurray, Alberta (Figure 2-1). BML is a man-made lake that consist of an old mine-out pit (~60m) filled with fluid fine tailings (FFT) (~30-50m) and then capped with a 9-10m water cap composed of fresh water and OSPW. The dimensions are roughly 3.5 km by 2.4 km for a total area of 8.2 km². All the sampling done for this thesis has been done at one of the three platforms installed on the lake: Platform 1 (P1, Center of the lake), Platform 2 (P2, North-East) and Platform 3 (P3, South-West) (Figure 2-2). The lake was commissioned in 2013 which means the input of tailings was stopped, however the lake still has an inlet and outlet to regulate water level before the integration of the lake to the watershed. The water inlet is located close to the

docks on the south-west end of the lake while the outlet is located at the north-east end. All water input in BML comes from Beaver Creek reservoir located 300m south of the lake. The water of the lake was very murky in 2015 and 2016 with a lot of suspended particles of clay and silt that did not settle. On most quiet days, patches of residual oil can be seen on floating on the surface.

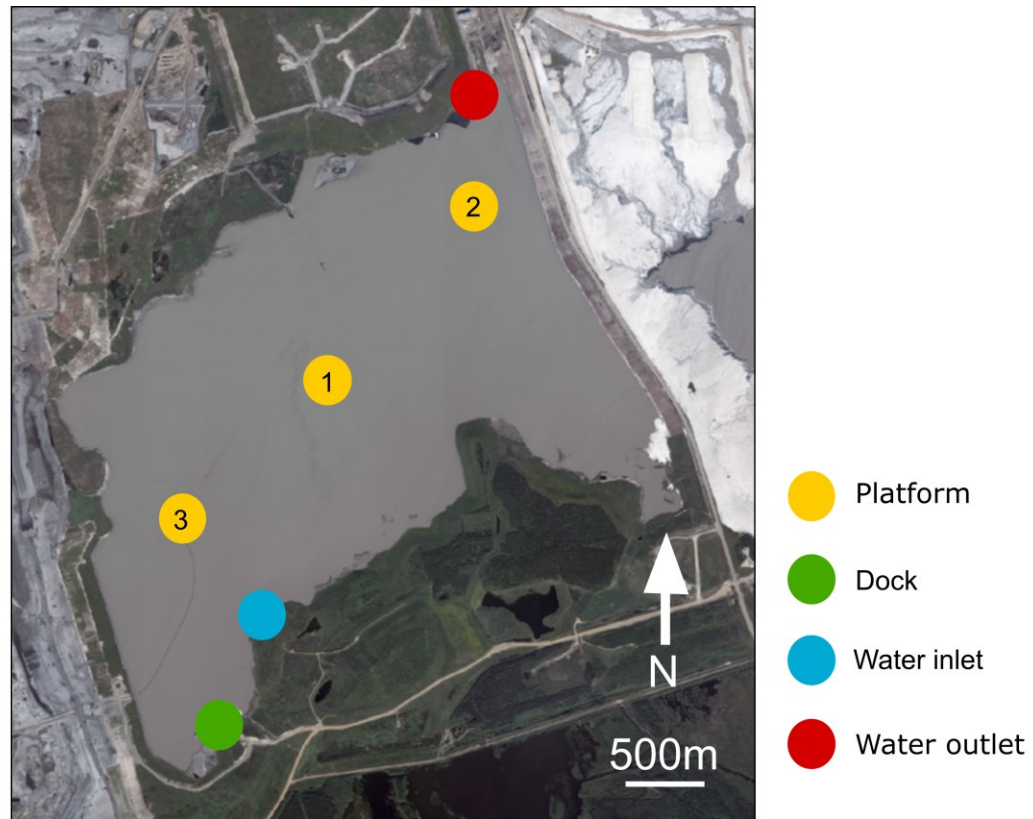


Figure 2-2: Aerial view of BML. The Platform (P1, P2 and P3) are represented by the yellow dots, the dock is represented as the green dot, the water inlet as a blue dot and water outlet as a red dot.

2.2 Field sampling



Figure 2-3: Photo of platform 1 on BML on which most of the data in 2016 was gathered.

All the data for this thesis was collected during three field campaigns: June to August 2015, July to September 2016 and February 2017. During the first field season from June 4th 2015 to August 31st 2015, BML was sampled approximately once a week or more alternating between one of the three platforms. A total of 43 sampling campaigns were carried out for which a physicochemical profile of the water cap and three water samples were collected. A minimum of three water samples were gathered for geochemical analyses at relevant depths using the information of water profile for that day. Sampling depths were chosen by picking depths with different oxygen concentration to reflect the potential geochemical zonation. All physicochemical profiles were produced by taking measurements every 50 cm through the whole water cap using a YSI Professional Plus 6-Series Sonde (YSI Incorporated). pH, temperature, dissolved oxygen, specific conductivity, ORP, turbidity and salinity was collected for each depth and each profile. Additional data from Golder Associates™ were used to fill in missing physicochemical data for May, June and September 2015. For the second field season from July 6th to September 2nd, a total of 36 sampling campaigns were carried out at platform one with only one sampling campaign at platform two and three. The focus on Platform 1 was due to the lack of significant difference in physicochemical and geochemical parameters (ANOVA, $p < 0.05$) for the year of 2015. This also allowed the sampling to be much more focus on collecting water for geochemical analyses at a higher depth resolution. An average of seven to eight water samples were collected weekly at Platform 1 in addition to the

physicochemical profile. Additional physicochemical data from Hatfield Consultants™ in September was used to fill in missing data for the fall. Delay in the field season in 2016 was caused by the Fort McMurray wild fire which prevent all field work activity and data collection from early May to early July. The last field season was February 14th and 15th 2017 and only two physicochemical profiles and one geochemical profile of eight depths were collected under ice. The sampling campaign was carried out beside platform one on the frozen lake were the usual sampling would have been performed on the boat for the summer. An ice Auger was used to drill through an average of 50 to 85 cm of ice to be able to collect water. All depths were measured starting from the bottom of the ice under water.



Figure 2-4: Cutting ice at platform one for winter sampling on BML.

2.3 Geochemical sampling procedure

Water samples were retrieved on the boat or on the ice after collection using a Van Dorn (Figure 2-5) from the desired depth. Upon retrieval, a three-way stop cock valve was inserted into the Van Dorn tube for sampling water without opening the bottle to the atmosphere and thus avoiding oxidation of redox sensitive species and degassing of aqueous dissolved species. CH₄ was the first species sampled immediately after recovery of the Van Dorn using an acid-cleaned 60 mL plastic syringe (soaked for >8h in a 5% v/v HCl bath, rinsed 7 times with ultrapure water: 18.2 $\Omega\text{m cm}^{-1}$, Milli-Q, Millipore) by rinsing it three times with water directly from the three-way valve. 30 mL was then extracted and injected into a stoppered, vacuumed 60 mL serum bottle fixed with 3.7 mg of saturated HgCl₂ solution to avoid microbial oxidation of methane and then stored in the dark at ambient temperature until analysis back at McMaster University. Samples for $\Sigma\text{H}_2\text{S}$ were then extracted in an acid-clean plastic syringe pre-spiked with reagent 1 (stabilizing Reagent 1, 60% w/w H₂SO₄) and filtered (0.45 μm , Acrodisc with Supor Membrane, 25 mm diameter, Pall Life Sciences, Mississauga, Canada) in 15 mL polypropylene tube for colorimetric analysis via methylene blue analysis (Hach Method 8131) using a HACH portable spectrophotometer (Hach DR/2800 or HACH DR/2700 spectrophotometer, HACH Company, Loveland, CO, USA). $\Sigma\text{H}_2\text{S}$ were conducted directly on the boat or on the ice to minimize as much as possible its oxidation (Figure 2-6). Collection of samples for Fe(II) and Fe(III) followed up using another 60 mL acid-clean plastic syringe to collect and filter water (0.45 μm) into a pre-spiked (2% v/v Optima grade HCl) 15 mL polypropylene tube. The samples were then stored in a cooler until the end of the sampling activity for the day and stored at 4°C until further analysis back at McMaster. TOC/DOC samples were collected using carbon-clean amber glass 120 mL bottles. Bottles were cleaned with detergent, rinsed with Milli-Q, then ethanol, and placed in a 10% HCl bath for >8 hours. After seven rinses with Milli-Q water, bottles were placed in a muffle furnace at 450°C for 8h to remove any residual carbon. Lids were rinsed with a 1:1:1 mixture of dichloromethane, hexane, and methanol and allowed to evaporate. In the field, each bottle was rinsed twice with sample before filling and then frozen at -20°C until filtration for dissolved organic carbon (DOC) characterization in the laboratory back at McMaster. Finally, a 1L sample was collected in an acid-clean Nalgene bottle for SO₄²⁻, NO₃⁻, NO₂⁻ and NH₄⁺ analyses and stored on ice until on water activities were finished for the day. The samples were then filtered using a 0.45 μm Acrodisc filter (32 mm diameter, Pall Life Sciences, Mississauga, Canada) in a clean 50 mL polypropylene tube and stored at 4°C until analysis in the field laboratory at Mildred Lake.



Figure 2-5: Van Dorn used to collect water for all geochemical sampling.



Figure 2-6: Florent Risacher carrying out sulfide analysis aboard the boat on BML.

2.4 Laboratory analyses

Laboratory analysis for SO_4^{2-} , NO_3^- , NO_2^- and NH_4^+ were performed in the field laboratory set up at the environmental research complex on Syncrude site at Mildred Lake by spectrophotometry. Filtered water samples were pipetted using a 5 mL pipette into a polypropylene 15 mL tube to be diluted by a factor of two (NO_3^- and NO_2^-) or five (SO_4^{2-} and NH_4^+) by adding ultra pure water ($18.2 \Omega\text{m cm}^{-1}$, Milli-Q, Millipore). Three replicates were analysed per species using a HACH DR/2800 or HACH DR/2700 spectrophotometer

(HACH Company, Loveland, CO, USA). USEPA method 8051, 8171, 8507 and 8155 from HACH Company (Loveland, CO, USA) were used to analyse for SO_4^{2-} , NO_3^- , NO_2^- and NH_4^+ respectively. All methods consist of a powder pillows reagent added to the 15 mL tube containing a pre-diluted 10 mL samples to react with the analyte in order to be read at a specific wave length after reaction (Figure 2-7). A new set of standard curves were produced a maximum of one month prior or after a new sample batch were run to ensure accuracy.



Figure 2-7: Ammonia analysis following the HACH method 8155.

The dissolved iron (II) and iron (III) were analyzed using the modified methods from Viollier et al. (2000) at McMaster University. The protocol uses the reaction between ferrozine (monosodium salt hydrate of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-p,p'-disulfonic acid) and iron(II) to form a complex that can be measured using a spectrophotometer at an wavelength of 562 nm. The method is a sequential method that measures iron(II) in the initial sample before reducing the iron (III) to iron (II) to be measured therefore determining the concentration of both using standard curves. A new set of standard curves were produced a maximum of one month prior or after a new sample batch were run to ensure accuracy.

The CH₄ analysis were performed at McMaster University by Corey Goad. Prior to sample analysis each serum bottle containing the sample was brought to atmospheric pressure through addition of high purity helium (Alphagaz 99.999%). CH₄ was then analyzed through withdrawal of 1 mL of gaseous headspace and run on a SRI-GC (Model 8610C) equipped with a 3' (1m) silica gel column and an FID (Flame ionization detector). All samples were run in triplicate, with intervening standards to ensure sample reproducibility.

Samples for carbon analysis were thawed and immediately filtered with a syringe-driven 0.7µm GF/F glass microfiber filter unit (13mm, GE Life Sciences). The filtrate was analyzed for TOC on a Shimadzu TOC-L Total Organic Carbon Analyzer with an autosampler ASI-L (Mandel Scientific, Guelph, Ontario, Canada) using the 680°C combustion catalytic oxidation method as per manufacturer recommended protocols. Particulate organic carbon and inorganic carbon were measured on the 0.7µm filters by combustion in the solid sampler SSM-5000A attachment for the Shimadzu TOC-Analyzer. Four to seven replicates were analyzed for all constituents. All samples were compared against a corresponding standard curve for either total C or inorganic C with a correlation value (R²) of 0.99 or higher. New standard curves were made prior to each analysis. Organic carbon values were obtained by subtracting the inorganic C values from the total C values. Dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) were analyzed on each sample.

2.5 Statistical analyses

All Figures and statistical analysis were performed under R studio (Version 1.0.143 – © 2009-2016 RStudio, Inc.) using the R-core base version 3.3.2 to 3.4.0 (R Core Team, 2017). A list of all packages used can be found in Table 2-1. All statistical analyses significance were tested using an alpha level of 0.05.

Table 2-1: Packages used for the analysis and figures

Package	Version	Description	Authors
akima	0.6-2	akima is a list with components x, y and z which represents a smooth surface of z values at selected points irregularly distributed in the x-y plane.	Hiroshi Akima, Albrecht Gebhardt, Thomas Petzold and Martin Maechler
car	2.1-3	Functions and Datasets to Accompany J. Fox and S. Weisberg, <i>An R Companion to Applied Regression</i> , Second Edition, Sage, 2011.	John Fox and Sanford Weisberg.
ggplot2	2.2.0	A system for 'declaratively' creating graphics, based on "The Grammar of Graphics". You provide the data, tell 'ggplot2' how to map variables to aesthetics, what graphical primitives to use, and it takes care of the details.	Hadley Wickham and Winston Chang
gridExtra	2.2.1	Provides a number of user-level functions to work with "grid" graphics, notably to arrange multiple grid-based plots on a page, and draw tables.	Baptiste Auguie and Anton Antonov
fields	8.15	Fields is a collection of programs for curve and function fitting with an emphasis on spatial data and spatial statistics. The major methods implemented include cubic and thin plate splines, universal Kriging and Kriging for large data sets. One main feature is any covariance function implemented in R code can be used for spatial prediction. Another important feature is that fields will take advantage of compactly supported covariance functions in a seamless way through the spam package.	Douglas Nychka, Reinhard Furrer, John Paige and Stephan Sain
pastecs	1.3-18	Regulation, decomposition and analysis of space-time series.	Philippe Grosjean, Frederic Ibanez and Michele Etienne

plyr	1.8.4	A set of tools that solves a common set of problems: you need to break a big problem down into manageable pieces, operate on each piece and then put all the pieces back together. For example, you might want to fit a model to each spatial location or time point in your study, summarise data by panels or collapse high-dimensional arrays to simpler summary statistics.	Hadley Wickham
unstackR	1.0	Split then merge a data frame by a factor with different length.	Florent Risacher

Chapter 3: The interplay of methane and ammonia as key oxygen consuming constituents in early stage development of Base Mine Lake, the first pilot Oil Sands pit lake

3.1 Introduction

The Athabasca Oil Sands region (AOSR) covers over 140,200 km² 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 & Foght, 2010). Clay particles in FFT remain in suspension and settle slowly over decades (MacKinnon, 1989). The large volume of oil sands 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 m³ (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 & 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 $\Sigma\text{H}_2\text{S}$ 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 et al., 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 $\Sigma\text{H}_2\text{S}$ 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). 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.

