

Analysis of Athabasca Oil Sands Process Water by ESI and APPI FT-ICR mass spectrometry

Mark Barrow¹, Matthias Witt²,
John Headley³ and Kerry M. Peru³

¹ Department of Chemistry, University of Warwick, Coventry, United Kingdom
² Bruker Daltonik GmbH, Bremen, Germany
³ Environment Canada, Saskatoon, Canada

Introduction

As the demand for petroleum has continued to increase, it has been necessary to turn to previously non-viable sources of oil. One such source is the oil sands of the Athabasca region of Canada, which is believed to represent 174 billion barrels of bitumen. Processing of the oil sands requires approximately three barrels of fresh water per barrel of oil produced. The exploitation of the Athabasca oil sands is therefore placing a burden upon the aquatic ecosystem in particular. Amongst the environmental concerns is the presence of naphthenic acids within the oil. Naphthenic acids are defined as carboxylic acids which include one or more saturated ring structures, though the definition has become more loosely used to describe the range of organic acids found within crude oil. The elemental composition for such acids has often been described by $C_nH_{2n+2}O_z$, where "Z" is referred to as the "hydrogen deficiency" and is a negative, even integer. Crude oils typically contain naphthenic acids in quantities of up to 4% by weight, while the carboxylic acid fraction is about 2% in unrefined Athabasca bitumen. The petroleum industry is concerned with the presence of naphthenic acids in crude oils due to their implication in corrosion. It has been stated that the price of oil could be decreased by several dollars per barrel if corrosion due to naphthenic acids was better understood. Disposal of naphthenic acids is problematic, as they are known to be toxic towards aquatic organisms; the aquatic toxicity is associated with their concentration and their surfactant characteristics. Naphthenic acids may enter surface water systems through such mechanisms as groundwater mixing and erosion of riverbank oil deposits in oil producing regions. Ambient levels in northern Alberta rivers in the Athabasca oil sands are generally below 1 mg/L; tailings pond waters, however, may contain as much as 110 mg/L. As the pressure for sources of petroleum grows, the quality of sources of petroleum has been declining and the problems associated with naphthenic acids, for example, have become increasingly significant. Characterization of the acids present within petroleum-related samples has therefore become a topic of great interest, and Fourier transform ion cyclotron resonance (FTICR) mass spectrometry has become established as amongst the leading methods for the analysis of complex mixtures.

Methods

- Oil sands process water (OSPW) sample from oil sands region of Athabasca River Basin, Alberta, Canada; concentrate was produced and dissolved 1 mg of extract in 1 mL of water/ acetonitrile (1:1)
- 12 T solarix Fourier transform ion cyclotron resonance (FTICR) mass spectrometer (Bruker Daltonik, Bremen, Germany)
- Positive-ion and negative-ion modes
- Electrospray ionization (ESI) using an Apollo II ion source (Bruker Daltonik, Bremen, Germany)
- Atmospheric pressure photoionization (APPI) using a PhotoMate APPI ion source (Syagen Technology, Inc., Tustin, CA, USA)
- Broadband raw data acquired as 4 MW datasets
- Data were primarily processed using a combination of DataAnalysis 4.0 SP2 (Bruker Daltonics, Billerica, MA, USA), Composer 1.0.2 (Sierra Analytics, Modesto, CA, USA), and Aabel 3.0.2 (Gigawiz Ltd. Co., Tulsa, OK, USA)

