Effect of Diluent Levels on Greenhouse Gases and Reduced Sulfur Compound Emissions from Oil Sands Tailings

by

Kathleen Frances Ming-tze Day Gee

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

in

Environmental Engineering

Department of Civil and Environmental Engineering
University of Alberta

ABSTRACT

A well-known issue of tailings is that they have poor consolidation properties, which, *in situ*, may require several decades or more before the material can be reclaimed. With the accumulation of tailings in the tailings ponds, one unintended consequence of this long-term storage is the evolution of emissions in the ponds. Studies in the last decade have indicated that methane, a greenhouse gas, is produced by methanogen microorganisms in the tailings and that emissions are more readily stimulated by the hydrocarbons in naphtha diluent that is leftover from the bitumen extraction process. More recent studies have also found black, sulfidic zones in the tailings where toxic, hydrogen sulfide gas may be being produced in considerable amounts, but it is unknown how much hydrogen sulfide or other reduced sulfur compound emissions are being released from the ponds or whether these emissions are also stimulated by naphtha diluent. The objectives of this study were as follows: 1) Determine whether there are advantages to further reducing the diluent concentrations in the tailings with respect to methane, carbon dioxide, and reduced sulfur compound emissions; 2) Between methane, carbon dioxide, and reduced sulfur compound emissions, which are the most concerning quantity wise under a worst case, high diluent scenario; and 3) Aside from diluent, are there other chemical factors that play a role in the types of emissions generated from tailings.

A mesocosm experiment was conducted using Suncor Energy Inc. Pond 2/3 mature fine tailings, pond water (Pond 2/3 or surrogate pond water), with naphtha diluent amendments of 0% w/v, 0.2% w/v, 0.8% w/v, and 1.5% w/v. Chromatography gas analysis revealed that all greenhouse gases and reduced sulfur compound emissions increased with increasing naphtha diluent concentrations. Therefore, further reducing the concentration of residual diluent in the tailings ponds is anticipated to decrease the amount of greenhouse gases and reduced sulfur compound emissions that are produced in tailings. With respect to the quantities of emissions produced, at a worst-case diluent scenario of 1.5% w/v, methane emissions were the highest, followed by carbon dioxide, and then the combined amount of reduced sulfur compounds. Within the reduced sulfur compounds, amounts emitted from highest to lowest were in the order of hydrogen sulfide and 2-methylthiophene > 2,5-dimethylthiophene > 3-methylthiophene > thiofuran > butyl mercaptan > carbonyl sulfide, with hydrogen sulfide and 2-methylthiophene combined making up 81% of the total reduced sulfur compound emissions. The remaining sulfate concentrations within the tailings samples was also an important factor with regards to the types of emissions produced as there was a system shift from sulfur emissions production to methanogenesis after sulfate became depleted. Lastly, our results indicated that hydrogen sulfide, methane, and carbon dioxide were produced from biological sources associated with the mature fine tailings whereas the remaining reduced sulfur compounds appeared to originate from the naphtha diluent. In conclusion, this study has provided further insights to gas evolution in tailings that contain naphtha diluent.

DEDICATION

To my father, Norman Gee, my grandmother, Frances Gee (deceased), and my happy bunny, Whiskey (deceased), for their love and support over the years.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter 1. INTRODUCTION

1.1 Oil Sands Overview

The oil sands deposits in Alberta are the third largest in the world after Saudi Arabia and Venezuela; currently there are approximately 166 billion barrels of oil contained in these deposits (GoA 2015a). Bitumen extraction has been ongoing in Alberta since the 1960s. Surface-mined bitumen is commonly extracted from the oil sands ore using the Clark Hot Water Extraction Process (Arkell et al. 2015) where the oil sands ore is digested in caustic, hot water at temperatures up to 93^{o}C (Small et al. 2015). A drawback to this method is that a significant amount of tailings waste is produced. It is estimated that approximately 0.1–0.2 m^3 of tailings is generated per ton of oil sands processed (Lo et al. 2003; Paslawski et al. 2009; Small et al. 2015) or approximately 1 million m^3 of tailings is produced per day (Siddique et al. 2014). These tailings, which are an alkaline slurry mixture of process water, sand, silt, clays, organics, inorganics, and unrecovered bitumen and diluent (MacKinnon 1989; Small et al. 2015) are stored in large settling basins called 'tailings ponds' (MacKinnon and Sethi 1993; GoA 2014). After several years, the tailings roughly separate into three zones (MacKinnon 1989) that include a water cap, a fluid fine tailings zone (~10% wt solids)(Arkell et al. 2015), and a mature fine tailings zone (~30% wt solids) at the bottom of the pond (Arkell et al. 2015).

A well-known issue of tailings is that they have poor consolidation properties, which, *in situ*, may require several decades or more before the material sufficiently consolidates for use in reclamation (BGC 2010). As a result, there are significant volumes of tailings accumulating in the tailings ponds; in 2013, this amount was estimated to be 976 million m^3 (GoA 2015b). One effect of long-term storage of tailings is that the tailings properties change over time. This has resulted in unintended issues such as the evolution of emissions in the tailings ponds.

1.2 Emissions from Tailings Ponds

As depicted in Figure 1-1, tailings pond emissions can be released into the environment through several processes, including volatilization, aerosolization, and production from microbial sources within the tailings (Small et al. 2015). Volatilization is largely associated with volatile organic compound (VOC) emissions from the residual diluent in the tailings (Small et al. 2015). Diluent is an organic solvent that is used to lower the bitumen's viscosity for purification and transportation purposes (Rao and Liu 2013; Small et al. 2015). While the majority of the diluent is recovered, a small amount of diluent (<1 % mass) is lost to the tailings (Penner and Foght 2010). In general, organic compounds with relatively high vapor pressures will have a greater tendency to partition into the gas phase (Suthersan 1996). For example, the BTEX compounds (benzene, toluene, ethyl benzene, and xylenes) that are present in naphtha diluent (Siddique et al. 2007) are considered relatively volatile (Suthersan 1996) and would contribute to VOC emissions. Vapor pressure is a temperature dependent parameter as increases of 5^{o}C to 10^{o}C can markedly increase vapor pressure, which in turn may result in increased emissions (Hemond and Fechner-Levy 2000). Therefore, higher VOC emissions due to volatilization would be expected to occur at a tailings outfall where the freshly discharged tailings have warm temperatures of up to 60^{o}C (Penner and Foght 2010) or during the spring or summer seasons when ambient temperatures are greater (Small et al. 2015).

Aerosolization is another process that may result in tailings pond emissions and also occurs at the surface of tailings ponds. Physical processes such as splashing due to tailings discharge, bursting bubbles at the pond surface, or environmental factors such as rainfall or wind generated waves (Small et al. 2015) can result in the formation of tiny droplets (Ehrenhauser et al. 2014). These tiny droplets are ejected into the air at high velocities and evaporate, which leaves behind tiny aerosols that may contain contaminants (Thoroddsen 2012) that are carried away by the wind. For larger organic compounds that are not particularly volatile or accessible to microbial degradation, such as residual bitumen in the tailings ponds (Small et al. 2015), aerosolization may be an important transport process (Ehrenhauser et al. 2014).

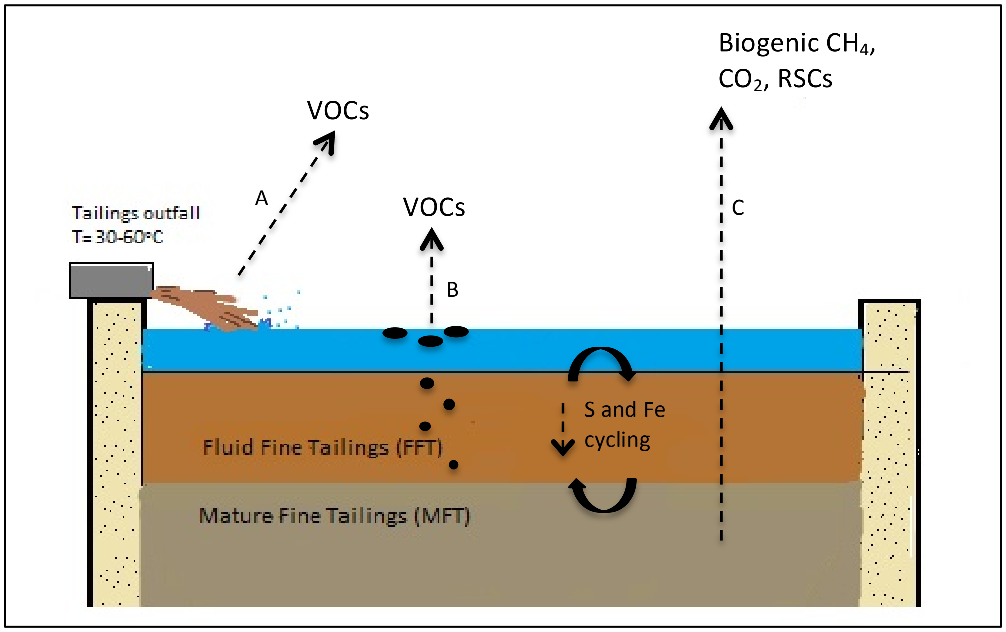


Figure 1-1: Theoretical emissions sources for an oil sands tailings pond. A) Volatilization and aerosolization of low molecular weight organics due to splashing and warm temperatures at the tailings outfall; B) Volatilization and aerosolization from oily films or residual bitumen due to wind, rain, or temperature changes; C) Biogenic gas production from microorganisms in the MFT. Sulfur and iron cycling in the tailings may decrease the rate of biogenic gases being released from the pond (image modified from Small et al. 2015).

In the last few decades, an emergence of methane (CH_4) emissions from the tailings ponds has garnered great interest. CH_4 was first detected approximately fifteen years after operation at two primary tailings ponds at Syncrude Canada Ltd. and Suncor Energy Ltd. between the 1980s and 1990s (Salloum et al. 2002; Yeh et al. 2010). It is suspected that this is partially due to changes in tailings discharge practices (Guo 2009) and the deposition of froth treatment tailings (FTT); more specifically, the hydrocarbons contained in the FTT diluent appear to be important substrates that are stimulating methane-producing microorganisms within the ponds (Burkus et al. 2014). CH_4 evolution is now present in most tailings ponds tested to date (Yeh et al. 2010; Siddique et al. 2012). The release of carbon dioxide (CO_2) has also been reported from a number of tailings ponds (Small et al. 2015). It is suspected of being largely biological (Small et al. 2015), however the oxidation of minerals such as pyrite and siderite in aerobic conditions may also contribute to CO_2 emissions (Burkus et al. 2014). The oil sands industry in Alberta has received criticism from various groups (Burkus et al. 2014) and internationally over the release of CH_4 and CO_2 from the tailings ponds, as these are greenhouse gases (GHGs). The production of CH_4 also potentially presents operational issues that may affect reclamation plans (ie. wet landscape) such as promoting the transport of toxic compounds and decreasing oxygen levels in water (Salloum et al. 2002), which is important due to new government policies aimed at decreasing the amount of accumulated tailings.

As of 2009, several government policies have been implemented to manage the accumulation of tailings for all oil sands operators (*Directive 074* and *Tailings Management Framework for Mineable Athabasca Oil Sands*), including specifying the performance criteria for tailings reduction and reclamation (ERCB 2015; GoA 2015b). In response, the oil sands industry has placed greater focus on the development of cost-effective techniques for the treatment of tailings (Siddique et al. 2014). One treatment that is used to increase MFT densification rates uses the additive, gypsum (Ramos-Padrón et al. 2011). The use of gypsum increases the sulfate concentrations in a tailings pond, an important substrate for sulfate-reducing bacteria (SRB) in the tailings, and may lead to an increased production of biogenic hydrogen sulfide (H_2S) gas (Chalaturnyk et al. 2002). As described by the Agency for Toxic Substances & Disease Registry (2014), H_2S is a “flammable, colorless gas that smells like rotten eggs”. Exposure to low concentrations can induce a variety of symptoms, including irritation to the eyes and throat, headaches, memory loss, and at high concentrations, may result in unconsciousness or death (ATSDR 2014). Currently, H_2S is hypothesized to largely remain within the tailings ponds (Ramos-Padrón et al. 2011) however there is a lack of peer-reviewed literature on the production of H_2S from tailings.

1.3 Research Objectives

A large majority of tailings pond emissions studies have reported on the biological production of methane (Holowenko et al. 2000; Fedorak et al. 2002, 2003; Siddique et al. 2006, 2007, 2011, 2012; Stasik and Wendt-Potthoff 2014) but there is little peer-reviewed literature regarding the production of other emissions such as reduced sulfur compounds (RSCs, including H_2S) and CO_2, which may potentially or are known to be released from the tailings ponds as well. To address this knowledge gap, (3) research questions were considered for this thesis dissertation:

1. ‘Are there advantages to further reducing the diluent concentrations in the tailings with regards to the emission of CO_2 and RSCs?’. As CO_2 is thought to be largely due to biological sources (Small et al. 2015), we hypothesize that CO_2 emissions will increase with increasing diluent concentrations. Similarly, based on slight increases in sulfate-reduction rates following substrate amendments as reported in Stasik and Wendt-Potthoff (2014), we hypothesize that RSC emissions will also increase with greater naphtha amendments but not to the same extent as CH_4 and CO_2.

2. ‘Between CH_4, CO_2, and RSC emissions, which are the most concerning quantity-wise to tailings pond operators in a worst case scenario, high diluent concentration?’. We hypothesize that the RSC emissions will be relatively minor in comparison to CH_4 and CO_2 emissions based on the low RSC concentrations (<ppb) that are typically found in the general environment (Wardencki 1998). Additionally, based on previous CH_4 studies, it is anticipated that CH_4 will be the greatest concern to tailings pond operators due to increased microbial stimulation at higher diluent concentrations.

3. ‘Aside from the diluent, are there other chemical factors that play a role in the types of emissions generated from tailings?’. A study by Fedorak et al. (2002) had previously reported a relationship between sulfate depletion and the start of methanogenesis. Based on this, we hypothesize that there will be a system shift from sulfur emissions to methane emissions when sulfate concentrations become depleted in the tailings.

To answer the research questions of this study the overall goals were to 1) characterize GHGs (CH_4 and CO_2) and select RSC emissions from tailings samples amended with varying naphtha concentrations; and 2) monitor select chemical parameters over time to determine whether there are any observed trends during gas evolution. In a similar fashion to previous CH_4 studies, this experiment was carried out in the laboratory using mesocosms to study the emissions generated directly from the tailings (ie. prior to exposure to aerobic conditions). The tailings materials used in this study included MFT, pond water, and naphtha diluent provided by Suncor Energy Ltd. Naphtha diluent was chosen due to its common use among different oil sands operators (Small et al. 2015), and the treatment levels ranged from 0% w/v to 1.5% w/v based on the typical naphtha diluent concentrations (<1 % mass naphtha) in the tailings (Penner and Foght 2010). Emissions were characterized by gas chromatograph (GC) methods, and the chemical parameters monitored over time included redox, pH, conductivity, dissolved organic carbon, alkalinity, and sulfate and nitrate concentrations.

To the author's knowledge, this study will be one of the first to present sulfur emissions data from tailings. By examining RSCs and CO_2 production at residual diluent concentrations as a 'baseline' it will yield further insight as to whether the addition of known substrates to the tailings ponds (ie. SO_4^{2-}) would result in emissions that require consideration in current or future tailings remediation plans.

1.4 Research Outline

This thesis consists of five chapters. A literature review regarding the current knowledge on the general physical and chemical characteristics of tailings, and information regarding the production of methane, carbon dioxide, and sulfur emissions from tailings ponds is presented in chapter 2. The experimental set-up for this study is described in chapter 3. The results obtained from this study are presented and discussed in chapter 4. Lastly, conclusions from this research and recommendations for future research are presented in chapter 5.

1.5 Chapter 1 References

Agency for Toxic Substances & Disease Registry (ATSDR). 2014. Hydrogen sulfide – ToxFAQs^{TM} [online]. Available from http://www.atsdr.cdc.gov/toxfaqs/tfacts114.pdf [cited 7 September 2015].

Arkell, N., Kuznetsov, P., Kuznetsova, A., Foght, J.M., and Siddique, T. 2015. Microbial metabolism alters pore water chemistry and increases consolidation of oil sands tailings. Journal of Environmental Quality, **44**: 145–153.

BGC Engineering Inc. 2010. Review of reclamation options for oil sands tailings substrates. Available from the Oil Sands Research and Information Network, University of Alberta, School of Energy and the Environment, Edmonton, Alta. OSRIN Report No. TR-2. pp 59.

Burkus, Z., Wheler, J., and Pletcher, S. 2014. GHG emissions from oil sands tailings ponds: overview and modelling based on fermentable substrates. Part I: Review of the tailings ponds facts and practices [online]. Alberta Environment and Sustainable Resource Development. Available from http://hdl.handle.net/10402/era.40125 [cited 15 August 2015].

Chalaturnyk, R.J., Scott, J.D., and Özüm, B. 2002. Management of oil sands tailings. Petroleum Science and Technology, **20**(9–10): 1025–1046.

Ehrenhauser, F.S., Avij, P., Shu, X., Dugas, V., Woodson, I., Liyana-Arachchi, T., Zhang, Z., Hung, F.R., and Valsaraj, K.T. 2014. Bubble bursting as an aerosol generation mechanisms during an oil spill in the deep-sea environment: laboratory experimental demonstration of the transport pathway. Environmental Science: Processes & Impacts, **16**: 65–73.

Energy Resources Conservation Board (ERCB). 2015. Directive 074: Tailings performance criteria and requirements for oil sands mining schemes [online]. Available from https://www.aer.ca/documents/directives/Directive074.pdf [cited 14 September 2015].

Fedorak, P.M., Coy, D.L., Salloum, M.J., and Dudas, M.J. 2002. Methanogenic potential of tailings samples from oil sands extraction plants. Canadian Journal of Microbiology, **48**(1): 21–33.

Fedorak, P.M., Coy, D.L., Dudas, M.J., Simpson, M.J., Renneberg, A.J., and MacKinnon, M.D. 2003. Microbially-mediated fugitive gas production from oil sands tailings and increased tailings densification rates. Journal of Environmental Engineering & Science, **2**(3): 199–211.

Government of Alberta (GoA). 2014. Tailings [online]. Available from http://www.oilsands.alberta.ca/tailings.html [cited 6 July 2015].

Government of Alberta (GoA). 2015a. Facts and statistics [online]. Available from http://www.energy.alberta.ca/oilsands/791.asp [cited 29 Sept 2015].

Government of Alberta (GoA). 2015b. Lower Athabasca region tailings management framework for the mineable Athabasca oil sands [online]. Available from http://esrd.alberta.ca/focus/cumulative-effects/cumulative-effects-management/management-frameworks/documents/LARP-TailingsMgtAthabascaOilsands-Mar2015.pdf [cited 6 July 2015].

Guo, C. 2009. Rapid densification of the oil sands mature fine tailings (MFT) by microbial activity. Ph.D. thesis, The University of Alberta, Edmonton, Alta.

Hemond, H.F., and Fechner-Levy, E.J. 2000. Chemical fate and transport in the environment. 2nd ed. Elsevier, San Diego, Calif.

Holowenko, F.M., MacKinnon, M.D., and Fedorak, P.M. 2000. Methanogens and sulfate-reducing bacteria in oil sands fine tailings waste. Canadian Journal of Microbiology, **46**(10): 927–937.

Lo, C.C., Brownlee, B.G., and Bunce, N.J. 2003. Electrospray-mass spectrometric analysis of reference carboxylic acids and Athabasca oil sands naphthenic acids. Analytical Chemistry, **75**: 6394–6400.

MacKinnon, M.D. 1989. Development of the tailings pond at Syncrude's oil sands plant: 1978–1987. AOSTRA Journal of Research, **5**: 109–133.

MacKinnon, M., and Sethi, A. 1993. A comparison of the physical and chemical properties of the tailings ponds at the Syncrude and Suncor oil sands plants. *In* Proceedings of the Fine Tailings Symposium: Oil Sands – Our Petroleum Future Conference, Edmonton, Alta., 4–7 April 1993. AOSTRA Publications, Edmonton, Alta. Paper No. 57.

Paslawski, J.C., Headley, J.V., Hill, G.A., and Nemati, M. 2009. Biodegradation kinetics of trans-4-methyl-1-cyclohexane carboxylic acid. Biodegradation, **20**: 125–133.

Penner, T.J., and Foght, J.M. 2010. Mature fine tailings from oil sands processing harbour diverse methanogenic communities. Canadian Journal of Microbiology, **56**(6): 459–470.

Ramos-Padrón, E., Bordenave, S., Lin, S., Bhaskar, I.M., Dong, X., Sensen, C.W., Fournier, J., Voordouw, G., and Gieg, L.M. 2011. Carbon and sulfur cycling by microbial communities in a gypsum-treated oil sands tailings pond. Environmental Science & Technology*,* **45**(2): 439–446.

Rao, F., and Liu, Q. 2013. Froth treatment in Athabasca oil sands bitumen recovery process: a Review. Energy Fuels*,* **27**(12): 7199–7207.

Salloum, M.J., Dudas, M.J., and Fedorak, P.M. 2002. Microbial reduction of amended sulfate in anaerobic mature fine tailings from oil sand. Waste Management & Research, **20**(2): 162–171.

Siddique, T., Fedorak, P.M., and Foght, J.M. 2006. Biodegradation of short-chain *n*-alkanes in oil sands tailings under methanogenic conditions. Environmental Science & Technology, **40**(17): 5459–5464.

Siddique, T., Fedorak, P.M., MacKinnon, M.D., and Foght, J.M. 2007. Metabolism of BTEX and naphtha compounds to methane in oil sands tailings. Environmental Science & Technology, **41**(7): 2350–2356.

Siddique, T., Penner, T., Semple, K., and Foght, J.M. 2011. Anaerobic biodegradation of longer-chain *n*-alkanes coupled to methane production in oil sands tailings. Environmental Science & Technology, **45**(13): 5892–5899.

Siddique, T., Penner, T., Klassen, J., Nesbø., and Foght, J.M. 2012. Microbial communities involved in methane production from hydrocarbons in oil sands tailings. Environmental Science & Technology, **46**(17): 9802–9810.

Small, C.C., Cho, S., Hashisho, Z., and Ulrich, A.C. 2015. Emissions from oil sands tailings ponds: review of tailings pond parameters and emission estimates. Journal of Petroleum Science and Engineering, **127**: 490–501.

Stasik, S., and Wendt-Potthoff, K. 2014. Interaction of microbial sulphate reduction and methanogenesis in oil sands tailings ponds. Chemosphere, **103**: 59–66.

Suthersan, S.S. 1996. Remediation engineering design concepts. CRC Press.

Thoroddsen, S.T. 2012. The making of a splash. Journal of Fluid Mechanics, **690**: 1–4.

Wardencki, W. 1998. Problems with the determination of environmental sulphur compounds by gas chromatography. Journal of Chromatography A, **793**(1): 1–19.

Yeh, S., Jordaan, S.M., Brandt, A.R., Turetsky, M.R., Spatari, S., and Keith, D.W. Land use greenhouse gas emissions from conventional oil production and oil sands. Environmental Science & Technology, **44**(22): 8766–8772.

Chapter 2. LITERATURE REVIEW

2.1 Tailings Pond Overview

Bitumen from surface-mined oil sands is commonly extracted using the Clark Hot Water Extraction Process (Chalaturnyk et al. 2002; Arkell et al. 2015). Briefly, this method involves crushing the mined ore and then mixing it with caustic, hot water at temperatures from 40°C to 93°C (Small et al. 2015). Depending on the ore quality and grade, the amount of caustic soda (NaOH) required varies from less than 0.04 kg/t to 0.11 kg/t of oil sands (MacKinnon and Sethi 1993). After hot water treatment, the resulting slurry is pumped to 'separation' stage(s). Due to the air trapped within the oil sands, the bitumen floats up and forms froth (Chalaturnyk et al. 2002) that is approximately 60 wt % bitumen, 30 wt % water, and 10 wt % mineral solids (Rao and Liu 2013). The froth is then collected by skimming rakes (Chalaturnyk et al. 2002) and is transported to froth treatment. At this stage the bitumen froth is typically treated with diluent (naphtha or paraffins) to remove residual water and solids, and to decrease the bitumen's viscosity for ease of transport before further processing (Rao and Liu 2013; Small et al. 2015).

The wastes from the bitumen extraction process, called 'tailings': an alkaline slurry of process water, sand, silt, clays, organics, inorganics, and unrecovered bitumen and diluent (MacKinnon 1989; Small et al. 2015) are transported to large settling basins called 'tailings ponds' for storage (MacKinnon and Sethi 1993; GoA 2014). Once deposited, the coarse solids fraction of the tailings (>44μm) quickly settles out to form beaches (Chalaturnyk et al. 2002; Small et al. 2015). The remaining wastes are left to settle, and over time they will separate into three zones within the tailings pond as seen in Error! Reference source not found.: 1) Water cap; 2) Fluid fine tailings zone; and 3) ature fine tailings zone (MacKinnon 1989).

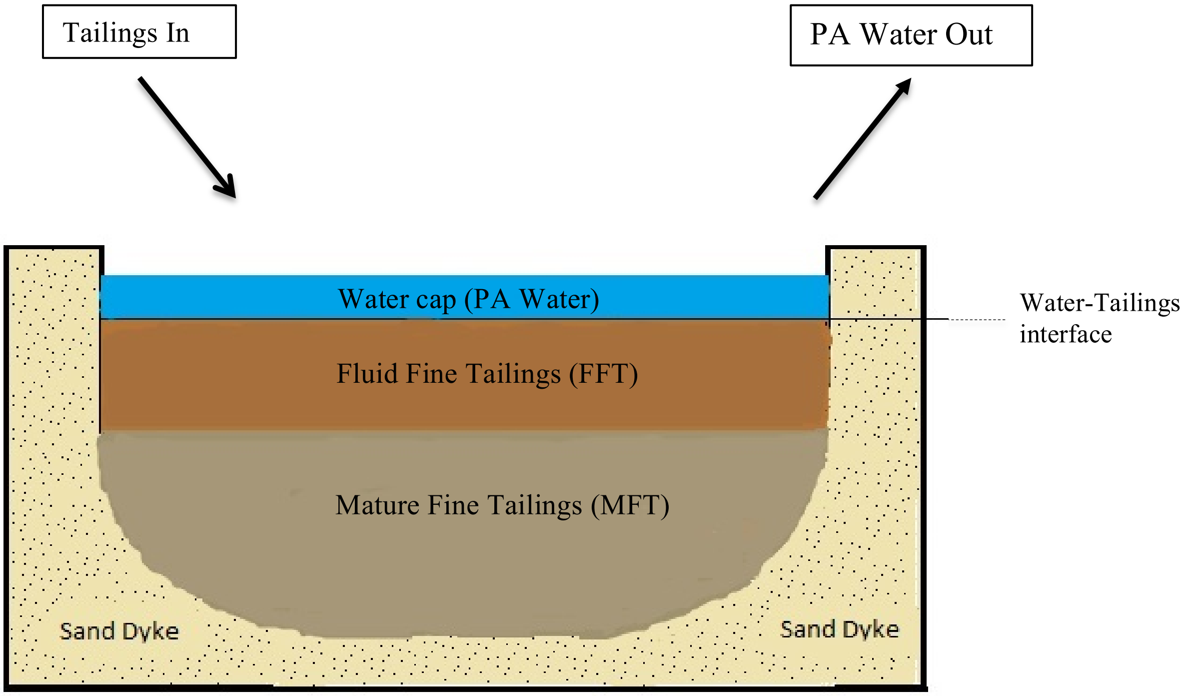


Figure 2-1: A general tailings pond depicting three zones that form as the tailings settle over time: Water cap, fluid fine tailings zone, and a mature fine tailings zone (Image modified from Small et al. (2015)).

The water cap is the upper-most layer in the tailings pond, and is composed of process-affected (PA) water that is released as the tailings settle (MacKinnon 1989). In general this zone is shallow; depths typically range from 2 m to 5 m (MacKinnon and Sethi 1993; Holowenko et al. 2000).

After the initial settling, the remaining process water and fines (primarily clay and silts, 20–80 wt % of fines)(Small et al. 2015) form an aqueous suspension called fluid fine tailings (FFT)(Small et al. 2015). After 2–4 years of settling, the solids content of the FFT increases to approximately 30 wt % solids, also known as mature fine tailings (MFT)(Arkell et al. 2015). Depending on the pond, the depth of the FFT and MFT zones can vary widely. In a study by MacKinnon and Sethi (1993), the tailings ponds studied at the time had total depths of up to 60 m.

The reason why tailings ponds have such a large footprint is in part due to the quantities of tailings produced in the bitumen extraction process. It is estimated that approximately 0.1–0.2 m^3 of tailings is generated per ton of oil sands processed (Lo et al. 2003; Paslawski et al. 2009; Small et al. 2015) or approximately 1 million m^3 of tailings is produced per day (Siddique et al. 2014). Given that the Alberta oil sands produced approximately 1.9 million barrels of oil per day in 2012 (GoA 2015a) and that the companies operate under a 'zero discharge' policy (MacKinnon and Sethi 1993), a significant amount of tailings has been accumulating within the ponds. As of 2013, the Alberta Government estimated that there were approximately 976 million m^3 of tailings being stored in the ponds (GoA 2015b). The issues behind the accumulation of these tailings are related to the tailings' physical and chemical properties, which are discussed in the following section.

2.2 Physical and Chemical Properties of Tailings

Due to their size and stratification, tailings ponds are heterogeneous environments. This means that the physical and chemical parameters of the tailings stored within a pond can vary significantly depending on the time, depth, and location a sample is taken. In addition to this, tailings' composition is also influenced by any modifications in the bitumen extraction process between oil sands companies, such as the use of additives, and the composition of the oil sands ore from which the bitumen was extracted (MacKinnon and Sethi 1993; Small et al. 2015). As such, this section will only summarize the general physical and chemical parameters of tailings found within literature. A brief summary regarding the water cap will be discussed first, followed by a discussion of tailings properties below the water:tailings interface.

As previously mentioned, the water cap is comprised of PA water that has been released from the consolidating tailings (MacKinnon 1989). Depending on the pond depth and residence time, the solids content of the PA water is typically less than 1% (MacKinnon and Sethi 1993). With respect to chemical composition, the PA water has been reported to contain high concentrations of sodium, chloride, and sulfate ions (Stasik et al. 2014; Small et al. 2015). As the ponds are operated outdoors, this shallow water layer is subject to environmental factors including seasonal fluctuations in temperature (25^{o}C in summer to ice cover in winter), wind mixing, mixing due to tailings discharge into the pond (MacKinnon and Sethi 1993), and interactions with the atmosphere (Small et al. 2015). The PA water from the water cap is recycled by oil sands operators and is reused in plant processes (MacKinnon 1989).

With regards to the tailings below the water:tailings interface, a summary of some commonly reported physical and chemical parameters from select tailings ponds are given in Table 2-1. Properties of tailings from Syncrude's Mildred Lake Settling Basin (MLSB) are frequently reported in peer-reviewed literature, and thus have been summarized in Table 2-1. Information regarding tailings from Suncor Energy Ltd.'s tailings ponds is less frequently reported on in peer-reviewed literature but the physical and chemical parameters found for Ponds 1, 2, and 3 are also included in Table 2-1.