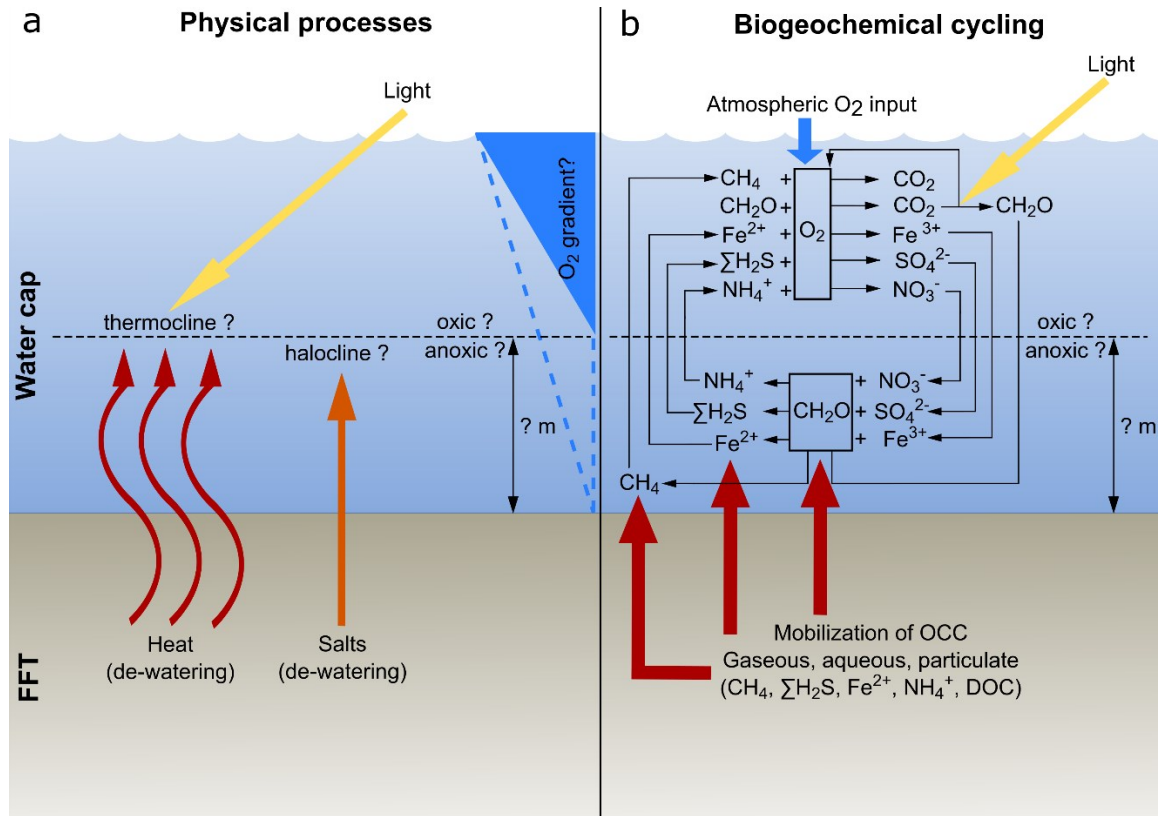


Figure 3-1: Schematic of potential water cap physical processes (a) and biogeochemical cycling associated with OCC mobilization (b) that can occur within an oil sand pit lake. A hypothetical oxic-anoxic zone is shown to occur within the water cap but depending on the extent of OCC mobilization and stratification pattern this region could be at the FFT-water interface (FWI).

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 CH₄ or ΣH₂S within FFT pore water (Holowenko et al., 2000; Stasik et al., 2014; Chen et al., 2013; Ramos-Padrón et al., 2010), this source of *oxygen consuming constituents* (OCC) could persist, precluding a positive developmental trajectory over substantial timescales. Indeed, ΣH₂S and CH₄ 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 (Figure 3-1; Quagraine et al., 2005, Westcott, 2007, Siddique et al., 2014). These compounds may be variably mobilized from the FFT into the overlying water

cap 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., 1985). 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 et al., 2010; Siddique et al., 2012, Foght et al., 2017). Over the last three decades, MLSB has developed from a primarily $\Sigma\text{H}_2\text{S}$ driven system in terms of oxygen consumption to now include CH_4 generated through microbial activity *in situ* (Foght et al., 1985; Sobolewski et al., 1992; Sobolewski et al., 1997). Interactions between methanogens and sulfate reducers have since been identified more widely in oil sands tailings 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 et al., 2012).

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 (~10m) compared to the typical <5m 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 $[\text{O}_2]$ 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.

3.2 Material and methods

3.2.1 Site description

BML is located on the Syncrude Canada Ltd Mildred lake lease, 40 km north of Fort McMurray, Alberta, Canada (Figure 3-2). BML, consists of a mixture of fresh water

and oil sands process water (OSPW; $\sim 500 \text{ mg/L Cl}^-$) water cap circa 10 meters in depth, covering an up to $\sim 40\text{m}$ layer of FFT (transferred from a tailings settling basin) in a 7 km^2 manmade lake (Figure 3-2; Dompierre et al. 2016). Three permanent platforms, Platform 1 (P1), Platform 2 (P2) and Platform 3 (P3) have been installed on the lake (Figure 3-2). 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 sampled per campaign (5-7 depths throughout the water cap compared to 3 depths in 2015).

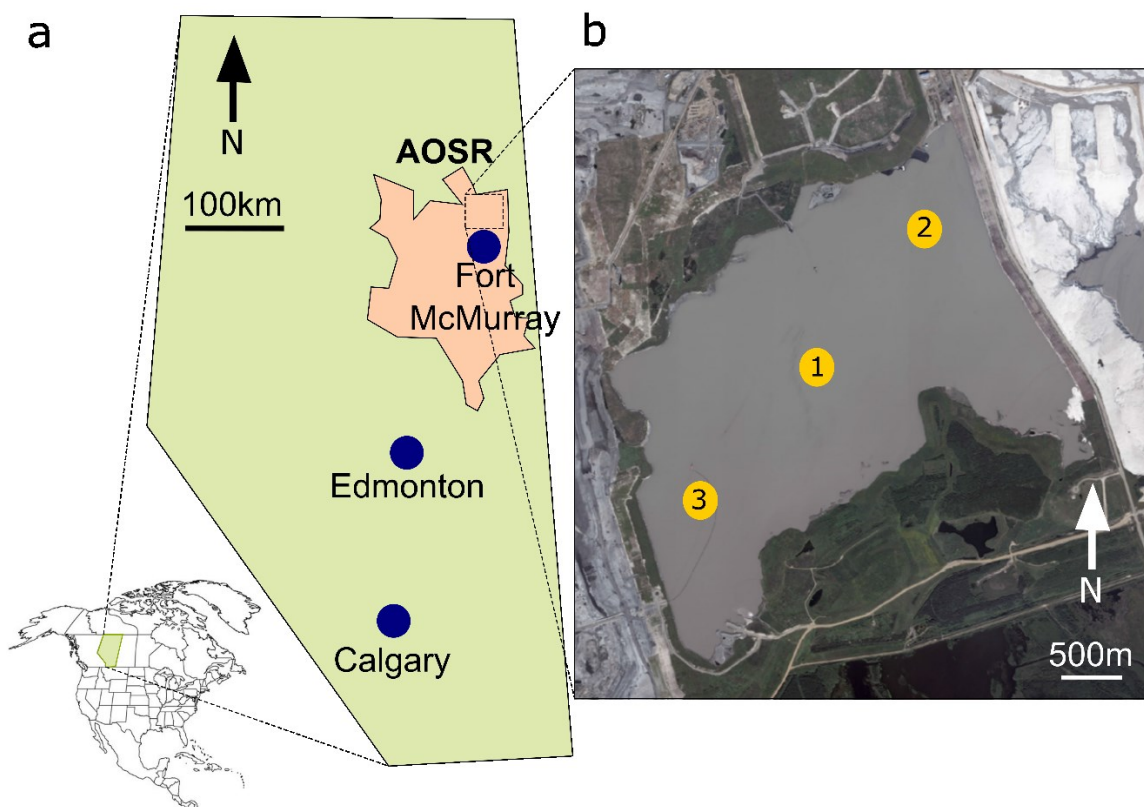


Figure 3-2: Location of AOSR (orange) in Alberta including major cities (a)(blue). Aerial photo of Base Mine Lake identifying the sampling sites (b) (yellow; platform 1, 2 and 3). Aerial photo, courtesy of Tara Penner.

3.2.2 Physicochemical Characterization of the Water Cap

For each sampling campaign, prior to water sampling, physicochemical profiling of the BML water cap (~9-10m of depth) was conducted. Profiles were collected at ~ 50 cm intervals from the BML surface to the FFT-water interface (FWI) at each platform for: pH, temperature, dissolved oxygen, specific conductivity, Oxidation Reduction Potential (ORP), turbidity and salinity (YSI Professional Plus 6-Series Sonde, YSI Incorporated). Additional YSI profiles provided from Golder Associates and Hatfield consultants for May, September and October in both years were incorporated into the results.

3.2.3 Sample Collection, Preservation and On Water Analyses

All sample collection, preservation and analyses followed well-established protocols developed in our research groups (Reid and Warren, 2016; Warren et al., 2016; Slater 2008). Briefly, all sampling equipment and sample containers were prepared by soaking in 5% (v/v) HCl for about 12 h followed by seven rinses with ultra-pure water (18.2 Ω m cm⁻¹, Milli-Q, Millipore) (inorganic analytes). Water samples were collected from three depths spanning the epilimnion, metalimnion and hypolimnion as identified from the physico-chemical profile for each sampling campaign using a 6.2L sampling Van Dorn (WaterMark, Forestry supplies). Upon retrieval of the Van Dorn to the boat, sample collection proceeded in the following order: CH₄, Σ H₂S, Fe²⁺, Fe³⁺, and a bulk water sample for NO₃⁻, NO₂⁻, NH₄⁺ and SO₄²⁻.

Samples for CH₄ were collected immediately upon retrieval of the sampling Van Dorn on the boat, by syringing 30 mL of sample directly from the closed Van Dorn via the embedded sampling tube, using a 3-way stop cock into a 60 mL plastic syringe. The water was then transferred by injection into a pre-evacuated 60 mL serum bottle (Wheaton) crimp sealed with a 20 mm chlorobutyl stopper (Bellco glass). The chlorobutyl stoppers were pre-treated by boiling in 1 M NaOH for one hour prior to use. The serum bottles were pre-treated with ~ 3.7 mg of saturated mercuric chloride solution to halt any microbial activity after sampling. Samples were stored refrigerated and subsequently analyzed upon return to McMaster University.

For Σ H₂S analyses, water samples were collected into acid washed plastic 60 mL syringes from the sampling Van Dorn sampling tube and filtered directly through 0.45 μ m sterile syringe filters (Supor membrane) into sample containers containing reagents to fix the Σ H₂S and analyzed via the methylene blue method directly on the boat using a HACH portable spectrophotometer (Hach DR/2800 spectrophotometer, HACH Company, Loveland, CO, USA). Samples for Fe²⁺ and Fe³⁺ were collected into acid washed 15 mL tubes and preserved by the addition of 2% v/v Optima-Grade hydrochloric acid and stored refrigerated until return to McMaster University for analyses.

A further sample was collected into a 1 liter, acid washed Nalgene bottle for SO_4^{2-} , NO_3^- , NO_2^- and NH_4^+ analyses and stored at 4°C until on water activities were finished for the day. These samples were stored refrigerated until analyses were performed either on site within the field laboratory or upon return to McMaster University.

3.2.4 Laboratory Analyses

Three to seven replicates were analyzed for all geochemical analytes. Field blanks (filtered and preserved ultrapure water on site) and process blanks were collected and analyzed for each analyte. Samples for ferrous and ferric iron were analyzed colorimetrically by a modified ferrozine method from Viollier et al. (2000) at McMaster University. CH_4 was analyzed following the modified method described by Lollart et al. (2006). The CH_4 was analyzed on an SRI GC (model 8610C) equipped with a 3' (1m) silica gel column and an FID (flame ionization detector) at McMaster University. SO_4^{2-} , NO_3^- , NO_2^- and NH_4^+ were analysed by spectrophotometry (Method 8051, Method 8171, Method 8507 and 8155; Hach DR/2800 spectrophotometer, HACH Company, Loveland, CO, USA) either in the field laboratory on site at Mildred Lake, or back at McMaster University.

3.2.5 Statistical Analyses

Differences of geochemical properties between platforms for 2015 were tested using ANOVAs to compare the means of each species individually, separated by zone. ANOVAs were also used to test for differences in mean CH_4 , NH_4^+ and $\sum\text{H}_2\text{S}$ concentration between layers. A paired t-test was used to compare mean concentrations of species between years, pairing by layers. Linear and multiple linear models were created to highlight trends in oxygen consumption by using the natural logarithm of the oxygen concentration as y and the natural logarithm of the concentration of NH_4^+ , CH_4 or both as x, separated by years. All statistical analyses (T-tests, ANOVA and models) were performed and figures produced using R studio (version 0.99.902, RStudio Team, 2015) working with R-base (version 3.3.2, R Development Core Team, 2008). A list of all packages used can be found in Table 2-1. Significance for all statistical analyses was set at an alpha value of 0.05.

3.3 Results and discussion

3.3.1 BML Water Cap Physicochemical Zonation

Contrasting typically shallower (i.e. < 5m) oil sands tailings ponds, which receive on-going FFT inputs (Wells 2011; MacKinnon 1989), the BML ~10m water cap thermally stratified in both summers investigated, with fall turnover initiating in mid-August (Figure

3-3). For both 2015 and 2016, a similar depth profile was observed with the epilimnetic region (0-4m; ~20-22°C) separated from the hypolimnion (6-9m; ~10-12°C) by a ~2m thick metalimnion (4-6m) (Figure 3-3). Similar trends in pH, turbidity (NTU), ORP (mV) and conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$) profiles were also observed for both summers (Table 3-1). Reflecting the alkaline nature of oil sands tailings, BML exhibited circumneutral water cap pH values, decreasing from 8.3 at the surface to 7.7 near the FWI (Table 3-1). Turbidity (NTU) showed a slight increase towards the FWI, with values of 131-145 NTU compared to the rest of the water cap (42-111 NTU). ORP (mV) and conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$) showed no depth dependence with similar values throughout the water cap (Table 3-1). ORP values were in the ~150 mV range and conductivity values averaged $2800 \mu\text{S}\cdot\text{cm}^{-1}$ across depth, site and sampling time (Table 3-1).

