On-Line Solid Phase Extraction – HPLC – Orbitrap Mass Spectrometry for Screening and Quantifying Targeted and Non-Targeted Analytes in Oil Sands Process-Affected Water and Natural Waters in the Athabasca Oil Sands Region

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- **Industry** with ready access to an integrated view of research that will help them make and execute environmental management plans – a view that crosses disciplines and organizational boundaries

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REPORT SUMMARY

In response to mounting evidence of local environmental contamination around the Alberta oil sands industry, the Alberta Environmental Monitoring Panel announced a new *world class environmental monitoring program* for the Alberta oil sands region in early 2011, and a new monitoring system is now being delivered jointly by the Government of Canada and the Government of Alberta. This new program involves much more frequent sampling of water at many locations around oil sands activity. However, a particular challenge remains that there are currently no proven or validated analytical methods for characterizing the highly complex mixture of organic compounds in bitumen-impacted waters which meet requirements for qualitative and quantitative accuracy, sensitivity, precision, and high throughput.

To address this need, an on-line solid phase extraction (SPE) technique was developed for oil sands process-affected water (OSPW), and for natural surface and groundwater samples in the Athabasca oil sands region. The on-line SPE method was connected directly to a high pressure liquid chromatography – Orbitrap mass spectrometry (SPE-HPLC-Orbitrap MS) instrumental system, allowing comprehensive profiling of thousands of dissolved organic compounds, and quantitative analysis of naphthenic acids (NAs), with only 5 mL of a natural water sample. The new method improves upon existing methods by reducing sample volume requirements, eliminating sample preparation time, reducing the possibility of contamination, and increasing the accuracy and precision without sacrificing chromatographic performance, method sensitivity, or method quantitative quality.

The new method is anticipated to be useful for high-throughput environmental water monitoring for purposes of current or future environmental compliance by industry, or for forensic source elucidation by monitoring programs and researchers. The method requires a small investment in equipment to setup, but can pay for itself in terms of cost (e.g., solvents and disposable SPEs), and time savings (cost of technician's time in manual solid phase extraction or other extraction step), not to mention the more precise and higher quality data that are resultant. Considering the capital cost of any HPLC-ultra-high resolution mass spectrometer system (e.g., minimum $600k), it is the opinion of the authors that the minor additional cost of on-line solid phase extraction can be well justified for Provincial and/or Federal water monitoring around oil sands development.

ACKNOWLEDGEMENTS

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1 INTRODUCTION

In response to scientific reports of environmental pollution around the Canadian oil sands industry (Kelly et al. 2009, 2010), the Alberta Environmental Monitoring Panel announced a new *world class environmental monitoring program* for Alberta in early 2011 (Government of Alberta 2011). Details of the new program are still in development, but a new monitoring system is now being delivered jointly by the Government of Canada and the Government of Alberta and involves much more frequent sampling of air and water at many locations around oil sands activity (Environment Canada n.d.). However, for water monitoring in the oil sands region of Alberta, where water may contain a highly complex mixture of bitumen-derived organic compounds, a particular challenge for environmental analytical chemists is that there are currently no standard analytical techniques, or gold-standard methods. Methods are now needed that can meet requirements for accuracy, sensitivity, reliability, and high throughput.

In 2012, Ross et al. reported on the quantitative and qualitative analysis of naphthenic acids (NAs) in surface waters and groundwaters from the Athabasca oil sands region using liquid-liquid extraction and high-pressure liquid chromatography (HPLC)-time-of-flight mass spectrometry; a "high resolution" mass spectrometry technique[1]. Using this highly selective method, this study showed that ambient NA concentrations in surface water (< 2 to 80.8 μg/L) were 100-fold lower than previously reported by "low resolution" mass spectrometry used by the Regional Aquatics Monitoring Program[2].

Nevertheless, there is still much room for improvement in the methods of Ross et al. (2012). First, Ross et al. were only able to report on the profiles of NAs ($C_nH_{2n-Z}O_2$; where n is the number of carbon atoms, and Z represents the deficiency of hydrogen atoms caused by double bonds or rings), even though thousands of other sulfur, nitrogen, and polyoxygenated compounds are known to be present in bitumen-impacted waters (i.e., natural water and tailings pond water) in the region (Birks et al 2013, Gibson et al. 2011); as determined by FTICR-MS; an "ultra-high resolution" mass spectrometry technique. Second, the liquid-liquid extraction procedure used by Ross et al. (2012) for NAs in water samples was not highly quantitative and furthermore required a large water sample volume (~1L for each individual sample), used large volumes of toxic organic solvent for extraction, and was overall highly laborious and time consuming (Pereira et al. 2013, Ross et al. 2012). It is also known that different extraction solvents yield different results for the same sample (Headley et al. 2013), thus no liquid-liquid extraction method will be ideal. Furthermore, inherent to all liquid-liquid extraction techniques is the high probability of contaminating a sample with the solvents, glassware, detergents, or ambient air in the lab. Thus, the current available techniques for water monitoring around oil sands activity in the Athabasca River, or its tributaries, are still far from *world class*. Improvements in the extraction and

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[1] For more information on a variety of analytical methods see Zhao, B., R. Currie and H. Mian, 2012. Catalogue of Analytical Methods for Naphthenic Acids Related to Oil Sands Operations. OSRIN Report No. TR-21. 65 pp. http://hdl.handle.net/10402/era.26792

[2] See http://www.ramp-alberta.org/RAMP.aspx

comprehensive detection of NAs, and of the highly complex mixture of other organic compounds, in bitumen-impacted waters was the goal of the current work.

For environmental trace analysis of most organic compounds in water, an extraction step is generally required prior to analysis to achieve suitably low detection limits. Solid phase extraction (SPE) is a now the most popular technique of choice for analysis of organic compounds in environmental water samples. SPE relies on the affinity of the targeted analytes for a solid matrix. The water sample (e.g., 10 to 1000 mL) is slowly passed over the solid matrix (typical flows are up to 5 mL of sample per minute), and the trapped analytes can then be eluted with a few mL of organic solvent, a portion of which can then be analyzed by HPLC with mass spectrometry (HPLC-MS). This has advantages over liquid-liquid extraction including much lower organic solvent use (e.g., 1 to 2 mL for SPE, versus 0.5 to 1 L for liquid-liquid extraction), better precision, and higher throughput. However, manual SPE is still relatively slow (e.g., a 1 L water sample may require 2 to 3 hours) and is still prone to contamination from solvents or the solid matrix itself. Since each environmental sample is also processed on a different disposable SPE column, batch-to-batch manufacturing variability, and manual control of the sample extraction flow rate can adversely affect precision of the analysis.

On-line solid phase extraction is a technique that improves upon manual SPE by automating and combining the water extraction step with the HPLC- MS analysis. Briefly, using an upgraded injection system and an additional valve, an HPLC system can be converted to inject an environmental water sample to a reusable SPE column device. Targeted analytes are trapped by the same principle as above, but are eluted by backflushing the on-line SPE directly to the analytical HPLC column. This provides significant advantages over manual SPE, or liquid-liquid extraction, by further minimizing solvent use, by increasing precision through automation, and increasing throughput by virtually eliminating the separate extraction step. Also, by eliminating many manual processing steps and contact with laboratory glassware and reagents, on-line SPE also offers the possibility of less sample contamination. Furthermore, relatively smaller water sample volumes (e.g., 5 to 40 mL) are needed for on-line SPE (Trenholm et al. 2009) to obtain equivalent detection limits of manual SPE (e.g., 500 to 1000 mL). For all these reasons, over the last decade the use of on-line SPE coupled to HPLC-MS has increased, and several methods have been applied for environmental analysis of different organic compounds in water samples, including pesticides (Kuster et al. 2006, Marín et al. 2006, Postigo et al. 2010, Singer et al. 2010), pharmaceutical residues (Bones et al. 2006, Farré et al. 2012, López-Serna et al. 2012), illicit drugs (Fontanals et al. 2013, Jurado et al. 2012, Repice et al. 2013), and antibiotics (Díaz-Cruz et al. 2008, García-Galán et al. 2010, 2012, Gros et al. 2013).

The major aim of this work was to establish an automated method that allows the routine and high-throughput quantitative analysis of NAs, while also providing qualitative analysis of other dissolved organics in natural or bitumen-impacted water samples using best-available technologies. The specific objectives were to improve on the method of Ross et al. (2012) by increasing sample throughput and precision, minimizing contamination, and by increasing the range of detected analytes without sacrificing sensitivity or quantitative applications for NAs. Here we combined on-line SPE with high-pressure liquid chromatography coupled to Orbitrap

MS (a form of “ultra-high” resolution mass spectrometry) (SPE-HPLC-Orbitrap-MS) for such a purpose.

2 EXPERIMENTAL

The SPE-HPLC-Orbitrap-MS method required the following apparatus, standards and reagents.

2.1 Apparatus

Most of the apparatus used is listed in Table 1, while components are listed in Table 2.

Table 1. Apparatus.

Apparatus	Manufacturer, Country
Adjustable Pipettes (P200 and P5000)	Eppendorf, USA
Disposable plastic pipettes tips – Labtip Yellow (range 5 to 200 µL), & WHIT Blue (range 200 to 1000 µL)	Fisher Scientific, USA
Scintillation vials, 20 mL	Cole-Parmer, CA
15 mL Falcon conical centrifugal tubes	Fisher Scientific, CA
10 mL Autosampler glass vials and caps	Fisher Scientific, CA
Vortex mixer	Fisher Scientific, CA
Centrifuge	Fisher Scientific, CA
Analytical balance (± 0.01 mg) model LE225D	Sartorius, USA

Table 2. Components.

Component	Manufacturer, Country	Model
Liquid Chromatography System	Thermo Fisher, CA, USA	ARIA MX
Mass spectrometer	Thermo Fisher, CA, USA	Orbitrap Elite

2.2 Standards and Reagents

Similar to the method of Ross et al. (2012) for quantitation of NAs, a commercial technical mixture of NAs (Refined Merichem) was used for calibration curves, and an authentic pure isotopically-labelled NA internal standard (Dodecanoic-D23 Acid) was added to each sample, blank, and standard prior to analysis. The identity and source of the standards is shown in Table 3. Table 4 shows all general reagents used for preparation of stock solutions or HPLC mobile phases.

Table 3. Reference standard information.

Standard	Purpose	Supplier
Commercial naphthenic acids (Refined Merichem)	Calibration curve	Merichem
Dodecanoic-D23 Acid $C_{12}HD_{23}O_2$; m.w. = 223.46	Internal Standard	Sigma-Aldrich

Table 4. Reagents for solutions and mobile phases.

Reagent	Description	Manufacturer, Country
Methanol	LCMS Optima grade	Fisher Scientific, CA
Water	LCMS Optima grade	Fisher Scientific, CA
Acetic acid	LCMS Optima grade	Fisher Scientific, CA

2.3 Master Stock Solutions

Master stock solutions of the internal standard and Refined Merichem were prepared in volumetric flasks and stored at 4 ^{o}C. An accuracy of ± 0.01 mg for the weighing of standards was used. All weighing references and additional dilutions were recorded in a laboratory notebook.

2.3.1 *General Procedure for Preparing the Commercial Naphthenic Acid (Refined Merichem) Master Stock Calibration Standard*

Commercial NA oil (Refined Merichem) was accurately weighed into a volumetric flask and diluted to volume with methanol. For the present study, the concentration of master stock solution for commercial naphthenic acid (Refined Merichem) was 50,000 µg/mL.

