



Methane Oxidation in Tailings Ponds and Impact on Fugitive Greenhouse Gas (GHG) Emissions

Background

Compared to the majority of tailings generated during hot water extraction of bitumen from mined oil sands, froth treatment tailings (FTT) are a relatively small waste stream that contain several components that can lead to specific biogeochemical concerns that may affect the operations, tailings management, and final closure and reclamation of the oil sands site. These include elevated levels of sulfide minerals that under some circumstances may lead to acid rock drainage (ARD), naturally occurring radioactive materials (NORMs) [1], and hydrocarbons that can result in gas generation due to biological activity ([2], [3], [4], [5]). These materials must be managed appropriately throughout the life of the mine to ensure closure objectives for the site are met.

Froth treatment tailings are similar to other tailings slurries in that they contain various mineral solids and small amounts of unrecovered bitumen. However, they also contain residual quantities of light hydrocarbons such as naphtha or paraffinic diluents that are used in froth treatment. After deposition of FTT in a tailings pond, the residual hydrocarbons can be degraded through many complex biological processes including aerobic, iron reducing, and sulphate reducing processes, as well as through methanogenesis ([3], [4], [6], [7], [8]). These processes can result in the generation of gases such as carbon dioxide, hydrogen sulphide and methane ([2], [8], [9]) which may be present in dissolved or ex-solved form. Transport of gases may affect tailings dewatering and consolidation. Ebullition of gas bubbles to the surfaces of deposits contributes to the GHG emissions of an oil sands site.

Microbial degradation of light hydrocarbons in FTT-affected tailings has been investigated in several laboratory studies using both model and field samples ([7], [10], [11], [12], [13], [14]). Work completed by COSIA [15] established a regional picture of some pertinent degradation pathways and the involved microbial communities. Other work addressed the circumstances that result in gas bubble evolution and release ([2], [3], [15], [16], [17]). The sources of GHGs, reduced sulphur compounds (RSCs) and volatile organic compounds (VOCs) were related to the chemistry of FTT and the various microbial processes involved in the degradation of light hydrocarbons in a recent review by Van Dongen et. al. [5].

Predicting gas generation from FTT-affected deposits has received more attention in the last few years as gases produced from biological activity may result in surface emissions of GHGs, which have been reported in several studies ([2], [6], [18], [19], [20]). Modelling and predicting GHG emissions from tailings ponds is challenging for numerous reasons; including the fact that tailings are heterogeneous and may occur as mixed deposits of FTT and other extraction tailings ([5], [21]). The biological processes involved are complex and may occur concurrently. A significant lag can also exist between the establishment of relevant microbial communities and observed gas generation [3]. Phenomena related to the transport and release of gas at surface must be understood in addition to gas generation mechanisms.

Models depicting gas generation from tailings have been developed in recent years; notably, a kinetic model was established by Siddique [12], with improvements proposed a decade later [21], while an equilibrium model relating emission intensity to diluent loss and the properties of diluent was proposed by Burkes [4]. In the latter, methane and carbon dioxide emissions were estimated based on the properties and amount of fermentable substrate originating from residual diluent, as well as assumptions about losses to VOC, consumption of carbon during aerobic degradation, sulphate reduction, and methanogenesis. The fugitive GHG intensity from FTT-affected tailings ponds was estimated to be less than 1 g CO₂eq/MJ bitumen produced for a typical oil sands operation.

Much study has been devoted to understanding methane generation in tailings ponds and potential future emissions profiles. It is important to note that interception and conversion of methane, produced during anaerobic degradation, to carbon dioxide in oxic, shallower environments prior to efflux may result in a reduction in GHG emission intensity due to the lower global warming potential of carbon dioxide compared to methane ([22], [23]). Methane oxidation has been observed in many natural sites such as lakes, ponds and swamps ([24], [25], [26]); see also other references within Le Mer and Roger [27]. This phenomenon has also been noted at agricultural sites such as rice fields [28]; see other references within Le Mer and Roger [27] and industrial sites with oil-impacted soils ([29], [30]) and those references within. In the oil sands context, methane oxidation in diluent degradation phenomena has been noted [6], specifically Saidi-Mehrabad et al. investigated methanotrophic communities that were detected in surface waters of a tailings pond [31]. They measured methanotrophic potential of surface waters and identified several environmental factors influencing the presence of methanotrophic species, such as alkalinity, salinity, ammonia and oxygen content, and temperature.

