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Use of Two-Dimensional Gas Chromatography to Supplement the Evaluation of Natural Attenuation at Petroleum Release Sites

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Presentation Overview

1. Project Objectives
2. Theoretical Background and Analytical Protocol (4)
3. Case study
4. Conclusions
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Project Objectives

- Evaluate petroleum biodegradation by GCXGC-TOF-MS technology and study how important it is at sites with historical releases
- Present a case study on the application of the technology and interpretation of the results consistent with the **multiple lines of evidence approach** to evaluate Natural Attenuation

Key points:
- GCXGC-TOF-MS is a cutting edge tool to show natural attenuation/biodegradation is occurring.
- GCXGC-TOF-MS is an (expensive) tool in the toolbox that may not be needed for the majority of petroleum release sites.

TOF-MS - Gas Chromatography by gas chromatography, time of flight, mass spectrometry.

Quick Theoretical Background: What is Extractable TPH?

"TPH" is not total, not only petroleum and not only hydrocarbons

TPH is defined by the method

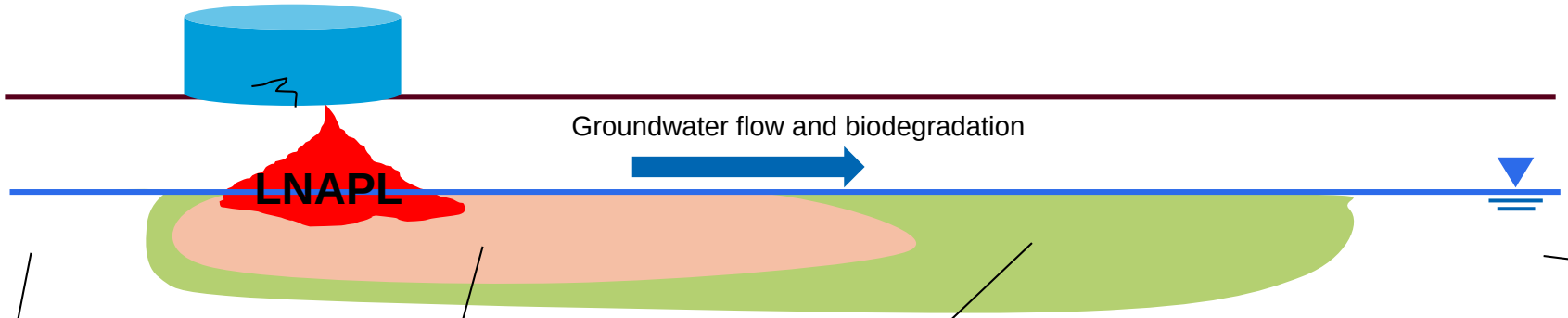
- TPH has been measured by very different analytical methods that quantify in different ways petroleum hydrocarbons as well as non-hydrocarbons as a bulk "TPH" concentration. Results depend on the solvent used, type of detector and fuel standard.
- Non-hydrocarbons (polars) are compounds with oxygen, sulfur and/or nitrogen
- Non-hydrocarbons can be separated from hydrocarbons in the extractable TPH by a silica gel cleanup step (e.g. EPA Method 3630c; SGC)

❑ITRC TPH Team expected to publish TPH guidance in 2018

- TPH is a measure of extractable organics.
- TPH methods vary across different regulatory jurisdictions, labs and methods.
- SGC can separate the polar from the hydrocarbon fraction
- Non-hydrocarbons = NSO compounds = Polar compounds

TPH – Total Petroleum Hydrocarbons
NSO compounds – Nitrogen, Sulphur and Oxygen containing compounds

"TPH" plumes measured as Extractable TPH in groundwater and natural attenuation



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

2. Dissolved HC plume:
TPH =
+ **HC**
+ **HC metabolites**
+ *Background organics*

3. Dissolved metabolites from HC biodegradation:
TPH =
+ **HC metabolites**
+ *Background organics*

4. Downgradient from HC metabolite plume:
TPH =
+ *Background organics*

LNAPL – Light Non Aqueous Phase Liquids
HC – Hydrocarbons
NSO compounds – Nitrogen, Sulphur and Oxygen containing compounds

Analytical Testing Protocol for Metabolites

Collection of groundwater samples from monitoring wells from 16 fuel terminals and 5 service station sites **with biodegrading sources and shrinking/stable plumes**

