

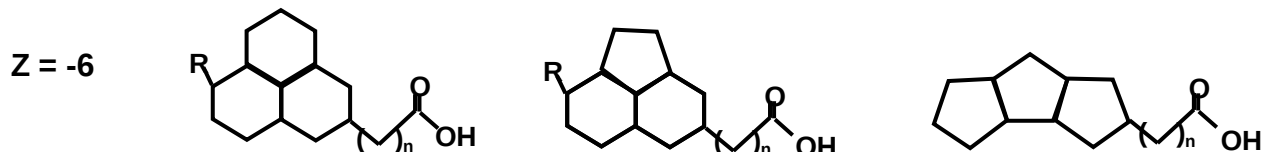
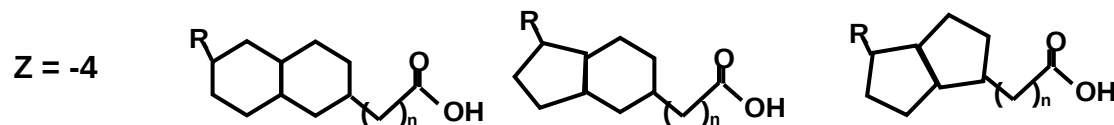
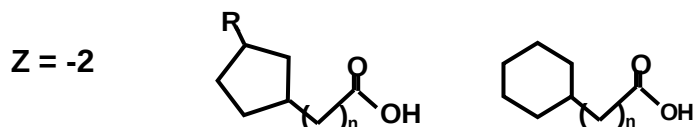
Advances in High Resolution Mass Spectrometry Analyses of Naphthenic Acids

John V. Headley, Kerry M Peru and Jonathan Bailey

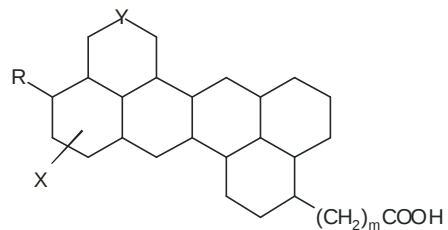
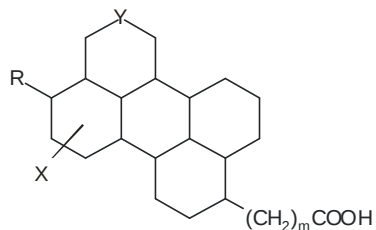
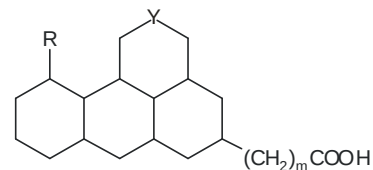
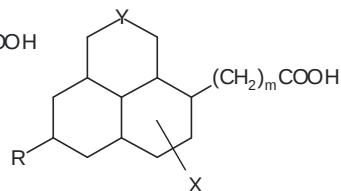
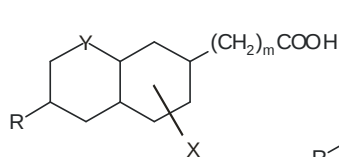
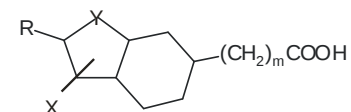
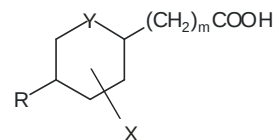
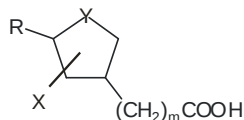
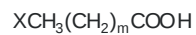
**Water Science and Technology Directorate
Environment Canada**

What are Naphthenic Acids?

- Complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids
- Chemical formula of $C_nH_{2n-Z}O_2$ in which n is the number of carbon atoms and Z is zero or a negative even number and represents the number of hydrogen atoms lost as the structures become more cyclic.



NAFCs



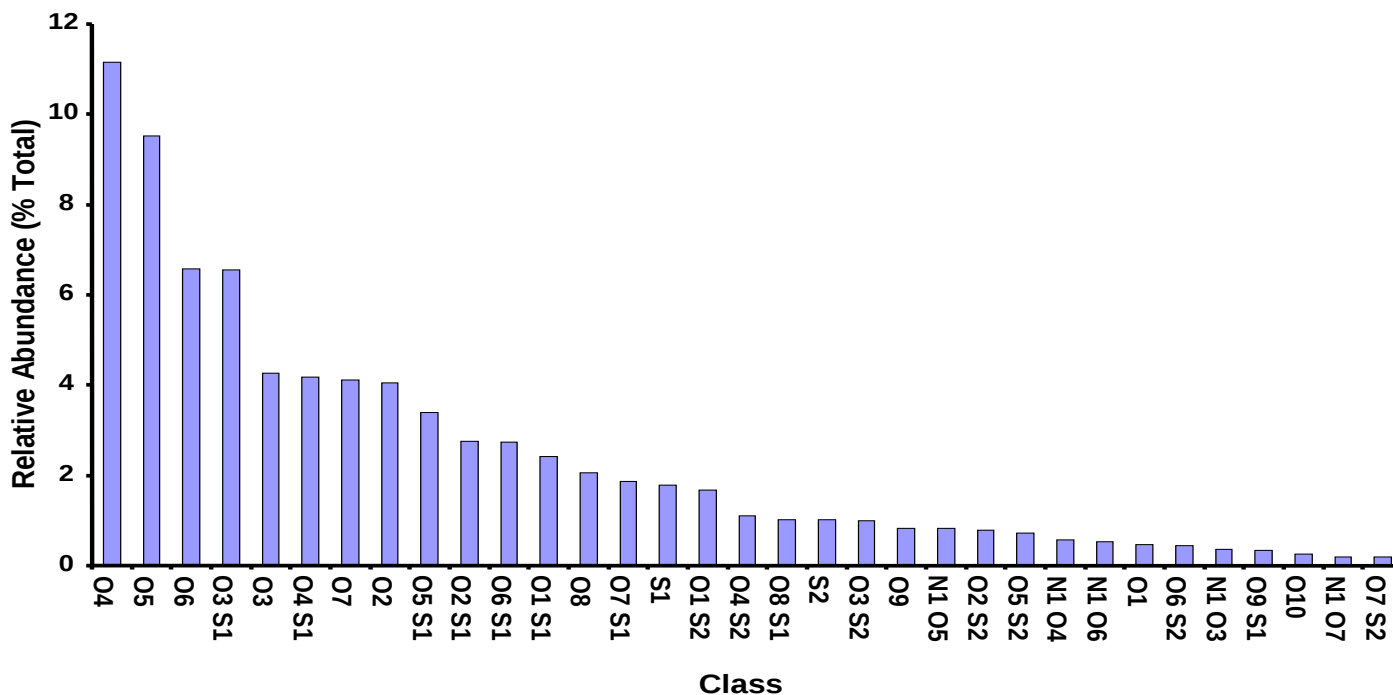
R = alkyl group
 X = COOH, R, OH, SO_x, NO_x, SH
 Y = C, S, N
 note: ring structures may not be fully saturated

