

# Athabasca Oil Sands Process Water: Characterization by Atmospheric Pressure Photoionization and Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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The Athabasca oil sands in Canada are a less conventional source of oil which have seen rapid development. There are concerns about the environmental impact, with particular respect to components in oil sands process water which may enter the aquatic ecosystem. Naphthenic acids have been previously targeted for study, due to their implications in toxicity toward aquatic wildlife, but it is believed that other components, too, contribute toward the potential toxicity of the oil sands process water. When mass spectrometry is used, it is necessary to use instrumentation with a high resolving power and mass accuracy when studying complex mixtures, but the technique has previously been hindered by the range of compounds that have been accessible via common ionization techniques, such as electrospray ionization. The research described here applied Fourier transform ion cyclotron resonance mass spectrometry in conjunction with electrospray ionization and atmospheric pressure photoionization, in both positive-ion and negative-ion modes, to the characterization of oil sands process water for the first time. The results highlight the need for broader characterization when investigating toxic components within oil sands process water.

Crude oil is used for a diverse range of products, including fuels, plastics, solvents, waxes, lubricants, and dyes, among others, and is, therefore, a vital resource for many industries. As the worldwide demand for petroleum continues to grow, previously nonviable sources of oil are increasingly pursued. One such source is the Athabasca oil sands in Canada and, with 174 billion barrels of bitumen available using current technology, it represents the second largest known reserve in the world. Canada is currently the top supplier of oil to the U.S.A. Oil sands are a mixture of clay, sand, water, and bitumen. The bitumen is extracted from the oil sands raw material prior to being “upgraded” to a synthetic oil. Approximately three barrels of water are required for produc-

tion of one barrel of oil. The oil sands process water is recycled and is stored in vast tailings ponds.

Among the components of crude oils, naphthenic acids are of particular interest due to their implication in corrosion<sup>1,2</sup> and toxicity toward wildlife.<sup>3–7</sup> These compounds have traditionally been defined as carboxylic acids which contain one or more saturated ring structures; they are also frequently defined by the empirical formula:  $C_nH_{2n+Z}O_2$ , where  $Z$  is a negative, even integer;  $Z$  may also be referred to as the measure of the “hydrogen deficiency” of the molecule. The petroleum industry is concerned with the presence of naphthenic acids in crude oils due to their implication in corrosion.<sup>2</sup> Disposal of the acids is problematic due to the toxicity toward aquatic organisms. The aquatic toxicity is associated with the concentration and surfactant characteristics of the naphthenic acids. Crude oils typically contain naphthenic acids in quantities up to 4% by weight, while the carboxylic acid fraction is approximately 2% in unrefined Athabasca bitumen. While ambient levels of naphthenic acids in Alberta rivers are generally below 1 mg/L, levels in oil sands process water (OSPW) may reach 110 mg/L. Naphthenic acids may enter surface water systems through such mechanisms as groundwater mixing and erosion of riverbank oil deposits in oil producing regions. Mass spectrometry has played an important role in the characterization of naphthenic acids from a range of sources<sup>8–22</sup> and has been affording insight into such phenomena as the presence of the ARN (an old Norwegian

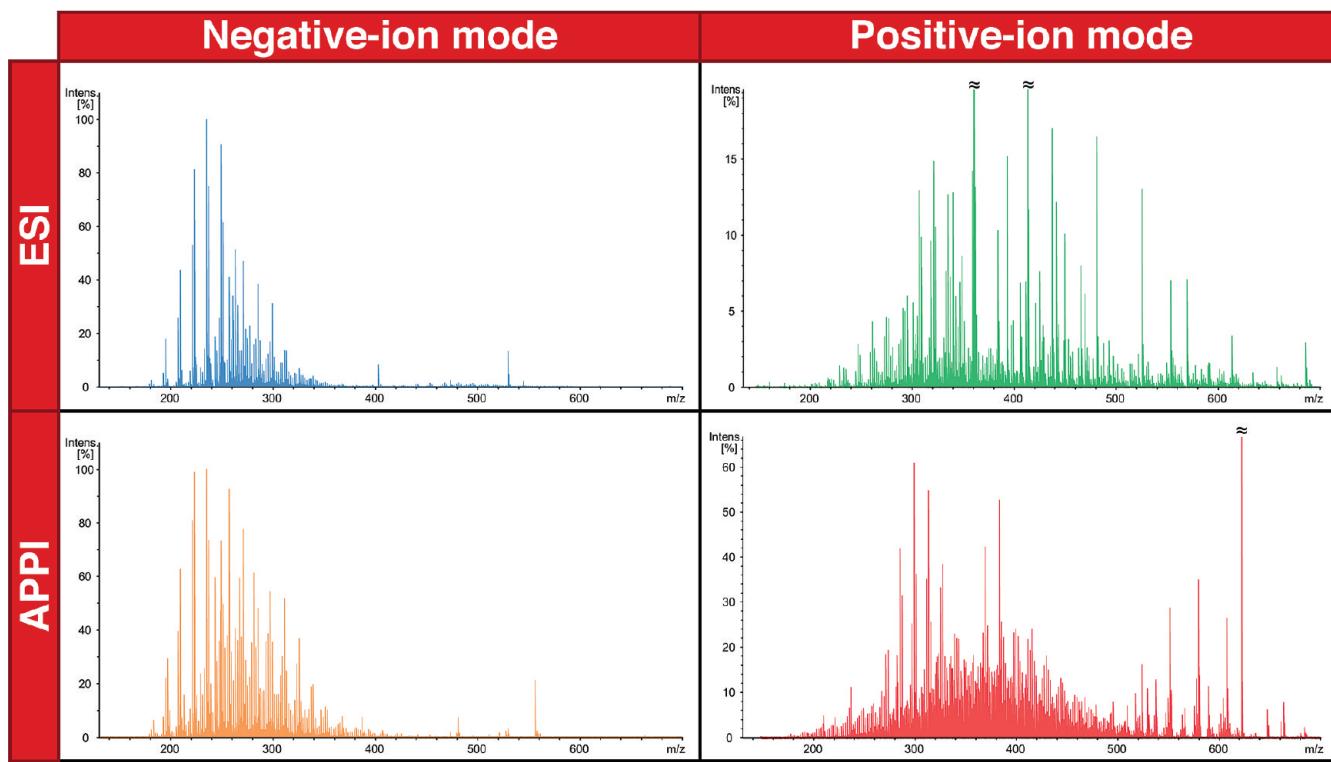
- (1) Slavcheva, E.; Shone, B.; Turnbull, A. *Br. Corros. J.* **1999**, *34*, 125–131.
- (2) Turnbull, A.; Slavcheva, E.; Shone, B. *Corrosion* **1998**, *54*, 922–930.
- (3) Rogers, V. V.; Wickstrom, M.; Liber, K.; MacKinnon, M. D. *Toxicol. Sci.* **2002**, *66*, 347–355.
- (4) Leung, S. S.; MacKinnon, M. D.; Smith, R. E. H. *Aquat. Toxicol.* **2003**, *62*, 11–26.
- (5) Clemente, J. S.; Fedorak, P. M. *Chemosphere* **2005**, *60*, 585–600.
- (6) Nero, V.; Farwell, A.; Lee, L. E. J.; Van Meer, T.; MacKinnon, M. D.; Dixon, D. G. *Ecoxicol. Environ. Saf.* **2006**, *65*, 252–264.
- (7) Lo, C. C.; Brownlee, B. G.; Bunce, N. J. *Water Res.* **2006**, *40*, 655–664.
- (8) Dzidic, I.; Somerville, A. C.; Raia, J. C.; Hart, H. V. *Anal. Chem.* **1988**, *60*, 1318–1323.
- (9) Fan, T. P. *Energy Fuels* **1991**, *5*, 371–375.
- (10) St. John, W. P.; Rughani, J.; Green, S. A.; McGinnis, G. D. *J. Chromatogr., A* **1998**, *807*, 241–251.
- (11) Hsu, C. S.; Dechert, G. J.; Robbins, W. K.; Fukuda, E. K. *Energy Fuels* **2000**, *14*, 217–223.
- (12) Rudzinski, W. E.; Oehlers, L.; Zhang, Y.; Najera, B. *Energy Fuels* **2002**, *16*, 1178–1185.