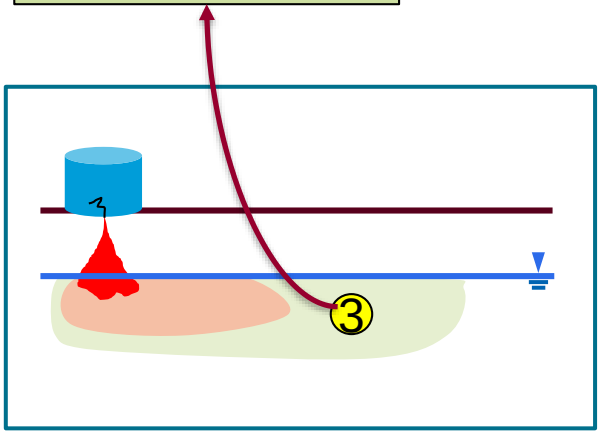
Extraction (3) with DCM (EPA Method 3510)

Silica gel cleanup (EPA Method 3630)

Extract (hydrocarbon +polars fraction) DRO Method 8015 & Method 8270C

Methanol eluate from the SGC (polars fraction)

Three extracts and one methanol eluate analyzed by GCXGC-TOFMS (Mohler et al., 2013)



All extractable organics and organics in the SGC were tested by GCXGC-TOF-MS

SGC – Silica Gel Cleanup

Analytical Testing Protocol for Metabolites

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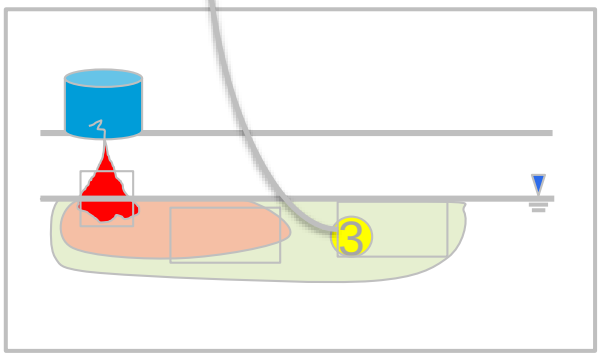
Extraction (3) with DCM (EPA Method 3510)

Silica gel cleanup (EPA Method 3630)

Extract (hydrocarbon +polars fraction) DRO Method 8015 & Method 8270C and GC-MS Targeted Search

Methanol eluate from the silica gel column (polars fraction)



Three extracts and one methanol eluate analyzed by GCXGC-TOFMS List of TIC classified by:

- **Molecular family**
  - **Alcohols/diols**
  - **Acids/esters**
  - **Ketones**
  - **Aldehydes**
  - **Phenols**
- Molecular structural class
- Name, chemical formula
- Oxygen, carbon and hydrogen ratios
- SMILES designation

- GCXGC –TOFMS result gives you compound family/structural class identification
- GCXGC results: detections, not concentration

TIC – Tentatively Identified Compounds with a similarity number >750
(Zemo et al., 2016)
GCXGC
SMILES - Simplified Molecular Input Line Entry System
SGC – Silica Gel Cleanup

