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Use of Advanced Tools to Measure the Composition of Extractable Oxygenated Organics at a Historic Crude Oil Release Site

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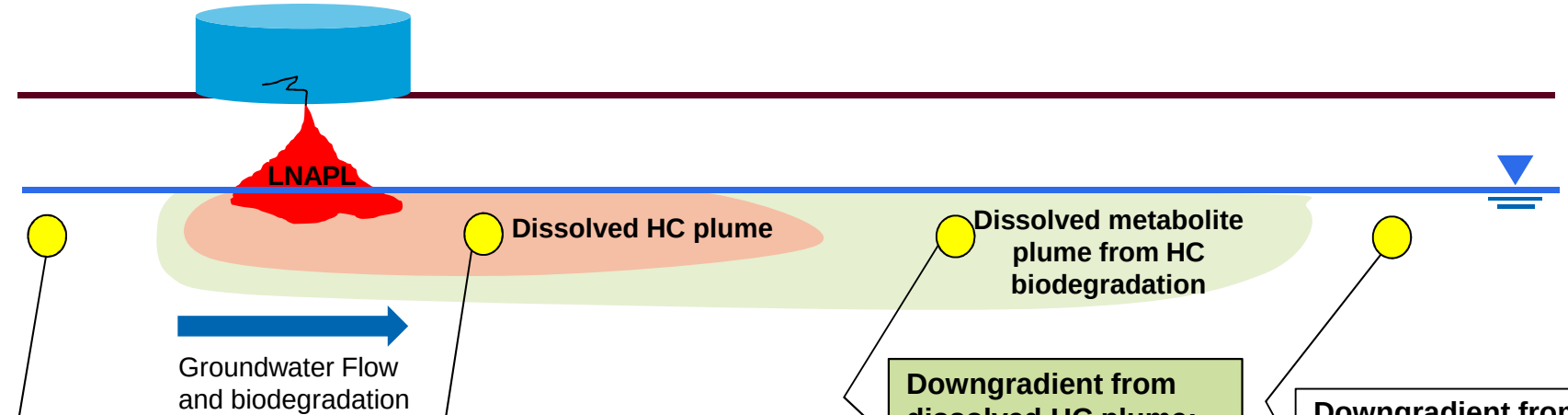
Conceptual "TPH" plume in groundwater and natural attenuation

Dissolved organics measured as Extractable TPH (Modified EPA 8015)



Upgradient from HC plume:
TPH =
+ *Naturally occurring organics*
+ *Background anthropogenic contamination*
+ *Lab/sampling artifacts*

Dissolved HC plume:
TPH =
+ **HC (and NSOs in case of crude oil)**
+ **HC metabolites**
+ *Naturally occurring organics*
+ *Background anthropogenic contamination*
+ *Lab/sampling artifacts*

Downgradient from dissolved HC plume:
TPH =
+ **HC metabolites**
+ *Naturally occurring organics*
+ *Background anthropogenic contamination*
+ *Lab/sampling artifacts*

Downgradient from HC metabolite plume:
TPH =
+ *Naturally occurring organics*
+ *Background anthropogenic contamination*
+ *Lab/sampling artifacts*

LNAPL – Light Non Aqueous Phase Liquids
TPH – Total Petroleum Hydrocarbons

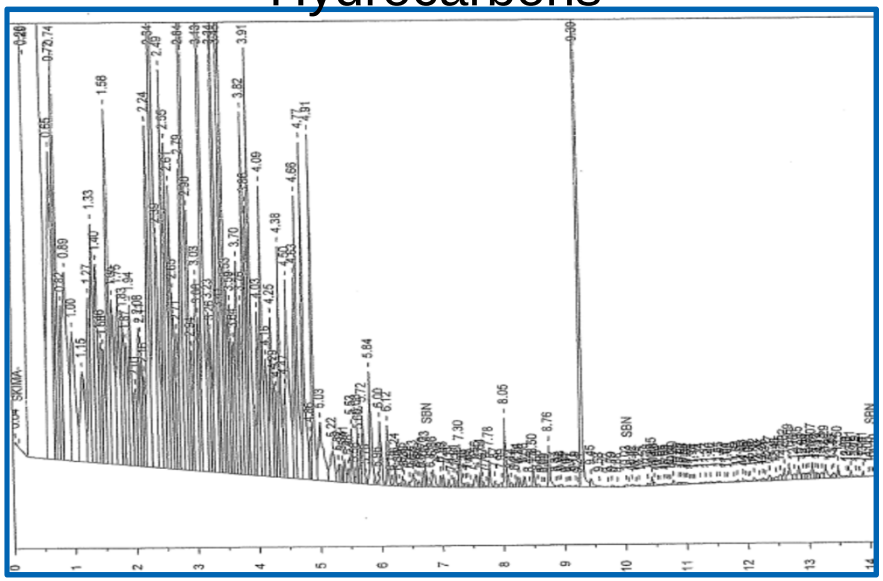
HC – Hydrocarbons
NSO compounds – Nitrogen, Sulphur and Oxygen containing compounds

Chromatograms Provide Insight into Presence of Non-Hydrocarbons

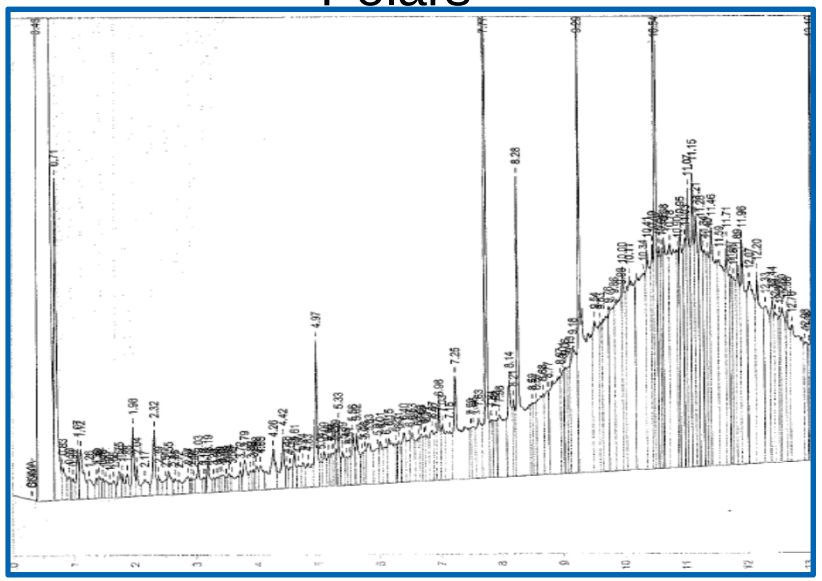
- Dissolved hydrocarbons will consist of compounds with carbon numbers less than 15 and will not show a UCM