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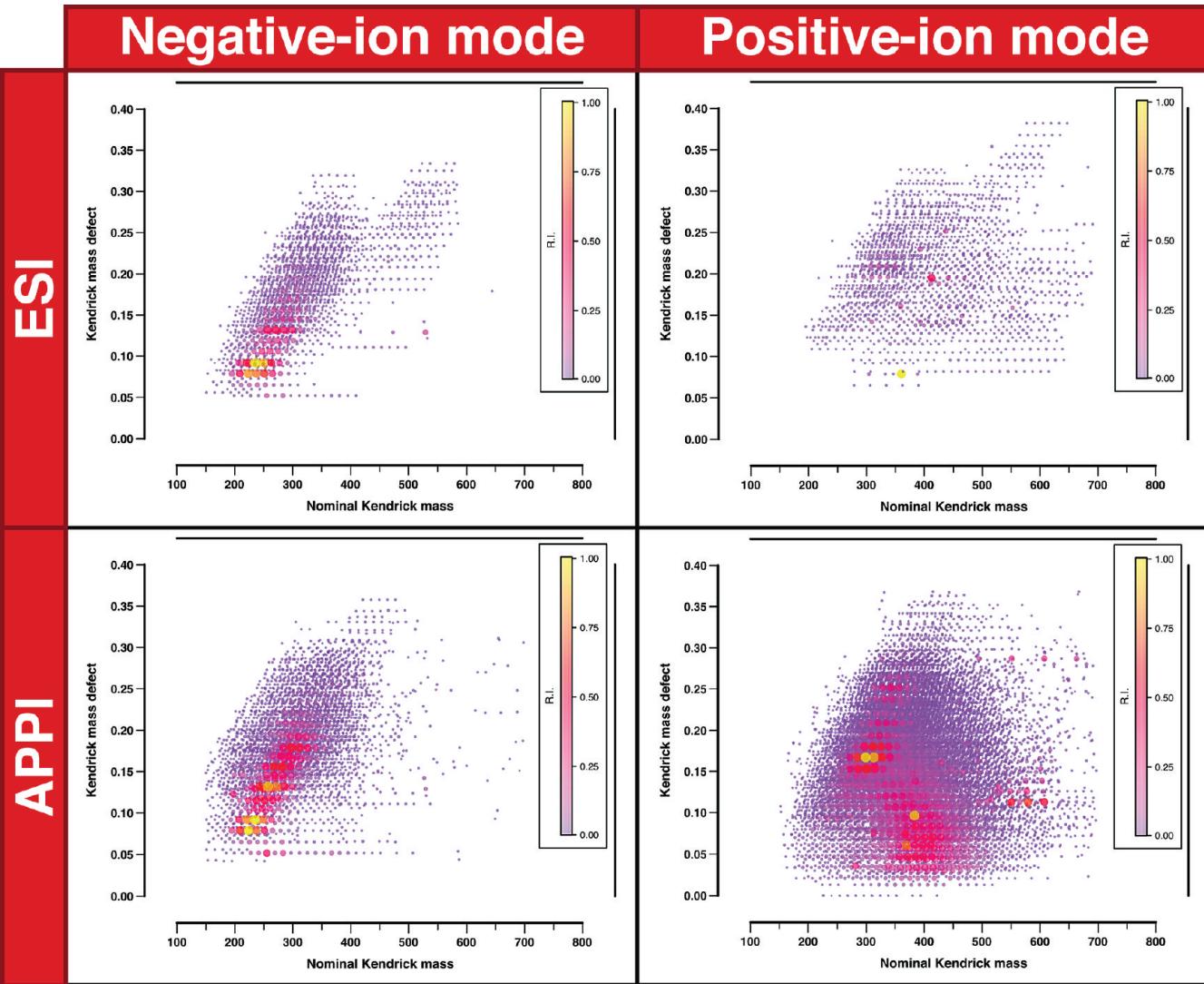
**Figure 1.** Broadband mass spectra of an Athabasca oil sands process water sample using a 12 T FTICR mass spectrometer in both positive-ion and negative-ion modes, coupled to an ESI or APPI source.

word for “eagle”) family of acids in deposits<sup>23,24</sup> in oilfield separators and the formation of aggregates.<sup>25,26</sup>

The components in oil vary in terms of size, structure, heteroatom content, and acidity/basicity. As a result, the different components will not be equally amenable to one set of experimental parameters, such as the choice of ionization method. Electrospray ionization (ESI) is among the most common ionization methods and is best suited to ionic or highly polar species in

solution. Zhan and Fenn<sup>27</sup> demonstrated usage of ESI for the analysis of fossil fuels, and the technique has proved invaluable for the characterization of petroleum-related samples.<sup>7,13,17,18,28–37</sup> A more recent technique is atmospheric pressure photoionization (APPI),<sup>38–42</sup> which has the advantage of being suitable for less polar molecules and is known to generate radical ions in addition to protonated/deprotonated ions.<sup>42,43</sup> Marshall and co-workers