For parameters of bitumen content, solids content, and temperature, there have been some general trends observed. Firstly, the residual bitumen content within tailings has consistently been found within a narrow range of values. In 1992, the bitumen content in Suncor's Pond 2 and Pond 3 ranged from less than 0.5–5 mass % at depths less than 6 m (Table 2-1). These values are similar to the bitumen content reported in tailings samples taken from the MLSB (1.1–2.7 mass %) in 1998 and 2004. In some cases, however, the residual bitumen content may exceed the typical range such as in the case of Suncor's Pond 1, in which a tailings sample was reported to contain 9.0 mass % of bitumen content. The reason for this elevation may be due to the sample being retrieved at a lesser depth (3.5 m) where relatively fresh tailings tend to reside.

Solids content, as noted in Table 2-1, has been found to increase with depth across all tailings ponds. This is due to the slow settling of the aqueous suspension of fines within the ponds (Holowenko et al. 2000). The degree of settling at a specific depth, however, is not consistent. For example, the solids content reported at a depth of 20 m could potentially range anywhere from 25.8 to 58.6 mass % (Table 2-1). This once again demonstrates the heterogeneity of the ponds.

Table 2-1: Select physical and chemical parameters with respect to depth for tailings in the Mildred Lake Settling Basin (Syncrude), and Ponds 1, 2, and 3 (Suncor).

Tailings pond	MLSB				Pond 2			Pond 3				Pond 1
Depth (m)	~6	10	20	30	6	19	28	6	18	29	52	3.5
Bitumen (g/100g)	2.57[c] – 2.7[b]	1.8[a]–2.24[c]	1.68[c]	1.11[c]	5.0 [d]	4.0[d]	-	0.3[d]	3.2[d]	4.1[d]	0.5[d]	9.0[b]
Solids (g/100g)	28.7[b] – 40.7[c]	25.0[a]–42.5[c]	58.6[c]	71.6[c]	27.9[d]	45.7[d]	43.1[d]	14.8[d]	25.8[d]	36.7[d]	75.7[d]	30.0[b]
Temperature (°C)	12[c]–16[b]	12.5[a]–16.9[c]	11.5[a]–22[c]	21.2[c]	16[d]	22[d]	20[d]	20[d]	18[d]	19[d]	18[d]	-
pH	7.37[c] – 8.3[a]	7.00[c]–8.3[a]	7.54[c]–8.5[a]	7.96[c]	8.2[d]	8.2[d]	8.3[d]	8.2[d]	8.0[d]	8.2[d]	8.1[d]	7.5[b]
HCO_3^- (mg/L)	1530[b]–1700[c]	970[a]–1790[c]	1220[c]	1470[c]	890[d]	874[d]	890[d]	874[d]	874[d]	874[d]	813[d]	1800[b]
NO_3^- (mg/L)	<1.0[c]	<1.0[c]	<1.0[c]	<1.0[c]	-	-	-	-	-	-	-	ND[b]
SO_4^{2-} (mg/L)	0.1[c] – 19[b]	12.8[c]–68[a]	19.6[c]	36.0[c]	108[d]	47[d]	44[d]	81[d]	43[d]	56[d]	137[d]	34[b]
DOC (mg/)	44[c] – 70[b]	44[c]	50[c]	56[c]	67[d]	60[d]	63[d]	69[d]	68[d]	63[d]	83[d]	68[b]
Naphtha (g/100g)	0.25[c] – 0.21[b]	0.21[c]	0.17[c]	0.03[c]	-	-	-	-	-	-	-	0.6[b]

Note: MLSB, Mildred Lake Settling Basin; DOC, dissolved organic carbon; ND, non-detectable

[a] From Holowenko et al. (2000), MFT sampled in July 1998.

[b] From Fedorak et al. (2002), MFT sampled in Sept 1998.

[c] From Penner and Foght (2010), MFT sampled in May 2004.

[d] Data for Ponds 2 and 3 were modified from MacKinnon and Sethi (1993), reported values in 1992.

Temperature of the tailings can vary considerably depending upon the pond, depth, and year the tailings were sampled (Table 2-1). In comparison to the water cap, the temperature of the tailings appears to be relatively consistent for depths less than 5 m at a given point in time (MacKinnon and Sethi 1993). Holowenko et al. (2000) analyzed tailings from the MLSB at depths of 5 m, 10 m, 15 m, and 20 m below the water surface in August 1997 and July 1998. In August 1997, the tailings samples had temperatures ranging from 17.7°C to 21.2°C (avg 19.3°C). Approximately a year later, at similar depths but different locations, the tailings temperature was found to be between 11.0°C and 14.0°C (avg 12.3°C). While a comparison between the two years yields a large temperature range within the MLSB, the temperature range of the tailings within each sampling period (1997, 1998) was relatively narrow and consistent at depths below the water:tailings interface.

With regards to chemical parameters, there are several notable trends as well. Tailings' pH was within a narrow range of approximately 7.0 to 8.5. Small fluctuations in pH can occur from the addition of fresh tailings, which have a pH of 9.0–10 (MacKinnon and Sethi 1993).

In addition to elevated levels of sodium and chloride, tailings also contain bicarbonate (HCO_3^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}) ions. Bicarbonate is the dominant anion in tailings (MacKinnon and Sethi 1993); concentrations are typically greater than 870 mg/L but in more recent studies bicarbonate concentrations of up to 1,800 mg/L have been reported (Table 2-1). Bicarbonate is of interest as it is a by-product of microbial respiration (MacKinnon and Sethi 1993; Salloum et al. 2002), and may be used as an indicator of microbial activity. Nitrate and sulfate are also of interest as they are potential electron acceptors for microorganisms under anaerobic conditions (Singleton 1993; Salloum et al. 2002; Dou et al. 2008) that are present in the tailings pond environment. Nitrate concentrations within the tailings, in general, are low. As can be seen in Table 2-1, nitrate concentrations typically measured less than 1 mg/L but concentrations up to 16 mg/L have been reported (Salloum et al. 2002). In comparison, sulfate is typically present in appreciable amounts. Several studies have reported sulfate concentrations to be the highest in the water cap and then rapidly decrease with depth in the tailings (MacKinnon and Sethi 1993; Holowenko et al. 2000; Salloum et al. 2002; Stasik et al. 2014). For example, Stasik et al. (2014) reported a decrease in sulfate concentrations starting at approximately 450 mg/L in the water cap to less than 50 mg/L in the tailings. Interestingly, Penner and Foght (2010) found sulfate concentrations to increase with depth in the MLSB. This increase appeared to coincide with decreasing numbers of sulfate-reducing bacteria that were also measured in this study.

Organics are also present within the tailings, however this fraction is not well characterized. This is partially due to the size of the tailings ponds (Small et al. 2015) and the complexity of the organic mixtures, which makes separation of the components time consuming and difficult (Selucky et al. 1977; Holowenko et al. 2001). Some organics that have been reported in tailings are associated with the unrecovered bitumen and diluent from the bitumen extraction process (MacKinnon and Sethi 1993; Siddique et al. 2007). Unrecovered bitumen is potentially contributing a fair amount of linear alkanes ($<C_{19}$) in the tailings ponds. Siddique et al. (2011) estimated that approximately 4,500 tonnes of linear alkanes ended up in the MLSB in 2011 from the unrecovered bitumen. Burkus et al. (2014) estimated that this amount was likely closer to 800 tonnes. Diluent is also a

source of organics within tailings ponds, especially naphtha due to its common use (Small et al. 2015). Naphtha is a complex mixture with 280 different hydrocarbons that includes compounds such as *n*-alkanes, BTEX (benzene, toluene, ethylbenzene, and xylenes), and other low molecular weight hydrocarbons (Siddique et al. 2007). Typically there is less than 1 mass % of residual naphtha in the tailings (Table 2-1**)**. Tailings also contain dissolved organic carbon (DOC), which is defined as organic matter that passes through a 0.45µm filter (MacKinnon 1989). The DOC concentrations within tailings typically range from 40–70 mg/L (Table 2-1), but concentrations up to 120 mg/L have been reported (Holowenko et al. 2001). Potentially, much of the DOC may be contributed by naphthenic acids (Fedorak et al. 2002; Penner and Foght 2010), which originate from the oil sands (Holowenko et al. 2001).

In summary, a significant amount of tailings waste is generated when bitumen is extracted from the oil sands (GoA 2015b). Tailings composition, which is a complex, alkaline mixture of process water, sand, silt, clays, organics and inorganics (MacKinnon 1989; Small et al. 2015), is largely influenced by the oil sand's ore composition and differences in the bitumen extraction process between oil sands operators (MacKinnon and Sethi 1993). Furthermore, analyzing the physical and chemical parameters of tailings is further complicated by the heterogeneity and size of the tailings ponds (Stasik et al. 2014; Small et al. 2015). Despite these difficulties, the physical and chemical parameters of tailings are of importance as the MFT *in situ* is expected to require decades of settling before it can be used for reclamation purposes (BGC 2010). One effect of such long-term storage is that the properties of the tailings change over time. This has resulted in unintended issues, such as the emission of gases from the ponds.

2.3 Gas Emissions from Tailings Ponds

2.3.1 Methane Emissions

One of the earliest documented reports of methane (CH_4) in the ponds was in the 1990s when CH_4 was first detected in Syncrude's MLSB (Holowenko et al. 2000). The MLSB began operation in 1978 (Burkus et al. 2014), and was Syncrude's primary tailings pond (Holowenko et al. 2000). In 1994, tailings discharge practices shifted from tailings being distributed around the pond to being mostly in the southern end (Guo 2009). Several years after this change, there was a noticeable increase in temperature in this area of the pond. Tailings temperatures at Sta. 1 (one of MLSB's three sampling stations) ranged from ~10^oC to 16^oC pre–1994, and increased up to ~23.5^oC in 1997 (Guo 2009). By 1999, bubbling was observed in the south-end of the MLSB and there was an estimated daily CH_4 flux of 17 L/m^2 being emitted from the pond (Fedorak et al. 2003; Holowenko et al. 2000). It is suspected that because the warm tailings were concentrated in the south end of the pond, the pond's temperature increased and this may have accelerated microbial activity to produce CH_4 emissions (Guo 2009).

Currently, most tailings ponds that have been tested are also producing CH_4 (Siddique et al. 2012). CH_4 evolution is a concern for several reasons. Not only is CH_4 a greenhouse gas (GHG) and may pose an ignition hazard near pumping equipment (Fedorak et al. 2003), but CH_4 bubbles may also negatively impact tailings reclamation efforts by re-suspending fines, increasing oxygen demand in the water layer, which can lead to anoxic conditions (Fedorak et al. 2002), and enhancing the transport of toxic compounds (Salloum et al. 2002; Ramos-Padrón et al. 2011).

2.3.1.1 Factors Affecting Methane Emissions From Tailings

MFT are known to harbor diverse microbial communities (Penner and Foght 2010). In MFT samples containing methanogenic microorganisms, CH_4 was reportedly produced under anaerobic conditions without additional supplements (no culture medium or extra substrates added) (Holowenko et al. 2000; Penner and Foght 2010). Furthermore, CH_4 production was enhanced when the MFT was amended with additional substrates (Siddique et al. 2006; Siddique et al. 2007; Siddique et al. 2011), and was undetected in instances where the MFT was sterilized (Siddique et al. 2006). Considering such observations, microbial communities within the tailings ponds have been implicated in the production of CH_4 though the biological mechanisms remain speculative (Siddique et al. 2012). Regardless, a number of studies have investigated the factors that influence CH_4 emissions and such factors include the 1) type of substrates, 2) availability of substrates, 3) temperature of the tailings, and 4) presence of carbon dioxide (CO_2).

Firstly, there have been several studies within the last decade that have investigated whether components of unrecovered bitumen or naphtha were being utilized by the microorganisms as substrates to produce CH_4 within the tailings ponds. Siddique et al. (2007) amended MFT from the MLSB with naphtha at concentrations of 0.5% w/v and 1.0% w/v, and found that the majority of the naphtha did not degrade under methanogenic conditions. After 46 weeks of incubation, only the BTEX compounds and *n*-alkanes (C_7-C_9) associated with the naphtha were degraded. The BTEX components in this study were preferentially degraded in the order of toluene > o-xylene > *m*-and-*p*-xylene > ethylbenzene > benzene (Siddique et al. 2007). These results slightly differ from those of Dou et al. (2008) which found that BTEX degraded with toluene > ethylbenzene

> *m*-xylene > *o*-xylene > benzene > *p*-xylene using a bacterial consortium from gasoline-contaminated soil under anaerobic conditions. The short chain *n*-alkanes in Siddique et al. (2007) also had a preferential degradation order of $C_9 > C_8 > C_7$. These results are consistent with those in Siddique et al. (2006) who investigated the degradation of *n*-alkanes in microcosms with MFT (also from MLSB) spiked with *n*-alkanes mixtures containing C_6, C_7, C_8, and C_{10}. Siddique et al. (2006) found that *n*-alkanes were degraded in the order of $C_{10} > C_8 > C_7 > C_6$.

Longer chain *n*-alkanes associated with bitumen have also been investigated as potential substrates as well. Siddique et al. (2011) amended MFT (from MLSB) with *n*-alkanes mixtures containing C_{14}, C_{16}, and C_{18}, and reported that there was a simultaneous sharp increase in CH_4 production when the concentrations of the *n*-alkanes started to decrease after 255 days. Unlike the short-chained *n*-alkanes and BTEX, however, there was no clear pattern of preferential degradation with the longer-chain *n*-alkanes (Siddique et al. 2011). The authors also noted that methanogenesis from the short chain *n*-alkanes occurred sooner than the longer chain *n*-alkanes; methanogenesis from the short-chain *n*-alkanes occurred within 10 days whereas there was a lag period of over 200 days before methanogenesis production increased with the longer-chain *n*-alkanes (Siddique et al. 2011). This indicates that the low molecular weight components of naphtha (BTEX, short chain *n*-alkanes) may be a preferred source of substrates for the microorganisms residing in the tailings. Interestingly, Burkus et al. (2014) also noted that ponds that receive froth treatment tailings (FTT), which are tailings that contain an assortment of hydrocarbons and diluent, appeared to be particularly prone to intensive bubbling.

Lastly, naphthenic acids (NAs), which may contribute to the DOC in tailings (Holowenko et al. 2001; Penner and Foght 2010), were also investigated for methanogenic potential as well. Holowenko et al. (2001) amended tailings samples with NAs extracted from the MLSB surface water in concentrations of 0 mg/L, 150 mg/L, 300 mg/L, and 500 mg/L. The authors found no evidence that the extracted NAs supported methanogenesis in their experiment. On the contrary, methanogenesis was inhibited with increasing NA concentrations.

The second factor that may affect methanogenesis in tailings is the availability of substrates. For example, it is important to note that the *n*-alkanes used in Siddique et al. (2006, 2011) were pure *n*-alkanes. Natural *n*-alkanes in the tailings contain isomers that may affect the bioavailability of the compounds to the microorganisms (Burkus et al. 2014).

Methanogenesis has also been documented to rapidly occur when certain substrates are depleted or added. For instance, rapid methanogenesis was observed when endogenous sulfate became depleted in marsh sediments (Winfrey and Ward 1983). Fedorak et al. (2002) also demonstrated that non-methanogenic MFT could be induced to become methanogenic through the repeated amendment of acetate and glucose. As the concentrations of acetate and glucose became depleted over time, sulfate concentrations also decreased. The authors eventually detected CH_4 in the microcosms by 153 days and 170 days for acetate and glucose, respectively (Fedorak et al. 2002). Environments with high sulfate concentrations are also known to inhibit CH_4 production (Holowenko et al. 2000). Despite this, methanogenesis can be stimulated if adequate substrates are present.

This was observed when Winfrey and Ward (1983) amended high-sulfate marsh sediments with 10mM of methylamine and reported enhanced CH_4 production.

Finally, the temperature of the tailings and the presence CO_2 are also potential factors for methanogenesis but perhaps to a lesser extent. Holowenko et al. (2000) investigated the effect of temperature on methanogenesis by incubating tailings samples at 14^{o}C and 22^{o}C. Although the rate of methanogenesis at 22^{o}C was greater than that at 14^{o}C, the total CH_4 produced after 516 days was similar. Therefore, the effect of temperature on methanogenesis, given enough time, is expected to be minimal. CO_2 gas generated within the tailings ponds (Small et al. 2015) may also contribute to CH_4 emissions as some methanogens are suspected of utilizing CO_2 to produce CH_4 (Siddique et al. 2012; Stasik and Wendt-Potthoff 2014).

2.3.1.2 Methane and Carbon Dioxide Emission Estimates From Tailings Ponds

The GHG emissions from tailings ponds are estimated to be a small percentage of the overall GHGs emissions from the oil sands. Cai et al. (manuscript 2015) assessed four well-to-refinery (WTR) oil sands production pathways for GHG emissions: 1) surface mining synthetic crude oil (SCO), (2) *in situ* bitumen, (3) surface mining bitumen, and (4) *in situ* SCO. For the surface mining bitumen pathway, Cai et al. (manuscript 2015) found that the amount of GHG emissions from the tailings ponds contributed 6% to the overall WTR GHG emissions.

Regarding specific GHG emission estimates from the tailings ponds, these estimates are reported to vary widely (Cai et al. manuscript 2015). Small et al. (2015) compiled CH_4 and CO_2 emissions data obtained from flux chamber measurements by oil sands companies between 2010 and 2011. For this literature review, only estimates for Suncor ponds (1A, 2/3, 5, 6, 7, 8A, 8B, STP) and Syncrude's (MLSB) will be discussed (refer to Table 2-2). The types of tailings contained in these ponds are also provided in Table 2-2.

Table 2-2: CH_4 and CO_2 emissions estimates and tailings types for Suncor Ponds (1A, 2/3, 5, 6,7, 8A, 8B, STP) and Syncrude's MLSB.

Tailings Pond	Tailings type [a]	GHG Emissions (t/ha/y)		
		CO_2 [b]	CH_4 [b] (CO_{2eq})	Total CO_{2eq} [b]
1A	OSPW, MFT	17.66	1.25 (26.25)	43.91
2/3	FTT	59.69	9.45 (198.45)	258.14
5	CT	46.53	0.19 (3.99)	50.52
6	CT	3.71	0.04 (0.84)	4.55
7	CT	4.47	0.03 (0.63)	5.1
8A	CT, MFT	7.66	0.13 (2.73)	10.39
8B	MFT	66.06	0.32 (6.72)	72.78
STP	N/A	23.46	0.13 (2.73)	26.19
MLSB	FTT, FFT/MFT, S	52.85	26.22 (550.62)	603.47

Note: $CO_{2eq} = CO_2 + (CH_4 \text{ x Global Warming Potential})$, where GWP = 21 (Small et al. 2015)

STP - South Tailings Pond

MLSB - Mildred Lake Settling Basin

OSPW - Oil Sands Process-affected Water

MFT – Mature Fine Tailings

FTT - Froth Treatment Tailings

CT – Composite Tailings

FFT – Fluid Fine Tailings

N/A – Not applicable (not reported)

[a] Modified from Burkus et al. (2014)

[b] Modified from Small et al. (2015)

As can be seen in Table 2-2, CO_2 emissions contribute more CO_{2eq} than CH_4 emissions in the majority of the tailings ponds. The exception to this is in Suncor's ponds 1A and 2/3, and Syncrude's MLSB, where methane's CO_{2eq} contribution was greater. As previously mentioned, Burkus et al. (2014) noted that ponds that receive FTT were prone to intensive bubbling. This was observed in Pond 2/3 and the MLSB, which received FTT tailings and had the highest GHG emission estimates. In addition to the increased temperature in the MLSB in 1997 (Guo 2009), microbial activity in these ponds may have been stimulated by the hydrocarbons and diluent within the FTT (Siddique et al. 2006, 2007, 2011; Burkus et al. 2014).

2.3.2 Sulfur Emissions

One treatment that is used to increase the densification of MFT is mixing the MFT with sand from the underflow of a cyclone and calcium (Ca^{2+}, in the form of gypsum: $CaSO_4{\bullet}2H_2O$) to create a product called 'composite' (or consolidated) tailings (CT)(Fedorak et al. 2003). The required dosage of gypsum for this method is approximately 1 kg $CaSO_4/m^3$ tailings (Ramos-Padrón et al. 2011). As a result of treating MFT with gypsum, the released waters from the CT process, which are deposited into tailings ponds, contain elevated concentrations of sulfate (Chalaturnyk et al. 2002). Depending upon the oil sands operator, the sulfate concentrations in CT samples can range from 700 mg/L to 1,271 mg/L greater than that of MFT samples (Fedorak et al. 2002).

The increase of sulfate concentrations in tailings is a concern due to the potential increase of hydrogen sulfide (H_2S) and other reduced sulfur compound (RSC) emissions from the ponds (Chalaturnyk et al. 2002; Salloum et al. 2002). H_2S is a toxic gas (Stasik et al. 2014) and is generally the most discussed sulfur gas with respect to sulfur emissions from tailings (Ramos-Padrón et al. 2011; Stasik and Wendt-Potthoff 2014; Stasik et al. 2014; Small et al. 2015). This is likely due to H_2S being a by-product of microbial activity, which has also been implicated in the production of CH_4 emissions (Ramos-Padrón et al. 2011). In recent years, several studies have identified the presence of a black, sulfidic zone in tailings beneath the water:tailings interface at depths of up to 15 m in the ponds (Ramos-Padrón et al. 2011; Chen et al. 2013; Chi Fru et al. 2013; Stasik et al. 2014). These sulfide-rich zones are also characterized by the abundance of sulfate-reducing bacteria (SRB)(Stasik et al. 2014). It is suspected that the SRB communities are driving these sulfidic zones; not only were these zones absent in sterilized tailings samples (Chen et al. 2013; Chi Fru et al. 2013) but the SRB are potentially consuming sulfate and producing considerable amounts of H_2S gas within the sulfidic zone (Stasik et al. 2014).

Sulfur gas analysis from tailings is complicated by the highly reactive nature of sulfur. Sample loss can occur through a number of ways such as irreversible adsorption or reactions with other materials and compounds that it comes into contact with during storage, handling, and analysis (Wardencki 1998). Currently there are few peer-reviewed studies that have reported on sulfur emissions from tailings. Small et al. (2015) also summarized total reduced sulfur compounds (TRS) and H_2S emissions data that was obtained from flux chamber measurements by oil sands companies between 2010 and

2011. In general, sulfur emissions were low (<0.5 t/ha/y) or below the detection limits of the instruments used. H_2S emissions were also lower than TRS emissions, which may be attributed to sulfur cycling within the tailings ponds, instrument detection limits, and whether the naphtha was treated (Small et al. 2015). Salloum et al. (2002) conducted a microcosm experiment, and also observed a small amount of H_2S in their microcosm headspace on their last sampling date. They found that the amount of H_2S produced was approximately 3% of the total sulfate reduced. Most of the sulfide produced was in the form of acid-volatile sulfide (AVS), which may be due to the formation of insoluble iron sulfides (Fedorak et al. 2002; Stasik et al. 2014).

Although there is a knowledge gap with regards to sulfur emissions, H_2S is thought to be largely contained within the tailings ponds due to two main processes: 1) incorporation of sulfide into various forms of iron sulfide; and 2) chemical or microbial oxidation of sulfide in the ponds' surface waters (Stasik and Wendt-Potthoff 2014; Stasik et al. 2014). Under anaerobic conditions, H_2S emission is often prevented through the incorporation of H_2S into iron sulfides (Salloum et al. 2002; Stasik et al. 2014). One parameter that is used as an indicator of the relative amount of this incorporation is AVS, which is defined as the "sulfide fraction that is evolved from sediment when treated with acid" (Hammerschmidt and Burton 2010). Several studies have found high fractions of AVS within tailings samples (Stasik and Wendt-Potthoff 2014; Stasik et al. 2014), which support the hypothesis that H_2S is immobilized within the tailings ponds.

The second process that may prevent H_2S emissions from tailings ponds is the chemical and microbial oxidation of H_2S in the water cap (Ramos-Padrón et al. 2011; Stasik and Wendt-Potthoff 2014; Stasik et al. 2014). Ramos-Padrón et al. (2011)

hypothesized that if H_2S is generated within the tailings, the gas may migrate to the surface of the tailings pond with rising CH_4 bubbles. Once encountering oxygen within the water cap, however, H_2S might be oxidized back into sulfate – an occurrence that may be contributing to the high sulfate concentrations seen in the water cap of the tailings ponds (Ramos-Padrón et al. 2011). Other factors that may increase H_2S production in the tailings ponds include a lack of available metals to form metal sulfides with and/or low pH (Saloum et al. 2002). While sulfur emissions are hypothesized to largely remain within the tailings ponds, the changing landscape of tailings treatment technology and the lack of peer-reviewed published data for emissions still present important knowledge gaps that require further research.

2.3.3 Impact of Sulfate on Gas Emissions

As previously mentioned, microbial communities living within the tailings have been implicated in the production of emissions from tailings ponds (Ramos-Padrón et al. 2011). However, the dominance of a particular gas is dependent upon the substrates available to these microorganisms (Stasik and Wendt-Potthoff 2014). In particular, for CH_4 and sulfur emissions a key factor appears to be sulfate.

SRB and methanogens, which are suspected of producing sulfur and CH_4 emissions, respectively, are known to compete for similar electron donors such as hydrogen (Salloum et al. 2002). In most instances, the SRB will out-compete the methanogens as they derive more energy from the same substrates (Holowenko et al. 2000; Stasik and Wendt-Potthoff 2014). Equations [2-1] and [2-2] from Salloum et al. (2002) depicts the energy yields from sulfate reduction and methanogenesis in an instance where hydrogen is used as an electron donor. A negative notation on the standard Gibbs free energy, ΔG^o (P=1 atm and T= 25°C) indicates that a reaction will readily proceed in the left to right direction. The greater the negative number, the more readily the reaction will proceed in this direction. As the standard Gibbs free energy for sulfate reduction is more negative than that for methanogenesis, this indicates that if there is competition for the same electron donor (in this case, H_2), then sulfate reduction will be the favorable process.

[2-1] $4H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O$

$\Delta G^o = -152$ kJ/reaction, sulfate reduction

[2-2] $4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O$

$\Delta G^o = -135$ kJ/reaction, methanogenesis

Where ΔG^o = Standard Gibbs free energy of formation

The effect of sulfate on methanogenesis has also been investigated in several laboratory studies. Fedorak et al. (2002) amended non-methanogenic MFT and CT samples with acetate or glucose to determine the remaining sulfate concentration when methanogenesis began. In general, they found that CH_4 production occurred when there was 17–20 mg/L of sulfate remaining within the samples. The inhibition of methanogenesis by sulfate-addition has also been investigated. Holowenko et al. (2000) added 8,000 mg/L sulfate to several microcosms that contained tailings and found that methanogenesis was significantly inhibited after 7–45 days. Therefore, considering the findings in literature, sulfate appears to be an important parameter with regards to when methane production will begin within tailings materials.

In summary, the production of greenhouse gases (CH_4 and CO_2), and sulfur emissions from the tailings is not well understood. A large majority of tailings pond emissions studies have focused on CH_4. The production of CH_4 in tailings can be influenced by four factors, such as 1) type of substrates (particularly the presence of BTEX and short chain *n*-alkanes from naphtha diluent), 2) availability of substrates, 3) temperature of the tailings, and 4) presence of carbon dioxide (CO_2). In contrast, there is little peer-reviewed literature reporting the production of CO_2 and RSCs (including H_2S) from tailings. In recent studies, a black, sulfidic zone in the tailings beneath the water:tailing interface was found and was reported to contain an abundance of SRB, which potentially might be producing considerable amounts of toxic, H_2S gas. It is currently hypothesized that H_2S is largely contained within the tailings ponds, however emission estimates are required to verify this.

2.4 Chapter 2 References

Arkell, N., Kuznetsov, P., Kuznetsova, A., Foght, J.M., and Siddique, T. 2015. Microbial metabolism alters pore water chemistry and increases consolidation of oil sands tailings. Journal of Environmental Quality, **44**(1): 145–153.

BGC Engineering Inc. 2010. Review of reclamation options for oil sands tailings substrates. Available from the Oil Sands Research and Information Network, University of Alberta, School of Energy and the Environment, Edmonton, Alta. OSRIN Report No. TR-2. pp 59.

Burkus, Z., Wheler, J., and Pletcher, S. 2014. GHG emissions from oil sands tailings ponds: overview and modelling based on fermentable substrates. Part I: review of the tailings ponds facts and practices [online]. Alberta Environment and Sustainable Resource Development. Available from http://hdl.handle.net/10402/era.40125 [cited 15 August 2015].

Cai, H., Brandt, A.R., Yeh, S., Englander, J.G., Han, J., Elgowainy, A., and Wang, M.Q. 2015. Well-to-Wheels greenhouse gas emissions of Canadian oil sands products: implication for U.S. petroleum fuels. Environmental Science & Technology. Accepted Manuscript.

Chalaturnyk, R.J., Scott, J.D., and Özüm, B. 2002. Management of oil sands tailings. Petroleum Science and Technology, **20**(9–10): 1025–1046.

Chen, M., Walshe, G., Chi Fru, E., Ciborowski, J.J.H., Weisener, C.G. 2013. Microcosm assessment of the biogeochemical development of sulfur and oxygen in oil sands fluid fine tailings. Applied Geochemistry, **37**: 1–11.

Chi Fru, E., Chen, M., Walshe, G., Penner, T., and Weisener, C. 2013. Bioreactor studies predict whole microbial population dynamics in oil sands tailings ponds. Applied Microbiology & Biotechnology, **97**(7): 3215–3224.

Dou, J., Liu, X., Hu, Z., and Deng, D. 2008. Anaerobic BTEX biodegradation linked to nitrate and sulfate reduction. Journal of Hazardous Materials, **151**(2): 720–729.

Fedorak, P.M., Coy, D.L., Salloum, M.J., and Dudas, M.J. 2002. Methanogenic potential of tailings samples from oil sands extraction plants. Canadian Journal of Microbiology, **48**(1): 21–33.

Fedorak, P.M., Coy, D.L., Dudas, M.J., Simpson, M.J., Renneberg, A.J., and MacKinnon, M.D. 2003. Microbially-mediated fugitive gas production from oil sands tailings and increased tailings densification rates. Journal of Environmental Engineering & Science, **2**(3): 199–211.

Government of Alberta (GoA). 2014. Tailings [online]. Available from http://www.oilsands.alberta.ca/tailings.html [cited 6 July 2015].

Government of Alberta (GoA). 2015a. Oil sands [online]. Available from http://www.energy.alberta.ca/ourbusiness/oilsands.asp [cited 6 July 2015].

Government of Alberta (GoA). 2015b. Lower Athabasca region tailings management framework for the mineable Athabasca oil sands [online]. Available from http://esrd.alberta.ca/focus/cumulative-effects/cumulative-effects-management/management-frameworks/documents/LARP-TailingsMgtAthabascaOilsands-Mar2015.pdf [cited 6 July 2015].

Guo, C. 2009. Rapid densification of the oil sands mature fine tailings (MFT) by microbial activity. Ph.D. thesis, The University of Alberta, Edmonton, Alta.

Hammerschmidt, C.R., and Burton, G.A. Jr. 2010. Measurements of acid volatile sulfide and simultaneously extracted metals are irreproducible among laboratories. Environmental Toxicology and Chemistry, **29**(7): 1453–1456.

Holowenko, F.M., MacKinnon, M.D., and Fedorak, P.M. 2000. Methanogens and sulfate-reducing bacteria in oil sands fine tailings waste. Canadian Journal of Microbiology, **46**(10): 927–937.