Orbitrap and FTICR ESI MS

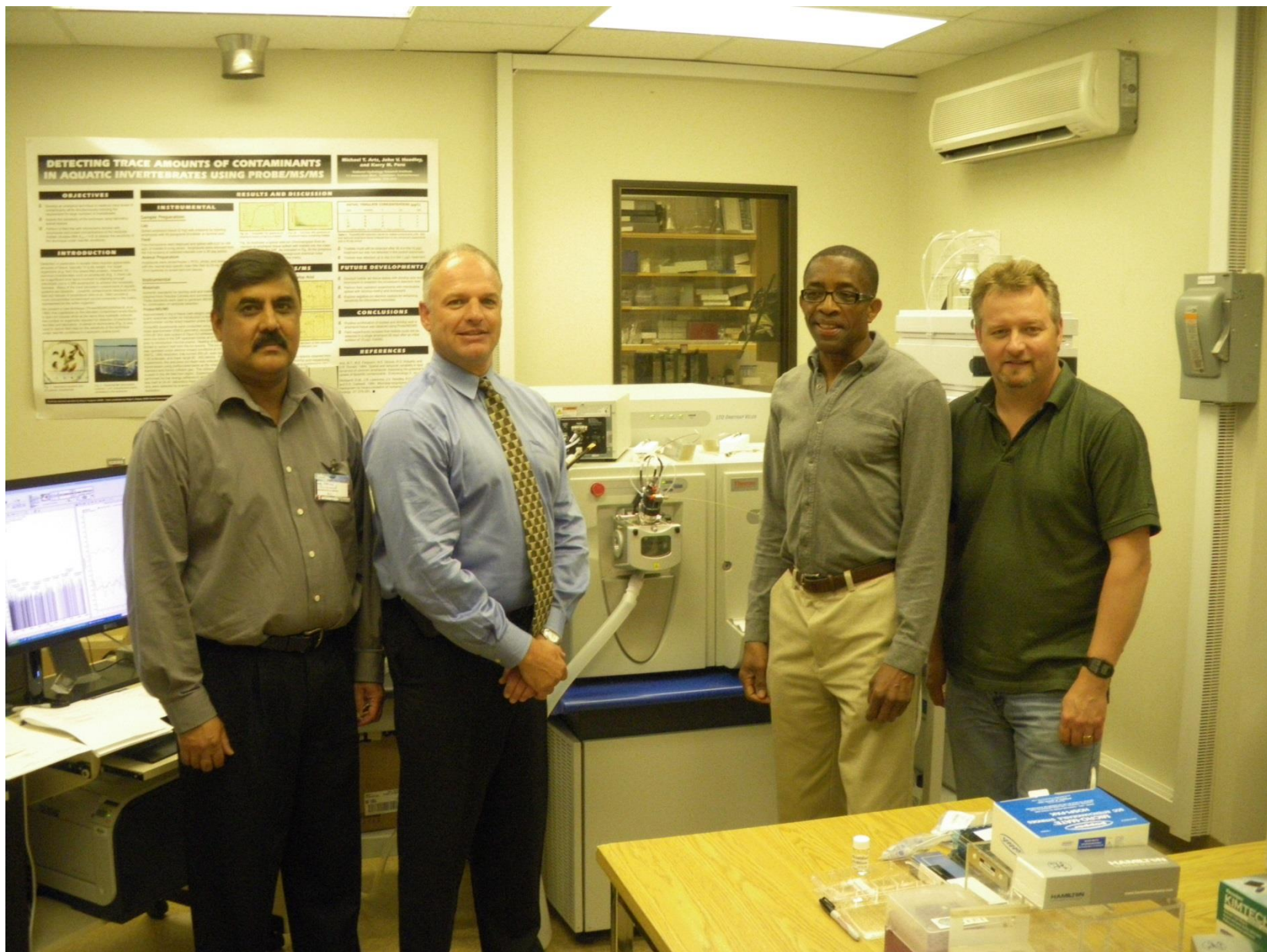
- Ultra High Resolution MS – 100,000+ resolution
- Enables empirical formula determination with less than 2ppm error

Class Graph for 5-3-1 -ESI

(-) Ion 9.4 T ESI FT-ICR MS







Extracting Oil Sands NAs



- An adapted liquid-liquid extraction process developed by Rogers, Liber, & MacKinnon (*Chemosphere*, 48:519)
- Acidify TPW
- Shake with DCM
- Separate from emulsion
- Rotoevaporate off DCM
- Filter 3x (final with molecular weight filter)

ESI MS

- Mass spectrometry with electrospray ionization in negative ion mode
- Loop injection
- External standard method
- Prior to analysis samples cleaned up using solid phase extraction (SPE)
- Removes background ions for improved analysis



