

Evaluation of NAs distribution and sources within the water column in BML

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Summary

Understanding the sources and fates of Naphthenic acids (NAs) is an important component of oil sand tailings reclamation. NAs are present in oil sands ore and are extracted and concentrated in oil sands process water (OSPW) and tailings. These compounds are also considered as the most hazardous components in the tailings, and thus understanding their fate is an important component of reclamation of tailings and oil sands sites. Syncrude has undertaken the first full scale reclamation of oil sands tailing using water capped tailing technology via the commissioning of a pit lake, Base Mine Lake (BML). The end goal of BML is the establishment of a self-sustaining ecosystem that naturally releases surface water to the Athabasca River. Understanding the presence and persistence of NAs in the water column of BML is a necessary part of assessing the overall functioning of the lake and the potential for future water release.

Accordingly, this study aimed to investigate the potential source(s) of NAs in the water column of BML. Potential sources of NAs in the water column of BML include the underlying fluid fine tailings (FFT) or the OSPW originally used as a part of the water column. In addition, ongoing microbial activity within the FFT and water cap may result in production of NA during partial degradation of organic residues or in the removal of NAs via biodegradation. Through comparing the molecular fingerprints of NA isomers for the different potential sources, the extent to which they may have contributed to NA in BML surface water can be assessed.

Theory / Method / Workflow

Naphthenic acids are defined as alicyclic monocarboxylic acids and are considered as one of the most toxic constituents in tailings. NAs are present in tailings as complex mixtures and co-exist with other heteroatomic (O, N, S) chemical species. Consequently, the identification of NAs has been hindered due to the analytical difficulties associated with resolving these compounds. The first studies that attempted to identify NAs were only able to resolve the degree of cyclicity and carbon numbers (Herman et al., 1994; Hsu et al., 2000; Holowenko et al., 2001; Scott et al., 2005). Comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC×GC/TOFMS) provides greater chromatographic resolution of naphthenic acids and has facilitated the firm identification of identify various families of NAs in oil sand ponds (Rowland et al., 2011a; Rowland et al., 2011b; Bowman et al., 2014; Wilde et al., 2015). In this system, two columns with different stationary phases are connected sequentially in a GC oven and a modulator is used to fractionate effluent from the primary to the secondary column throughout the run (Frysiner, 2002; Ong and Marriott, 2002; Stauffer et al., 2008; Vazquez-Roig and Pico, 2012). The first-dimension separation is based on the volatility of the compounds, while the second-dimension separation is driven by polarity. This added dimension of separation greatly enhances resolution of individual compounds from complex mixtures, and specifically enables resolution of isomers of individual compounds.

The analysis was implemented by collecting water column samples from BML covering the 3 platforms (P1, P2, P3) (Figure 1) over the span of 3 years (2015-2018). The samples were collected from the Epilimnion (1.5m), Metalimnion (5m), Hypolimnion (9-10m). Additionally, FFT samples were collected from the FFT-water interface (10-11 m) and deeper FFT (16m). Additional analysis of OSPW and raw bitumen ore for comparison is ongoing.

