



## Monitoring Biogeochemical Cycling in an Oil Sand Pit Lake via High Resolution Spatial Distribution of Organic Chemicals

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### Summary

Surface mining operations in the Athabasca Region in Northern Alberta, create large open pits to access oil sands deposits where crude oil is present in the form of bitumen<sup>1</sup>. To extract bitumen from the sands, the cretaceous ore is combined with hot water and sodium hydroxide in a process referred to as the 'Clark Hot Water Extraction'<sup>2</sup>. Although only 20% of all bitumen reserves are extracted with this protocol<sup>1</sup>, over 1.18 trillion liters of by product has been produced in the form of Fluid Fine Tailings (FFT) and Oil Sands Process Water (OSPW)<sup>3</sup>. The Tailing Management Framework (TMF) issued by the Alberta Energy Regulators in 2015<sup>4</sup> has emboldened oil sands operators to continue their investigation into management strategies for the reduction of tailings and reclamation of open pit mines. To promote the reclamation of these oil sands pits and the by-products of bitumen extraction, oil sands operators are currently investigating the use of pit lakes (PL). These lakes are constructed by introducing tailings into open pit mines and capping with several meters of water and allowing the FFT to steadily densify over time<sup>5</sup>. Freshwater inputs, including precipitation and runoff, and in situ biogeochemical processes are expected to improve the quality of the water cover over time leading to the establishment of a boreal lake ecosystem<sup>6</sup>. A challenge that arises is that as FFT settles and densifies porewater containing reduced species is released to the overlying water cap, which can in turn lead to decreases in water cap oxygen concentrations and may impede lake development<sup>7,8,9</sup>. To monitor the progression of this reclamation strategy, our research group is working collaboratively with Syncrude Canada to assess the spatial variability in organic compounds within the FFT to understand their potential biodegradation and the associated potential for release of reduced species and biogeochemical outcomes.