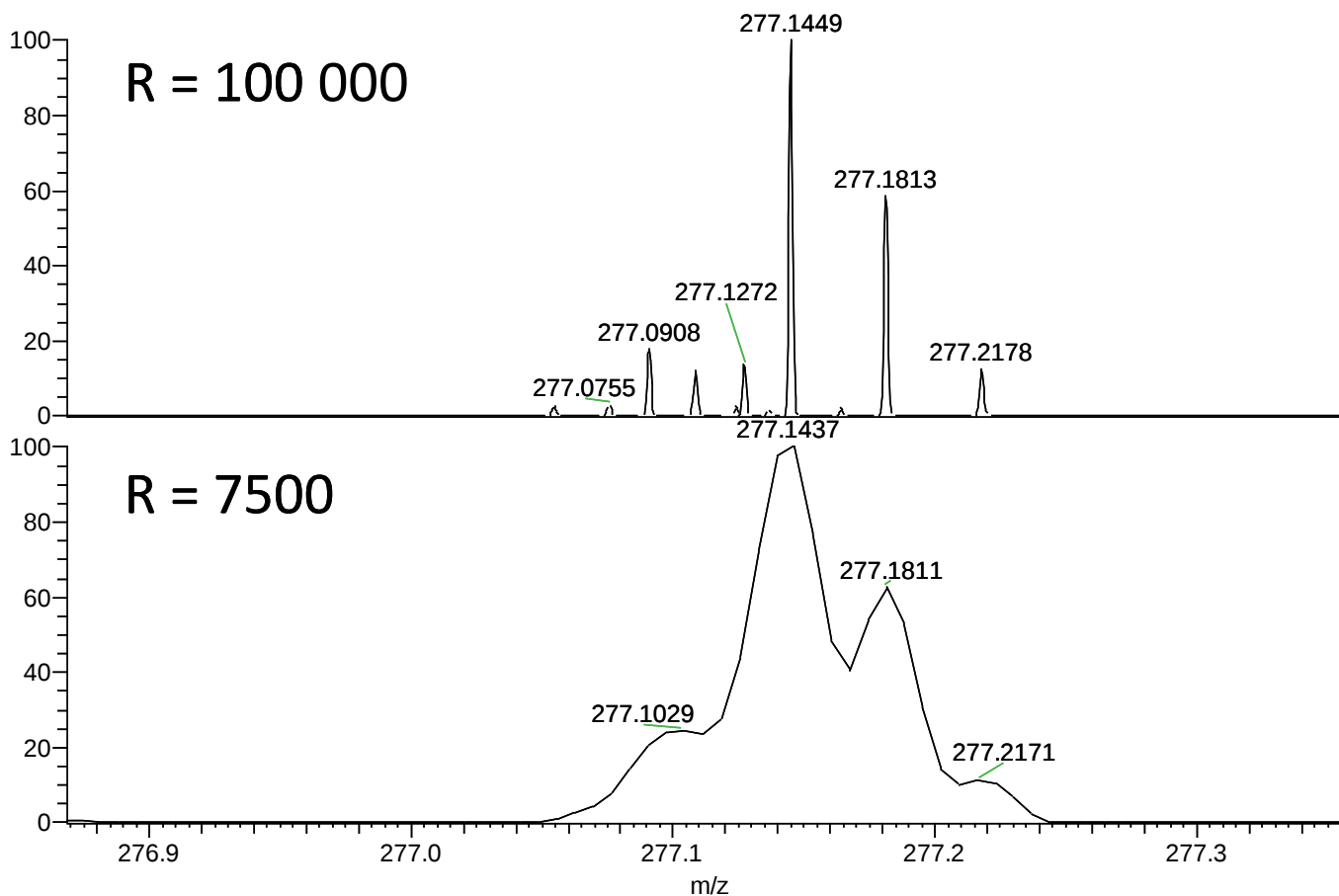
MS Experiments

Calibration standard

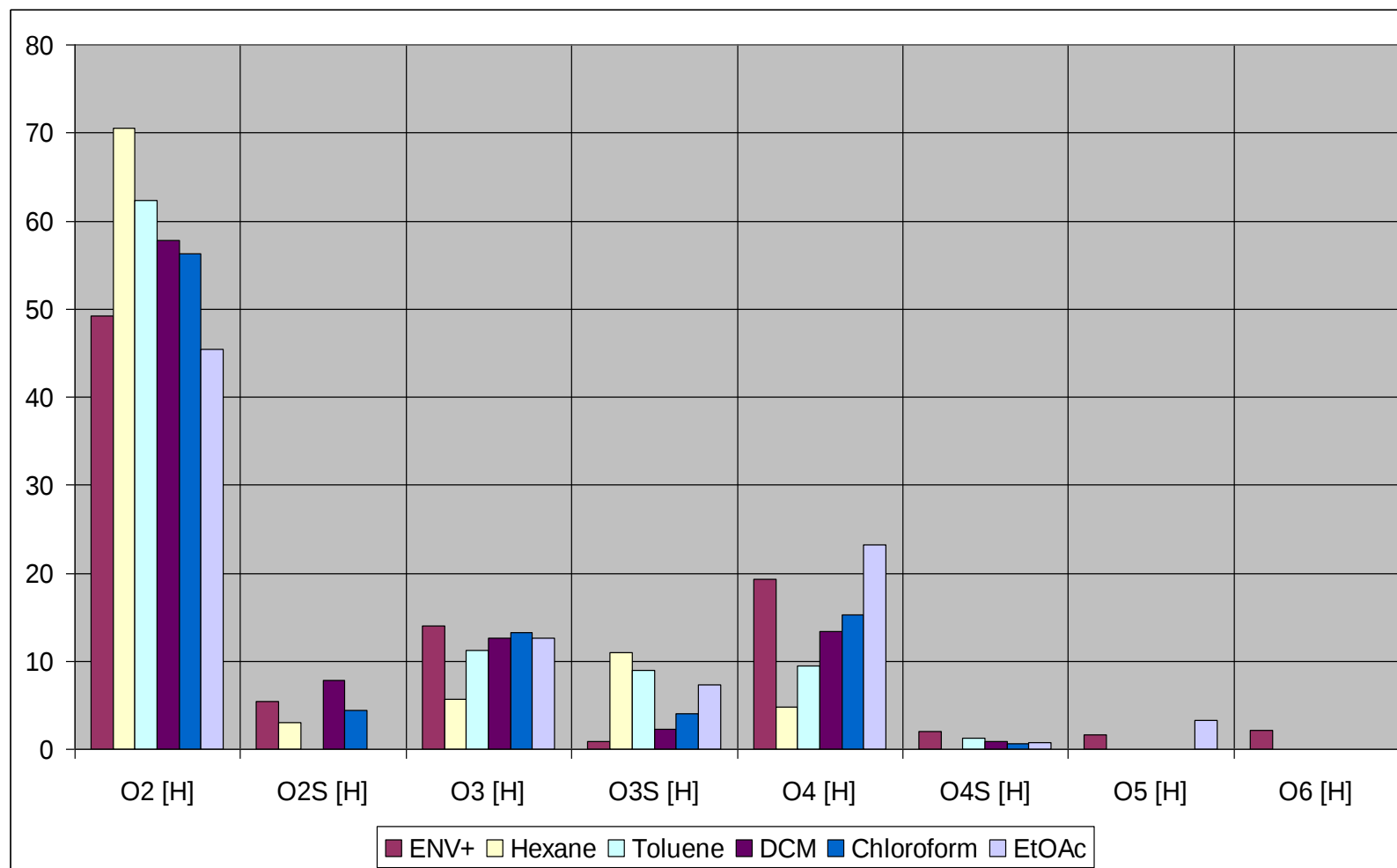
- **NAs extracted from Syncrude OSPW** - prepared in 50:50 acetonitrile:water (ACN:H₂O) containing 0.1% ammonium hydroxide(NH₄OH)
- No separation- flow injection analysis
- 250K resolution at m/z 200 detection
- full scan mode (m/z 100-600).

Orbitrap High Resolution ESI MS

- Ability to distinguish isobaric (same nominal MW) components.