- “Polars” are more soluble than hydrocarbons and compounds with carbon number greater than 15 can be in dissolved phase

Hydrocarbons



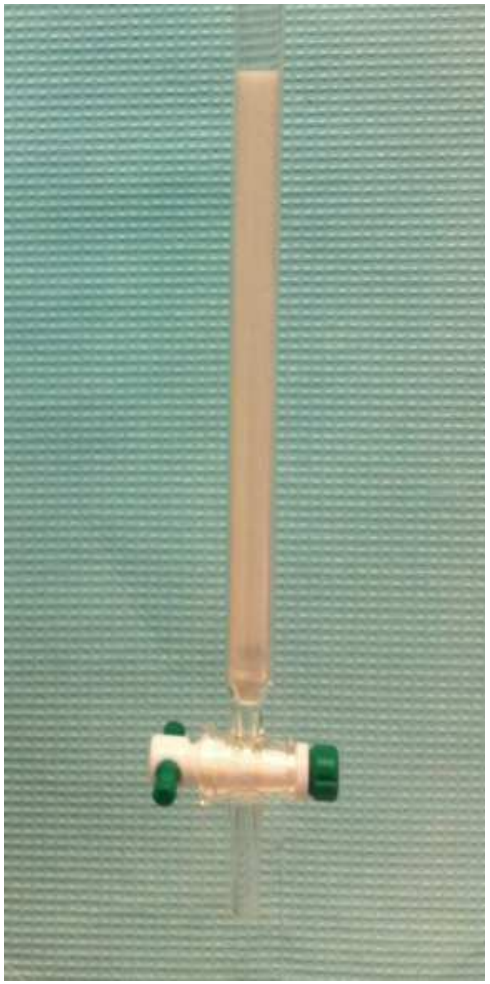
“Polars”



Silica Gel Cleanup (EPA Method 3630C)

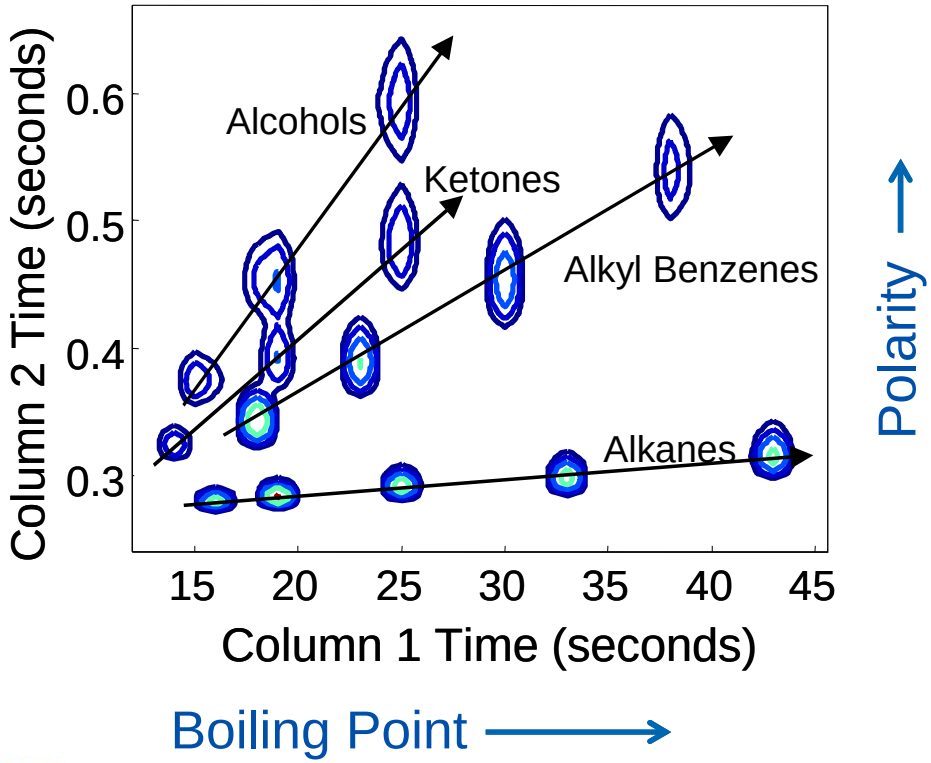
- Compounds trapped depend on the solvent
- Silica gel columns trap polars and allow petroleum hydrocarbons to pass through.
- Surrogates allows tracking of hydrocarbons removal and retention of polars

TPHd – C10-C28 (µg/l)	TPHd with S.G. (µg/l)	% Polars
3300	810	75
220	N.D.	**100**
14000	13000	7
53000	2900	95
2100	340	84
2900	N.D.	**100**
3500	1600	54



Introduction to GCxGC

- Similar to traditional gas chromatography except that the compounds in the sample are subjected to two separations
- *Simultaneous* separation of analytes using two complementary (unrelated) separation mechanisms while preserving the first dimension separation
- Assume:
  - GC_1 can separate 5 compounds
  - GC_2 can separate 3 compounds
- Then:
  - GC_1xGC_2 can separate 5 x 3, so 15 compounds!