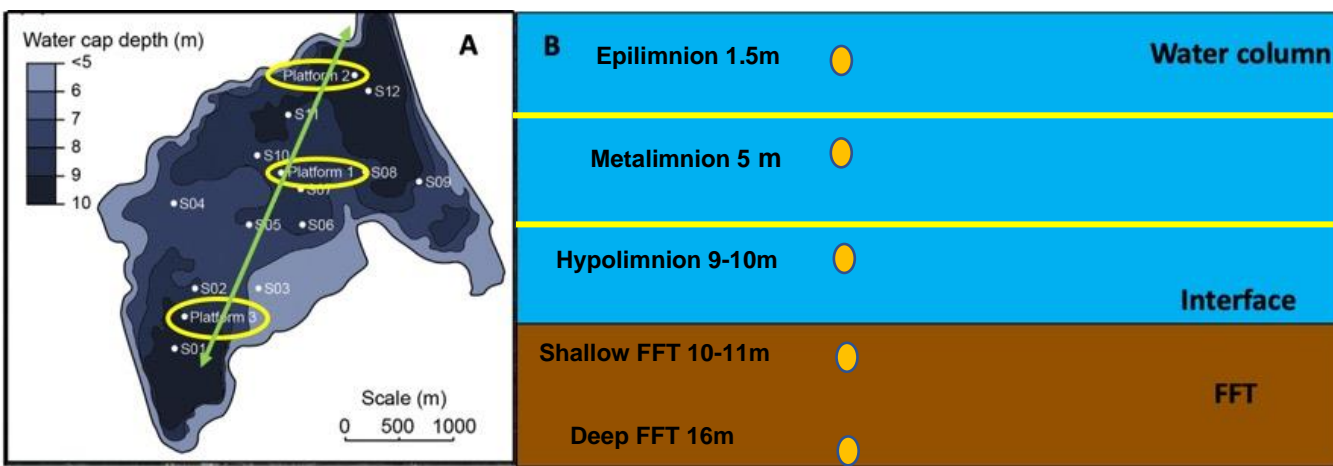


Figure 1: (A) A satellite image of BML that shows P1, P2, P3 Modified from (Dompierre and Barbour, 2016) (B) A cross section of BML that shows water column and FFT, sample depths interval across all platforms is indicated in orange circles.

Results, Observations, Conclusions

Using the GC×GC/TOFMS, the NAs isomer profiles were identified in the shallow and deep water column samples from 2015 -2018. The identified NAs isomers in the water cap of BML include several alkylated groups of Cyclohexane, bicyclic, and adamantane carboxylic acids. Preliminary results have indicated that overall there was no pronounced temporal variability for these identified compounds from 2015-2018 (Figure 2). However, two samples from 2018 at 5m and 2m showed a slight separation on PC1 (68.5%) due to their higher relative peak abundances for the C-9 bicyclic acids (168 m/z), methyl-adamantane carboxylic acids (208 m/z), and C₃-Cyclohexane carboxylic acids (184 m/z).

The overall stability of the distributions of these compounds over three years either indicates either that there were no additional inputs of NAs from the FFT during this period or potentially that the NAs detected are those remaining after biodegradation has removed NAs that would create distinct fingerprints. The minor variability observed for the isomers of the 2018 samples may indicate a specific input from a new NA source at this time that has yet to be degraded to be consistent with the overall water cap fingerprint. Ongoing analysis will resolve

and identify the NAs isomers and assess their variability of in the FFT, in addition to OSPW, and bitumen samples. Comparison of water cap NA profiles with the FFT samples will enable assessment of NAs transport upwards from the FFT through advection to the water column and whether biodegradation is affecting these inputs. Characterization of OSPW NA profile with the water cap profile will assess whether the observed profile may be dominated by inputs that occurred when OSPW originally filled the lake. Finally, comparison of these NA profiles to that of raw bitumen will confirm the extent to which biodegradation or mixing has affected OSPW and FFT porewater profiles. This research will elucidate NA source and the potential for their biodegradation within the BML system and thereby inform management decisions for BML and potentially other pit lakes in the Athabasca oil sands region.

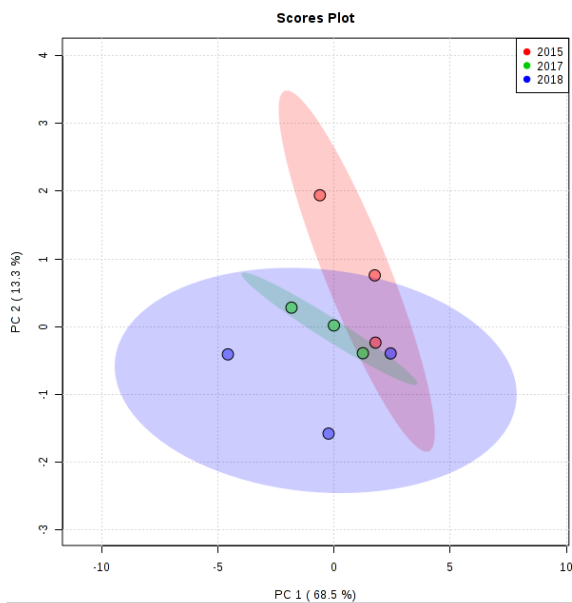


Figure 2: PCA plot for the relative abundance of NAs isomer profiles between 2015, 2017,2018