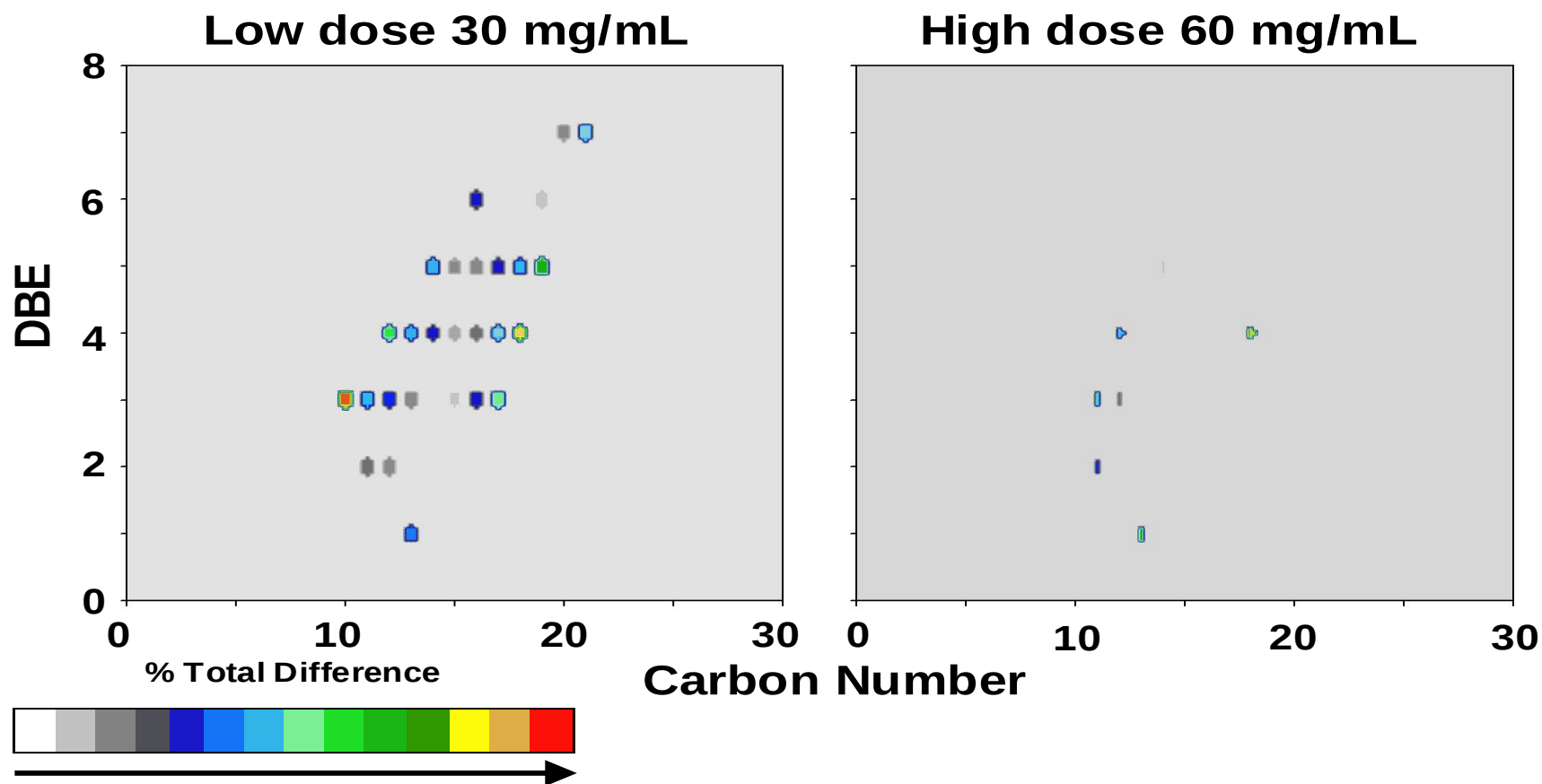


Orbitrap MS of Selective Solvent Extraction of NAFCs in OSPW



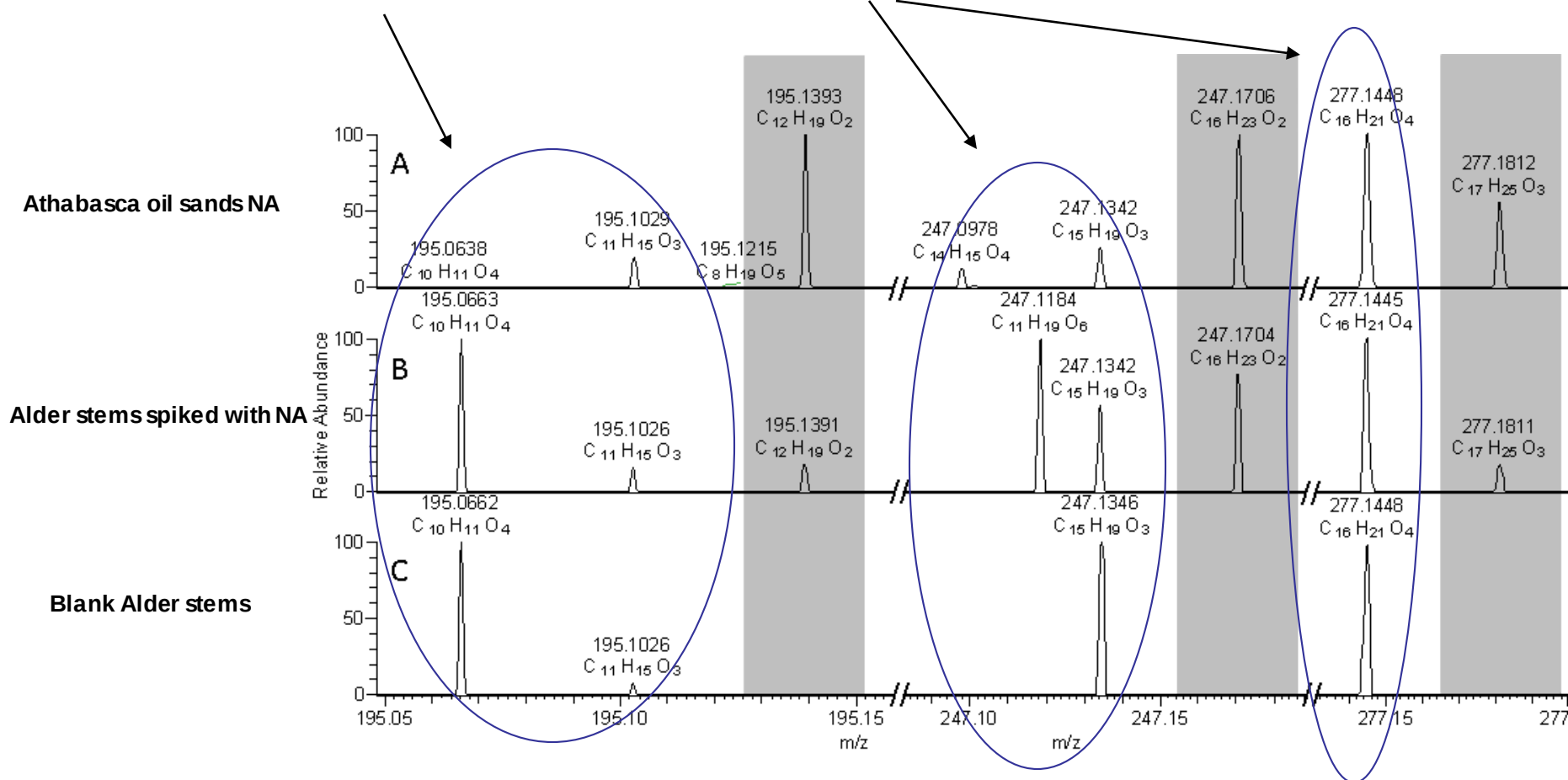
Biota Induced Dissipation NAs

Dissipation of NA in Plants



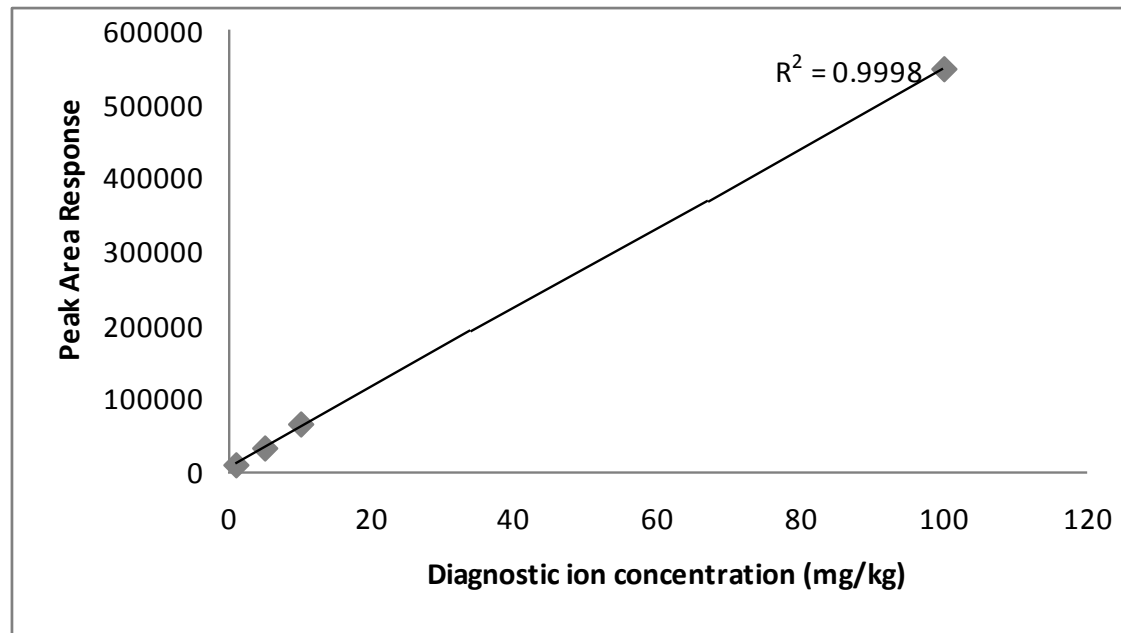
Orbitrap ESI MS of Plant Tissue

Low resolution would lead to misidentification

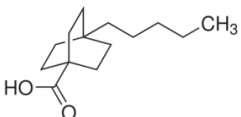