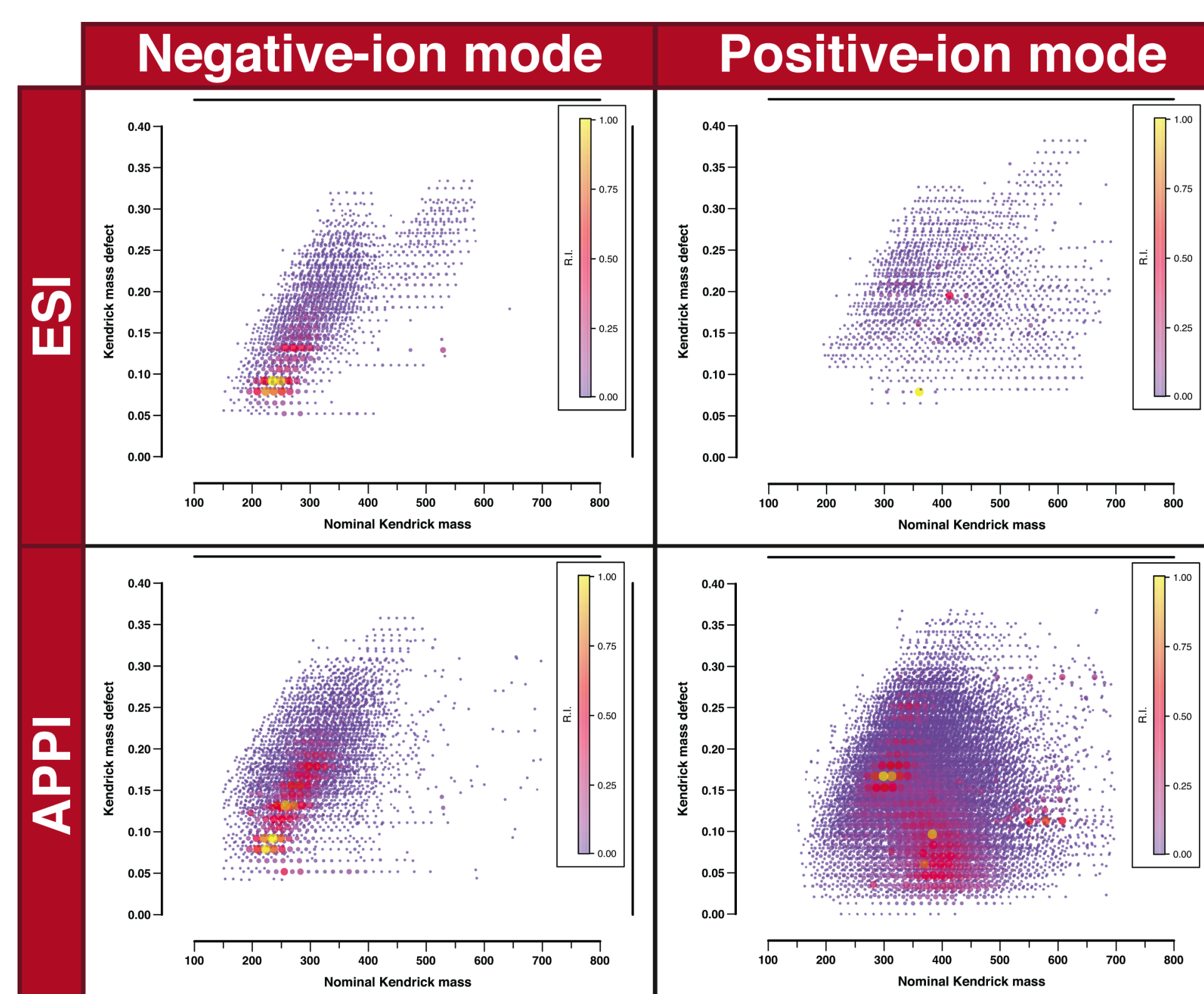


Figure 1: Plots of Kendrick mass defect versus Kendrick nominal mass. Relative intensity is represented by data point size (area of circle) and by color coding. Homologous series of compounds lie along horizontal lines, where adjacent data points differ by an additional CH_2 contribution.

Results

Broadband mass spectra of the OSPW sample were acquired using ESI and APPI in both the positive-ion and negative-ion modes. A greater number of signals were observed when using APPI, when compared to ESI; the positive-ion mode APPI mass spectrum contained approximately 19,000 peaks. For visualization of large numbers of data points arising from the analysis of complex mixtures, it can be convenient to plot data according to their Kendrick nominal mass and Kendrick mass defect (see Figure 1). Assignments for each peak can be made and the classes observed are summarized in Figure 2, which shows that O_x species are predominant and compounds which were previously inaccessible using ESI can be observed using APPI. Ionization can occur via different routes when using APPI (such as the observation of both radical ions and protonated ions). For instance, hydrocarbon compounds which do not include a heteroatom could be observed using positive-ion mode APPI. The majority of species observed using positive-ion mode ESI were sodiated, while negative-ion ESI was most amenable to the study of O_x species such as naphthenic acids.