- (13) Headley, J. V.; Peru, K. M.; McMartin, D. W.; Winkler, M. *J. AOAC Int.* **2002**, *85*, 182–187.
- (14) Barrow, M. P.; McDonnell, L. A.; Feng, X.; Walker, J.; Derrick, P. J. *Anal. Chem.* **2003**, *75*, 860–866.
- (15) Clemente, J. S.; Prasad, N. G. N.; MacKinnon, M. D.; Fedorak, P. M. *Chemosphere* **2003**, *50*, 1265–1274.
- (16) Barrow, M. P.; Headley, J. V.; Peru, K. M.; Derrick, P. J. *J. Chromatogr., A* **2004**, *1058*, 51–59.
- (17) Bataineh, M.; Scott, A. C.; Fedorak, P. M.; Martin, J. W. *Anal. Chem.* **2006**, *78*, 8354–8361.
- (18) Headley, J. V.; Peru, K. M.; Barrow, M. P.; Derrick, P. J. *Anal. Chem.* **2007**, *79*, 6222–6229.
- (19) Smith, B. E.; Lewis, C. A.; Belt, S. T.; Whitby, C.; Rowland, S. J. *Environ. Sci. Technol.* **2008**, *42*, 9323–9328.
- (20) Smith, B. E.; Rowland, S. J. *Rapid Commun. Mass Spectrom.* **2008**, *22*, 3909–3927.
- (21) Barrow, M. P.; Headley, J. V.; Peru, K. M.; Derrick, P. J. *Energy Fuels* **2009**, *23*, 2592–2599.
- (22) Headley, J. V.; Peru, K. M.; Barrow, M. P. *Mass Spectrom. Rev.* **2009**, *28*, 121–134.
- (23) Baugh, T. D.; Wolf, N. O.; Mediaas, H.; Vindstad, J. E.; Grande, K. *Abstr. Pap. Am. Chem. Soc.* **2004**, *228*, U172–U172.
- (24) Smith, B. E.; Sutton, P. A.; Lewis, C. A.; Dunsmore, B.; Fowler, G.; Krane, J.; Lutnaes, B. F.; Brandal, Ø.; Sjöblom, J.; Rowland, S. J. *J. Sep. Sci.* **2007**, *30*, 375–380.
- (25) Smith, D. F.; Schaub, T. M.; Rahimi, P.; Teclamariam, A.; Rodgers, R. P.; Marshall, A. G. *Energy Fuels* **2007**, *21*, 1309–1316.
- (26) Da Campo, R.; Barrow, M. P.; Shepherd, A. G.; Salisbury, M.; Derrick, P. J. *Energy Fuels* **2009**, *23*, 5544–5549.
- (27) Zhan, D.; Fenn, J. B. *Int. J. Mass Spectrom.* **2000**, *194*, 197–208.
- (28) Qian, K.; Robbins, W. K.; Hughey, C. A.; Cooper, H. J.; Rodgers, R. P.; Marshall, A. G. *Energy Fuels* **2001**, *15*, 1505–1511.
- (29) Stanford, L. A.; Kim, S.; Rodgers, R. P.; Marshall, A. G. *Energy Fuels* **2006**, *20*, 1664–1673.
- (30) Klein, G. C.; Kim, S.; Rodgers, R. P.; Marshall, A. G.; Yen, A. *Energy Fuels* **2006**, *20*, 1973–1979.
- (31) Teravainen, M. J.; Pakarinen, J. M. H.; Wickstrom, K.; Vainiotalo, P. *Energy Fuels* **2007**, *21*, 266–273.
- (32) Qian, K.; Edwards, K. E.; Dechert, G. J.; Jaffe, S. B.; Green, L. A.; Olmstead, W. N. *Anal. Chem.* **2008**, *80*, 849–855.
- (33) Smith, D. F.; Schaub, T. M.; Kim, S.; Rodgers, R. P.; Rahimi, P.; Teclamariam, A.; Marshall, A. G. *Energy Fuels* **2008**, *22*, 2372–2378.
- (34) Hughey, C. A.; Minardi, C. S.; Galasso-Roth, S. A.; Paspalof, G. B.; Mapolelo, M. M.; Rodgers, R. P.; Marshall, A. G.; Ruderman, D. L. *Rapid Commun. Mass Spectrom.* **2008**, *22*, 3968–3976.
- (35) Kim, S.; Rodgers, R. P.; Blakney, G. T.; Hendrickson, C. L.; Marshall, A. G. *J. Am. Soc. Mass Spectrom.* **2009**, *20*, 263–268.
- (36) Lo, C. C.; Brownlee, B. G.; Bunce, N. J. *Anal. Chem.* **2003**, *75*, 6394–6400.
- (37) Mapolelo, M. M.; Stanford, L. A.; Rodgers, R. P.; Yen, A. T.; Debord, J. D.; Asomaning, S.; Marshall, A. G. *Energy Fuels* **2009**, *23*, 349–355.
- (38) Robb, D. B.; Covey, T. R.; Bruins, A. P. *Anal. Chem.* **2000**, *72*, 3653–3659.
- (39) Kauppila, T. J.; Kotiaho, T.; Kostainen, R.; Bruins, A. P. *J. Am. Soc. Mass Spectrom.* **2004**, *15*, 203–211.
- (40) Kauppila, T. J.; Kostainen, R.; Bruins, A. P. *Rapid Commun. Mass Spectrom.* **2004**, *18*, 808–815.
- (41) Kauppila, T. J.; Bruins, A. P.; Kostainen, R. *J. Am. Soc. Mass Spectrom.* **2005**, *16*, 1399–1407.
- (42) Raffaelli, A.; Saba, A. *Mass Spectrom. Rev.* **2003**, *22*, 318–331.

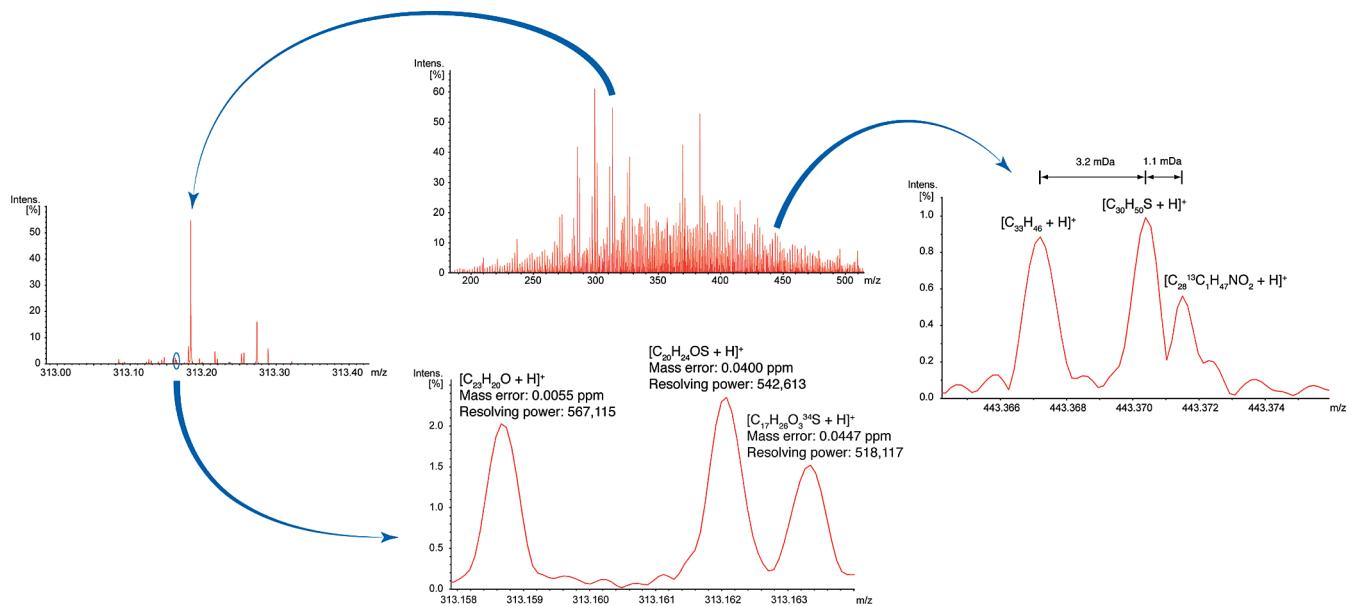


**Figure 2.** Plots of Kendrick mass defect versus nominal Kendrick mass for the four mass spectra shown in Figure 1.

have demonstrated the applicability to studying petroleum,<sup>43,44</sup> and miniaturized variants of APPI sources have also been developed.<sup>45,46</sup> Traditionally, field ionization/field desorption<sup>47,48</sup> was required for the ionization of the less acidic or basic components of a crude oil, such as sulfur-containing species; APPI, however, makes these species accessible for detection without the need for prior chemical derivatization.<sup>49</sup>