Holowenko, F.M., Mackinnon, M.D., and Fedorak, P.M. 2001. Naphthenic acids and surrogate naphthenic acids in methanogenic microcosms. Water Research*,* **35**(11): 2595–2606.

MacKinnon, M.D. 1989. Development of the tailings pond at Syncrude's oil sands plant: 1978–1987. AOSTRA Journal of Research, **5**: 109–133.

MacKinnon, M., and Sethi, A. 1993. A comparison of the physical and chemical properties of the tailings ponds at the Syncrude and Suncor oil sands plants. *In* Proceedings of the Fine Tailings Symposium: Oil Sands – Our Petroleum Future Conference, Edmonton, Alta., 4–7 April 1993. AOSTRA Publications, Edmonton, Alta. Paper No. 57.

Penner, T.J., and Foght, J.M. 2010. Mature fine tailings from oil sands processing harbour diverse methanogenic communities. Canadian Journal of Microbiology, **56**(6): 459–470.

Ramos-Padrón, E., Bordenave, S., Lin, S., Bhaskar, I.M., Dong, X., Sensen, C.W., Fournier, J., Voordouw, G., and Gieg, L.M. 2011. Carbon and sulfur cycling by microbial communities in a gypsum-treated oil sands tailings pond. Environmental Science & Technology*,* **45**(2): 439–446.

Rao, F., and Liu, Q. 2013. Froth treatment in Athabasca oil sands bitumen recovery process: a review. Energy Fuels*,* **27**(12): 7199–7207.

Salloum, M.J., Dudas, M.J., and Fedorak, P.M. 2002. Microbial reduction of amended sulfate in anaerobic mature fine tailings from oil sand. Waste Management & Research, **20**(2): 162–171.

Selucky, M.L., Chu, Y., Ruo, T., and Strausz, O.P. 1977. Chemical composition of Athabasca bitumen. Fuel, **56**(4): 369–381.

Siddique, T., Fedorak, P.M., and Foght, J.M. 2006. Biodegradation of short-chain *n*-alkanes in oil sands tailings under methanogenic conditions. Environmental Science & Technology, **40**(17): 5459–5464.

Siddique, T., Fedorak, P.M., MacKinnon, M.D., and Foght, J.M. 2007. Metabolism of BTEX and naphtha compounds to methane in oil sands tailings. Environmental Science & Technology, **41**(7): 2350–2356.

Siddique, T., Penner, T., Semple, K., and Foght, J.M. 2011. Anaerobic biodegradation of longer-chain *n*-alkanes coupled to methane production in oil sands tailings. Environmental Science & Technology, **45**(13): 5892–5899.

Siddique, T., Penner, T., Klassen, J., Nesbø., and Foght, J.M. 2012. Microbial communities involved in methane production from hydrocarbons in oil sands tailings. Environmental Science & Technology, **46**(17): 9802–9810.

Singleton, R. Jr. 1993. The Sulfate-Reducing Bacteria: An Overview. *In* The sulfate-reducing bacteria: contemporary perspectives. *Edited by* J.M. Odom and R. Singleton Jr. Springer-Verlag, New York. pp. 1–20.

Small, C.C., Cho, S., Hashisho, Z., and Ulrich, A.C. 2015. Emissions from oil sands tailings ponds: review of tailings pond parameters and emission estimates. Journal of Petroleum Science and Engineering, **127**: 490–501.

Stasik, S., and Wendt-Potthoff, K. 2014. Interaction of microbial sulphate reduction and methanogenesis in oil sands tailings ponds. Chemosphere, **103**: 59–66.

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

Wardencki, W. 1998. Problems with the determination of environmental sulphur compounds by gas chromatography. Journal of Chromatography A, **793**(1): 1–19.

Winfrey, M.R., and Ward, D.M. 1983. Substrates for sulfate reduction and methane production in intertidal sediments. Applied and Environmental Microbiology, **45**(1): 193–199.

Chapter 3. EXPERIMENTAL SECTION

3.1 Experiment Overview

To answer the research questions of this thesis dissertation, the overall objectives of this experiment were to 1) characterize greenhouse gases (methane and carbon dioxide) and select reduced sulfur compound emissions from tailings samples amended with varying naphtha concentrations; and 2) monitor select chemical parameters over time to determine whether there are any observed trends during gas evolution.

This experiment was carried out in the laboratory using mesocosms made with 1000 mL PYREX® glass bottles (Corning, No. 1395). Based on a typical residual naphtha concentration of less than 1 % mass in the tailings (Penner and Foght 2010) and a total liquid volume (MFT and PA water) of 800 mL, the mesocosms were amended with diluent concentrations ranging from 0% w/v to 1.5% w/v as shown in Table 3-1. The naphtha was provided by Suncor Energy Inc. and was determined in our laboratory to have a specific gravity of 0.7731 (T=20^{o}C, P=1 atm).

Due to a limited amount of tailings pond water, surrogate pond water (SPW) was also used in this experiment. The SPW was prepared in the laboratory by Yaxin Jiang based on a recipe provided by Dr. Hamed Mahdavi (protocol is given in Appendix A). As a result, the treatments were divided into a Pond 2/3–pond water group and SPW group. As there was more SPW available than Pond 2/3 water, the SPW group tested all diluent concentration levels whereas the Pond 2/3 group only tested the most relevant tailings ponds diluent levels (0.8% w/v) as shown in Table 3-1.

Table 3-1: A summary of the mesocosm treatments used in this experiment. Treatments included MFT+SPW with naphtha additions from 0% to 1.5% w/v, MFT + Pond 2/3 water with diluent additions of 0% and 0.8% w/v, and no-MFT controls for both pond waters groups at 0.8% w/v naphtha. Symbols of (✔) indicates that a parameter was investigated whereas (-) indicates that a parameter was not investigated.

	SPW					Pond 2/3		
	MFT	Naphtha (% w/v)				MFT	Naphtha (% w/v)	
		0%	0.2%	0.8%	1.5%		0%	0.8%
1	✔	✔	-	-	-	✔	✔	-
2	✔	-	✔	-	-	-	-	-
3	✔	-	-	✔	-	✔	-	✔
4	✔	-	-	-	✔	-	-	-
5	-	-	-	✔	-	-	-	✔

In addition to the no-diluent control group, a no-MFT control group was also included (Table 3-1). MFT was omitted for this control instead of using autoclaved MFT in order to avoid potential heat-induced physical and chemical changes to the samples (Arkell et al. 2015). A no-MFT control was done for both pond water groups, and consisted of 800 mL pond water (Pond 2/3 or SPW) with 0.8% w/v naphtha. The 0.8% w/v naphtha concentration was chosen to represent the typical residual diluent concentration in the tailings ponds.

3.2: Materials and Methods

3.2.1: MFT and Pond Water

The MFT and Pond 2/3 water came from Suncor Energy Inc.'s Pond 2/3. Originally being two separate ponds, the berm between Pond 2 and Pond 3 was removed in 1992. This allowed the surface waters of the two ponds to connect (MacKinnon and Sethi 1993). Currently, Pond 2/3 receives approximately 3 Mm^3 of FTT annually and this is expected to continue until at least 2020 (Suncor 2009). The pond is also used as a contingency water supply; Suncor Energy Inc. plans to maintain a water cap of 2.5 m to 3 m on the pond during its operation (Suncor 2009). The MFT used in this experiment was sampled from Pond 2/3 in June 2012 at a depth of 12 meters below the water surface. Both the MFT and Pond 2/3 water was stored in sealed plastic buckets at $4^{o}C$ until use. The SPW was stored in a 20 L container (70% ethanol disinfected) at $4^{o}C$ prior to use.

3.2.2: Experimental Mesocosm Set Up

It is important to note that all of the mesocosm materials will eventually be transferred into an anaerobic chamber. In order to minimize oxygen introduction into the chamber, the materials are typically required to sit in the chamber's airlock for several hours before being taken inside.

3.2.2.1 Glass Cleaning

Before assembling the mesocosms, the glassware was cleaned and sterilized. Twelve 1 L PYREX® glass bottles and three 2 L PYREX® glass bottles (Corning, No. 1395) were (i) general washed (hand washed with Fisherbrand® Sparkleen For Manual Washing 1, rinsed with deionized water (x3), followed by a ultrapure water rinse (x3)); (ii) soaked in a 5% HCl acid bath for several days, then rinsed with ultrapure water; (iii) rinsed with acetone; and (iv) autoclaved. The Corning® caps for the mesocosms were prepared in a similar fashion and were also modified to fit black butyl septa (Geo-Microbial Technologies, Cat no. 1313). Additionally, all beakers used for the preparation of the mesocosms were at a minimum general washed and disinfected with 70% ethanol.

3.2.2.2 Pond Water Preparation

Approximately 1.6 L of Pond 2/3 water and 3.2 L of SPW were transferred into the three 2 L bottles. During the transfer, the aluminum foil covering the mouth of the 2 L bottles was parted only enough to allow the water in – this was done to minimize aerosol microbial contamination. Following this, the water-filled bottles were purged of oxygen with Argon gas (Praxair, ultra high purity 5.0) for an hour (Figure 3-1). The Argon gas was funneled into the bottles using a sterile 10 mL plastic pipette. The pipettes had gauze padding at its base, which may help to filter out any contaminants flowing out of the Argon cylinder.

Figure 3-1: 2 L bottles filled with Pond 2/3 water and surrogate pond water that are being purged of oxygen at the purging station. The purging gas used was 5.0 Argon.

3.2.2.3 MFT Preparation

The items used to transfer Pond 2/3 MFT into the 1 L bottles included the following: a small shovel, a stainless steel spoon, a funnel, and a glass rod. All items were rinsed with ultrapure water and disinfected with 70% ethanol before coming into contact with the MFT (Figure 3-2). The shovel was used to homogenize the MFT before transferring. After mixing, the aluminum foil covering the mouth of the 1 L bottle was removed and replaced by the funnel. Using the spoon, approximately 400 mL of MFT was transferred into the bottle. Occasionally, there were small rocks in the MFT that became lodged in the funnel's neck. In this event, the glass rod was used to dislodge and drop the pebbles directly into the 1 L bottle.

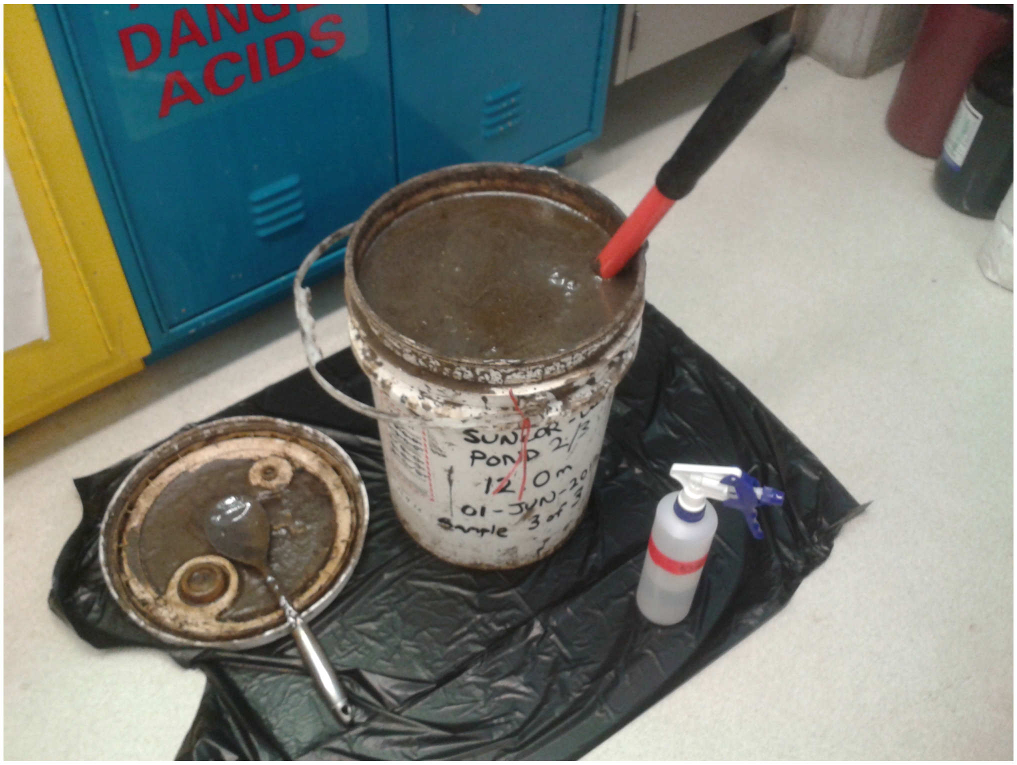


Figure 3-2: Pond 2/3 MFT bucket that was mixed with a shovel. The stainless steel spoon, which was used to scoop out the MFT, is also depicted. All items were rinsed with ultrapure water and disinfected with 70% ethanol before coming into contact with the MFT.

After transferring the MFT, the aluminum foil covering was replaced and the 1 L bottle was purged of oxygen in the fume hood using 5.0 Argon for ten minutes. Following purging, the sterile 10 mL plastic pipette was removed from the bottle in an upwards spiraling motion to minimize oxygen re-entry into the bottle. The bottle was then promptly capped with one of the autoclaved Corning® caps. The MFT in the bucket was remixed, and the preparation process was repeated until six of the mesocosm bottles were done.

The MFT was then amended with naphtha diluent in the fume hood. The naphtha concentrations (% w/v) required were: 0% (no diluent), 0.2% (1.6 mL naphtha), 0.8% (8 mL naphtha), and 1.5% (16 mL naphtha). As duplicate mesocosms were prepared, the total amount of naphtha required for all twelve 1 L mesocosms was 67.2 mL. The naphtha was pipetted out of the diluent canister and into a glass beaker using sterile, 10 mL plastic pipettes attached to a Brand® Macro Pipette Controller II.[1]

3.2.2.4 Mesocosm Assembly in the Anaerobic Chamber

All materials were placed into the chamber airlock (caps loose to avoid pressure issues) and cycled with gases that were ordered from Praxair. The gases used to cycle the airlock were 5.0 Nitrogen (first two cycles) followed by a final cycle of gas mixture (5% CO_2, 5% H_2, nitrogen balance). At this point, the oxygen sensor within the chamber had reported an oxygen level of 38 ppm. The bottles were left inside the chamber (caps loose) until the chamber catalyst scavenged out the oxygen to a level of 0 ppm before proceeding to the next step.

With a glass beaker, approximately 400 mL of Pond 2/3 water was poured into each of the Pond 2/3 mesocosms. The bottles were capped and then sealed with parafilm tape. The SPW mesocosms were also prepared in a similar way. Once all of the mesocosm bottles were complete, they were gently inverted several times to mix their contents and were then covered by an opaque black blanket. Unless certain testing was required, the mesocosms were left in the anaerobic chamber in this manner.

---

[1] Glass pipettes are ideal to prevent the breakdown of the pipette.

3.2.3. No-MFT Control Group Mesocosm Set Up

After the experimental mesocosm trial was completed it was noted that there was a large difference in the emissions generated between the Pond 2/3 and SPW groups. As a result, the no-MFT mesocosm control group was added. The materials required for this group included four 1 L PYREX® (Corning, No. 1395) bottles, 1.6 L of Pond 2/3 water, 1.6 L of SPW, and 32 mL of naphtha diluent.

In summary, the no-MFT mesocosms were prepared in a similar manner to the experimental mesocosm group. Some key differences are 1) The required pond water amount (Pond 2/3 or SPW) was directly transferred into the 1 L bottles and oxygen purged with 5.0 Argon for 30 minutes; and 2) The required diluent was added to the 1 L bottles (filled with oxygen purged pond water) in the fume hood before being placed into the anaerobic chamber airlock.

3.2.4. Chemical Analyses

Several days before an analytical time point, the mesocosms were gently inverted several times and allowed to re-settle. Typically, a depth of 50 mL to 100 mL of water was released by the sampling date. Liquid samples were removed from the mesocosms inside of the anaerobic chamber (sampling protocol is provided in Appendix B). Additionally, all probes and instruments used for the liquid analyses described herein were calibrated before each use.

REDOX Redox measurements of the liquid samples were conducted in the anaerobic chamber. An Accumet redox probe was used (Cat no. 13-620-81) with a 4 M KCl saturated with AgCl internal solution (Cat no. SP135-500). The oxidation-reduction potential (ORP) standard used was Orion 967901. Measurements were done in 'relative mV mode' and adjusted to E_H values after testing. The internal temperature of the anaerobic chamber where the mesocosms were incubated was used to convert the relative mV redox values to E_H. In the case of this experiment, the temperature value used was 24°C.

After redox testing the liquid samples were removed from the anaerobic chamber and centrifuged at 8,000 x g for 5 minutes at 20°C. This resulted in two layers: a large water layer and a thin solids layer. The water layer was removed and filtered with 0.45μm nylon syringe filters (Thermo Scientific) into 25x95mm acid and acetone rinsed, glass vials (Fisherbrand®, Cat no. 03-339-21H).

pH AND CONDUCTIVITY pH and conductivity were measured using a ExStik®II pH/Conductivity/TDS Meter (EC500) from Extech Instruments. As there was a limited amount of liquid sample, approximately 15 mL of the liquid sample was transferred into a 20 mL glass beaker in order to measure pH and conductivity. After testing, the liquid sample was re-combined with the remaining sample.

ALKALINITY Alkalinity was measured using a Mettler Toledo DL53. A diluted sample (1 mL aliquot and 34 mL of boiled ultrapure water) was titrated with 0.02N H_2SO_4.

DISSOLVED ORGANIC CARBON Dissolved organic carbon samples, which have already been filtered with 0.45µm filters, were analyzed with a Shimadzu TOC-L CPH using the Non-Purgeable Organic Carbon (NPOC) analysis method (Shimadzu 2015).

SULFATE AND NITRATE Sulfate and nitrate samples were filtered with 0.22µm filters and then diluted with ultrapure water, if necessary. The samples were analyzed with a Dionex ICS-2100 using the AS18 32 mM ISO method (Standard Methods 2000). Due to technical issues, a number of sulfate and nitrate samples were analyzed at the Department of Biological Sciences at the University of Alberta. These particular samples were measured with a Dionex DX600 Ion Chromatography (Sunnyvale, CA, USA) using EPA method 300.1 (USEPA 1997).

3.2.5. Gas Characterization of the Mesocosm Headspace

3.2.5.1 Methane and Carbon Dioxide

GC METHOD Methane (CH_4) and carbon dioxide (CO_2) emissions from the mesocosms were measured using a thermal conductivity detector (TCD) attached to a 7890A GC. Helium 5.0 (Praxair) was used as the carrier gas. The column used was a Supelco, 80/100 Hayesep Q column, 10FT x 1/8 IN SS. The parameters for the TCD method used to characterize the CH_4 and CO_2 emissions in the mesocosms are given in Table 3-2 (method was modified from Christina Small's notes (unpublished) and Wang (2010)). Modifications to the TCD method involved adjusting the column flow and reference flows to 15 mL/min and 30 mL/min, respectively, as other compound peaks may elute with the CH_4 peak in low flow conditions. Overall the total run time per sample for the method described in Table 3-2 is approximately 7 minutes with an additional ten minutes for the oven temperature to cool back to 25°C.

Table 3-2: TCD method used to characterize CH_4 and CO_2 emissions within the mesocosm headspace (modified from Christina Small's notes (unpublished) and Wang (2010)).

Component	Parameter	Values
Inlet	Temperature	200°C
	Total flow	15 mL/min
	Septum purge flow	3 mL/min
Detector	Temperature	200°C
	Reference flow	30 mL/min
	Make-up flow	2 mL/min
Oven	Temperature	25°C (hold for 3 mins)
	Ramp 1	50°C/min to 110°C (hold for 2 mins)
Signal	Frequency/min	5 Hz/ 0.04 min

CALIBRATION Between the instrument not working, time constraints on the instrument, and issues with the sulfur gas standard, gas calibrations for this experiment were done when able. All gas calibration data for greenhouse gases and reduced sulfur compound (RSC) emissions are provided in Appendix C.

Calibration mixtures for TCD analysis were made using 3.7 CH_4 (Advanced Gas Technologies, ultra high purity) and 3.0 CO_2 (Praxair, bone dry) gases. A small amount of CH_4 and CO_2 gas was transferred into Tedlar gas sample bags (SKC Inc., Cat no. 232-02) and used as stock bags. These gases were then used to make varying CH_4 and CO_2 mixtures (% volume) as outlined in Table 3-3.

Table 3-3: Calibration gas mixtures to produce %volume to peak area calibration curves for CH_4 and CO_2.

Calibration Gas Mixture	Volume of CH_4 added	Volume of CO_2 added
100% CH_4	Withdrawn from stock bag	None
100% CO_2	None	Withdrawn from stock bag
50% CH_4, 50% CO_2	30 mL	30 mL
25% CH_4, 75% CO_2	15 mL	45 mL
25% CO_2, 75% CH_4	45 mL	15 mL
5% CH_4, 95% CO_2	3 mL	57 mL
5% CO_2, 95% CH_4	57 mL	3 mL

Gas-tight 0.5 mL syringes with a sample lock were used to inject 50 μL of gas from each of the calibration mixtures. To account for methanol rinsing between experimental sample injections, the 0.5 mL syringes were methanol rinsed between calibration injections as well. Based on the mixtures in Table 3-3, the resulting calibration curves for CH_4 and CO_2 yielded peak areas for the following % volume gas: 5%, 25%, 50%, 75%, 95% and 100%.

HEADSPACE SAMPLING Methanol-rinsed 0.5 mL syringes were taken into the anaerobic chamber. The syringe needles and mesocosm septa were disinfected with 70% ethanol and blotted dry with a Kimwipe. In order to pierce the septa, the syringe needle was fitted through a sterile 18G needle head to act as a guide. To minimize gas escape from using an 18G needle head, the needles were inserted into the septa at a 45-degree angle. Once inside the mesocosm headspace, the syringe was flushed with the headspace gas several times before a 50 μL gas sample was withdrawn and the syringe was locked. The 18G needle and the syringe were then removed from the mesocosm septa together to prevent any additional gas loss.

After running the gas samples through the TCD, the pressures in the mesocosms were measured using a Cecomp Electronics Digital Pressure Gauge (model DPG1000B+/-15PSIG-10). It is very important to take these pressure measurements for each time point as these values are required to convert the data from % volume into a mole per volume concentration. Knowing the pressure, temperature, and headspace volume of the mesocosms at each analytical time point, the Ideal Gas equation was used to find the corresponding density of CH_4 and CO_2 for each mesocosm, which was then used to convert % volume to the amount of moles of CH_4 and CO_2 in the mesocosm headspace.[2]

---

[2] Concurrent to this experiment, MFT samples was taken by another student (S.Poon) after weeks 5 and week 11 for DNA analysis. At this time the bottles (all but the no-MFT controls) were opened in a glove bag and were assumed to have vented. These disturbances were taken into account when estimating the gas concentrations over time.

3.2.5.2 Sulfur Gas Analysis

Seven sulfur compounds were studied in this experiment: 1) Hydrogen sulfide; 2) Carbonyl sulfide; 3) Thiofuran; 4) Butyl mercaptan; 5) 2-Methylthiophene; 6) 3-Methylthiophene; and 7) 2,5-Dimethylthiophene. These compounds were chosen based on a list of targeted RSCs from a Clearstone Engineering Ltd. report (attributed by Dr. Hashisho to a report by Clearstone Engineering Ltd. in 2012), and on whether the standard gas mixture could be made by gas manufacturers.

GC METHOD The sulfur emissions were measured using an Agilent Technologies 355 sulfur chemiluminescence detector (SCD) that was fitted onto a 7890A GC. The gases used to run the SCD were 5.0 Hydrogen and Ultra zero air from Praxair. The column that was used was a DB-1 column from Agilent with dimensions of 30 m in length, 0.320 mm diameter, and had a film of 5 μm (part no. 123-1035). Christina Small developed the SCD method used in this experiment (unpublished), and this information is provided in Table 3-4. Overall the total run time per sample for the method described in Table 3-4 is approximately 18 minutes with an additional ten minutes for the oven temperature to return to 30°C.

To note, a modification was made to the SCD to bypass the controller box so that the gas flow rates would be moderated by pressure settings rather than the controller box turn dials. For this particular SCD, the optimum flows (and corresponding pressure settings) are also provided in Table 3-4.

Table 3-4: SCD method used to characterize sulfur emissions in the mesocosm headspace.[3]

Component	Parameter	Values
Inlet	Temperature	210^{o}C
	Pressure	4.706 psi
	Total flow	15 mL/min
	Septum purge flow	3 mL/min
	Split flow ratio	5:1
Aux EPC 1 (H$_2$)	Flow rate	39 sccm (pressure set to 81 psi)
Aux EPC 2 (Air)	Flow rate	59.7 sccm (pressure set to 9 psi)
Dual plasma controller	Temperature	800 ^{o}C
Oven	Temperature	30^{o}C (hold for 3 mins)
	Ramp 1	15^{o}C/min to 185^{o}C (hold for 5 mins)
Signal	Frequency/min	20 Hz/ 0.01 min

CALIBRATION For calibration the following equipment was used: Flex Foil, 1 L gas sampling bags (SKC Inc., Cat. no. 252-01), 40 mL EPA vials with volatiles quality assurance (Thermo Scientific, Cat. no. 02-912-376) and fitting Mininert$^{®}$ caps (Supelco, Cat. no: 33304), a 10 mL gas-tight syringe, and a sulfur gas standard containing the sulfur compounds purchased from Air Liquide. The sulfur gas standard had the following compound concentrations: 1) Hydrogen sulfide (151 ppmv); 2) Carbonyl sulfide (5.09 ppmv); 3) Thiofuran (15.3 ppmv); 4) Butyl mercaptan (10.1 ppmv); 5) 2-Methylthiophene (91.6 ppmv); 6) 3-Methylthiophene (40.7 ppmv); and 7) 2,5-Dimethylthiophene (61.1 ppmv).

3. For SCDs in general, it is best to leave the machine on once it is running; otherwise, a 1–2 day stabilization period may be required before the samples can be analyzed (P. Kulmatycki 2014, Personal Communication).

Due to odor and toxicity of the sulfur gas mixture, the gas sample bag was filled with sulfur gas standard in a well-ventilated fume hood (the gas sample bag was also left in the fume hood when not in use). The dilution factors used to construct the calibration curves were 0X, 2X, 4X, 7X, and 20X. As sulfur is highly reactive (Wardencki 1998) a 'syringe dilution' method was used where possible as this method was found to yield more consistent dilution results. However, a 'vial dilution' method was also used for the 20X and several of the 7X dilutions as measuring such small gas sample volumes with a 10 mL syringe resulted in large deviations from the expected dilution value. A total volume of 5 mL was injected for each of the calibration gas mixtures. The volumes of gas used to make the calibration mixtures for each respective dilution method are provided in Table 3-5 and Table 3-6.

Table 3-5: Syringe dilution method for sulfur calibration. Volumes of sulfur gas standard were diluted with 4.8pp Nitrogen in a syringe to form 5 mL calibration mixtures.

Dilution Factor	Volume of Sulfur Gas	Volume of 4.8pp Nitrogen
0X	5 mL	None
2X	2.5 mL	2.5 mL
4X	1.25 mL	3.75 mL
7X	0.73 mL	4.27 mL

For the syringe dilution method, the 5 mL calibration mixtures were made with a 10 mL gas-tight syringe. With respect to the vial dilution method, the 40 mL EPA vials were placed into an anaerobic chamber airlock (Mininert® caps loose) and the airlock was cycled with 5.0 Nitrogen gas several times. After a minimum of an hour, the vials were brought into the anaerobic chamber to tighten the caps. A 10 mL gas-tight syringe was used to transfer the required volume of sulfur gas standard into the vials. The gases were allowed to mix for approximately 5 minutes before 5 mL of diluted sample was withdrawn and injected into the SCD.

Regardless of the dilution method, the syringe was methanol rinsed between injections. Additionally, before withdrawing sulfur gas samples (standard gas or dilution mixtures containing sulfur) the 10 mL syringe was flushed with 4.8 Nitrogen (Praxair) to minimize sample loss due to contact with oxygen.

Table 3-6: Vial dilution method for sulfur calibration. Volumes of sulfur gas standard were diluted in 40 mL EPA vials (43 mL total volume) filled with 5.0 Nitrogen to form calibration mixtures for 7X and 20X dilution.

Dilution Factor	Volume of Sulfur Gas	Volume of 5.0 Nitrogen
7X	7.1 mL	43 mL
20X	2.25 mL	43 mL

HEADSPACE SAMPLING 5 mL of gas sample from the mesocosms was used for sulfur gas analysis. A 10 mL gas-tight syringe was used to measure out the sample. As the syringe was not equipped with a sample lock, the mesocosms were removed from the anaerobic chamber for headspace sampling. The procedure for gas sampling was similar to the TCD procedure, however several modifications were made in an attempt to minimize oxygen contact with the sulfur samples (see Appendix B for detailed sampling procedure).

Undiluted samples from all of the mesocosms were run first. If any of the targeted compounds topped out on the chromatograph, which was often the case, diluted samples were run until the peak areas fell within the calibration range. To dilute the samples, 40 mL EPA vials filled with 5.0 Nitrogen were used (see vial preparation in the 'vial dilution' method as described in the Calibration section).

3.3 Standard Deviation Formula for Duplicate Results

As all mesocosm treatments were done in duplicate, a standard deviation formula for duplicate results was used to evaluate the data. This formula is given in equation [3-1] (Synek 2008; Small et al. 2012).

$$[3\text{-}1] \qquad \mathbf{s} = \sqrt{\frac{\sum_{\mathbf{i=1}}^{\mathbf{n}}(\mathbf{x_{i1}} - \mathbf{x_{i2}})^{\mathbf{2}}}{\mathbf{2n}}}$$

Where 'x_{i1}' and 'x_{i2}' are measurements in a duplicate set, and 'n' is the number of duplicate measurement sets.

3.4 Chapter 3 References

Arkell, N., Kuznetsov, P., Kuznetsova, A., Foght, J.M., and Siddique, T. 2015. Microbial metabolism alters pore water chemistry and increases consolidation of oil sands tailings. Journal of Environmental Quality, **44**(1): 145–153.

MacKinnon, M., and Sethi, A. 1993. A comparison of the physical and chemical properties of the tailings ponds at the Syncrude and Suncor oil sands plants. *In* Proceedings of the Fine Tailings Symposium: Oil Sands – Our Petroleum Future Conference, Edmonton, Alta., 4–7 April 1993. AOSTRA Publications, Edmonton, Alta. Paper No. 57.

Penner, T.J., and Foght, J.M. 2010. Mature fine tailings from oil sands processing harbour diverse methanogenic communities. Canadian Journal of Microbiology, **56**(6): 459–470.

Shimadzu. 2015. TOC-L, 680°C Combustion catalytic oxidation method measurement principles [online]. Available from http://www.shimadzu.com/an/toc/lab/toc-l4.html [cited 30 August 2015].

Small, C.C., Ulrich, A.C., and Hashisho, Z. 2012. Adsorption of acid extractable oil sands tailings organics onto raw and activated oil sands coke. Journal of Environmental Engineering, **138**: 833–840.

Standard Methods. 2000. 4110 Determination of anions by ion chromatography [online]. Available from http://www.standardmethods.org/store/ProductView.cfm?ProductID=31 [cited 3 December 2015].

Suncor. 2009. Annual tailings management plan [online]. Available from https://www.aer.ca/documents/oilsands/tailings-plans/Suncor_2009_TailingsPlans.pdf [cited 29 August 2015].