2.3.2 *Procedure for Preparing Dodecanoic-D23 Acid Master Stock Solution*

Dodecanoic-D23 acid was accurately weighed into a volumetric flask and diluted to volume with an appropriate amount of methanol. For the present study, the concentration of the master solution of dodecanoic-D23 acid internal standard was 500 µg/mL.

2.4 Working Solutions

To fulfill the needs for pre-study and study validation, the following working solutions were prepared by dilution of the corresponding master solution. The final concentration, resultant volume, dilution and source solution details are presented in each of the following tables.

2.4.1 *Commercial NA Working Solutions for Calibration*

All working solutions (A to J in Table 5) were prepared by dilution of the master commercial naphthenic acid (Refined Merichem) stock solution using methanol/water (50/50; v/v) as the diluent.

Table 5. Naphthenic acid working solutions for use in calibration.

	Final Concentration (in µg/mL)	**Stock Solution Used**		**Volume of Diluent (in mL)**	**Final Volume (in mL)**	**Dilution Factor**
		Added Volume (in mL)	Concentration (in µg/mL)			
A	10,000	2.00	50,000 (master)	8.00	10	5
B	5,000	1.00	50,000 (master)	9.00	10	10
C	2,000	0.40	50,000 (master)	9.60	10	25
D	1,000	1.00	10,000	9.00	10	10
E	500	1.00	5,000	9.00	10	10
F	200	1.00	2,000	9.00	10	10
G	100	1.00	1,000	9.00	10	10
H	50	1.00	500	9.00	10	10
I	20	1.00	200	9.00	10	10
J	10	1.00	100	9.00	10	10

2.4.2 *Dodecanoic-D23 Internal Standard Working Solution*

Working solutions of dodecanoic-D23 internal standard were prepared by diluting the master solution 50x with methanol (Table 6).

Table 6. Dodecanoic-D23 working solution.

	Final Concentration (in µg/mL)	**Source Master Solution**		**Volume of Diluent (in mL)**	**Final Volume (in mL)**	**Dilution Factor**
		Added Volume (in mL)	Concentration (in µg/mL)			
A	10.00	0.2	500	9.8	10	50

2.5 Preparation of Aqueous Acetic Acid Mobile Phase

A fresh aqueous solution of aqueous acetic acid (mobile phase A) was prepared as needed for each analysis by adding 1 mL of acetic acid into a volumetric flask (1,000 mL capacity) containing 200 mL of water and diluting to volume with water in a fumehood.

2.6 Chromatographic Conditions

The chromatographic conditions used are listed in Table 7 and the online SPE conditions used are listed in Table 8. The typical internal standard retention time by the current method was 13.8 minutes.

Table 7. Chromatographic conditions.

Parameters	Description
Mobile phase	(A) Acetic acid 0.1% in water and (B) Methanol
Analytical column	Hypersil Gold C18 5 cm x 2.1 mm 1.9 µm
SPE column	Hypersil Gold aQ (C18 type column) 2 cm x 2.1 mm 12 µm
Autosampler temperature	12°C
Back pressure	Max 800 Bar
Column temperature	40 °C
Split	not used
Injection volume	5 mL
Total run time	25 minutes

Table 8. Online-SPE and HPLC flow conditions.
The information includes total flow rate (ml/min), composition of mobile phase A and B (%A, %B), gradient mode (Grad: step function or linear ramp), and timing of the valve which switches from “load position” to “elute position” at 3.67 min for the on-line SPE (also see Figure 1).

	Online-SPE					Analytical Column			
Time (min)	Flow (mL/min)	Grad	%A	%B	Valve	Flow (mL/min)	Grad	%A	%B
0.00	2.00	Step	99.0	1.0	-	0.50	Step	100	0
3.67	0.25	Step	0	100	switch	0.50	Step	100	0
7.67	0.25	Step	0	100	-	0.50	Step	100	0
8.17	0.50	Step	0	100	-	0.50	Ramp	10	90
17.00	0.50	Step	99.0	1.0	-	0.50	Ramp	1	99
22.00	0.50	Step	99.0	1.0	-	0.50	Ramp	100	0
25.00	0.50	Step	99.0	1.0	-	0.50	Ramp	100	0

2.7 Mass Spectrometric Conditions

The Orbitrap Elite was operated in negative electrospray ionization (ESI-) mode. Acquisition was performed in scan mode from m/z 100 to m/z 500 with the conditions shown in Table 9.

Table 9. Orbitrap Elite conditions.

Parameters	Description
Capillary Temperature (°C)	300
Vaporizer Temperature (°C)	350
Sheath Gas Flow (Arbitrary units)	40
Auxiliary Gas Flow (Arbitrary units)	5
Sweep Gas Flow (Arbitrary units)	2
Source Voltage (kV)	5

2.8 Analyte Identification

For quantification and generation of profiles, individual NA homologues were identified using a two-tiered approach. First, individual homologues were identified based on the exact mass, using the criteria of ±0.02 daltons. Second, analyte retention times for each homologue must have corresponded to within ± 0.5 minutes with retention times for the same homologue in commercial Refined Merichem NAs.

2.9 Quantification

All chromatograms were processed automatically using Xcalibur 2.2 software/QuanBrowser (Thermo Fisher) using the same processing parameters such as integration type, smooth, peak-to-peak amplitude and peak detection for all samples. Manual integration was performed only when necessary.

Total O_2 naphthenic acid concentrations were calculated based on external calibration. A calibration curve was generated from serial dilutions of a stock commercial naphthenic acid solution (Refined Merichem). Total peak area ratios for all homologues, based on the sum peak area ratio (peak area of analyte divided by the peak area of the internal standard) for all identified homologues from C_7 to C_{22} and Z = 0 to Z = -20 were fit to a least squares regression.

Total naphthenic acid peak area ratios were then interpolated based on the linear calibration function, to provide concentrations for total naphthenic acids. The calculated value was rounded off to 3 (three) significant figures using an Excel worksheet formula.

2.10 Profiles

Homologue profiles of O_2 naphthenic acids were generated by plotting the peak area ratio for all for all identified homologues from C_7 to C_{22} and Z = 0 to Z = -20 in Microsoft Excel.

2.11 Determination of the Limit of Quantification (LOQ)

The lowest standard on the calibration curve was accepted as the Limit of Quantification (LOQ) if the following conditions were met:

1. No interference present in blanks at the retention time of the analytes, or the response of this lowest standard is 5 times greater than any interference in blanks at that retention time.
2. Analyte peak is identifiable, discrete and with an accuracy of 80% to 120% in relation to the nominal standard concentration.
3. If duplicate standards were available and approved, the calculated precision was within 20%.

The LOQ of this method for total O_2 naphthenic acids was determined to be 1 µg/L.

3 HIGH VOLUME INJECTION SPE VERSUS LIQUID/LIQUID EXTRACTION

3.1 Chromatographic Performance and Efficiency

In the present method, 5 mL of the sample is injected into the chromatographic system and the target compounds are concentrated into the SPE column by a stream of mobile phase water with 0.1% of acetic acid in water:methanol (99:1, v/v)) at 2 mL/min. Thereafter, the six-port switching valve was activated and the analytes were transferred from the SPE column to the analytical column using the same mobile phases as in the previous step through both columns (Figure 1). When the transfer was finished, the analytes were separated analytically in a conventional manner. Water spiked at 50 µg/L of Refined Merichem oil was used as a surrogate in the water samples to evaluate the impact of the injection volume and SPE concentration step on chromatographic performance.

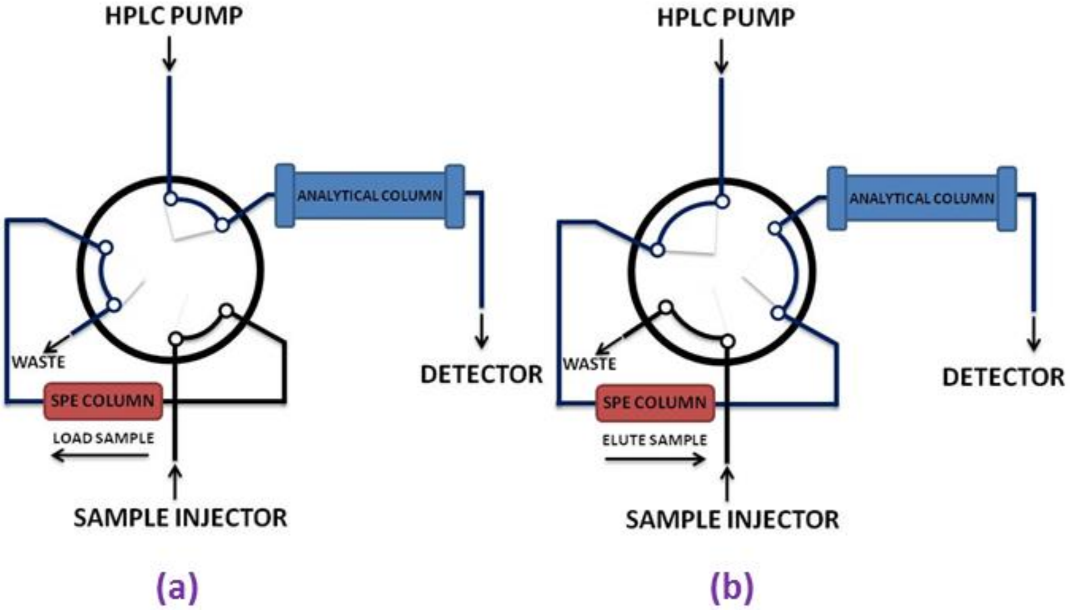


Figure 1. Schematic of the online-SPE valve.
(a) Load position; (b) Elute position.

