Analysis of Petroleum Metabolites in Groundwater using GCxGC-TOFMS

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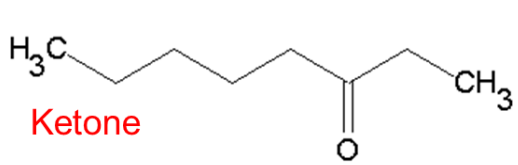
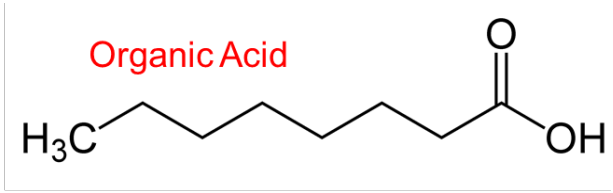
Outline

- Background/ Purpose of Study
- Overview of Study
- GCxGC results
- Summary

Background

- Refined petroleum products contain hydrocarbons and only very small amounts of heteroatoms (NSOs).
  - Hydrocarbons contain only carbon and hydrogen
- Biodegradation of petroleum results in molecules that contain oxygen and thus are “polar”
  - Metabolites





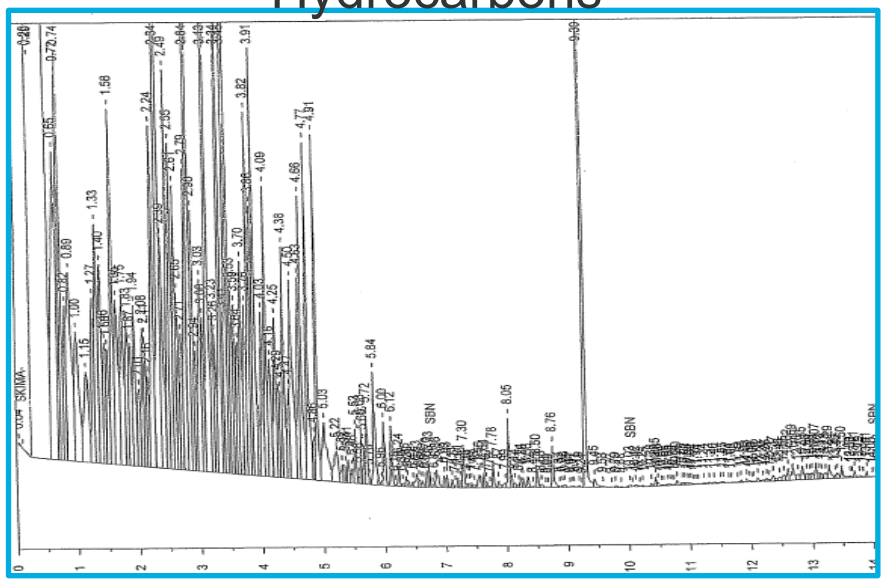
- Solvent extraction using dichloromethane will extract all organics
- At historic release sites, the composition of material in groundwater can shift from mostly hydrocarbons to mostly “polars”.
- Silica gel will remove “polars” from the extract without retaining the hydrocarbons

Dissolved Hydrocarbons vs. Dissolved “Polars”

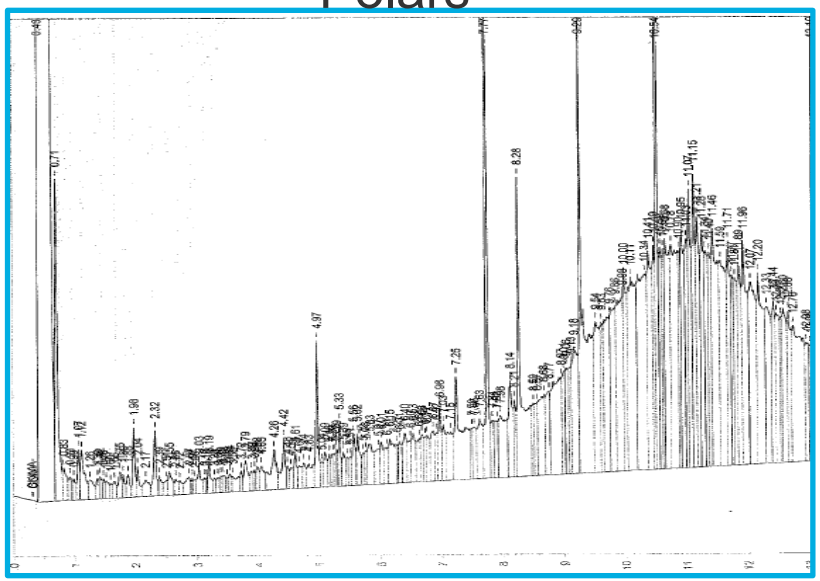
- Dissolved hydrocarbons will consist of compounds with carbon numbers less than 15 and will not show a UCM