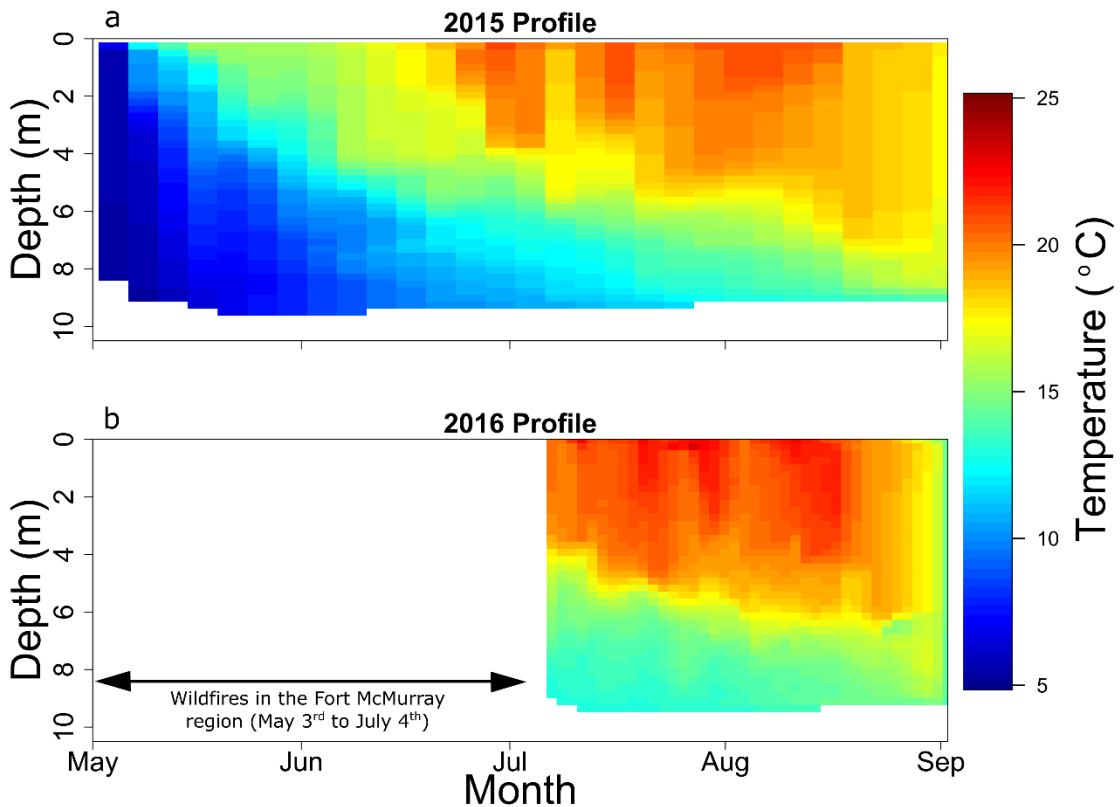


Figure 3-3 : Heatmaps showing thermal profiles for BML sampling platform 1 (P1) in 2015 (a) and 2016 (b). Thermal profiles collected on each sampling day ($N=454$ observations 2015) and ($N=494$ observations, 2016) are plotted on a temperature scale ranging between 5°C (blue) to 25°C (red). The data was linearly interpolated to create the heatmaps.

The deeper water cap and cessation of FFT inputs in BML resulted in higher oxygen saturation (70-90% maximum saturation in the epilimnetic region; Figure 3-4), than typically observed in active tailings ponds, where commonly $<5\%$ O_2 persists by 1m,

resulting in a largely anoxic water column and an anoxic FWI zone (Stasik et al., 2014). Further, BML depth dependent oxygen profiles were evidently constrained by thermal zonation (Figure 3-4). Oxygen concentrations decreased rapidly through the metalimnion from epilimnetic values of ~70% (2015) or 85% (2016) to ~10% saturation at the top of the hypolimnion (6m; 1 mg/L, 32 μM). Hypolimnetic oxygen concentrations also followed a similar profile in both years, decreasing to 1-5% saturation (0.25 mg/L, 8 μM) at the FWI (Figure 3-4). Mean epilimnetic chlorophyll a (chl-a) concentrations more than doubled from 1.9 to 4.8 $\mu\text{g/L}$ (Table 3-2, t-test, d.f. =4, $p < 0.05$) from 2015 to 2016 consistent with an increase in primary productivity leading to higher epilimnetic oxygen saturation from ~70% saturation (6.4 mg/L, 200 μM) in 2015, to ~85% saturation (8.1 mg/L, 250 μM) in 2016.

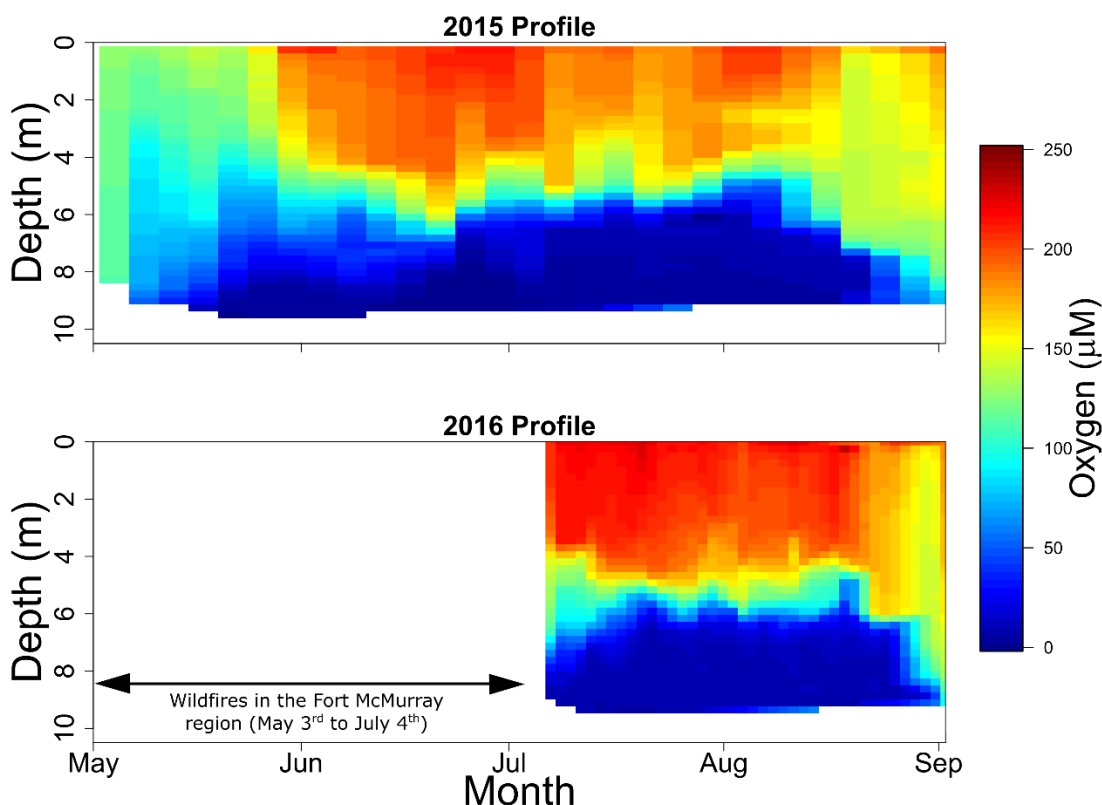


Figure 3-4: Heatmaps showing oxygen profiles for BML sampling platform 1 (P1) in 2015 (a) and 2016 (b). Thermal profiles collected on each sampling day ($N=454$ observations 2015) and ($N=494$ observations, 2016) are plotted on a concentration scale ranging between 0 μM (blue) to 250 μM (red). The data were linearly interpolated to create the heatmaps.

Table 3-1: Summary of physicochemical parameters of BML for the summer of 2015 and 2016.

Parameter	2015			2016		
	Epilimnion	Metalimnion	Hypolimnion	Epilimnion	Metalimnion	Hypolimnion
pH	8.26±0.02	8.11±0.01	7.94±0.02	8.29±0.02	8.14±0.04	8±0.03
Turbidity (NTU)	85±5	112±6	131±10	42±9	69±11	146±9
ORP (mV)	145±6	575±423	29±23	110±10	102±8	73±17
Conductivity (µS.cm ⁻¹)	2690±70	2800±10	2760±80	2800±10	2810±40	2840±20

3.3.2 Depth Dependent and Annual Water Cap Geochemical Trends

No evident depth dependent or annual trends in either SO_4^{2-} (high observed concentrations >2000 µM) or Fe^{3+} (low concentrations < 3 µM) emerged (Table 3-2). BML water cap Fe^{2+} concentrations were low with an observable decrease in concentration from 2015 (< 1 µM) to 2016 (< 0.1 µM; Table 3-2) (Paired t-test, d.f. = 2, p-value>0.05). In contrast, depth dependent and annual trends for potentially important OCC, CH_4 , $\sum\text{H}_2\text{S}$ and NH_4^+ were observed. The highest concentrations of CH_4 , $\sum\text{H}_2\text{S}$ and NH_4^+ occurred at the deepest depths sampled, consistent with the underlying FFT acting as the source of these potential OCC. Water cap concentrations significantly decreased from observed hypolimnetic maximum values to their minimum epilimnetic concentrations for CH_4 and NH_4^+ (ANOVA, d.f. =2, p<0.05) (Figure 3-5; Table 3-2). BML FWI aqueous concentrations of CH_4 of up to 105 µM (2015) and 150 µM (2016) decreased to lower hypolimnetic concentrations of ~20-40 µM; comparable to those observed in oil sands tailings pond water caps (Siddique et al., 2012; Penner and Foght 2010; Holowenko et al., 2000). However, in BML, aqueous CH_4 concentrations rapidly decreased moving up into the overlying water cap away from the FWI. The CH_4 profile is consistent with the underlying FFT layer being the primary source of CH_4 to the water cap and consumption of CH_4 by aerobic methanotrophy leading to an evident decreasing concentration profile up into the water cap. While the water cap concentrations decrease rapidly moving up into the water cap from the FWI, given that the porewaters of the ~40m FFT layer in BML are saturated with CH_4 (>1.4 mM, Dompierre et al., 2016), the FFT layer could act as a source of CH_4 to the overlying BML water cap for some considerable time to come, with likely strong impacts on BML water cap oxygen concentrations, as discussed below.

Concentrations of $\sum\text{H}_2\text{S}$ are rapidly extinguished above the FWI, consistent with the oxic water column. While BML water cap $\sum\text{H}_2\text{S}$ concentrations are lower than those noted in active tailings ponds (1-86 µM) (Stasik et al., 2014; Chen et al., 2013; Salloum et al., 2002), most oil sands tailings ponds water caps are dominantly anoxic which would

enable $\Sigma\text{H}_2\text{S}$ to persist until it reached the oxic-anoxic boundary where its influence on oxygen consumption would be rapid. In BML, as oxygen persists to the FWI in both years, the majority of $\Sigma\text{H}_2\text{S}$ oxidation would occur directly within the FWI, as abiotic oxidation of $\Sigma\text{H}_2\text{S}$ is rapid (Stasik et al., 2014). Consistent with this hypothesis, concentrations of $\Sigma\text{H}_2\text{S}$ within BML FFT porewater of $17\ \mu\text{M}$ have been identified (Dompierre et al., 2016), higher than those observed here at the FWI ($< 1\ \mu\text{M}$) (Table 3-2).

The mean 2015 hypolimnetic concentration of NH_4^+ ($53 \pm 4\ \mu\text{M}$) is significantly higher than that of CH_4 ($40 \pm 5\ \mu\text{M}$) or $\Sigma\text{H}_2\text{S}$ ($0.72 \pm 0.2\ \mu\text{M}$) (ANOVA, d.f. =2, $p < 0.05$) (Table 3-2). Ammonia concentrations in oil sands tailings pond water caps have been detected as high as $500\ \mu\text{M}$ (Chen et al., 2013), up to 10x higher than the maximum concentrations observed within the BML water cap $\sim 50\text{-}100\ \mu\text{M}$ (Table 3-2). However, unlike $\Sigma\text{H}_2\text{S}$ and CH_4 , ammonia has not been shown to be an important OCC affecting oxygen concentrations in tailings ponds (Chen et al., 2013; Reid et al., 2016; Saidi-Mehrabad et al., 2013). In keeping with methanotrophy playing a more dominant role in oxygen consumption than nitrification, the decrease in the mean 2015 CH_4 concentration from the hypolimnetic maxima to epilimnetic minima were greater than those observed for NH_4^+ concentrations (Figure 3-5, Table 3-2). The mean metalimnetic CH_4 concentration was reduced to 3% and the epilimnetic mean CH_4 concentration was reduced to $< 1\%$ of the hypolimnetic CH_4 concentration. In contrast, the mean metalimnetic NH_4^+ concentration was 68% and the mean epilimnetic NH_4^+ concentration was 47% of the mean hypolimnetic concentration (Table 3-2).

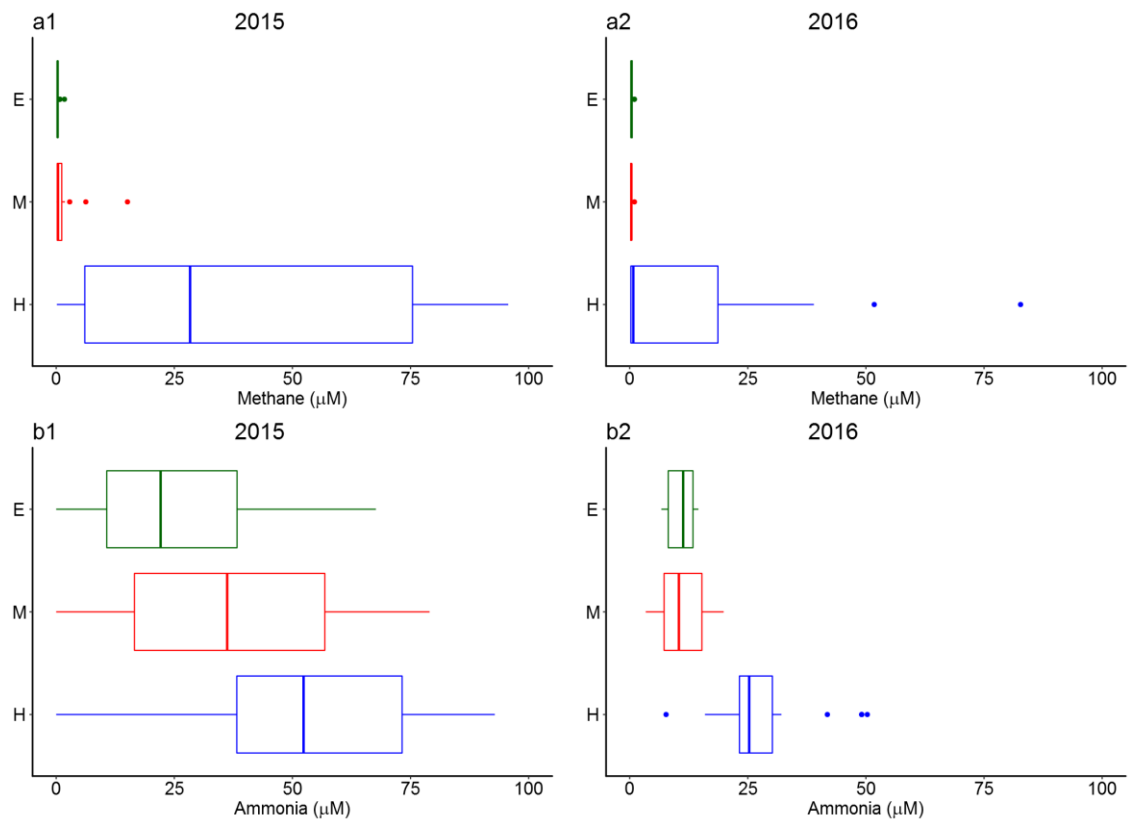


Figure 3-5: Summer BML water cap 2015 (a1, b1) and 2016 (a2, b2) whisker box plots for methane and ammonia concentrations in the epilimnion, E, (green), metalimnion, M, (red) and hypolimnion, H, (blue). (The vertical lines indicate median concentrations, the edges of the box represent the first and third quartiles, the whiskers represent the highest values within 1.5*IQR and the dots represent the outliers)

Table 3-2 : Summary of the geochemistry of BML for the summer of 2015 and 2016.