The chromatographic separation and peak shape obtained using the high volume injection online SPE-LC system were comparable to those obtained by direct HPLC analysis (i.e., similar to the existing method of Ross et al. (2012)), confirming good chromatographic performance, and good analyte focusing and transfer to the analytical column without significant band broadening. Figure 2A shows a total ion chromatogram (TIC) of Merichem oil in water at 50 µg/L where 5 mL is injected to the on-line SPE column. This can be directly compared to the TIC in Figure 2B, where 5 µL of Refined Merichem oil (in methanol at 50 mg/L) is injected directly to the analytical column. In both analyses, 250 ng of the Refined Merichem oil was introduced to the system, and the chromatograms show a high similarity, suggesting that the chromatographic performance of both analyses is similar. However, due to the known complexity of the sample, TICs cannot be used for further chromatographic evaluation, thus extracted ion chromatograms of three naphthenic acids in the sample are shown in Figure 3:

1. $C_{10}H_{16}O_2$
2. $C_{12}H_{20}O_2$
3. $C_{14}H_{24}O_2$

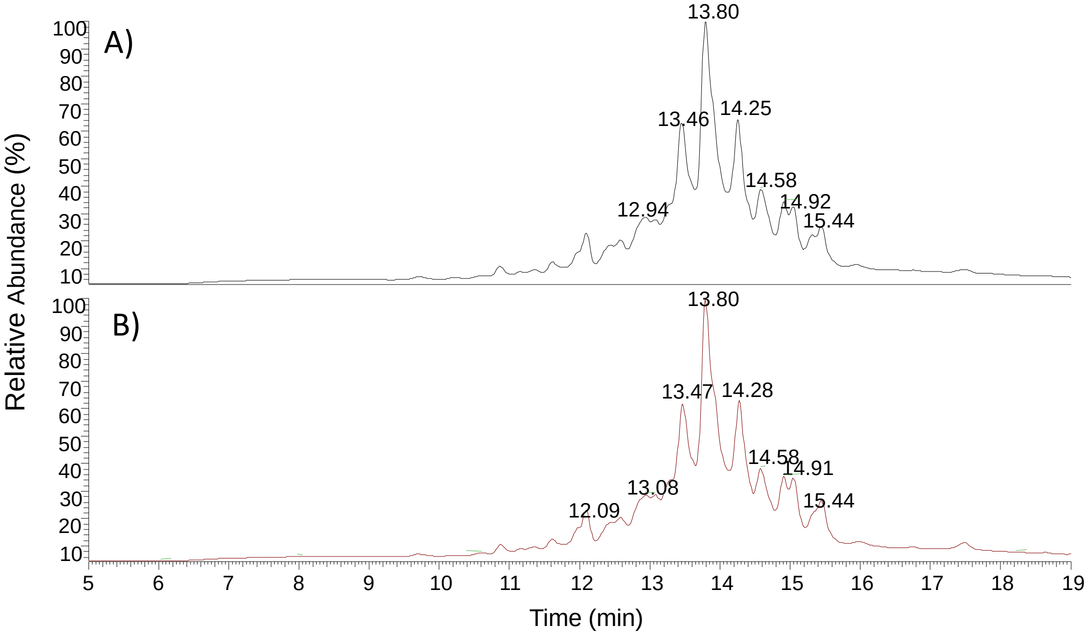


Figure 2. Total ion chromatograms of Refined Merichem oil in water and methanol.
A) TIC of Refined Merichem oil in water at 50 µg/L where 5 mL is injected to the on-line SPE column.
B) TIC of Refined Merichem oil in methanol at 50 mg/L where 5 µL is injected directly to analytical column.

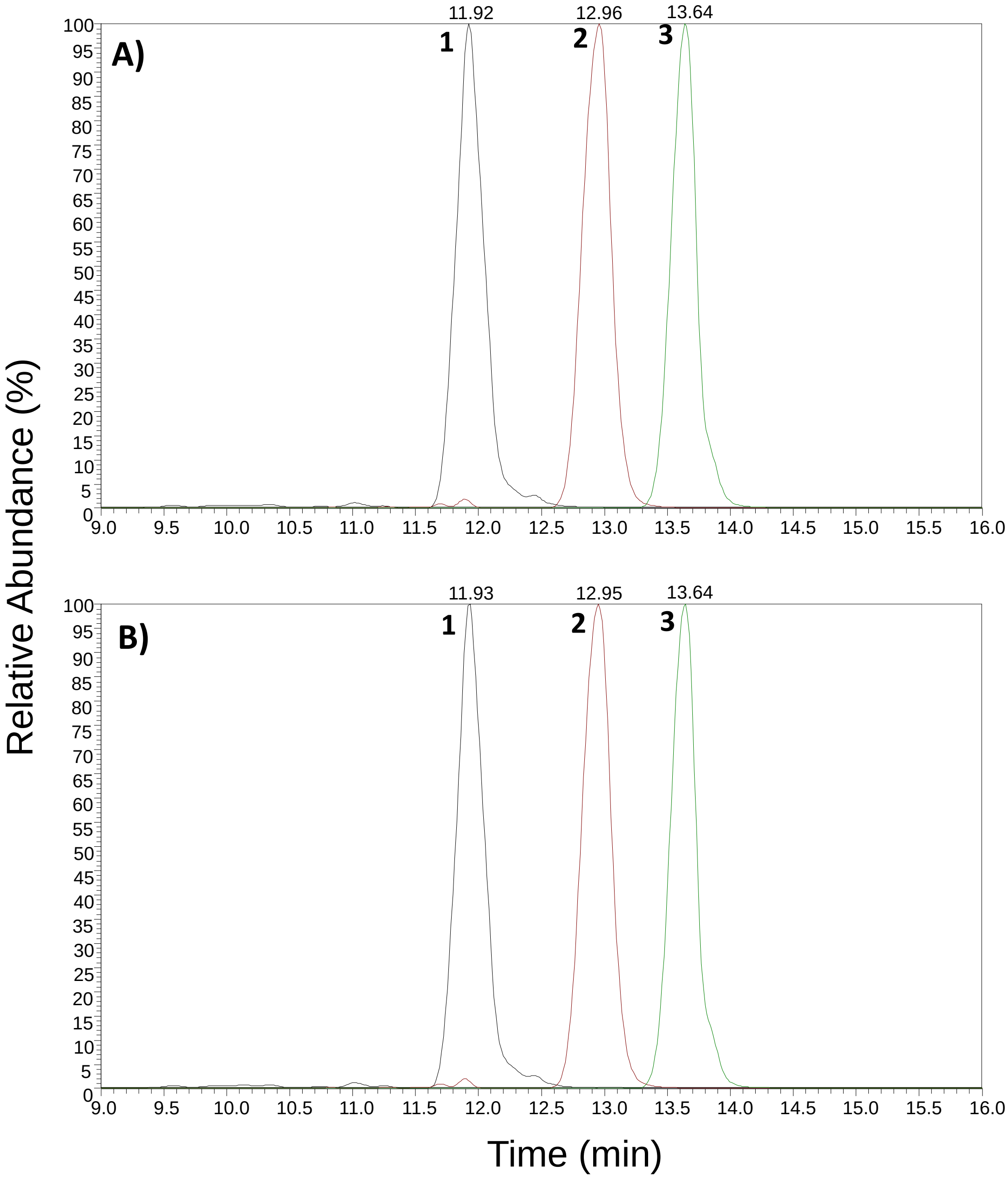


Figure 3. Extracted ion chromatograms of specific naphthenic acids in Refined Merichem oil. [1] – $C_{10}H_{16}O_2$, [2] – $C_{12}H_{20}O_2$, and [3] – $C_{14}H_{24}O_2$.
(A) Refined Merichem oil in water at 50 µg/L, with 5 mL injected to the on-line SPE column.
(B) Refined Merichem oil in methanol at 50 mg/L, with 5 µL injected directly to the analytical column.

The number of theoretical plates (N, equation 1) is an objective measure of chromatographic performance, and is specifically a measure of chromatographic efficiency. It is desirable to maximize N, thus N was calculated for the on-line SPE method according to the following equation, and compared to direct injection.

(1) $$N = 5.545(t_R/W_h)^2$$

Where
t_R is the retention time and
W_h is the width at half the peak height.

Based on the retention times for compound 2, and the widths at half the peak height, the calculated Ns are very similar: 12,567 for the online-SPE and 12,650 for direct injection to the analytical column (Figure 3). For columns with porous particle packing materials, the column performance has a relationship with particle diameter (equation 2), and both the above results are very close to the maximum theoretical value of N (13,160) for a column with 5 cm of length (L) and a particle diameter (dp) of 1.9 µm.

(2) $$N \approx L/2dp$$

Another objective measure of chromatographic performance is the ability of the system to separate any two compounds, and this can be measured by calculating the resolution (Rs, equation 3) for any two analytes. Considering chromatographic peaks 1 and 2, and 2 and 3 (Figure 3), the resolution was nearly identical in the two systems: Rs of 2.31 for peaks 1 and 2, and Rs of 1.51 for peaks 2 and 3, by the on-line SPE analysis, and Rs of 2.32 for peaks 1 and 2, and Rs of 1.53 for peaks 2 and 3 obtained by direct injection to the analytical column.

(3) $$Rs = 1.18((t_{R2} - t_{R1})/(W_{h1}+W_{h2})$$

Therefore, at least for NAs, it is possible to conclude that the online-SPE step did not create any significant band broadening (i.e., widening of the peaks), nor did it have an impact on the chromatographic efficiency or general performance of the method.

3.2 Sensitivity and Linearity

Using the new on-line SPE method, the linearity of the calibration curves constructed for total NAs by the analysis of water spiked with Refined Merichem oil, between 1 and 1,000 µg/L, was good, with correlation coefficients always higher than 0.99 (Figure 4).

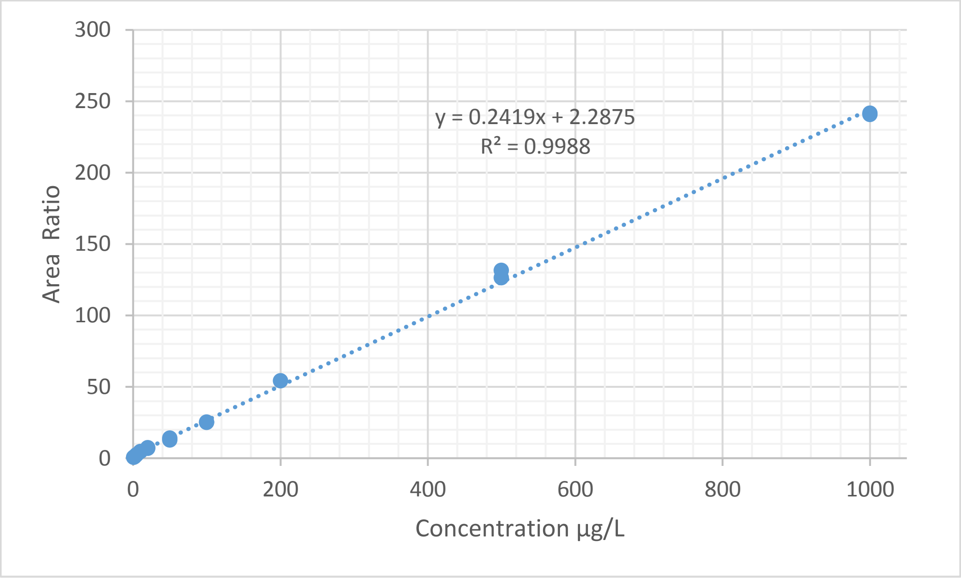


Figure 4. Typical calibration curve for commercial naphthenic acids (Refined Merichem). The area ratio (y-axis) is calculated by the total response of NAs divided by the response of the internal standard.

The sensitivity for the present method is approximately 2 times better than the previous HPLC-QTOF method of Ross et al. (2012) (comparing equivalent mass injected to the system), used for the analysis of NAs in natural waters samples. Other advantages include the very low sample manipulation, and the fact that this Orbitrap mass spectrometer has a much higher resolving power (8 to 10 times) compared to the QTOF instrument for the same compounds (Pereira et al. 2013).

3.3 Analyte Recoveries

The online-SPE recovery was evaluated by calculating the total peak area of NAs from Refined Merichem oil (3 concentrations), compared to equivalent samples that were extracted by the liquid/liquid procedure of Ross et al. (2012) and injected directly. Specifically, liquid/liquid extraction of 1 L of spiked water was performed by reducing the pH to 2 using 98% H_2SO_4, and shaken twice with 200 mL of dichloromethane. The combined extract (400 mL) was then evaporated to near dryness with a rotary evaporator, the remaining volume transferred to a 10 mL glass vial and taken to dryness under a gentle stream of nitrogen at 40 °C. The residue was dissolved in 1 mL of acetone and transferred to a 2 mL vial for analysis, and 5 µL was injected direct to the analytical column using the same conditions described in Table 8.

Figure 5 shows the overall results at 3 concentrations (each in triplicate), and indicates that the recovery by online-SPE is higher and also has lower variability than the common liquid-liquid extraction method.