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

Hydrocarbons



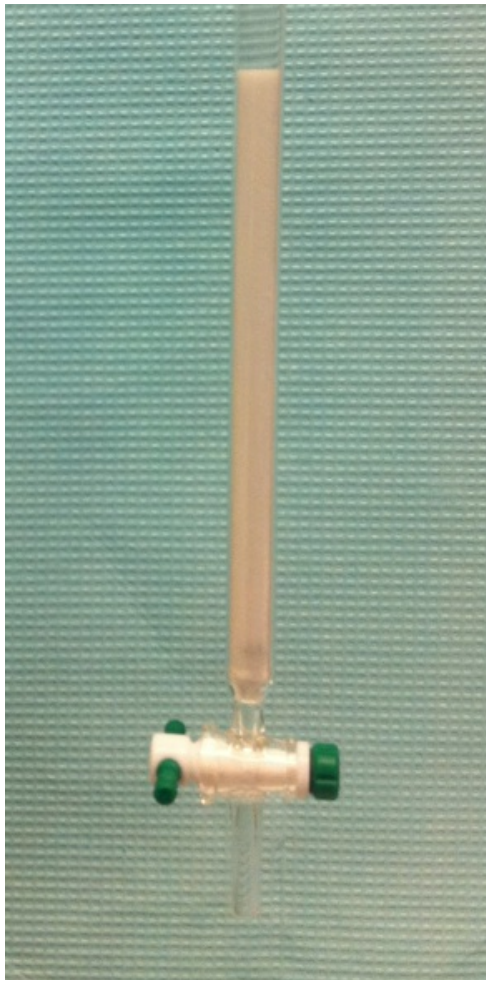
“Polars”