K. J. Johnson et. al. *J. Sep. Sci.* (2002), 25, 297-303.

Importance of Advanced Characterization

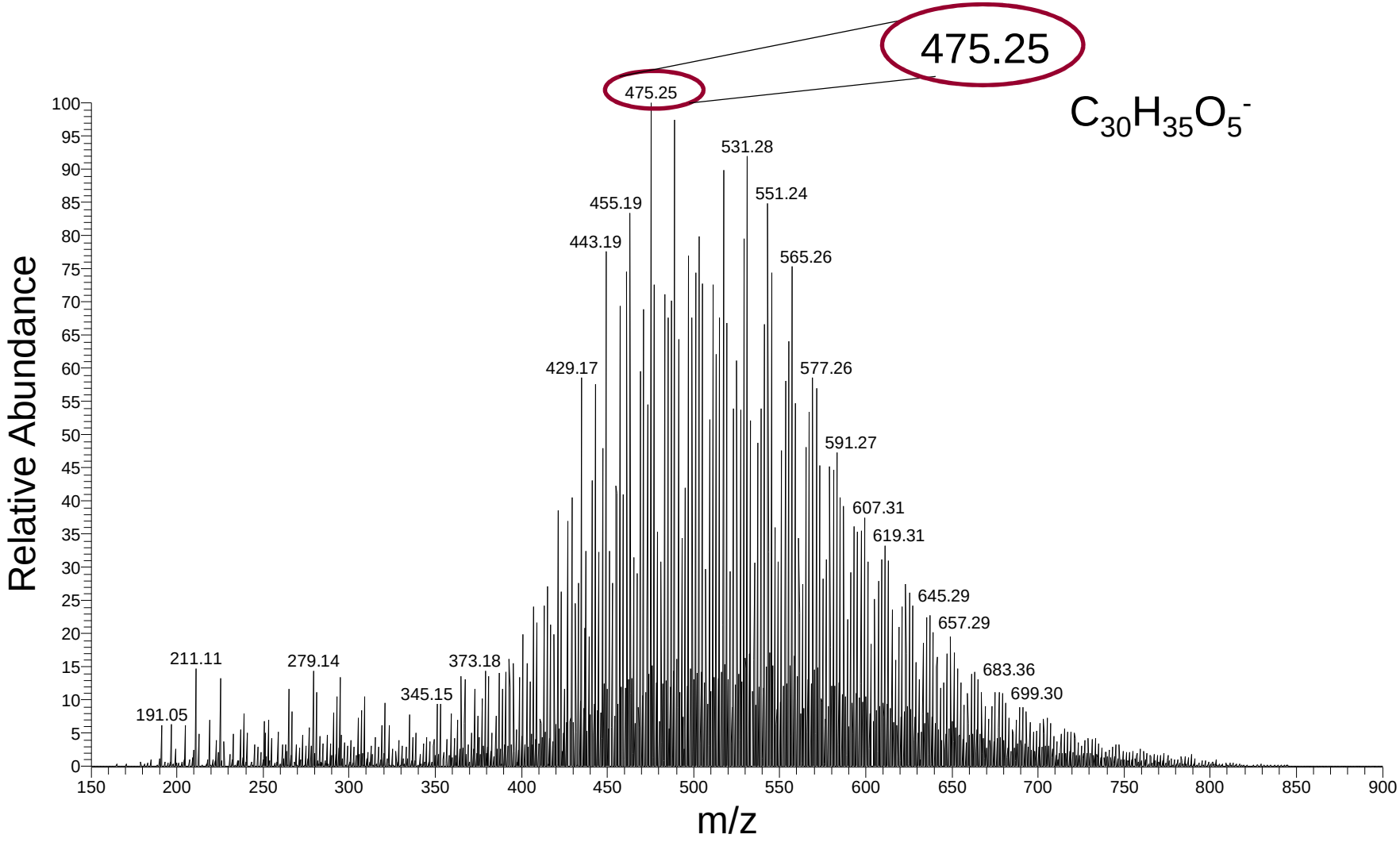
Well	DRO ug/l	DRO wSGC ug/l	Target Polars	# Tentatively Identified Polar Compounds (TIPCs) (metabolites only) in each class (Commercial Lab GC-MS Library Search)					# Tentatively Identified Polar Compounds (TIPCs) (metabolites only) in each class (GCxGC-MS Results)				
				K	P	Ald	Alc	Acid	K	P	Ald	Alc	Acid
MW-3	3200	<96	**All ND**	0	0	0	0	**9**	**22**	**0**	**5**	**19**	**15**
MW-3 dup	2900	<120	**All ND**	0	0	0	0	**3**	**14**	**0**	**4**	**13**	**14**
MW-41	3300	<96	**All ND**	0	0	0	0	**1**	**13**	**0**	**3**	**13**	**18**
MW-26	210	<100	**All ND**	0	0	0	0	**3**	**2**	**1**	**0**	**4**	**12**
MW-31	470	<100	**All ND**	0	0	0	0	**2**	**0**	**1**	**0**	**1**	**7**

Identification is based on retention time and mass spectra, not by using standards. K= ketones, P= phenols, Ald= aldehydes, Alc= alcohols, Acids= acids and esters

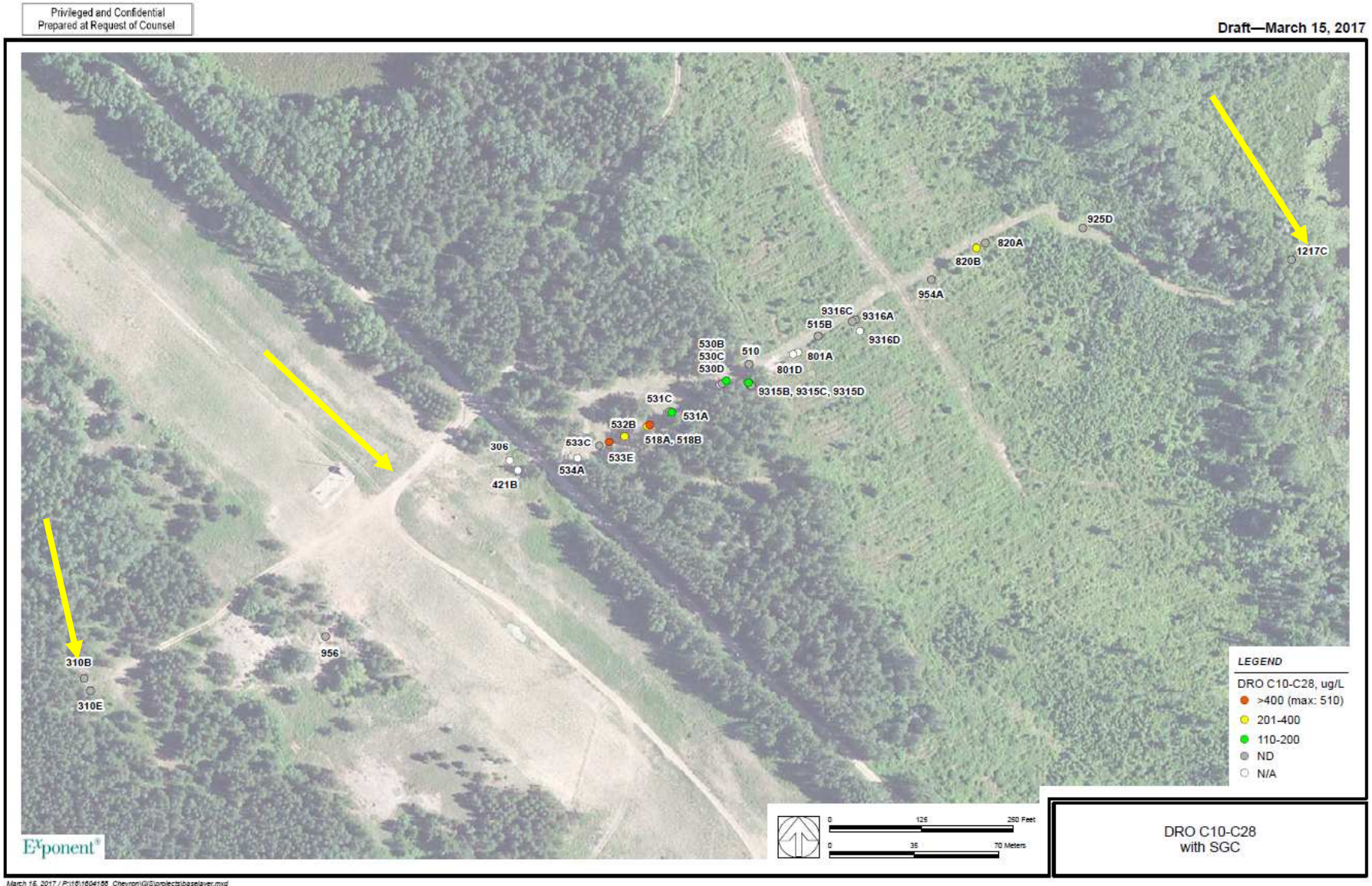
Introduction to Orbitrap High Resolution Mass Spectrometry