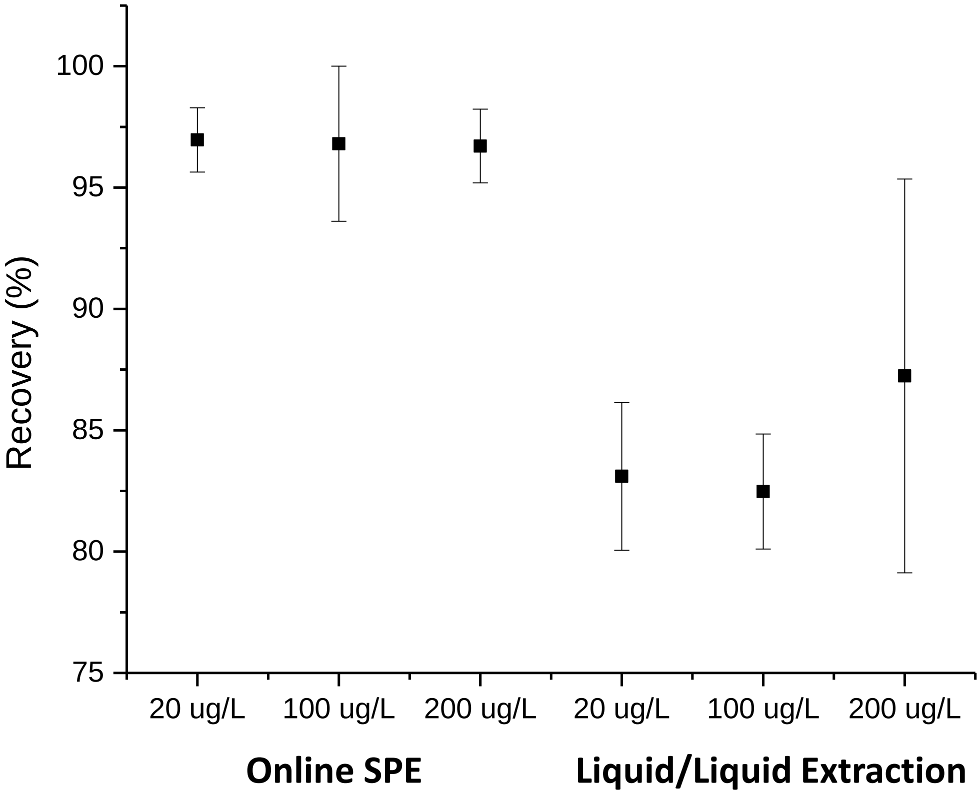


Figure 5. Recovery and precision (plotted as standard deviation) for the online-SPE and liquid/liquid extraction at three concentrations in triplicate.

3.4 Method Precision

The overall method precision (i.e., the repeatability) was calculated as the relative standard deviation (RSD) for the replicate (n = 3) analyses of an authentic OSPW sample diluted 100 times in optima grade HPLC water. This sample can be considered a surrogate for a bitumen-impacted natural water sample in the Athabasca region, as it not only has NAs (~200 µg/L) but also contains other heteroatom-containing species such as O_3, O_4, O_2S, etc… (details about the chemical composition of this sample are provided in Section 3.6). The TIC of three consecutive analyses (injecting 5 mL of the sample to the on-line SPE each time) is shown in Figure 6. These three TIC chromatograms are basically the same, showing high precision of the developed method.

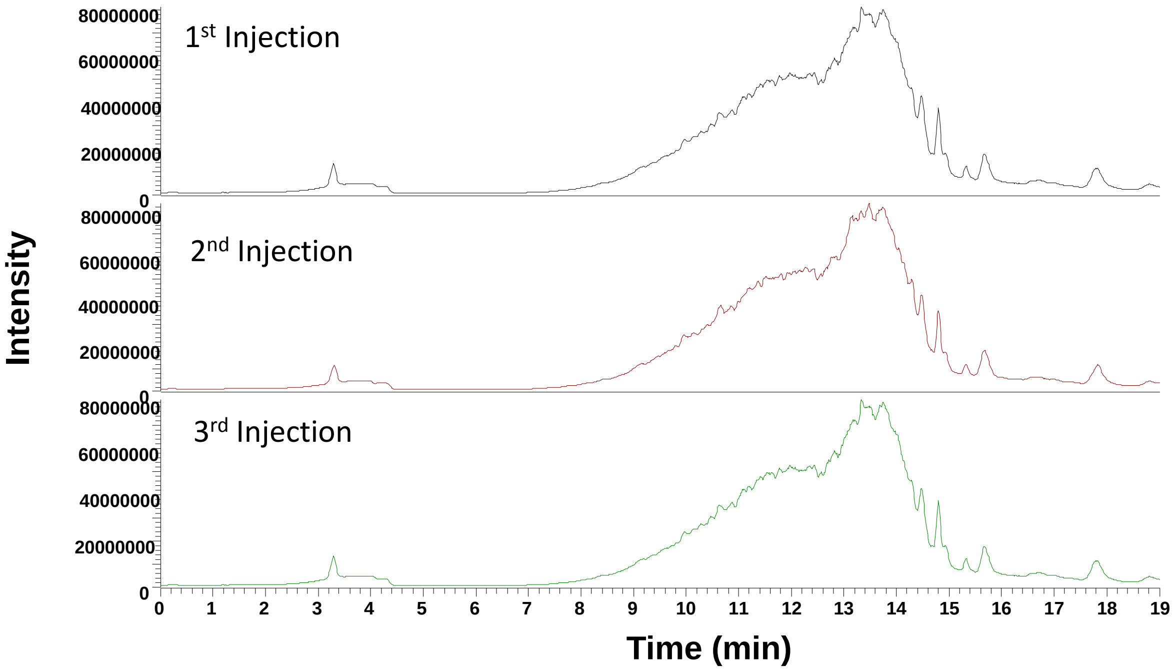


Figure 6. The TIC of three consecutive analyses of an OSPW sample diluted 100 times (5 mL injected on the on-line SPE system).

A more detailed analysis of the method precision was performed by examining individual compound peaks, as shown in Figure 7. The peaks corresponding to an NA ($C_{14}H_{24}O_2$) in three consecutive analyses were near perfectly superimposed (Figure 7A), as was the case for more oxygenated species present in the OSPW. For example, the relative standard deviations of the peak areas were lower than 2.0% (without internal standard correction), as illustrated for $C_{14}H_{20}O_3$ (Figure 7B) and $C_{14}H_{24}O_4$ (Figure 7C).

Precision of results is one of the main advantages of an automated on-line method like this, and can be attributed to little or no manipulation of the sample by any off-line manual method prior to injection.

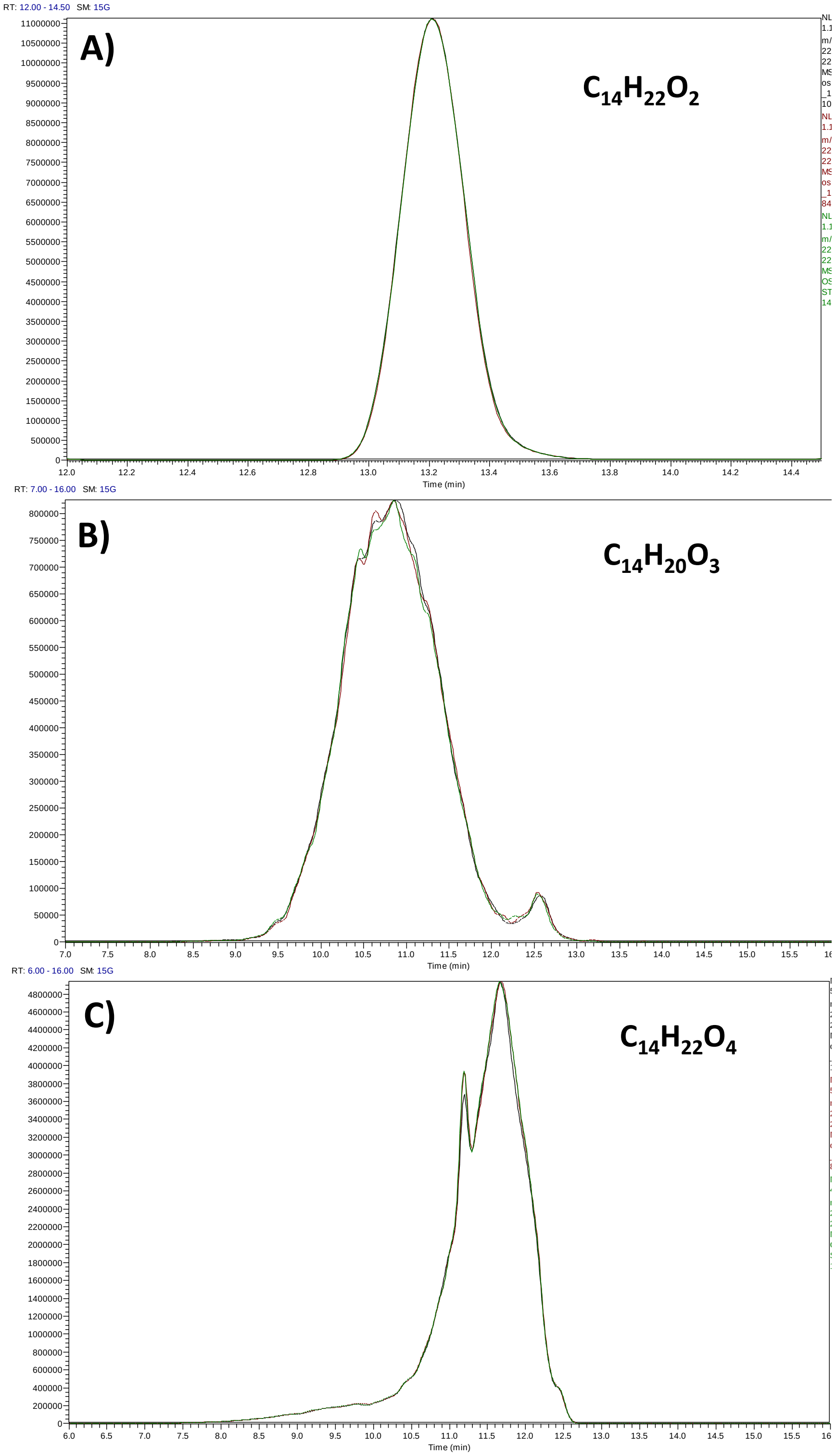


Figure 7. Three superimposed extracted ion chromatograms (black, green, and red trace) for an OSPW sample that was diluted 100 times, of which 5 mL was injected to the on-line SPE system in triplicate.
(A) $C_{14}H_{22}O_2$, (B) $C_{14}H_{20}O_3$ and (C) $C_{14}H_{22}O_4$.

3.5 Naphthenic Acid Profile

To demonstrate the qualitative abilities of the method we compared the NA profiles for a sample of Refined Merichem oil in water at 50 µg/L injected to the on-line SPE column (5 mL injection volume) to a Refined Merichem oil sample dissolved in methanol (50 mg/L) and injected directly to the analytical column (5 µL injection volume). The results (Figure 8) show no evident distortion of the NA profile. This result contributes to the validation of the use of the present method for the NA profiling and consequently as an analytical tool to evaluate the fate or source of a wide range of NAs in the Athabasca region, as is possible with the method of Ross et al. (2012).

