



# Investigation of the impact of organic solvent type and solution pH on the extraction efficiency of naphthenic acids from oil sands process-affected water



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## HIGHLIGHTS

- Liquid–liquid extraction of OSPW NAs using six solvents at three pHs (2.0, 8.5, 12.0).
- n-pentane, n-hexane, cyclohexane, dichloromethane, ethyl ether, and ethyl acetate.
- Extractability of molecules depends on polarity and ions on water solubility.
- Ethyl ether is an alternative to dichloromethane for extraction of O<sub>x</sub>–NAs (2 ≤ x ≤ 4).
- Dichloromethane use can be discontinued to limit human health risk.

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## ABSTRACT

Naphthenic acids (NAs) from oil sand process-affected water (OSPW) were liquid–liquid extracted using six organic solvents (n-pentane, n-hexane, cyclohexane, dichloromethane, ethyl ether, and ethyl acetate) at three pHs (2.0, 8.5, and 12.0). The NAs exist in ionic (ions) and non-ionic (molecules) forms in the water phase depending on their dissociation constants and the solution pH. Results showed the extractability of NA molecules depends on the solvent polarity and the extractability of NA ions on the water solubility in solvent. The organic solvent type and solution pH were found to not only impact the extracted amounts of each NA species, but also the NAs distribution in terms of molecule carbon number and hydrogen deficiency. Overall, it is concluded that ethyl ether can be used as an alternative to dichloromethane (DCM) given their similar extraction efficiencies and extracted NA profiles. This is important since DCM is known to have metabolic toxicity and transitioning to the safer ethyl ether would eliminate laboratory DCM exposures and risk to human health. Despite the higher extraction efficiency of NAs at pH 2.0, extraction at pH 12.0 could be useful for targeted extraction of low-concentration nonpolar organic compounds in OSPW. This knowledge may assist in the determination of the specific NAs species that are known to have chronic, sub-chronic and acute toxicity to various organisms, and the potential targeting of treatment to these NAs species.

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## 1. Introduction

The rapid growth of the oil sands industry in Alberta, Canada has led to the production of huge volumes of oil sands process-affected water (OSPW) containing suspended particles, salts, metal ions, and organic compounds (Kelly et al., 2009, 2010). The organics include naphthenic acids (NAs) that are persistent toxic compounds

of concern due to their high concentrations in OSPW and their potential to adversely affect the environmental and public health if released (Kim et al., 2012; Hudson, 2013; Kurek et al., 2013). Acute, sub-chronic and chronic toxicity of NAs have been assessed for organisms including goldfish, larval zebrafish, *Pimephales promelas*, *Vibrio fischeri*, and the mammalian immune system (Hagen et al., 2012; He et al., 2012; Scarlett et al., 2013; Wang et al., 2013). NAs are a complex mix of hundreds of compounds having the empirical formula  $C_nH_{(2n+Z)}O_x$  where “n” is the carbon number ( $7 \leq n \leq 26$ ), “Z” is zero or an even negative integer ( $0 \leq -Z \leq 18$ ) that specifies the hydrogen deficiency resulting from ring or double bond formation, and “x” represents the number of oxygen atoms. In addition, recent studies indicate the presence of aromatic NAs as a part of  $O_x$ -NAs and also the identification of low abundance sulphur and nitrogen-containing NAs (Nyakas et al., 2013; Barrow et al., 2015).

For many comprehensive analytical and toxicological studies, OSPW NAs are typically separated from the OSPW matrix using solid phase extraction (SPE) and/or liquid–liquid extraction (Garcia-Garcia et al., 2012; Reinardy et al., 2013; Scarlett et al., 2013; Wang et al., 2013). Although SPE separation has been successfully applied to separate different NAs species (Reinardy et al., 2013; West et al., 2014), for studies requiring larger amounts of a more comprehensive range of NAs (e.g. chronic toxicity or in-vivo toxicity tests), liquid–liquid extraction is a more appropriate and convenient extraction method. Given NAs are weak acidic compounds, liquid–liquid extraction of NAs has typically been performed at pH 2.0 using dichloromethane (DCM) as the extraction solvent (Garcia-Garcia et al., 2011, 2012; Wang et al., 2013). The optimal extraction of NAs at acidic conditions (pH 2.0) has recently been shown by Barrow et al. (2015). Despite the ubiquity of its use, the efficacy of DCM as an extraction solvent has not been thoroughly investigated for OSPW extraction despite the complexity of NA species (i.e., widely varying physicochemical properties). In addition, DCM is a known carcinogen to the human body through pathways including inhalation/ingestion and skin absorption, making the consideration of other extraction solvents necessary to decrease human health risks related to DCM use in the laboratory setting (Graves et al., 1995). Headley et al. (2013) investigated the extraction efficiency of NAs using solvents with differing polarity (DCM, ENV+, hexane, toluene, chloroform, ethyl acetate/dichloromethane, and ethyl acetate) and indicated the preference of solvent for extraction depends on the targeted NA species, though the composition of the individual fractions from such extractions using different solvents has not been characterized previously.