Synek, V. 2008. Evaluation of the standard deviation from duplicate results. Accreditation and Quality Assurance: Journal for Quality, Comparability and Reliability in Chemical Measurement, **13**: 335–337.

United States Environmental Protection Agency (USEPA). 1997. Method 300.1 Determination of inorganic anions in drinking water by ion chromatography [online]. Available from http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_07_10_methods_method_300_1.pdf [cited 30 August 2015]

Wang, C. 2010. Simultaneous analysis of greenhouse gases by gas chromatography [online]. Available from http://www.chem-agilent.com/pdf/5990-5129EN.pdf [cited 20 May 2015].

Wardencki, W. 1998. Problems with the determination of environmental sulphur compounds by gas chromatography. Journal of Chromatography A, **793**(1): 1–19.

Chapter 4. RESULTS AND DISCUSSION

To briefly recap, the objectives of this study were to 1) characterize the greenhouse emissions (methane and carbon dioxide) and select reduced sulfur compound emissions from tailings samples amended with varying naphtha concentrations; and 2) monitor select chemical parameters over time to determine whether there are any observed trends during gas evolution. A summary of the mesocosm treatments used in this experiment is presented in Table 4-1. Treatments included mature fine tailings (MFT)+surrogate pond water (SPW) with naphtha diluent additions from 0% to 1.5% w/v; MFT+Pond 2/3 water with naphtha diluent additions of 0% w/v and 0.8% w/v; and no-MFT controls for both pond water groups with a naphtha diluent concentration of 0.8% w/v.

Table 4-1: A summary of the mesocosm treatments used in this experiment. Symbols of (✔) indicates that a parameter was investigated whereas (-) indicates that a parameter was not investigated. Each treatment was conducted with duplicate mesocosms.

	SPW					**Pond 2/3**		
	MFT	Naphtha (% w/v)				MFT	Naphtha (% w/v)	
		0%	0.2%	0.8%	1.5%		0%	0.8%
1	✔	✔	-	-	-	✔	✔	-
2	✔	-	✔	-	-	-	-	-
3	✔	-	-	✔	-	✔	-	✔
4	✔	-	-	-	✔	-	-	-
5	-	-	-	✔	-	-	-	✔

4.1 Sample Properties Prior to Naphtha Amendment

Some of the physical and chemical properties of the MFT and pond water samples prior to naphtha amendment are presented in Table 4-2. The MFT samples consisted of 2.5 wt % bitumen content, 51 wt % solids content, and 37 wt % water, which are similar to the values reported for tailings samples from other tailings ponds (Table 2-1). Considering that oxygen levels rapidly decrease below the water-tailings interface (Chen et al. 2013), and the high solids content and depth at which the sample was taken, this indicates that the tailings sample used in this study originated from the anaerobic, MFT zone of Pond 2/3.

For clarity, the chemical analyses in this study were conducted on a mixture of released water and pore water but we will define this water fraction as oil sands process water (OSPW) for this discussion. Regarding the no-diluent controls (MFT and pond water only), which represent the initial properties of the tailings samples, pH and conductivity were relatively consistent between treatments: pH was slightly alkaline and conductivity ranged from 3.29 to 3.36 mS/cm. A slightly alkaline pH is the result of fresh tailings with a pH ~9-10 (MacKinnon and Sethi 1993) being buffered by the high alkalinity concentrations in the tailings ponds (Table 2-1). As expected, the Pond 2/3 samples in this study also contained high initial alkalinity concentrations, which ranged from 779 (±7) mg $CaCO_3$/L to 895 (±6) mg $CaCO_3$/L. The high conductivity values of the samples were likely due to the accumulation of salts (sodium, chloride, and sulfate) in the tailings pond from the bitumen extraction process (Small et al. 2015).

Redox potentials were also measured and were found to be largely positive (190±22 mV to 369±12 mV). As the standard redox potential (pH 7 and T=25°C) for an oxygen to water coupling is significantly more positive at +820 mV (Liebensteiner et al. 2014), this indicates that a small amount of oxygen was introduced into the Pond 2/3 tailings sample when it was removed from the tailings pond. With respect to dissolved organic carbon (DOC) content, the Pond 2/3 samples had an initial DOC concentration of 92 (±0.3) mg/L – this is nearly three times greater than that found in the SPW samples. As the SPW by itself contains no DOC, the 33 ± 3.8 mg/L measured in the no-MFT controls was contributed by the MFT. In general, DOC concentrations in tailings samples are 70 mg/L or less (Table 2-1); therefore the DOC content in the Pond 2/3 OSPW was slightly higher than the typically reported values.

Additionally, the OSPW was analyzed for nitrate and sulfate concentrations, which are important electron acceptors for microbial processes in the tailings ponds. As nitrate concentrations at t=0 were less than 1 mg/L, nitrate reduction by microorganisms is unlikely to be significant in this study (Penner and Foght 2010). However, sulfate was not only present in adequate amounts but was also at greater concentrations than those previously reported for tailings samples (Holowenko et al. 2000; Penner and Foght 2010; Stasik et al. 2014). Sulfate concentrations in the Pond 2/3 and SPW groups at t=0 were approximately 224 (±5) mg/L and 376 (±2) mg/L, respectively. In Fedorak et al. (2002) a 'young' MFT sample from Shell Canada was found to have a sulfate concentration of 170 mg/L. At the depth the Pond 2/3 tailings sample was taken, it is unlikely that fresh MFT mixing was occurring. Rather, the elevated sulfate concentrations in the MFT may have been due to exposure to oxygen in the water cap when the sample was removed from Pond 2/3 and this resulted in H_2S conversion to sulfate (Ramos-Padrón et al. 2011). It was also noted that the SPW group had 150 mg/L more sulfate than the Pond 2/3 samples, and this was likely attributed to the SPW being based on Syncrude Canada Ltd.'s West In Pit (WIP) pond OSPW. Regardless, sulfate reduction will likely be a significant microbial process in both the Pond 2/3 and SPW groups due to the high initial sulfate concentrations.

Table 4-2: Summary of the physical and chemical parameters for the MFT and pond water samples used in this study prior to naphtha amendment. Measurements are average values from duplicate mesocosms.

Parameter	Pond 2/3 with MFT	SPW with MFT	MFT
Bitumen (%)	-	-	2.5
Solids (%)	-	-	51
Water (%)			37
Redox, E_H (mV)*	369 ± 12	190 ± 22	-
pH*	7.84 ± 0.01	7.91 ± 0.02	-
Conductivity (mS/cm)*	3.29 ± 0.01	3.36 ± 0.04	-
Alkalinity (mg $CaCO_3$/L)*	779 ± 7	895 ± 6	-
DOC (mg/L)*	92 ± 0.3	33 ± 3.8	-
NO_3^- (mg/L)*	0.25 ± 0.05	0.19 ± 0.01	-
SO_4^{2-} (mg/L)*	224 ± 5	376 ± 2	-

Note: MFT, mature fine tailings; DOC, dissolved organic carbon; NO_3^-, nitrate; SO_4^{2-}, sulfate.
* OSPW

4.2 Chemical Properties of the Samples Over 11-weeks

The chemical parameters described in Table 4-2 were monitored in the mesocosms over an 11-week period to determine whether there are any observed trends during gas production. The results for pH and conductivity are provided in Figure 4-1.

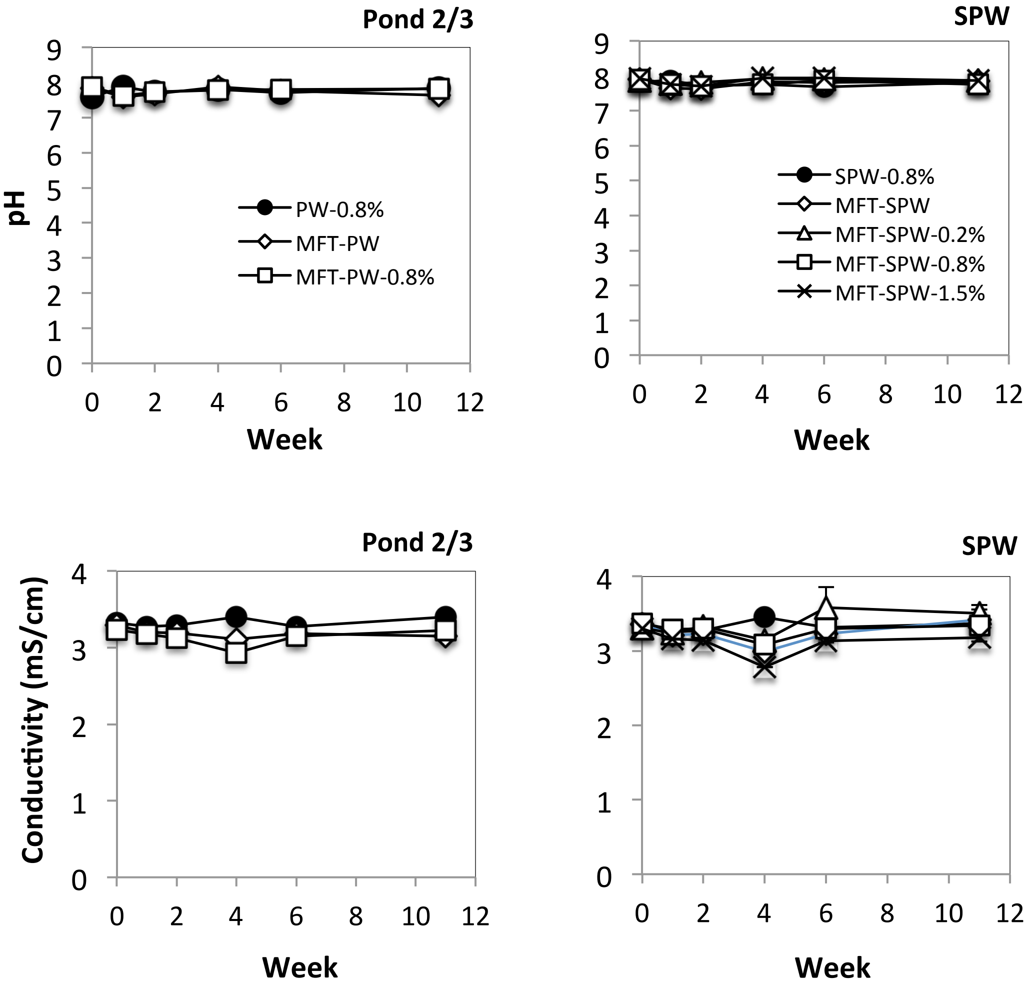


Figure 4-1: pH and conductivity measurements for the Pond 2/3 and surrogate pond water groups over the 11-week study period. The measurements for the MFT containing mesocosms at weeks 1, 2, and 4 represent one measurement. All other values are averages from duplicate measurements and standard deviation bars, where visible, are plus and minus one standard deviation.

In general, pH and conductivity did not deviate significantly from the t=0 values and remained relatively constant throughout the experiment: pH ranged from 7.59 (±na[1]) to 7.95 (±0.09), and conductivity ranged from 2.78 (±na) to 3.59 (±0.28) mS/cm for both pond water groups over the 11-weeks. This indicates that any microbial processes occurring within the tailings are being buffered by the high alkalinity concentrations of the samples (Figure 4-2). Additionally, the relatively stable conductivity values also indicate that no significant ion release occurred within the mesocosms that affected the initial conductivity values during the 11-weeks.

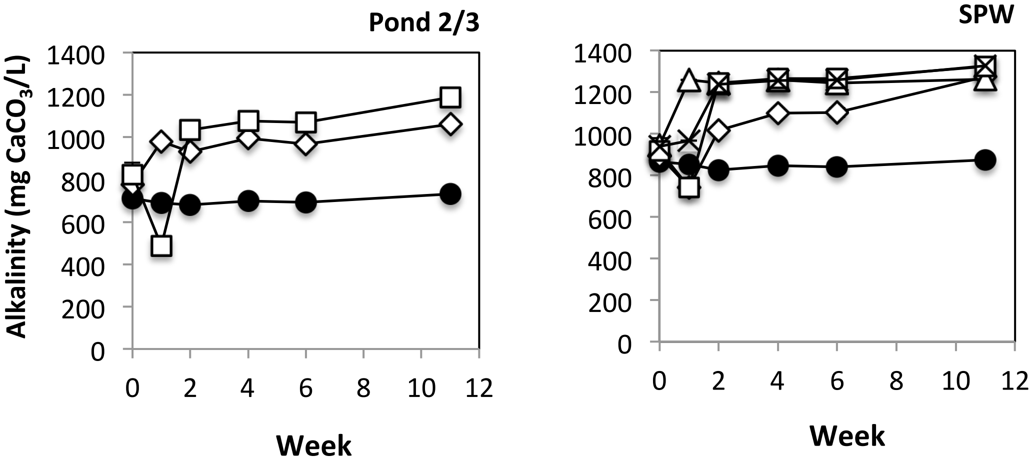


Figure 4-2: Alkalinity measurements for the Pond 2/3 and surrogate pond water groups over the 11-week study period. The measurements for the MFT containing mesocosms at weeks 1, 2, and 4 represent one measurement. All other values are averages from duplicate measurements and standard deviation bars, where visible, are plus and minus one standard deviation.

In contrast, there were significant shifts observed in redox, and nitrate and sulfate concentrations within the first few weeks of the study (Figure 4-3).

---

1. 'na' = not available; represents one sample measurement.

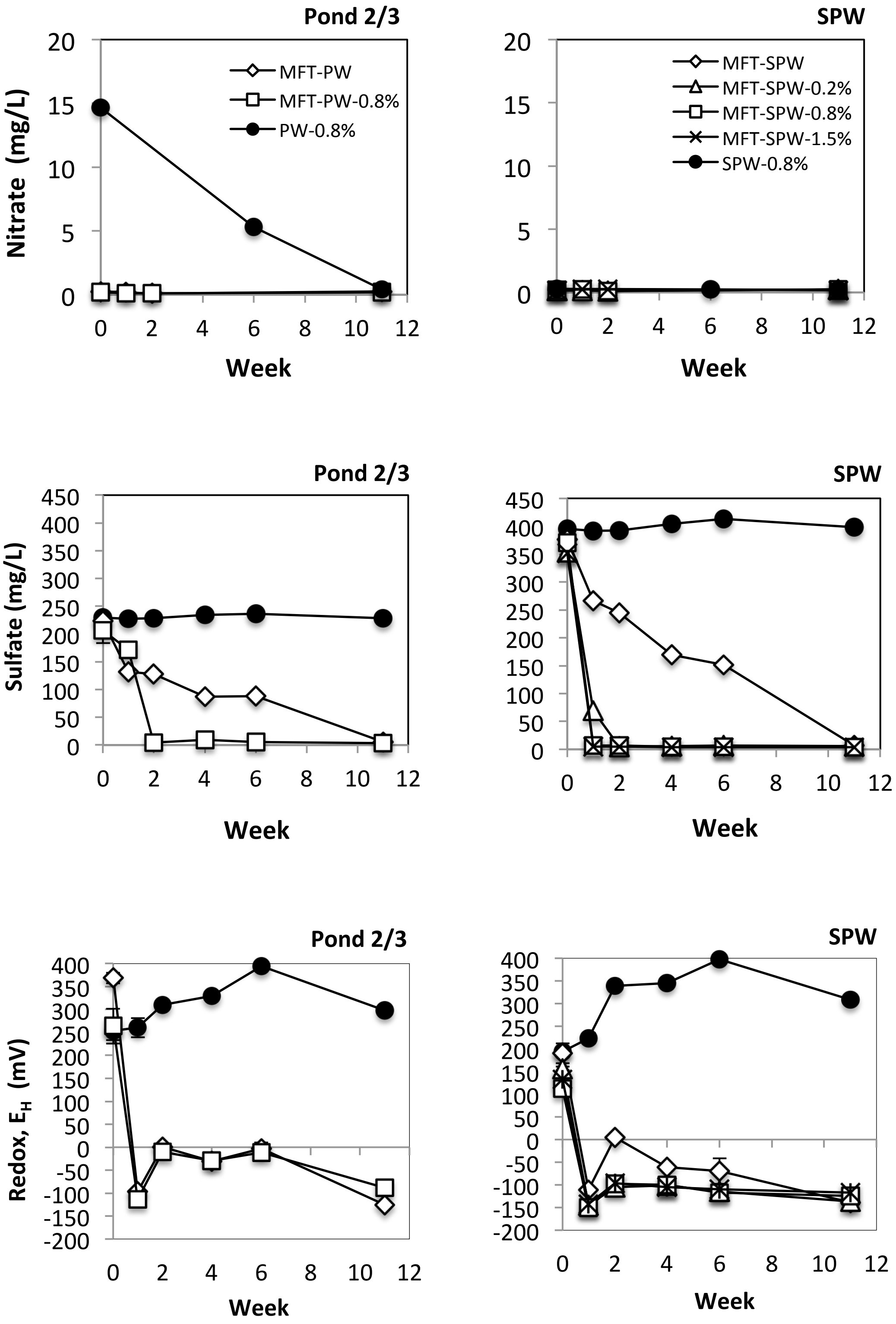


Figure 4-3: Nitrate, sulfate, and redox measurements for the Pond 2/3 and surrogate pond water groups over the 11-week study period. The measurements for the MFT containing mesocosms at weeks 1, 2, and 4 represent one measurement. All other values are averages from duplicate measurements and standard deviation bars, where visible, are plus and minus one standard deviation.

As previously mentioned, the initial redox potentials in the mesocosms were all largely positive prior to naphtha amendment. While the redox potentials in the no-MFT controls (pond water and diluent only) remained largely positive after the addition of naphtha for the 11-weeks, the redox potentials in all of the MFT-containing mesocosms markedly decreased in the first week and were negative for the remainder of the study. This decrease in redox values coincided with a decrease in sulfate concentrations and increase in alkalinity, which indicates that there was an increase in microbial activity. A similar drop in redox values were also observed by Chen et al. (2013) after one week in unamended fluid fine tailings (FFT) samples from Syncrude Canada Ltd.'s WIP pond and the authors suspected that this was due to the production of highly reducing sulfide compounds by sulfate reducing bacteria (SRB). In general, microbial processes that are thermodynamically favorable (ie. yield higher energies) will proceed first (Roychoudhury and Merrett 2006). In terms of electron acceptors, the energy yielded from oxygen is the highest, followed by nitrate, manganese, iron, and sulfate (Roychoudhury and Merrett 2006). Based on the standard reduction potentials (E^0) described in (Liebensteiner et al. 2014) the redox couples O_2/H_2O, Fe^{3+}/Fe^{2+}, MnO_2/Mn^{2+}, NO_3^-/NO_2^- all have redox potentials greater than +400 mV whereas SO_4^{2-}/HSO_3^- occurs at a E^0 around -516 mV. Although our redox values for the MFT bottles did not appear to decrease below -145 (±na) in the first two weeks during sulfate depletion, it should be noted that the redox measurements for this experiment were conducted on OSPW and not a whole MFT sample. The difference between redox values in pore water samples can be up to 215 mV higher compared to those in a whole MFT sample (Salloum et al. 2002). This suggests that the redox values in the MFT of the mesocosms, where microbial activity is occurring, is likely much lower than what was measured in this study. Therefore, given the change in redox, sulfate, and alkalinity concentrations, and the high initial sulfate concentrations and low nitrate concentrations in the MFT mesocosms at t=0, the results of our study indicate that microbial sulfate reduction is occurring during the first two weeks of this study.

The rate of sulfate depletion between the analytical time points for each of the diluent treatment levels was determined and is summarized in Table 4-3. Sulfate reduction rates (SRRs) were highest in the SPW, MFT-naphtha amended mesocosms during the first week of incubation; SRRs for the typical naphtha concentration in tailings ponds (0.8% w/v) and the worst case diluent scenario (1.5% w/v) were 270 nmol/mL MFT/day and 258 nmol/mL MFT/day, respectively, during the first week and then decreased to less than 1 nmol/mL MFT/day by week 2 when sulfate had become depleted (<7 mg/L). For the Pond 2/3 0.8% w/v mesocosms, there was a one week delay before the SRR increased to a similar rate as seen in the SPW mesocosms, 290 nmol/mL MFT/day, but rates also decreased when sulfate had become depleted at the end of week 2. One possibility for the lag is that there may be toxic compounds in the Pond 2/3 water that temporarily inhibited the SRB before the microorganisms acclimatized to the added naphtha and began to rapidly consume the sulfate. Despite this, sulfate became depleted in all of the MFT-diluent mesocosms by week 2. In contrast to the no-diluent controls, sulfate depletion did not occur until towards the end of week 11. These results suggest that the naphtha diluent stimulated sulfate reduction by the SRB.

Table 4-3: Sulfate reduction rates in nmol SO_4^{-2}/mL MFT/day for the MFT-containing mesocosms. A (-) rate indicates that sulfate was consumed between analytical time points.

Week interval	MFT-Pond 2/3-Naphtha		MFT-SPW-Naphtha			
	0% w/v	0.8% w/v	0% w/v	0.2% w/v	0.8% w/v	1.5% w/v
W0-W1	-68	-26	-82	-212	-270	-258
W1-W2	-8	-290	-38	-112	0.4	-0.7
W2-W4	-26	4	-49	0.5	-2	-0.6
W4-W6	1	-5	-20	0.9	0	0.5
W6-W11	-27	-0.6	-47	0	-0.3	-0.1

While sulfate reduction was occurring in all of the MFT mesocosms, this did not appear to be the case for the Pond 2/3 no-MFT controls. At t=0, the Pond 2/3 no-MFT control was the only treatment that contained nitrate (~15±0.04 mg/L). Nitrate was then observed to gradually decrease over time, and was less than 1 mg/L after the 11-week study period. Given that the redox values in the Pond 2/3 no-MFT controls were largely positive throughout the study (254±20 mg/L to 395±0.8 mg/L), it is likely that microbial nitrate reduction was taking place in these mesocosms over the 11-weeks (Liebensteiner et al. 2014). It is possible that there was similar nitrate concentrations in the Pond 2/3 water of the MFT mesocosms prior to t=0 but as there was a several day settling period between assembling the mesocosms and taking the t=0 liquid samples, the nitrate may have been utilized by nitrate reducers before the start of the experiment.

With respect to the DOC content of the samples, the results were characterized by small decreases in DOC and sudden, significantly large increases in DOC concentrations over time. The no-MFT controls were the exception to this, as these mesocosms had relatively stable DOC concentrations between 42 (±0.9) mg/L and 79 (±7.6) mg/L throughout the 11-weeks. Unlike the other chemical parameters measured in this study, there were large variations observed between the duplicate measurements for the MFT mesocosms at a few of the analytical time points. Rather than averaging these values, the individual DOC values were plotted for both pond water groups and are given in Figure 4-4.

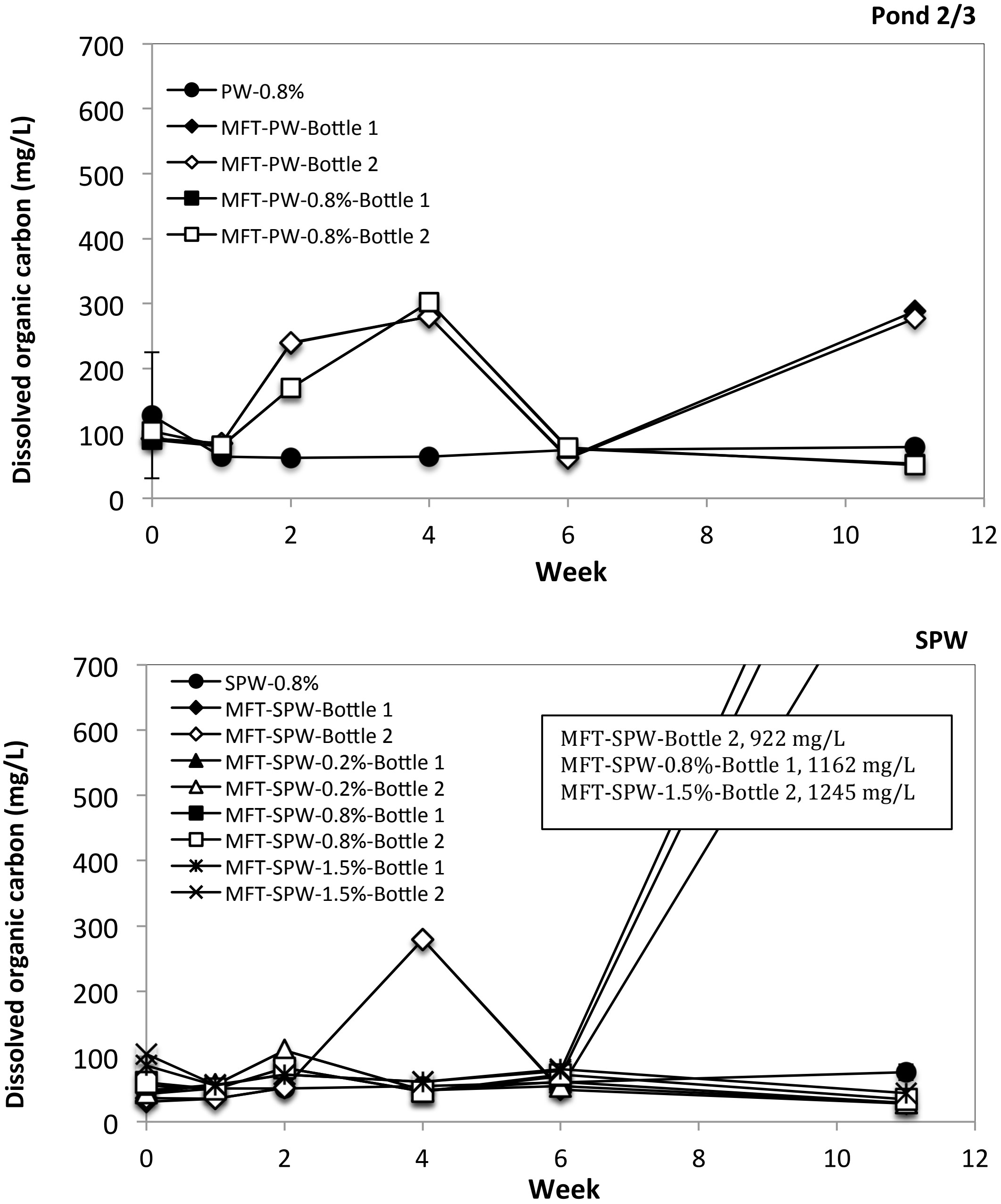


Figure 4-4: **Dissolved organic carbon measurements for the Pond 2/3 and surrogate pond water groups over the 11-week study period. The no-MFT controls are averages from duplicate measurements. For all other treatments, the points represent a single measurement.**

In the Pond 2/3 group, the no-diluent and 0.8% w/v naphtha mesocosms had DOC concentrations of 92 (±0.3) mg/L and 97 (±9.0) mg/L, respectively, at t=0. Concentrations initially decreased in week 1 but then greatly increased to 280 mg/L and 302 mg/L by week 4. Thereafter, the DOC concentrations decreased to below t=0 concentrations except for week 11 when the DOC concentrations in the no-diluent controls spiked once again (283±8.2 mg/L). For the SPW mesocosms, the DOC concentrations at t=0 for the no-diluent, 0.2% w/v, 0.8% w/v, and 1.5% w/v naphtha mesocosms were 33 (±3.8) mg/L, 47 (±2.5) mg/L, 58 (±3.3) mg/L, and 95 (±12.2) mg/L, respectively. For the first 6 weeks of the study there was relatively little change; DOC concentrations for all the SPW mesocosms fluctuated between 33 (± 3.8) mg/L and 109 (±na) mg/L (the no-diluent controls spiked at week 4, 279±na mg/L). At week 11, however, the DOC content in a number of the SPW mesocosms sharply increased to concentrations of up to 1,245 mg/L. Interestingly, this sharp increase was observed in approximately half of the mesocosms and was not restricted to any particular naphtha treatment group. The SPW samples were tested for DOC again at week 20 and concentrations had returned to approximately t=0 ranges (data not shown).

In general, DOC concentrations decreased very slightly unless a significant spike in DOC concentrations preceded it. Based on these observations, one possibility is that the DOC content in the samples at t=0 are largely recalcitrant (Penner and Foght 2010) and that the increases in DOC are due to the growth of microorganisms living within the tailings. Some microorganisms have the ability to excrete extracellulur polymeric substances (EPS), such as polysaccharides, proteins, lipids, and nucleic acids (Flemming and Wingender 2001). One function of EPS is that is can be used by microorganisms to emulsify hydrocarbons, thereby increasing hydrocarbon bioavailability (Vasconcellos et al. 2011). Bordenave et al. (2010) investigated the sedimentation of tailings samples and found that tailings aggregates formed under various conditions (methanogenesis, nitrate reduction, and sulfate reduction) contained fine clays, microbial cells, and EPS. It is postulated that during tailings aggregation, microorganisms excrete EPS or other polymers (Vasconcellos et al. 2011) to emulsify the hydrocarbons and this results in increased DOC concentrations in the pore water. As EPS does not appear to be a readily available carbon source for microorganisms (Flemming and Wingender 2001), and given that the DOC concentrations promptly decline after a spike in concentrations, it is unlikely then that the source of this DOC is the EPS. One possibility is that the DOC spikes reflect readily available DOC that is promptly taken up by the microorganisms.

Overall, the chemical analysis results indicate that microbial nitrate reduction and sulfate reduction was taking place within the mesocosms during this study. Based on the differences in initial nitrate concentrations for the Pond 2/3 no-MFT controls and t=0 MFT mesocosms, nitration reduction likely occurred in the MFT mesocosms before the t=0 analytical time point. After t=0, sulfate reduction began in the MFT mesocosms. Sulfate reduction rates were highest in the MFT-naphtha amended mesocosms, and promptly decreased after two weeks when sulfate became depleted.

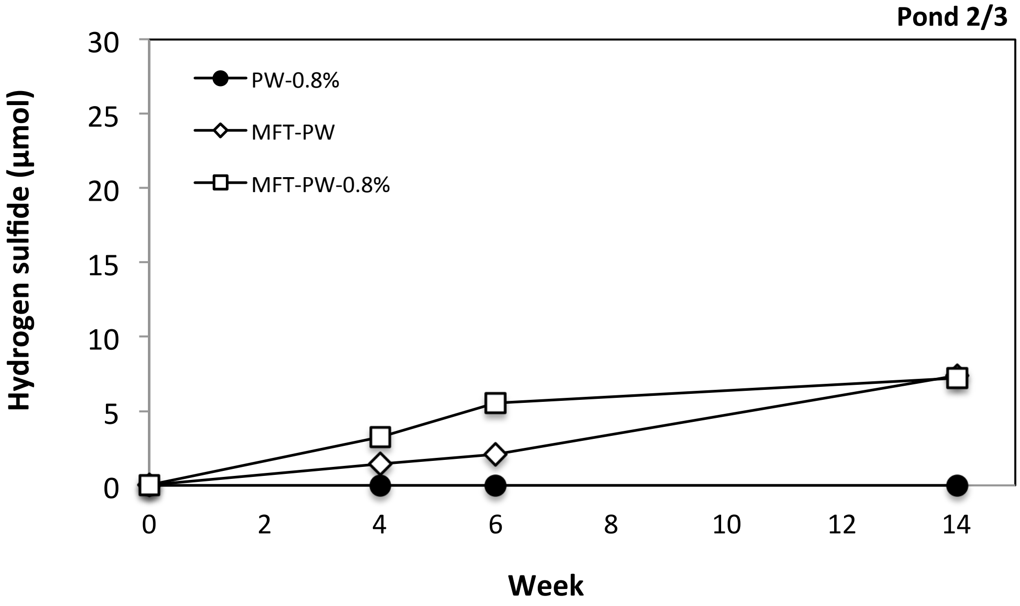
As previously mentioned, it was anticipated that methanogenesis would begin in the mesocosms when the remaining sulfate concentrations in the samples decreased to 17–20 mg/L (Fedorak et al. 2002). In this study, sulfate became depleted in the MFT-naphtha amended mesocosms for both pond water groups after 2 weeks of incubation.