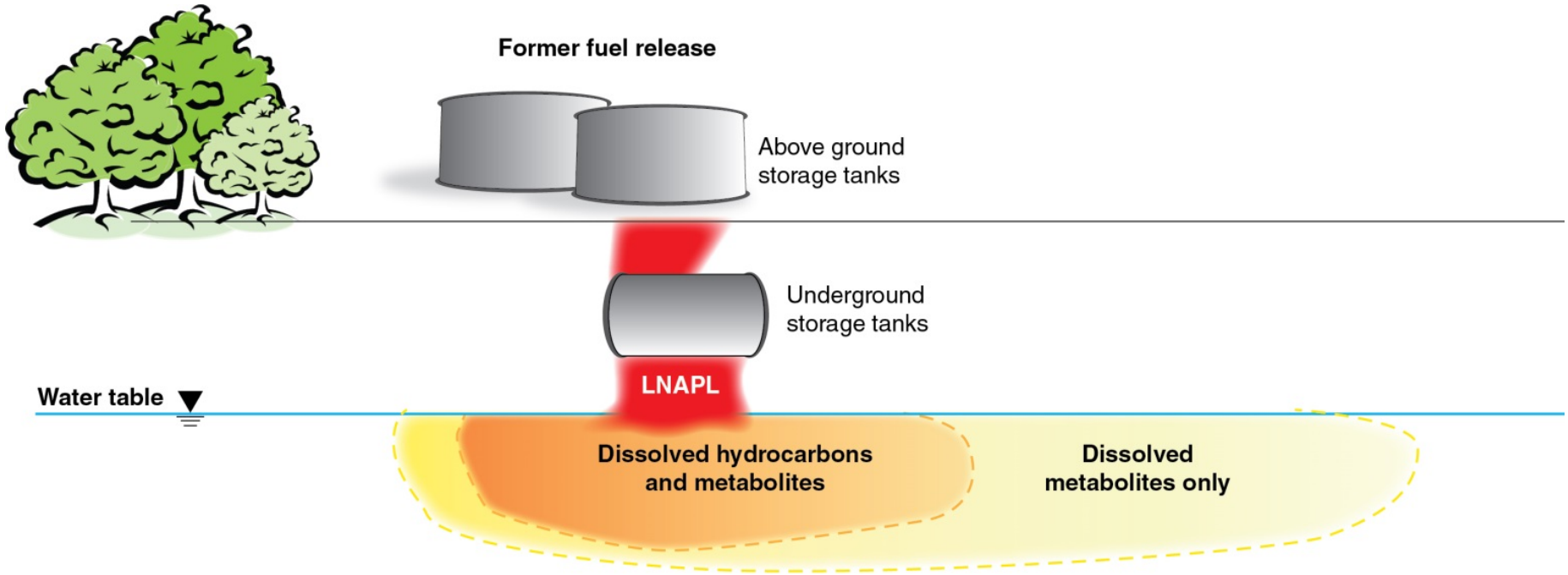
Silica Gel Cleanup

- 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

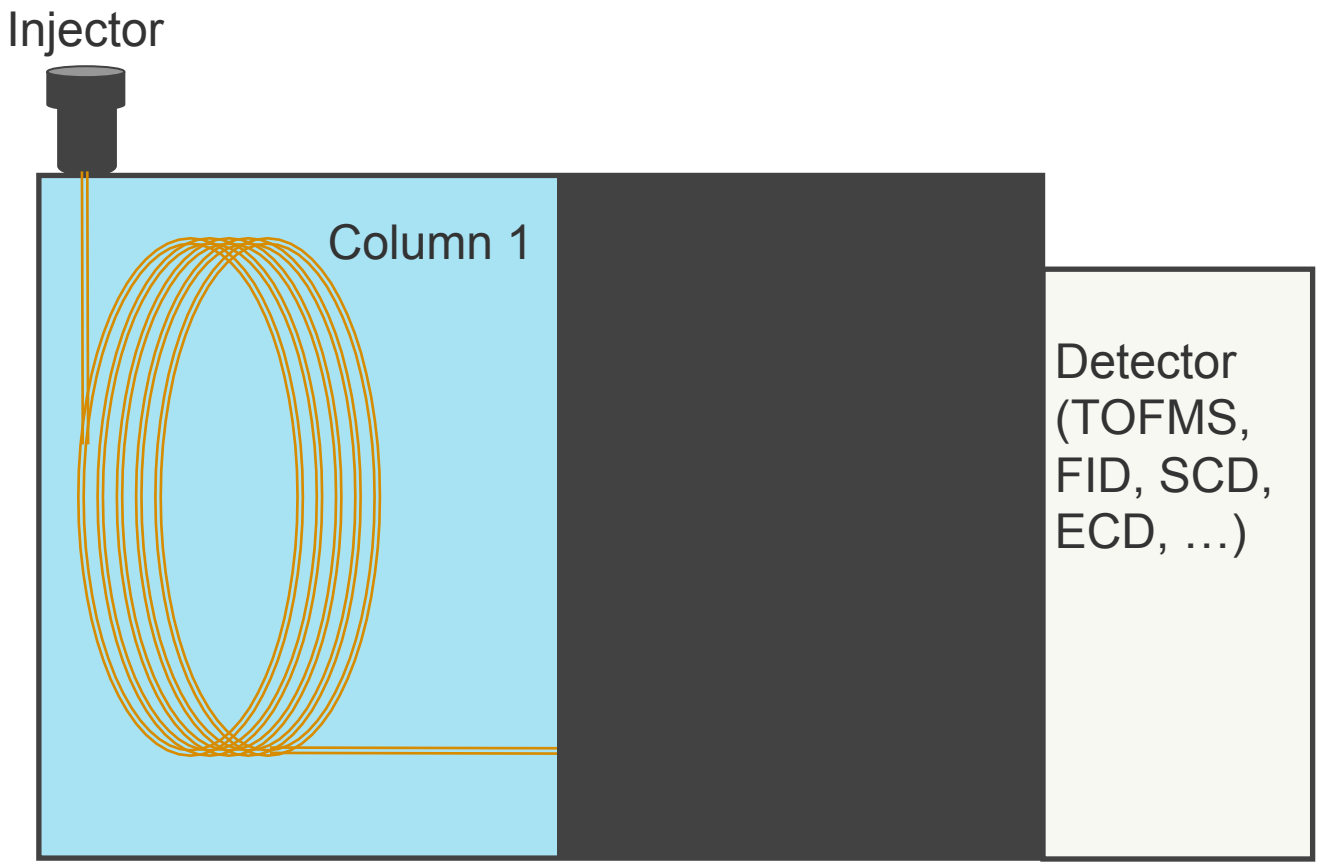


Project Description



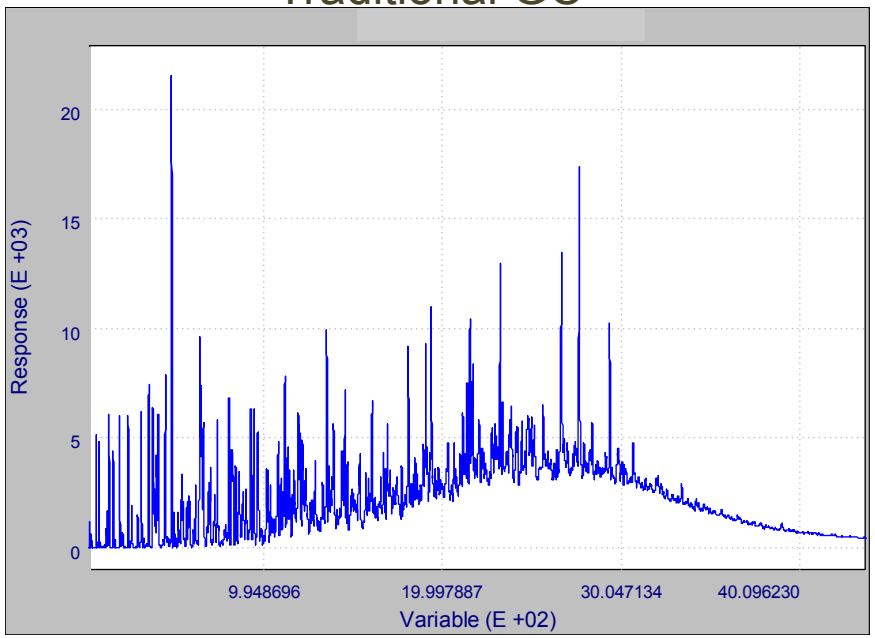
- Project goal: Evaluate the nature, toxicity, and fate of petroleum metabolites found in groundwater at fuel release sites.
- Project Purpose: Improve risk management and optimize closure of sites with TPH/DRO plumes.