3.6 Full Chemical Profile

An additional advantage of the present analytical method, over Ross et al. (2012) is the high resolution of the mass spectrometer used. The resolving power in mass spectrometry is the ability of an instrument to discriminate ions of similar m/z. It can be calculated as $m/\Delta m$, where m is the nominal mass of a given molecule and Δm is the width of the peak at half of its maximum height. For the Orbitrap Elite mass spectrometer, the nominal resolving power was 240,000 at m/z 400, allowing empirical chemical formulas (i.e., $C_nO_xS_yN_z$) to be assigned to each resolved peak with errors (difference between the theoretical and measured m/z) less than 2 ppm.

Figure 9 shows total ion mass spectra (i.e., mass spectra are summed across the entire chromatogram) for a sample of OSPW diluted 100 times and injected to the online-SPE, compared to the same OSPW sample (no dilution) injected directly to the analytical column. The two total ion mass spectra are very similar, and consequently result in very similar full chemical profiles (Figure 10). No quantitative calibration was attempted, thus these data are primarily qualitative, however the online-SPE step did not create any obvious distortion in the distribution of OSPW-derived chemical compounds.

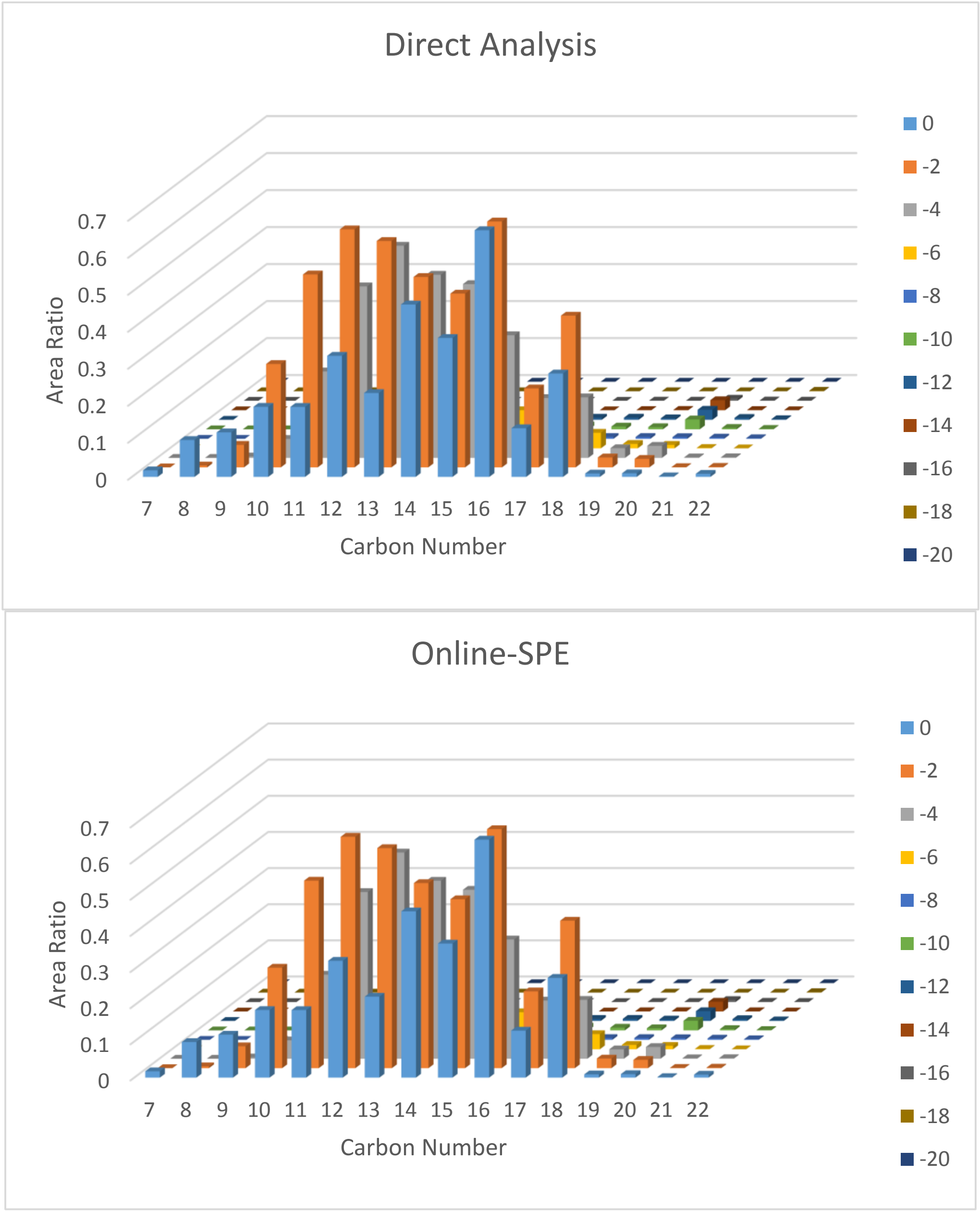


Figure 8. NA profiles ($C_nH_{2n\text{-}Z}O_2$) of Refined Merichem oil dissolved in methanol and injected directly to the analytical column (top panel) compared to the same sample diluted 100x and injected to the on-line SPE system (bottom panel).
Each colour represents a different Z, as indicated in the legends.

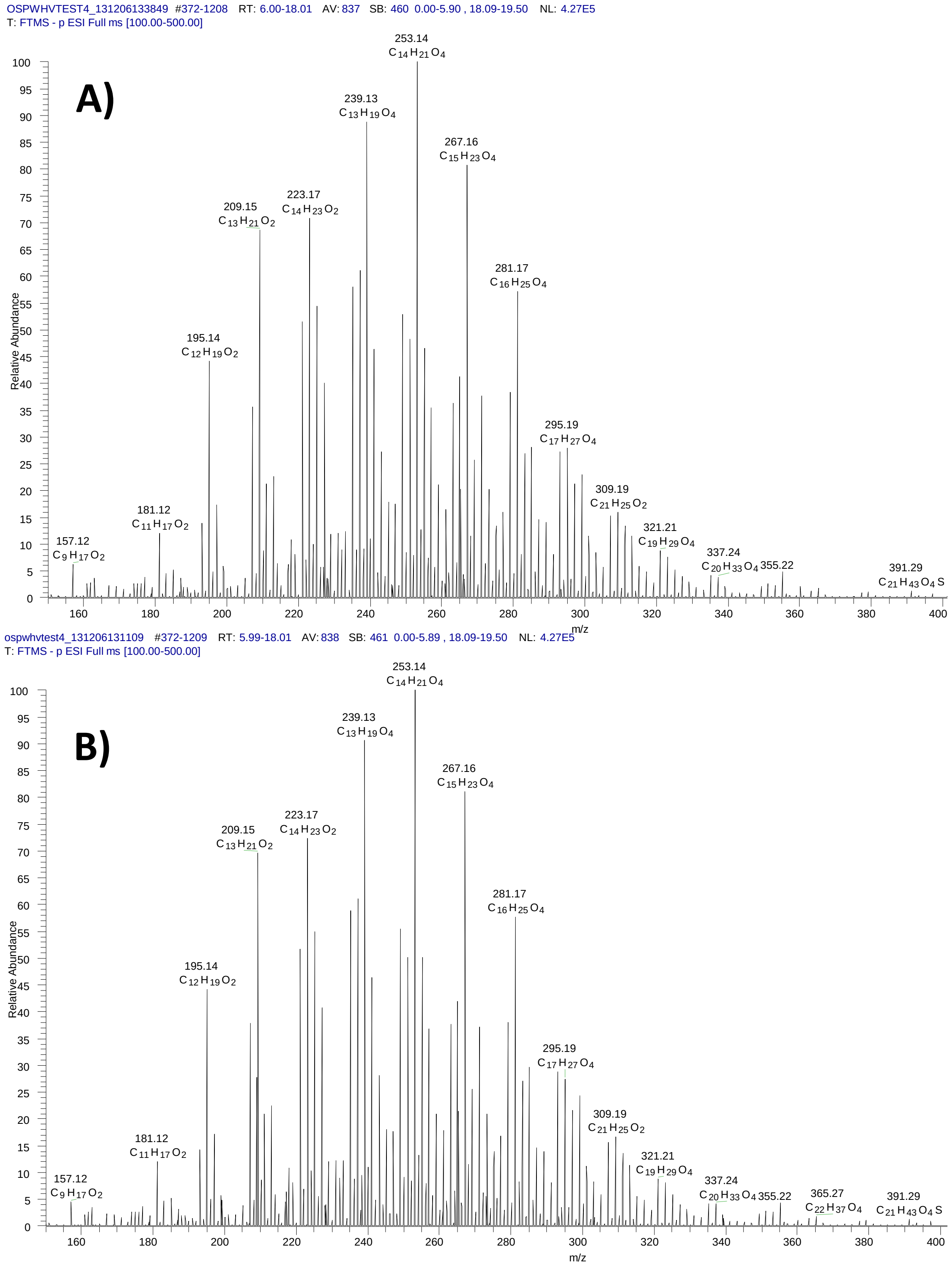


Figure 9. Total mass spectra of OSPW chromatograms acquired by electrospray negative mode.

(A) OSPW diluted 100 times and injected to the online-SPE, and (B) OSPW injected directly to the analytical column.

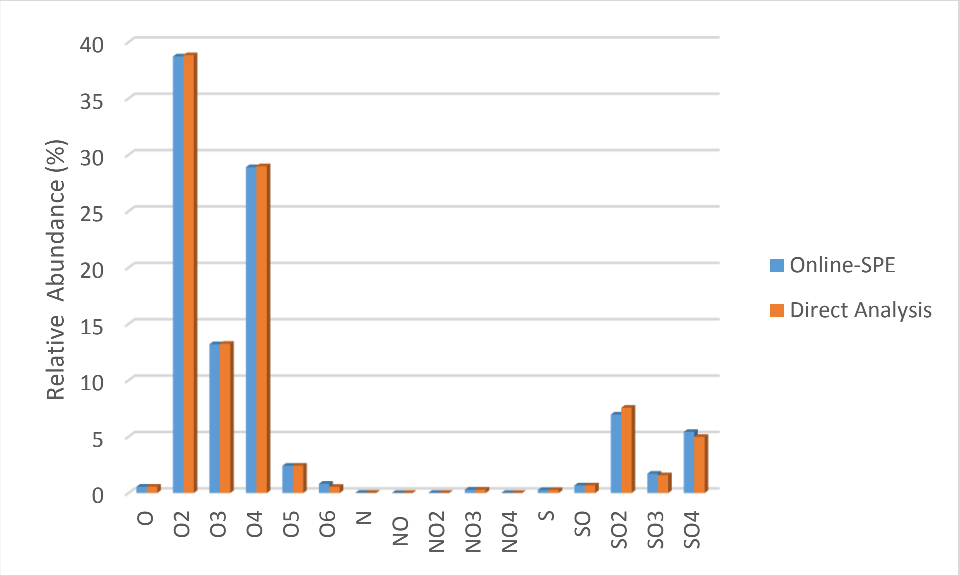


Figure 10. Comparison of total heteroatom class peak area abundance.
Top panel – analysis of OSPW diluted 100 times and injected to the online-SPE.
Bottom panel – sample of OSPW (without dilution) injected directly to the analytical column

4 ANALYSIS OF REAL SAMPLES

The application of the present method to real samples is demonstrated through the analysis of a set of three surface water samples and three groundwater samples collected in the Athabasca oil sands region. Total NA concentration (Table 10) is reported for all water samples, and is based on "adjusted profiles", see below, that are not blank subtracted. However, total response in the blank is very low (<1 µg/L).