Statement of Research Opportunity

While methane oxidation has been researched in other contexts and to some degree in the oil sands application, the relative importance of methane oxidation as a mechanism that may influence GHG emissions from a tailings pond is not well understood. It is of interest to comprehend the significance of methane oxidation on the GHG emission profile of a tailings pond, by better understanding the biogeochemical conditions that lead to methane oxidation and the potential impact of concurrent biological processes occurring in anoxic and oxic zones of tailings deposits.

Desired Results

An understanding of the relationship between methane oxidation and other gas generating phenomena that occur in deep and shallower zones of tailings ponds is sought, including ideally a quantitative assessment as to the proportion of anaerobically generated methane that may be intercepted and oxidized before it reaches the surface as a GHG emission.

A better understanding of the circumstances favoring methane oxidation, relative to other metabolic pathways, is also sought, including knowledge of the conditions within a tailings pond that lead to methane interception and subsequent oxidation. For example, understanding how temperature, geochemistry, presence of certain biological communities, relative thickness and/or location of FTT affected tailings within a pond, as well as properties of overlying surface waters, affect the likelihood that anaerobically generated methane will be oxidized before being emitted as a surface GHG may be relevant.

Another goal could be to understand the relative importance of methane oxidation in FTT-affected fluid fine tailings deposits, typically overlaid by surface water, when compared to FTT-affected beach above water deposits that may be only partially saturated.

Works Cited

- [1] Lindsay, M.B.J., Vessey, C.J., and Robertson, J.M. 2019. Mineralogy and Geochemistry of oil sands froth treatment tailings: implications for acid generation and metal(loid) release. *Applied Geochemistry* (Vol. 102, pp. 186-196). doi:10.1016/j.apgeochem.2019.02.001.
- [2] Small, C.C., Cho, S., Hashisho, Z., and Ulrich, A.C. 2015. Emissions from oil sands tailings ponds: Review of tailings ponds parameters and emission estimates, *Journal of Petroleum Science and Engineering*, (Vol.127, pp. 490-501). doi:10.1016/j.petrol.2014.11.020.
- [3] Burkus, Z., Wheler, J., and Pletcher, S. 2014. GHG Emission from Oil Sands Tailings Ponds: Overview and Modelling Based on Fermentable Substrates Part I: Review of the Tailings Ponds Facts and Practices. Alberta Environment and Sustainable Resource Development. doi: <https://doi.org/10.7939/R3F188>.
- [4] Burkus, Z. 2014. GHG Emissions from Oil Sands Tailings Ponds: Overview and Modelling Based on Fermentable Substrates. Part II: Modeling of GHG Emissions from Tailings Ponds Based on Fermentable Substrates. Alberta Environment and Sustainable Resource Development. doi:<https://doi.org/10.7939/R3F188>.
- [5] Van Dongen, A., Samad, A., Heshka, N.E., Rathie, K., Martineau, C., Bruant, G., and Degenhardt, D. 2021. A Deep Look into the Microbiology and Chemistry of Froth Treatment Tailings: A Review. *Microorganisms: Basel*. (Vol. 9(5), pp. 1091). doi:10.3390/microorganisms9051091.
- [6] Holowenko, F.M., MacKinnon, M.D., and Fedorak, P.M. 2000. Methanogens and sulfate-reducing bacteria in oil sands fine tailings waste. *Can. J. Microbiol.* (Vol. 46(10), pp. 927-937). doi:10.1139/cjm-46-10-927.
- [7] Gee, K.F., Poon, H.Y., Hashisho, Z. and Ulrich, A.C. 2017. Effect of naphtha diluent on greenhouse gases and reduced sulfur compounds emissions from oil sands tailings. *Science of the Total Environment*, (Vol. 598, pp. 916-924). doi:10.1016/j.scitotenv.2017.04.107.