Methane (CH_4) emissions were observed after week 2; however it was preceded by a system shift from sulfur emissions, which will be discussed in the following section.

4.3 Sulfur Gas Production in the Mesocosms

Six of the most abundant biogenic, reduced sulfur compounds (RSCs) in the environment are reported to be hydrogen sulfide (H_2S), carbonyl sulfide (COS), methane thiol (or methyl mercaptan, MeSH), dimethyl sulfide (DMS), carbon disulfide (CS_2), and dimethyl disulfide (DMDS)(Wardencki 1998; Pandey and Kim 2009). Originally there were twelve sulfur compounds to be analyzed in this study, including H_2S, COS, MeSH, DMS, and CS_2. RSC concentrations were expected to be low as those in the environment are typically <ppb levels (Wardencki 1998; Pandey and Kim 2009). By week 4, however, concentrations for a number of sulfur species exceeded the 1 ppmv concentrations in the calibration standard. As the MeSH, DMS, and CS_2 concentrations were less than 1 ppmv or not detectable up to week 4, the number of compounds to be analyzed was narrowed down to the seven sulfur species that were present at greater concentrations. These were H_2S, COS, thiofuran, butyl mercaptan, 2-methylthiophene, 3-methylthiophene, and 2,5-dimethylthiophene.

Sulfur emissions in the mesocosms were monitored over a 14-week period. Sulfur analysis was terminated after 14 weeks as the tailings system shifted from sulfur production to methanogenesis around week 5 of this experiment. Out of the RSCs analyzed in this study, H_2S was distinct as there was no H_2S detected in the no-MFT controls; only the mesocosms containing MFT saw H_2S production (Figure 4-5). This indicates that the production of H_2S was due to microbial activity.



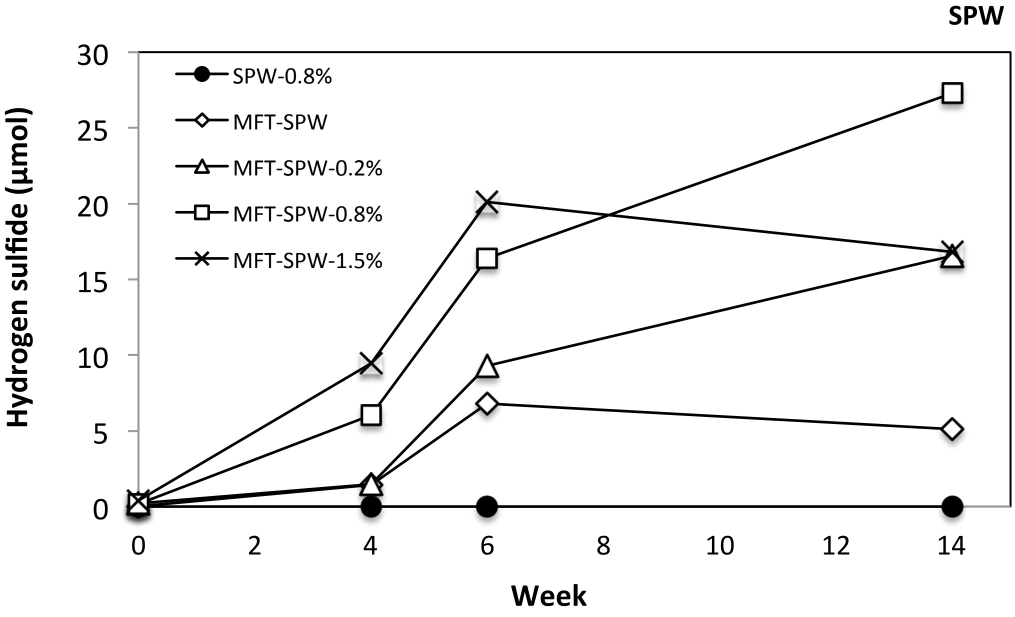


Figure 4-5: Hydrogen sulfide measurements for the Pond 2/3 and surrogate pond water groups over a 14-week study period. The values for MFT (PW, PW-0.8%, SPW, SPW-0.2%, and SPW-0.8%) at week 0 are averages from duplicate measurements. For all other points, only one measurement is represented.

The majority of H_2S in the MFT mesocosms was produced in the first 6 weeks before CH_4 emissions began to increase. Therefore, the first six weeks of this experiment is considered the sulfur emissions production time frame and will be the focus for the RSC analysis. The H_2S production rates (and corresponding maximum SRRs, in µmol/mL MFT/day), and the total amount of H_2S produced during the first six weeks are given in Table 4-4. A comparison of the rates between the diluent amended mesocosms and the no-diluent controls are also described in Table 4-5.

Table 4-4: Maximum sulfate reduction rates (SRR), H_2S production rates, and the total amount of H_2S produced in the MFT mesocosms for the first six weeks of the study.

Treatment	Max SRR (µmol/mL MFT/d)	H_2S production rates		Total H_2S Weeks 0 to 6 (µmol)
		Weeks 0 to 4 (µmol/mL MFT/d)	Weeks 4 to 6 (µmol/mL MFT/d)	
MFT-PW	0.07	1.5E-04	1.2E-04	2.1
MFT-PW-0.8%	0.29	3.4E-04	4.3E-04	5.5
MFT-SPW	0.08	1.5E-04	1.0E-03	6.8
MFT-SPW-0.2%	0.21	1.3E-04	1.5E-03	9.1
MFT-SPW-0.8%	0.27	6.1E-04	2.0E-03	16.3
MFT-SPW-1.5%	0.26	9.4E-04	2.1E-03	19.7

Table 4-5: Difference in SRR rates, H_2S production rates, and H_2S amounts produced between the diluent amended mesocosms and the no-diluent controls.

Treatment	Max SRR (µmol/mL MFT/d)	H_2S production rates		Total H_2S Weeks 0 to 6 (µmol)
		Weeks 0 to 4 (µmol/mL MFT/d)	Weeks 4 to 6 (µmol/mL MFT/d)	
MFT-PW-0.8%	4.1	2.3	3.6	2.7
MFT-SPW-0.2%	2.6	0.9	1.5	1.3
MFT-SPW-0.8%	3.4	4.1	1.9	2.4
MFT-SPW-1.5%	3.2	6.3	2.0	2.9

Note: Rate difference = rate in diluent mesocosms / rate in no-diluent control

In comparison to the no-diluent controls, the addition of naphtha diluent in the mesocosms increased SRRs by approximately 2.6 to 4 times. With respect to the maximum SRR, rates were 0.21–0.29 μmol/mL MFT/day for all MFT-diluent mesocosms regardless of the pond water group. In contrast there was a noticeable difference in H_2S production rates immediately following sulfate depletion. H_2S production rates in the mesocosms ranged from 0.9 times (0.2% w/v) to 6.3 times (1.5% w/v) higher than the no-diluent controls. Furthermore, the effect of diluent concentrations on H_2S production was also observed in the total amount of H_2S produced. After six weeks, H_2S production in the SPW no-diluent, 0.2% w/v, 0.8% w/v, and 1.5% w/v mesocosms were found in increasing amounts of 6.8 μmol, 9.1 μmol, 16.3 μmol, and 19.7 μmol, respectively. The amount of H_2S produced in the Pond 2/3 0.8% w/v mesocosms was also greater than the no-diluent controls but was only about a third of the SPW 0.8% w/v mesocosms (5.5 μmol). These results further support that naphtha diluent stimulates sulfate reduction by the SRB, and this in turn results in increased H_2S emissions within the tailings.

It is also worth mentioning that the amount of H_2S found in the mesocosms' headspace was considerably higher than the anticipated <ppb concentrations (Wardencki 1998). As noted by Salloum et al. (2002) the release of H_2S from the tailings would be an issue if the pH was low or if there was an insufficient amount of metals available to form metal sulfides. Given the slightly alkaline pH of our tailings samples, the release of H_2S may be due to the latter. The concentrations for the other five RSCs measured in this study are plotted in Figure 4-6 and Figure 4-7.

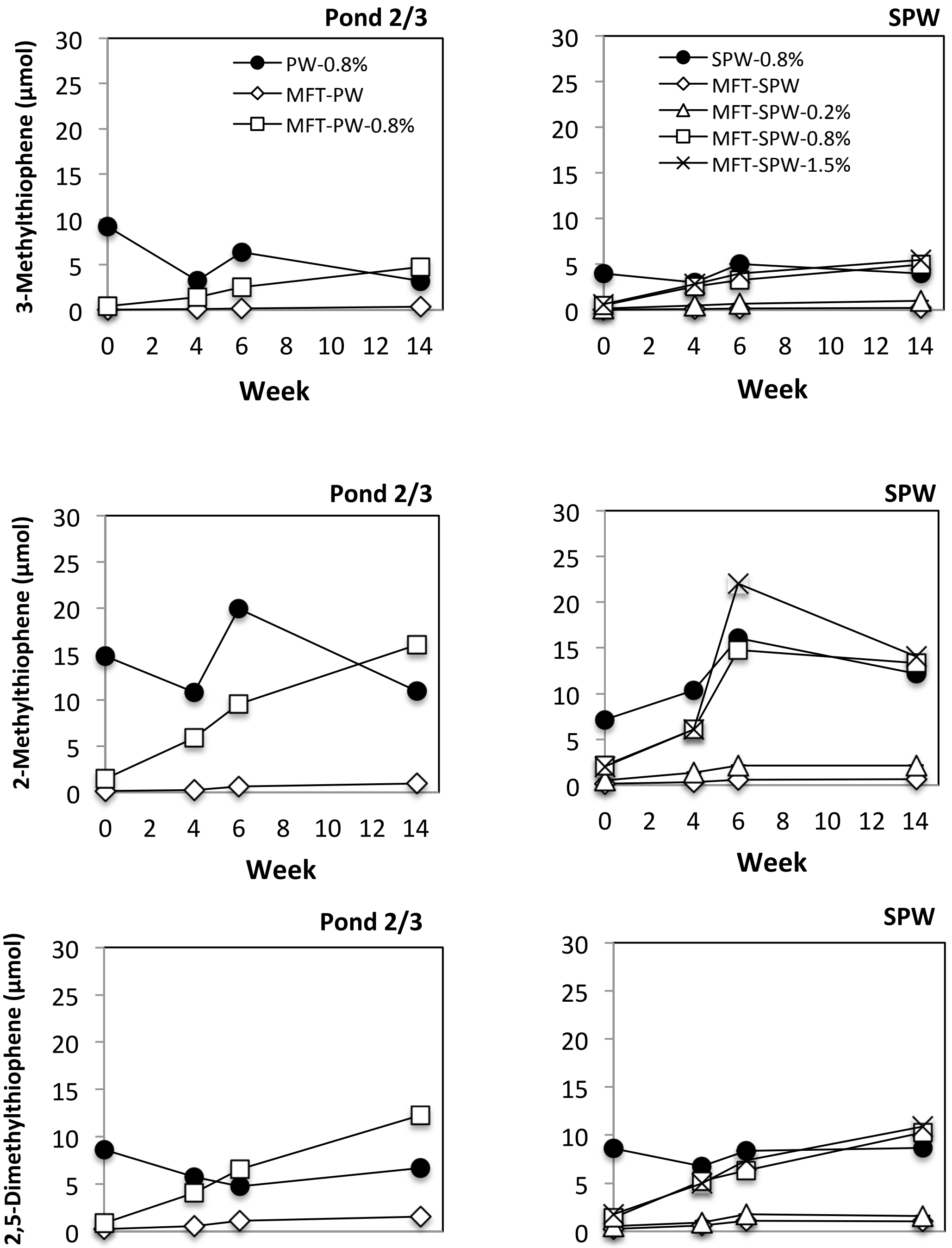


Figure 4-6: 3-Methylthiophene, 2-methylthiophene, and 2,5-dimethylthiophene concentrations for the Pond 2/3 and surrogate pond water groups over a 14-week study period. The values for MFT (PW, SPW, and SPW-0.2%) are averages from duplicate measurements. For all other mesocosms, only one measurement is represented.

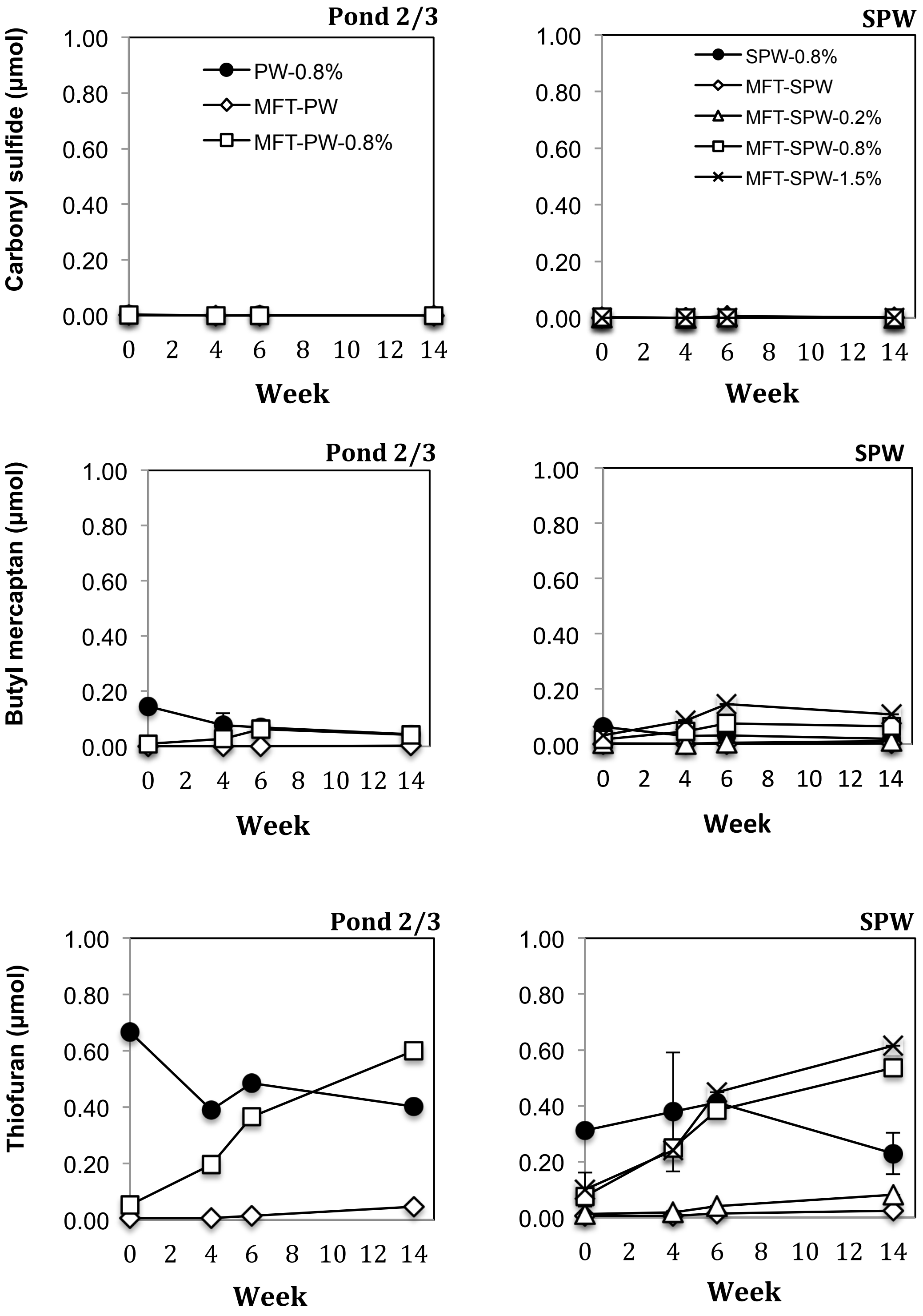


Figure 4-7: Carbonyl sulfide, butyl mercaptan, and thiofuran concentrations for the Pond 2/3 and surrogate pond water groups over a 14-week study period. The values for butyl mercaptan (PW-0.8% at W0) and thiofuran (PW-0.8%, all; MFT-SPW-0.8% at W6; MFT-PW-0.8% at W4 and W14; MFT-SPW-0.8% at W4; and MFT-SPW-1.5% at W4) represent one measurement. All other values are averages from duplicate measurements and the error bars (where visible) represent plus and minus one standard deviation.

Unlike H_2S, the other five RSCs measured in this study (excluding COS, <0.1 μmol throughout the study), 2-methylthiophene, 3-methylthiophene, 2,5-dimethylthiophene (Figure 4-6), thiofuran and butyl mercaptan (Figure 4-7) were not only detected in the no-MFT controls at t=0 but these concentrations were significantly higher than those found in the MFT mesocosms. The reason as to why these RSC emissions are higher in the no-MFT controls might be explained by partitioning. The Henry's law constant for 2-methylthiophene and thiofuran at 25°C are estimated to be 4.2×10^{-1} M/atm (H=10.7) and 4.4×10^{-1} M/atm (H=10.2) (Sander 1999), respectively, which indicates that some of these sulfur compounds have a tendency to remain in the liquid phase. Additionally, the organic carbon partition coefficient, K_{oc}, value for thiofuran was reported in Toxnet (2014) as 230 and as 54 in Suthersan (1996), which also indicates that there is some potential for the RSCs to sorb to the MFT as well. As the partitioning coefficients for the RSCs in this study are largely unavailable in literature, further research would be required to verify whether sorption of these compounds is an important environmental fate process.

A second important observation is that the final concentrations at week 14 in the MFT-diluent mesocosms were similar to those observed in the no-MFT controls at t=0. As this was the case in both pond water groups, these results suggest that the RSC emissions other than H_2S originated from the naphtha diluent. Furthermore, based on the differences in emissions produced between the MFT-diluent mesocosms and the no-diluent controls (Table 4-6 to Table 4-11), the diluent concentration in the tailings appears to be a particularly important factor with respect to the release of these RSCs over time. In the case of H_2S, the amount emitted increased by a factor 3 times the no-diluent control emissions at a worst-case diluent scenario of 1.5% w/v. For 2-methylthiophene, 3-methylthiophene, 2,5-dimethylthiophene, and thiofuran, the total amount of RSC emissions increased by a minimal factor of 4 at 0.2% w/v and reached up to 45 times that of the no-diluent control emissions at 1.5% w/v. Again, the substantial difference in emissions produced may be due to these RSCs originating from the diluent and that there is a greater amount of diluent in some of the treatments. One possibility is that there is a sorption and release mechanism that is occurring between the RSCs and the MFT over time. It is unclear what role microbial activity may be playing in this process, but several studies have found that microbial activity coincides with changes in tailings properties and increased MFT consolidation rates (Bordenave et al. 2010; Arkell et al. 2015). As RSC emissions were the greatest in the diluent mesocosms where microbial activity is stimulated, perhaps these changes in tailings properties also influence the release of the RSCs over time.

In general, all RSC emissions increased with increasing naphtha diluent concentrations in the MFT mesocosms. Considering a worst case diluent scenario of 1.5% w/v, the amount of RSCs produced from highest to lowest between weeks 0 and week 6 were in the order of H_2S and 2-methylthiophene > 2,5-dimethylthiophene > 3-methylthiophene > thiofuran > butyl mercaptan > COS. Of the total RSCs produced at 1.5% w/v (49 μmol), H_2S and 2-methylthiophene combined made up 81% of the emissions. Based on our results, further reducing the concentration of residual diluent in the tailings ponds is anticipated to reduce the amount of RSCs produced in the tailings.

Table 4-6: 3-Methylthiophene production rates, total µmol produced between weeks 0 and 6, and comparison to the no-diluent control values.

Treatment	Production Rates			Comparison to no-diluent rates		
	Weeks 0 to 4 (µmol/mL MFT/d)	Weeks 4 to 6 (µmol/mL MFT/d)	Total µmol Weeks 0 to 6	Weeks 0 to 4	Weeks 4 to 6	Total µmol Weeks 0 to 6
MFT-PW	6.6E-06	1.6E-05	0.1	1	1	1
MFT-PW-0.8%	1.0E-04	2.2E-04	2.1	16	13	14
MFT-SPW	7.2E-06	1.5E-05	0.1	1	1	1
MFT-SPW-0.2	3.4E-05	4.3E-05	0.6	5	3	4
MFT-SPW-0.8	2.1E-04	1.4E-04	2.8	30	10	19
MFT-SPW-1.5	2.3E-04	2.2E-04	3.3	32	15	23

Table 4-7: 2-Methylthiophene production rates, total µmol produced between weeks 0 and 6, and comparison to the no-diluent control values.

Treatment	Production Rates			Comparison to no-diluent rates		
	Weeks 0 to 4 (µmol/mL MFT/d)	Weeks 4 to 6 (µmol/mL MFT/d)	Total µmol Weeks 0 to 6	Weeks 0 to 4	Weeks 4 to 6	Total µmol Weeks 0 to 6
MFT-PW	1.3E-05	6.3E-05	0.5	1	1	1
MFT-PW-0.8%	4.7E-04	7.0E-04	8	35	11	18
MFT-SPW	1.7E-05	5.6E-05	0.5	1	1	1
MFT-SPW-0.2	9.1E-05	1.5E-04	1.7	6	3	4
MFT-SPW-0.8	4.1E-04	1.7E-03	13	25	30	28
MFT-SPW-1.5	4.2E-04	3.1E-03	20	26	55	45

Table 4-8: 2,5-Dimethylthiophene production rates, total µmol produced between weeks 0 and 6, and comparison to the no-diluent control values.

Treatment	Production Rates			Comparison to no-diluent rates		
	Weeks 0 to 4 (µmol/mL MFT/d)	Weeks 4 to 6 (µmol/mL MFT/d)	Total µmol Weeks 0 to 6	Weeks 0 to 4	Weeks 4 to 6	Total µmol Weeks 0 to 6
MFT-PW	2.9E-05	1.2E-04	0.9	1	1	1
MFT-PW-0.8%	3.3E-04	4.7E-04	5.7	11	4	6
MFT-SPW	3.7E-05	9.5E-05	0.9	1	1	1
MFT-SPW-0.2	4.4E-05	1.6E-04	1.2	1	2	1
MFT-SPW-0.8	4.0E-04	2.1E-04	4.9	11	2	6
MFT-SPW-1.5	3.3E-04	4.7E-04	5.6	9	5	7

Table 4-9: Carbonyl sulfide production rates, total µmol produced between weeks 0 and 6, and comparison to the no-diluent control values. A (-) rate indicates that concentrations decreased between two time points. Na = a zero production rate, or the amount of total µmol is negligible.

Treatment	Production Rates			Comparison to no-diluent rates		
	Weeks 0 to 4 (µmol/mL MFT/d)	Weeks 4 to 6 (µmol/mL MFT/d)	Total µmol Weeks 0 to 6	Weeks 0 to 4	Weeks 4 to 6	Total µmol Weeks 0 to 6
MFT-PW	-8.7E-08	0	-8.3E-04	na	na	na
MFT-PW-0.8%	-1.4E-07	0	-1.3E-03	na	na	na
MFT-SPW	-2.6E-08	1.2E-06	6.2E-03	na	1	1
MFT-SPW-0.2	-1.9E-07	9.9E-07	3.3E-03	na	1	0.5
MFT-SPW-0.8	-1.2E-07	0	-1.2E-03	na	na	na
MFT-SPW-1.5	-7.9E-08	0	-7.6E-04	na	na	na

Table 4-10: Butyl mercaptan production rates, total µmol produced between weeks 0 and 6, and comparison to the no-diluent control values. A (-) rate indicates that concentrations decreased between two time points. Na = a zero production rate in the no-diluent control.

Treatment	Production Rates			Comparison to no-diluent rates		
	Weeks 0 to 4 (µmol/mL MFT/d)	Weeks 4 to 6 (µmol/mL MFT/d)	Total µmol Weeks 0 to 6	Weeks 0 to 4	Weeks 4 to 6	Total µmol Weeks 0 to 6
MFT-PW	0	0	0	na	na	na
MFT-PW-0.8%	2.0E-06	6.7E-06	0.05	na	na	na
MFT-SPW	0	0	0	na	na	na
MFT-SPW-0.2	-3.1E-08	4.7E-07	0.002	na	na	na
MFT-SPW-0.8	3.0E-06	5.6E-06	0.06	na	na	na
MFT-SPW-1.5	5.5E-06	1.2E-05	0.11	na	na	na

Table 4-11: Thiofuran production rates, total µmol produced between weeks 0 and 6, and comparison to the no-diluent control values.

Treatment	Production Rates			Comparison to no-diluent rates		
	Weeks 0 to 4 (µmol/mL MFT/d)	Weeks 4 to 6 (µmol/mL MFT/d)	Total µmol Weeks 0 to 6	Weeks 0 to 4	Weeks 4 to 6	Total µmol Weeks 0 to 6
MFT-PW	-8.5E-08	1.8E-06	0.01	1	1	1
MFT-PW-0.8%	1.5E-05	3.3E-05	0.31	175	18	37
MFT-SPW	-5.5E-08	1.6E-06	0.01	1	1	1
MFT-SPW-0.2	6.8E-07	4.3E-06	0.03	12	3	4
MFT-SPW-0.8	1.8E-05	2.6E-05	0.31	328	16	39
MFT-SPW-1.5	1.5E-05	4.0E-05	0.35	266	25	44

4.4 Methane and Carbon Dioxide Production in the Mesocosms

Based on the results of Fedorak et al. (2002) it was hypothesized that CH_4 production in the mesocosms would be detected when there was approximately 17–20 mg/L of sulfate remaining within the samples. Although the initial sulfate concentrations in our samples were greater than 200 mg/L, small amounts of CH_4 (<205 μmol) were detected in all of the MFT mesocosms at t=0 (CH_4 was not detected in any of the no-MFT controls throughout the 11-weeks). Sulfate concentrations fell below 20 mg/L by week 2 of this study for all MFT-diluent amended mesocosms. CH_4 production began to rapidly increase after week 5, which indicates that there was a lag period of approximately 3 weeks between sulfate depletion and the start of methanogenesis. Further evidence of this system transition was exhibited by the stabilization or decline of H_2S emissions during increased methanogenesis after week 5. The redox values of the samples after week 5 were also indicating methanogenic conditions as well (Liebensteiner et al. 2014).

In general, the amount of CH_4 produced in this study was found to increase with increasing the naphtha concentrations (Figure 4-8). The total amount of CH_4 produced in the Pond 2/3 no-diluent and 0.8% w/v naphtha amended mesocosms after 11 weeks was 973 (±159) μmol and 10,870 (±692) μmol, respectively, and the CH_4 emissions in the SPW no-diluent, 0.2% w/v, 0.8% w/v, and 1.5% w/v naphtha amended mesocosms were 455 (±144) μmol, 919 (±444) μmol, 13,946 (±840) μmol, and 17,292 (±1,131) μmol, respectively. The CH_4 production rates (and carbon dioxide production rates) in this study were also determined and are given in Tables 4-12 and Table 4-13.

Table 4-12: Methane production rates, total µmol produced between weeks 5 and 11, and comparison to the no-diluent control values. Na = a zero production rate in the no-diluent control.

Treatment	Production Rates				Comparison to no-diluent rates			
	Weeks 2 to 5 (µmol/mL MFT/d)	Weeks 5 to 7 (µmol/mL MFT/d)	Weeks 7 to 11 (µmol/mL MFT/d)	Total µmol Weeks 5-11	Weeks 2-5	Weeks 5-7	Weeks 7-11	Total µmol Weeks 5-11
MFT-PW	0.03	0.02	0.06	751	1	1	1	1
MFT-PW-0.8%	0.09	0.50	0.62	9,928	2.5	25	11	13
MFT-SPW	-0.02	0.01	0.04	455	na	1	1	1
MFT-SPW-0.2	0.01	0.04	0.05	766	na	6	1	2
MFT-SPW-0.8	0.35	0.66	0.65	11,280	na	122	17	25
MFT-SPW-1.5	0.07	0.49	1.19	16,264	na	90	32	36

Table 4-13: Carbon dioxide production rates, total µmol produced between weeks 5 and 11, and comparison to the no-diluent control values. Na = a zero production rate in the no-diluent control.

Treatment	Production Rates				Comparison to no-diluent rates			
	Weeks 2 to 5 (µmol/mL MFT/d)	Weeks 5 to 7 (µmol/mL MFT/d)	Weeks 7 to 11 (µmol/mL MFT/d)	Total µmol Weeks 5-11	Weeks 2-5	Weeks 5-7	Weeks 7-11	Total µmol Weeks 5-11
MFT-PW	-0.02	0.08	0.02	682	na	1	1	1
MFT-PW-0.8%	0	0.11	0.05	1,259	na	1	3	2
MFT-SPW	-0.03	0.02	0.04	549	na	1	1	1
MFT-SPW-0.2	0	0.04	0.03	609	na	2	1	1
MFT-SPW-0.8	0.04	0.14	0.08	1,760	na	6	2	3
MFT-SPW-1.5	0	0.12	0.14	2,361	na	5	4	4

Immediately following the period of high SRRs, CH_4 production rates remained low until week 5 (Table 4-12). After week 5, CH_4 production rates increased and were highest towards the end of the study between weeks 7 and week 11; the highest rate observed was in the SPW 1.5% w/v mesocosms at 1.19 µmol/mL MFT/day. In comparison to the no-diluent controls, there were only slight increases in CH_4 production rates for the 0.2% w/v mesocosms between week 5 and week 11. However, there were significantly higher rates observed for the 0.8% w/v and 1.5% w/v mesocosms, ranging from 11 to 122 times greater than those found in the no-diluent controls. While the addition of diluent greatly increased CH_4 emissions in the tailings samples, it was noted that the majority of the CH_4 emissions produced over the 11 weeks (>75%) was produced between weeks 5 and week 11 for all MFT mesocosms including the no-diluent controls.

With respect to carbon dioxide (CO_2), it should be noted that small amounts of CO_2 was detected in all of the mesocosm at t=0, likely due to the 5% CO_2, 5% H_2, N_2 balance gas mixture inside of the anaerobic chamber where the mesocosms were assembled. If the entire mesocosm headspace was filled with gas mix while in the anaerobic chamber at t=0, the maximum amount of CO_2 which would be expected is 687 µmol. As seen in Figure 4-8, the CO_2 emissions in the mesocosms at t=0 were significantly lower than 687 µmol and ranged from 128 (±4) µmol to 249 (±122) µmol.