Instrumentation



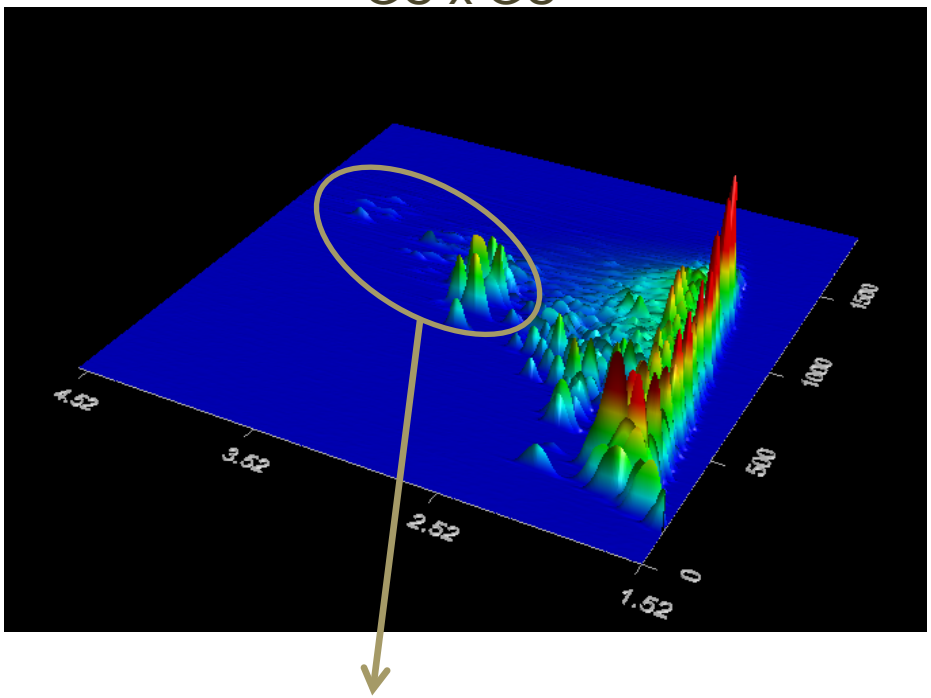
GCxGC-TOFMS offers improved resolution over traditional GC

Traditional GC



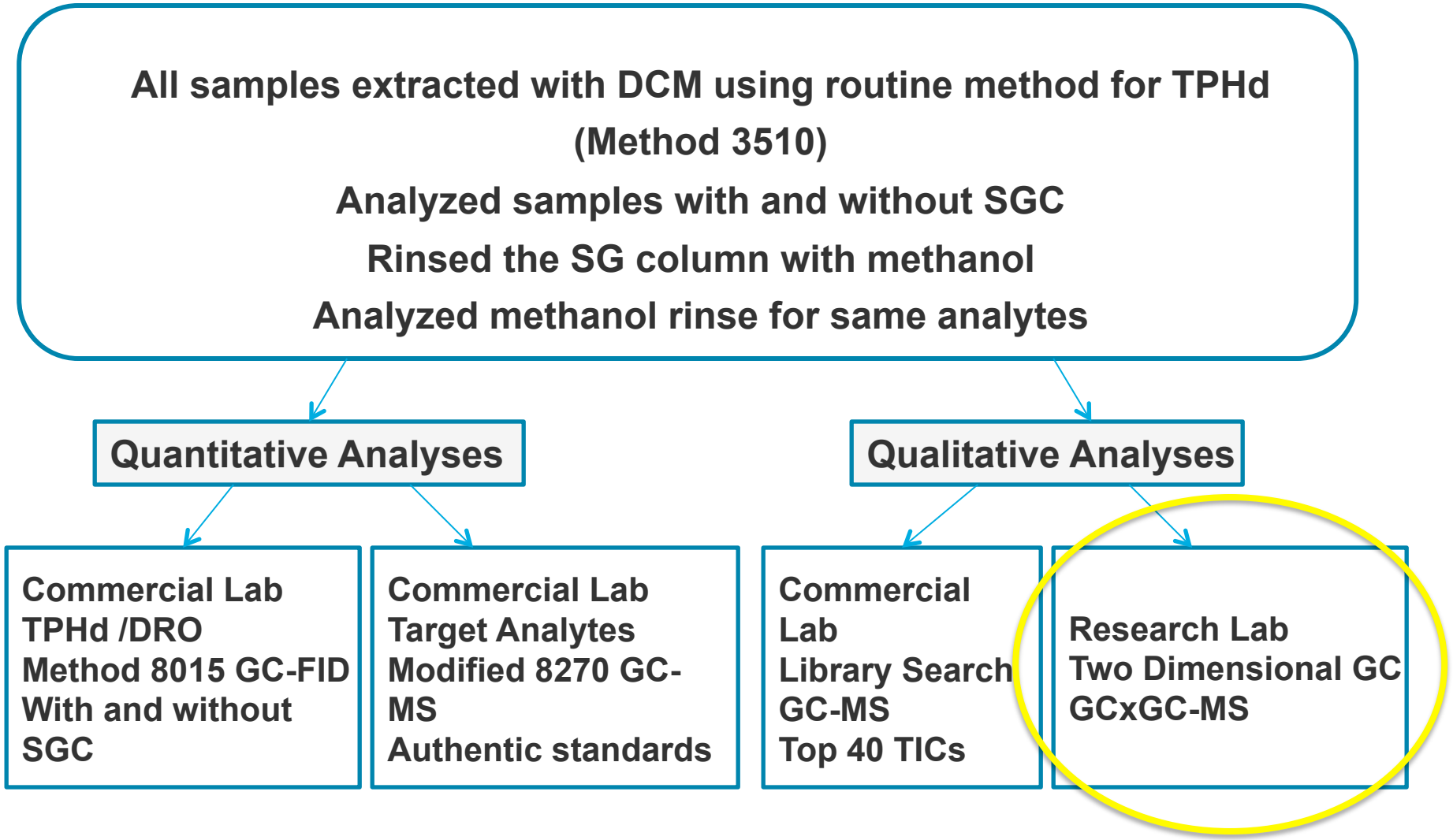
This unresolved complex mixture….