- [8] Foght, J.M., Gieg, L.M., and Siddique, T. 2017. The Microbiology of oil sands tailings: Past, present, future. *FEMS Microbiology Ecology*, (Vol. 93(5)). doi:10.1093/femsec/fix034
- [9] Siddique, T., Penner, T., Klassen, J., Nesbo, and C. Fought, J.M. 2012. Microbial Communities involved in Methane Production from Hydrocarbons in Oil Sands Tailings. *Environ. Sci., Technol.* (Vol. 46(17), pp. 9802-9810). doi:10.1021/es302202c.
- [10] Siddique, T., Fedorak, P.M., and Foght, J.M. 2006. Biodegradation of Short-Chain n-Alkanes in Oil Sands Tailings under Methanogenic Conditions. *Environ. Sci. Technol.* (Vol. 40, pp. 5459-5464). doi:10.1021/es060993m.
- [11] Siddique, T., Fedorak, P.M., Mackinnon, M., and Foght, J.M. 2007. Metabolism of BTEX and Naphtha Compounds to Methane in Oil Sands Tailings. *Environ. Sci. Technol.* (Vol. 41(7), pp. 2350-2356). doi:10.1021/es062852q.
- [12] Siddique, T., Gupta, R., Fedorak, P.M., Mackinnon, M., and Foght, J.M. 2008. A first approximation kinetic model to predict methane generation from an oil sands tailings settling basin. *Chemosphere* (Vol. 72(10), pp. 1573-1580). doi:10.1016/j.chemosphere.2008.04.036.
- [13] Mohamad Shahimin, M.F., Foght, J.M., and Siddique, T. 2016. Preferential methanogenic biodegradation of short-chain n-alkanes by microbial communities from two different oil sands tailings ponds. *Science of the Total Environment*. (Vol. 553, pp. 250-257). doi:10.1016/j.scitotenv.2016.02.061.
- [14] Mohamad Shahimin, M.F., and Siddique, T. 2017. Sequential Biodegradation of Complex Naphtha Hydrocarbons under Methanogenic Conditions in Two Different Oil Sands Tailings. *Environ. Pollut.* (Vol. 221, pp. 398-406). doi:10.1016/j.envpol.2016.12.002.
- [15] Budwill, K. June 3-4, 2019. Methanogenic Diluent Microcosm Study: Insights Into Diluent Degradation in Tailings Material. COSIA Oil Sands Innovation Summit.
- [16] Fawcett, S., Neune, M. (Golder Associates), Birks, J., and Budwill, K. (InnoTech). June 3-4 2019. Oil Sands Innovation Summit COSIA Froth Treatment Tailings Sampling Project: An overview of the 2018 program. COSIA Oil Sands Innovation Summit.
- [17] Neuner, M., Fawcett, S., and Moleswar, A. (Golder Associates). June 3-4 2019. Oil Sands Innovation Summit COSIA Froth Treatment Tailings Sampling Project: Gas Generation and Composition. COSIA Oil Sands Innovation Summit.
- [18] You, Y., Staebler, R.M., Moussa, S.G., Beck, J., and Mittermeier, R.L. 2021. Methane Emissions from an oil sands tailings pond: a quantitative comparison of fluxes derived by different methods. *Atmos. Meas. Tech.*, (Vol. 14(3) pp. 1879-1892). doi:10.5194/amt-14-1879-2021.
- [19] Zhang, L., Cho, S., Hashisho, Z., and Brown, C. 2019. Quantification of fugitive emissions from an oil sands tailings pond by eddy covariance. *Fuel (Guildford)*. (Vol. 237, pp. 457-464). doi:10.1016/j.fuel.2018.09.104.