Petroleum-related mixtures typically contain thousands or tens of thousands of components.<sup>50–53</sup> Due to this level of complexity, Fourier transform ion cyclotron resonance (FTICR) instruments have played a key role in the characterization of components due to the inherent ultrahigh resolving power and mass accuracy. While it is now possible to resolve this number of components, analysis and visualization of the data is another challenge.<sup>54</sup> Attempts to address this problem have included the usage of the Kendrick mass defect,<sup>55–57</sup> van Krevelen diagrams,<sup>58,59</sup> double

- (43) Purcell, J. M.; Hendrickson, C. L.; Rodgers, R. P.; Marshall, A. G. *Anal. Chem.* **2006**, *78*, 5906–5912.
- (44) McKenna, A. M.; Purcell, J. M.; Rodgers, R. P.; Marshall, A. G. *Energy Fuels* **2009**, *23*, 2122–2128.
- (45) Kauppila, T. J.; Ostman, P.; Marttila, S.; Ketola, R. A.; Kotiaho, T.; Franssila, S.; Kostiainen, R. *Anal. Chem.* **2004**, *76*, 6797–6801.
- (46) Haapala, M.; Purcell, J. M.; Saarela, V.; Franssila, S.; Rodgers, R. P.; Hendrickson, C. L.; Kotiaho, T.; Marshall, A. G.; Kostiainen, R. *Anal. Chem.* **2009**, *81*, 2799–2803.
- (47) Schaub, T. M.; Hendrickson, C. L.; Qian, K.; Quinn, J. P.; Marshall, A. G. *Anal. Chem.* **2003**, *75*, 2172–2176.
- (48) Schaub, T. M.; Hendrickson, C. L.; Quinn, J. P.; Rodgers, R. P.; Marshall, A. G. *Anal. Chem.* **2005**, *77*, 1317–1324.
- (49) Müller, H.; Andersson, J. T.; Schrader, W. *Anal. Chem.* **2005**, *77*, 2536–2543.
- (50) Hughey, C. A.; Rodgers, R. P.; Marshall, A. G. *Anal. Chem.* **2002**, *74*, 4145–4149.
- (51) Qian, K.; Robbins, W. K.; Hughey, C. A.; Cooper, H. J.; Rodgers, R. P.; Marshall, A. G. *Energy Fuels* **2001**, *15*, 1505–1511.
- (52) Qian, K.; Rodgers, R. P.; Hendrickson, C. L.; Emmett, M. R.; Marshall, A. G. *Energy Fuels* **2001**, *15*, 492–498.
- (53) Wu, Z.; Jernstrom, S.; Hughey, C. A.; Rodgers, R. P.; Marshall, A. G. *Energy Fuels* **2003**, *17*, 946–953.
- (54) Kind, T.; Fiehn, O. *BMC Bioinf.* **2007**, *8*, 105.
- (55) Hsu, C. S.; Qian, K. N.; Chen, Y. N. C. *Anal. Chim. Acta* **1992**, *264*, 79–89.
- (56) Hughey, C. A.; Hendrickson, C. L.; Rodgers, R. P.; Marshall, A. G.; Qian, K. *Anal. Chem.* **2001**, *73*, 4676–4681.



**Figure 3.** Broadband mass spectrum acquired using the APPI source and operating in positive-ion mode, highlighting the need for ultrahigh resolving power and mass accuracy in order to characterize complex mixtures.

bond equivalents,<sup>60,61</sup> plots of carbon number versus mass,<sup>62,63</sup> pseudograms,<sup>64</sup> and heat maps.<sup>21</sup>

Oil sands acid extractable organics (AEO) typically have a yellow-orange color, depending on the concentration of the extracts, and this color cannot be explained by the classical naphthenic acid structures alone. Furthermore, reduction of the toxicity of the oil sands process water does not always correlate with changes in concentration of the classical naphthenic acids. Previous research has focused on ESI for analysis of oil sands process water. There is thus a need to explore the use of other ionization methods for characterization of species which may be inaccessible using ESI. The coupling of APPI and FTICR mass spectrometry is expected to provide greater insight into the composition of OSPW mixtures. The research described here represents the first characterization<sup>65</sup> of Athabasca oil sands process water using the combination of ESI and APPI in both positive-ion and negative-ion modes, highlighting a broader range of components in addition to classical naphthenic acids.

## EXPERIMENTAL SECTION

A 12 T solariX Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) was

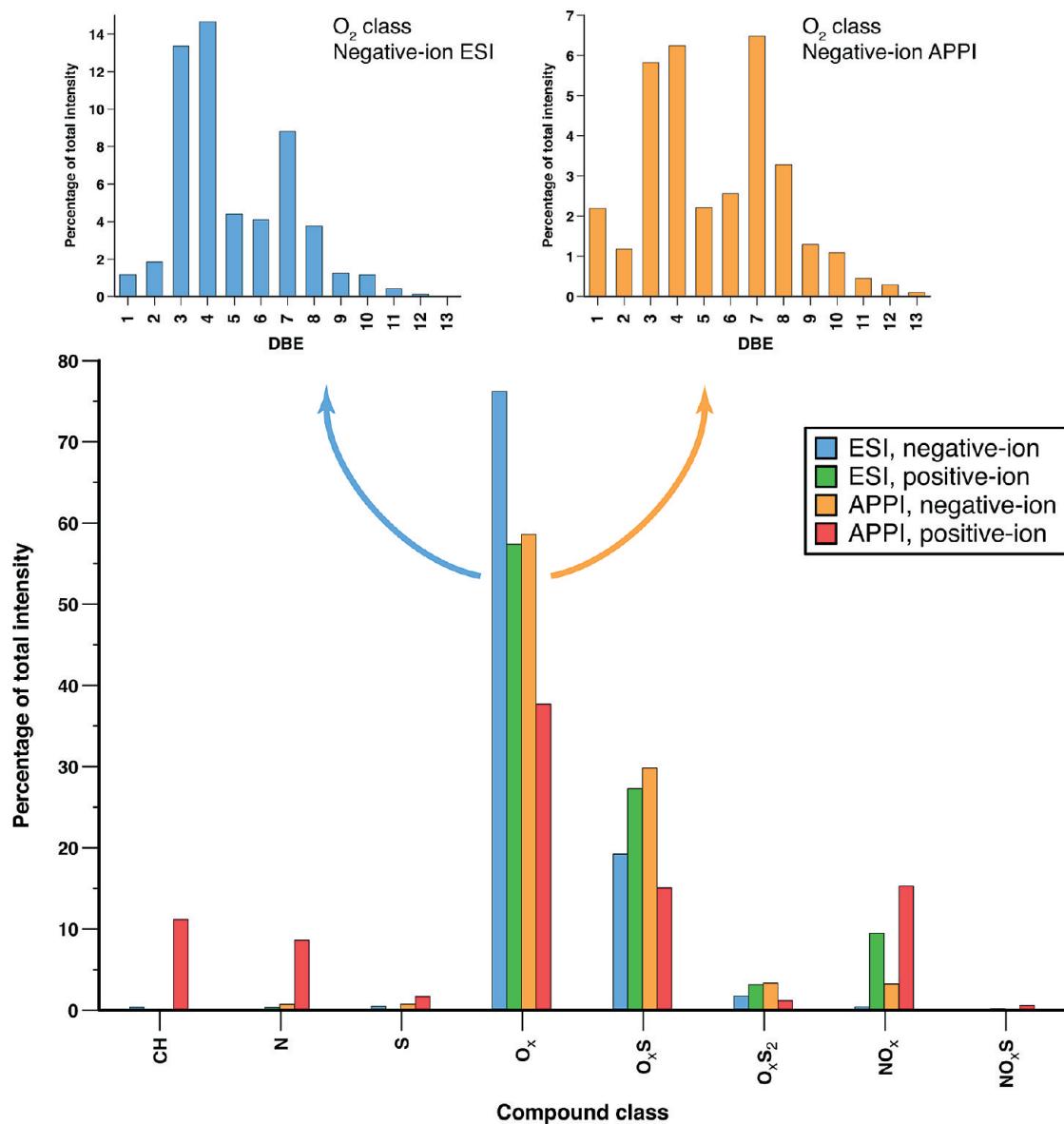
used for the analysis of the sample solutions. Electrospray ionization experiments were performed using an Apollo II ion source (Bruker Daltonik GmbH, Bremen, Germany), and atmospheric pressure photoionization experiments were performed using a PhotoMate APPI ion source (Syagen Technology, Inc., Tustin, CA, USA).