Constituent	2015			2016		
	Epilimnion	Metalimnion	Hypolimnion	Epilimnion	Metalimnion	Hypolimnion
CH ₄ (μM)	0.38±0.05	1.2±0.5	40±5	0.45±0.06	0.41±0.09	26±7
∑H ₂ S (μM)	0.2±0.2	0.3±0.2	0.7±0.2	BDL	BDL	0.5±0.3
NH ₄ ⁺ (μM)	25±3	36±4	53±4	11±1	11±2	27±2
NO ₃ ⁻ (μM)	25±2	36±5	40±15	44±5	40±6	27±3
NO ₂ ⁻ (μM)	2.3±0.2	4.4±2.1	2.5±0.5	2.3±0.3	3.7±0.6	5.0±0.8
SO ₄ ²⁻ (μM)	2049±96	2095±61	2176±113	2085±65	2103±104	2140±56
Fe(II) (μM)	0.9±0.3	0.8±0.2	0.9±0.3	0.04±0.01	0.09±0.04	0.09±0.04
Fe(III) (μM)	1.2±0.3	1.3±0.2	2.7±0.6	0.9±0.3	2.8±1.3	2.1±0.9
chl-a (mg/m ³)	1.9±1.0	-	-	4.8±2.7	-	-

* BDL: Below detection limits

In 2016, similar depth trends for all three potential OCC emerged as those seen in 2015, but the mean summer concentrations at every depth were lower (Figure 3-5, Table 3-2). While not significantly lower, the mean 2016 hypolimnetic ∑H₂S concentration of 0.5±0.3 μM was 38% lower, while the mean 2016 hypolimnetic CH₄ concentration of 26 ±7 μM was 35% lower than their respective 2015 values of 0.7±0.2 μM and 40±5 μM (Table 3-2). However, concentrations of NH₄⁺ in all three water cap regions were significantly lower in 2016 compared to 2015 (Paired t-test, p-value<0.05, d.f. =2). The mean 2016 hypolimnetic NH₄⁺ concentration of 27±1 μM showed the greatest decrease, 49% lower than the concentration of 53±4 μM observed in 2015.

Both (1) reduced mobilization of these OCC from the FFT layer and / or (2) greater redox biogeochemical cycling could contribute to the lower observed water cap concentrations seen in 2016. Information on underlying FFT porewater concentrations from 2015 and 2016 indicate similar concentrations (Dr. Matt Lindsay, personal communication) indicating that mobilization of OCC from the FFT, at least from diffusion processes, should be similar between the two summers. Further, comparison of the nitrogen species results indicates the emergence of active microbially driven nitrification occurring in 2016, which is not evident from 2015 results. The total nitrogen concentration (∑(NH₄⁺, NO₂⁻, NO₃⁻)) increases with depth in 2015 (Figure 3-6a). However, the relative proportions of ammonia and nitrate remain relatively static for each of the three regions consistent with a lack of microbial nitrogen cycling (Figure 3-6b). In contrast, in 2016 the total nitrogen concentration remains similar across the three depths (Figure 3-6c), however a clear depth dependent reversal in the relative proportions of NH₄⁺ and NO₃⁻ occur, consistent with progressive microbial nitrification moving up into the water cap (Figure 3-6d). NO₃⁻ concentrations (the redox end product of microbial NH₄⁺ oxidation) increase and its relative

contribution to the total nitrogen concentration increases from 48% in both the metalimnion and epilimnion in 2015, to 73% and 77% respectively in 2016, while absolute concentrations and relative contributions of NH_4^+ to total nitrogen concentrations show a corresponding decrease from 48% in both the metalimnion and epilimnion in 2015 to 20% and 19% respectively in 2016 (Figure 3-6).

The emergence of nitrification in 2016 suggests that there may have been some delay in the establishment of nitrifying Bacterial and/or Archaeal microorganisms in BML. Apart from N_2 fixation (Collins et al., 2016) the nitrogen cycle in the oil sands tailings ponds has been poorly studied. However, one study from Misiti et al. (2013) showed inhibition of microbial nitrification by naphthenic acids (NA), which was postulated to explain why this metabolism has not been identified to play an important role in oil sands tailings pond biogeochemical cycling. NA concentrations of 40 to 120 mg/L have been reported for oil sands tailings ponds (Headley and McMartin 2004; Rogers et al., 2002; Quagraine et al., 2005). These values are higher than the 2016 NA median concentration of 31 mg/L observed in BML. Misiti et al. (2013) detected significant nitrification inhibition in mixed cultures of nitrifiers and heterotrophs at a starting NA concentration of 80 mg/L. These findings would suggest that NA concentrations are not high enough in BML to suppress this guild, enabling them to establish and begin to thrive. To date, CH_4 and $\sum\text{H}_2\text{S}$ have been identified as the key OCC affecting oxygen concentrations within oil sands tailings ponds (Chen et al., 2013; Reid et al., 2016; Saidi-Mehrabad et al., 2013). Here, results from BML indicate that with cessation of further FFT inputs and a thicker water cap enabling stratification and zonation, nitrifying microorganisms appear to establish and thus NH_4^+ may be an important OCC that needs to be considered in addition to CH_4 and $\sum\text{H}_2\text{S}$ in oil sands pit lake water cap oxygen behavior over longer term developmental timescales.

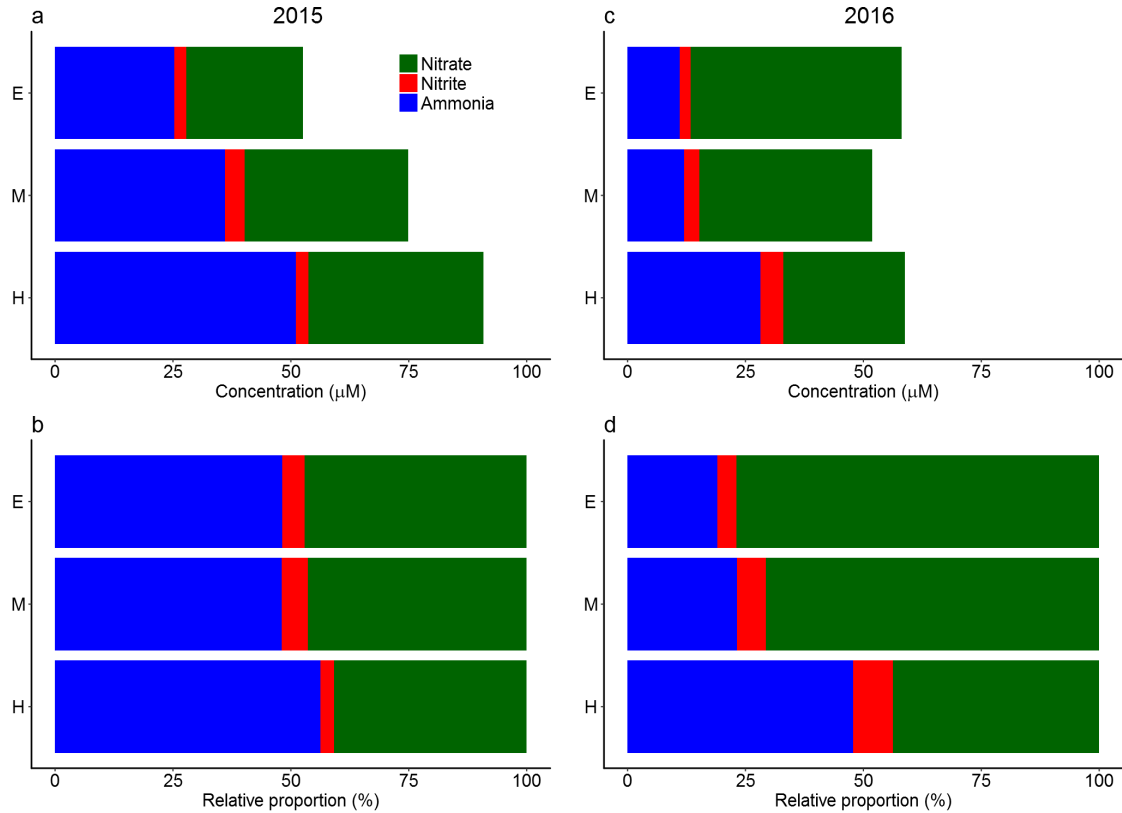


Figure 3-6 : Mean BML water cap epilimnetic (E), metalimnetic (M) and hypolimnetic (H) concentrations of the three N redox species, NH_4^+ (Blue), NO_2^- (Red), and NO_3^- (Green) (μM) and relative proportions for 2015 (a;b) and 2016 (c;d). Modeling BML water cap oxygen consumption

3.3.3 Modeling BML water cap oxygen consumption

To identify which OCC were important in determining BML water cap oxygen concentrations in each summer, linear regression modeling was used. Preliminary analysis on the limited number of samples for which detectable $\Sigma\text{H}_2\text{S}$ concentrations were available within the BML water cap (less than half of the samples for both years in the hypolimnion), identified that this parameter was not a significant factor in affecting BML water column oxygen concentrations, consistent with the likelihood that most $\Sigma\text{H}_2\text{S}$ is removed within the FWI region. However, detectable concentrations of both CH_4 and NH_4^+ extend higher up into the water column (Figure 3-5). Univariate linear regression modeling identified differences in the importance of these two potential OCC in 2015 versus 2016. While there is scatter in the data for both years, CH_4 was significantly negatively correlated to oxygen concentrations explaining 63% and 41% of the variation in oxygen concentrations in 2015 and 2016 respectively (Figure 3-7 a1, a2) indicating the greater the mobilization of CH_4 from the FFT, the greater the oxygen consumption observed within the BML water cap. In

contrast, NH_4^+ concentrations were not significantly correlated to 2015 BML water cap oxygen concentrations, but did emerge as significantly negatively correlated to BML water cap oxygen concentrations in 2016, explaining 54% of the variance (Figure 3-7 b1, b2).

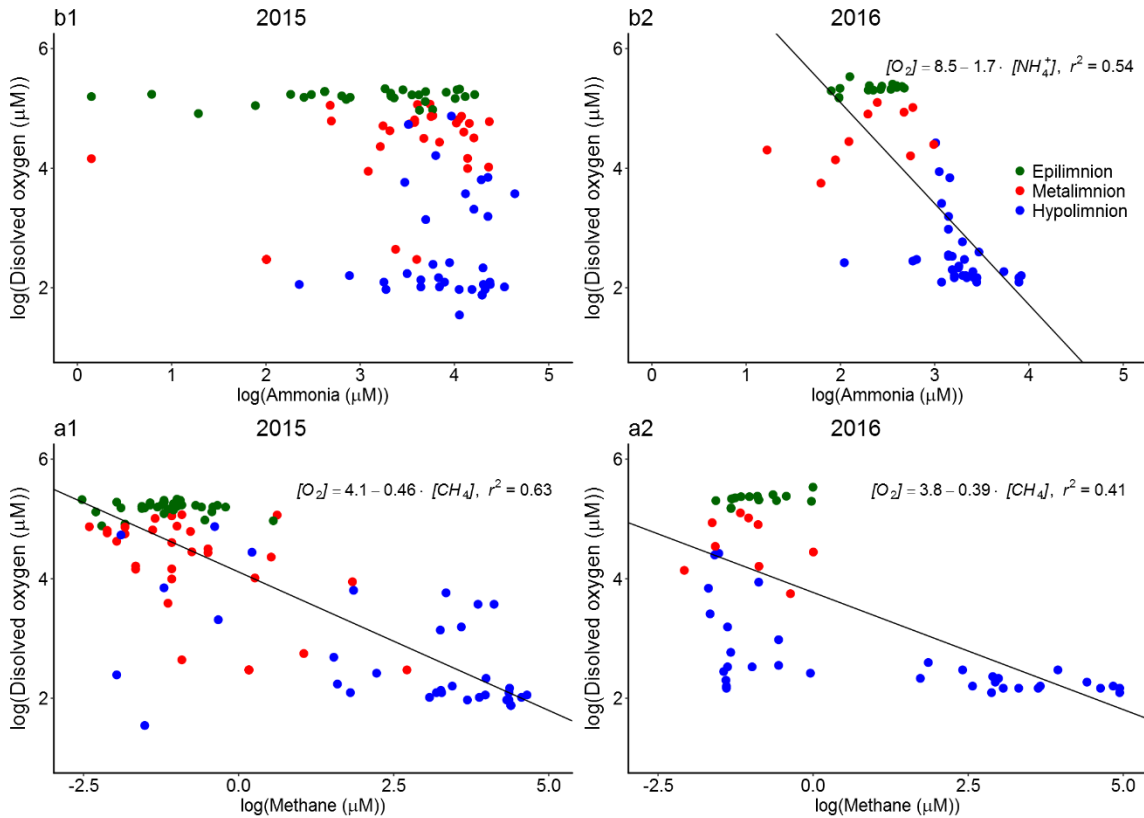
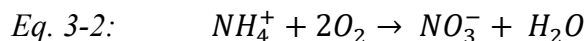
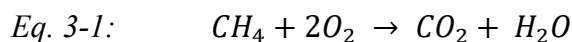


Figure 3-7 : Linear regression modeling of BML water cap O₂ concentrations versus water cap CH₄ (a) and NH₄⁺ (b) concentrations for 2015 (1) and 2016 (2). (data points are colour coded by thermal region: green (epilimnion), red (metalimnion) and blue (hypolimnion)).