After t=0, CO_2 emissions remained relatively stable until approximately week 7 when emissions noticeably began to increase (except in no-MFT controls) and continued to increase until the end of the 11-week incubation. At the end of 11-weeks, CO_2 emissions in the Pond 2/3 no-diluent and 0.8% w/v naphtha amended mesocosms was 1,067 (±34) µmol and 1,692 (±174) µmol, respectively, and the CO_2 emissions in the

SPW no-diluent, 0.2% w/v, 0.8% w/v, and 1.5% w/v naphtha amended mesocosms was 752 (±21) µmol, 1,103 (±125) µmol, 2,446 (±163) µmol, and 2,798 (±130) µmol, respectively. Similarly to CH_4, CO_2 production appeared to increase with increasing naphtha diluent but the amounts of CO_2 produced were markedly less than CH_4 throughout the 11-week study period. As previously noted in section 2.3.1.2 (Table 2-2), CO_2 emissions are typically greater than CH_4 emissions from the tailings ponds. There are a few possible reasons as to why our results are the opposite of this; Arkell et al. (2015) noted that such differences might be due to CO_2 having a higher solubility than CH_4. Another potential factor could be related to the different types of methanogen microorganisms within the tailings samples. Two proposed pathways outlined by Siddique et al. (2011) involve acetoclastic methanogens and hydrogenotrophic methanogens. Acetoclastic methanogens utilize acetate to form CH_4, while hydrogenotrophic methanogens utilize CO_2 and H_2 to form CH_4. The reactions are provided in equations [4-1] and [4-2].

[4-1] $CH_3COOH \rightarrow CH_4 + CO_2$ (Acetoclastic methanogens)

[4-2] $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ (Hydrogenotrophic methanogens)

If hydrogenotrophic methanogens were dominant within the tailings samples, this would also explain the lower CO_2 emissions. Alternatively as the emissions measured in our experiment represent those under anaerobic conditions, there may be other interactions occuring in the water cap of the tailings ponds.

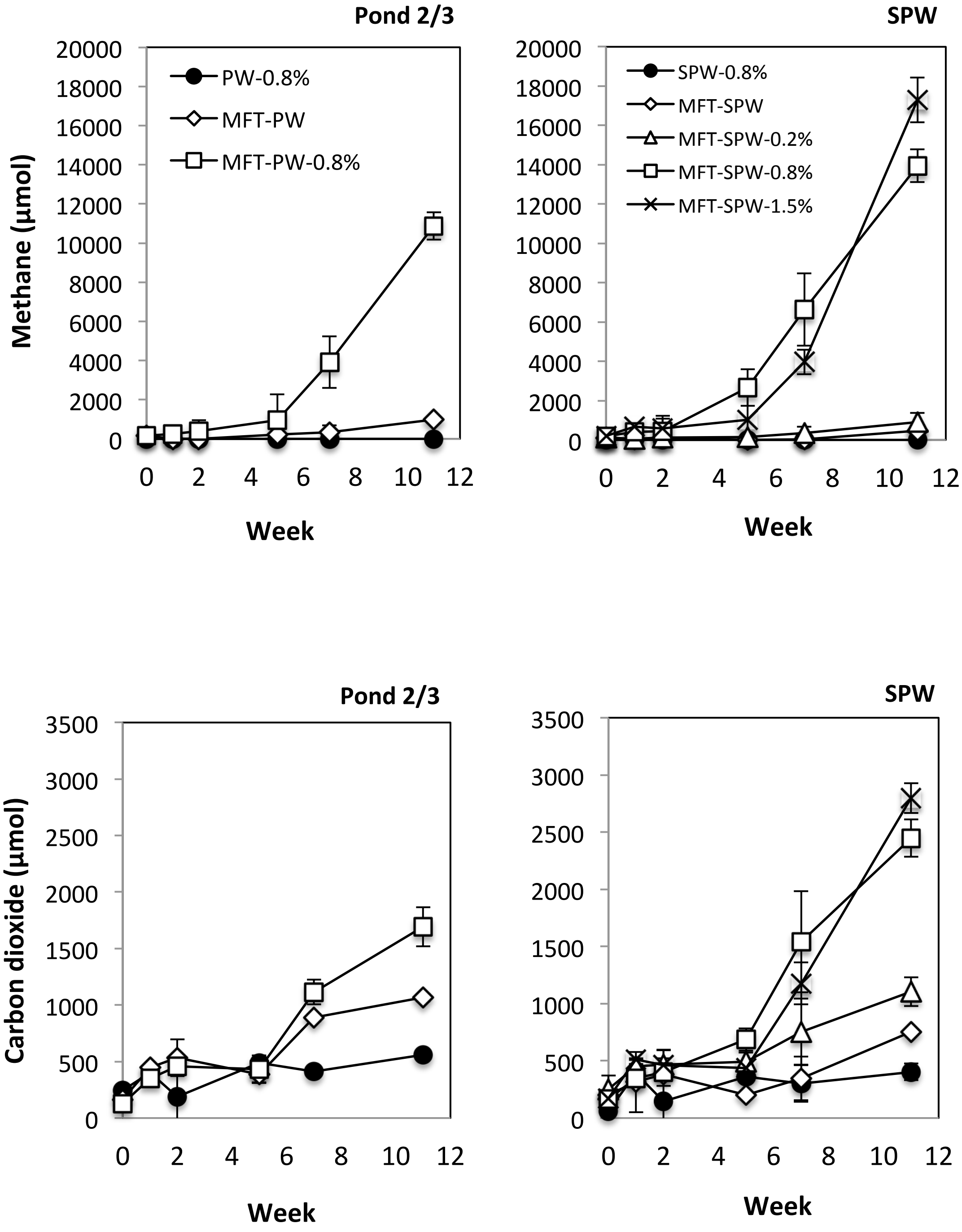


Figure 4-8: Methane and carbon dioxide emissions for the Pond 2/3 and surrogate pond water groups over an 11-week study period. The values are averages from duplicate measurements. The error bars (where visible) represent plus and minus one standard deviation.

In summary, there were three main stages that occurred within the MFT-diluent mesocosms of this study: 1) nitrate reduction (prior to t=0), 2) sulfate reduction between weeks 0 and week 2, followed by a spike in RSC emissions, and 3) methanogenesis between weeks 5 and week 11. The results of this study indicated that H_2S, CH_4, and CO_2 emissions were the result of microbial activity associated with the MFT whereas the other RSCs studied originated from the naphtha diluent. Furthermore, all RSC and CH_4 and CO_2 emissions were found to increase with increasing naphtha diluent concentrations. The total amount of RSCs produced per mL of MFT (between weeks 0 and week 6), and CH_4 and CO_2 produced per mL of MFT (between weeks 5 to week 11) for the MFT mesocosms are reported in Table 4-14. Quantity wise, CH_4 was the highest as hypothesized, followed by CO_2 emissions, and the then total combined RSC emissions. The results of this study demonstrate that there is a potential to reduce emissions from tailings by further reducing the amount of diluent being lost to the tailings ponds.

Table 4-14: Total amount of RSCs, CH_4, and CO_2 emissions produced per mL of MFT in the MFT mesocosms for the sulfur emissions time frame (week 0 to week 6) and the methanogenesis time frame (week 5 to week 11).

Treatment	Total emissions produced (µmol/mL MFT)		
	RSC	CH_4	CO_2
MFT-PW	0.01	1.9	1.7
MFT-PW-0.8%	0.06	24.8	3.1
MFT-SPW	0.02	1.1	1.4
MFT-SPW-0.2%	0.03	1.9	1.5
MFT-SPW-0.8%	0.09	28.2	4.4
MFT-SPW-1.5%	0.12	40.7	5.9

4.5 Chapter 4 References

Arkell, N., Kuznetsov, P., Kuznetsova, A., Foght, J.M., and Siddique, T. 2015. Microbial metabolism alters pore water chemistry and increases consolidation of oil sands tailings. Journal of Environmental Quality, **44**(1): 145–153.

Bordenave, S., Kostenko, V., Dutkoski, M., Grigoryan, A., Martinuzzi, R.J., and Voordouw, G. 2010. Relation between the activity of anaerobic microbial populations in oil sands tailings ponds and the sedimentation of tailings. Chemosphere, **81**(5): 663–668.

Chen, M., Walshe, G., Chi Fru, E., Ciborowski, J.J.H., Weisener, C.G. 2013. Microcosm assessment of the biogeochemical development of sulfur and oxygen in oil sands fluid fine tailings. Applied Geochemistry, **37**: 1–11.

Fedorak, P.M., Coy, D.L., Salloum, M.J., and Dudas, M.J. 2002. Methanogenic potential of tailings samples from oil sands extraction plants. Canadian Journal of Microbiology, **48**(1): 21–33.

Flemming, H.C., and Wingender, J. 2001. Relevance of microbial extracellulur polymeric substances (EPSs) – Part I: Structure and ecological aspects. Water Science and Technology, **43**: 1–8.

Holowenko, F.M., MacKinnon, M.D., and Fedorak, P.M. 2000. Methanogens and sulfate-reducing bacteria in oil sands fine tailings waste. Canadian Journal of Microbiology, **46**(10): 927–937.

Liebensteiner, M.G., Tsesmetzis, N., Stams, A.J.M., and Lomans, B.P. 2014. Microbial redox processes in deep subsurface environments and the potential application of (per)chlorate in oil reservoirs. Frontier in Microbiology, **5**(428): 1–13.

MacKinnon, M., and Sethi, A. 1993. A comparison of the physical and chemical properties of the tailings ponds at the Syncrude and Suncor oil sands plants. *In* Proceedings of the Fine Tailings Symposium: Oil Sands – Our Petroleum Future Conference, Edmonton, Alta., 4–7 April 1993. AOSTRA Publications, Edmonton, Alta. Paper No. 57.

Pandey, S.K., and Kim, K.H. 2009. A review of methods for the determination of reduced sulfur compounds (RSCs) in air. Environmental Science & Technology, **43**(9): 3020–3029.

Penner, T.J., and Foght, J.M. 2010. Mature fine tailings from oil sands processing harbour diverse methanogenic communities. Canadian Journal of Microbiology, **56**(6): 459–470.

Ramos-Padrón, E., Bordenave, S., Lin, S., Bhaskar, I.M., Dong, X., Sensen, C.W., Fournier, J., Voordouw, G., and Gieg, L.M. 2011. Carbon and sulfur cycling by microbial communities in a gypsum-treated oil sands tailings pond. Environmental Science & Technology, **45**(2): 439–446.

Roychoudhury, A.N., and Merrett, G.L. 2006. Redox pathways in a petroleum contaminated shallow sandy aquifer: iron and sulfate reductions. Science of The Total Environment, **366**(1): 262–274.

Salloum, M.J., Dudas, M.J., and Fedorak, P.M. 2002. Microbial reduction of amended sulfate in anaerobic mature fine tailings from oil sand. Waste Management & Research, **20**(2): 162–171.

Sander, R. 1999. Compilation of Henry’s Law constants for inorganic and organic species of potential importance in environmental chemistry [online]. Available from http://www.henrys-law.org/henry-3.0.pdf [cited 5 September 2015].

Siddique, T., Penner, T., Semple, K., and Foght, J.M. 2011. Anaerobic biodegradation of longer-chain *n*-alkanes coupled to methane production in oil sands tailings. Environmental Science & Technology, **45**(13): 5892–5899.

Small, C.C., Cho, S., Hashisho, Z., and Ulrich, A.C. 2015. Emissions from oil sands tailings ponds: review of tailings pond parameters and emission estimates. Journal of Petroleum Science and Engineering, **127**: 490–501.

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

Suthersan, S.S. 1996. Remediation engineering design concepts. CRC Press.

Toxnet. 2014. Thiophene [online]. Available from http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+130 [cited 11 October 2015].

Vasconcellos, S.P., Dellagnezze, B.M., Wieland, A., Klock, J.H., Santos Neto, E.V., Marsaioli, A.J., Oliveira, V.M., and Michaelis, W. 2011. The potential for hydrocarbon biodegradation and production of extracellulur polymeric substances by aerobic bacteria isolated from a Brazilian petroleum reservoir. World Journal of Microbiology & Biotechnology, **27**: 1513–1518.

Wardencki, W. 1998. Problems with the determination of environmental sulphur compounds by gas chromatography. Journal of Chromatography A, **793**(1): 1–19.

Chapter 5. CONCLUSIONS AND RECOMMENDATIONS

In conclusion, this study has provided insights to gas evolution in tailings that contain naphtha diluent. Over the course of this 11-week study, there were three stages observed in the MFT-diluent mesocosms: 1) nitrate reduction (prior to t=0), 2) sulfur emissions production between weeks 0 and week 6, and 3) methanogenesis between weeks 5 and week 11. The majority of reduced sulfur compound (RSC) emissions were produced between weeks 0 and week 6. Hydrogen sulfide (H_2S) emissions were detected in all of the MFT containing mesocosms at slightly alkaline pH conditions, and production was stimulated by naphtha diluent. The greatest amount of H_2S was found in the surrogate pond water 1.5% w/v treatment, which produced up to 3 times the amount of H_2S found in the no-diluent controls and had a production rate of 0.05 μmol/mL MFT. H_2S production also coincided with significant decreases in sulfate concentrations and spikes in alkalinity. Based on the chemical changes during this time and the absence of H_2S emissions in the no-MFT controls, biogenic sulfate-reduction by sulfate reducing bacteria was the likely cause of the H_2S release. With respect to the other six RSCs analyzed in this study, the initial and final concentrations in the mesocosms indicate that they originated from the naphtha diluent. In general these RSC emissions also increased with increasing naphtha concentrations; the amounts emitted increased by a factor of 4 at 0.2% w/v up to 45 times that of the no-diluent control emissions at 1.5% w/v. Considering a worst case diluent scenario of 1.5% w/v, the overall amount of RSCs produced from highest to lowest between weeks 0 and week 6 were in the order of H_2S and 2-methylthiophene > 2,5-dimethylthiophene > 3-methylthiophene > thiofuran > butyl mercaptan > carbonyl sulfide. The combined RSC production rate under these conditions was 0.12 μmol/mL MFT, with H_2S and 2-methylthiophene combined making up 81% of the total RSC emissions.

Methane (CH_4) and carbon dioxide (CO_2) emissions began to increase around week 5, several weeks after sulfate depletion, and appeared to be the result of microbial activity. Both CH_4 and CO_2 emissions also increased with increasing naphtha concentrations–the greatest amounts were found in the surrogate pond water 1.5% w/v mesocosms, with production rates of 41 μmol CH_4/mL MFT and 6 μmol CO_2/mL MFT. Of the emissions analyzed in this study, the amount of CH_4 emissions were the highest, as hypothesized, followed by CO_2, and then the combined total RSCs. Overall, the results of this study demonstrate that sulfate is a key factor with respect to the transition from sulfur emissions production to methanogenesis, and that naphtha diluent stimulates the production of CH_4, CO_2, and sulfur emissions in the tailings. Therefore, further reducing the concentration of residual diluent in the tailings ponds is anticipated to decrease the amount of greenhouse gases and RSC emissions that are produced in tailings.

One drawback to this study is that it does not address how much of the emissions generated in the tailings are released into the atmosphere, particularly concerning the sulfur compounds as they are highly reactive. Further study of this may involve conducting a column experiment that introduces known concentrations of sulfur emissions (from the results of this study) and measuring the change in sulfur quantities with respect to depth over time.

Regarding the sulfur compounds (excluding H_2S) in this study, which are thought to originate from the naphtha diluent, it was hypothesized that these emissions were being re-released as the MFT settles due to the similarity between the week 14 concentrations in the MFT-diluent mesocosms and t=0 concentrations in the no-MFT controls. A potential method to verify this hypothesis is to remake the 0.8% w/v naphtha mesocosms for both pond water groups but re-amend the mesocosms with sulfate (to extend sulfate reduction) and see whether the concentrations of 2-methylthiophene, 2,5-dimethylthiophene, 3-methylthiophene, thiofuran, butyl mercaptan, and carbonyl sulfide significantly exceed the t=0 concentrations of the no-MFT controls over time.

A last suggestion to further the research from this experiment is to repeat the study but with MFT, pond water, and diluent from other oil sands operators. In peer-reviewed studies, a number of microcosm experiments were conducted with materials from Syncrude Canada Ltd.'s Mildred Lake Settling Basin. This experiment used MFT and pond water from Suncor Energy Inc.'s Pond 2/3. Therefore, repeating this study with material from Shell Canada or investigating the use of paraffinic diluent may yield further insights to emissions production within the tailings ponds.

Bibliography

Agency for Toxic Substances & Disease Registry (ATSDR). 2014. Hydrogen sulfide – ToxFAQs^{TM} [online]. Available from http://www.atsdr.cdc.gov/toxfaqs/tfacts114.pdf [cited 7 September 2015].

Arkell, N., Kuznetsov, P., Kuznetsova, A., Foght, J.M., and Siddique, T. 2015. Microbial metabolism alters pore water chemistry and increases consolidation of oil sands tailings. Journal of Environmental Quality, **44**: 145–153.

BGC Engineering Inc. 2010. Review of reclamation options for oil sands tailings substrates. Available from the Oil Sands Research and Information Network, University of Alberta, School of Energy and the Environment, Edmonton, Alta. OSRIN Report No. TR-2. pp 59.

Bordenave, S., Kostenko, V., Dutkoski, M., Grigoryan, A., Martinuzzi, R.J., and Voordouw, G. 2010. Relation between the activity of anaerobic microbial populations in oil sands tailings ponds and the sedimentation of tailings. Chemosphere, **81**(5): 663–668.

Burkus, Z., Wheler, J., and Pletcher, S. 2014. GHG emissions from oil sands tailings ponds: overview and modelling based on fermentable substrates. Part I: Review of the tailings ponds facts and practices [online]. Alberta Environment and Sustainable Resource Development. Available from http://hdl.handle.net/10402/era.40125 [cited 15 August 2015].

Cai, H., Brandt, A.R., Yeh, S., Englander, J.G., Han, J., Elgowainy, A., and Wang, M.Q. 2015. Well-to-Wheels greenhouse gas emissions of Canadian oil sands products: implication for U.S. petroleum fuels. Environmental Science & Technology. Accepted Manuscript.

Chalaturnyk, R.J., Scott, J.D., and Özüm, B. 2002. Management of oil sands tailings. Petroleum Science and Technology, **20**(9–10): 1025–1046.

Chen, M., Walshe, G., Chi Fru, E., Ciborowski, J.J.H., Weisener, C.G. 2013. Microcosm assessment of the biogeochemical development of sulfur and oxygen in oil sands fluid fine tailings. Applied Geochemistry, **37**: 1–11.

Chi Fru, E., Chen, M., Walshe, G., Penner, T., and Weisener, C. 2013. Bioreactor studies predict whole microbial population dynamics in oil sands tailings ponds. Applied Microbiology & Biotechnology, **97**(7): 3215–3224.

Dou, J., Liu, X., Hu, Z., and Deng, D. 2008. Anaerobic BTEX biodegradation linked to nitrate and sulfate reduction. Journal of Hazardous Materials, **151**(2): 720–729.

Ehrenhauser, F.S., Avij, P., Shu, X., Dugas, V., Woodson, I., Liyana-Arachchi, T., Zhang, Z., Hung, F.R., and Valsaraj, K.T. 2014. Bubble bursting as an aerosol generation mechanisms during an oil spill in the deep-sea environment: laboratory experimental demonstration of the transport pathway. Environmental Science: Processes & Impacts, **16**: 65–73.

Energy Resources Conservation Board (ERCB). 2015. Directive 074: Tailings performance criteria and requirements for oil sands mining schemes [online]. Available from https://www.aer.ca/documents/directives/Directive074.pdf [cited 14 September 2015].

Fedorak, P.M., Coy, D.L., Salloum, M.J., and Dudas, M.J. 2002. Methanogenic potential of tailings samples from oil sands extraction plants. Canadian Journal of Microbiology, **48**(1): 21–33.

Fedorak, P.M., Coy, D.L., Dudas, M.J., Simpson, M.J., Renneberg, A.J., and MacKinnon, M.D. 2003. Microbially-mediated fugitive gas production from oil sands tailings and increased tailings densification rates. Journal of Environmental Engineering & Science, **2**(3): 199–211.

Flemming, H.C., and Wingender, J. 2001. Relevance of microbial extracellulur polymeric substances (EPSs) – Part I: Structure and ecological aspects. Water Science and Technology, **43**: 1–8.

Government of Alberta (GoA). 2014. Tailings [online]. Available from http://www.oilsands.alberta.ca/tailings.html [cited 6 July 2015].

Government of Alberta (GoA). 2015a. Facts and statistics [online]. Available from http://www.energy.alberta.ca/oilsands/791.asp [cited 29 Sept 2015].

Government of Alberta (GoA). 2015b. Lower Athabasca region tailings management framework for the mineable Athabasca oil sands [online]. Available from http://esrd.alberta.ca/focus/cumulative-effects/cumulative-effects-management/management-frameworks/documents/LARP-TailingsMgtAthabascaOilsands-Mar2015.pdf [cited 6 July 2015].

Guo, C. 2009. Rapid densification of the oil sands mature fine tailings (MFT) by microbial activity. Ph.D. thesis, The University of Alberta, Edmonton, Alta.

Hammerschmidt, C.R., and Burton, G.A. Jr. 2010. Measurements of acid volatile sulfide and simultaneously extracted metals are irreproducible among laboratories. Environmental Toxicology and Chemistry, **29**(7): 1453–1456.

Hemond, H.F., and Fechner-Levy, E.J. 2000. Chemical fate and transport in the environment. 2nd ed. Elsevier, San Diego, Calif.

Holowenko, F.M., MacKinnon, M.D., and Fedorak, P.M. 2000. Methanogens and sulfate-reducing bacteria in oil sands fine tailings waste. Canadian Journal of Microbiology, **46**(10): 927–937.

Holowenko, F.M., Mackinnon, M.D., and Fedorak, P.M. 2001. Naphthenic acids and surrogate naphthenic acids in methanogenic microcosms. Water Research, **35**(11): 2595–2606.

Liebensteiner, M.G., Tsesmetzis, N., Stams, A.J.M., and Lomans, B.P. 2014. Microbial redox processes in deep subsurface environments and the potential application of (per)chlorate in oil reservoirs. Frontier in Microbiology, **5**(428): 1–13.

Lo, C.C., Brownlee, B.G., and Bunce, N.J. 2003. Electrospray-mass spectrometric analysis of reference carboxylic acids and Athabasca oil sands naphthenic acids. Analytical Chemistry, **75**: 6394–6400.

MacKinnon, M.D. 1989. Development of the tailings pond at Syncrude's oil sands plant: 1978–1987. AOSTRA Journal of Research, **5**: 109–133.

MacKinnon, M., and Sethi, A. 1993. A comparison of the physical and chemical properties of the tailings ponds at the Syncrude and Suncor oil sands plants. *In* Proceedings of the Fine Tailings Symposium: Oil Sands – Our Petroleum Future Conference, Edmonton, Alta., 4–7 April 1993. AOSTRA Publications, Edmonton, Alta. Paper No. 57.

Pandey, S.K., and Kim, K.H. 2009. A review of methods for the determination of reduced sulfur compounds (RSCs) in air. Environmental Science & Technology, **43**(9): 3020–3029.

Paslawski, J.C., Headley, J.V., Hill, G.A., and Nemati, M. 2009. Biodegradation kinetics of trans-4-methyl-1-cyclohexane carboxylic acid. Biodegradation, **20**: 125–133.

Penner, T.J., and Foght, J.M. 2010. Mature fine tailings from oil sands processing harbour diverse methanogenic communities. Canadian Journal of Microbiology, **56**(6): 459–470.

Ramos-Padrón, E., Bordenave, S., Lin, S., Bhaskar, I.M., Dong, X., Sensen, C.W., Fournier, J., Voordouw, G., and Gieg, L.M. 2011. Carbon and sulfur cycling by microbial communities in a gypsum-treated oil sands tailings pond. Environmental Science & Technology, **45**(2): 439–446.

Rao, F., and Liu, Q. 2013. Froth treatment in Athabasca oil sands bitumen recovery process: a Review. Energy Fuels, **27**(12): 7199–7207.

Roychoudhury, A.N., and Merrett, G.L. 2006. Redox pathways in a petroleum contaminated shallow sandy aquifer: iron and sulfate reductions. Science of The Total Environment, **366**(1): 262–274.

Salloum, M.J., Dudas, M.J., and Fedorak, P.M. 2002. Microbial reduction of amended sulfate in anaerobic mature fine tailings from oil sand. Waste Management & Research, **20**(2): 162–171.

Sander, R. 1999. Compilation of Henry's Law constants for inorganic and organic species of potential importance in environmental chemistry [online]. Available from http://www.henrys-law.org/henry-3.0.pdf [cited 5 September 2015].

Selucky, M.L., Chu, Y., Ruo, T., and Strausz, O.P. 1977. Chemical composition of Athabasca bitumen. Fuel, **56**(4): 369–381.

Shimadzu. 2015. TOC-L, 680°C Combustion catalytic oxidation method measurement principles [online]. Available from http://www.shimadzu.com/an/toc/lab/toc-l4.html [cited 30 August 2015].

Siddique, T., Fedorak, P.M., and Foght, J.M. 2006. Biodegradation of short-chain *n*-alkanes in oil sands tailings under methanogenic conditions. Environmental Science & Technology, **40**(17): 5459–5464.

Siddique, T., Fedorak, P.M., MacKinnon, M.D., and Foght, J.M. 2007. Metabolism of BTEX and naphtha compounds to methane in oil sands tailings. Environmental Science & Technology, **41**(7): 2350–2356.

Siddique, T., Penner, T., Semple, K., and Foght, J.M. 2011. Anaerobic biodegradation of longer-chain *n*-alkanes coupled to methane production in oil sands tailings. Environmental Science & Technology, **45**(13): 5892–5899.

Siddique, T., Penner, T., Klassen, J., Nesbø., and Foght, J.M. 2012. Microbial communities involved in methane production from hydrocarbons in oil sands tailings. Environmental Science & Technology, **46**(17): 9802–9810.

Siddique, T., Kuznetsov, P., Kuznetsova, A., Li, C., Young, R., Arocena, J.M., and Foght, J.M. 2014. Microbially-accelerated consolidation of oil sands tailings. Pathway II: solid phase biogeochemistry. Frontier in Microbiology, **5**: 1–13.

Singleton, R. Jr. 1993. The Sulfate-Reducing Bacteria: An Overview. *In* The sulfate-reducing bacteria: contemporary perspectives. *Edited by* J.M. Odom and R. Singleton Jr. Springer-Verlag, New York. pp. 1–20.

Small, C.C., Ulrich, A.C., and Hashisho, Z. 2012. Adsorption of acid extractable oil sands tailings organics onto raw and activated oil sands coke. Journal of Environmental Engineering, **138**: 833–840.

Small, C.C., Cho, S., Hashisho, Z., and Ulrich, A.C. 2015. Emissions from oil sands tailings ponds: review of tailings pond parameters and emission estimates. Journal of Petroleum Science and Engineering, **127**: 490–501.

Standard Methods. 2000. 4110 Determination of anions by ion chromatography [online]. Available from http://www.standardmethods.org/store/ProductView.cfm?ProductID=31 [cited 3 December 2015].

Stasik, S., and Wendt-Potthoff, K. 2014. Interaction of microbial sulphate reduction and methanogenesis in oil sands tailings ponds. Chemosphere, **103**: 59–66.

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

Suncor. 2009. Annual tailings management plan [online]. Available from https://www.aer.ca/documents/oilsands/tailings-plans/Suncor_2009_TailingsPlans.pdf [cited 29 August 2015].

Suthersan, S.S. 1996. Remediation engineering design concepts. CRC Press.

Synek, V. 2008. Evaluation of the standard deviation from duplicate results. Accreditation and Quality Assurance: Journal for Quality, Comparability and Reliability in Chemical Measurement, **13**: 335–337.

Thoroddsen, S.T. 2012. The making of a splash. Journal of Fluid Mechanics, **690**: 1–4.

Toxnet. 2014. Thiophene [online]. Available from http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+130 [cited 11 October 2015].

United States Environmental Protection Agency (USEPA). 1997. Method 300.1 Determination of inorganic anions in drinking water by ion chromatography [online]. Available from http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_07_10_methods_method_300_1.pdf [cited 30 August 2015].

Vasconcellos, S.P., Dellagnezze, B.M., Wieland, A., Klock, J.H., Santos Neto, E.V., Marsaioli, A.J., Oliveira, V.M., and Michaelis, W. 2011. The potential for hydrocarbon biodegradation and production of extracellulur polymeric substances by aerobic bacteria isolated from a Brazilian petroleum reservoir. World Journal of Microbiology & Biotechnology, **27**: 1513–1518.

Wang, C. 2010. Simultaneous analysis of greenhouse gases by gas chromatography [online]. Available from http://www.chem-agilent.com/pdf/5990-5129EN.pdf [cited 20 May 2015].

Wardencki, W. 1998. Problems with the determination of environmental sulphur compounds by gas chromatography. Journal of Chromatography A, **793**(1): 1–19.

Winfrey, M.R., and Ward, D.M. 1983. Substrates for sulfate reduction and methane production in intertidal sediments. Applied and Environmental Microbiology, **45**(1): 193–199.

Yeh, S., Jordaan, S.M., Brandt, A.R., Turetsky, M.R., Spatari, S., and Keith, D.W. Land use greenhouse gas emissions from conventional oil production and oil sands. Environmental Science & Technology*,* **44**(22): 8766–8772.

APPENDIX A: SURROGATE POND WATER RECIPE

Dr. Hamed Mahdavi provided the protocol for making the surrogate pond water (SPW) used in this experiment in personnel communications (2014), which is also provided here. The individual components are listed in Table A-1 and Table A-2. Yaxin Jiang prepared the SPW prior to this study.

Table A-1: Non-metal components of the surrogate pond water.

Compound	mM	MW	Weight (g/L)	g for 10 L
NH_4Cl	0.307	53.49	0.0164	0.1640
KCl	0.379	74.55	0.0283	0.2828
NaCl	10.000	58.44	0.5844	5.8440
$MgSO_4$	0.471	120.37	0.0567	0.5673
Na_2SO_4	3.886	142.04	0.5520	5.5200
$NaHCO_3$	15.572	84.01	1.3082	13.0818
$CaCl_2$	0.518	110.98	0.0575	0.5750
NaF	0.155	41.99	0.0065	0.0652
KBr	0.005	119.00	0.0005	0.0054
$SrCl_2 \bullet 6H_2O$	0.009	266.62	0.0024	0.0239
LiCl	0.039	42.39	0.0016	0.0165

Table A-2: Trace metal solution for the surrogate pond water.

Metal	Atomic mass	Formula	MW	Conc. in SPW (mg/L)	M (mol/L)	g of chemicals in 1 L water
Cr	52.00	K_2CrO_4	194.19	0.0064	1.22E-07	2.38E-05
Mn	54.94	$MnCl_2 \bullet 4H_2O$	197.90	0.0407	7.41E-07	1.47E-04
Co	58.93	$CoCl_2 \bullet 6H_2O$	237.93	0.0013	2.26E-08	5.37E-06
Ni	58.69	$NiCl_2 \bullet 6H_2O$	237.69	0.0095	1.61E-07	3.84E-05
Cu	63.55	$CuCl_2 \bullet 2H_2O$	170.48	0.0054	8.46E-08	1.44E-05
Zn	65.41	$ZnCl_2$	136.31	0.0071	1.08E-07	1.47E-05
As	74.92	As_2O_3	197.84	0.0132	1.77E-07	1.75E-05
Se	78.96	$H_2SeO_4 \bullet 10H_2O$	325.13	0.0053	6.69E-08	2.18E-05
Cd	112.41	$CdCl_2$	183.32	0.0001	9.86E-10	1.81E-07
Sb	121.76	$KSbO \bullet C_4H_4O_6$	324.94	0.0015	1.20E-08	3.88E-06
Ba	137.33	$BaCl_2 \bullet 2H_2O$	244.26	0.3653	2.66E-06	6.50E-04
Mo	95.94	$Na_2MoO_4 \bullet 2H_2O$	241.95	0.1180	1.23E-06	2.98E-04
Ag	107.87	Ag_2SO_4	311.80	0.0000	2.78E-10	8.67E-08
B	10.81	$Na_2B_4O_7 \bullet 10H_2O$	381.37	2.8900	2.67E-04	2.55E-02
Si	28.09	$NaSiO_3 \bullet 9H_2O$	261.21	3.0000	1.07E-04	2.79E-02

Instructions for making the SPW provided by H. Mahdavi (personal communications, 2014) are as follows:

1. Dissolve each chemical in a small amount of deionized (DI) water separately. You want enough DI water that the chemical is completely dissolved.