- [20] Baray, S., Darlington, A., Gordon, M., Hayden, K.L., Leithead, A., Li, S-M., Liu, P.S.K., Mittermeie, R.L., Moussa, S.G., O'Brien, J., Staebler, R., Wolde, M., Worthy, D., and McLaren, R. 2018. Quantification of methane sources in the Athabasca Oil Sands Region of Alberta by aircraft mass balance. *Atmos. Chem. Phys.* (Vol. 18(10), pp. 7361-7378). doi:10.5194/acp-18-7361-2018.
- [21] Kong, J.D., Wang, H., Siddique, T., Foght, J., Semple, K., Burkus, Z., and Lewis, M.A. 2019. Second-generation stoichiometric mathematical model to predict methane emissions from oil sands tailings. *Science of the Total Environment*. (Vol. 694, pp. 133645-133645). doi:10.1016/j.scitotenv.2019.133645.
- [22] Sinke, A.J.C., Cottaa, F.H.M., Buis, K., and Keizer, P. 1992. Methane oxidation by methanotrophs and its effects on phosphate flux over the sediment-water interface in a eutrophic lake. *Microbiol. Ecol.* (Vol. 24(3), pp.259-269). doi:10.1007/BF00167785.
- [23] Wang, Z., Zeng, D., and Patrick Jr, W.H. 1996. Methane emissions from natural wetlands. *Environ. Monitor. Assess.*, (Vol. 42(1-2), pp.143-161). doi:10.1007/BF00394047.
- [24] King, G.M. 1994. Association of Methanotrophs with roots of rhizomes of aquatic vegetation. *Appl. Environ. Microbiol.* (Vol. 60(9), pp. 3220-3227). doi:10.1128/AEM.60.9.3220-3227.1994.
- [25] Roslev, P. and King, G.M. 1996. Regulation of methane oxidation in a freshwater wetland by water table changes and anoxia. *FEMS Microbio. Ecol.* (Vol. 19(2), pp. 105-115). doi:10.1016/0168-6496(95)00084-4.
- [26] Fernandes Sanches, L., Guenet, B., Cardoso Marinho, C., Barros, N., and de Assis Esteves, F. Global Regulation of Methane Emission from Natural Lakes. *Scientific Reports*. (Vol. 9, pp. 255). doi:10.1038/s41598-018-36519-5.
- [27] Le Mer J. and Roger, P. 2001. Production, oxidation, emission and consumption of methane by soils: A review. *Eur. J. Biol.* (Vol. 37(1), pp. 25-50). doi:10.1016/S1164-5563(01)01067-6.
- [28] Conrad, R. and Rothfuss, F. 1991. Methane oxidation in the soil surface layer of a flooded ricefield and the effect of ammonium. *Biol. Fert. Soils.* (Vol. 12, pp 28-32). doi:10.1007/BF00369384.
- [29] Amos, R.T., Bekins, B.A., Delin, G.N., Cozzarelli, I.M., Blowes, D.W., and Kirshtein, J.D. 2011. Methane oxidation in a crude oil contaminated aquifer: Delineation of aerobic reactions at the plume fringes. *Journal of Contaminant Hydrology.* (Vol. 125(1), pp. 13-25). doi:10.1016/j.jconhyd.2011.04.003.
- [30] Garg, S., Newell, C.J., Kulkarni, P.R., King, D.C., Adamson, D.T., Irianni Renno, and M., Sale, T. 2017. Over-view of Natural Source Zone Depletion: Processes, Controlling Factors and Composition Change. *Groundwater Monitoring and Remediation* (Vol. 37(3), pp. 62-81). doi:10.1111/gwmr.12219.
- [31] Saidi-Mehrabad, A., He, Z., Tamas, I., Sharp, C.E., Brady, A.L., Rochman, F.F., Bodrossy, L. Abell, G.C.J., Penner, T., Dong, X., Sensen, C.W., and Dunfield, J.F. Methanotrophic bacteria in oil sands tailings ponds of northern Alberta. *The ISME Journal.* (Vol. 7, pp. 908-921). doi:10.1038/ismej.2012.163.