

## Selective solvent extraction and characterization of the acid extractable fraction of Athabasca oils sands process waters by Orbitrap mass spectrometry

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### ABSTRACT

The developments of oil sands activities in western Canada have increased the need for improved risk assessment and monitoring of water quality in surface and ground waters. Efforts have focused on the monitoring of naphthenic acids as principal toxicants of oil sands processed waters (OSPW). The complexity of naphthenic acids (NAs) has led to a surge in research to study their occurrence, fate and aquatic toxicity along with increased efforts to better characterize components in environmental samples. Developments in selective solvent extraction combined with negative-ion electrospray Orbitrap mass spectrometry are shown to be well-suited for the characterization of NAs and naphthenic acid fraction compounds (NAFCs) in Athabasca basin OSPW. Detailed characterization of the mixtures is critical for development of methods for the analyses of NAs and NAFCs. Improved methods for the characterization of NAFCs in turn will help improve the understanding of their measured toxicity, fate and transport in the environment.

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### 1. Introduction

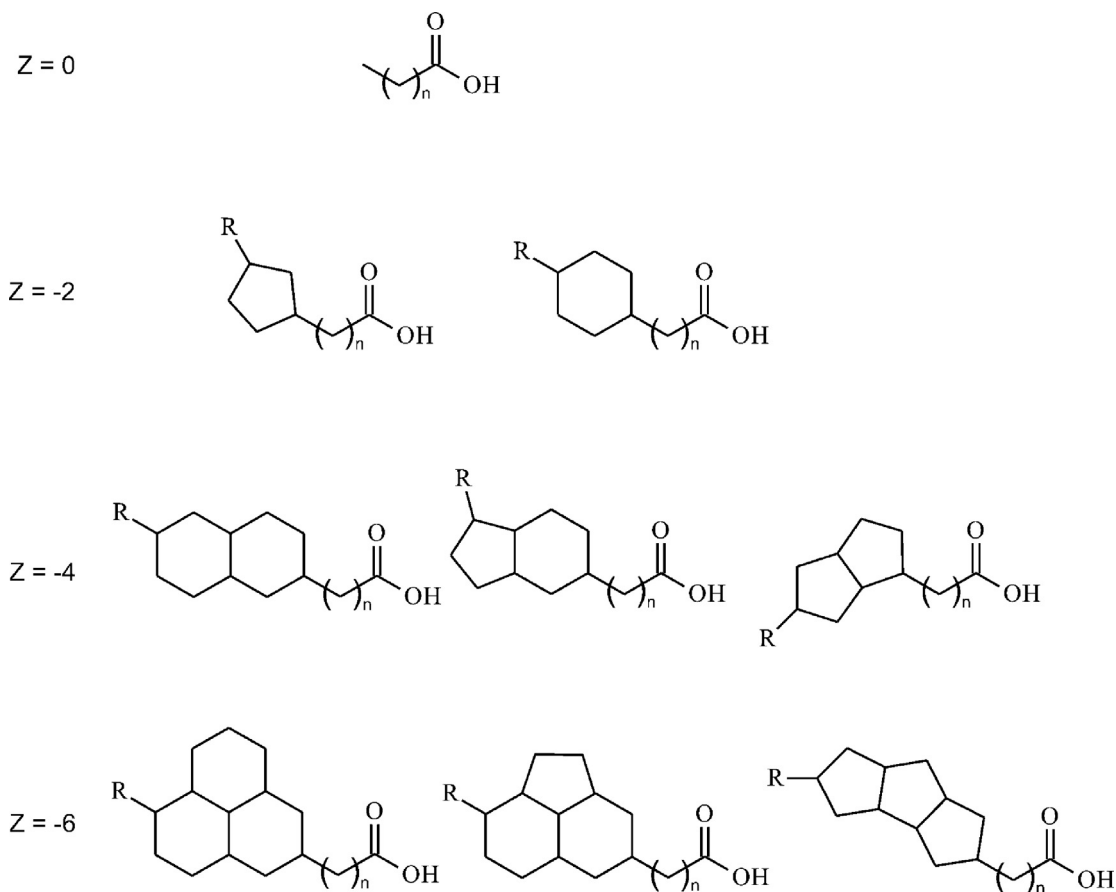
The main Canadian oil sands formations cover an area of about 142,000 km<sup>2</sup> in the province of Alberta, where oil sands reserves are estimated to be about 170 billion barrels – the third-largest proven crude oil reserve in the world, after Saudi Arabia and Venezuela. The present Athabasca oil sands surface mining operations have disturbed about 600 km<sup>2</sup> of a total 4800 km<sup>2</sup> that is surface-mineable [1]. The economic scale and rate of resource development is reflected in the \$22.8 billion net value of the resource for 2008, up from about 5 billion dollars in 2000 [2]. Recent reviews of oil sands activities [2–6] have highlighted the need for risk assessment of the complex mixtures to improve the monitoring of surface and ground waters and most have mentioned the role of naphthenic acids (NAs) as an important toxicant of oil sands processed waters (OSPW). Allen [7] provides a review of NA occurrence in OSPW in tailings ponds (30–70 mg/L) and discusses toxicity and treatment options. Other reviews of NA occurrence, fate and toxicology have highlighted the complexity of this group of chemicals [8,9] and their associated analytical difficulties [10].