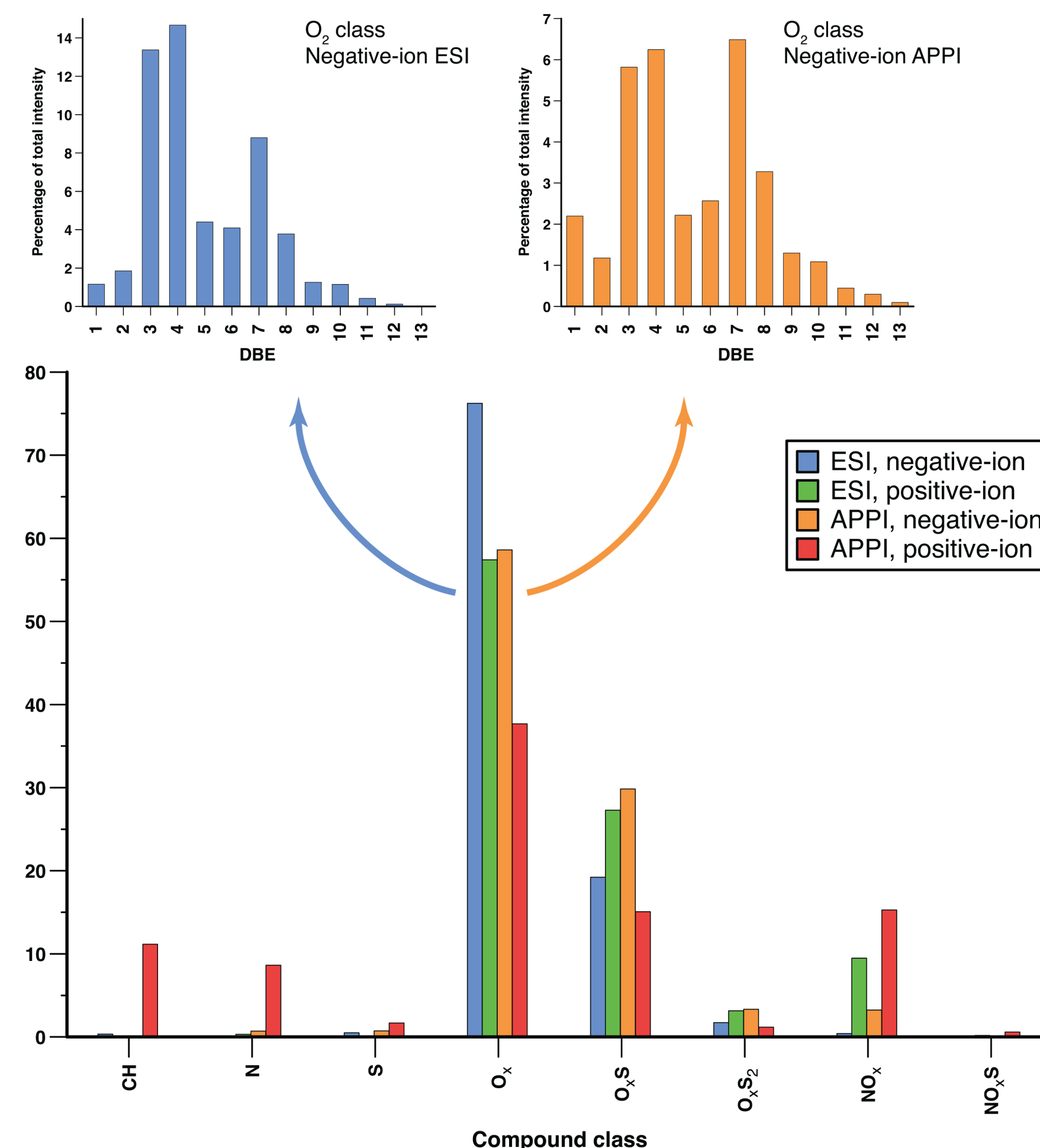