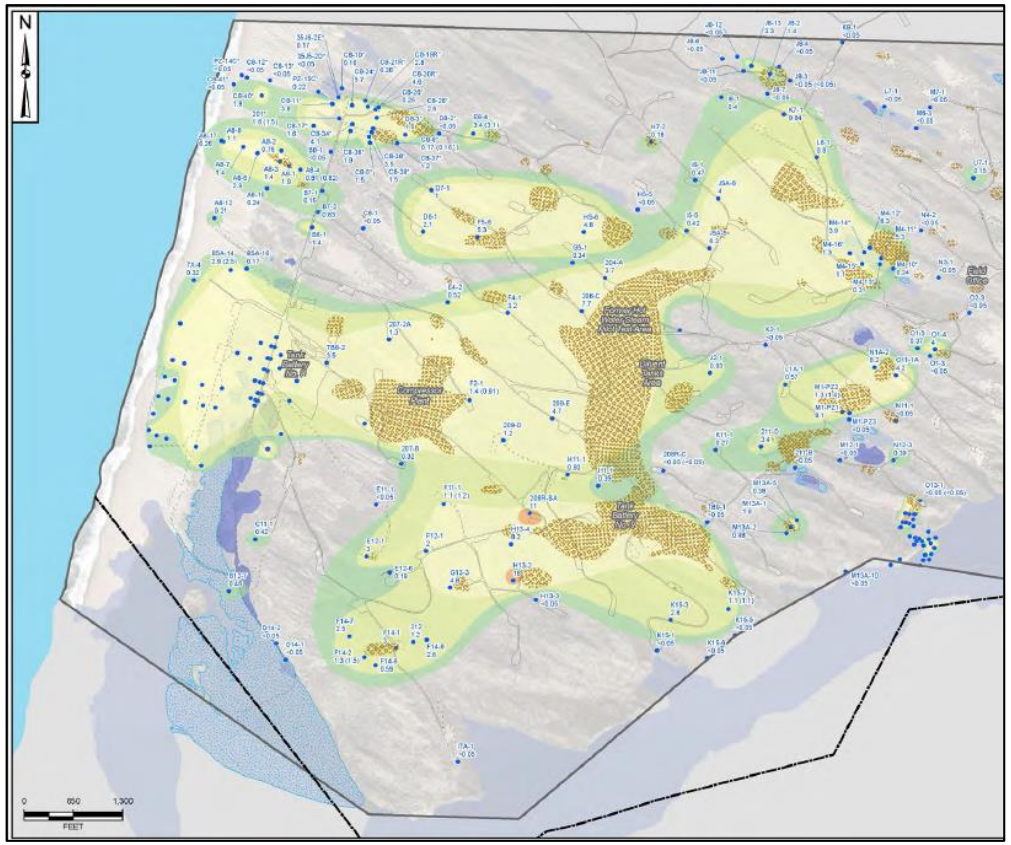
Case Study

- Former oil field ~2800 acre site at the Pacific Ocean shoreline
- Oil field operations from late 1940s to early 1990s
- Historical releases of a mid-distillate product (C10-C28) and heavy crude
- Active remediation and LNAPL recovery has been conducted at several locations of the site
- TPH in unconfined aquifer is evaluated under MNA

➢MNA evaluated with multiples lines of evidence, in a tiered approach.

1. Concentration in GW vs. time (TPH w/wo SGC)
2. Geochemistry (not shown here)
3. **GCXGC-TOFMS for metabolites in groundwater, soil and LNAPL**

TPH without SGC in Groundwater
(191 monitoring wells)



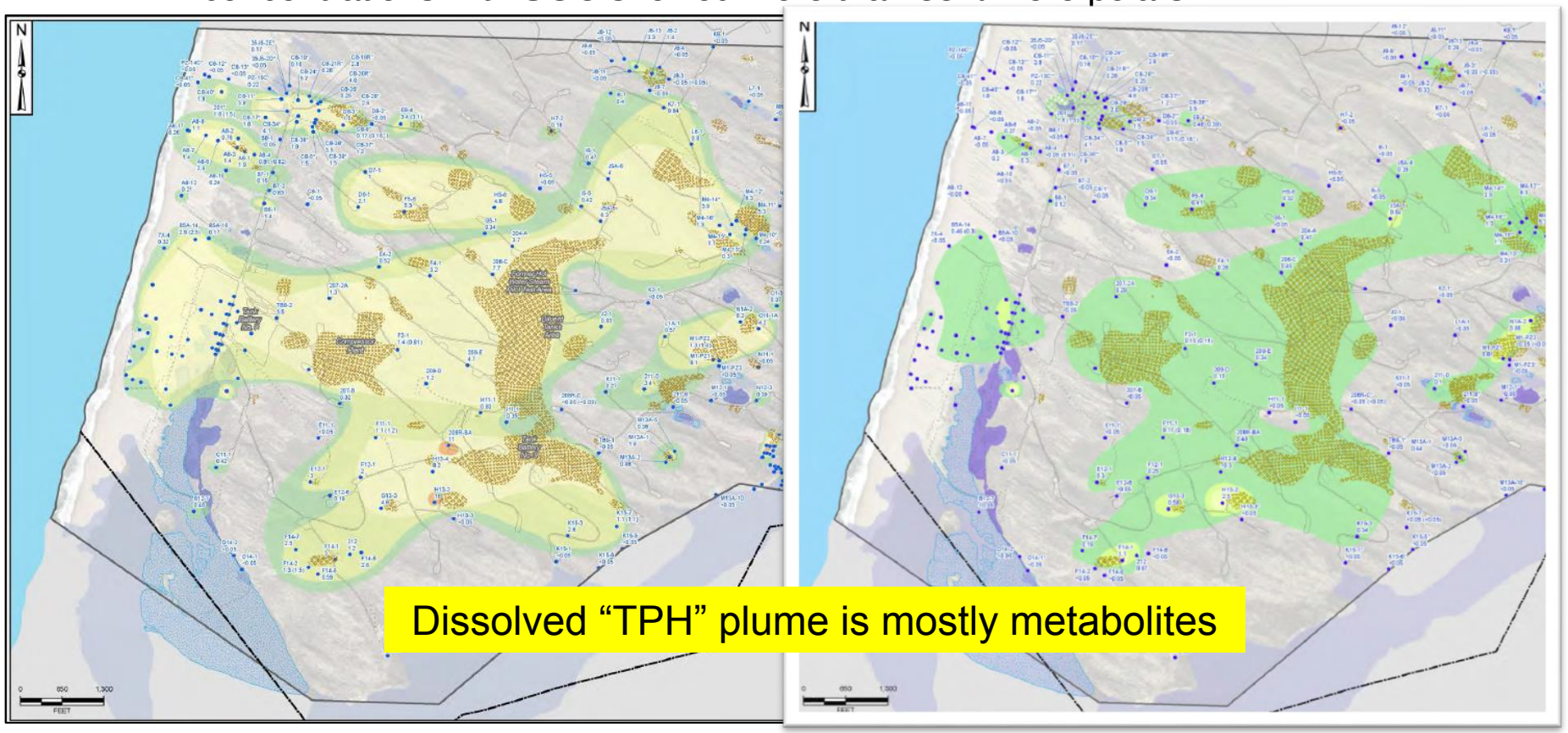
TPH (mg/L)