Table 10. Naphthenic acid concentration in real samples.

Sample	Concentration (µg/L)
Blank01	<LOQ
Surface Water Samples	
SW01	4.00
SW02	17.6

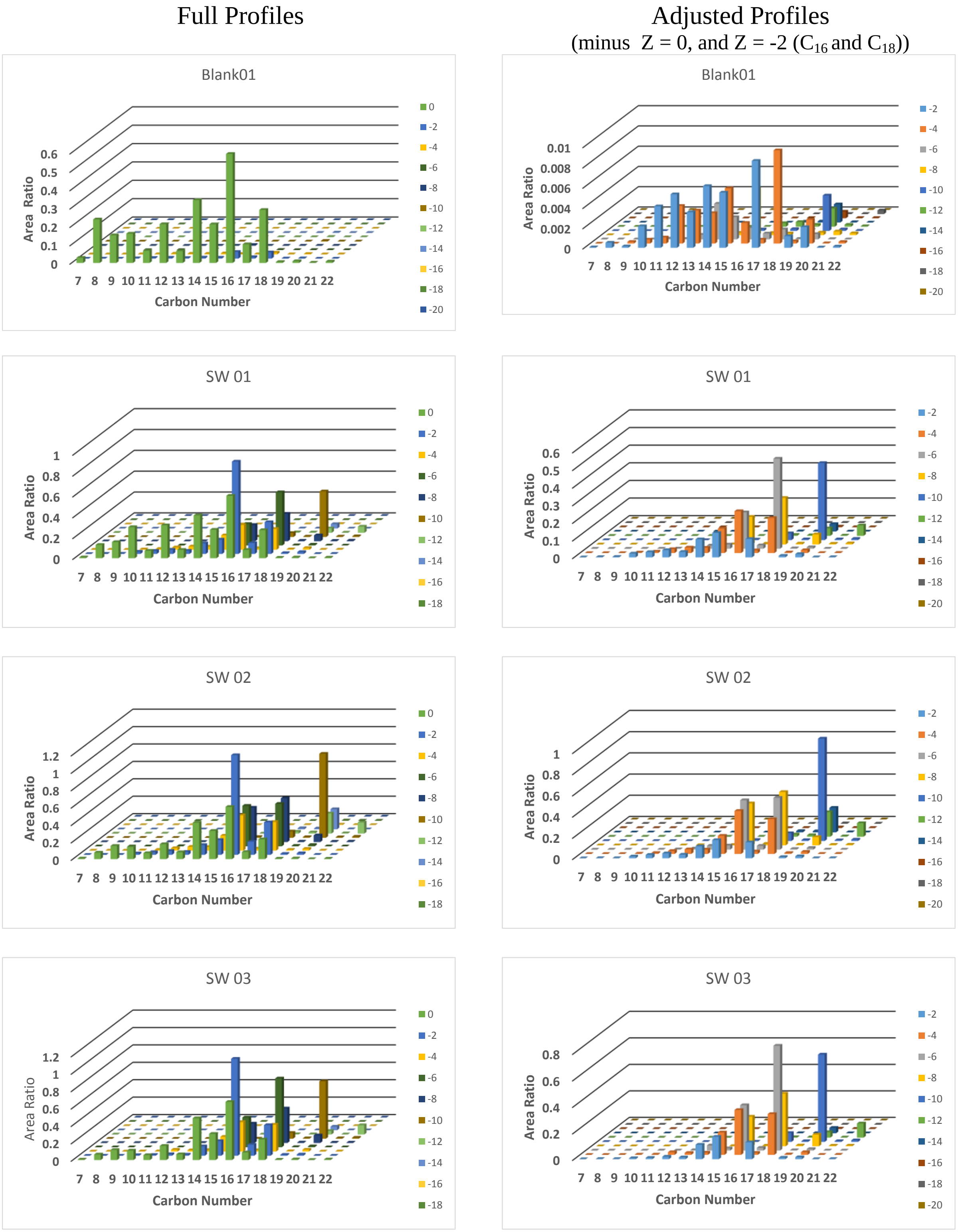
Sample	**Concentration (µg/L)**
SW03	11.1
Groundwater Samples	
GW01	12.8
GW02	30.7
GW03	236

The qualitative homologue profiles are also shown below for all surface water (Figure 11) and groundwater (Figure 12) samples. The full profiles (all NA data) and "adjusted profiles" are shown. The adjusted profiles are made by removing all the signal from Z = 0 NAs, and Z = -2 NAs (C_{16} and C_{18} only), as these are highly influenced by natural (biological) sources, and are only minor NAs in oil sands process-affected water. Thus the adjusted profiles are most useful for tracking bitumen-derived sources of NAs.

5 CONCLUSIONS

The present analytical method has minimal sample manipulation which contributes to enhanced precision and accuracy of quantitative and qualitative NA measurements in water samples, while diminishing the potential for contamination of samples prior to analysis. In the developed method, the on-line SPE pre-concentration and transfer of the extract to the chromatographic system did not affect chromatographic efficiency, and improved limits of detection. High sensitivity and specificity was achieved by the use of Orbitrap mass spectrometry, providing even greater reliability to the data. The method is anticipated to be useful in high-throughput environmental water monitoring for purposes of future environmental compliance by industry, or for forensic source elucidation by monitoring programs and researchers.

The method requires a small investment in equipment to setup ($30 to $50k), but should pay for itself in terms of cost (e.g., solvents and disposable SPEs), and time savings (cost of technician's time in manual SPE or other extraction step), not to mention the more precise and higher quality data that are resultant. Considering the capital cost of any HPLC-ultra-high resolution mass spectrometer system (e.g., minimum $600k), it is the opinion of the authors that the minor additional cost of on-line SPE can be well justified for Provincial and/or Federal water monitoring around oil sands development.



Full Profiles

Adjusted Profiles

(minus Z = 0, and Z = -2 (C_{16} and C_{18}))

Blank01

SW 01

SW 02

SW 03

Figure 11. Three Athabasca River surface water samples analyzed by SPE-HPLC-Orbitrap MS.

Full Profiles

Adjusted Profiles
(minus Z = 0, and Z = -2 (C_{16} and C_{18}))

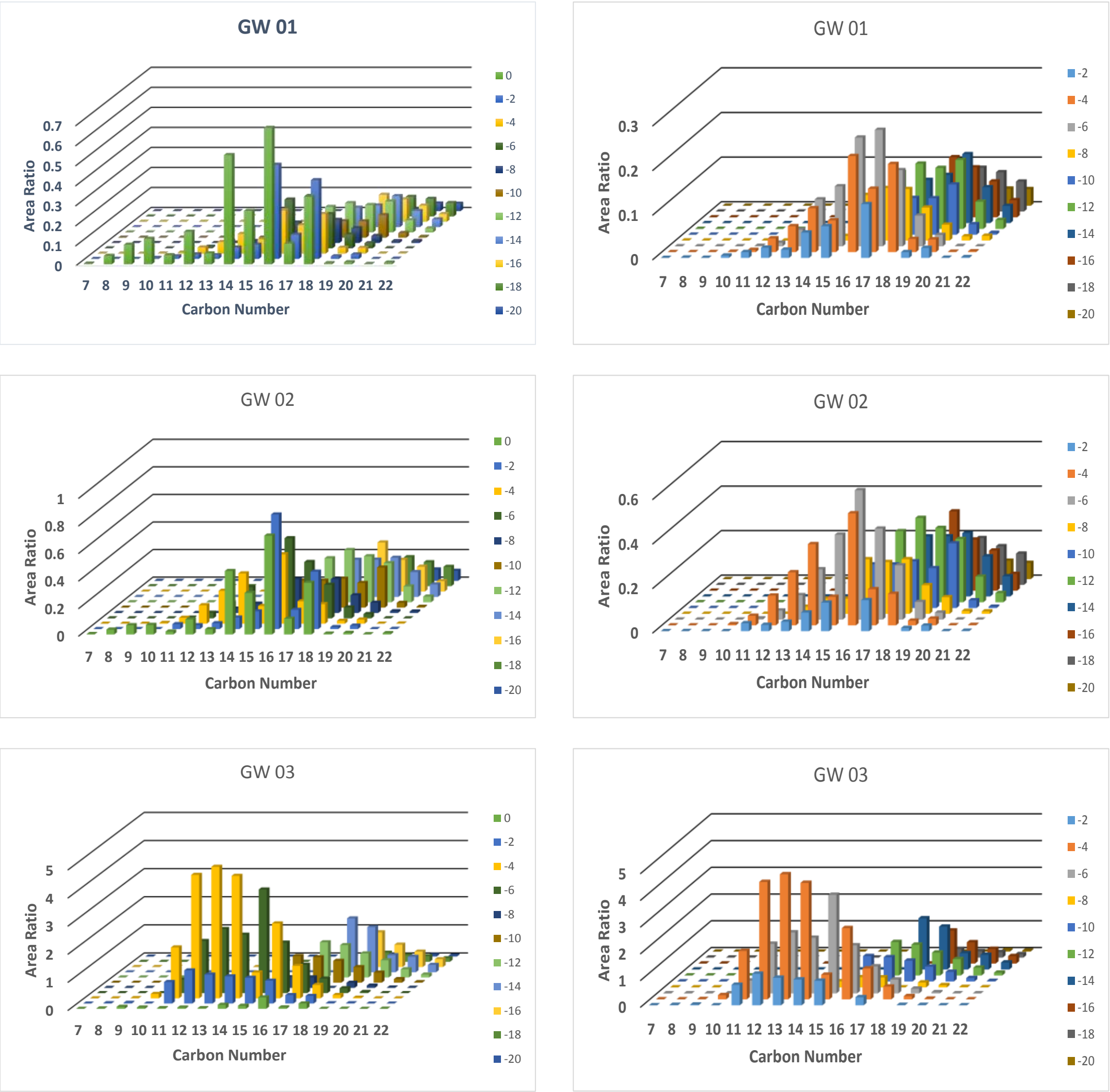


Figure 12. Three bitumen-impacted groundwater samples analyzed by SPE-HPLC-Orbitrap MS.

6 REFERENCES

Birks, S.J., Y. Yi, S. Cho, J.J. Gibson and R. Hazewinkel, 2013. Characterizing the Organic Composition of Snow and Surface Water in the Athabasca Region. Oil Sands Research and Information Network, School of Energy and the Environment, University of Alberta, Edmonton, Alberta. OSRIN Report No. TR-40. 62 pp. http://hdl.handle.net/10402/era.36643 [Last accessed January 2, 2014].

Bones, J., K. Thomas, P.N. Nesterenko and B. Paull, 2006. On-line preconcentration of pharmaceutical residues from large volume water samples using short reversed-phase monolithic cartridges coupled to LC-UV-ESI-MS. Talanta 70(5): 1117-1128.

Díaz-Cruz, M.S., M.J. García-Galán and D. Barceló, 2008. Highly sensitive simultaneous determination of sulfonamide antibiotics and one metabolite in environmental waters by liquid chromatography-quadrupole linear ion trap-mass spectrometry. Journal of Chromatography A 1193(1-2): 50-59.