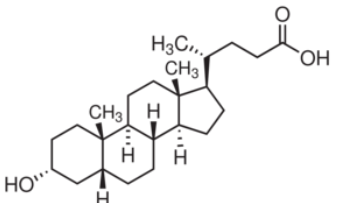
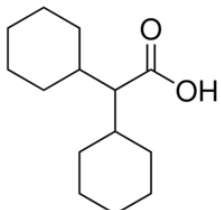


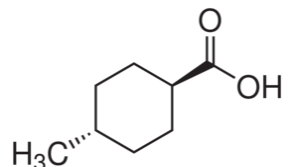
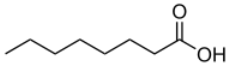
Orbitrap - Quantification

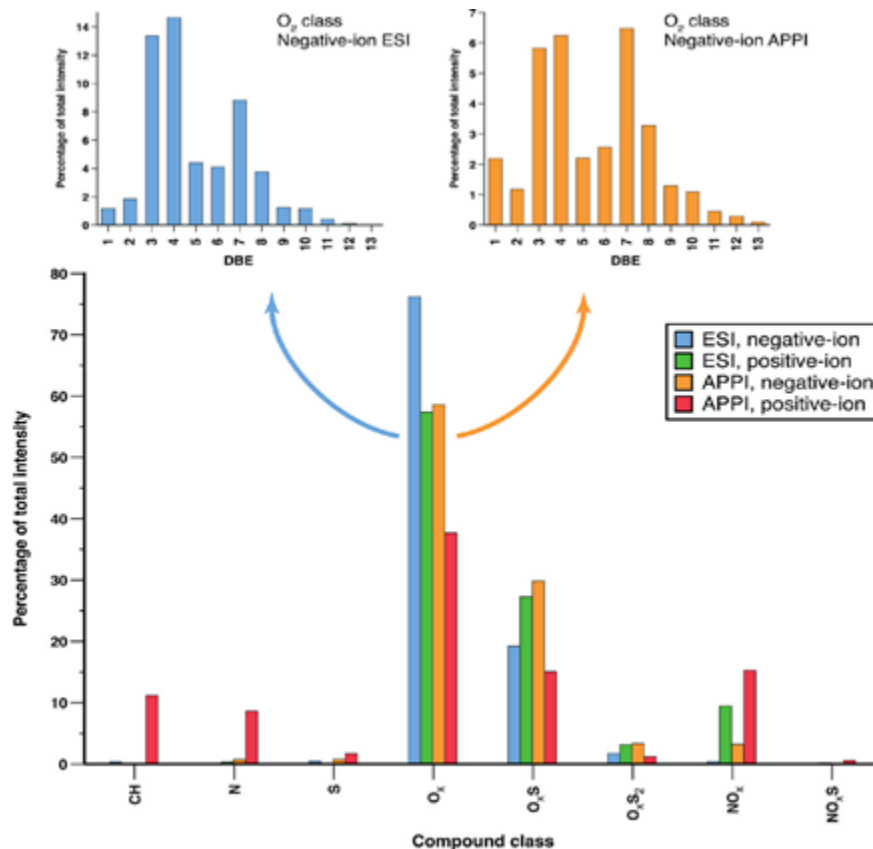
- In addition to providing mass resolution of up to 400,000, the orbitrap allows for quantification