0.05 – 0.5 0.5 – 1.0 1.0 – 2.5 LNAPL

TPH – Total Petroleum Hydrocarbons
SGC – Silica gel cleanup by EPA Method 3630

TPH with SGC in Groundwater

- 54% of the samples with TPH detections were non-detect (<50 ug/L) with TPH with SGC
- TPH concentrations with SGC showed more than 85% were polars



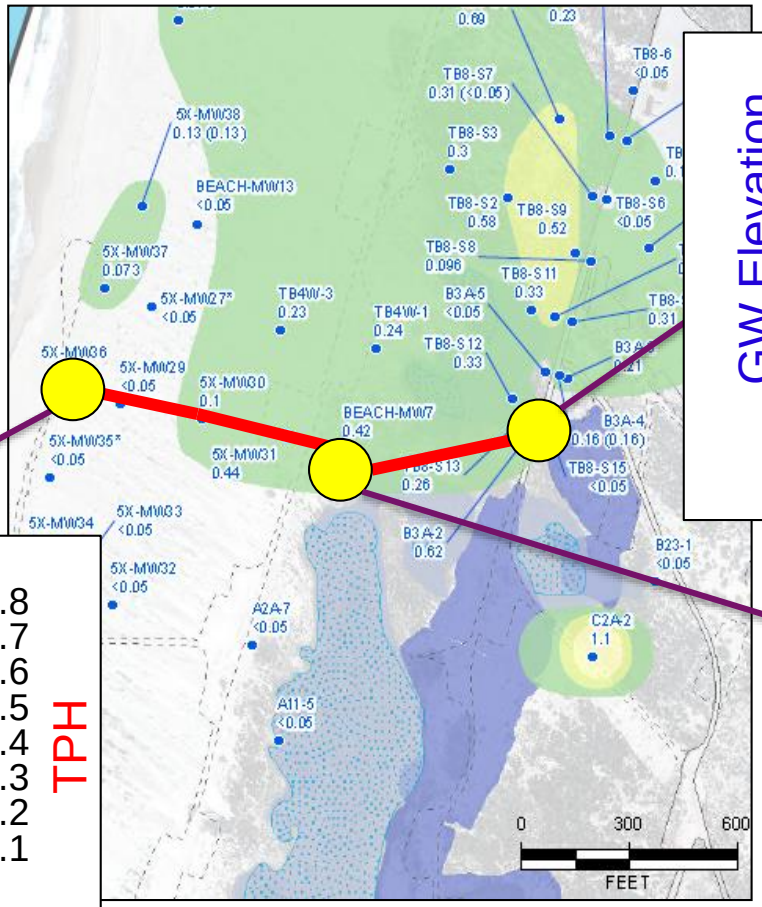
TPH (mg/L)