2. Slowly combine the dissolved chemical solutions. There should be no precipitation. Closely monitor the pH when adding each separate solution; if the pH increases, add HCl acid to decrease it back to 7-8. After combining the chemicals top up the mixture with DI water to a final volume of 9 L (For example, if your combined chemical mixture had a volume of 4 L, add another 5 L of DI water to get a total volume of 9 L).

3. Dissolve your target naphthenic acids (NAs) in 300-500mL of 4.083566176 gr NaOH. It will take around 30 minutes or so to completely dissolve depending on the NAs. After the NAs are completely dissolved, reduce the pH to around 9 to 9.5 by adding HCl acid.

4. Slowly add your NAs solution to the 9 L solution that you prepared in step 2. The pH should not exceed 8.3 (the final target pH). If it does, again, add HCl acid. You want a final volume of 10 L.

Other notes:

- All addition steps must be in a vigorous mixing condition. Be sure to add solutions as slowly as possible.
- Be careful when adding HCl acid; the pH can change very quickly. You can use a diluted HCl acid solution but keep in mind that the more diluted it is the more you will need to add. For ex. 1 N HCl is too dilute. You might exceed the final 10 L target.

APPENDIX B: LIQUID SAMPLING AND SULFUR GAS SAMPLING PROTOCOLS

LIQUID SAMPLING PROCOTOL

The materials used were 70% ethanol, a box of Kimwipes, a 2 L ‘waste’ glass beaker, and sterile 18G needles, 30 mL plastic syringes, and 50 mL Corning® polypropylene centrifuge tubes.

First, the mesocosm septa was disinfected with 70% ethanol and blotted dry with a Kimwipe. The mesocosm was then carefully tilted onto its side. It is important not to agitate the contents during this step or the MFT may re-suspend and clog the syringe. A 30 mL plastic syringe fitted with an 18G needle was inserted through the septa and was used to withdraw approximately 20 mL of liquid sample (Figure B-1). The liquid sample was then deposited into a 50 mL centrifuge tube and capped.

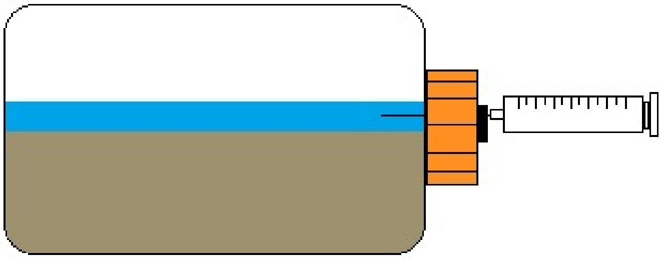


Figure B-1: Liquid sampling from the mesocosms’ water fraction. Approximately 20 mL of liquid sample was withdrawn for each time point.

SULFUR GAS SAMPLING PROCOTOL

Undiluted sulfur gas samples from all of the mesocosms were run first. If any of the target compounds topped out on the chromatograph, which was often the case, diluted samples were then run until the peak areas fell within the calibration range. For undiluted gas samples the following steps were taken for sulfur gas sampling:

1. Rinse the syringe with methanol and let it dry for at least 30 minutes.
2. Gently invert the mesocosm several of times to re-distribute the gases.
3. Flush the syringe with 4.8pp Nitrogen gas, and then withdraw approximately 10 mL of the nitrogen gas into the syringe.
4. Disinfect the syringe needle and the mesocosm septa with 70% ethanol and blot dry with a Kimwipe.
5. Place the syringe needle at the base of an 18G needle head and depress the syringe piston to push the nitrogen gas through the needle head. Then pierce the septa with the 18G needle guide at a 45-degree angle to minimize gas loss.
6. Flush the syringe with the headspace gas before withdrawing 5 mL of gas sample. Quickly remove the needle guide and syringe from the septa (together), put down the 18G needle head, and inject the gas sample into the SCD.

For dilution of the sulfur gas samples, step 1 to step 5 are the same as the undiluted sample run. Thereafter, the following steps are taken:

6. Flush the syringe with the headspace gas before withdrawing the desired volume of gas sample for dilution. Quickly remove the needle guide and syringe from the septa, put down the 18G needle head, and inject the gas sample into a 5.0 nitrogen-filled, 40 mL EPA vial. Lock the EPA vial.

7. Wait five minutes to let the gases mix.

8. Flush the syringe with 4.8pp Nitrogen, withdraw 5 mL of diluted gas sample, and immediately inject it into the SCD.

Note:

- See section 3.2.5.2 Sulfur Gas Analysis for further information on the syringe dilution method.

APPENDIX C: CALIBRATION DATA

TCD CALIBRATION FOR METHANE AND CARBON DIOXIDE

Calibrations for methane and carbon dioxide on the TCD were done in % volume. The calibration equations for the MFT mesocosms and the no-MFT controls are provided in Table C-1 and Table C-2. Calibration curves for methane and carbon dioxide obtained in this study are also plotted in Figures C-1 to Figure C-3.

Table C-1: Methane and carbon dioxide calibration equations for MFT mesocosms.

	Test week applied to					
Date	CH_4	CO_2	CH_4 eqn	R^2	CO_2 eqn	R^2
Oct 8/14	5	0, 1, 2, 5	y = 124.41x	0.9878	y = 203.08x	0.9916
Oct 24/14	0, 1, 2, 7	7	y = 143.8x	0.9952	y = 206.3x	0.9840
Nov 21/14	11	11	y = 115.43x	0.9957	y = 181.34x	0.9898

Table C-2: Methane and carbon dioxide calibration equations for the no-MFT controls.

Date	Week	CH_4 eqn	R^2	CO_2 eqn	R^2
Dec 19/14	0	y = 113.92x	0.98057	y = 159.15x	0.9851
Dec 24/14	1	y = 121.57x	0.98747	y = 169.68x	0.9682
Dec 30/14	2	y = 104.99x	0.98243	y = 184.2x	0.9892
Jan 20/15	5	y = 118.12x	0.99075	y = 191.56x	0.9883
Feb 5/15	7	y = 118.12x	0.99075	y = 193.11x	0.9801
Mar 5/15	11	y = 96.806x	0.98572	y = 186.3x	0.9937

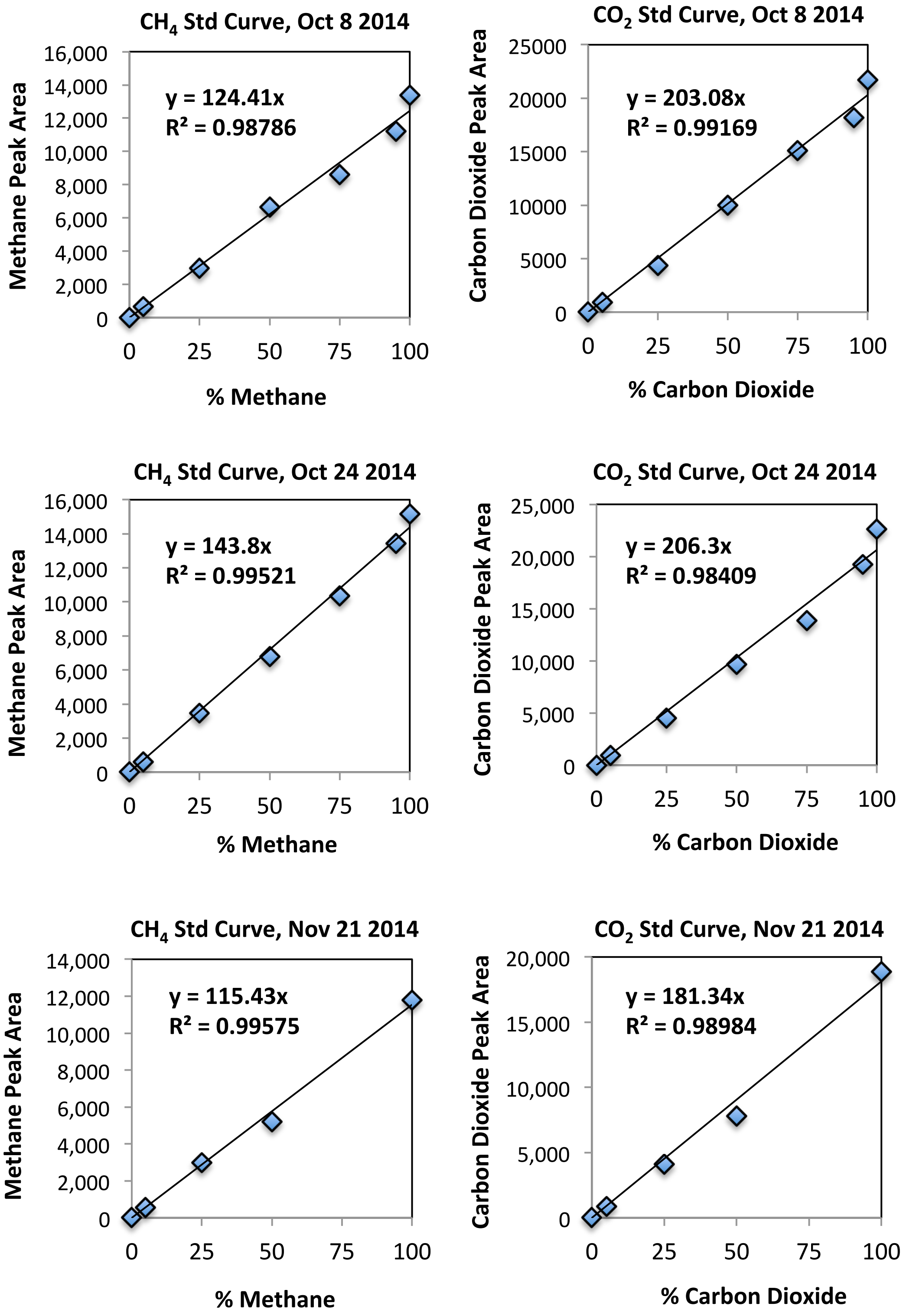


Figure C-1: MFT mesocosm calibration curves for methane and carbon dioxide. The three dates used were Oct 8/14, Oct 24/14, and Nov 21/14.

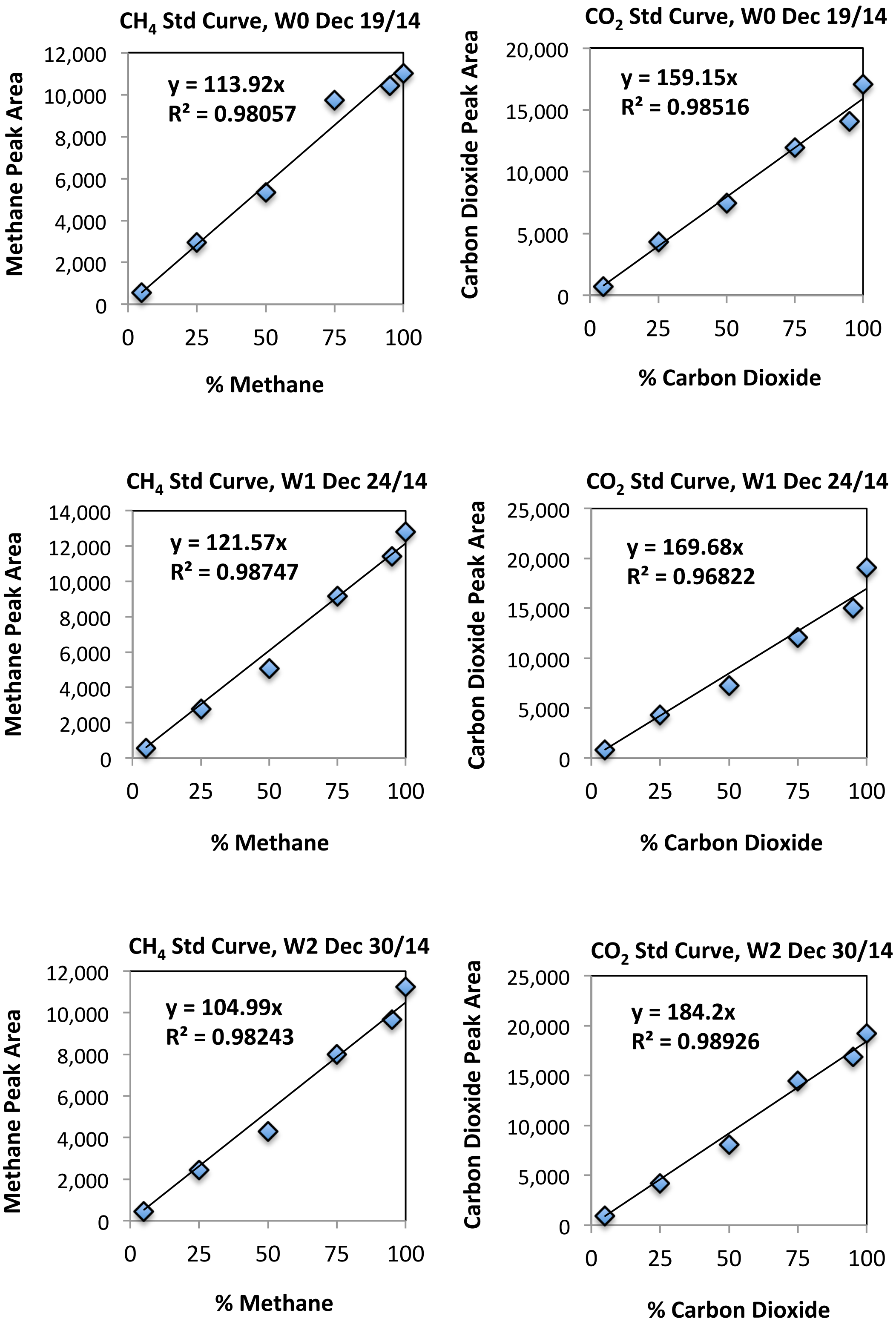


Figure C-2: No-MFT calibration curves for weeks 0, 1, and 2, for methane and carbon dioxide.

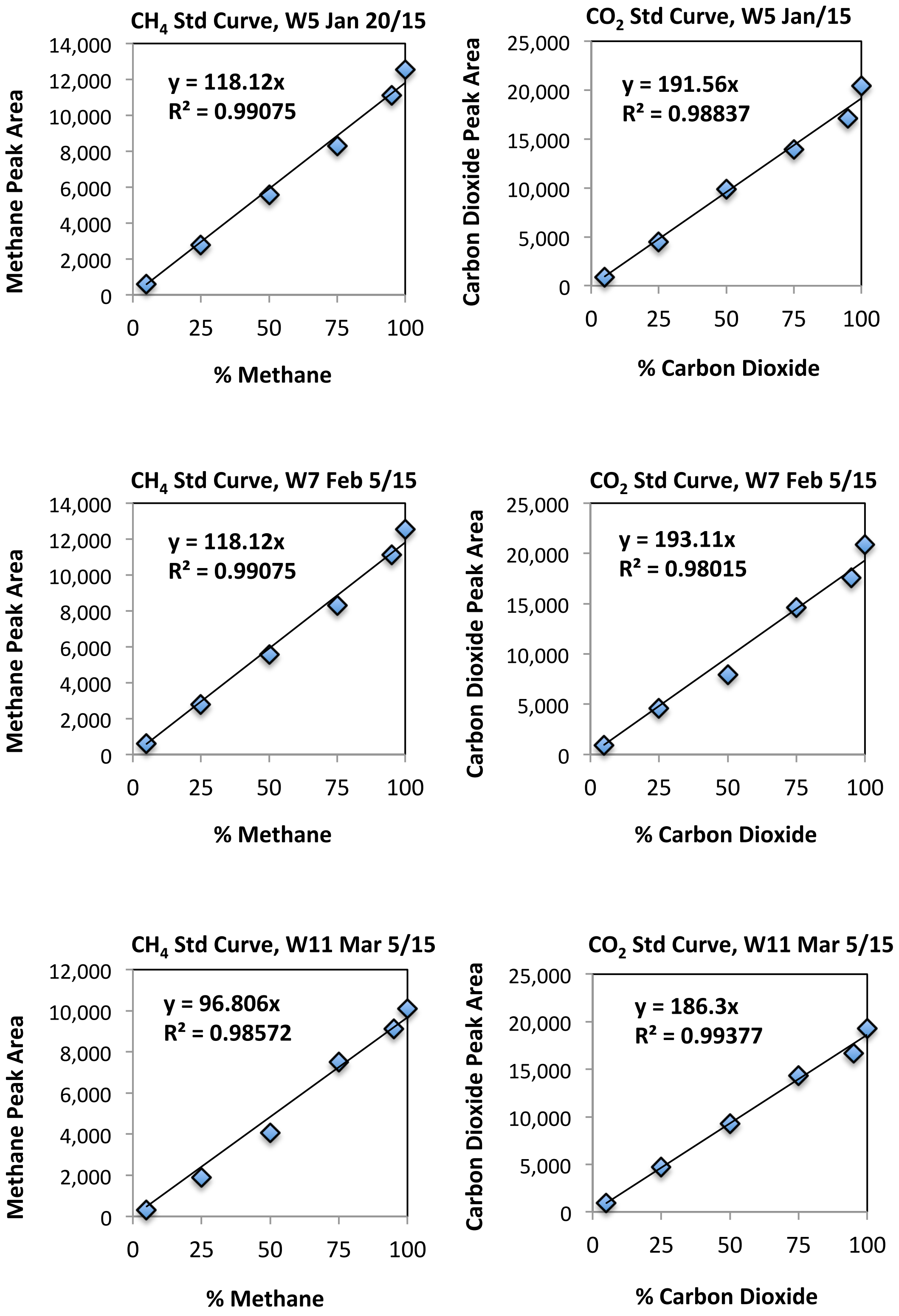


Figure C-3: No-MFT calibration curves for weeks 5, 7, and 11, for methane and carbon dioxide.

SCD CALIBRATION FOR SULFUR EMISSIONS

An initial sulfur gas standard containing 1 ppmv of hydrogen sulfide, carbonyl sulfide, thiofuran, butyl mercaptan, 2-methylthiophene, 3-methylthiophene, and 2,5-dimethylthiophene was used at the start of the experiment. Several weeks into the study, however, a number of these compounds' concentrations were consistently exceeding those of the 1 ppmv standard calibration. While a new sulfur gas standard was being ordered, a liquid sulfur standard from Agilent was used to approximate the shifts in compound peaks between time points. For example, if the Agilent standard's peak areas at week 0 was ~30% greater than the same standard during the new sulfur standard calibration, then the new calibration curves were adjusted by 30% to approximate the week 0 curves. The calibration equations and peak areas resulting from the new sulfur gas standard are provided in Table C-3 and Table C-4.

Table C-3: Calibration equations for the sulfur gas compounds analyzed in this study from the new sulfur gas standard.

Compound	New sulfur std (ppmv)	Equation	R^2
Hydrogen sulfide	151	7,899.9x	0.97852
Carbonyl sulfide	5.09	8,262.9x	0.99797
Thiofuran	15.3	2,968.2x	0.99824
Butyl mercaptan	10.1	1,523.8x	0.9914
2-Methylthiophene	91.6	1,389.3x	0.99066
3-Methylthiophene	40.7	1,354.5x	0.98761
2,5-Dimethylthiophene	61.1	486.92x	0.9144

Table C-4: Sulfur concentrations and corresponding peak areas in the new sulfur gas standard at 0X, 2X, 4X, 7X, and 20X dilution factors.

Dilution Factor	Hydrogen sulfide*		Carbonyl sulfide		Thiofuran		Butyl mercaptan		2-Methylthiophene		3-Methylthiophene		2,5-Dimethylthiophene	
	Conc.	PA	Conc.	PA	Conc.	PA	Conc.	PA	Conc.	PA	Conc.	PA	Conc.	PA
0X	151	N/A	5.09	41,937	15.3	45,289	10.1	15,924	91.6	124,287	40.7	53,977	61.1	27,355
2X	75.5	N/A	2.5	20,940	7.65	22,323	5.05	6948	45.8	65,487	20.35	28,483	30.6	18,378
4X	37.75	312,401	1.27	11,683	3.83	12,722	2.53	3,548	22.9	38,809	10.18	16,996	15.3	10,328
7X	22.01	154,196	0.74	5,303	2.23	6,457	1.47	1,822	13.4	19,179	5.93	6,494	8.9	3,800
20X	7.55	46,175	0.25	1,993	0.77	2,210	0.51	299	4.58	10,447	2.04	5,029	3.1	9,207

Note: Conc., Concentration (in ppmv); PA, Peak areas.

* Hydrogen sulfide only has a 3-point calibration curve as the peak areas at the 151 ppmv and 75.5 ppmv concentrations topped out on the chromatograph.

Table C-5: MFT mesocosms, Agilent standard peak areas at the analytical time points and during calibration with the new sulfur gas standard.

Time point (TP)	Agilent std at TP		Agilent std at new calibration		Diff b/t TP and new calibration		Modification Factor used
	Peak 1	Peak 2	Peak 1	Peak 2	Peak 1	Peak 2	
Week 0	N/A	N/A	102,068	145,804	N/A	N/A	None
Week 4	31,316	61,413			-69%	-58%	-58%
Week 6	136,606	189,722			34%	30%	34%
Week 14	210,347	295,089			106%	102%	102%

Table C-6: No-MFT controls, Agilent standard peak areas at the analytical time points and during calibration with the new sulfur gas standard.

Time point (TP)	Agilent std at TP		Agilent std at new calibration		Diff b/t TP and new calibration		Modification Factor used*
	Peak 1	**Peak 2**	**Peak 1**	**Peak 2**	**Peak 1**	**Peak 2**	
Week 0	235,219	318,690	102,068	145,804	130%	119%	130%
Week 4	128,606	182,672			26%	25%	26%
Week 6	173,226	241,988			70%	66%	70%
Week 14	108,169	157,998			6%	8%	8%

* The % differences between the Agilent standard values are slightly different for each compound. The value chosen as the modification factor was the one that would yield a more conservative estimate of the sulfur concentrations.

Hydrogen sulfide calibration curves (MFT mesocosms)

The hydrogen sulfide calibration curves for the MFT mesocosms are plotted in Figure C-4 (hydrogen sulfide was not detected in the no-MFT controls). Calibration equations and R^2 values for carbonyl sulfide, thiofuran, butyl mercaptan, 2-methylthiophene, 3-methylthiophene, and 2,5-dimethylthiophene for weeks 0, 4, 6, and 14 is provided in Table C-7 and Table C-8.

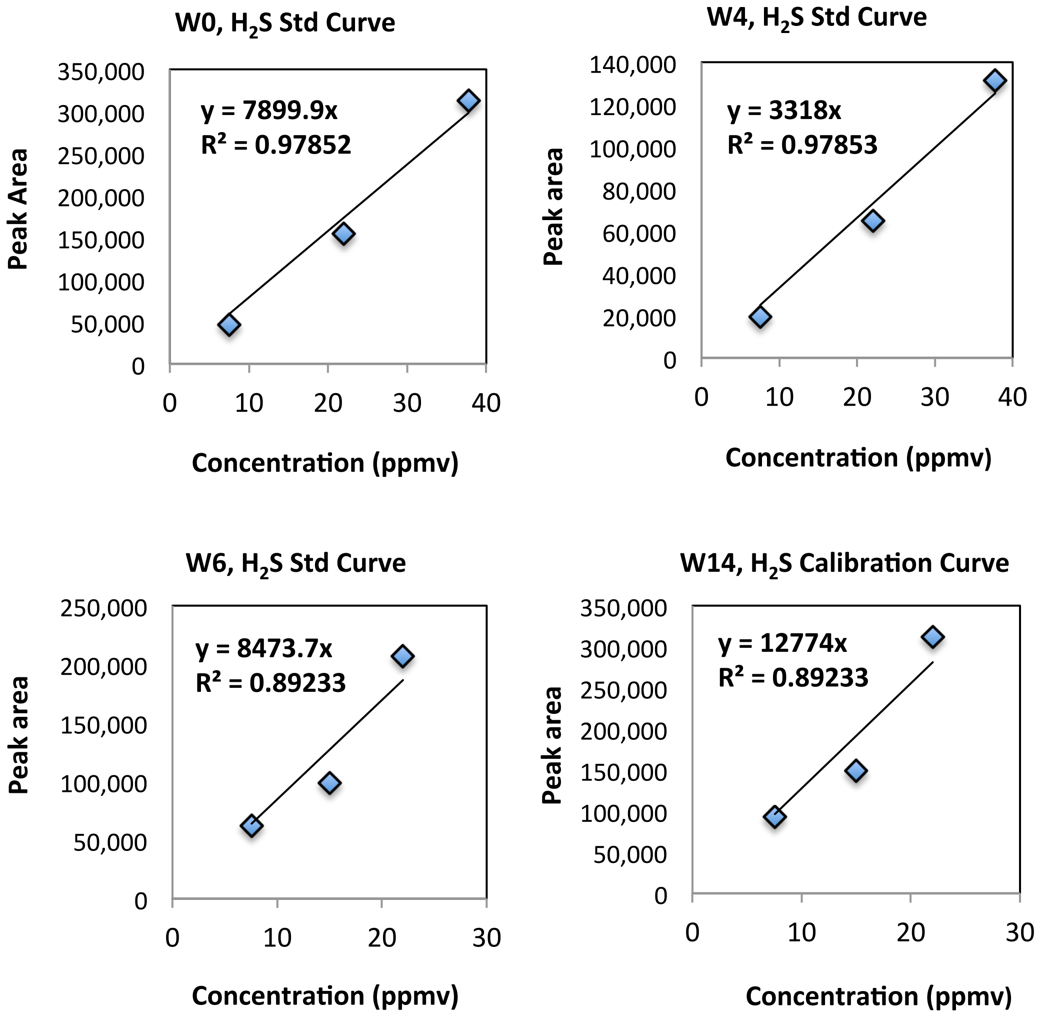


Figure C-4: Hydrogen sulfide calibration curves for the MFT mesocosms. Sampling times in this experiment were week 0, 4, 6, and 14.

Table C-7: MFT mesocosms sulfur calibration equations and R^2 values for weeks 0, 4, 6, and 14.

Compound	Conc. range (ppmv)	MFT mesocosms			
		Week 0	Week 4	Week 6	Week 14
Carbonyl sulfide	0 to 5.09	8,263x; $R^2 = 0.998$	3,470x; $R^2 = 0.998$	10,742x; $R^2 = 0.998$	16,691x; $R^2 = 0.998$
Thiofuran	0 to 15.3	2,968x; $R^2 = 0.998$	1,247x; $R^2 = 0.998$	3,859x; $R^2 = 0.998$	5,996x; $R^2 = 0.998$
Butyl mercaptan	0 to 10.1	1,524x; $R^2 = 0.991$	640x; $R^2 = 0.991$	1,981x; $R^2 = 0.991$	3,078x; $R^2 = 0.991$
2-Methylthiophene	0 to 91.6	1,389x; $R^2 = 0.991$	584x; $R^2 = 0.991$	1,806x; $R^2 = 0.991$	3,001x; $R^2 = 0.976$
3-Methylthiophene	0 to 40.7	1,355x; $R^2 = 0.988$	569x; $R^2 = 0.988$	1,761x; $R^2 = 0.988$	2,736x; $R^2 = 0.988$
2,5-Dimethylthiophene	0 to 61.1	487x; $R^2 = 0.914$	205x; $R^2 = 0.914$	633x; $R^2 = 0.914$	984x; $R^2 = 0.914$

Table C-8: No-MFT controls sulfur calibration equations and R^2 values for weeks 0, 4, 6, and 14.

Compound	Conc. range (ppmv)	No-MFT controls			
		Week 0	Week 4	Week 6	Week 14
Carbonyl sulfide	0 to 5.09	19,005x; $R^2 = 0.998$	10,411x; $R^2 = 0.998$	14,047x; $R^2 = 0.998$	8,924x; $R^2 = 0.998$
Thiofuran	0 to 15.3	6,827x; $R^2 = 0.998$	3,740x; $R^2 = 0.998$	5,046x; $R^2 = 0.998$	3,206x; $R^2 = 0.998$
Butyl mercaptan	0 to 10.1	3,505x; $R^2 = 0.991$	1,920x; $R^2 = 0.991$	2,590x; $R^2 = 0.991$	1,646x; $R^2 = 0.991$
2-Methylthiophene	0 to 91.6	3,417x; $R^2 = 0.976$	1,751x; $R^2 = 0.991$	2,362x; $R^2 = 0.991$	1,500x; $R^2 = 0.991$
3-Methylthiophene	0 to 40.7	3,115x; $R^2 = 0.988$	1,707x; $R^2 = 0.988$	2,303x; $R^2 = 0.988$	1,463x; $R^2 = 0.988$
2,5-Dimethylthiophene	0 to 61.1	1,120x; $R^2 = 0.914$	614x; $R^2 = 0.914$	828x; $R^2 = 0.914$	526x; $R^2 = 0.914$

REDOX CALIBRATION CHECK

ORP standard, E = 220 mV ± 3 mV

Table C-9: Redox ORP Standard before and after testing check for MFT mesocosms.

Week	Before test ORP (mV)	% Diff from E,std	After test ORP (mV)	% Diff wrt before
0	214.0	2.73	215.6	0.74
1	217.4	1.18	218.7	0.6
2	215.7	1.95	218.1	1.1
4	216.5	1.59	217.1	0.28
6	216.7	1.50	216.7	0.00
11	219.8	0.09	219.6	0.09

Table C-10: Redox ORP Standard before and after testing check for no-MFT controls.