An oil sands process water sample was obtained from a tailings pond at an oil sands extraction site in Ft. McMurray, Alberta, Canada. Using the method described by Rogers et al.,<sup>66</sup> a concentrate was produced and dissolved as 1 mg of extract in 1 mL of water/acetonitrile (1:1). As no components were added during the extraction process or during sample handling, the compounds detected during subsequent analysis should, therefore, originate from the oil sands. A sample solution was prepared by dissolving the concentrate in the relevant solvent system, using a ratio of 0.01 mg of concentrate per 1 mL of solvent. For ESI, the solvent system was acetonitrile/methanol (1:1), and no acids/bases were added to aid protonation/deprotonation. The solvent system for APPI was acetonitrile/toluene (1:1), as toluene assists the ionization process through efficient absorption of the photons from the krypton lamp and subsequent action as a charge carrier.

The FTICR mass spectrometer was operated in both the positive-ion and negative-ion modes, with detection of ions in the range of  $m/z$  147.4–3000. Data was acquired in broadband mode, using 4 megaword data sets (4 194 304 data points), with each mass spectrum resulting from the sum of 300 scans. Following acquisition of the time domain data, the data was zero-filled once; sine-bell apodization was applied, and a fast Fourier transform (FFT) was used to produce the frequency domain data, which was then used to produce the mass spectrum. The mass spectra were first externally calibrated, using “ES Tuning Mix” (part number G2421A; Agilent, Palo Alto, CA, USA), and subsequently internally calibrated, using a known series of compounds that were present within the sample. For data processing, a combination of

- (57) Stenson, A. C.; Marshall, A. G.; Cooper, W. T. *Anal. Chem.* **2003**, *75*, 1275–1284.
- (58) Kim, S.; Kramer, R. W.; Hatcher, P. G. *Anal. Chem.* **2003**, *75*, 5336–5344.
- (59) Wu, Z.; Rodgers, R. P.; Marshall, A. G. *Anal. Chem.* **2004**, *76*, 2511–2516.
- (60) Wu, Z.; Rodgers, R. P.; Marshall, A. G.; Strohm, J. J.; Song, C. *Energy Fuels* **2005**, *19*, 1072–1077.
- (61) Klein, G. C.; Angström, A.; Rodgers, R. P.; Marshall, A. G. *Energy Fuels* **2006**, *20*, 668–672.
- (62) Reemtsma, T.; These, A.; Venkatachari, P.; Xia, X.; Hopke, P. K.; Springer, A.; Linscheid, M. *Anal. Chem.* **2006**, *78*, 8299–8304.
- (63) Reemtsma, T.; These, A.; Springer, A.; Linscheid, M. *Environ. Sci. Technol.* **2006**, *40*, 5839–5845.
- (64) Panda, S. K.; Schrader, W.; al-Hajji, A.; Andersson, J. T. *Energy Fuels* **2007**, *21*, 1071–1077.
- (65) Barrow, M. P.; Witt, M.; Headley, J. V.; Peru, K. M. In *Analysis of Athabasca Oil Sands Process Water by ESI and APPI Fourier Transform Ion Cyclotron Resonance Mass Spectrometry*, Proceedings of the 18th International Mass Spectrometry Conference, Bremen, Germany, August 30–September 4, 2009.

- (66) Rogers, V. V.; Liber, K.; MacKinnon, M. D. *Chemosphere* **2002**, *48*, 519–527.



**Figure 4.** Plot of compound classes within the Athabasca oil sands process water sample, as observed using the ESI and APPI sources in both positive-ion and negative-ion modes. APPI generally provided accessibility to a greater range of compounds. As an example of a further breakdown of the data, the insets highlight the range of double bond equivalents (calculated for the neutral state) associated with the O<sub>2</sub> species observed within the negative-ion mode ESI and APPI data.

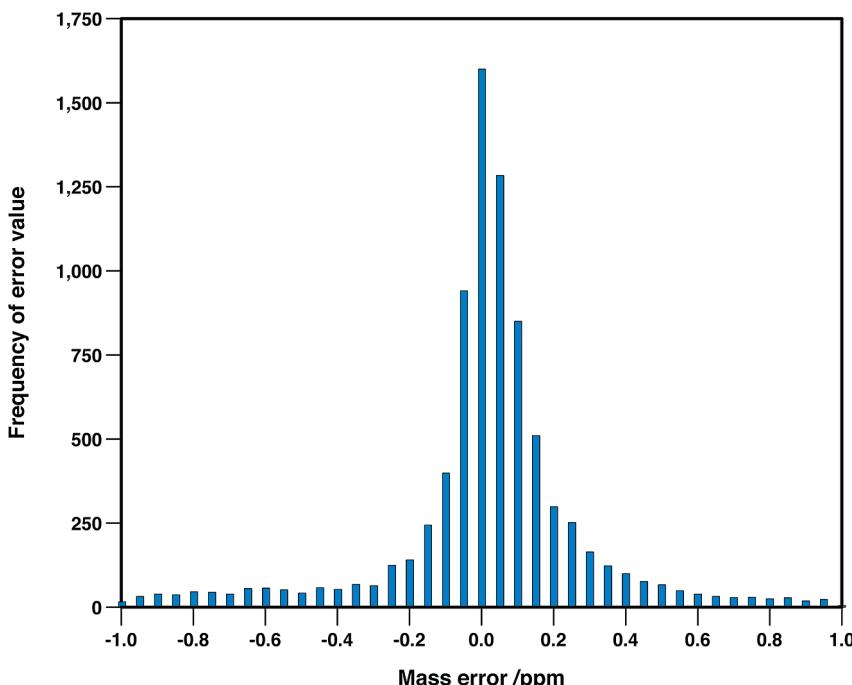
DataAnalysis 4.0 SP2 (Bruker Daltonik GmbH, Bremen, Germany), Composer 1.0.2 (Sierra Analytics, Modesto, CA, USA), Excel (Microsoft Corporation, Redmond, WA), and Aabel 3.0.3 (Gigawiz Ltd. Co., Tulsa, OK, USA) was used.