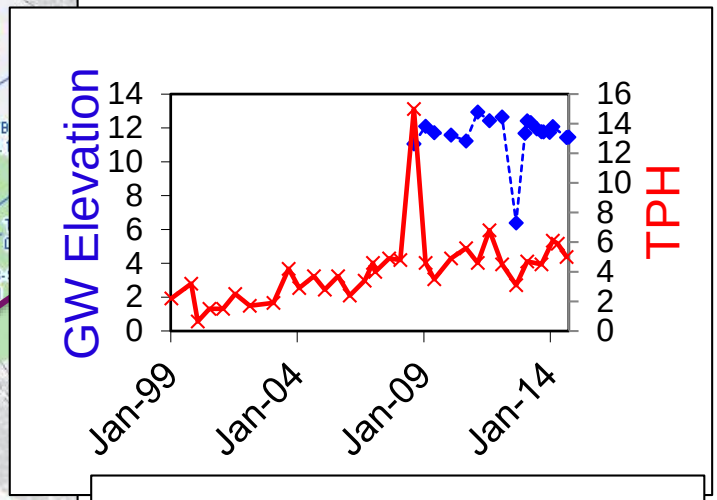
0.05 – 0.5 0.5 – 1.0 1.0 – 2.5 LNAPL

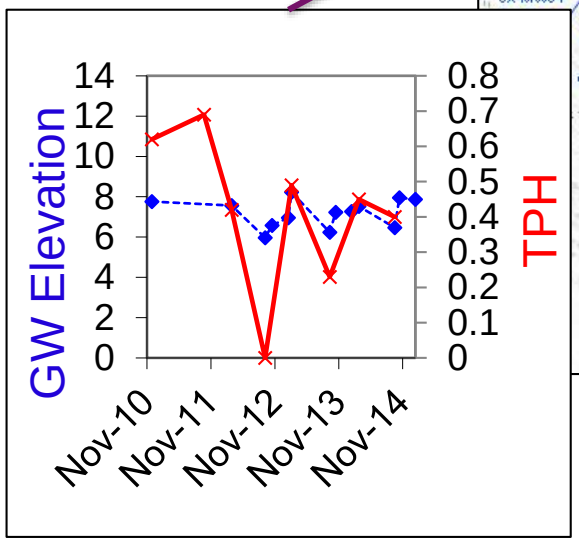
TPH w/o SGC - trends in Transect 1

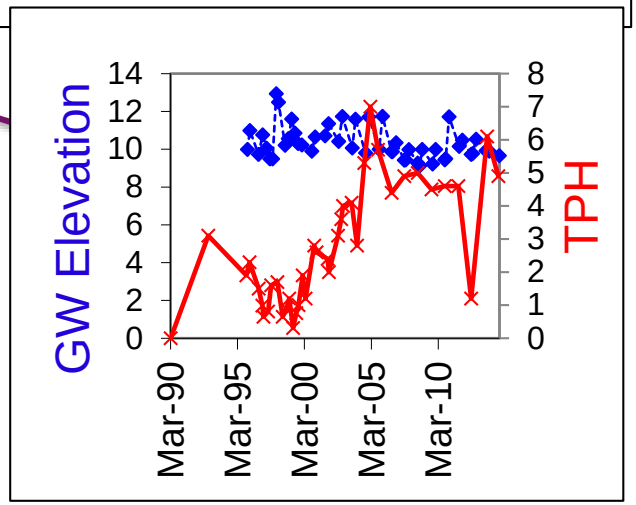
Historical Groundwater Elevation and TPH