- Molecules are directly infused into the mass spectrometer
- Molecules are ionized and separated based on their mass to charge ratio (m/z)
  - Negative mode: acidic species
  - Positive Mode: basic species
  - Non-polar molecules will not be detected
- The mass spectrometer provides molecular formulas but cannot differentiate isomers

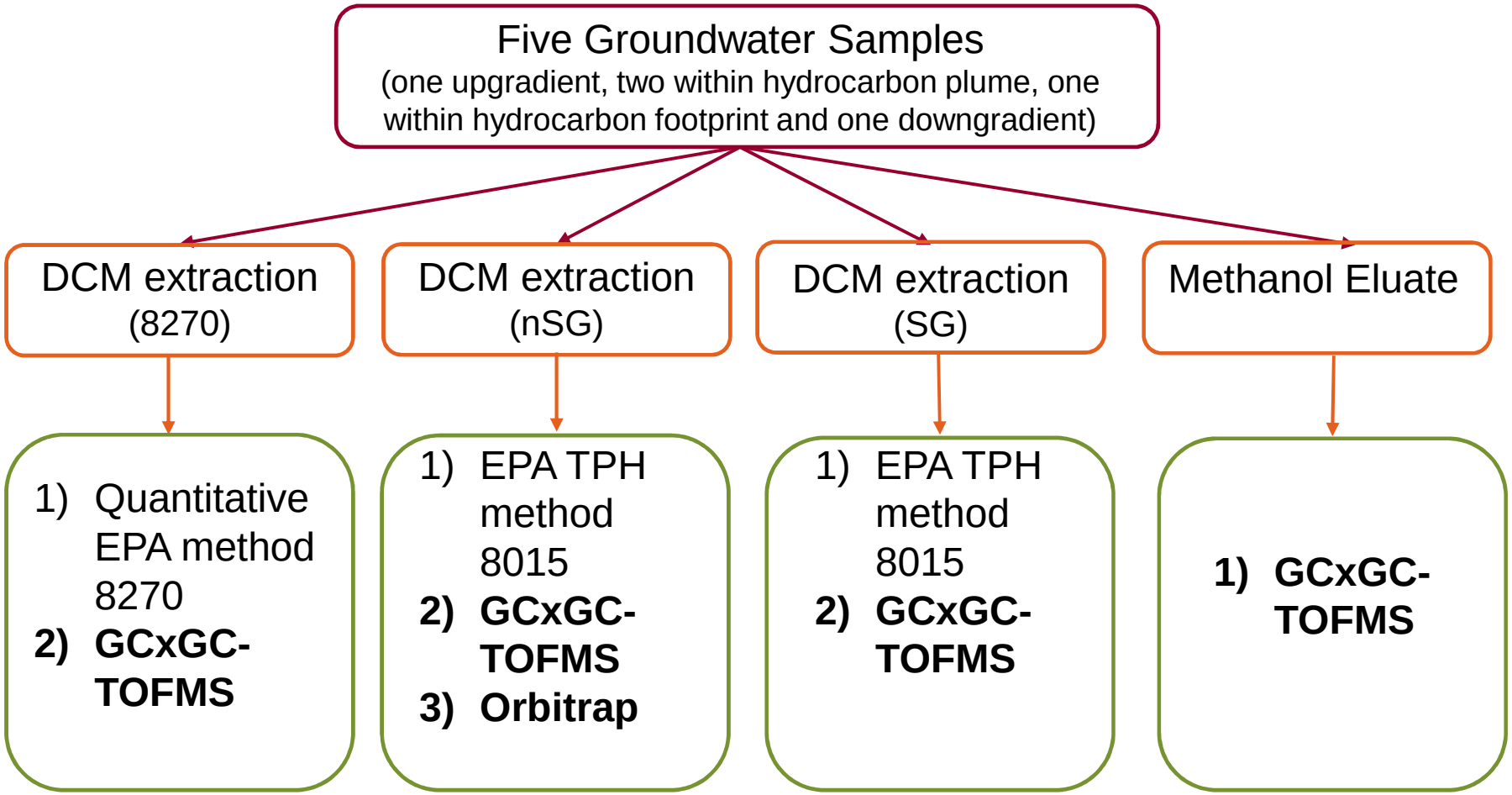
High Resolution Mass Spectrum using ESI in Negative Mode



