



## Comparison of methods for determination of total oil sands-derived naphthenic acids in water samples



Sarah A. Hughes<sup>a, b, c, \*, 1</sup>, Rongfu Huang<sup>d, 1</sup>, Ashley Mahaffey<sup>e</sup>, Pamela Chelme-Ayala<sup>d</sup>, Nikolaus Klammerth<sup>d</sup>, Mohamed N.A. Meshref<sup>d</sup>, Mohamed D. Ibrahim<sup>d</sup>, Christine Brown<sup>f</sup>, Kerry M. Peru<sup>g</sup>, John V. Headley<sup>g</sup>, Mohamed Gamal El-Din<sup>d</sup>

<sup>a</sup> Shell Health – Americas, Shell Oil Company, 910 Louisiana Street, Houston, TX 77002, USA

<sup>b</sup> Department of Biological Sciences, University of Alberta, Edmonton, AB, T6G 1H9, Canada

<sup>c</sup> Department of Forestry and Environmental Conservation, Clemson University, Clemson, SC, 29634, USA

<sup>d</sup> Department of Civil and Environmental Engineering, University of Alberta, Edmonton, AB, T6G 1H9, Canada

<sup>e</sup> Coral Waters Consulting Inc, Shell Technology Centre Calgary, 3655 36 St NW, Calgary, AB, T2L 1Y8, Canada

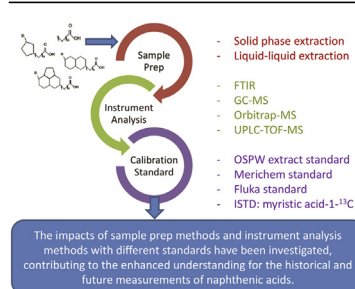
<sup>f</sup> Shell Canada Ltd. Shell Technology Centre Calgary, 3655 36 St NW, Calgary, AB, T2L 1Y8, Canada

<sup>g</sup> Environment and Climate Change Canada, 11 Innovation Boulevard, Saskatoon, SK, S7N 3H5, Canada

### HIGHLIGHTS

- Naphthenic acids (NAs) in OSPW and groundwater samples were analyzed for comparison.
- Solid phase and liquid-liquid extractions were compared for sample pretreatment.
- FTIR, GC-MS, UPLC-TOF-MS, and Orbitrap-MS were compared for determination of NAs.
- Different external and internal standards were compared for calibration.
- Total NA concentration measured depends on inherent differences of the method used.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 17 May 2017

Received in revised form

18 August 2017

Accepted 22 August 2017

Available online 23 August 2017

Handling Editor: Keith Maruya

#### Keywords:

Oil sands

Oil sands process-affected water

Groundwater

Naphthenic acids

### ABSTRACT

There are several established methods for the determination of naphthenic acids (NAs) in waters associated with oil sands mining operations. Due to their highly complex nature, measured concentration and composition of NAs vary depending on the method used. This study compared different common sample preparation techniques, analytical instrument methods, and analytical standards to measure NAs in groundwater and process water samples collected from an active oil sands operation. In general, the high- and ultrahigh-resolution methods, namely high performance liquid chromatography time-of-flight mass spectrometry (UPLC-TOF-MS) and Orbitrap mass spectrometry (Orbitrap-MS), were within an order of magnitude of the Fourier transform infrared spectroscopy (FTIR) methods. The gas chromatography mass spectrometry (GC-MS) methods consistently had the highest NA concentrations and greatest standard error. Total NAs concentration was not statistically different between sample preparation of solid phase extraction and liquid-liquid extraction. Calibration standards influenced quantitation results. This work provided a comprehensive understanding of the inherent differences in the various techniques

\* Corresponding author. Shell Health – Americas, Shell Oil Company, 910 Louisiana Street, Houston, TX 77002, USA.

E-mail address: [s.hughes@shell.com](mailto:s.hughes@shell.com) (S.A. Hughes).

<sup>1</sup> S.H. and R.H. contributed equally to this study.

available to measure NAs and hence the potential differences in measured amounts of NAs in samples. Results from this study will contribute to the analytical method standardization for NA analysis in oil sands related water samples.

© 2017 Published by Elsevier Ltd.

## 1. Introduction

In north-eastern Alberta Canada, bitumen is mined from oil sands deposits to produce synthetic crude oil. During the warm-water extraction process that separates the bitumen from the sand, naphthenic acids (NAs) in bitumen are dissolved into the process-water. Oil sands NAs are a highly complex mixture of organic compounds naturally present with bitumen and in groundwater associated with bitumen deposits. Oil sands NAs contain classical NAs (with the formula  $C_nH_{2n+2}O_2$ ) as well as oxidized NAs (e.g.  $O_x$ ), aromatic and heteroatomic NAs (containing sulfur or nitrogen atoms) (Barrow et al., 2009, 2015; Headley et al., 2009; Grewer et al., 2010; Huang et al., 2016a). These compounds are known to have aquatic toxicity (Swigert et al., 2015) and recent studies have confirmed classical NAs as primary toxic compounds present in oil sands NAs (Morandi et al., 2015; Yue et al., 2015; Hughes et al., 2017).