GC x GC

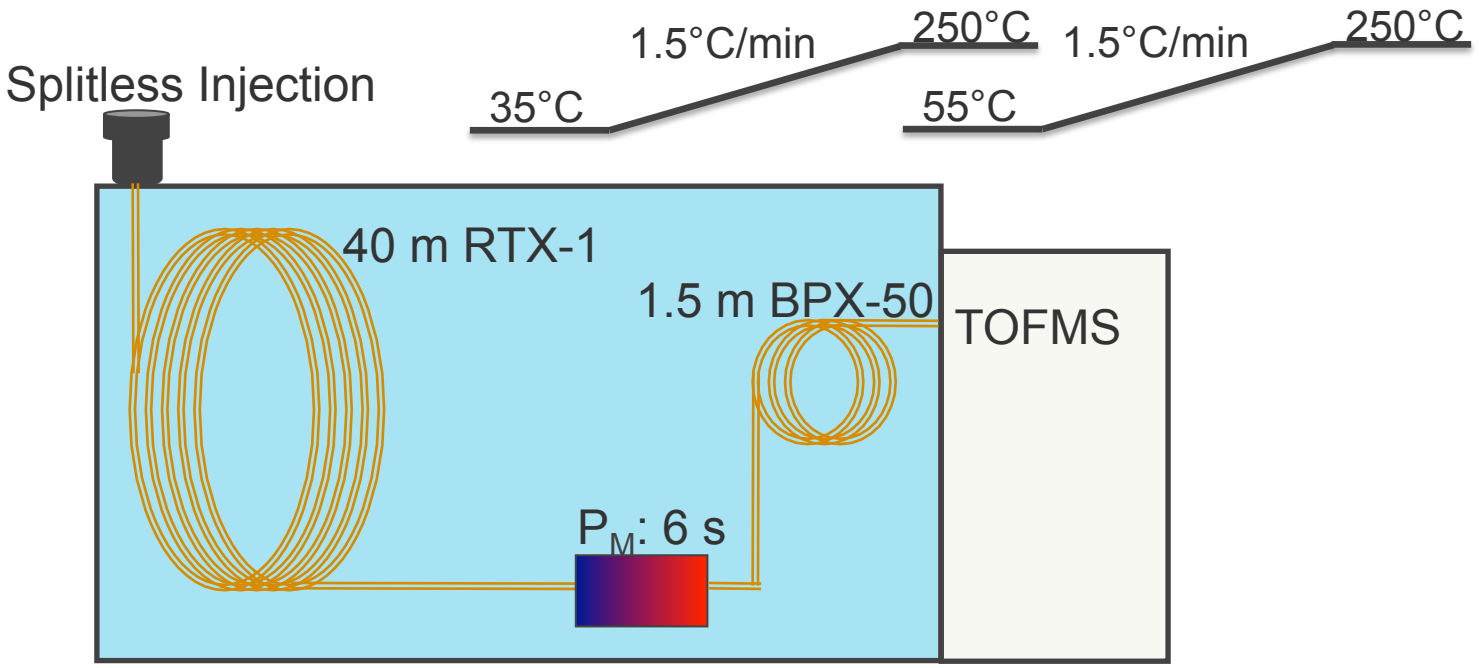


…can be separated with a 2D separation space and in this case is determined to contain a significant amount of diaromatics

Overview of Study



Overview of the GCxGC Method



- Data Analysis
  - Removed peaks with S/N <5
  - Compiled peak tables from the 4 sample extracts
  - Confirmed the identification of peaks with mass spectral similarity value greater than 850
  - Tentatively identified peaks with a mass spectral similarity value down to 750

Calculation of Limit of Quantitation

- Analyzed 28 standards spread over the five classes of interest
- Integrated the total ion count
- Calculated the limit of quantitation (LOQ) assuming a linear response and a signal to noise ratio of 10

Compound Class	Carbon Range	Number of Compounds	Average LOQ (μg/l)
Acids	C7-C8	3	3
Alcohols	C7-C10	7	1
Aldehydes	C7-C12	7	2
Ketones	C9-C13	4	2
Phenols	C8-C15	7	3

Classes of Polar Compounds Identified, Terminals
(2011-2012)