Crude Oil Site

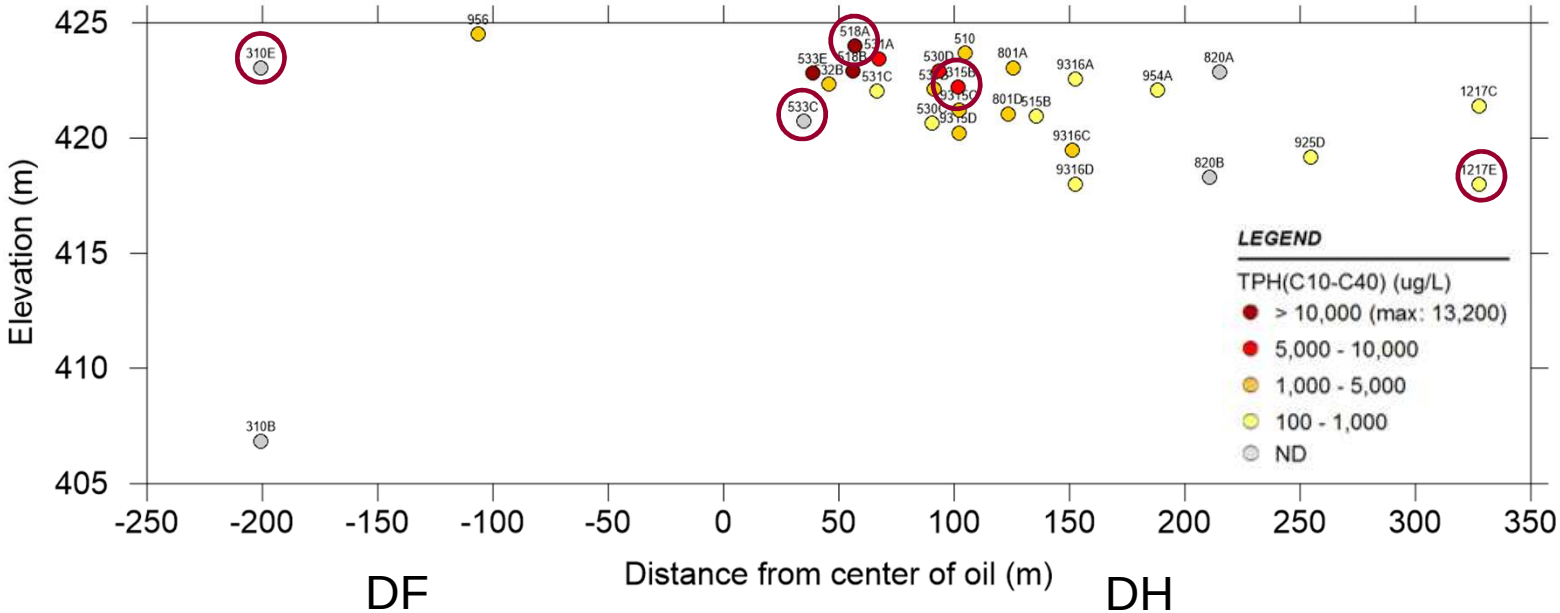


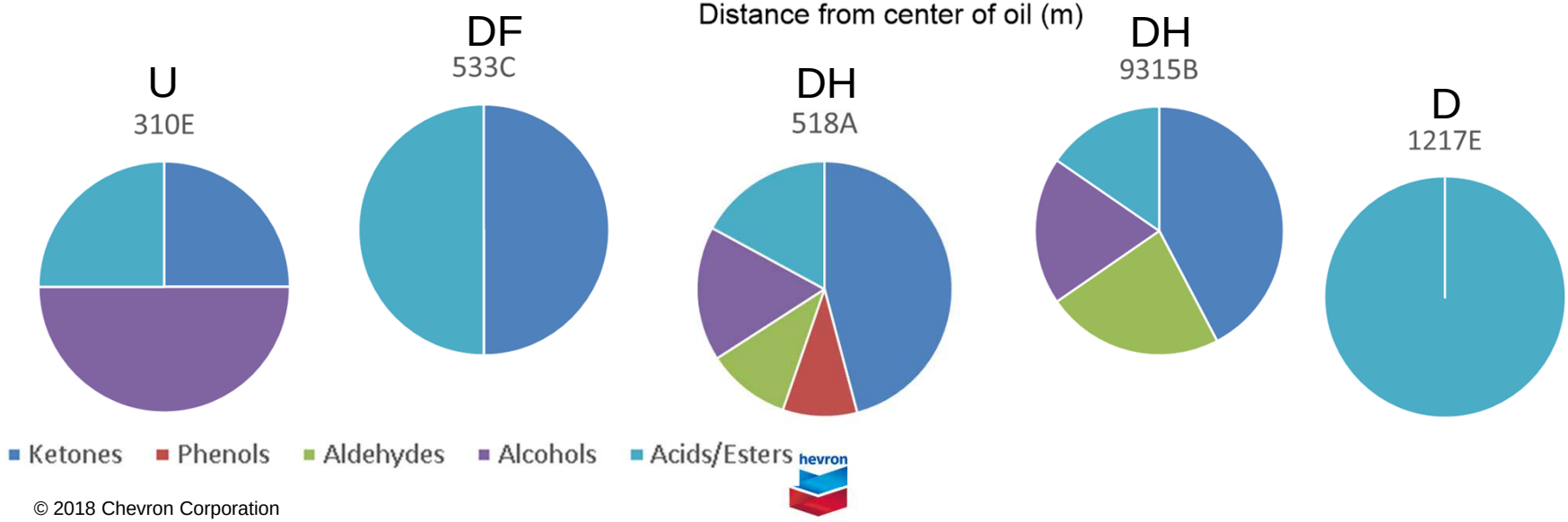
Analytical Approach



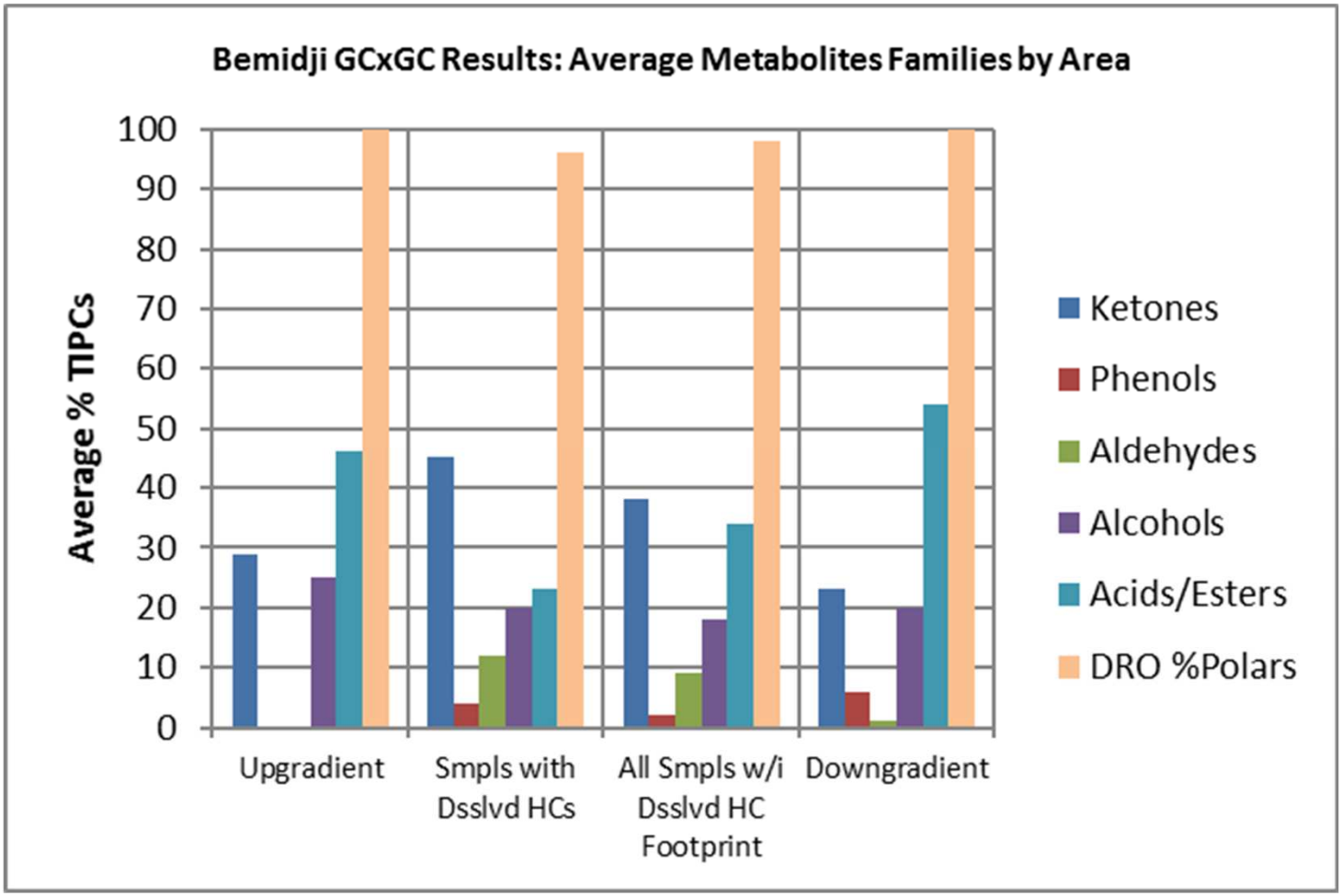
Two LNAPL samples were also collected and analyzed on the Orbitrap

Composition of Organics Becomes more Like Background in the Downgradient Wells





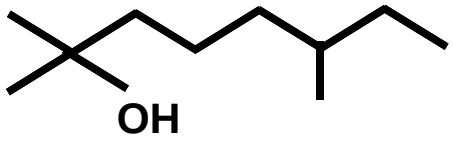
GCxGC Groundwater Results



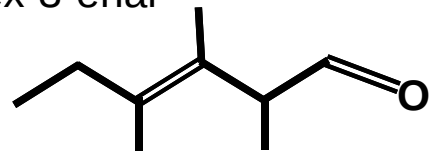
Tentatively Identified Compounds Identified by GCxGC-TOFMS

- 2016 Bemidji data set contains 178 unique TICs of which 158 (89%) are in our fuels database

