

Spatial and Temporal Assessment of Naphthenic Acid Fraction Compounds (NAFC) across an Oil Sands End Pit Lake Network: Novel insights into NAFC degradation and production via FTICR-MS Analysis

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The reclamation of mining by-products in Alberta's Oil Sands Region (AOSR) is a strictly regulated responsibility for oil producers, with various integrated mine closure strategies ensuring that reclaimed landscapes can resemble local, functioning ecosystems in the long-term. Base Mine Lake (BML), the first AOSR pit lake, is the large-scale demonstration of Syncrude Canada Ltd.'s water capped tailings technology which aims to store and reclaim fluid fine tailings (FFT) under a sufficient layer of water in decommissioned mine pits. Ongoing research and monitoring of the chemical and biological indicators within BML have shown that acid extractable organics (AEOs), which include Naphthenic Acid Fraction Compounds (NAFC), residual hydrocarbon/bitumen, and dissolved organic matter (DOM), play a crucial role governing the development of major biogeochemical cycles within BML. In this study, we applied negative mode electrospray ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (Neg-ESI FT ICR MS) to assess trends in the AEOs across two depths (epilimnion and hypolimnion) in BML's water cap over 10 years. Furthermore, the temporal BML results were compared to a local freshwater source (BCR), an active tailings pond (MLSB), and a 30-year-old pit lake demonstration pond (DP) to highlight molecular differences and provide further insights into AEO sources and cycling across oil sands management systems. In general, BML was dominated by NAFCs, specifically O_x and O_xS_x classes, from which highly unsaturated and aliphatic compounds were highly prevalent and stable over time. Recalcitrant NAFCs, like diamondoid acids, were previously investigated in BML, and we identified numerous formulas suspected to be biodegradation intermediates within BML and DP. In addition, oxygenated-NAFCs (O_{3-6}) were observed to be increasing over time to a greater extent in BML surface waters compared to bottom water samples, suggesting the occurrence of biodegradation. N-containing and highly oxygenated (O_8 to O_{20}) compounds were strongly represented in BCR and DP, as compared to MLSB, and we conjecture these compounds signal higher DOM representation in the AEO and are important