Week	Before test ORP (mV)	% Diff from E,std	After test ORP (mV)	% Diff wrt before
0	219.9	0.05	220.6	0.32
1	220.5	-0.23	221.6	0.5
2	219.5	0.23	219.8	0.1
4	217.5	1.14	220.2	1.23
6	216.7	1.50	219.5	1.28
11	216.4	1.64	218.0	0.73

DOC CALIBRATION CURVES - MFT mesocosms

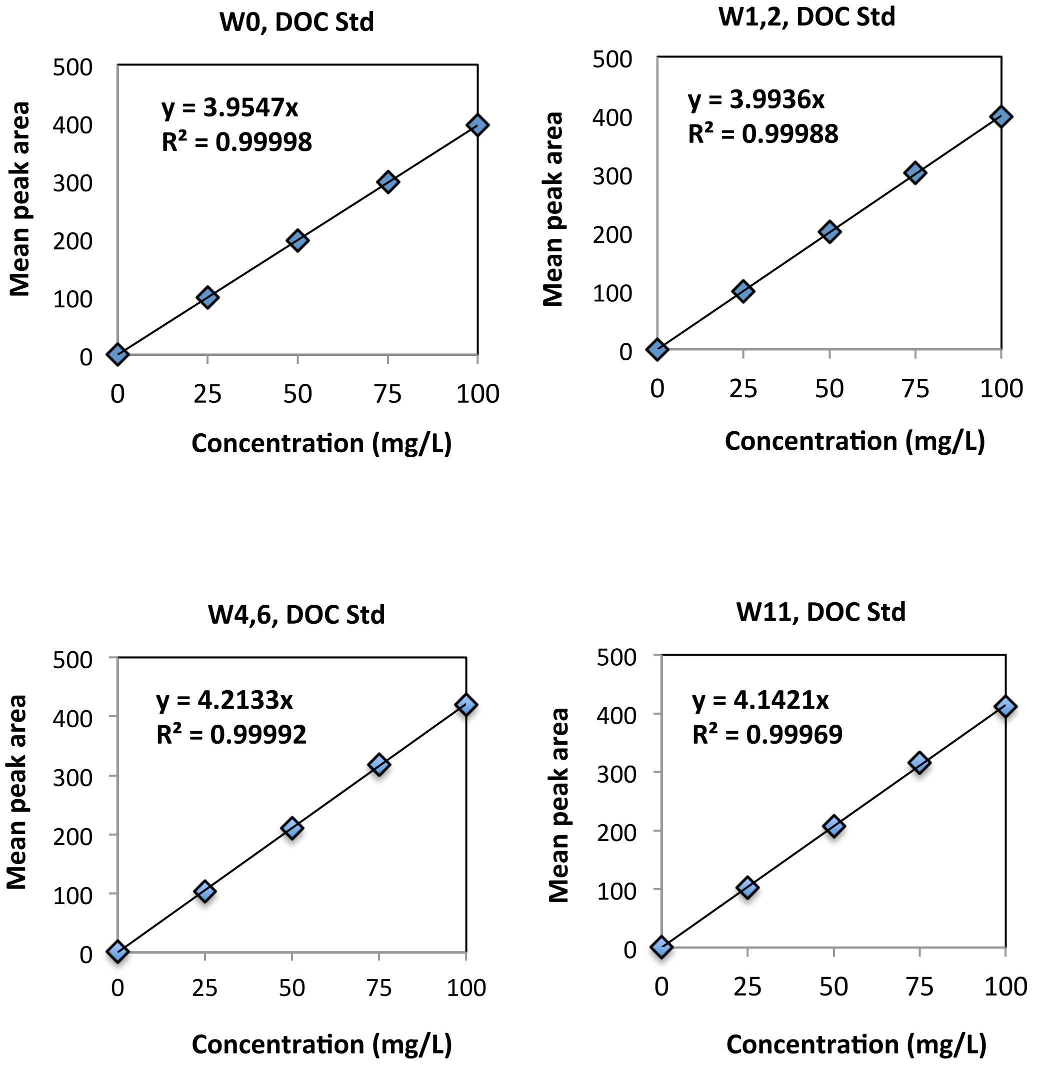


Figure C-5: Dissolved organic carbon calibration curves for the MFT mesocosms. Some curves were used for multiple time points as these samples were all run at the same time.

DOC CALIBRATION CURVES – No-MFT controls

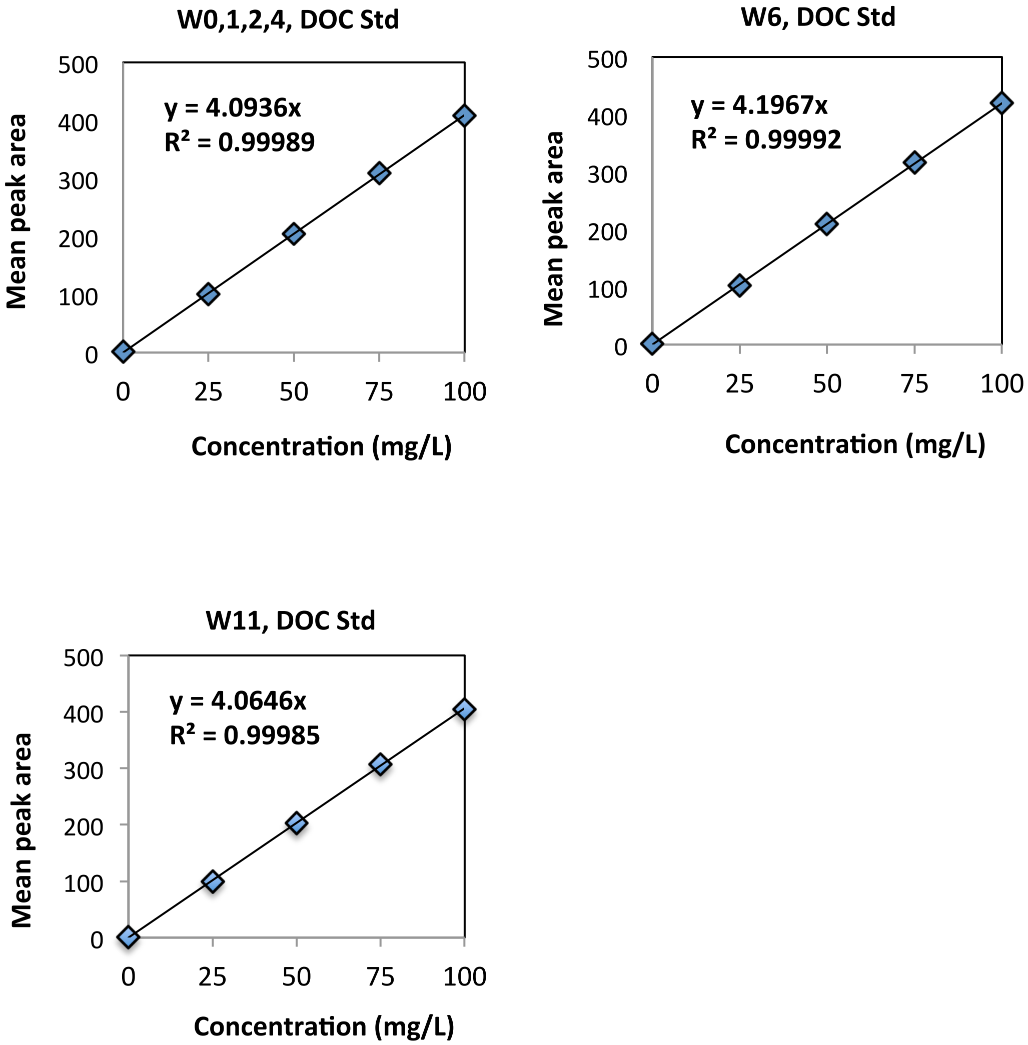


Figure C-6: Dissolved organic carbon calibration curves for the no-MFT controls. Some curves were used for multiple time points as these samples were all run at the same time.

APPENDIX D: RAW DATA

CHEMICAL DATA

Table D-1: Redox E_H values (mV) in the Pond 2/3 mesocosms and the no-MFT controls over the 11-week study.

Week	Pond 2/3 MFT Mesocosms				No-MFT Controls			
	PW1	PW2	PW-0.8%1	PW-0.8%2	PW-0.8%1	PW-0.8%2	SPW-0.8%1	SPW-0.8%2
0	360	377	291	237	268	239	199	189
1	-97	N/A	N/A	-114	275	246	232	215
2	N/A	1	-10	N/A	317	303	344	334
4	-31	N/A	-29	N/A	328	332	346	345
6	7	-14	-1	-23	394	396	398	397
11	-125	-126	-92	-84	294	304	315	303

Table D-2: Redox E_H values (mV) in the MFT-SPW mesocosms over the 11-week study.

Week	SPW1	SPW2	SPW-0.2% 1	SPW-0.2% 2	SPW-0.8%1	SPW-0.8%2	SPW-1.5%1	SPW-1.5% 2
0	206	175	159	154	104	119	126	140
1	N/A	-112	-145	N/A	N/A	-150	N/A	-142
2	5	N/A	N/A	-105	-97	N/A	-96	N/A
4	N/A	-61	-101	N/A	-101	N/A	-105	N/A
6	-50	-89	-112	-118	-115	-120	-111	-108
11	-136	-141	-136	-138	-125	-123	-118	-117

*All redox measurements were conducted on the pore water samples. ORP values are converted to E_H values based on temperature. The anaerobic chamber temperature was **24ºC**. Based on the ORP standard's manufacturer's label, a value of 420 was added to convert the ORP values to E_H.

Table D-3: pH measurements in the Pond 2/3 mesocosms and the no-MFT controls over the 11-week study.

Week	Pond 2/3 MFT Mesocosms				No-MFT Controls			
	PW1	PW2	PW-0.8%1	PW-0.8%2	PW-0.8%1	PW-0.8%2	SPW-0.8%1	SPW-0.8%2
0	7.84	7.83	7.88	7.87	7.53	7.65	7.81	7.84
1	7.59	N/A	N/A	7.62	7.86	7.88	7.91	7.84
2	N/A	7.67	7.72	N/A	7.69	7.77	7.80	7.63
4	7.88	N/A	7.79	N/A	7.77	7.84	7.83	7.70
6	7.82	7.72	7.78	7.82	7.72	7.70	7.82	7.55
11	7.66	7.63	7.93	7.71	7.87	7.82	7.81	7.83

Table D-4: pH measurements in the MFT-SPW mesocosms over the 11-week study.

Week	SPW1	SPW2	SPW-0.2% 1	SPW-0.2% 2	SPW-0.8%1	SPW-0.8%2	SPW-1.5%1	SPW-1.5% 2
0	7.92	7.89	7.83	7.89	7.88	7.88	7.89	7.94
1	N/A	7.65	7.77	N/A	N/A	7.76	N/A	7.75
2	7.63	N/A	N/A	7.81	7.71	N/A	7.71	N/A
4	N/A	7.84	7.92	N/A	7.76	N/A	7.94	N/A
6	7.82	7.81	7.89	7.91	7.82	7.92	7.88	8.01
11	7.83	7.88	7.97	7.77	7.73	7.77	7.89	7.85

Table D-5: Conductivity measurements (mS/cm) in the Pond 2/3 mesocosms and the no-MFT controls over the 11-week study.

Week	Pond 2/3 MFT Mesocosms				No-MFT Controls			
	PW1	PW2	PW-0.8%1	PW-0.8%2	PW-0.8%1	PW-0.8%2	SPW-0.8%1	SPW-0.8%2
0	3.30	3.28	3.22	3.25	3.37	3.29	3.36	3.37
1	3.20	N/A	N/A	3.18	3.28	3.28	3.26	3.25
2	N/A	3.19	3.13	N/A	3.29	3.29	3.28	3.26
4	3.11	N/A	2.93	N/A	3.45	3.36	3.48	3.42
6	3.21	3.16	3.16	3.15	3.30	3.25	3.31	3.32
11	3.11	3.20	3.23	3.22	3.41	3.39	3.37	3.37

Table D-6: Conductivity measurements (mS/cm) in the MFT-SPW mesocosms over the 11-week study.

Week	SPW1	SPW2	SPW-0.2% 1	SPW-0.2% 2	SPW-0.8%1	SPW-0.8%2	SPW-1.5%1	SPW-1.5% 2
0	3.33	3.39	3.25	3.37	3.38	3.35	3.33	3.27
1	N/A	3.21	3.24	N/A	N/A	3.29	N/A	3.16
2	3.23	N/A	N/A	3.33	3.30	N/A	3.14	N/A
4	N/A	2.99	3.14	N/A	3.08	N/A	2.78	N/A
6	3.19	3.27	3.39	3.78	3.32	3.27	3.12	3.15
11	3.28	3.56	3.47	3.54	3.34	3.34	3.21	3.14

Table D-7: Alkalinity measurements (mg $CaCO_3$/L) for all mesocosms over the 11-week study.

Sample	**Alkalinity (mg $CaCO_3$/L)**					
	Week 0	Week 1	Week 2	Week 4	Week 6	Week 11
MFT-PW 1	773	979	N/A	994	960	1055
MFT-PW 2	784	N/A	932	N/A	976	1066
MFT-PW-0.8% 1	863	N/A	1034	1077	1064	1182
MFT-PW-0.8% 2	780	486	N/A	N/A	1075	1192
MFT-SPW 1	891	N/A	1016	N/A	1088	1295
MFT-SPW 2	899	742	N/A	1099	1118	1254
MFT-SPW-0.2% 1	969	1259	N/A	1258	1247	1256
MFT-SPW-0.2% 2	923	N/A	1246	N/A	1242	1269
MFT-SPW-0.8% 1	922	N/A	1243	1266	1263	1323
MFT-SPW-0.8% 2	914	743	N/A	N/A	1266	1324
MFT-SPW-1.5% 1	946	N/A	1237	1256	1255	1321
MFT-SPW-1.5% 2	933	968	N/A	N/A	1267	1335
PW-0.8% 1	715	692	682	693	693	733
PW-0.8% 2	707	688	678	704	694	733
SPW-0.8% 1	866	853	837	849	839	874
SPW-0.8% 2	866	854	815	846	842	874

Note 1: Boiled ultrapure water was used as blanks and to the dilute samples for all alkalinity measurements. Diluted samples were (1 mL sample + 34 mL boiled ultrapure water). The titrant used was 0.02 N H_2SO_4.

Note 2: Checked dilution by running a diluted OSPW sample (1 mL sample + 34 mL boiled ultrapure water) against an undiluted OSPW sample (34 mL). After correcting for the blank, there was a less than 2% difference between the two samples.

Table D-8: Dissolved organic carbon measurements (mg/L) for all mesocosms over the 11-week study.

Sample	DOC (mg/L)					
	Week 0	Week 1	Week 2	Week 4	Week 6	Week 11
MFT-PW 1	92.4	84.7	N/A	279.9	63.3	288.37
MFT-PW 2	92.0	N/A	239.4	N/A	61.5	276.78
MFT-PW-0.8% 1	90.6	N/A	170.3	301.7	76.1	53.37
MFT-PW-0.8% 2	103.3	80.4	N/A	N/A	78.2	51.27
MFT-SPW 1	30.6	N/A	52.2	N/A	49.0	28.3
MFT-SPW 2	36.0	35.1	N/A	270.1	50.6	922.2
MFT-SPW-0.2% 1	48.3	56.6	N/A	48.3	61.2	28.48
MFT-SPW-0.2% 2	44.8	N/A	109.0	N/A	54.6	28.42
MFT-SPW-0.8% 1	55.7	N/A	82.4	46.2	69.3	1162.4
MFT-SPW-0.8% 2	60.3	49.7	N/A	N/A	72.4	34.5
MFT-SPW-1.5% 1	86.0	N/A	72.0	61.3	80.3	44.3
MFT-SPW-1.5% 2	103.2	56.5	N/A	N/A	77.8	1244.5
PW-0.8% 1	196.2	66.8	61.9	62.8	70.4	73.7
PW-0.8% 2	59.2	62.3	61.7	65.0	77.6	84.4
SPW-0.8% 1	43.0	53.0	49.9	56.1	62.2	84.1
SPW-0.8% 2	41.7	48.5	52.0	53.6	58.5	67.4

*Ultrapure water was used as the blanks and for diluting the samples. 2-5 mL of sample was diluted with ultrapure water to a total volume of 25 mL to fit a 0–100 mg/L calibration curve. Concentrations were then back calculated to determine the original DOC concentration of the sample.

Table D-9: Nitrate concentrations (mg/L) in the Pond 2/3 mesocosms and the no-MFT controls over the 11-week study.

Week	Pond 2/3 MFT Mesocosms				No-MFT Controls			
	PW1	PW2	PW-0.8%1	PW-0.8%2	PW-0.8%1	PW-0.8%2	SPW-0.8%1	SPW-0.8%2
0	0.21	0.28	0.14	0.26	14.72	14.60	0.24	0.29
1	0.21	N/A	N/A	0.13	N/A	N/A	N/A	N/A
2	N/A	0.11	0.11	N/A	N/A	N/A	N/A	N/A
4	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
6	N/A	N/A	N/A	N/A	5.33	N/A	0.26	N/A
11	0.26	N/A	0.19	N/A	N/A	0.42	N/A	0.18

Table D-10: Nitrate concentrations (mg/L) in the MFT-SPW mesocosms over the 11-week study.

Week	SPW1	SPW2	SPW-0.2% 1	SPW-0.2% 2	SPW-0.8%1	SPW-0.8%2	SPW-1.5%1	SPW-1.5% 2
0	0.18	0.20	0.14	0.14	0.17	0.19	0.15	0.19
1	N/A	0.19	0.16	N/A	N/A	0.25	N/A	0.24
2	0.17	N/A	N/A	0.12	0.09	N/A	0.26	N/A
4	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
6	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
11	N/A	0.26	N/A	0.26	0.26	N/A	0.17	N/A

*The initial nitrate concentrations were low (except in the Pond 2/3 no MFT controls) so nitrate analysis was done only periodically to verify that they remained low during the study. Nitrate samples were analyzed at the Department of Biological Sciences at the University of Alberta.

Table D-11: Sulfate concentrations (mg/L) in the Pond 2/3 mesocosms and the no-MFT controls over the 11-week study.

Week	Pond 2/3 MFT Mesocosms				No-MFT Controls			
	PW1	PW2	PW-0.8%1	PW-0.8%2	PW-0.8%1	PW-0.8%2	SPW-0.8%1	SPW-0.8%2
0	227.3	220.5	190.0	222.4	230.5	228.4	393.1	397.2
1	132.1	N/A	N/A	171.18	224.7	229.8	391.33	392.4
2	N/A	127.5	4.2	N/A	227.3	229.4	393.4	390.6
4	87.2	N/A	9.6	N/A	231.2	236.7	401.9	406.5
6	87.9	88.1	5.5	4.7	235.0	238.2	411.2	414.2
11	5.6921	6.0582	3.0497	3.4495	228.2	228	398.8	N/A

Table D-12: Sulfate concentrations (mg/L) in the MFT-SPW mesocosms over the 11-week study.

Week	SPW1	SPW2	SPW-0.2% 1	SPW-0.2% 2	SPW-0.8%1	SPW-0.8%2	SPW-1.5%1	SPW-1.5% 2
0	377.6	374.5	332.4	375.4	368.4	372.1	350.0	354.3
1	N/A	266.36	69.17	N/A	N/A	6.74	N/A	4.93
2	244.4	N/A	N/A	4.9	7.0	N/A	4.6	N/A
4	N/A	169.1	5.58	N/A	4.6	N/A	3.7	N/A
6	169.3	134.2	5.8	6.8	4.8	4.5	4.0	4.3
11	7.1066	6.8105	6.3288	6.1648	4.0302	3.5141	3.3227	4.1255

*Sulfate samples were diluted with ultrapure water if necessary to fit a 0–100 mg/L calibration curve, then back calculated to the original concentration.

METHANE DATA

Table D-13: Methane emissions (µmol) from the Pond 2/3 mesocosms and the no-MFT controls over the 11-week study.

Week	Pond 2/3 MFT Mesocosms				No-MFT Controls			
	PW1	PW2	PW-0.8%1	PW-0.8%2	PW-0.8%1	PW-0.8%2	SPW-0.8%1	SPW-0.8%2
0	150	150	162	137	0.0	0.0	0.0	0.0
1	0	0	368	128	0.0	0.0	0.0	0.0
2	0	0	0	792	0.0	0.0	0.0	0.0
4	0	443	0	1,883	0.0	0.0	0.0	0.0
6	100	580	2,993	4,863	0.0	0.0	0.0	0.0
11	860	1,085	10,380	11,359	0.0	0.0	0.0	0.0

Table D-14: Methane emissions (µmol) from the MFT-SPW mesocosms over the 11-week study.

Week	SPW1	SPW2	SPW-0.2% 1	SPW-0.2% 2	SPW-0.8%1	SPW-0.8%2	SPW-1.5%1	SPW-1.5% 2
0	159	0	93	149	183	193	193	204
1	0	57	106	0	496	313	563	759
2	77	131	220	0	0	886	124	1,048
4	0	0	152	154	2,009	3,322	0	2,057
6	65	0	152	575	5,336	7,941	4,417	3,527
11	557	353	604	1,233	14,540	13,352	18,092	16,492

*Methane was converted from a peak area to a %volume. Then the %volume was converted (using bottle pressure and headspace volume, gas constant R, Temperature, and MW of CH_4) to mg CH_4 and then to µmol using the MW.

CARBON DIOXIDE DATA

Table D-15: Carbon dioxide emissions (μmol) Pond 2/3 mesocosms and the no-MFT controls over the 11-week study.

Week	Pond 2/3 MFT Mesocosms				No-MFT Controls			
	PW1	PW2	PW-0.8%1	PW-0.8%2	PW-0.8%1	PW-0.8%2	SPW-0.8%1	SPW-0.8%2
0	154	175	131	125	154	175	131	125
1	438	459	397	302	438	459	397	302
2	649	419	420	495	649	419	420	495
4	336	433	345	520	336	433	345	520
6	866	912	1,037	1,193	866	912	1,037	1,193
11	1,091	1,043	1,568	1,815	1,091	1,043	1,568	1,815

Table D-16: Carbon dioxide emissions (μmol) from the MFT-SPW mesocosms over the 11-week study.

Week	SPW1	SPW2	SPW-0.2% 1	SPW-0.2% 2	SPW-0.8%1	SPW-0.8%2	SPW-1.5%1	SPW-1.5% 2
0	185	218	335	163	159	173	180	164
1	128	501	468	437	377	320	510	519
2	369	392	560	378	315	485	369	552
4	195	212	550	437	618	754	434	440
6	483	212	550	961	1,227	1,854	1,308	1,046
11	767	738	1,191	1,014	2,561	2,331	2,890	2,705

*See methane note; same conversion but with MW of CO_2.

SULFUR EMISSIONS DATA

Table D-17: Hydrogen sulfide measurements for all mesocosms in weeks 0, 4, 6, and 14, of the 14-week study.

Sample ID	Week 0 (µmol)	Week 4 (µmol)	Week 6 (µmol)	Week 14 (µmol)
MFT-PW 1	0.015	N/A	0.63	N/A
MFT-PW 2	0.034	1.45	N/A	5.94
MFT-PW-0.8% 1	0.025	N/A	2.26	N/A
MFT-PW-0.8% 2	0.039	3.27	N/A	3.95
MFT-SPW 1	0.003	1.45	N/A	3.67
MFT-SPW 2	0.019	N/A	5.36	N/A
MFT-SPW-0.2% 1	0.127	N/A	7.85	N/A
MFT-SPW-0.2% 2	0.255	1.45	N/A	15.12
MFT-SPW-0.8% 1	0.163	N/A	10.37	N/A
MFT-SPW-0.8% 2	0.136	6.03	N/A	21.27
MFT-SPW-1.5% 1	0.392	N/A	10.68	N/A
MFT-SPW-1.5% 2	N/A	9.44	N/A	7.35
PW-0.8% 1	0.0	0.0	0.0	0.0
PW-0.8% 2	0.0	0.0	0.0	0.0
SPW-0.8% 1	0.0	0.0	0.0	0.0
SPW-0.8% 2	0.0	0.0	0.0	0.0

*After week 0, the H_2S peak areas in the MFT mesocosms all topped out for the remaining weeks. Diluted samples were run to estimate these concentrations (see chapter 3 for dilution methods).

Table D-18: Carbonyl sulfide measurements for all mesocosms in weeks 0, 4, 6, and 14, of the 14-week study.

Sample ID	Week 0 (µmol)	Week 4 (µmol)	Week 6 (µmol)	Week 14 (µmol)
MFT-PW 1	9.91E-04	0.0	0.0	0.0
MFT-PW 2	6.78E-04	0.0	0.0	0.0
MFT-PW-0.8% 1	1.75E-03	0.0	0.0	0.0
MFT-PW-0.8% 2	9.40E-04	0.0	0.0	0.0
MFT-SPW 1	5.04E-04	0.0	5.29E-03	0.0
MFT-SPW 2	0.0	0.0	7.52E-03	3.66E-03
MFT-SPW-0.2% 1	1.96E-03	0.0	0.0	0.0
MFT-SPW-0.2% 2	1.70E-03	0.0	1.03E-02	0.0
MFT-SPW-0.8% 1	1.11E-03	0.0	0.0	0.0
MFT-SPW-0.8% 2	1.20E-03	0.0	0.0	0.0
MFT-SPW-1.5% 1	1.52E-03	0.0	0.0	0.0
MFT-SPW-1.5% 2	0.0	0.0	0.0	0.0
PW-0.8% 1	3.00E-03	0.0	7.00E-04	5.00E-04
PW-0.8% 2	2.00E-03	0.0	8.00E-04	0.0
SPW-0.8% 1	2.00E-03	0.0	0.0	6.00E-04
SPW-0.8% 2	1.00E-03	0.0	5.00E-04	4.00E-04

Table D-19: Thiofuran concentrations measurements for all mesocosms in weeks 0, 4, 6, and 14, of the 14-week study.

Sample ID	Week 0 (µmol)	Week 4 (µmol)	Week 6 (µmol)	Week 14 (µmol)
MFT-PW 1	0.007	0.006	0.01	0.05
MFT-PW 2	0.005	0.005	0.007	0.03
MFT-PW-0.8% 1	0.06	0.20	0.20	N/A
MFT-PW-0.8% 2	0.05	N/A	0.14	0.40*
MFT-SPW 1	0.007	0.003	0.007	0.02
MFT-SPW 2	0.005	0.007	0.01	0.02
MFT-SPW-0.2% 1	0.01	0.02	0.03	0.08
MFT-SPW-0.2% 2	0.01	0.02	0.02	0.04
MFT-SPW-0.8% 1	0.09	N/A	0.14	0.27
MFT-SPW-0.8% 2	0.06	0.25*	0.13	0.31*
MFT-SPW-1.5% 1	0.14	N/A	0.27	0.39*
MFT-SPW-1.5% 2	0.06	0.24*	0.15	0.36*
PW-0.8% 1	0.67*	N/A	0.49*	N/A
PW-0.8% 2	N/A	0.39*	N/A	0.40*
SPW-0.8% 1	0.31*	0.23	0.41*	0.28*
SPW-0.8% 2	N/A	0.53*	N/A	0.18

* Concentrations were estimated from diluted values.

Table D-20: Butyl mercaptan measurements for all mesocosms in weeks 0, 4, 6, and 14, of the 14-week study.

Sample ID	Week 0 (µmol)	Week 4 (µmol)	Week 6 (µmol)	Week 14 (µmol)
MFT-PW 1	0.0	0.0	0.0	0.003
MFT-PW 2	0.0	0.0	0.0	0.003
MFT-PW-0.8% 1	0.01	0.02	0.04	0.01
MFT-PW-0.8% 2	0.009	0.04	0.03	0.02
MFT-SPW 1	0.0	0.0	0.0	0.002
MFT-SPW 2	0.0	0.0	0.0	0.002
MFT-SPW-0.2% 1	0.002	0.003	0.003	0.01
MFT-SPW-0.2% 2	0.002	0.0	0.002	0.006
MFT-SPW-0.8% 1	0.02	0.05	0.03	0.02
MFT-SPW-0.8% 2	0.01	0.04	0.03	0.02
MFT-SPW-1.5% 1	0.04	0.09	0.07	0.03
MFT-SPW-1.5% 2	0.03	0.08	0.05	0.02
PW-0.8% 1	N/A	0.11	0.06	0.06
PW-0.8% 2	0.14	0.05	0.08	0.03
SPW-0.8% 1	0.06	0.02	0.03	0.02
SPW-0.8% 2	0.06	0.04	0.03	0.02

Table D-21: 2-Methylthiophene measurements for all mesocosms in weeks 0, 4, 6, and 14, of the 14-week study.

Sample ID	Week 0 (µmol)	Week 4 (µmol)	Week 6 (µmol)	Week 14 (µmol)
MFT-PW 1	0.18	0.31	0.41	N/A
MFT-PW 2	0.13	0.25	0.25	0.70
MFT-PW-0.8% 1	N/A	N/A	3.6*	N/A
MFT-PW-0.8% 2	1.5*	5.9*	N/A	10.1*
MFT-SPW 1	0.17	0.15	0.22	0.35
MFT-SPW 2	0.15	0.48	0.36	0.35
MFT-SPW-0.2% 1	0.57	1.3	0.97	N/A
MFT-SPW-0.2% 2	0.42	1.4	0.62	0.79*
MFT-SPW-0.8% 1	2.2*	N/A	8.7*	N/A
MFT-SPW-0.8% 2	N/A	6.1*	N/A	7.3*
MFT-SPW-1.5% 1	N/A	N/A	16*	N/A
MFT-SPW-1.5% 2	2*	6.1*	N/A	8*
PW-0.8% 1	14.8*	N/A	19.9*	N/A
PW-0.8% 2	N/A	10.9*	N/A	11*
SPW-0.8% 1	7.2*	10.3*	16.1*	12.2*
SPW-0.8% 2	N/A	N/A	N/A	N/A

* Concentrations were estimated from diluted values.

Table D-22: 3-Methylthiophene measurements for all mesocosms in weeks 0, 4, 6, and 14, of the 14-week study.

Sample ID	Week 0 (µmol)	Week 4 (µmol)	Week 6 (µmol)	Week 14 (µmol)
MFT-PW 1	0.04	0.11	0.11	0.32
MFT-PW 2	0.03	0.10	0.07	0.19
MFT-PW-0.8% 1	0.45	N/A	1.14*	N/A
MFT-PW-0.8% 2	0.38	1.41*	N/A	3.37*
MFT-SPW 1	0.04	0.05	0.06	0.09
MFT-SPW 2	0.04	0.16	0.10	0.09
MFT-SPW-0.2% 1	0.15	0.44	0.27	0.80
MFT-SPW-0.2% 2	0.11	0.49	0.17	0.27
MFT-SPW-0.8% 1	N/A	N/A	0.74*	N/A
MFT-SPW-0.8% 2	0.52	2.55*	N/A	2.39*
MFT-SPW-1.5% 1	N/A	N/A	1.13*	N/A
MFT-SPW-1.5% 2	0.63*	2.85*	N/A	2.66*
PW-0.8% 1	9.22*	N/A	6.38*	N/A
PW-0.8% 2	N/A	3.22*	N/A	3.21*
SPW-0.8% 1	4.16*	3.13*	4.76*	3.65*
SPW-0.8% 2	N/A	N/A	N/A	N/A

* Concentrations were estimated from diluted values.

Table D-23: 2,5-Dimethylthiophene measurements for all mesocosms in weeks 0, 4, 6, and 14, of the 14-week study.

Sample ID	Week 0 (µmol)	Week 4 (µmol)	Week 6 (µmol)	Week 14 (µmol)
MFT-PW 1	0.29	0.58	0.71	N/A
MFT-PW 2	0.21	0.49	0.49	1.1*
MFT-PW-0.8% 1	N/A	N/A	2.5*	N/A
MFT-PW-0.8% 2	0.88*	4.1*	N/A	8.2*
MFT-SPW 1	0.27	0.29	0.39	0.41
MFT-SPW 2	0.25	0.94*	0.60	0.46
MFT-SPW-0.2% 1	0.62	N/A	1.0	N/A
MFT-SPW-0.2% 2	0.42	0.95*	0.62	0.67
MFT-SPW-0.8% 1	1.4*	N/A	1.1*	N/A
MFT-SPW-0.8% 2	N/A	5.3*	N/A	5.0*
MFT-SPW-1.5% 1	N/A	N/A	2.4*	N/A
MFT-SPW-1.5% 2	1.8*	5.0*	N/A	5.9*
PW-0.8% 1	8.7*	N/A	4.8*	N/A
PW-0.8% 2	N/A	5.8*	N/A	6.7*
SPW-0.8% 1	8.6*	6.8*	8.4*	8.7*
SPW-0.8% 2	N/A	N/A	N/A	N/A

* Concentrations were estimated from diluted values.