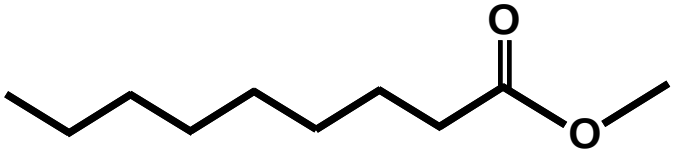
2,6 dimethyl, 2 octanol

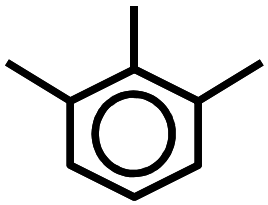


2,3,4 trimethyl, hex-3-enal

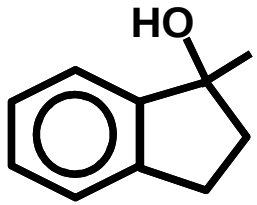


Octanoic acid, methyl ester

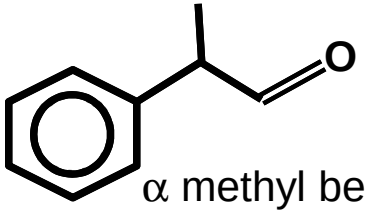




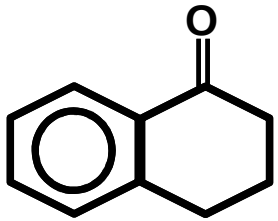
2,3 dimethyl phenol



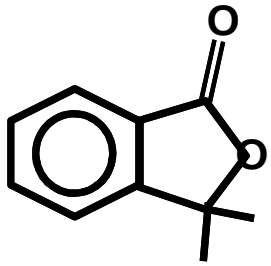
1-methyl,
1-indanol



α methyl benzenealdehyde

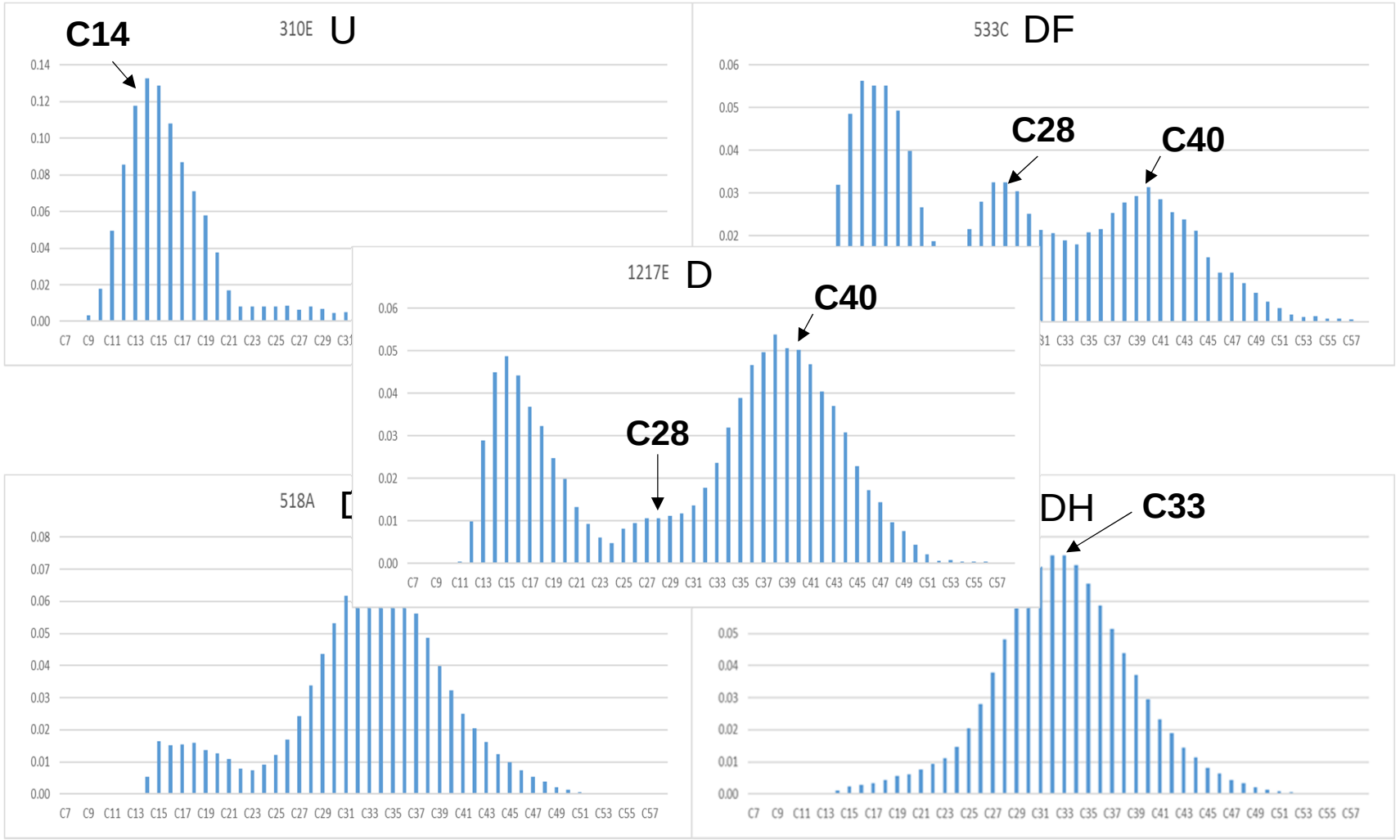


1 (2H)
Naphthalenone,
3,4 dihydro



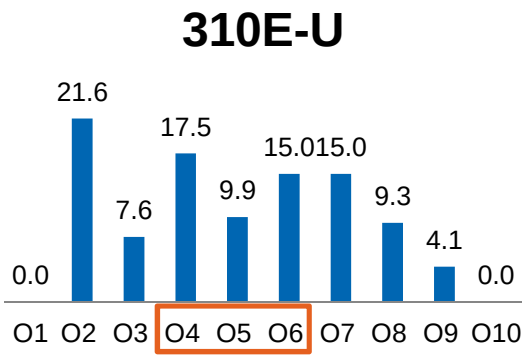
1(3H)
Isobenzofuranone,
3,3 dimethyl

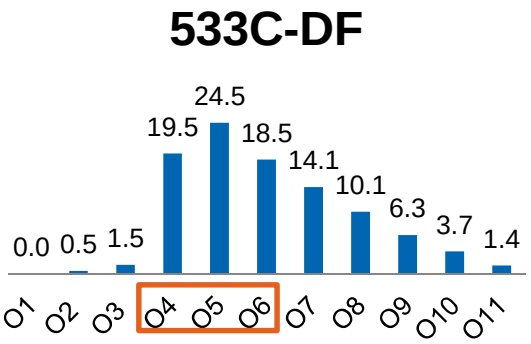
Orbitrap Carbon Number Distribution is Different Based on location within the Plume