Using multivariate linear regression modeling, the relative importance of CH₄ and NH₄⁺ and their possible interaction in determining 2016 BML water cap oxygen values was assessed (Figure 3-8). The best fit model incorporated both OCC and explained a larger percentage of the variance in observed BML water cap O₂ concentrations, 66%, than either OCC alone (Figure 3-7, Figure 3-8). Stoichiometric equations for O₂ consumption by either CH₄ (Eq. 3-1) or NH₄⁺ (Eq. 3-2; assuming oxidation to NO₃⁻, as supported by results in Table 3-2, Figure 3-6) indicates 2 moles of oxygen should be consumed for every mole of either OCC. However, the coefficients determined by the model of -1.2 for CH₄ and -1.5 for NH₄⁺ are less than this; $\frac{2}{3}$ and $\frac{3}{4}$ of the expected values respectively; indicating inputs of oxygen moderate the overall net oxygen concentrations observed (Figure 3-8). Interestingly the model also identifies a positive CH₄ and NH₄⁺ interaction coefficient (Figure 3-8; coefficient +0.32) indicating a positive effect on [O₂] as the product of CH₄

and NH_4^+ concentrations increase. This occurs at the deepest depths, close to the FFT source of these two OCC and where oxygen concentrations are the lowest (Figure 3-3, Figure 3-4, Table 3-2). We interpret this interaction term as an indication that (1) competition between methanotrophs and nitrifying microorganisms for highly limited oxygen may be occurring and/or (2) inhibition of one or both microbial metabolisms occur at the low oxygen levels observed at the FWI. The ability of methanotrophs to outcompete nitrifying microorganisms has been demonstrated in both fresh and marine systems. High methane concentrations ($\geq 84 \mu\text{M}$) at the freshwater sediment water interface have been shown to suppress nitrification, indicating methanotrophs outcompete nitrifying microorganisms when oxygen is limited (Roy et al., 1996). In marine sediments, similar processes have been observed where sediments ($\sim 250 \mu\text{M NH}_4^+$, $\sim 100 \mu\text{M CH}_4$) amended with ammonium ($300 \mu\text{M}$) and methane ($80 \mu\text{M}$) showed similar nitrification rates but higher methanotrophy rates compared to unamended controls suggesting inhibition of nitrifiers by methanotrophs (Carini et al., 2003).



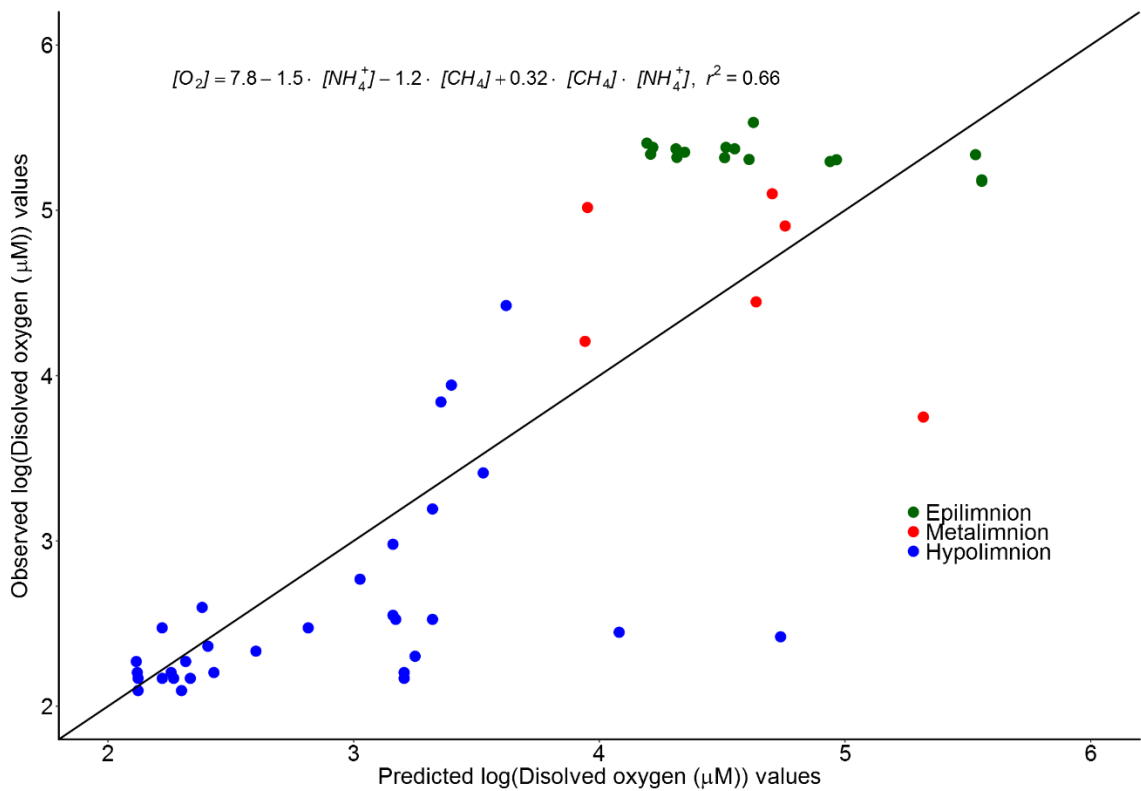


Figure 3-8 : Observed BML water cap oxygen concentrations versus those predicted by the best model fit through multiple linear regression modeling. (data points are colour coded by thermal region: green (epilimnion), red (metalimnion) and blue (hypolimnion)).

Results here for the first full-scale demonstrated oil sands pit lake, Base Mine Lake, confirm that the FFT will be an important source of oxygen consuming constituents into the overlying water cap where they affect extant oxygen concentrations. The thicker water cap and lack of perturbation by ongoing tailings inputs of BML relative to more shallow oil sands tailings impoundments, enabled summer thermal stratification and oxygen zonation, with epilimnetic oxygen saturations reaching 70% (2015) and 85% (2016) while hypolimnetic oxygen saturation decreased to < 5%, but did not go anoxic at the FFT water interface (Figure 3-4). The observed summer epilimnetic oxygen concentrations, especially in 2016, would well support a number of warm water fish species and macrofauna. An increase in chl-a concentrations from 2015 to 2016 consistent with higher levels of primary productivity, is in accordance with the increased epilimnetic oxygen concentrations observed in 2016. This will be an important oxygen producing process for this pit lake to moderate oxygen consumptive processes currently occurring in the deeper zone, driven by mobilization of OCC from the underlying FFT layer. In both years, mobilization of expected potential OCC: CH_4 , ΣH_2S and NH_4^+ was observed with intense redox cycling and oxidation occurring right at the FFT water interface (FWI), where oxygen

concentrations are lowest; resulting in near complete removal of $\sum\text{H}_2\text{S}$ within a small distance from the FFT water interface (Figure 3-9). In contrast, both CH_4 and NH_4^+ are detectable in the overlying water column; but the loss of CH_4 moving away from the FWI is more rapid, resulting in near complete CH_4 removal by the metalimnion, while NH_4^+ persists up into the epilimnion. While CH_4 concentrations alone best explain the consumption of oxygen within the BML water cap in 2015; both NH_4^+ and CH_4 were important in explaining water cap decreases in oxygen concentration in 2016.

The emergence of microbial nitrification processes as important to oxygen consumption within the BML water cap in 2016 indicates that this process will be an important player in determining oil sands pit lake water column oxygen concentrations over the longer development trajectory (Figure 3-9). Nitrifying microorganisms have not been observed to be highly active in oil sands tailings ponds, despite high concentrations of ammonia; the absence of this microbial metabolism has been attributed to naphthenic acids (NA) toxicity in these tailings ponds. Here, results indicate that the lower observed NA concentrations in BML likely enable nitrifying microorganisms to establish and have a detectable impact on oxygen concentrations within four years of commissioning BML. Our results suggest that oxygen concentrations are an important control on this metabolism. In early pit lake development, it may take some time for nitrifying microorganisms to establish and/or methanotrophs may outcompete nitrifying microorganisms for highly limited oxygen at the FFT water interface where the most intense redox cycling occurs, and/or methanotrophs may tolerate lower oxygen concentrations better. Metagenomics characterization of the epilimnetic, metalimnetic and hypolimnetic microbial communities from the summers of 2015 and 2016 is currently underway and will elucidate whether both metabolisms are present in both years, and identify any shifts in community diversity from 2015 to 2016. Collectively, results here indicate that pit lake design will have to consider the interplay of physicochemical zonation and biogeochemical cycling on oxygen status within pit lake water caps. The legacy concentrations of OCC within FFT disposed of within pit lakes and the clear evidence here of their mobilization into the BML water cap indicate that biogeochemical cycling is likely to continue for some time to come. Further the rapid developmental shift from methane alone to both methane and ammonia affecting oxygen concentrations indicate that pit lake behavior cannot be reliably predicted from what is currently known about tailings pond biogeochemical cycling.

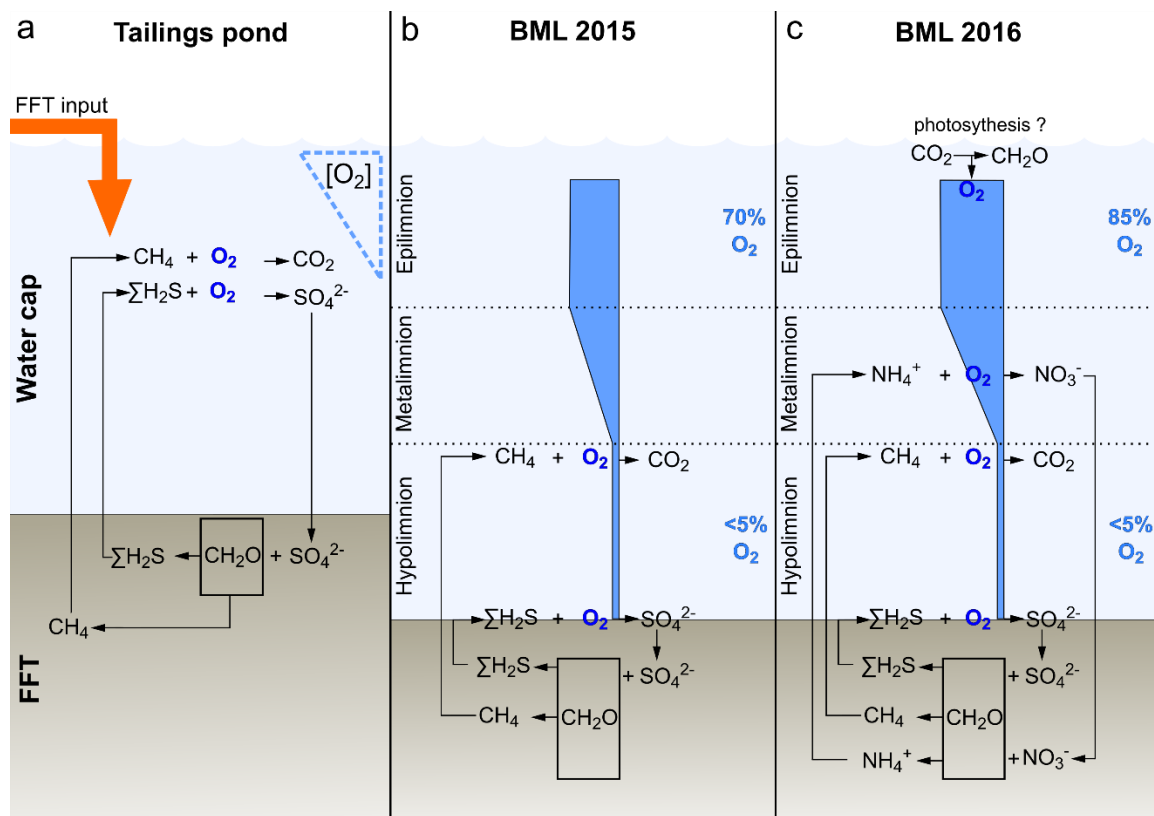


Figure 3-9 Comparison of the physicochemistry and oxygen consumption dynamics between a tailings pond (a) and BML for the summers of 2015 (b) and 2016 (c). Pore water concentration for CH_4 , NH_4^+ and $\Sigma\text{H}_2\text{S}$ is 1.4 mM, 300 μM and 17 μM respectively for both years (FFT porewater concentration data courtesy of Dr. Matt Lindsay; University of Saskatchewan).

Chapter 4: Seasonal influence of oxygen and methane on nitrification in the first commercial scale Oil Sand Pit Lake, Base Mine Lake.

4.1 Introduction

Athabasca's oil sand region (AOSR) located in northern Alberta, Canada is the third largest oil reserve in the world with currently an estimated 300 billion barrels of recoverable bitumen (Alberta Energy, 2013). Associated with the surface mining and oil extraction process is the production of tailings; a slurry of sand, silt, clay, residual oil and process-affected water; that is currently being discharged in holding ponds where the coarser material is allowed to settle very slowly over years (Chalaturnyk et al., 2002; MacKinnon, 1989). This densification results in a brackish, fluid-like slurry called fluid fine tailings (FFT), which is then transferred to tailings pond (Penner & Foght, 2010). To date the tailings ponds are estimated to hold volumes of tailings exceeding 700 millions m³ therefore emphasizing the need for storage and isolation (Dominski, 2007). Presently, water capped tailings technology (WCTT) is being assessed as a reclamation strategy in the oil sands, with the commission of the first full scale pit lake, Base Mine Lake (BML) in December 2012. BML consist of an old mined out pit in which ~ 40m of FFT were deposited over decades, and then subsequently capped with a 10m water cap, with no further discharge of tailings post commission (Boerger et al. 1992, Westcott & Watson, 2007). The reclamation goal for BML is to provide long term storage and isolation of the FFT as part of the closure strategy for the mine through the establishment of a self sustaining ecosystem similar to a natural lake. Currently, approximately 30 pit lakes have been planned in the AOSR and as the development of the oil sand expands, more will be underway (Westcott, 2007).

In order to successfully achieve reclamation status and develop in to a natural ecosystem, BML must be able to support macrofauna, which requires the establishment of an oxic zone within the water cap that will persist over seasonal and developmental scales. However, due to the reductive nature of FFT, potential concerns for the development of an oxic water cap and therefore for the success of WCTT as a reclamation strategy have been identified. Indeed, studies of oil sands tailings ponds have identified mobilization of reductants such as CH₄ and Σ H₂S from FFT porewater into the water column where they rapidly consume oxygen (Holowenko et al., 2000; Stasik et al., 2014; Chen et al., 2013; Ramos-Padrón et al., 2010). The same concern exists for BML, that the underlying FFT layer will be a substantive source of oxygen consuming constituents (OCC) that can be mobilized in the overlying water cap and decrease oxygen concentrations below those that can support macrofauna. Diverse microbial communities have been identified in the FFT

of tailings ponds which are also likely to be present in BML and actively drive biogeochemical cycling (Foght et al., 1985). Anaerobic microbes such as methanogens, sulfate reducing bacteria (SRB), nitrate reducing bacteria (NRB) and iron reducing bacteria (IRB) have all been found to generate reduced compounds in the FFT of tailings ponds (Holowenko et al., 2000; Penner et al., 2010; Siddique et al., 2012, Foght et al., 2017), providing an array of potential OCC that can be mobilized into the BML water cap where biogeochemical cycling can occur.