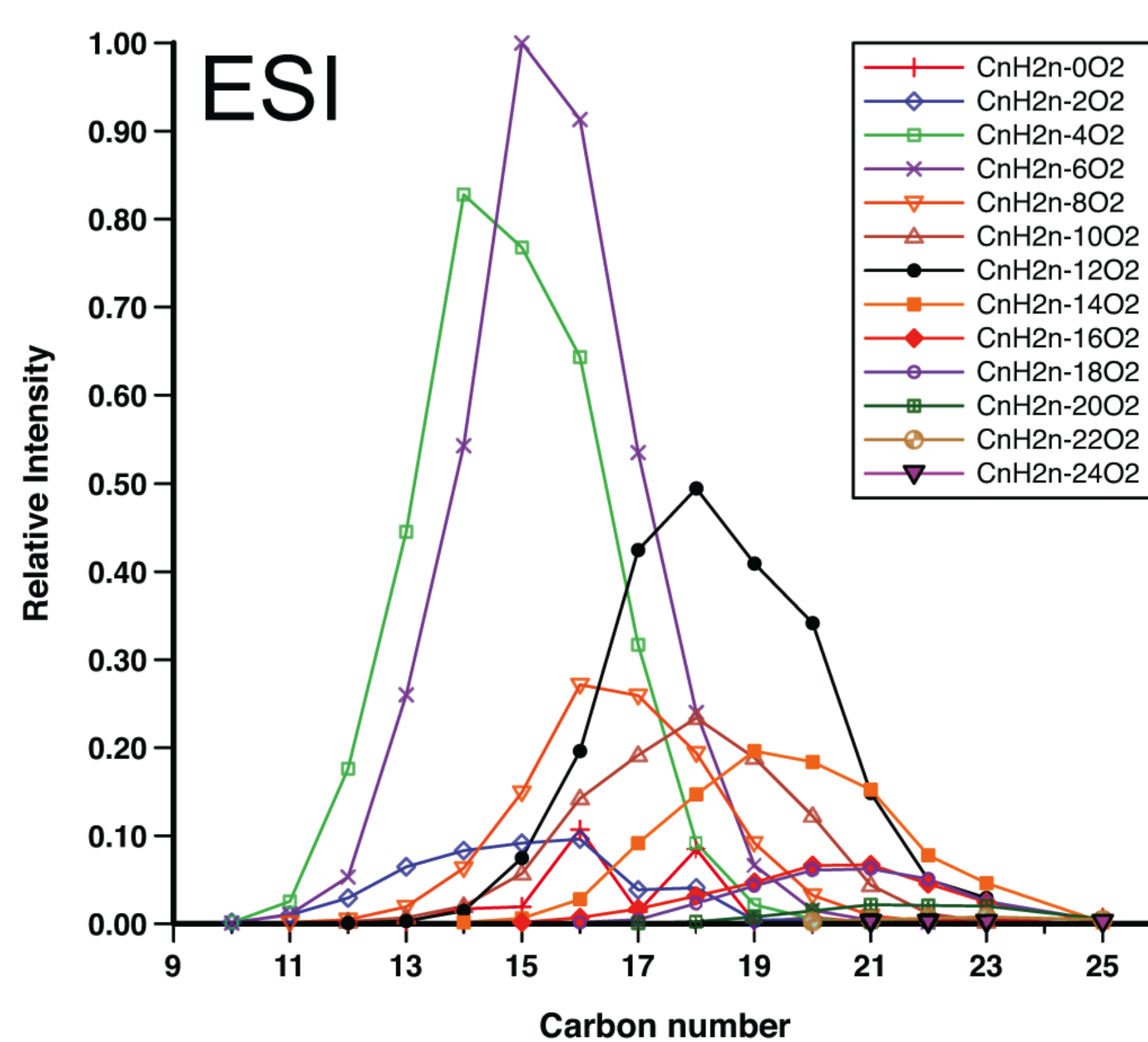