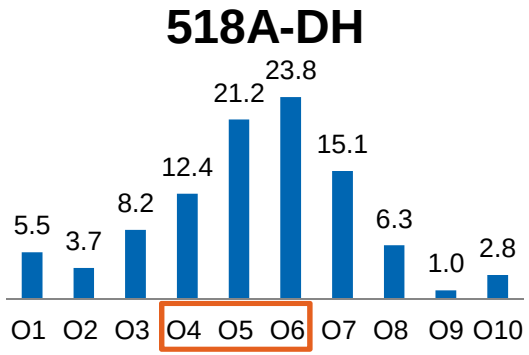


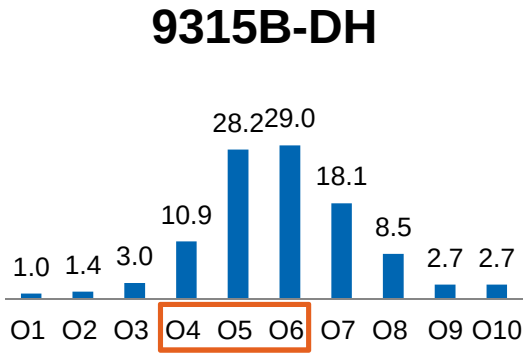
Compounds with 4-7 Oxygens Dominate

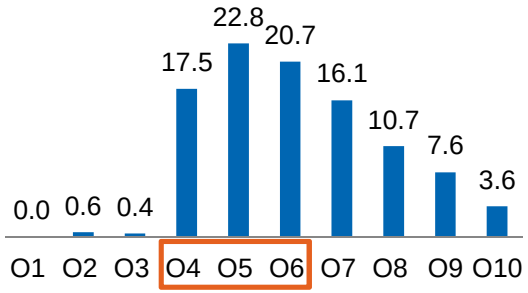
ESI Negative Ion Mode



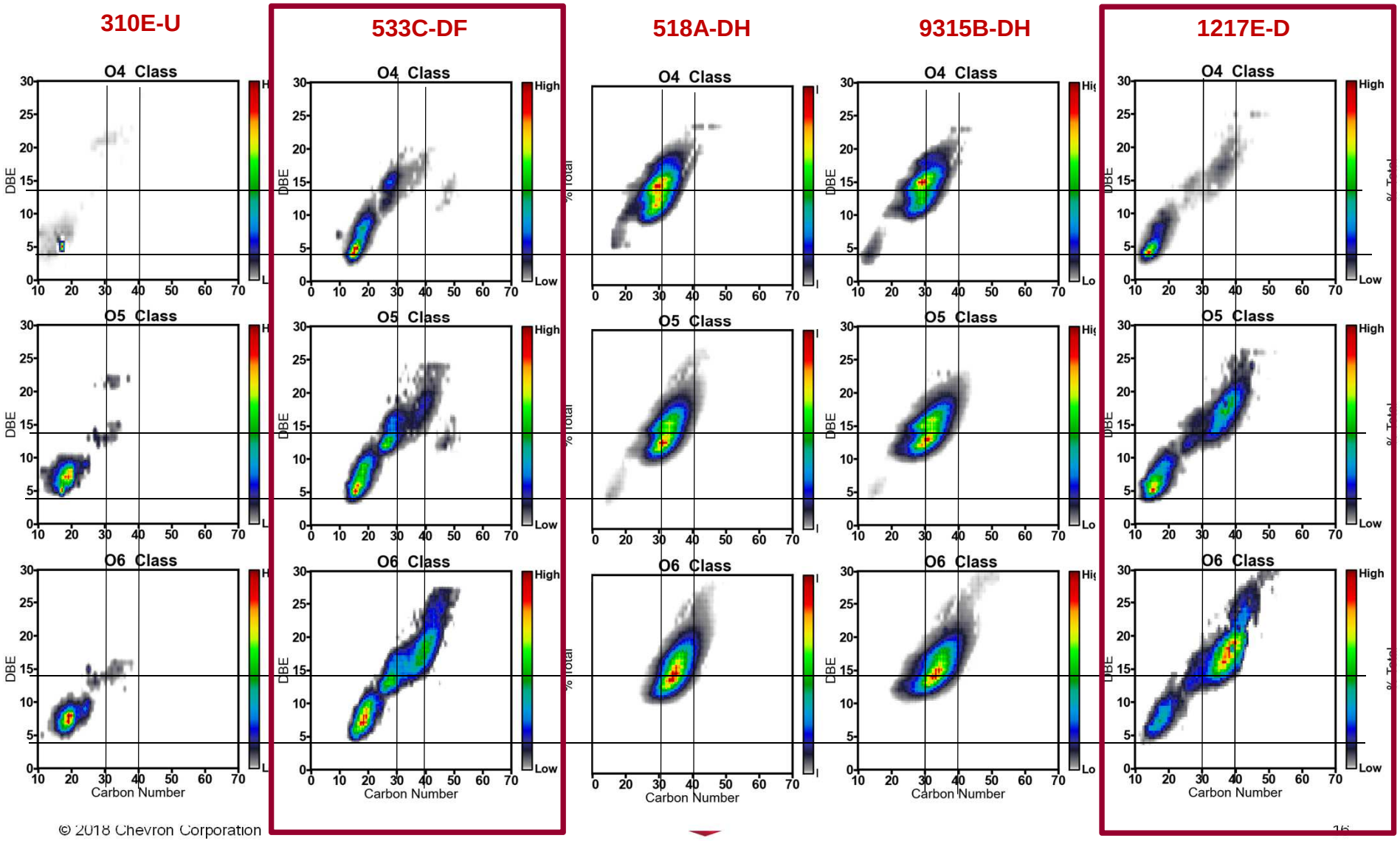




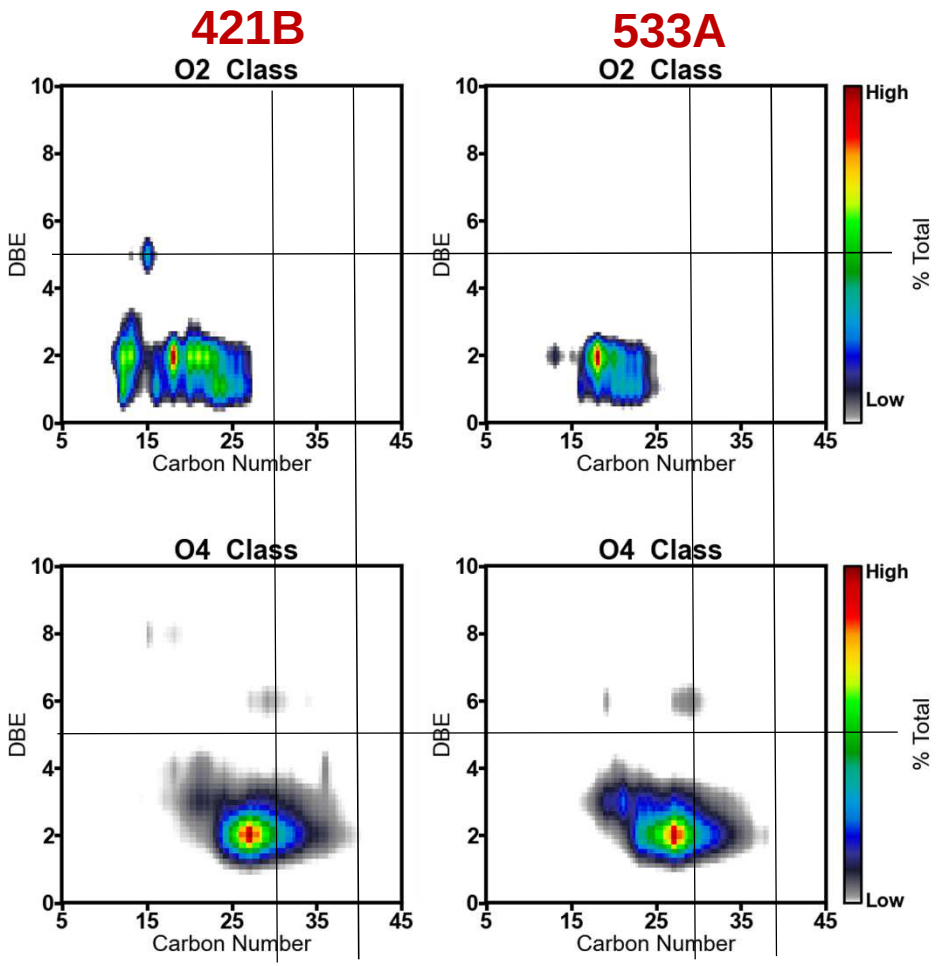




Oxygen containing organics vary across the site



Acids profile in LNAPL is much different from what is present in the groundwater



Appears to be a mixture of paraffinic and mononaphthenic carboxylic acids based on DBE

Appears to be mainly paraffinic dicarboxylic acids based on DBE

Summary

- TPH is a complex mixture of organic compounds
  - Metabolite compounds found at Bemidji have been found at fuel release sites.
- Advanced characterization tools indicate
  - Composition of oxygen containing compounds in groundwater at historic crude oil release site are similar to fuel releases (GCxGC-TOFMS)
  - Solvents can extract oxygen containing compounds with carbon numbers up to C50 (Orbitrap)
  - Oxygen containing compounds downgradient can have very few similarities to hydrocarbons that were part of the original release (Orbitrap)

Acknowledgements

- Chevron Environmental Management Company:
  - Project managers
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  - Matthew Hurt
  - Jeff Curtis
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- Barbara Bekins, Jared Trost, and Andrew Berg of the USGS for site background information and field support