A previous study from Risacher et al. (2017) established that CH_4 and NH_4^+ are the main oxygen consuming constituents (OCC) in the water cap of BML during the summer stratification period (Figure 4-1). These compounds, mobilized from the underlying FFT layer were linked to decreasing oxygen concentrations in the lake and were identified as a risk to the success of WCTT in the oil sands as the high concentrations within the FFT porewaters are sufficient to impair oxygen concentrations for some time to come within BML. However, unlike oil sands tailings ponds water caps, which are predominantly anoxic, the water cap of BML was oxic from the surface (~80-95% saturation) to the FFT water interface (< 5% saturation) during summer stratification (Figure 4-1). The consumption of oxygen was predominantly constrained to the hypolimnion of BML, where the concentrations of FFT derived OCC were the highest and oxygen concentrations were the lowest.

It is currently unknown whether the BML water cap is stratified and/or goes anoxic during winter months when the lake is ice-covered (Figure 4-1). An ice cap would limit the oxygen input from atmospheric diffusion into the BML surface waters, as well as trap any gaseous OCC species such as CH_4 and $\Sigma\text{H}_2\text{S}$ within the water cap (Figure 4-1). The potential accumulation of OCC under ice could exacerbate the consumption of oxygen leading to anoxia. Thus, the objective of this study is to characterize the BML winter water cap geochemistry under ice and provide a better understanding of the implications of seasonal stratification on water cap oxygen concentrations within this pilot pit lake.

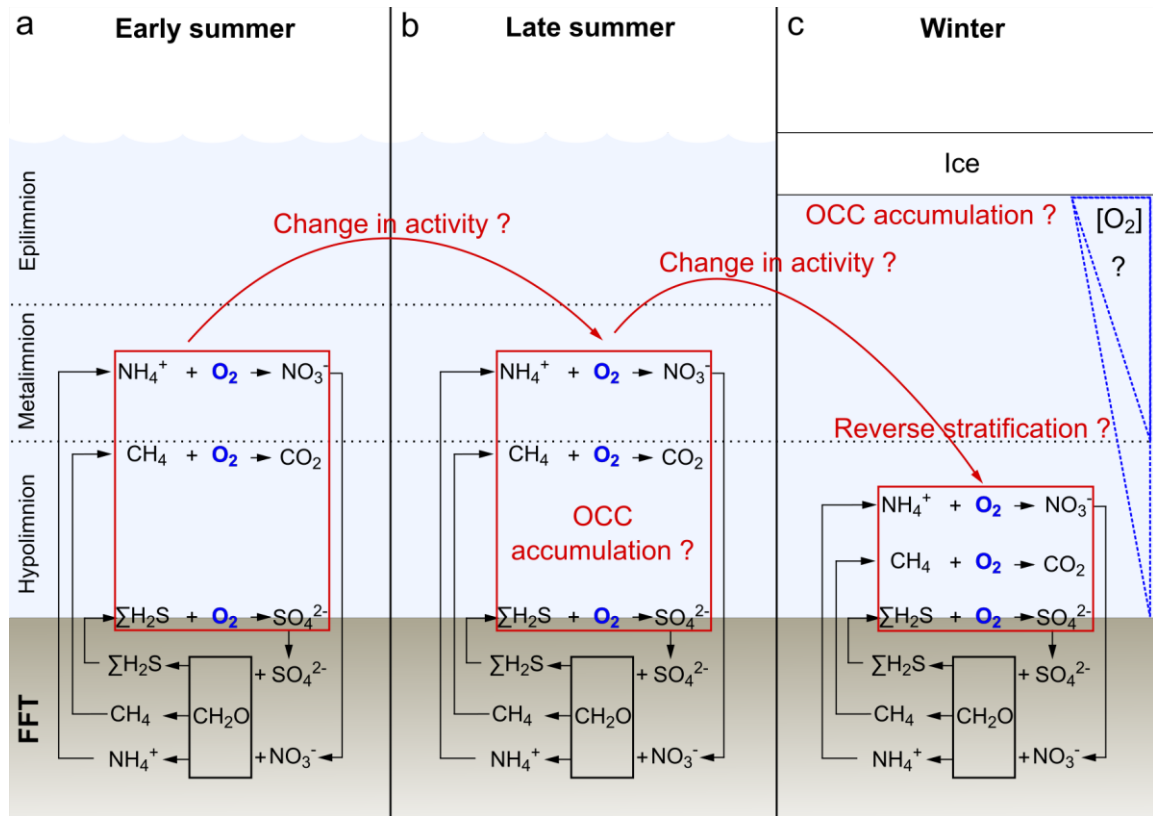


Figure 4-1: Schematic of seasonal oxygen consumption dynamics of BML. The questions are in red.

4.2 Material and methods

4.2.1 Site Description

As Base Mine Lake (BML) has been fully described in Risacher et al. 2017, only a brief overview of the field site will be presented here. Base Mine Lake (BML) is a man-made lake located approximately 40 km North of Fort McMurray, Alberta (Figure 4-2a), on Syncrude Canada ltd lease. BML has a water cap of ~10m overlying 30 to 60m of FFT that has been deposited in an old mined-out pit over the past decades (Dompierre et al. 2016). Three platforms have been installed on the lake for sampling purposes: P1 (Platform 1, center), P2 (Platform 2, North-West) and P3 (Platform 3, South-East; Figure 4-2a). All reported results here were taken at the central Platform 1, P1, as results from earlier sampling in 2015 across all 3 platforms identified no statistically significant differences in geochemistry (Risacher et al. 2017).

4.2.2 Seasonal Sampling Campaigns 2016-2017

Sampling campaigns were carried out between July 6th to September 1st 2016 capturing summer stratification and over February 13th to 17th 2017, capturing winter stratification. For each sampling campaign, prior to water sampling, physicochemical profiling of the BML water cap at Platform 1 (~9-10m of depth) was conducted. Profiles were collected at ~ 50 cm intervals from the BML water cap surface or the bottom of the ice cover to the FFT-water interface (FWI) for: pH, temperature, dissolved oxygen, specific conductivity, ORP, turbidity and salinity (YSI Professional Plus 6-Series Sonde, YSI Incorporated). For the winter sampling campaign, sampling was performed under the ice beside Platform 1 (Figure 4-2b), following the same protocol employed during the summer from the boat (Figure 4-2c), by coring through the ice first using an ice Auger. All depths in winter are measured starting below the ice, which was ~ 50 to 85 cm thick.

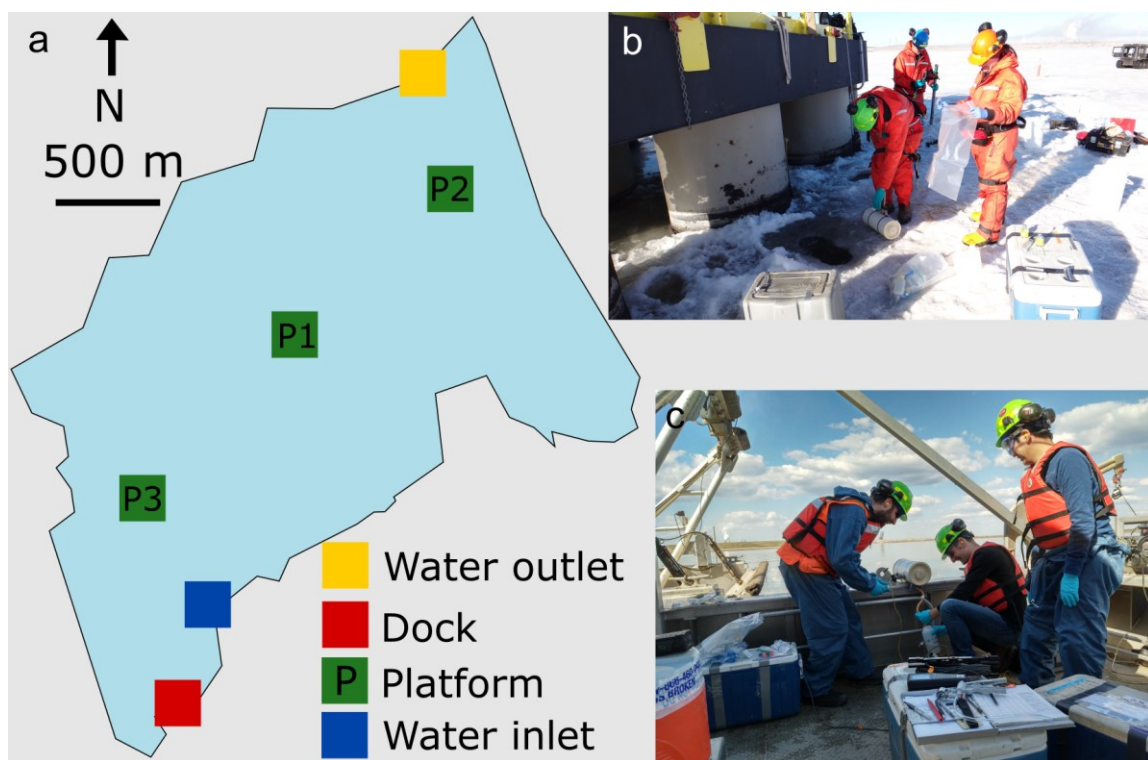


Figure 4-2: Sketch map of BML (a) with location of platforms (green) and dock (red). Photo of winter sampling campaign (b) and summer sampling campaign (c).

4.2.3 Geochemical Sample Collection, preservation and Analyses

Sample collection, preservation and analyses were performed following established protocols in our research groups (Slater 2008; Reid and Warren, 2016; Warren et al., 2016)

and well described in Risacher et al. 2017. Briefly, all sampling equipment and containers were acid cleaned by soaking in 5% (v/v) HCl for 12 h and rinsed with ultra-pure water (18.2Ωm cm-1, Milli-Q, Millipore). The physico-chemical profiles obtained by the YSI were used to identify depths for geochemical characterization (CH_4 , $\Sigma\text{H}_2\text{S}$, SO_4^{2-} , Fe^{2+} , Fe^{3+} , NH_4^+ , NO_2^- , NO_3^-) during summer open water or under ice sampling. Water samples were then collected from seven to eight depths for each sampling campaign (35 summer; 1 winter) spanning the water cap surface to the FWI, using a 6.2L sampling Van Dorn (PVC, WaterMark, Forestry supplies). Following the retrieval of the Van Dorn to the boat or to the ice surface, sample collection proceeded in the subsequent order: CH_4 , $\Sigma\text{H}_2\text{S}$, $\text{Fe}^{2+}/\text{Fe}^{3+}$, and a bulk water sample for NO_3^- , NO_2^- , NH_4^+ and SO_4^{2-} as outlined in Risacher et al. 2017. A minimum of three replicates was analyzed for each analytical constituent. Field blanks (filtered and preserved ultrapure water (18.2Ωm cm-1, Milli-Q, Millipore) on site) and process blanks were collected and analyzed for each chemical species.

4.2.4 Statistical analyses

Full details and results of the 35 summer sampling campaigns carried out in 2016 are reported in Risacher et al. 2017. Here, for the purposes of comparison with the winter sampling campaign, a representative sampling campaign for July (early summer stratification; July 6th -7th 2016) and for August (established summer stratification; August 4th – 5th 2016) were selected for comparison to the under ice, winter February data (February 14th -15th 2017). This comparison was used for the physico-chemical and geochemical profiles. However, subsequent analyses were performed with all data from July and August 2016. Linear models were built and analysed to compare the consumption of oxygen by different OCC. All statistical tests and all figures in this paper have been produced using R Studio (version 1.0.143, RStudio Team, 2016) working with R-base (version 3.4.0, R Development Core Team, 2017). Significance level for all statistical analysis was set at an alpha value of 0.05.

4.3 Results and discussion

4.3.1 Seasonal water cap physico-chemistry

The BML water cap evidenced a summer stratification pattern of ~ 5m thick 20°C epilimnion separated from the 13°C hypolimnion by a ~ 2m metalimnion (~5-7m) (Figure 4-3a). Under ice, the BML water cap showed a classic winter profile, increasing from 0°C at the ice-water interface to 4°C at about ~ 7.5m (Figure 4-3a). Summer dissolved oxygen concentration profiles show a decrease from ~85% saturation (200 μM, 7 mg/L) in the epilimnion to ~ <5% saturation in the hypolimnion just above the FWI (10 μM, 0.3 mg/L; Figure 4-3b, c). The winter under ice profile shows a similar oxygen decrease with depth

(Figure 4-3b, c), however absolute concentrations are higher (epilimnetic 300 μM ; hypolimnetic above the FWI, 50 μM). Interestingly, the relative saturation within the epilimnion under ice is only 67%, compared to the summer open water epilimnetic saturation of $\sim 85\%$, while the winter hypolimnetic O_2 saturation is 10-30%, higher than that observed for the summer stratification period (Figure 4-3b, c).

pH profiles were similar for both summer and winter, evidencing circumneutral values with a slightly higher epilimnetic pH (8.2-8.5) than that observed in the hypolimnion (7.8-8.2; Figure 4-3d, Table 4-1). Conductivity values show very little change with depth in both seasons, however values in the summer (2800 $\mu\text{S}/\text{cm}$) are considerably higher than those observed under ice (1800 $\mu\text{S}/\text{cm}$; Figure 4-3c, Table 4-1). Turbidity values are relatively constant also throughout the water cap, except for an increase near the FWI for both seasons; and again showing a seasonal decrease from summer values (50-100 NTU) to observed winter values (3-4 NTU; Figure 4-3e, Table 4-1). The lower conductivity and turbidity values observed in winter at least partially reflect the addition of aluminum sulfate (flocculent) added in the fall of 2016 to settle out suspended solids and improve clarity of the water cap.