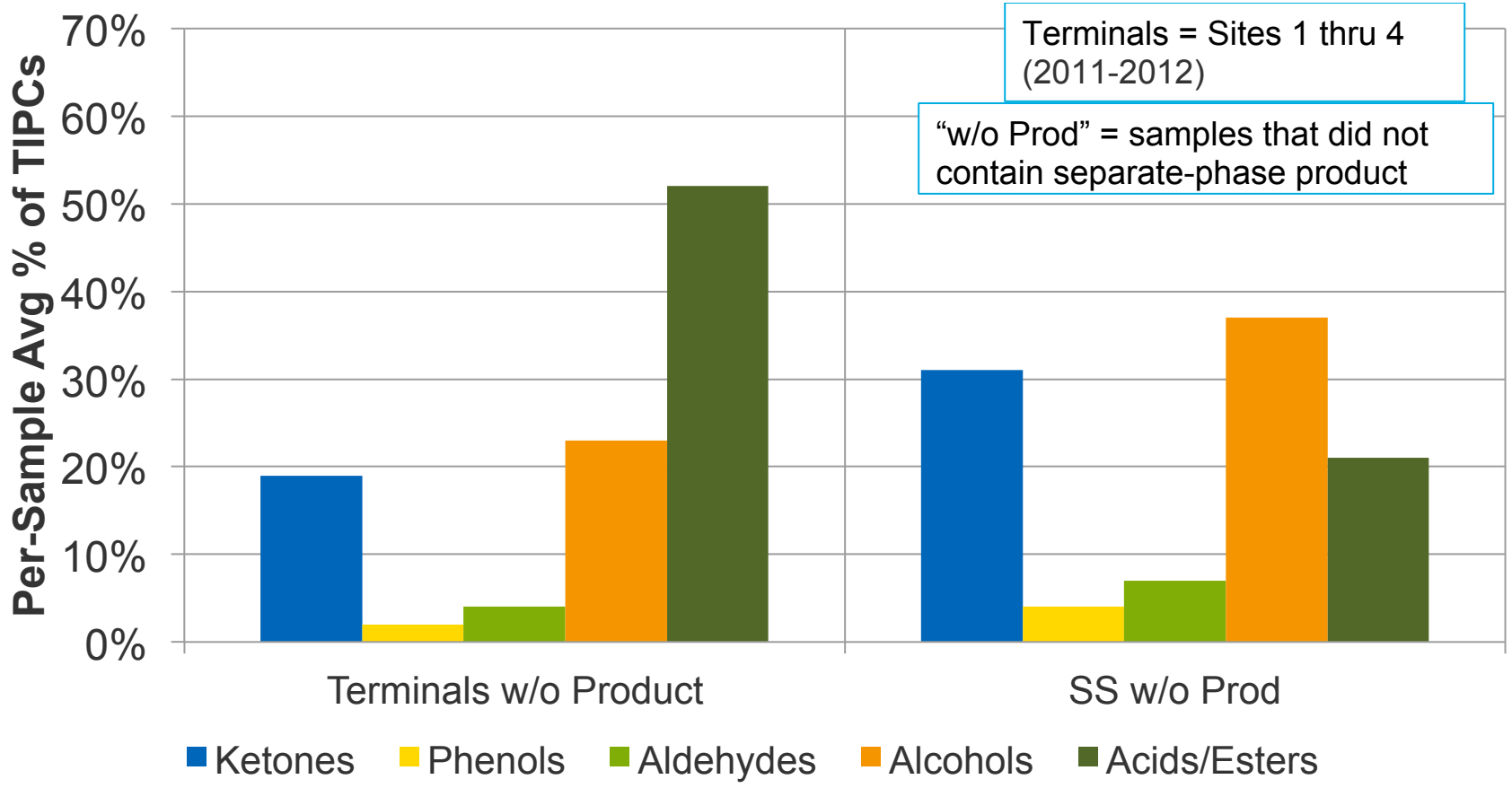
Name	Formula	# Sites	Classifications
Benzothiazole	C7H5NS	5	Other
Nonanoic acid, methyl ester	C10H20O2	4	acid/ester
Octanoic Acid	C8H16O2	3	acid/ester
Octanoic acid, methyl ester	C9H18O2	3	acid/ester
Ethanol, 2-(2-butoxyethoxy)-	C8H18O3	3	alcohol
1,2-Benzenedicarboxylic acid	C8H6O4	2	acid/ester
Tridecanoic acid, methyl ester	C14H28O2	2	acid/ester
1-Adamantanol	C10H16O	2	alcohol
1-Dodecanol, 3,7,11-trimethyl-	C15H32O	2	alcohol
Nonanal	C9H18O	2	aldehyde
1H-Inden-1-one, 2,3-dihydro-	C9H8O	2	ketone

Acids/esters, Alcohols, Aldehydes, Ketones, Phenols

Classes of Polars Identified, Service Stations

Name	Formula	# Sites	Classifications
1,2-Benzenedicarboxylic acid, diisooctyl ester	C24H38O4	5	acid/ester
1H-Indenol, 2,3-dihydro-	C9H10O	5	alcohol
1-Methylindan-2-one	C10H10O	5	ketone
2-Cyclopenten-1-one, 2,3-dimethyl-	C7H10O	5	ketone
2-Heptanol, 2-methyl-	C8H18O	5	alcohol
2-Hexanol, 2-methyl-	C7H16O	5	alcohol
Benzeneacetaldehyde, à-methyl-	C9H10O	5	aldehyde
Cyclohexanone	C6H10O	5	ketone
Decanoic acid, methyl ester	C11H22O2	5	acid/ester
Dodecanoic acid, methyl ester	C13H26O2	5	acid/ester
Phenol, 2-(1-methylethyl)-	C9H12O	5	phenol
trans-3,4-Dimethylcyclopentanone	C7H12O	5	ketone