## RESULTS AND DISCUSSION

Examples of broadband mass spectra obtained using combinations of negative-ion and positive-ion mode, electrospray ionization, and atmospheric pressure photoionization are shown in Figure 1. The base peak within the positive-ion mode APPI mass spectrum resulted from a calibration compound and was excluded during the normalization of the relative intensities of the peaks relating to the process water sample. A greater number of peaks were observed in positive-ion mode than negative-ion mode, and more peaks were observed using APPI than using ESI. These trends are evident in the plots of the Kendrick mass defect versus

nominal Kendrick mass, as shown in Figure 2. The plots provide an indication of the number of species present in each case and families of compounds, where the heteroatom content and Z-homologues are constant and lie along horizontal lines, with adjacent data points differing by one CH<sub>2</sub> unit.

The ultrahigh resolving power and mass accuracy associated with high field FTICR mass spectrometry result in the technique being uniquely suitable for the direct analysis of complex mixtures within a single mass spectrum. Figure 3 shows the successive enlargement of the positive-ion mode APPI mass spectrum, where approximately 19 000 peaks were observed. The need for ultrahigh resolving power is evident, due to the need to resolve the thousands of components present and to observe the isotopomers that can provide diagnostic information during the assignment of species. The ability to resolve the species and their isotopomers,



**Figure 5.** Histogram showing examples of mass errors, in this case associated with assignments for the positive-ion mode APPI data. High mass accuracy is essential for characterization of complex mixtures.

coupled with the level of mass accuracy afforded by the technique, lead to an unrivaled degree of confidence in the assignment of empirical formulas.

Following the assignment of compositions associated with the peaks within each of the mass spectra, it is possible to create a chart which describes the contribution from different compound classes, as shown in Figure 4. The samples investigated here are known to have a high salt content. The presence of salts in turn can lead to suppression effects when ESI is used or influence the observation of the different classes of compounds under the conditions used; many of the ions observed in the positive-ion mode using ESI were sodiated, for example. Negative-ion mode is more amenable for the study of acidic components, where deprotonated naphthenic acids, for example, can be readily observed under these conditions. In contrast, positive-ion mode is more suitable for the characterization of basic components and ions observed can often result from different processes, including protonation or the formation of adducts with metal ions, making the mass spectrum more complex. When comparing the four sets of conditions, the  $O_x$  classes of hydrocarbon predominated in each case, and the  $O_xS$  classes were also particularly abundant in each of the four mass spectra. While positive-ion mode ESI was well-suited for the observation of  $O_x$ ,  $O_xS$ ,  $O_xS_2$ , and  $NO_x$  classes, negative-ion mode ESI mass spectra were dominated by  $O_x$  classes (and, to a lesser degree,  $O_xS$ ), making it particularly useful for the study of naphthenic acids. Plots of the percentage of the relative intensity for  $O_2$  species of varying double bond equivalents<sup>54,67–69</sup> (for the neutral state of the compounds) are shown in the insets for Figure 4, comparing negative-ion mode ESI and APPI data. It can be seen that the species of DBE = 1 ( $Z = 0$ ) and DBE = 7 to 13 ( $Z = -12$  to -24)

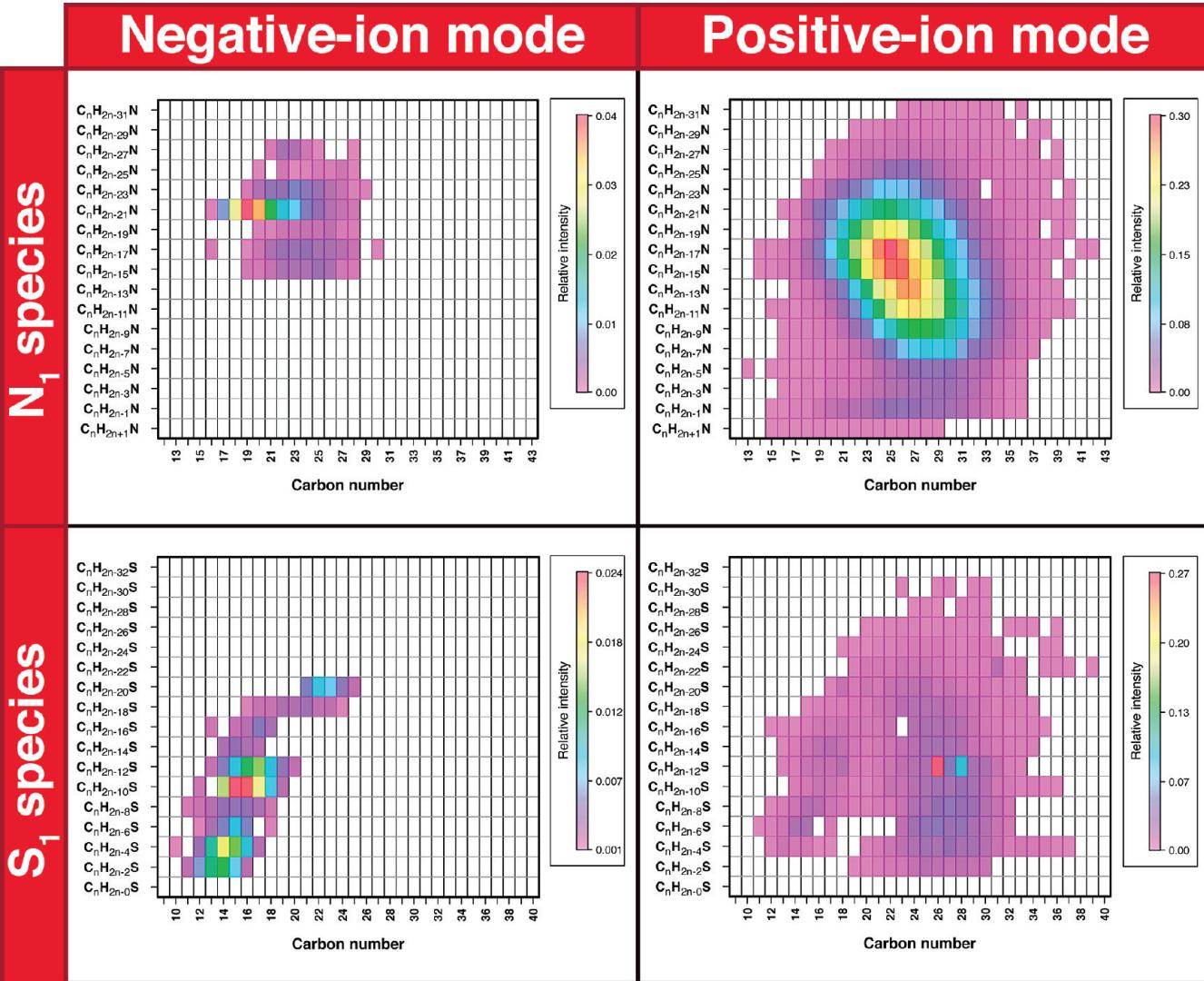
were more pronounced when APPI is used; the increased intensity of the ions of the latter, higher DBE range potentially demonstrate that naphthenoaromatic<sup>32</sup> species are more amenable to analysis by APPI than by ESI. The positive-ion mode APPI mass spectrum was notable for the greater intensity of the  $NO_x$  classes but also for the N class and the observation of hydrocarbons which did not contain a heteroatom. One of the advantages of APPI is that it affords the ability to observe compounds which would otherwise be inaccessible through ESI, such as aromatic hydrocarbons which do not include a heteroatom. The usage of toluene to aid the ionization process can also influence the observation of different classes of compounds, as solvents are known to play a significant role.<sup>18</sup> Figure 5 is a histogram of the mass errors associated with assignments, using the positive-ion mode APPI mass spectrum as the example. As illustrated, typical mass errors were significantly below 1 ppm (rms value of 0.27 ppm), with more than three-quarters of the assignments having an associated mass error within the range of -0.2 to +0.2 ppm.