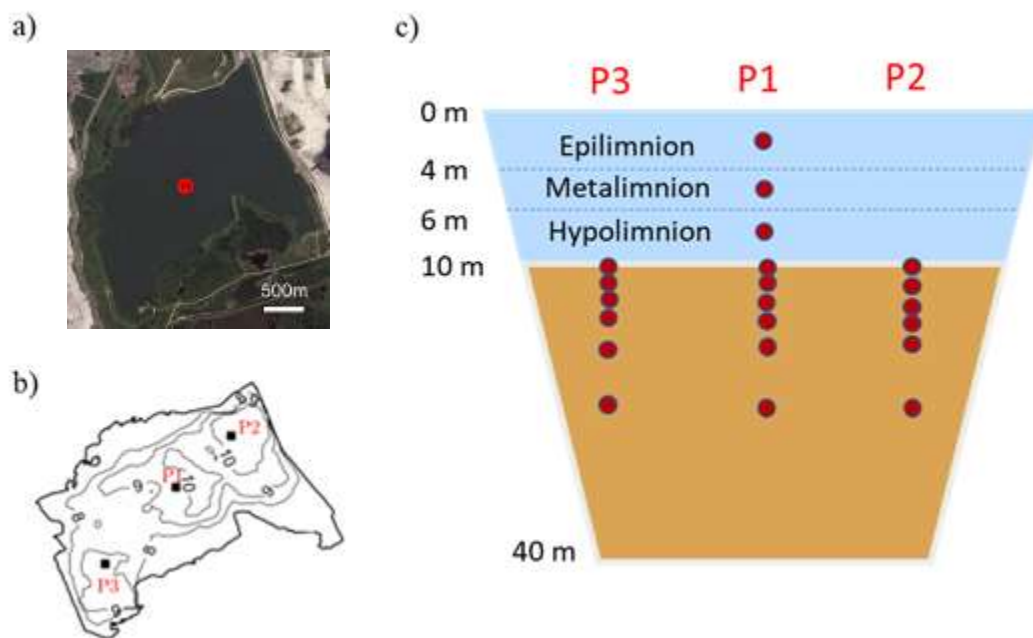
### Theory / Method / Workflow

Gas chromatography coupled to low resolution mass spectrometry (GC/LRMS) has been applied to numerous studies examining the organic constituents within FFT<sup>12,13</sup>. The limitation with this analytical method is that the organic constituents elute in an unresolved complex mixtures (UCM) in the total ion current (TIC) chromatogram. These UCMs correspond to a raised baseline hump with unresolved chromatographic peaks and overlaying mass spectra. Although GC/LRMS remains a workhorse for the analysis of many environmental samples, development of improved methods for identifying and quantifying UCM components will allow improved understanding of biogeochemical processing within the FFT. As a compensation for the insufficient peak capacity associated with GC/LRMS, complex and time-consuming sample preparation methods have been established (example, ASTM D2549)<sup>15</sup>. In response to these analytical challenges, our research group is applying comprehensive two-dimensional gas chromatography (GCxGC) to study high resolution depth profiling of the organic geochemistry within FFT deposits and at the water cap interface. GCxGC is a powerful tool in oil sands forensics as it offers unparalleled chromatographic separation, peak capacity and has been used in recent years to resolve individual constituents within complex mixtures, including structural isomers<sup>11</sup>. GCxGC has already been notably used in oil sands forensics to investigate the compositional difference

between various oil sands process water (OSPW)<sup>16</sup>, differentiation in groundwater systems from naturally occurring bitumen deposits<sup>17</sup> and assessment of the temporal and spatial variations of naphthenic acids in tailing ponds<sup>18</sup>. In this study our group is applying GCxGC to assess the spatial variability of organic compounds within the FFT and relate this to potential biogeochemical cycling.

The focus of this study is Base Mine Lake (BML) a PL that Syncrude commissioned in 2012<sup>10</sup> that was the first application of this reclamation strategy in the Athabasca Oil Sands Region (AOSR). As of October 2012, the FFT deposit underlying BML had reached a maximum thickness of 48 m and was submerged under a 52 Million m<sup>3</sup> water cover, with a surface area of approximately 8 km<sup>2</sup> and average depth of 6.5 m<sup>6</sup>. Densification of the FFT since 2012 has resulted in the settlement of FFT up to 6m, which has increased the average water depth to circa 10.5 m<sup>10</sup>. Yearly freshwater addition – ranging from 2 to 6 Million m<sup>3</sup> – to BML has been undertaken to simulate future water inflow from adjacent reclaimed landforms<sup>6</sup>. Water is currently pumped from the BML water cap for utilization in the oil sands extraction process such that the lake maintains a surface elevation of 308.7 ± 0.5 meters above sea level<sup>6</sup>.

Figure 1 presents a map of BML and the locations of the 3 sampling platforms (Platform 1, or P1; Platform 2, or P2; Platform 3, or P3), a schematic diagram of the spatial section of FFT studied and stratification of water cap. Eighteen FFT samples were collected from P1 (6 samples), P2 (6 samples), P3 (6 samples). Four samples from each platform were from close to the FFT-Water cap interface in increments of 0.2 m, one sample was collected 0.5 m from the previous set of samples and the deepest samples were collected ~ 15 m from the water surface (~ 5 m from FFT-Water interface). Three water samples were collected from P1 at the water-cap stratified zones (epilimnion, metalimnion, and hypolimnion).