Given the limitations of SPE and DCM liquid–liquid extraction outlined above, the goal of the current study was to compare and characterize the liquid–liquid extraction efficiency of OSPW NAs using six organic solvents (n-pentane, n-hexane, cyclohexane, DCM, ethyl ether, and ethyl acetate; see Table 1 for physicochemical properties) at three solution pH values (12.0, 8.5, and 2.0). The basic

pH conditions were tested to determine if specific NAs species are preferentially extracted at higher pH that may be present at lower concentrations in OSPW but may be more toxic than other NAs. This knowledge may be used for future research in elucidating the specific NAs species that are most toxic via various acute, sub-chronic and chronic toxicity assays.

## 2. Experimental

### 2.1. Reagents and materials

The six extraction solvents included n-pentane, n-hexane, and DCM (Fisher Scientific, ON), cyclohexane and ethyl acetate (Acros Organic, NJ), and ethyl ether (Sigma–Aldrich, ON). Optima-grade water, methanol, and acetonitrile (Fisher Scientific, ON) were used in ultrahigh performance liquid chromatography time-of-flight mass spectrometry (UPLC-TOFMS) analyses.

OSPW was collected in February 2011 from an oil sands tailings pond in Fort McMurray, Alberta, Canada. After arriving at the University of Alberta, the OSPW was stored at 4 °C and later brought to room temperature (~20 °C) prior to liquid–liquid extraction. OSPW was mixed uniformly using a motor driven paddle mixer before dividing into 100 mL sample aliquots. The samples were centrifuged at 10 000 RPM for 5 min to remove suspended particles.

### 2.2. Liquid–liquid extraction

The raw OSPW had a natural pH of 8.5.  $H_2SO_4$  (1.8 M) and NaOH ( $0.1 \text{ g mL}^{-1}$ ) solutions were added dropwise to adjust the pH of the samples immediately prior to extraction to 2.0 and 12.0, respectively. Six organic solvents were used to extract NAs from each 100 mL sample using three separate aliquots of 20 mL, 20 mL, and 10 mL (2:1 sample to solvent volume ratio). The organic solvent layers were separated from the water, combined, and air-dried in a fume hood. Each dried fraction was re-dissolved into 2 mL acetonitrile for quantification of  $O_x$ -NAs ( $2 \leq x \leq 4$ ) species. Duplicate OSPW extractions were performed at each specified pH value and for each organic solvent.

### 2.3. UPLC-TOFMS quantification analysis

A 1 mL volume of each re-dissolved fraction was centrifuged at 10 000 RPM for 5 min. The injection solution was prepared with 500  $\mu\text{L}$  of the supernatant, 100  $\mu\text{L}$  of  $4.0 \text{ mg L}^{-1}$  internal standard (myristic acid- $1\text{-}^{13}\text{C}$ ) in methanol, and 400  $\mu\text{L}$  methanol to reach a final sample volume of 1 mL. Chromatographic separations were performed using a Waters UPLC Phenyl BEH column ( $1.7 \mu\text{m}$ ,  $150 \text{ mm} \times 1 \text{ mm}$ ), with mobile phases of 10 mM ammonium acetate in water (A) and 10 mM ammonium acetate in 50/50 methanol/acetonitrile (B). The elution gradient was 0–2 min, 1% B; 2–3 min, increased from 1% to 60% B; 3–7 min, from 60% to 70% B; 7–13 min, from 70% to 95% B; 13–14 min, from 95% to 1% B, and hold 1% B until 20 min to equilibrate column with a flow rate of  $100 \mu\text{L min}^{-1}$ . The column temperature was set at 50 °C and the sample temperature at 4 °C. Samples were analyzed with an UPLC-TOFMS (Synapt G2, Waters) with the electrospray ionization (ESI) source operating in negative ion mode and TOF analyzer in high-resolution mode. Mass resolution was 40 000 with the investigated mass range of 100–600 (m/z). Data acquisition was controlled using MassLynx (Waters) and data extraction from spectra was performed using TargetLynx (Waters). The UPLC-TOFMS quantification method was developed previously (Hwang et al., 2013; Wang et al., 2013).

**Table 1**  
Properties of six organic solvents and water.

	Boiling point (°C)	Density <sup>a</sup> (g/mL)	Polarity index	Water solubility in solvent (%w)
n-pentane	36	0.626	0	0.010
n-hexane	69	0.655	0.1	0.010
Cyclohexane	81	0.779	0.2	0.012
DCM	40	1.327	3.1	0.17
Ethyl ether	35	0.713	2.8	1.3
Ethyl acetate	77	0.894	4.4	9.8
Water	100	0.998	10.2	–

<sup>a</sup> The solvent density was measured at 20 °C.

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