A comparison between negative-ion and positive-ion mode APPI data sets provides insights into the presence of species consisting of carbon, hydrogen, and a sole nitrogen or sulfur atom. The profiles associated with the two APPI mass spectra are shown as heat maps in Figure 6. While the species were of low relative intensity in the negative-ion mode mass spectra, a greater variety of species were observed in the positive-ion mode, and the signals were of greater relative intensity. For  $C_nH_{2n+Z}N$  compounds, the most intense peaks were associated with a range of carbon number 24–27, with  $Z$  values within the range of -13 to -17; for the  $C_nH_{2n+Z}S$  compounds, a range of carbon number between 26 and 28 and a  $Z$  value of -12 were among the most intense. For nitrogen-containing compounds, pyrrolic structures (where the nitrogen atom is incorporated into a five-membered ring) will be acidic and more readily observed in negative-ion

(67) Korsten, H. *AIChE J.* **1997**, *43*, 1559–1568.

(68) Pellegrin, V. *J. Chem. Educ.* **1983**, *60*, 626–633.

(69) Soffer, M. D. *Science* **1958**, *127*, 880.

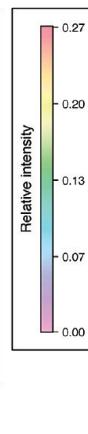
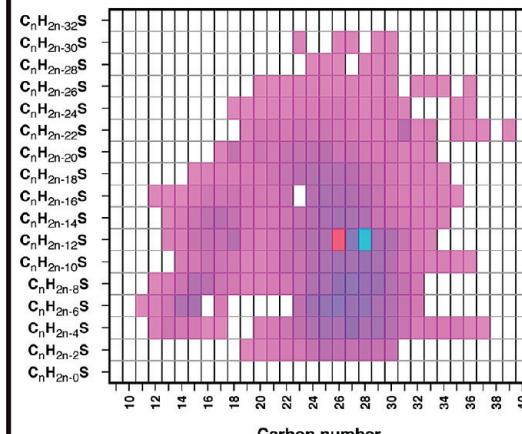
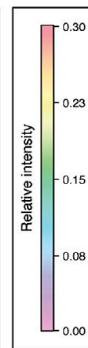
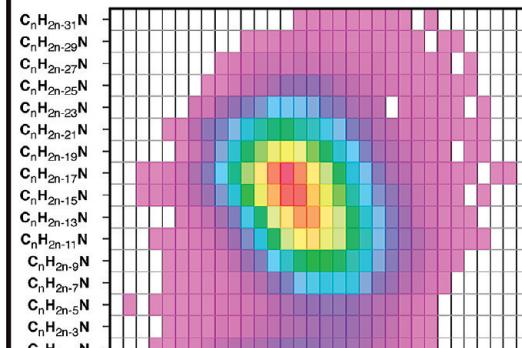


**Figure 6.** Heat maps of nitrogen- and sulfur-containing species observed using the APPI source in both positive-ion and negative-ion modes.

mode when ESI is used, while pyridinic structures (where the nitrogen atom is incorporated into a six-membered ring) will be basic and more readily observed in the positive-ion mode when ESI is used. APPI, however, can be used to observe both pyridinic and pyrrolic structures in the positive-ion mode, due to the possibility of forming both protonated ions and radical ions.<sup>70</sup> For the nitrogen-containing species, the vast majority of the signals observed using APPI in positive-ion mode were protonated ions, rather than radical ions, potentially indicating a more highly pyridinic nature. As sulfur-containing species are relatively less accessible using ESI, APPI has an additional advantage in being more amenable to the ionization of such species. In similarity to the results for the nitrogen-containing species, the ions observed for sulfur-containing species were predominantly protonated, rather than radical ions.

Figure 7 shows the heat maps associated with selected compound classes that were among the most abundant within the positive-ion mode APPI mass spectrum. In each case, there is a broad range of  $Z$  values, ranging from compounds of almost