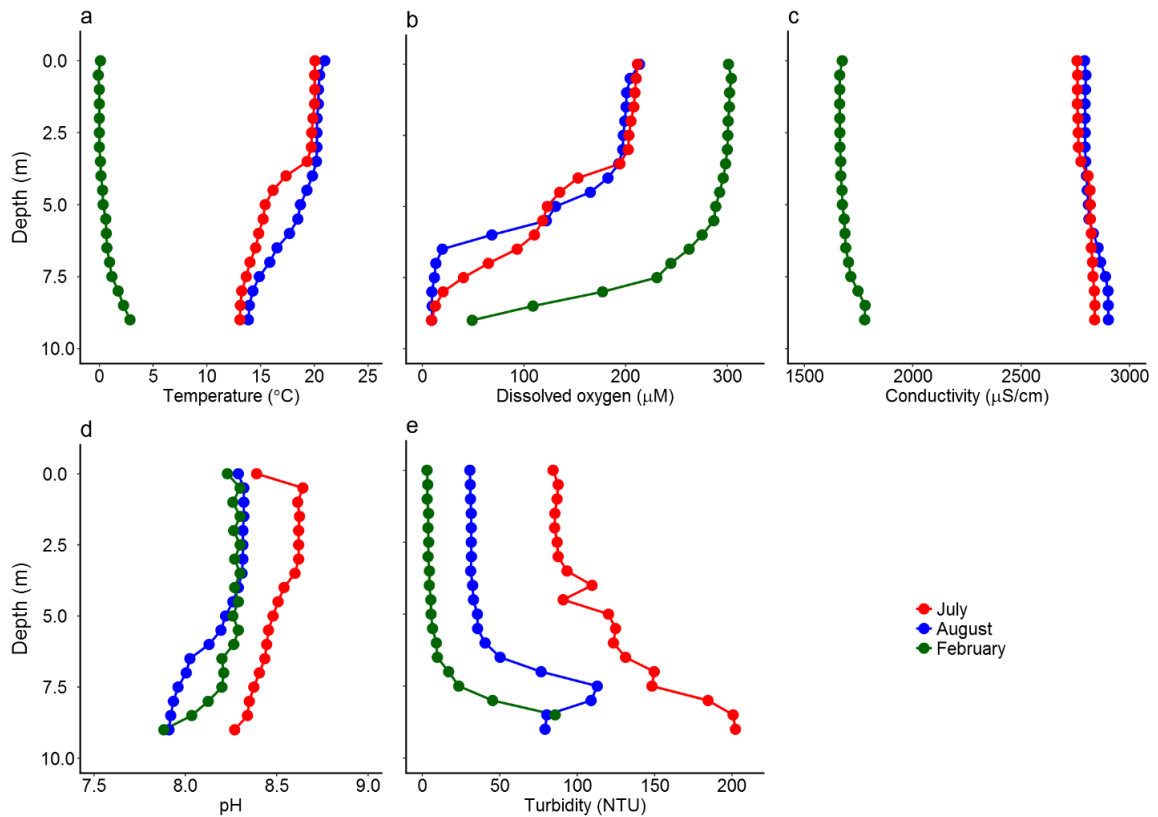


Figure 4-3: Physicochemical parameters of the BML water cap for July 2016 (red), August 2016 (blue), and February 2017 (green). Temperature (a), dissolved oxygen (b), conductivity (c), pH (d) and turbidity (e) are shown.

Table 4-1: Summary of physicochemical parameters of BML for July, August and February for each zone.

Parameter	Epilimnion			Metalimnion			Hypolimnion		
	July	August	February	July	August	February	July	August	February
Temperature (°C)	20.46±0.1	20.34±0.09	0.03±0.02	16.35±0.2	18.22±0.15	0.51±0.07	13.63±0.05	14.74±0.09	1.91±0.23
Conductivity (µS/cm)	2790±2	2818±4	1666±1	2837±3	2833±6	1682±3	2870±4	2895±6	1748±17
pH	8.34±0.01	8.28±0.01	8.27±0.01	8.15±0.02	8.16±0.01	8.26±0.01	7.97±0.02	7.91±0.01	8.07±0.05
Turbidity (NTU)	63±2	26.3±0.5	4±1	100±4	34±2	7±1	187±10	72±5	94±34
Oxygen saturation (%)	74±1	70±1	67±1	35±2	36±3	63±1	5±1	4±1	35±5
Dissolved oxygen (mg/L)	6.56±0.04	6.25±0.05	9.61±0.02	3.31±0.19	3.3±0.24	9.01±0.13	0.5±0.06	0.36±0.01	4.8±0.77
Dissolved oxygen (µM)	205±1	195±2	300±1	104±6	103±8	281±4	16±2	11±1	150±24

BDL: Below detection level

4.3.2 Seasonal water cap geochemistry

The two most important observed OCC negatively affecting oxygen concentrations within the BML water cap during the summer of 2016 were CH₄ and NH₄⁺ (Risacher et al 2017). Consistent with these previous findings, CH₄ concentrations for the summer were a maximum of ~ 100-150 µM at the FWI and rapidly reached < 1 µM by the lower metalimnion, as highlighted by the representative selected profiles for July and August of 2016 (Figure 4-4a) indicative of rapid CH₄ consumption in the hypolimnion. Winter CH₄ concentrations are statistically significantly higher (ANOVA, d.f. =2, p<0.05) (up to 300 µM) and extend all the way up to the ice-water interface where they are much higher than those observed in the epilimnion during the summer (i.e. < 1 µM; Figure 4-4a). Methane is the only parameter for which statistically significantly higher winter concentrations were observed.

Winter NH₄⁺ concentrations follow a similar depth profile to those observed in the summer, decreasing away from the FWI up into the water cap and range in concentration from 30-45 µM at the FWI to 10-18 µM in the epilimnion (Figure 4-4b; Table 4-2). The July NO₃⁻ profile shows a markedly higher epilimnetic concentration than either in August or under ice (ANOVA, d.f. =2, p<0.05) (Figure 4-4c, Table 4-2).

BML water cap ΣH₂S concentrations are low throughout the water column across all seasons (Figure 4-4f), consistent with the detectable presence of oxygen to the FWI, which would enable rapid abiotic oxidation. SO₄²⁻ concentrations are high relative to other analytes in the 2 mM range (Figure 4-4f, Table 4-2) and evidence an overall increase in absolute concentration to 2600 µM in February 2017 reflecting the addition of SO₄²⁻ from the aluminium sulfate treatment applied to BML during the fall of 2016.

No depth or seasonal dependent trends were observed for Fe²⁺ and Fe³⁺ in BML with very low observable concentrations <1 µM (Figure 4-4g, h, Table 4-2).

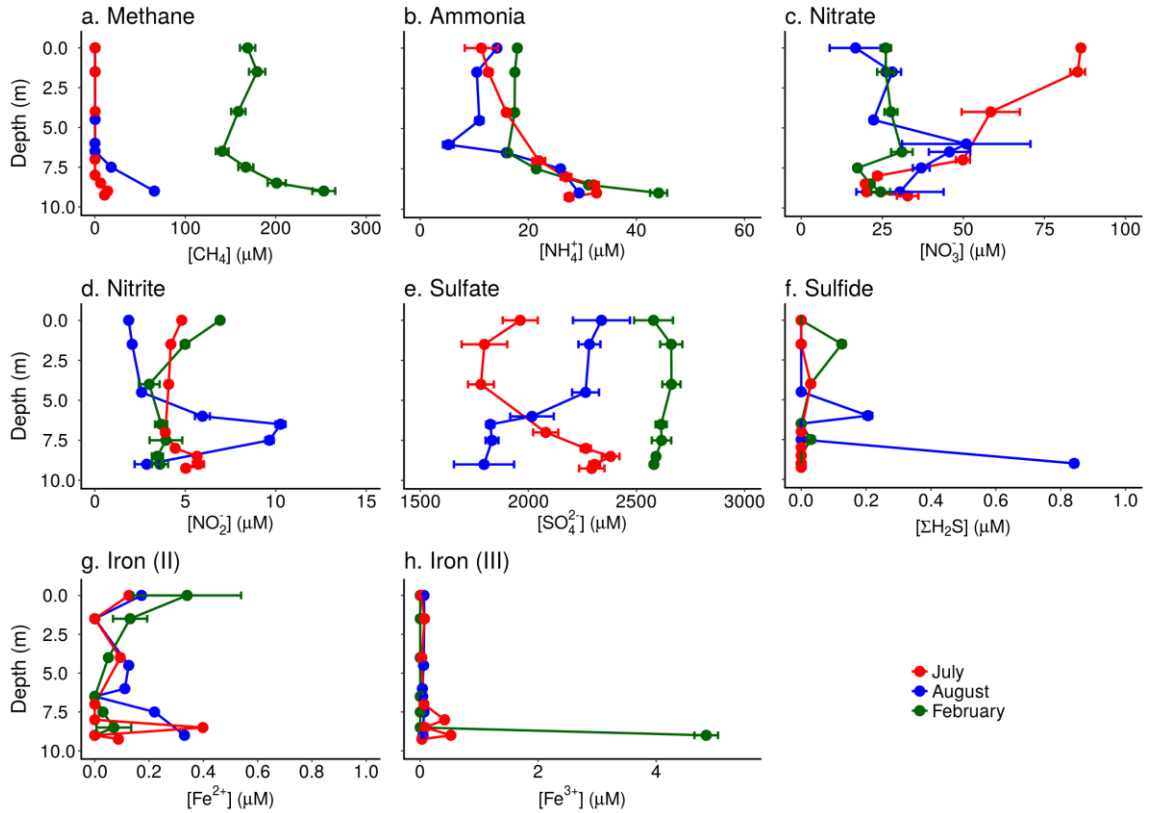


Figure 4-4: Geochemical parameters of the BML water cap for July 2016 (red), August 2016 (blue), and February 2017 (green). Methane (a), Ammonia (b), Nitrite (c), Sulfate (d), Sulfide (e), Iron(II) (g) and Iron(III) (h) are shown. Standard error of the mean is shown with the error bars.

Table 4-2: Summary of geochemical parameters of BML for July, August and February for each zone.

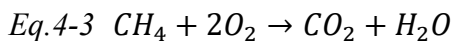
Constituent	Epilimnion			Metalimnion			Hypolimnion		
	July	August	February	July	August	February	July	August	February
CH_4 (μM)	0.36±0.03	0.6±0.1	169±6	0.31±0.05	0.5±0.1	141±NA	19±5	57±18	207±25
NH_4^+ (μM)	13.4±0.5	9.0±0.8	17.6±0.2	17.35±0.95	8.5±1.2	16.2±NA	28.6±1.0	29.3±5.1	32.2±6.6
NO_3^- (μM)	49.7±7.2	37.0±3.9	26.6±0.5	32±2	41.8±5.9	31.0±NA	24.1±2.0	28.7±6.1	21.1±2
NO_2^- (μM)	3.0±0.4	1.8±0.2	5.0±1.1	3.3±0.3	4.2±1.1	3.7±NA	5.1±0.7	3.8±1.2	3.7±0.1
SO_4^{2-} (μM)	2076±87	2137±92	2634±27	2240±75	2012±101	2614±NA	2270±46	1948±85	2596±11
$\Sigma\text{H}_2\text{S}$ (μM)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	1.42±0.91	BDL
Fe(II) (μM)	0.04±0.01	0.05±0.02	0.17±0.09	0.08±0.04	0.11±0.07	BDL	0.08±0.03	0.10±0.04	0.03±0.02
Fe(III) (μM)	0.74±0.17	1.0±0.5	BDL	2.5±1.6	1.6±1.1	BDL	1.4±0.4	3.8±3.2	1.2±1.8

*BDL: Below detection level

4.3.3 Seasonal roles of methane and ammonia in driving water cap oxygen concentrations

Here, to identify if CH_4 and NH_4^+ , both shown to be important in affecting water cap oxygen concentrations over the entire summer of 2016 (Risacher et al. 2017), are also both important under ice, linear regression analyses were performed between oxygen concentration and each OCC for each of the three seasons (Figure 4-5). Potential change in consumption dynamics between early and late summer will also be assessed to see if the accumulation of CH_4 in the hypolimnion plays a role in changing the major OCC. As the majority of water cap $\Sigma\text{H}_2\text{S}$ concentrations were below detection (Table 4-2), this OCC was not considered in these analyses.

CH_4 was negatively correlated with oxygen for August and February but the regression had a low R square for August (0.56) indicative of the limited importance of oxygen consumption in BML. Despite this, CH_4 concentrations in the hypolimnion have increased from July to August, indicative of accumulation in the hypolimnion also consistent with the negative correlation in August which is not seen in July. The poor results of the linear regression for CH_4 are not surprising because of the concentrations below $1 \mu\text{M}$ in the metalimnion and epilimnion. Unfortunately, not enough data points are present to run linear regression for the hypolimnion alone but results suggest that oxygen consumption through CH_4 oxidation is limited to this region. In contrast, the regression of CH_4 against O_2 for February has a high R square (0.81) showing that CH_4 seems to be an important OCC during the winter. It is however worth noting that some points do not fall on the linear regression because the CH_4 accumulating under ice is not being consumed. The slope of the regression for February is 3.5 which is higher than the expected stoichiometric ratio of 2 moles of O_2 consumed for each mole of CH_4 oxidized through methanotrophy (Eq. 4-3). This could be explained because of two processes that would influence the oxygen and/or the CH_4 concentration. Mixing is one of these factor that could potentially control the amount of oxygenated water mixing past the thermocline during winter, indeed this would limit the O_2 concentration in the hypolimnion therefore increasing the slope of the regression between CH_4 and O_2 . On the other hand, the mobilization rate of CH_4 from the FFT might be higher than the consumption rate in the hypolimnion, therefore the CH_4 would accumulate in the top 7.5m of the water cap creating a gradient that is sharper than the one expected from consumption alone.



Similarly to CH_4 , NH_4^+ is negatively correlated with oxygen for July, August and February consistent with NH_4^+ being an important OCC in the BML water cap. July and February show similar trends with high R squares (0.84 and 0.85). The slope of 3.6 for July is higher than the expected ratio of 2 from the stoichiometric equation of NH_4^+ oxidation

to NO_3^- (Eq. 4-1 and 4-2) while for February it is slightly lower than expected (1.7). The higher slope could be indicative of additional processes going on aside from consumption similar to the ones mentioned for CH_4 in February such as a higher diffusion rate of NH_4^+ out of the FFT. On the other hand, August has a low R square (0.56) and a lower slope than July which indicates that as the summer progresses the dynamics of ammonia consumption changes. Despite the lower fit for the full water cap concentrations of NH_4^+ vs oxygen in August, NH_4^+ still seems to be higher at lower concentration of oxygen and lower at higher concentrations of oxygen. This could indicate that consumption processes are still active but are limited because of the lower oxygen concentration that develops in the hypolimnion as the summer proceeds. This is supported by the higher NO_2^- at the metalimnion-hypolimnion interface (Figure 4-4d) that indicate that only partial oxidation of NH_4^+ to NO_2^- is ongoing.