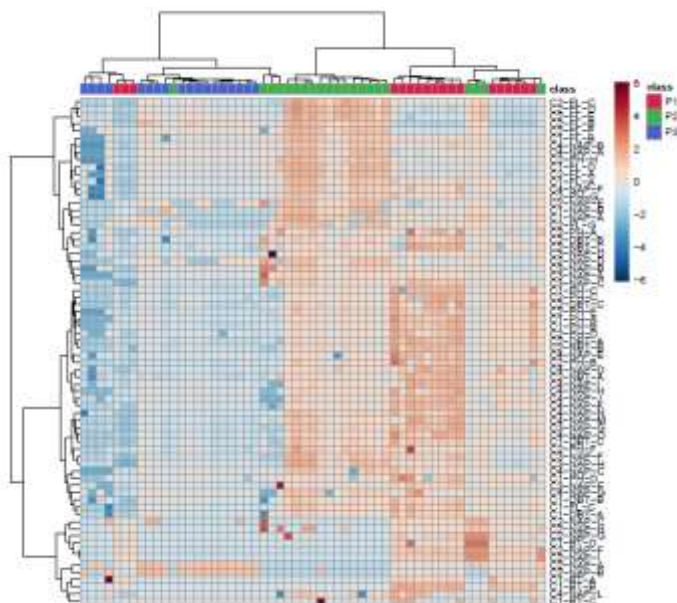


**Figure 1.** (a) Satellite view of BML site in 2017 (b) Bathymetry of BML with the locations of the three platforms (P1, P2, P3)<sup>19</sup> and (c) schematic diagram of sampling locations (red circles) within the spatial section of FFT and stratified water-cap.

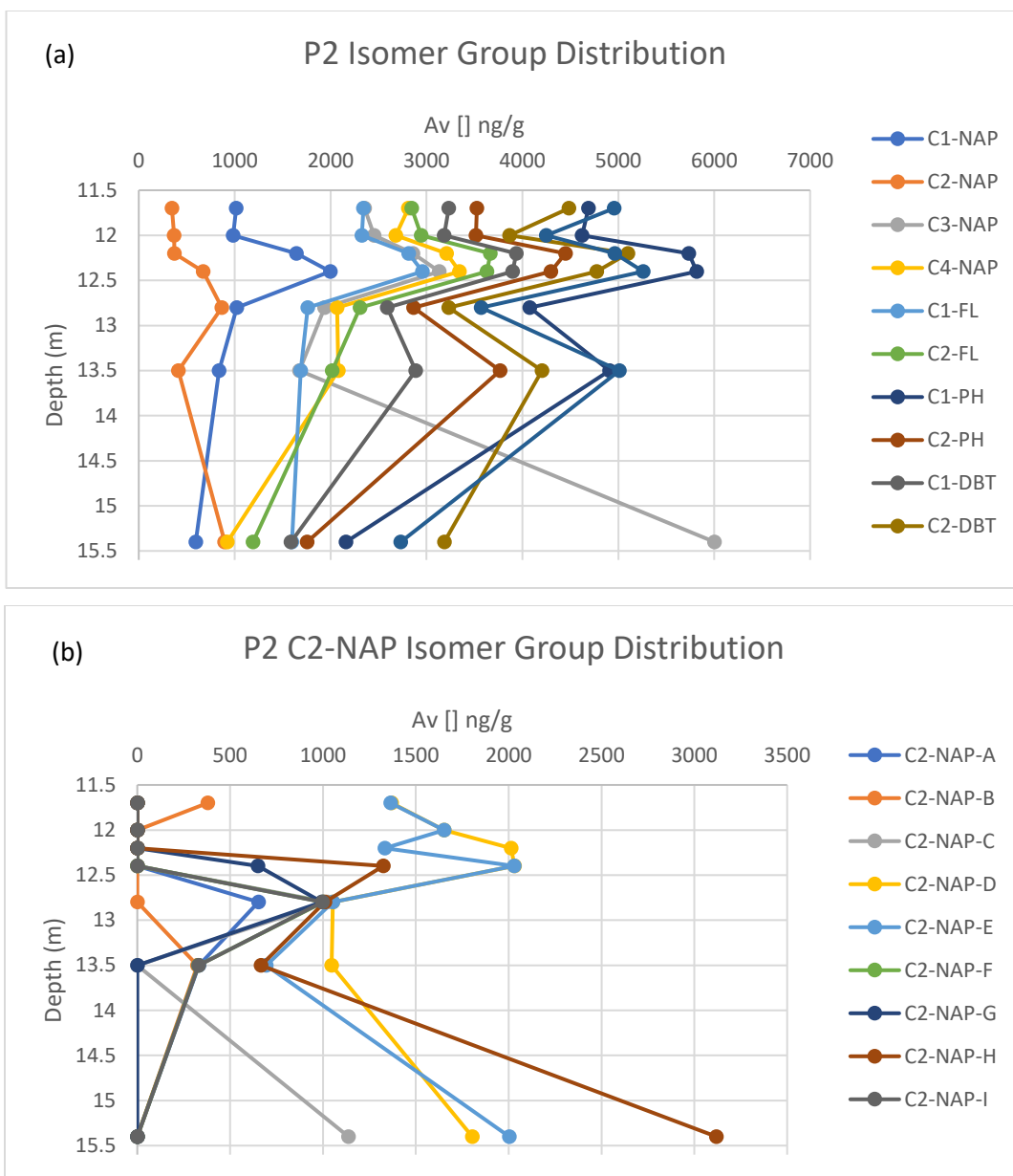
The FFT samples were extracted in triplicate with hexane to yield total lipid extracts (TLEs) at each depth interval. The extracts were analyzed with GCxGC/TOFMS to assess the spatial variability of the organics between the water cap stratification zones and FFT deposit. Individual isomer distributions of alkylated poly-aromatic hydrocarbons were obtained, and individual concentrations were semi-quantified using the closest available authentic standard. In total 69 individual alkylated poly-aromatic hydrocarbon isomers were semi-quantified: two isomers of C1-naphthalene, nine isomers of C2-naphthalene, eight isomers of C3-naphthalene, fourteen isomers of C4-naphthalene, four isomers of C1-fluorene, five isomers of C2-fluorene, four isomers of C1-phenanthrene, eight isomers of C2-phenanthrene, four isomers of C1-benzothiophene, 3 isomers of dibenzothiophenes and six isomers of C2-dibenzothiophene. The resulting distribution of alkylated poly-aromatic hydrocarbon for each class and individual isomers were compared using chemometric approaches.