Comparison of “Polars” Tentatively Identified at Service Stations and Terminals

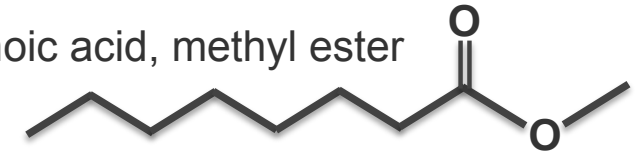


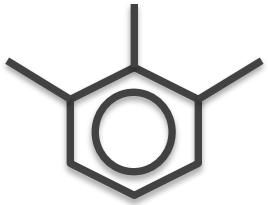
Polar Structures Identified

2-hexyl, 1 decanol

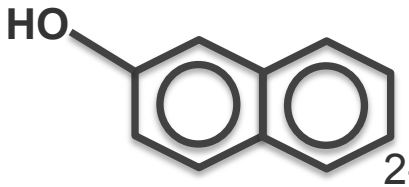
Nonanal

Octanoic acid, methyl ester

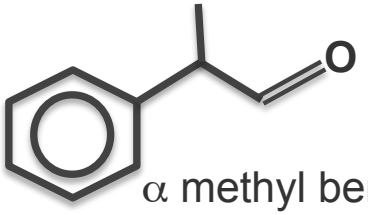




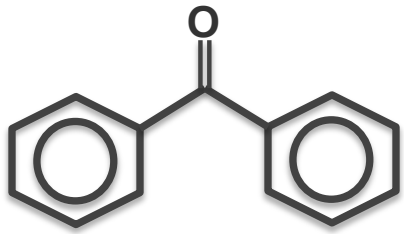
2,3 dimethyl phenol



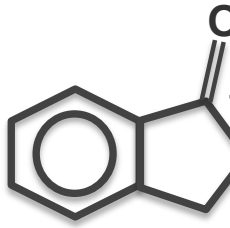
2-Naphthalenol



α methyl benzenealdehyde



Benzophenone



1-Indanone

Table Highlighting Different Polars from 2011 and 2012 at one terminal: Acids/Esters

Compound	2011	2012	Formula	S/N
Octanoic acid, methyl ester	✓		C9H18O2	211.18
Oxalic acid, allyl octadecyl ester	✓	✓	C23H42O4	11.27
Oxalic acid, allyl hexadecyl ester	✓		C21H38O4	19.42
Nonanoic acid, methyl ester	✓	✓	C10H20O2	194.63
Dodecanoic acid, methyl ester	✓		C13H26O2	127.84
Octanoic Acid	✓		C8H16O2	17.28
Tridecanoic acid, methyl ester	✓		C14H28O2	83.49
Oxalic acid, isobutyl pentyl ester	✓		C11H20O4	259.89
1,2-Benzenedicarboxylic acid, diisooctyl ester	✓	✓	C24H38O4	42.18
Dodecyl acrylate		✓	C15H28O2	23.53

Table Highlighting Different Polars from 2011 and 2012 at one terminal: Alcohols

Compound	2011	2012	Formula	S/N
1-Decanol, 2-hexyl-	✓		C16H34O	292.92
1-Dodecanol, 3,7,11-trimethyl-	✓	✓	C15H32O	352.5 (13.3)
Ethanol, 2-(2-butoxyethoxy)-	✓		C8H18O3	19.859
2-Ethyl-1-dodecanol	✓		C14H30O	232.1
1-Tridecanol	✓		C13H28O	28.892
1-Adamantanol		✓	C10H16O	90.886
Benzeneethanol, à-methyl-		✓	C9H12O	39.098

- The number of compounds in each class might remain very similar with time, however, the actual compounds definitely change