Environment Canada, n.d. Backgrounder. Joint Canada-Alberta Implementation Plan for Oil Sands Monitoring. http://www.ec.gc.ca/default.asp?lang=En&n=D87FA775-1&news=DC1E489F-7A47-4241-96D3-2E37344833B6 [Last accessed December 11, 2013].

Farré, M., L. Kantiani, M. Petrovic, S. Pérez and D. Barceló, 2012. Achievements and future trends in the analysis of emerging organic contaminants in environmental samples by mass spectrometry and bioanalytical techniques. Journal of Chromatography A 1259: 86-99.

Fontanals, N., F. Borrull and R.M. Marcé, 2013. On-line weak cationic mixed-mode solid-phase extraction coupled to liquid chromatography-mass spectrometry to determine illicit drugs at low concentration levels from environmental waters. Journal of Chromatography A 1286: 16-21.

García-Galán, M.J., M.S. Díaz-Cruz and D. Barceló, 2010. Determination of 19 sulfonamides in environmental water samples by automated on-line solid-phase extraction-liquid chromatography-tandem mass spectrometry (SPE-LC-MS/MS). Talanta 81(1-2): 355-366.

García-Galán, M.J., T. Frömel, J. Müller, M. Peschka, T. Knepper, S. Díaz-Cruz and D. Barceló, 2012. Biodegradation studies of N 4-acetylsulfapyridine and N 4-acetylsulfamethazine in environmental water by applying mass spectrometry techniques. Analytical and Bioanalytical Chemistry 402(9): 2885-2896.

Gibson, J.J., S.J. Birks, M. Moncur, Y. Yi, K. Tattrie, S. Jasechko, K. Richardson, and P. Eby, 2011. Isotopic and Geochemical Tracers for Fingerprinting Process-Affected Waters in the Oil Sands Industry: A Pilot Study. Oil Sands Research and Information Network, School of Energy and the Environment, University of Alberta, Edmonton, Alberta. OSRIN Report No. TR-12. 109 pp. http://hdl.handle.net/10402/era.23000 [Last accessed January 2, 2014].

Government of Alberta, 2011. A world class environmental monitoring, evaluation and reporting system for Alberta. The Report of the Alberta Environmental Monitoring Panel. http://environment.gov.ab.ca/info/library/8381.pdf [Last accessed December 11, 2013].

Gros, M., S. Rodríguez-Mozaz and D. Barceló, 2013. Rapid analysis of multiclass antibiotic residues and some of their metabolites in hospital, urban wastewater and river water by ultra-high-performance liquid chromatography coupled to quadrupole-linear ion trap tandem mass spectrometry. Journal of Chromatography A 1292: 173-188.

Headley, J.V., K.M. Peru, B. Fahlman, A. Colodey and D.W. McMartin, 2013. Selective solvent extraction and characterization of the acid extractable fraction of Athabasca oils sands process waters by Orbitrap mass spectrometry. International Journal of Mass Spectrometry 345-347: 104-108.

Jurado, A., N. Mastroianni, E. Vàzquez-Suñé, J. Carrera, I. Tubau, E. Pujades, C. Postigo, M.L. de Alda and D. Barceló, 2012. Drugs of abuse in urban groundwater. A case study: Barcelona. Science of the Total Environment 424: 280-288.

Kelly, E.N., D.W. Schindler, P.V. Hodson, J.W. Short, R. Radmanovich and C.C. Nielsen, 2010. Oil sands development contributes elements toxic at low concentrations to the Athabasca River and its tributaries. Proceedings of the National Academy of Sciences 107(37): 16178-16183.

Kelly, E.N., J.W. Short, D.W. Schindler, P.V. Hodson, M. Ma, A.K. Kwan and B.L. Fortin, 2009. Oil sands development contributes polycyclic aromatic compounds to the Athabasca River and its tributaries. Proceedings of the National Academy of Sciences 106(52): 22346-22351.

Kuster, M., L.M. De Alda and D. Barceló, 2006. Analysis of pesticides in water by liquid chromatography-tandem mass spectrometric techniques. Mass Spectrometry Reviews 25(6): 900-916.

López-Serna, R., M. Petrović and D. Barceló, 2012. Direct analysis of pharmaceuticals, their metabolites and transformation products in environmental waters using on-line TurboFlow™ chromatography-liquid chromatography-tandem mass spectrometry. Journal of Chromatography A 1252: 115-129.

Marín, J.M., J.V. Sancho, O.J. Pozo, F.J. López and F. Hernández, 2006. Quantification and confirmation of anionic, cationic and neutral pesticides and transformation products in water by on-line solid phase extraction-liquid chromatography-tandem mass spectrometry. Journal of Chromatography A 1133(1-2): 204-214.

Pereira, A.S., S. Bhattacharjee and J.W. Martin, 2013. Characterization of oil sands process-affected waters by liquid chromatography Orbitrap mass spectrometry. Environmental Science and Technology 47(10): 5504-5513.

Postigo, C., M.J. López de Alda, D. Barceló, A. Ginebreda, T. Garrido and J. Fraile, 2010. Analysis and occurrence of selected medium to highly polar pesticides in groundwater of Catalonia (NE Spain): An approach based on on-line solid phase extraction-liquid chromatography-electrospray-tandem mass spectrometry detection. Journal of Hydrology 383(1-2): 83-92.

Repice, C., M.D. Grande, R. Maggi and R. Pedrazzani, 2013. Licit and illicit drugs in a wastewater treatment plant in Verona, Italy. Science of the Total Environment 463-464: 27-34.

Ross, M.S., A.D.S. Pereira, J. Fennell, M. Davies, J. Johnson, L. Sliva and J.W. Martin, 2012. Quantitative and qualitative analysis of naphthenic acids in natural waters surrounding the Canadian oil sands industry. Environmental Science and Technology 46(23): 12796-12805.

Singer, H., S. Jaus, I. Hanke, A. Lück, J. Hollender and A.C. Alder, 2010. Determination of biocides and pesticides by on-line solid phase extraction coupled with mass spectrometry and their behaviour in wastewater and surface water. Environmental Pollution 158(10): 3054-3064.

Trenholm, R.A., B.J. Vanderford and S.A. Snyder, 2009. On-line solid phase extraction LC-MS/MS analysis of pharmaceutical indicators in water: A green alternative to conventional methods. Talanta 79(5): 1425-1432.

7 GLOSSARY

7.1 Terms

Accuracy

The degree of closeness of measurements of a quantity to that quantity's actual (true) value.

Analyte

The chemical being analyzed.

Band Broadening

In chromatography, this is the result of the analyte's longitudinal diffusion within the analytical column, resulting in wider chromatographic peaks. This should always be minimized.

Efficiency

In chromatography, the efficiency of a system is effectively a measure of peak width, with smaller peak widths being most desirable. Efficiency can be measured quantitatively by the theoretical plates. Band broadening reduces efficiency.

Electrospray Negative Mode

Electrospray is an ionization source, which operates at the interface between HPLC and mass spectrometry. It is useful because it effectively removes charged analytes from solution (e.g., in HPLC the analytes are dissolved in water/solvent) into the gas-phase, such that they may enter the mass spectrometer and be analyzed. Acids, such as naphthenic acids, are negatively charged in solution, thus “negative mode” is used in the current work to analyze all negatively charged analytes.

Elute

To desorb the analytes from a solid matrix (e.g., SPE or analytical column), usually by means of a solvent.

Heteroatom

In organic chemistry, a heteroatom is any atom that is not carbon or hydrogen. Usually, the term is used to indicate that non-carbon atoms have replaced carbon in the backbone of the molecular structure. Typical heteroatoms are nitrogen, oxygen, sulfur, phosphorus, chlorine, bromine, and iodine.

Homologue

A series of compounds with a similar general formula, but varying by the length of a carbon chain (number of CH_2 groups). Because homologues typically have a fixed set of functional groups, these compounds have similar chemical and physical properties.

Mass Spectrometry

An instrumental method for identifying the chemical constitution of a substance by means of the separation of gaseous ions according to their differing mass and charge.

Refined Merichem Oil

This oil can be purchased commercially from the Merichem Company (Houston, TX) and is useful because it is a relatively pure form of naphthenic acids (a complex mixture of homologues, nevertheless) that can be used to calibrate or validate analytical methods designed to detect naphthenic acids in environmental samples.

Polyoxygenated Compounds

A compound or group of compounds containing more than two oxygen atoms.

Precision

The degree to which repeated measurements under unchanged conditions show the same results.

Retention Time

The amount of time elapsed from the injection of a sample into the chromatographic system to the recording of the peak elution (maximum) of the component in the chromatogram.

Theoretical Plates (N)

Also termed plate number. It is a number indicative of chromatographic column performance. Higher numbers of theoretical plates are desirable.

7.2 Acronyms

FTICR-MS	Fourier Transform Ion Cyclotron Resonance – Mass Spectrometry
HPLC	High Pressure Liquid Chromatography
LC-MS	Liquid Chromatography-Mass Spectrometry
LOQ	Limit of Quantification
NA	Naphthenic Acid
OSPW	Oil Sands Process-affected Water
OSRIN	Oil Sands Research and Information Network
QTOF	Quadropole Time of Flight
RSD	Relative Standard Deviation

SEE	School of Energy and the Environment
SPE	Solid Phase Extraction
TIC	Total Ion Chromatogram

7.3 Measurements

mg/L	milligram per litre
mL	millilitre
ng	nanogram
µg	microgram
µg/L	microgram per litre
µL	microlitre

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OSRIN Technical Reports – http://hdl.handle.net/10402/era.17507

BGC Engineering Inc., 2010. Oil Sands Tailings Technology Review. OSRIN Report No. TR-1. 136 pp. http://hdl.handle.net/10402/era.17555

BGC Engineering Inc., 2010. Review of Reclamation Options for Oil Sands Tailings Substrates. OSRIN Report No. TR-2. 59 pp. http://hdl.handle.net/10402/era.17547

Chapman, K.J. and S.B. Das, 2010. Survey of Albertans' Value Drivers Regarding Oil Sands Development and Reclamation. OSRIN Report TR-3. 13 pp. http://hdl.handle.net/10402/era.17584

Jones, R.K. and D. Forrest, 2010. Oil Sands Mining Reclamation Challenge Dialogue – Report and Appendices. OSRIN Report No. TR-4. 258 pp. http://hdl.handle.net/10402/era.19092

Jones, R.K. and D. Forrest, 2010. Oil Sands Mining Reclamation Challenge Dialogue – Report. OSRIN Report No. TR-4A. 18 pp. http://hdl.handle.net/10402/era.19091

James, D.R. and T. Vold, 2010. Establishing a World Class Public Information and Reporting System for Ecosystems in the Oil Sands Region – Report and Appendices. OSRIN Report No. TR-5. 189 pp. http://hdl.handle.net/10402/era.19093

James, D.R. and T. Vold, 2010. Establishing a World Class Public Information and Reporting System for Ecosystems in the Oil Sands Region – Report. OSRIN Report No. TR-5A. 31 pp. http://hdl.handle.net/10402/era.19094

Lott, E.O. and R.K. Jones, 2010. Review of Four Major Environmental Effects Monitoring Programs in the Oil Sands Region. OSRIN Report No. TR-6. 114 pp. http://hdl.handle.net/10402/65.20287

Godwalt, C., P. Kotecha and C. Aumann, 2010. Oil Sands Tailings Management Project. OSRIN Report No. TR-7. 64 pp. http://hdl.handle.net/10402/era.22536