After bitumen extraction, all process water is stored in tailings ponds along with other potentially NA-contaminated water streams from the site such as: groundwaters from around the ore deposit; connate water; surface run-off from precipitation, to name just a few. Collectively these waters in tailings ponds are known as oil sands process-affected water (OSPW). As a part of their approval permits, oil sands operators are required to remediate OSPW and upon mine closure return water in tailings ponds to the environment (Shell Canada Ltd, 2014). Notably, industry is investigating options for progressive reclamation by identifying select low risk water streams for return to the environment during mine operations (Shell Canada Ltd, 2014). As NAs have been recognized as the primary toxic constituents in OSPW, in order to safely return water to the environment, there is an urgent need to accurately measure NAs in water samples to verify they are adequately treated. Although as of yet there is no water quality guideline for NAs, it is envisaged that future discharge would likely involve both analytical assessment paired with whole effluent toxicity testing to demonstrate the safety of any water discharges. Furthermore, establishment of a NA guideline may one day be possible if improved and standardized analytical methods are established and used along with standardized toxicity testing.

Assuring accurate and appropriate determination of NAs is complicated by both the lack of a universal analytical standard for calibration, as well as the technological progression of analytical instrumentation over the years that have historically been used to measure oil sands NAs in natural and process water sources (for a comprehensive review see Zhao et al. (2012)). Moreover, due to their highly complex nature, both the concentration and composition of the NA for a given mixture varies depending on the analytical methods used (Martin et al., 2008; Grewer et al., 2010; Brunswick et al., 2015). This adds further to uncertainty surrounding NA toxicity, assessment of environmental risk, and targeting of monitoring efforts. Brown and Ulrich (2015) stated that research in all areas of NAs has been hampered by the lack of a uniformly accepted standard method for measurement of total NAs. Additionally, there is a need to place historical oil sands NA environmental research into perspective of present day information to permit read-across between studies old and new and understand

what is being measured in historical studies with different instrumentation, standards, etc.

This study aims to compare a suite of different common analytical standards, sample preparation techniques, and key analytical methods, to measure the methods influence on total NA concentration in water samples (OSPW and groundwater) from an active oil sands lease site. The analyses included a high- and ultrahigh-resolution methods: ultra performance liquid chromatography time-of-flight mass spectrometry (UPLC-TOF-MS) and Orbitrap mass spectrometry (Orbitrap-MS), respectively using both external (OSPW extracted naphthenic acids) and internal (myristic acid-1- $^{13}C$ ) standards; a unit resolution method: gas chromatography mass spectrometry (GC-MS) using a commercial NA mixture standard; and a spectroscopic method: Fourier transform infrared spectroscopy (FTIR) using two commercial NA mixtures (Fluka and Merichem) and one OSPW extract standard as calibrants. A schematic of the tests conducted is presented in Fig. 1. The goal of this work is to provide a comprehensive understanding of the inherent differences among the various techniques available to measure “total NAs”. To our knowledge there have been no reported studies which have comprehensively tested a suite of analytical parameters side-by-side for their influence on total NA concentration in a variety of water types from an active oil sands operation. This study builds upon earlier studies that compared the influence of instrument resolution (Martin et al., 2008; Headley et al., 2009) and type (Grewer et al., 2010) by incorporating main elements of present total NA analysis methods (e.g. sample preparation, instrument type, and calibration) as well as looking at the effect of these variables in wide range of water samples collected over a three-month period.

Although in some reports, chemical species were also detected using positive-ion electrospray ionization (ESI) mode, in addition to NA species using the negative-ion mode (Pereira et al., 2013), there is no available method to quantify these species using the positive-ion mode. Furthermore, the results of effects-directed analysis found these positive-ion species have minor toxicity compared to the toxicity of classical  $O_2$ -NAs species (Morandi et al., 2015, 2016; Zhang et al., 2016; Hughes et al., 2017). Therefore, this paper focuses on analysis of “total NAs” that include  $O_2$ -NAs, using the negative-ion mode, as it will become one of the metric used for water quality assessment and hazard/risk assessment purposes (Kovalchik et al., 2017). This study conducted qualitative comparisons among methods instead of quantitative comparisons, given limited number and types of water samples that have been tested and that these samples cannot be used to represent all of historical and future water types and matrices. Nevertheless, this work is a step forward towards the standardization of analytical methods for oil sands NAs and optimization of method selection for futures studies.

## 2. Methods

### 2.1. Sample collection

Samples were collected from Shell Canada Limited's (Shell) Albian Sands Oil Sands operations (Muskeg River Mine, MRM and

Download English Version:

<https://daneshyari.com/en/article/5746426>

Download Persian Version:

<https://daneshyari.com/article/5746426>

[Daneshyari.com](https://daneshyari.com)