Quantification Using Orbitrap

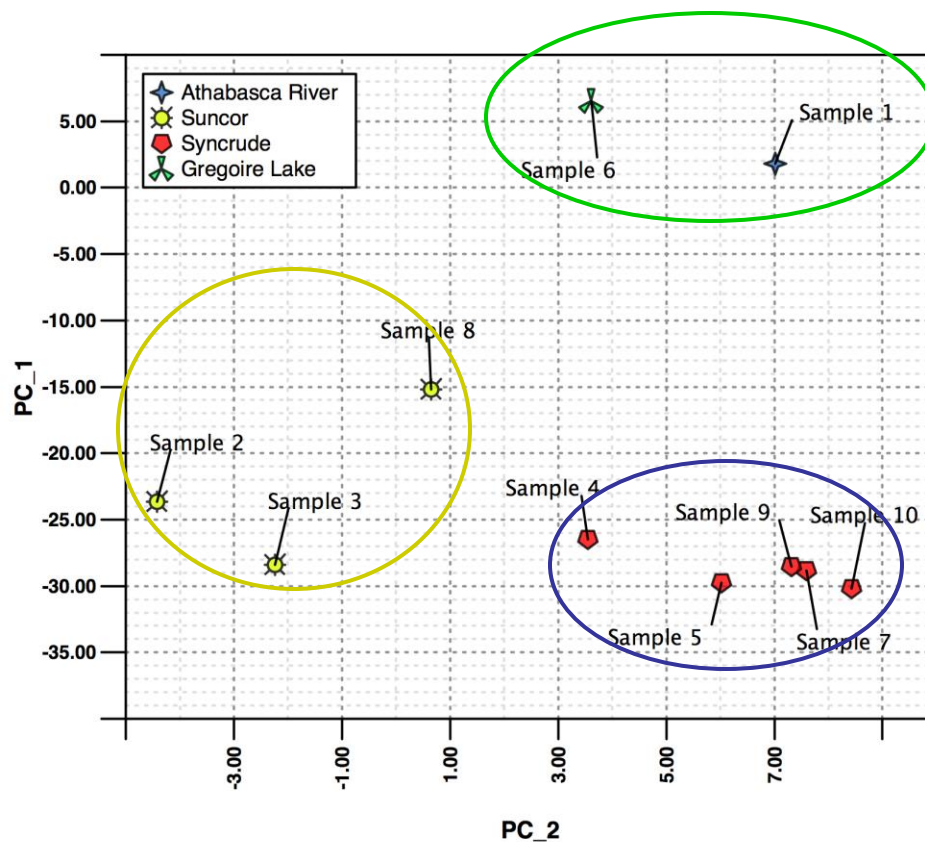
Compound	low res mg/L	high res mg/L
4-pentylbicyclo[2,2,2]octane-1-carboxylic acid	20.2	18.3
	25.2	22.7
	27.9	24.6
	31.5	28.2
	37.8	33.6
	46.3	36.0
	48.3	40.7
	4.5	6.3
	11.6	14.5
lithocholic acid	6.8	9.7
	10.6	13.0
	19.4	21.8
	16.2	13.4
	23.9	24.2
	29.9	30.3
	35.1	32.7
	38.9	37.5
	51.3	51.0
	4.1	6.6
dicyclohexylacetic acid	33.5	35.9
	53.6	54.6
	58	60.5
	64.2	68.0
	65.1	67.9
	65	63.5
	10.8	15.2
	18.4	23.7

Compound	low res mg/L	high res mg/L
4-methylcyclohexanecarboxylic acid	62.7	65.9
	57.1	51.2
	64.1	58.4
	3.4	6.9
	17.3	18.4
	37.5	35.6
	37.1	39.7
	48.4	41.7
	73.9	67.5
n-caprylic acid	24.5	24.7
	34.5	35.0
	43	40.4
	52.2	38.4
	56.1	53.0
	67.8	58.4
	72.5	67.1
	79	68.9

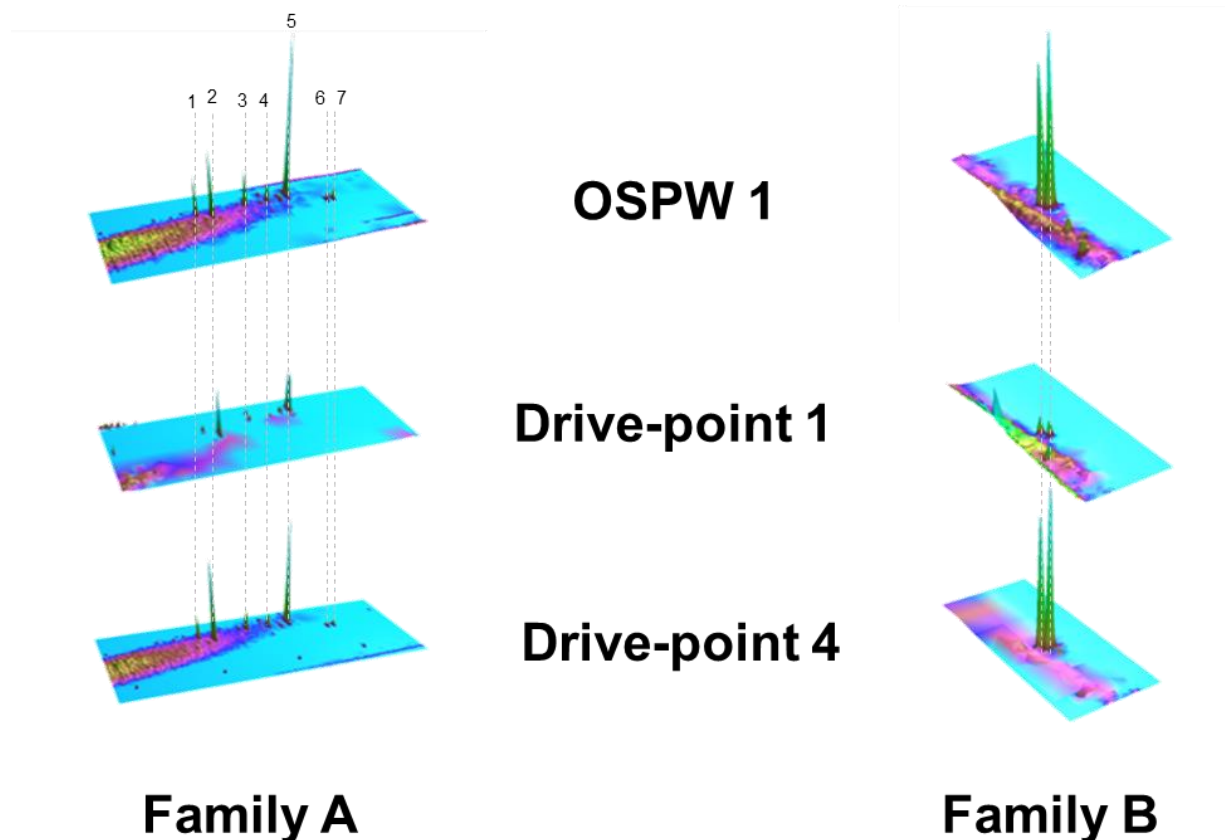


Contributions from different compound classes in a single OSPW sample as a function of the ionization method used.