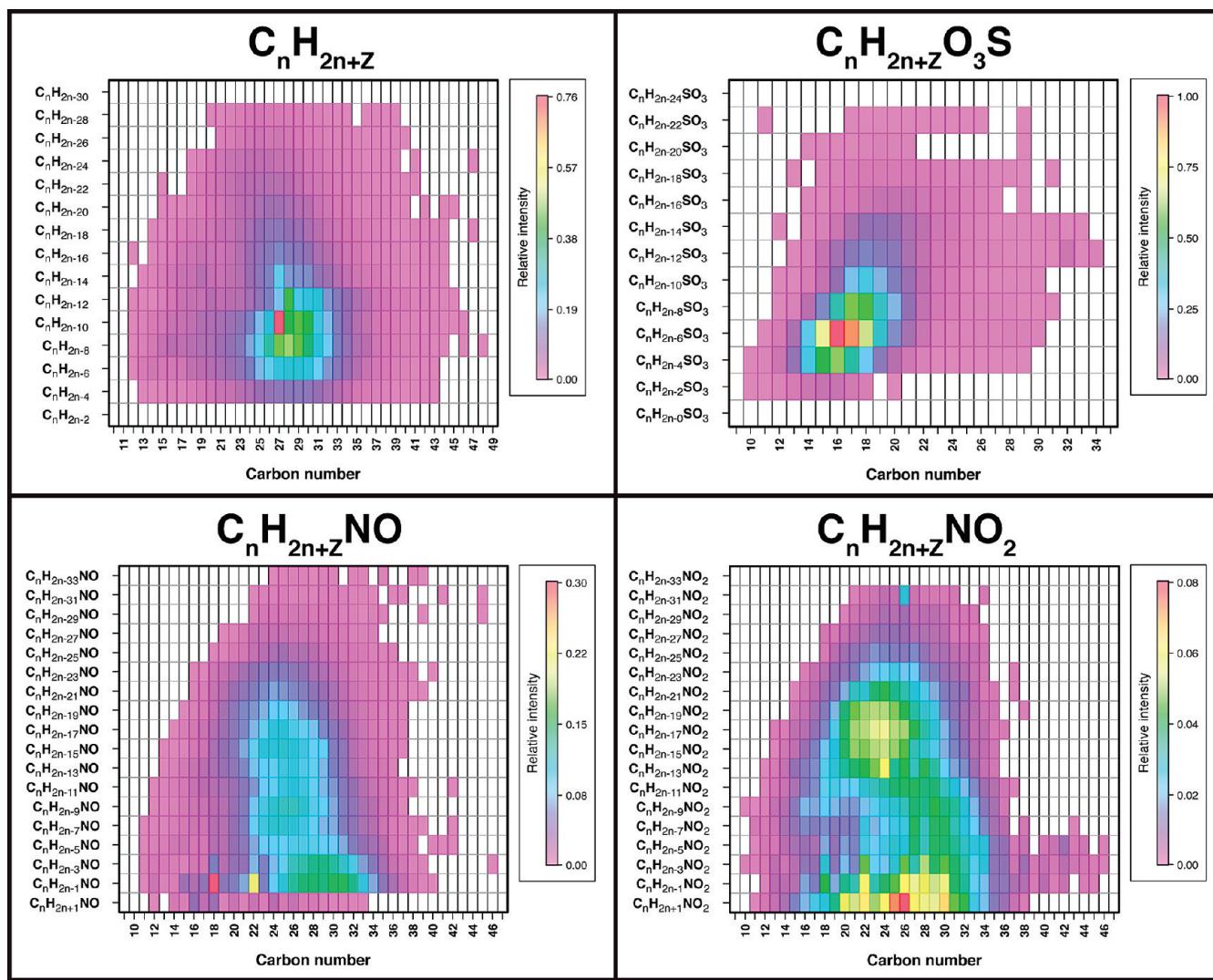
## Positive-ion mode



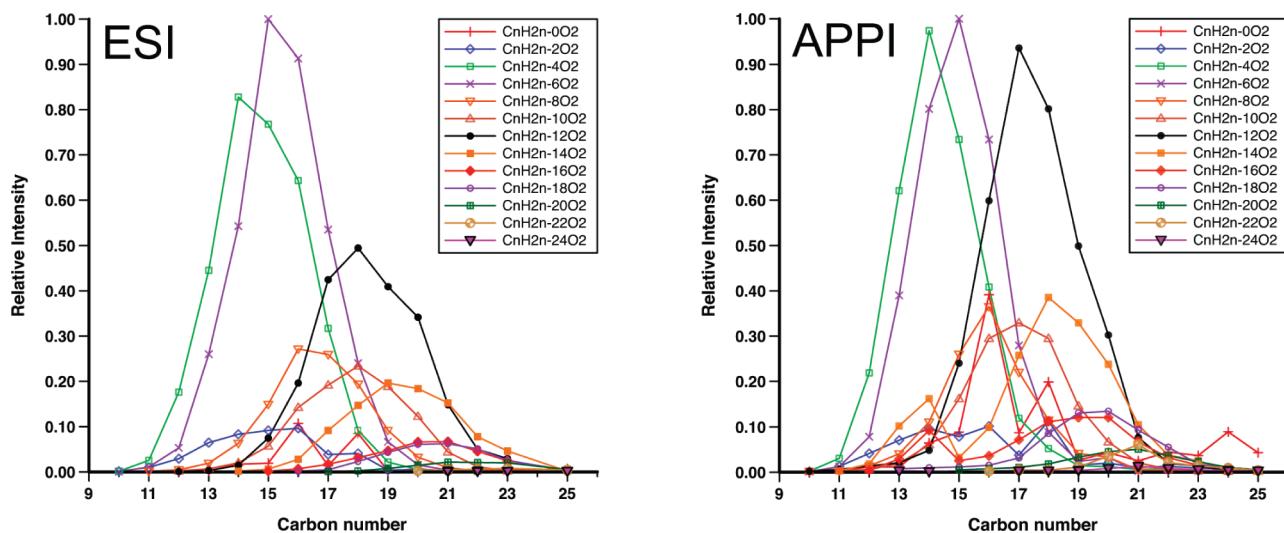
entirely aliphatic character (where the degree of hydrogen deficiency is low) to those of relatively aromatic character. The  $O_3S$  compound class (spanning a carbon number range of 10–34, and  $Z = -2$  to  $-22$ ) was one of the most intense within the mass spectrum, at a carbon number of 16 to 17 and a  $Z$  value of  $-6$ . The carbon number range of the pure hydrocarbon class was greater (12–48) and spanned a wider range of hydrogen deficiencies ( $Z = -4$  to  $-28$ ). The NO compound class was more abundant than the  $NO_2$  class, but the two profiles bore some similarity to one another in terms of the shape of the profile, the carbon number range, and the hydrogen deficiency range.

Naphthenic acids are among the compounds of particular interest within the oil sands process water, as they are known to be toxic toward aquatic organisms.<sup>3–7</sup> Negative-ion mode mass spectra are most convenient for investigating these acidic species, and the negative-ion mode ESI and APPI data (for the  $O_2$  compound class) were therefore compared, as shown in Figure 8. The profiles were similar with respect to the carbon number range and range of hydrogen deficiencies observed, although there were notable differences in terms of relative intensity. The

(70) Purcell, J. M.; Rodgers, R. P.; Hendrickson, C. L.; Marshall, A. G. *J. Am. Soc. Mass Spectrom.* 2007, 18, 1265–1273.



**Figure 7.** Heat maps of hydrocarbon,  $O_3S$ -containing, NO-containing, and  $NO_2$ -containing species observed when APPI is used in positive-ion mode.



**Figure 8.** Line plots of the  $O_2$ -containing species observed when ESI and APPI are used in the negative-ion mode.

$Z = -6$  family ( $DBE = 4$ ) was of decreased relative intensity within the APPI mass spectrum, compared to the ESI data set, but a number of species of higher hydrogen deficiency (such as

$Z = -8, -10, -12$ , and  $-14$ ;  $DBE = 5, 6, 7$ , and  $8$ , respectively) were of increased relative intensity. The species of higher hydrogen deficiency are likely to be of naphthenoaromatic

character.<sup>32</sup> A particularly notable difference involved the  $Z = -12$  family ( $\text{DBE} = 7$ ), where the relative intensity approximately doubled. The difference in intensities, when comparing the ESI and APPI data, can most likely be explained by two factors. The first is that the APPI data were acquired using toluene as a cosolvent, as this improves ionization efficiency. The usage of different solvents is known to introduce biases when studying complex mixtures,<sup>18</sup> and toluene could prove a more suitable solvent for naphthenoaromatic compounds. The second factor is that APPI is suitable for the study of polycyclic aromatic compounds, and the naphthenoaromatic species may prove more amenable to ionization using this technique, compared to using ESI.

## CONCLUSIONS

A 12 T FTICR mass spectrometer was coupled to ESI and APPI sources and utilized in both the positive-ion and negative-ion modes to analyze Athabasca oil sands process water. Usage of positive-ion APPI led to the observation of the greatest number of components, while usage of negative-ion mode ESI led to the observation of the fewest. As observed using both ESI and APPI,

the predominant components of the oil sands process water sample were oxygenated species, including naphthenic acids. Naphthenic acids of higher hydrogen deficiencies, potentially naphthenoaromatic compounds, were more intense when APPI was used than when ESI was used. Compounds that are less accessible when ESI is used, such as hydrocarbons which do not contain a heteroatom or sulfur-containing species, may be observed using APPI. The broader characterization of oil sands process water should be considered in the context of a need for research into a greater range of components, as the overall toxicity will not depend upon naphthenic acids alone.

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