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References

- Bowman D. T., Slater G. F., Warren L. A. and McCarry B. E. (2014) Identification of individual thiophene-, indane-, tetralin-, cyclohexane-, and adamantane-type carboxylic acids in composite tailings pore water from Alberta oil sands. *Rapid Commun. Mass Spectrom.* **28**, 2075–2083. Available at: <http://doi.wiley.com/10.1002/rcm.6996> [Accessed March 13, 2018].
- Dompierre K. A. and Barbour S. L. (2016) Characterization of physical mass transport through oil sands fluid fine tailings in an end pit lake: a multi-tracer study. *J. Contam. Hydrol.* **189**, 12–26. Available at: <http://dx.doi.org/10.1016/j.jconhyd.2016.03.006>.
- Frysjnger G. (2002) GCxGC—A New Analytical Tool For Environmental Forensics. *Environ. Forensics* **3**, 27–34. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S1527592202900777>.
- Herman D. C., Fedorak P. M., MacKinnon M. D. and Costerton J. W. (1994) Biodegradation of naphthenic acids by microbial populations indigenous to oil sands tailings. *Can. J. Microbiol.* **40**, 467–477.
- Holowenko F. M., MacKinnon M. D. and Fedorak P. M. (2001) Naphthenic acids and surrogate naphthenic acids in methanogenic microcosms. *Water Res.* **35**, 2595–2606.
- Hsu C. S., Dechert G. J., Robbins W. K. and Fukuda E. K. (2000) Naphthenic acids in crude oils characterized by mass spectrometry. *Energy and Fuels* **14**, 217–223.
- Ong R. C. Y. and Marriott P. J. (2002) A Review of Basic Concepts in Comprehensive Two-Dimensional Gas Chromatography. *J. Chromatogr. Sci.* **40**, 276–291. Available at: <https://academic.oup.com/chromsci/article-lookup/doi/10.1093/chromsci/40.5.276>.
- Rowland Steven J., Scarlett A. G., Jones D., West C. E. and Frank R. A. (2011) Diamonds in the rough: Identification of individual naphthenic acids in oil sands process water. *Environ. Sci. Technol.* **45**, 3154–3159.
- Rowland Steven J., West C. E., Scarlett A. G. and Jones D. (2011) Identification of individual acids in a commercial sample of naphthenic acids from petroleum by two-dimensional comprehensive gas chromatography/mass spectrometry. *Rapid Commun. Mass Spectrom.* **25**, 1741–1751.
- Scott A. C., MacKinnon M. D. and Fedorak P. M. (2005) Naphthenic acids in athabasca oil sands tailings waters are less biodegradable than commercial naphthenic acids. *Environ. Sci. Technol.* **39**, 8388–8394.
- Stauffer E., Dolan J. A., Newman R., Stauffer E., Dolan J. A. and Newman R. (2008) Gas Chromatography and Gas Chromatography—Mass Spectrometry. In *Fire Debris Analysis* Elsevier. pp. 235–293.
- Vazquez-Roig P. and Pico Y. (2012) Gas chromatography and mass spectroscopy techniques for the detection of chemical contaminants and residues in foods. In *Chemical Contaminants and Residues in Food* Elsevier. pp. 17–61. Available at: <http://linkinghub.elsevier.com/retrieve/pii/B9780857090584500025> [Accessed March 27, 2018].
- Wilde M. J., West C. E., Scarlett A. G., Jones D., Frank R. A., Hewitt L. M. and Rowland S. J. (2015) Bicyclic naphthenic acids in oil sands process water: Identification by comprehensive multidimensional gas chromatography-mass spectrometry. *J. Chromatogr. A* **1378**, 74–87.