The majority of the oil sands extraction to date is via open pit mining in areas where the overburden is less than 75 m. The process includes: ore crushing followed by formation of a 45–60 °C water-slurry which is hydro-transported and processed using sodium hydroxide which begins to liberate the bitumen before further separation via air floatation. After de-aeration the 60% bitumen froth mixture is further processed with solvent addition (naphtha or C<sub>5</sub>–C<sub>6</sub> paraffins) which lower the viscosity and the density of the bitumen and aids in concentrating bitumen to ca. 99% [2].

For each 1 m<sup>3</sup> of synthetic crude produced by surface mining, 11 t of oil sands are mined, 2.5 m<sup>3</sup> of hot water used (80% recycled from tailings pond), 3.3 m<sup>3</sup> raw oil sands tailings are added to the tailings ponds, which overtime become 2 m<sup>3</sup> mature fine tailings. Current tailings ponds cover an area of about 130 km<sup>2</sup> and contain around 720 million m<sup>3</sup> of tailings that are 1–3% bitumen, 20–30% sand-silt-clay and 70–80% water [2].

About 80% of the oil sands deposits are located deeper than 150 m and need to be accessed via in situ recovery using high pressure steam extraction at 250 °C [2]. Classical NAs as described using low resolution mass spectrometry [10,11] are carboxylic acids (Fig. 1) which include components with no rings (Z=0) and components with one or more saturated ring structures (Z=–2, –4, –6, etc.). Reported here is the first application of Orbitrap mass spectrometry for the characterization of selective solvent extraction of NAFCs in oil sands process waters. The high resolution of Orbitrap

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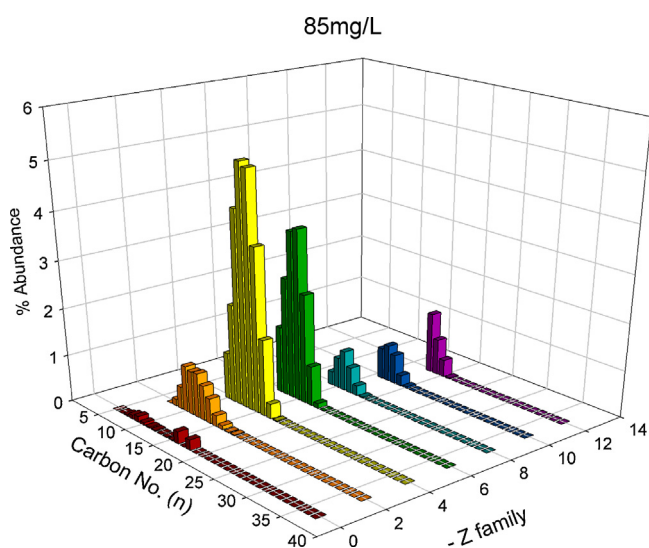


**Fig. 1.** Classical structures as defined by the general chemical formula  $C_nH_{2n-z}O_2$  of naphthenic acids reported for analyses of OSPW.

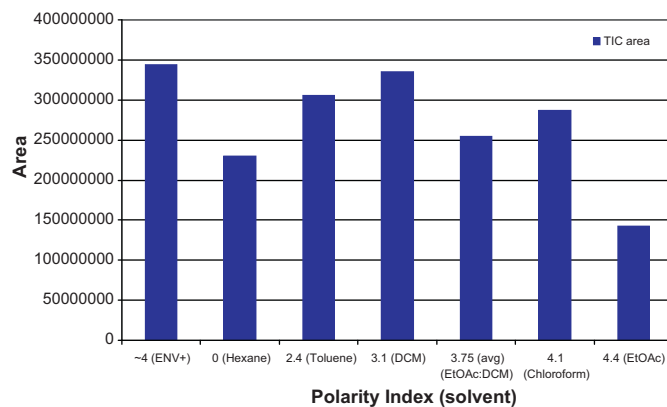
mass spectrometry (100,000 resolution at  $m/z$  400) is shown to be complementary to ultrahigh resolution methods ( $\sim 500,000$  resolution at  $m/z$  400) such as Fourier transform ion cyclotron resonance mass spectrometry (FTICRMS).

## 2. Experimental

A naphthenic acids standard was prepared as previously described by Rogers et al. [12] and Janfada et al. [13] from OSPW produced as a by-product of an oil sands extraction operation (Fort McMurray, AB, Canada). This standard comprised of the acid extractable components (which includes NAs) of OSPW has been previously characterized by FTICRMS [10,14–19]. Selective solvent extraction of OSPW was performed using the following solvents or solid phase extraction systems: (a) dichloromethane (3.1), (b) ENV+ ( $\sim 4$ ), (c) hexane (0), (d) toluene (2.4), (e) ethyl



**Fig. 2.** Distribution of naphthenic acids (NA) in OSPW extract observed using negative-ion electrospray ionization Orbitrap mass spectrometry.



**Fig. 3.** Naphthenic acid fraction components (NAFCs) total extraction area counts using selected solvent systems or SPE with various polarity indexes.

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