## Results, Observations, Conclusions

The lowest abundance of the 69 semi-quantified alkylated poly-aromatic hydrocarbons in the FFT depth profiles were associated with samples collected near the FFT – Water Cap interface. Beyond the FFT – Water Cap interface, the abundance of alkylated poly-aromatic hydrocarbons within the sampling platforms fluctuated between depth intervals with no distinct trend. The multivariate statistical analysis for the spatial alkylated poly-aromatic hydrocarbon variability within a sampling platform in the BML FFT deposit demonstrates the heterogeneity of the system (**Figure 2**). A distinct variability was observed in the abundance of the 69 semi-quantified alkylated poly-aromatic hydrocarbons between sampling platforms with P2 exhibiting elevated abundance and P3 exhibiting the lowest abundance. The elevated abundance of substrates capable of undergoing microbial metabolism in P2 indicates high potential for biogeochemical cycling, while decreased abundance of these substrates at these other sites indicates a lower potential, either due to lower initial inputs or to ongoing cycling reducing the abundances of the compounds originally present. Although isomer groups are generally elevated in P2, this trend does not correlate with all isomer species and isomers that are preferentially biogeochemically cycled can be identified (Figure 3). This highlights the advantage that GCxGC provides over conventional methods, which cannot resolve individual isomers.



**Figure 2** – Heat map of spatial poly-aromatic hydrocarbon variability between sampling platforms



**Figure 3** – (a) Distribution of isomer group within P2 (b) Distribution of C2-naphthalene isomers within P2

Principal Component Analysis (PCA) was applied to the abundance of 69 semi-quantified alkylated poly-aromatic hydrocarbons within the FFT depth profiles. The largest variability between isomer abundance influencing the PCA separation within the FFT depth profiles is associated with C2-naphthalene isomers.

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