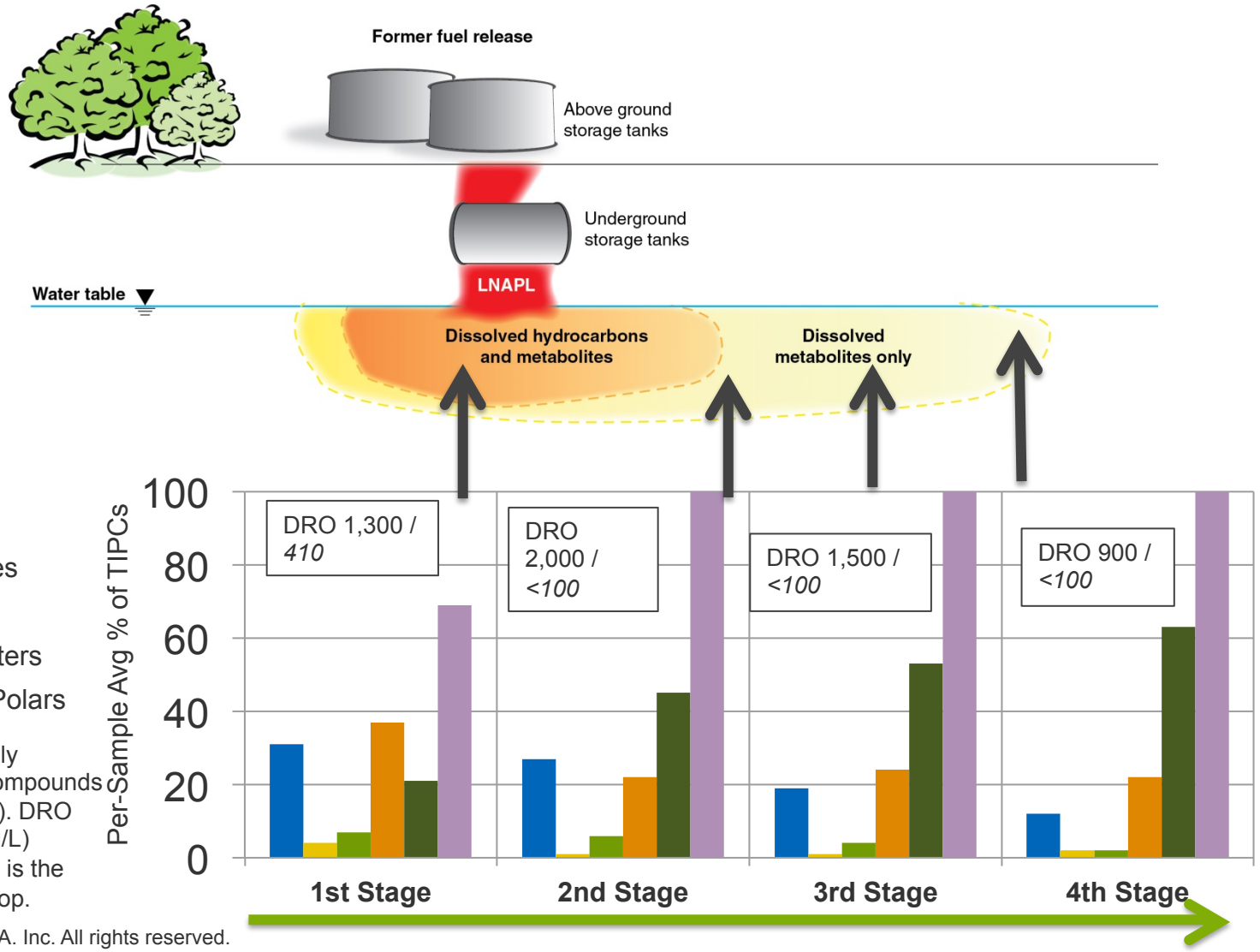
Importance of GCxGC Results

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**

Results are from samples collected in 2011. Wells are in order from source area (MW-3) to farthest downgradient (MW-31). Target Polars= 57 individual compounds, RLs typically 10ug/l. 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

Four Stages of Petroleum Biodegradation

(Terminals 1-4 2011-2012 and SSs 2013)



TIPCs = tentatively identified polar compounds (metabolites only). DRO concentration (ug/L) without/with SGC is the average for the pop.

Summary

- At historic release sites, the composition of material in groundwater shifts from mostly hydrocarbons to mostly “polars”.
- Solvent extraction using dichloromethane will extract all organics
- Silica gel will remove “polars” from the extract without retaining the hydrocarbons
- GCxGC can tentatively identify polar biodegradation metabolites with a variety of chemical structures in groundwater samples down to single digit detection limits
  - Allowed toxicity evaluation because we could get the structural classes
  - Technology is state of the art not state of the science
- Individual biodegradation metabolites are transient

Publications

- **Identification of ester metabolites from petroleum hydrocarbon biodegradation in groundwater using GCxGC-TOFMS.** *Environmental Toxicology and Chemistry,* accepted DOI:10.1002/etc.3022*,* Kirk T. O'Reilly, Rachel E. Mohler, Sungwoo Ahn, Asheesh K. Tiwary, Dawn A. Zemo, Renae I. Magaw, Catalina Espino Devine, Karen A. Synowiec.
- **Nature and Estimated Human Toxicity of Polar Metabolite Mixtures in Groundwater Quantified as TPHd/DRO at Biodegrading Fuel Release Sites.** Dawn A. Zemo, Kirk T. O'Reilly, Rachel E. Mohler, Asheesh K. Tiwary, Renae I. Magaw, Karen A. Synowiec . *Groundwater Monitoring and Remediation*. 2013, 33, 44-56
- **Non-Targeted Analysis of Petroleum Metabolites in Groundwater Using GCxGC-TOFMS.** Rachel E. Mohler, Kirk T. O'Reilly, Dawn A. Zemo, Asheesh K. Tiwary, Renae I. Magaw, Karen A. Synowiec. *Environmental Science and Technology*, 2013, 47, 10471-10476
- **Comparison of Shake and Column Silica Gel Cleanup Methods for Groundwater Extracts to be Analyzed for TPHd/DRO.** Dawn A. Zemo, Karen A. Synowiec, Renae, I Magaw, Rachel E. Mohler. *Groundwater Monitoring and Remediation,* 2013, 33, 108-112

Acknowledgements

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  - Provided funding
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