Welham, C., 2010. Oil Sands Terrestrial Habitat and Risk Modeling for Disturbance and Reclamation – Phase I Report. OSRIN Report No. TR-8. 109 pp. http://hdl.handle.net/10402/era.22567

Schneider, T., 2011. Accounting for Environmental Liabilities under International Financial Reporting Standards. OSRIN Report TR-9. 16 pp. http://hdl.handle.net/10402/era.22741

Davies, J. and B. Eaton, 2011. Community Level Physiological Profiling for Monitoring Oil Sands Impacts. OSRIN Report No. TR-10. 44 pp. http://hdl.handle.net/10402/era.22781

Hurndall, B.J., N.R. Morgenstern, A. Kupper and J. Sobkowicz, 2011. Report and Recommendations of the Task Force on Tree and Shrub Planting on Active Oil Sands Tailings Dams. OSRIN Report No. TR-11. 15 pp. http://hdl.handle.net/10402/era.22782

Gibson, J.J., S.J. Birks, M. Moncur, Y. Yi, K. Tattrie, S. Jasechko, K. Richardson, and P. Eby, 2011. Isotopic and Geochemical Tracers for Fingerprinting Process-Affected Waters in the Oil Sands Industry: A Pilot Study. OSRIN Report No. TR-12. 109 pp. http://hdl.handle.net/10402/era.23000

Oil Sands Research and Information Network, 2011. Equivalent Land Capability Workshop Summary Notes. OSRIN Report TR-13. 83 pp. http://hdl.handle.net/10402/era.23385

Kindzierski, W., J. Jin and M. Gamal El-Din, 2011. Plain Language Explanation of Human Health Risk Assessment. OSRIN Report TR-14. 37 pp. http://hdl.handle.net/10402/era.23487

Welham, C. and B. Seely, 2011. Oil Sands Terrestrial Habitat and Risk Modelling for Disturbance and Reclamation – Phase II Report. OSRIN Report No. TR-15. 93 pp. http://hdl.handle.net/10402/era.24547

Morton Sr., M., A. Mullick, J. Nelson and W. Thornton, 2011. Factors to Consider in Estimating Oil Sands Plant Decommissioning Costs. OSRIN Report No. TR-16. 62 pp. http://hdl.handle.net/10402/era.24630

Paskey, J. and G. Steward, 2012. The Alberta Oil Sands, Journalists, and Their Sources. OSRIN Report No. TR-17. 33 pp. http://hdl.handle.net/10402/era.25266

Cruz-Martinez, L. and J.E.G. Smits, 2012. Potential to Use Animals as Monitors of Ecosystem Health in the Oil Sands Region – July 2013 Update. OSRIN Report No. TR-18. 59 pp. http://hdl.handle.net/10402/era.25417

Hashisho, Z., C.C. Small and G. Morshed, 2012. Review of Technologies for the Characterization and Monitoring of VOCs, Reduced Sulphur Compounds and CH_4. OSRIN Report No. TR-19. 93 pp. http://hdl.handle.net/10402/era.25522

Kindzierski, W., J. Jin and M. Gamal El-Din, 2012. Review of Health Effects of Naphthenic Acids: Data Gaps and Implications for Understanding Human Health Risk. OSRIN Report No. TR-20. 43 pp. http://hdl.handle.net/10402/era.26060

Zhao, B., R. Currie and H. Mian, 2012. Catalogue of Analytical Methods for Naphthenic Acids Related to Oil Sands Operations. OSRIN Report No. TR-21. 65 pp. http://hdl.handle.net/10402/era.26792

Oil Sands Research and Information Network and Canadian Environmental Assessment Agency, 2012. Summary of the Oil Sands Groundwater – Surface Water Interactions Workshop. OSRIN Report No. TR-22. 125 pp. http://hdl.handle.net/10402/era.26831

Valera, E. and C.B. Powter, 2012. Implications of Changing Environmental Requirements on Oil Sands Royalties. OSRIN Report No. TR-23. 21 pp. http://hdl.handle.net/10402/era.27344

Dixon, R., M. Maier, A. Sandilya and T. Schneider, 2012. Qualifying Environmental Trusts as Financial Security for Oil Sands Reclamation Liabilities. OSRIN Report No. TR-24. 32 pp. http://hdl.handle.net/10402/era.28305

Creasey, R., 2012. Workshop on the Information that Professionals Would Look for in Mineable Oil Sands Reclamation Certification. OSRIN Report No. TR-25. 52 pp. http://hdl.handle.net/10402/era.28331

Alberta Innovates – Technology Futures, 2012. Investigating a Knowledge Exchange Network for the Reclamation Community. OSRIN Report No. TR-26. 42 pp. http://hdl.handle.net/10402/era.28407

Dixon, R.J., J. Kenney and A.C. Sandilya, 2012. Audit Protocol for the Mine Financial Security Program. OSRIN Report No. TR-27. 27 pp. http://hdl.handle.net/10402/era.28514

Davies, J., B. Eaton and D. Humphries, 2012. Microcosm Evaluation of Community Level Physiological Profiling in Oil Sands Process Affected Water. OSRIN Report No. TR-28. 33 pp. http://hdl.handle.net/10402/era.29322

Thibault, B., 2012. Assessing Corporate Certification as Impetus for Accurate Reporting in Self-Reported Financial Estimates Underlying Alberta's Mine Financial Security Program. OSRIN Report No. TR-29. 37 pp. http://hdl.handle.net/10402/era.29361

Pyper, M.P., C.B. Powter and T. Vinge, 2013. Summary of Resiliency of Reclaimed Boreal Forest Landscapes Seminar. OSRIN Report No. TR-30. 131 pp. http://hdl.handle.net/10402/era.30360

Pyper, M. and T. Vinge, 2013. A Visual Guide to Handling Woody Materials for Forested Land Reclamation. OSRIN Report No. TR-31. 10 pp. http://hdl.handle.net/10402/era.30381

Mian, H., N. Fassina, A. Mukherjee, A. Fair and C.B. Powter, 2013. Summary of 2013 Tailings Technology Development and Commercialization Workshop. OSRIN Report No. TR-32. 69 pp. http://hdl.handle.net/10402/era.31012

Howlett, M. and J. Craft, 2013. Application of Federal Legislation to Alberta's Mineable Oil Sands. OSRIN Report No. TR-33. 94 pp. http://hdl.handle.net/10402/era.31627

Welham, C., 2013. Factors Affecting Ecological Resilience of Reclaimed Oil Sands Uplands. OSRIN Report No. TR-34. 44 pp. http://hdl.handle.net/10402/era.31714

Naeth, M.A., S.R. Wilkinson, D.D. Mackenzie, H.A. Archibald and C.B. Powter, 2013. Potential of LFH Mineral Soil Mixes for Land Reclamation in Alberta. OSRIN Report No. TR-35. 64 pp. http://hdl.handle.net/10402/era.31855

Welham, C. and B. Seely, 2013. Oil Sands Terrestrial Habitat and Risk Modelling for Disturbance and Reclamation: The Impact of Climate Change on Tree Regeneration and Productivity – Phase III Report. OSRIN Report No. TR-36. 65 pp. http://hdl.handle.net/10402/era.31900

Eaton, B., T. Muhly, J. Fisher and S-L. Chai, 2013. Potential Impacts of Beaver on Oil Sands Reclamation Success – an Analysis of Available Literature. OSRIN Report No. TR-37. 65 pp. http://hdl.handle.net/10402/era.32764

Paskey, J., G. Steward and A. Williams, 2013. The Alberta Oil Sands Then and Now: An Investigation of the Economic, Environmental and Social Discourses Across Four Decades. OSRIN Report No. TR-38. 108 pp. http://hdl.handle.net/10402/era.32845

Watson, B.M. and G. Putz, 2013. Preliminary Watershed Hydrology Model for Reclaimed Oil Sands Sites. OSRIN Report No. TR-39. 193 pp. http://hdl.handle.net/10402/era.34250

Birks, S.J., Y. Yi, S. Cho, J.J. Gibson and R. Hazewinkel, 2013. Characterizing the Organic Composition of Snow and Surface Water in the Athabasca Region. OSRIN Report No. TR-40. 62 pp. http://hdl.handle.net/10402/era.36643

De Corby, R.G., 2013. Development of Silicon-Based Optofluidic Sensors for Oil Sands Environmental Monitoring. OSRIN Report No. TR-41. 19 pp. http://hdl.handle.net/10402/era.36936

Iqbal, M., T.K. Purkait, J.G.C. Veinot and G.G. Goss, 2013. Benign-by-Design: Synthesis of Engineered Silicon Nanoparticles and their Application to Oil Sands Water Contaminant Remediation. OSRIN Report No. TR-42. 30 pp. http://hdl.handle.net/10402/era.37308

Oil Sands Research and Information Network, 2013. Future of Shrubs in Oil Sands Reclamation Workshop. OSRIN Report No. TR-43. 71 pp. http://hdl.handle.net/10402/era.37440

Smreciu, A., K. Gould and S. Wood, 2013. Boreal Plant Species for Reclamation of Athabasca Oil Sands Disturbances. OSRIN Report No. TR-44. 23 pp. plus appendices. http://hdl.handle.net/10402/era.37533

OSRIN Videos – http://hdl.handle.net/10402/era.29304

Rooney Productions, 2012. Assessment Methods for Oil Sands Reclamation Marshes. OSRIN Video No. V-1. 20 minutes. Also available on the University of Alberta You Tube Channel (recommended approach).

Rooney Productions, 2012. Assessment Methods for Oil Sands Reclamation Marshes. OSRIN Video No. V-1. Nine-part mobile device version. Also available on the University of Alberta You Tube Channel (link to Part 1 - recommended approach).

OSRIN Staff Reports – http://hdl.handle.net/10402/era.19095

OSRIN, 2010. Glossary of Terms and Acronyms used in Oil Sands Mining, Processing and Environmental Management – December 2013 Update. OSRIN Report No. SR-1. 123 pp. http://hdl.handle.net/10402/era.17544

OSRIN, 2010. OSRIN Writer's Style Guide – November 2013 Update. OSRIN Report No. SR-2. 29 pp. http://hdl.handle.net/10402/era.17545

OSRIN, 2010. OSRIN Annual Report: 2009/2010. OSRIN Report No. SR-3. 27 pp. http://hdl.handle.net/10402/era.17546

OSRIN, 2010. Guide to OSRIN Research Grants and Services Agreements - June 2011 Update. OSRIN Report No. SR-4. 21 pp. http://hdl.handle.net/10402/era.17558

OSRIN, 2011. Summary of OSRIN Projects – December 2013 Update. OSRIN Report No. SR-5. 97 pp. http://hdl.handle.net/10402/era.20529

OSRIN, 2011. OSRIN Annual Report: 2010/11. OSRIN Report No. SR-6. 34 pp. http://hdl.handle.net/10402/era.23032

OSRIN, 2011. OSRIN's Design and Implementation Strategy. OSRIN Report No. SR-7. 10 pp. http://hdl.handle.net/10402/era.23574

OSRIN, 2012. OSRIN Annual Report: 2011/12. OSRIN Report No. SR-8. 25 pp. http://hdl.handle.net/10402/era.26715

OSRIN, 2013. OSRIN Annual Report: 2012/13. OSRIN Report No. SR-9. 56 pp. http://hdl.handle.net/10402/era.31211