PCA (principle component analysis) using HR ESI FTICR-MS

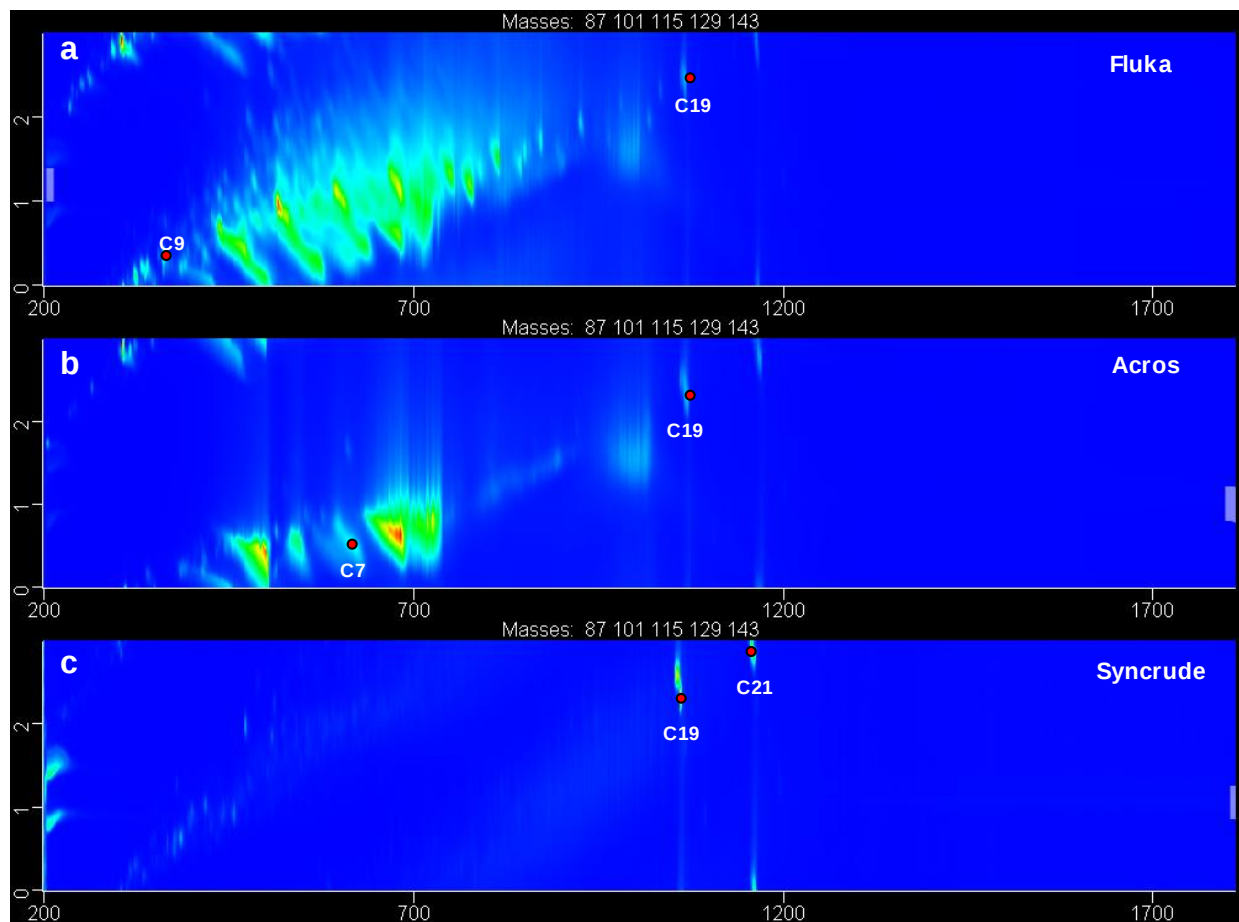


GC×GC-TOF/MS ion chromatograms for selected samples from OSPW, Far-field (Drive point 1) and Near-field (Drive-point 4) sites. Shown are the mono-aromatic m/z 145 (Family A) and m/z 237 and 310 (Family B) ions



Richard A. Frank, James W. Roy, Greg Bickerton, Steve J. Rowland, John V. Headley, Alan G. Scarlett, Charles E. West, Kerry M. Peru, Joanne L. Parrott, F. Malcolm Conly, and L. Mark Hewitt. *Environ. Sci Technol.*, **2014**, 48 (5), pp 2660-2670