Figure 2: Summary of the classes of compound observed using the positive and negative ion modes, coupled with electrospray ionization and APPI. The contribution has been normalized to create a percentage in each case.

Summary

- 12 T FTICR has been coupled to ESI and APPI to analyze an oil sands process water sample, obtained from the Athabasca River Basin region.
- Positive-ion APPI led to the observation of the greatest number of signals, while negative-ion mode ESI led to the observation of fewest; high resolving power and mass accuracy were essential.
- The predominant components of the oil sands process water sample were oxygenated species, such as naphthenic acids, which can be toxic towards aquatic organisms.
- Naphthenic acids of higher hydrogen deficiencies, potentially naphthenoaromatic compounds, were more intense when using APPI compared to ESI.

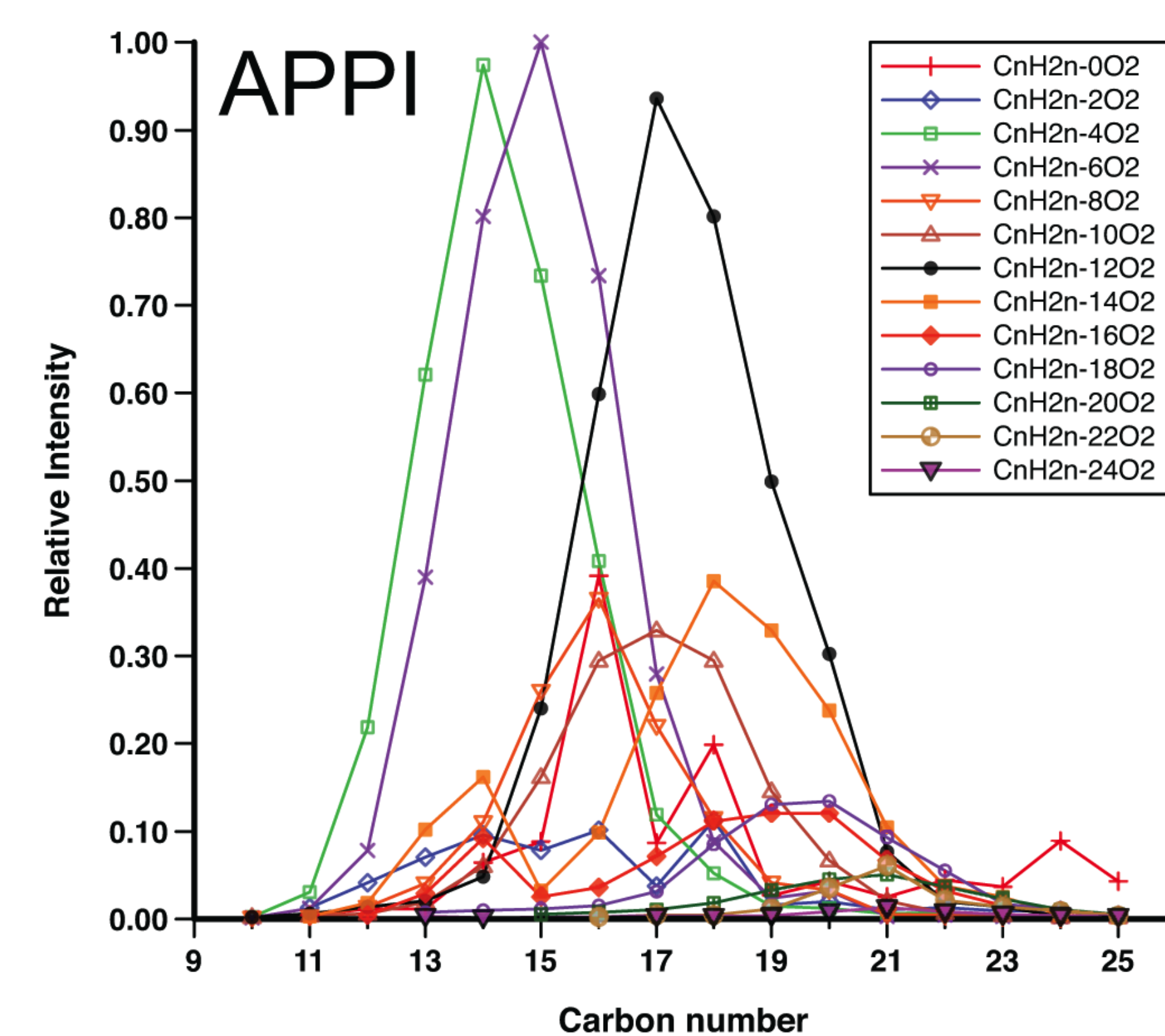


Figure 3: Plots of relative intensity versus carbon content, as function of hydrogen deficiency, for naphthenic acids within the Athabasca River Basin sample, when using negative-ion mode ESI and APPI.

To gain additional insight into the homologous series of naphthenic acids present and to further investigate the differences between ESI and APPI, the relative intensity of each peak was plotted versus carbon content, as a function of hydrogen deficiency (Figure 3). When comparing the ESI and APPI data, the ranges of the carbon contents observed are very similar. The $Z = -6$ series appears to be more intense when using ESI, but higher hydrogen deficiencies, such as $Z = -10$ to -22 , appear to be more intense when using APPI. Naphthenic acids of higher hydrogen deficiencies are likely to be naphthenoaromatic species.

Acknowledgements

The authors thank David Stranz (Sierra Analytics) and acknowledge the Program of Energy Research and Development (PERD) for providing funding.

Conclusions

Ultrahigh resolving power and mass accuracy associated with high field FT-ICR mass spectrometers make them uniquely suitable for the study of complex mixtures.

ESI FT-ICR MS