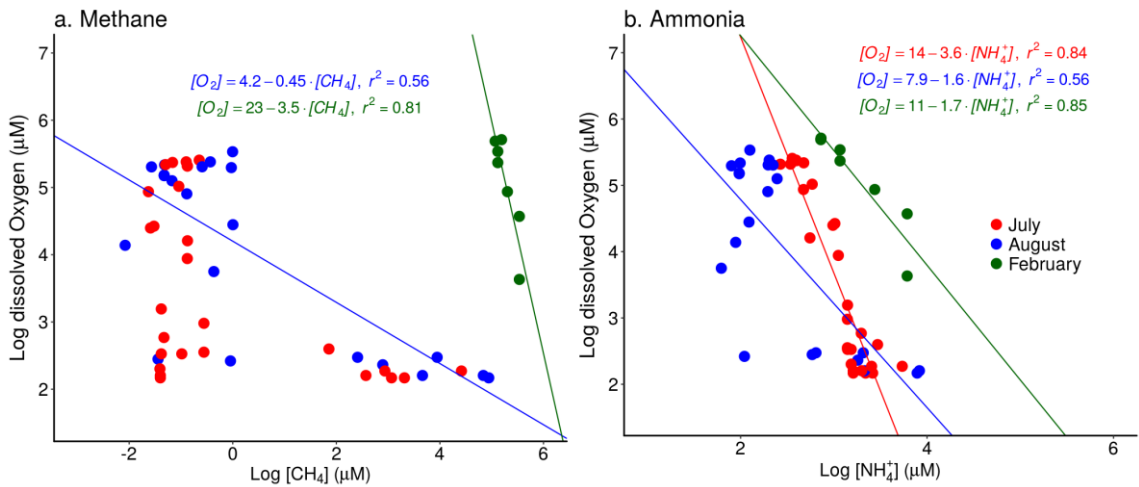


Figure 4-5: Models of dissolved oxygen vs Methane (a) or Ammonia (b) for July (red), August (blue) or February (green). The equations in each panels show the regression formula and the R-square value for each season.

4.3.4 Seasonal influence of oxygen and methane on nitrification

To understand what controls the observed change in consumption of NH_4^+ a regression between the log of the ratio of NO_3^- to NH_4^+ and the log of oxygen has been made to highlight the influence of oxygen on nitrification in the water cap (Figure 4-6). Since 2 moles of oxygen are consumed for each mole of NH_4^+ converted to NO_3^- a positive linear relationship between the log of oxygen and the log of the ratio of NH_4^+ to NO_3^- is expected. Results show a strong positive linear relationship between both for July and February (R square of 0.67 and 0.63 respectively) indicating that oxygen is the main control

on nitrification. For August, the fit is poor (R square of 0.43) hinting that nitrification is not as influenced by oxygen concentration as in July or February. The decrease in importance of oxygen on nitrification in August could be explained by the increased importance of CH₄ oxidation (Figure 4-5). Indeed, as both metabolism require oxygen, competition could develop, especially in the hypolimnion where oxygen in August is lower than in July. This supports the idea that had been proposed in Risacher et al. (2017) and Morris et al., 2017 where methanotrophs have a competitive advantage in oxygen uptake at low concentration compared to nitrifiers. Thus there is a potential oxygen consumption takeover by methanotrophs when oxygen in the hypolimnion is low.

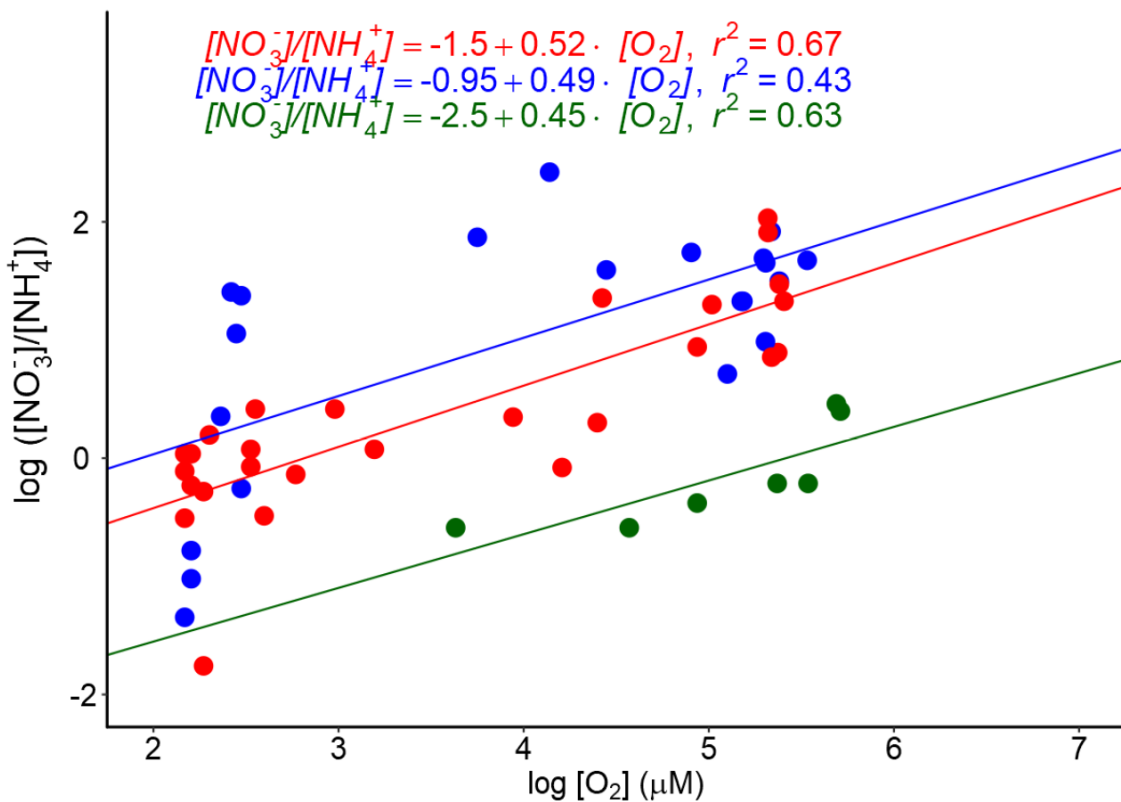


Figure 4-6: Models of log dissolved oxygen vs NH₄⁺ divided by NO₃⁻ for July (red), August (blue) or February (green). The equations show the regression formula and the R-square value for each season.

To test the effect of CH₄ on nitrification in the water cap a regression between the log of the ratio of NO₃⁻ to NH₄⁺ and the log of CH₄ has been made (Figure 4-7). Unlike the previous model where a positive relationship was expected based on the stoichiometric ratios of NH₄⁺ oxidation using oxygen, a negative relationship is expected here since CH₄ would have a negative impact on the conversion of NO₃⁻ to NH₄⁺. Results show that while indeed

for all seasons CH₄ has a negative effect on the ratio of NO₃⁻ to NH₄⁺, the strongest correlation is seen in August with a R square of 0.73 when in comparison February and July have a lower R square of 0.58 and 0.38 respectively. These results highlight that CH₄ concentration is the main control on nitrification in August compared to oxygen concentration which is the main control in July and February. This seasonal difference of the factor controlling nitrification can be explained by the change in physico-chemical and geochemical properties of the water cap throughout the summer. Indeed, as the summer progresses the stratification of the water cap limits the inputs of oxygen in the hypolimnion while OCC accumulate (Figure 4-3b and Figure 4-4a). These conditions have been hypothesised to be favorable to methanotrophs because of their competitive advantage against nitrifiers under low oxygen concentrations (Risacher et al., 2017; Morris et al., 2017; Carini et al., 2003; Roy et al., 1996). In comparison, February has higher oxygen level in the hypolimnion (Figure 4-3b) which allow nitrifiers to stay active despite the high amount of CH₄. For this reason, competition would not be limiting oxygen consumption as much as in late summer despite the OCC accumulation under ice.

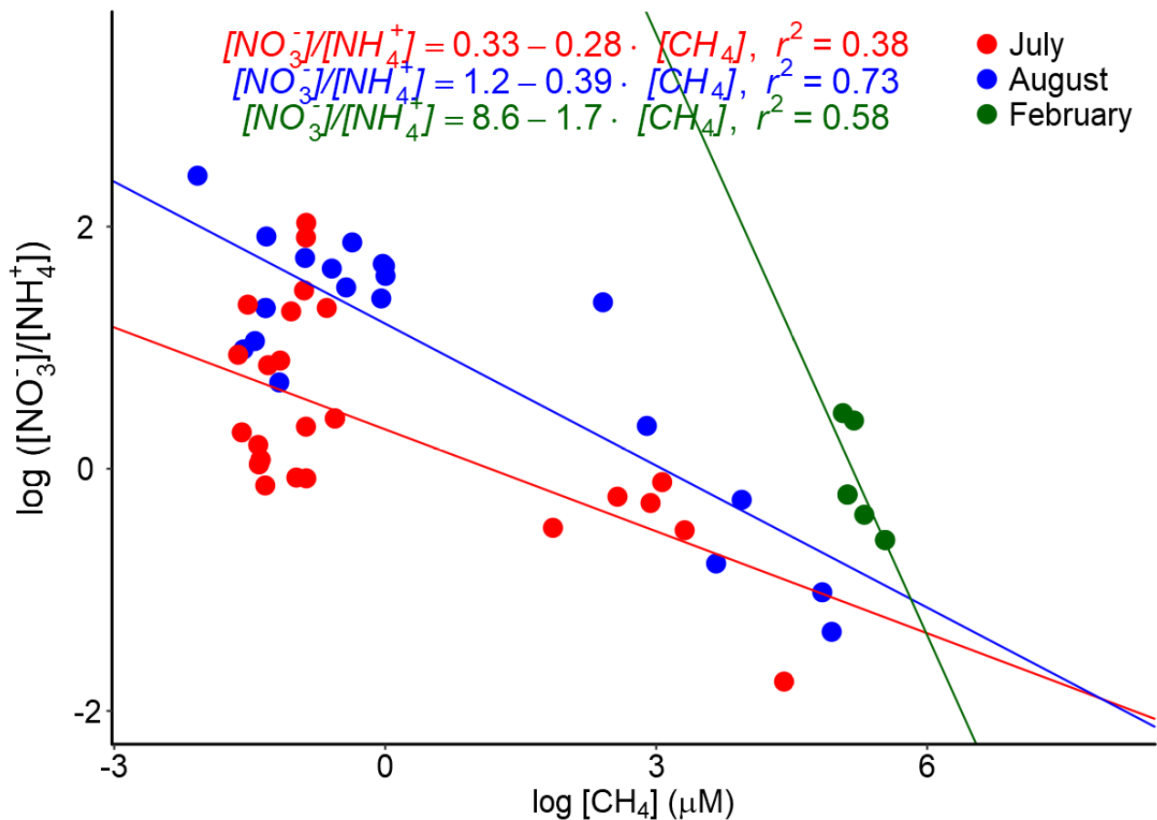


Figure 4-7: Models of log dissolved CH₄ vs NH₄⁺ divided by NO₃⁻ for July (red), August (blue) or February (green). The equations show the regression formula and the R-square value for each season.

Results here show that CH_4 and NH_4^+ are the two main OCC in BML throughout the water cap during the summer but also during winter, under ice. However, seasonal variations in their importance were observed with a higher preponderance of nitrification in early summer compared to late summer. This difference was explained by the accumulation of methane and depletion of oxygen in the hypolimnion as the summer progresses. Indeed, low oxygen concentrations have been previously linked to higher methanotrophs activity and lower nitrifiers activity because of their competitive advantage (Risacher et al., 2017; Morris et al., 2017). This is seen here in August where CH_4 becomes the dominant controlling factor on nitrification therefore limiting their activity. In winter, both NH_4^+ and CH_4 concentrations are high throughout the water cap and show signs of accumulation below ice. However, oxygen concentrations are high and consumption only takes place in the last 2.5m of the water cap thus limiting competition.

Characterization of the interactions between methanotrophs and nitrifiers will be a crucial next step in understanding the dynamics of oxygen consumption in pit lakes. As shown here, stratification creates the conditions suitable for competition to develop, therefore limiting the oxygen depletion of the water cap in summer. Rapid evolution of the factors controlling nitrification also highlighted the relative speed at which microbial interaction can change and impact the geochemical properties of the water cap. These concerns should be kept in mind as the potential for winter depletion of oxygen under ice is still very much present especially since both methanotrophs and nitrifiers have been shown to be active.

Chapter 5: Conclusion

The results of this thesis lay the foundation for early development for oil sands pit lakes through characterization of the first pilot AOSR pit lake, Base Mine lake (BML). Results confirmed that similarly to tailings ponds, the FFT is a source of oxygen consuming constituents (OCC) that are mobilized into the overlying water cap and affect oxygen concentration. Thermal stratification allowed by the thicker water cap and the lack of tailings input creates an oxygenated zoned that would be sufficient for life to thrive in the epilimnion during the summer but also during the winter under ice. Oxygen concentrations show evident decreases with depth, but persist albeit at low concentrations (i.e. < 1 mg/L) to the FFT water interface. Results identified that OCC accumulated in the hypolimnion during late summer as well as under ice. Analyses of OCC showed that CH_4 and NH_4^+ are the major constituent affecting oxygen concentration within water cap, while $\sum\text{H}_2\text{S}$ effects were constrained to the FFT water interface region. During the first year, 2015, CH_4 was the only significant OCC driving decreased oxygen concentrations within the water cap. However, in 2016, both NH_4^+ and CH_4 were significant OCC driving decreased BML water cap oxygen concentrations. The emergence of nitrifiers in Base Mine Lake is attributed to the lower naphthenic acid concentration compared to what is commonly found in tailings ponds where nitrification has not been observed despite high levels of NH_4^+ . Results here, have shown that accumulation of OCC in the hypolimnion through the summer is associated with decreased oxygen and a lower level of nitrification, indicating that methanotrophs outcompete nitrifiers at low oxygen concentrations. Change in the main factor controlling nitrification from oxygen in early summer to CH_4 in late summer also supports the idea of a competitive advantage of methanotrophs over nitrifiers under low oxygen conditions.

More than 50 pit lakes have been planned in the Athabasca oil sands and as the mining operations extend more will be underway. This underlines the importance of water capped tailings technology as a reclamation solution and the need to understand if this strategy is viable to sustain a full aquatic ecosystem. The main concern addressed by the results of this thesis was the potential for OCC mobilized from the underlying FFT layer within a pit lake to negatively impact oxygen concentrations and prevent the success of this possible reclamation strategy. Results have shown that despite active redox cycling in Base Mine Lake, the stratification observed during winter and summer allows for the top part of the water cap to have a constant oxygenated zone that could support macrofauna. The lake would therefore behave similarly to a productive boreal lake where the bottom is anoxic but fresh water fish populate the upper water cap. Despite these encouraging findings, the significant decrease and potential complete extinction of oxygen within the water cap still presents a risk for any ecosystem establishment, as the accumulation of OCC due to thermal stratification and/or ice cover could trigger significant oxygen decreases associated

with turn over and/or spring melt. Finally, the developmental trend observed from 2015 to 2016 of methane to methane and ammonia impacting BML water cap oxygen concentrations identifies a divergent microbially controlled biogeochemistry is developing within this pit lake compared to that seen in tailings ponds within the AOSR. As nitrification has never been shown to be active within AOSR tailings ponds, further characterization of both the microbial communities within BML as well as the continued developmental trajectory of the BML water cap is required to better constrain potential risks to water cap oxygen concentrations associated with FFT mobilized OCC and their subsequent biogeochemical redox cycling and thus better inform the design of future pit lakes for the region.

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