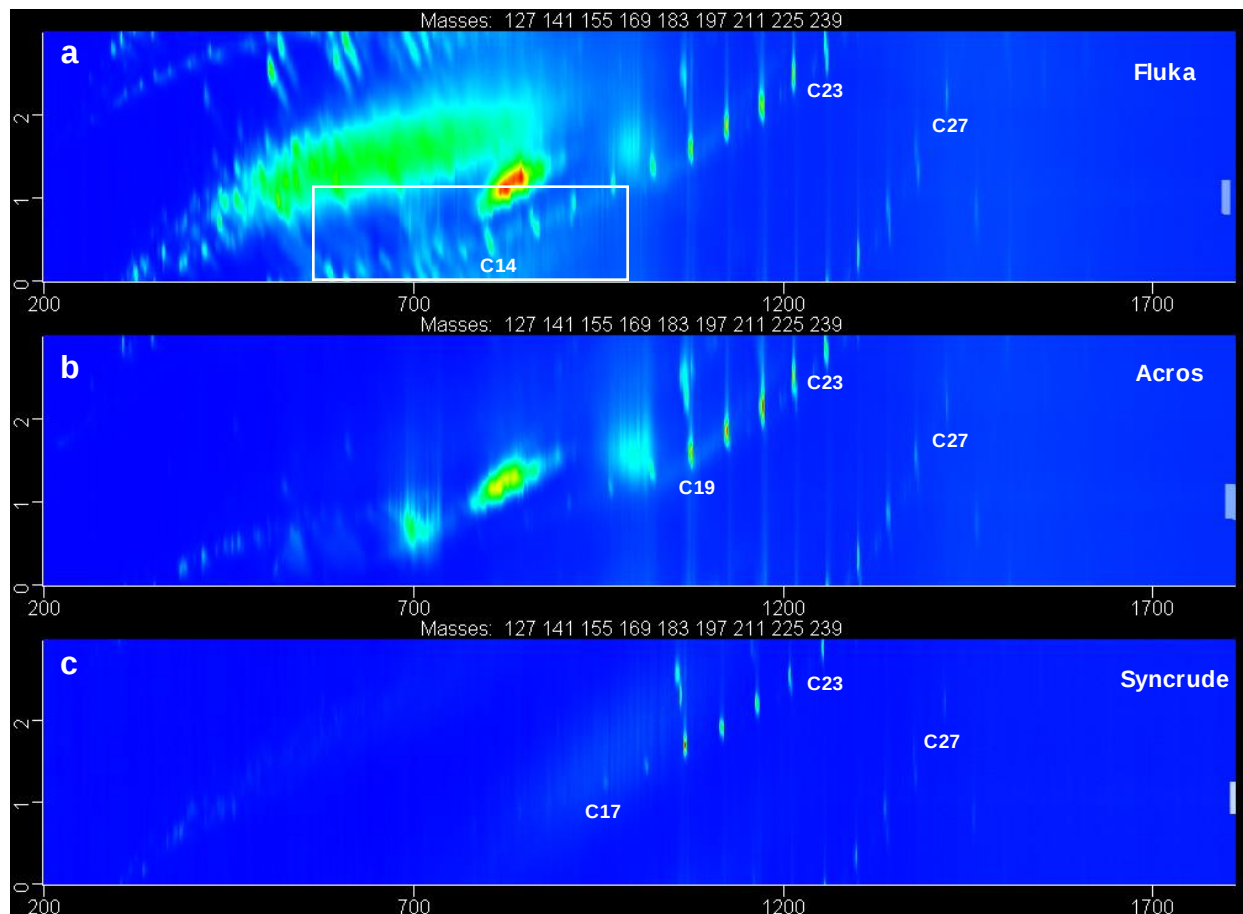
Z = 0



Contour plots of Z = 0 homolog obtained from methylated Fluka (a), Acros (b) and Syncrude (c) NAs.

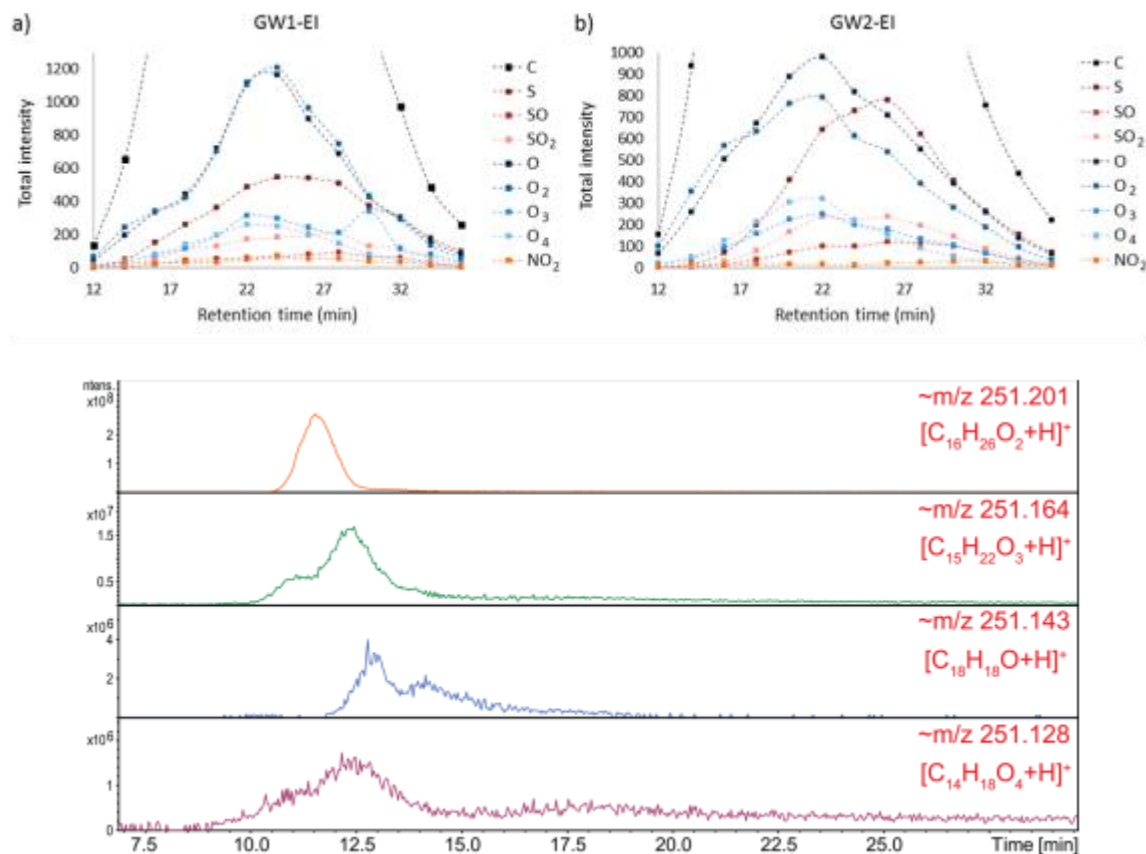
Chunyan Hao, John V. Headley , Kerry M. Peru , Richard Frank,Paul Yang, Keith R. Solomon.
Journal of Chromatography A, 1067 (2005) 277–284

$$Z = -2$$



Contour plots of $Z = -2$ homolog obtained from methylated Fluka (a), Acros (b) and Syncrude (c) NAs.

Chunyan Hao, John V. Headley , Kerry M. Peru , Richard Frank, Paul Yang, Keith R. Solomon. *Journal of Chromatography A*, 1067 (2005) 277–284



a) & b) GC-FTICR MS data illustrating different NAFC classes, c) GC-FTICR MS EIC monitoring of different isomers in OSPW.

a) & b) Xavier Ortiz, Karl J. Jobst, Eric J. Reiner, Sean M. Backus, Kerry M. Peru, Dena W. McMartin, Gwen O'Sullivan, Vince Y. Taguchi, and John V. Headley. *Anal. Chem.*, 2014, 86 (15), pp 7666–7673

c) Mark P. Barrow, Kerry M. Peru, and John V. Headley. *Anal. Chem.*, 2014, 86 (16), pp 8281–8288

Questions