TPH w/o SGC is a poor metric of biodegradation









Groundwater flow

TPH: mg/L
Groundwater (GW) Elevation: feet above mean sea level

GCXGC data - approx. % TIC in Transect 1

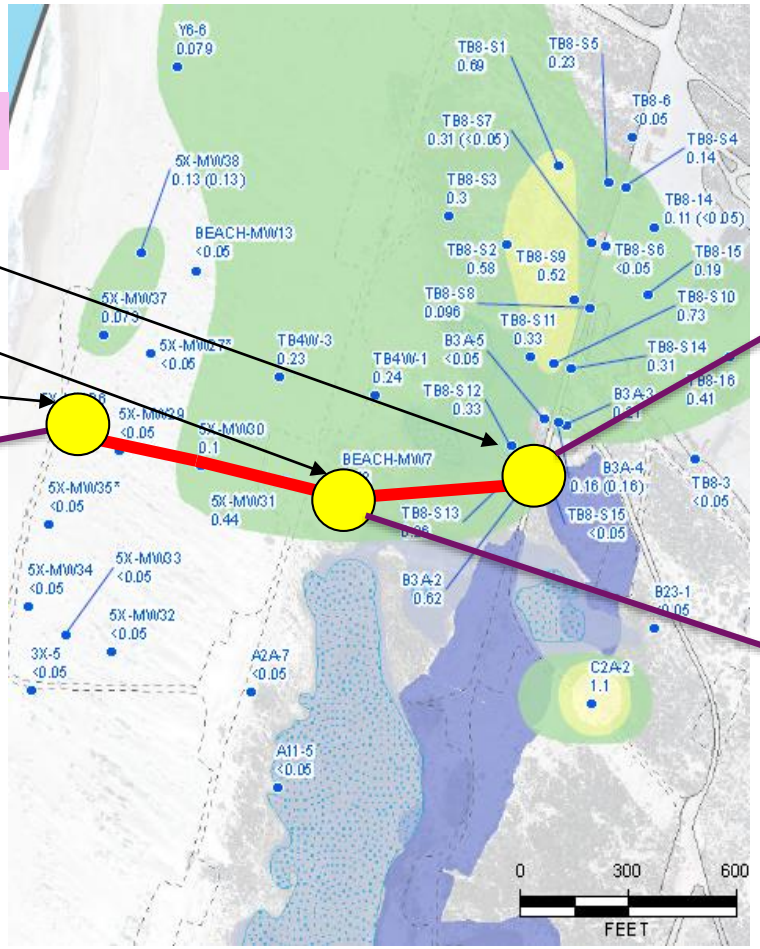
HC biodegradation occurring across the flow path

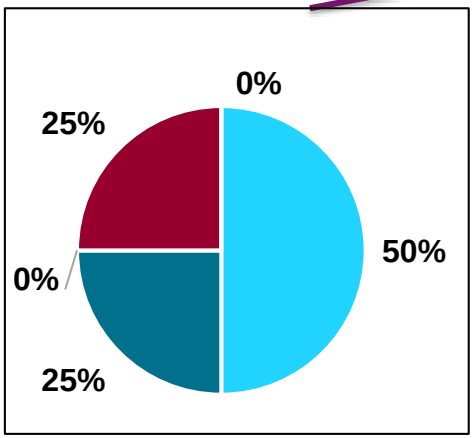
TPH/TPHwSGC (ug/L)

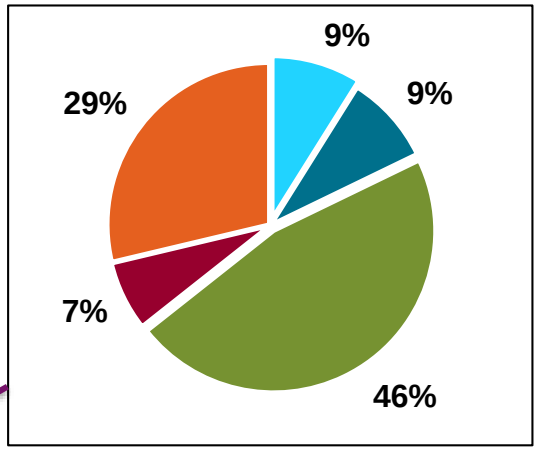
5000 / 620

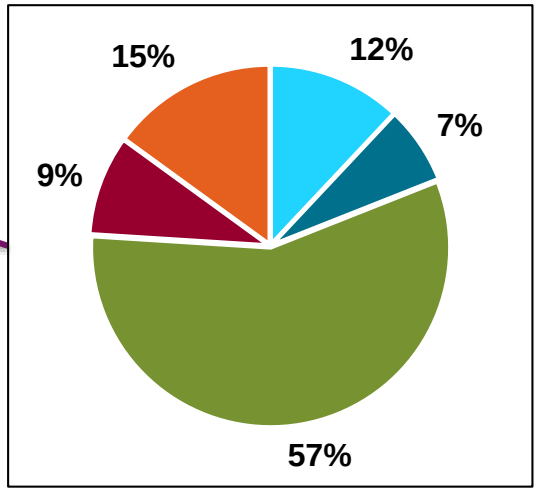
4900 / 420

400 / <50







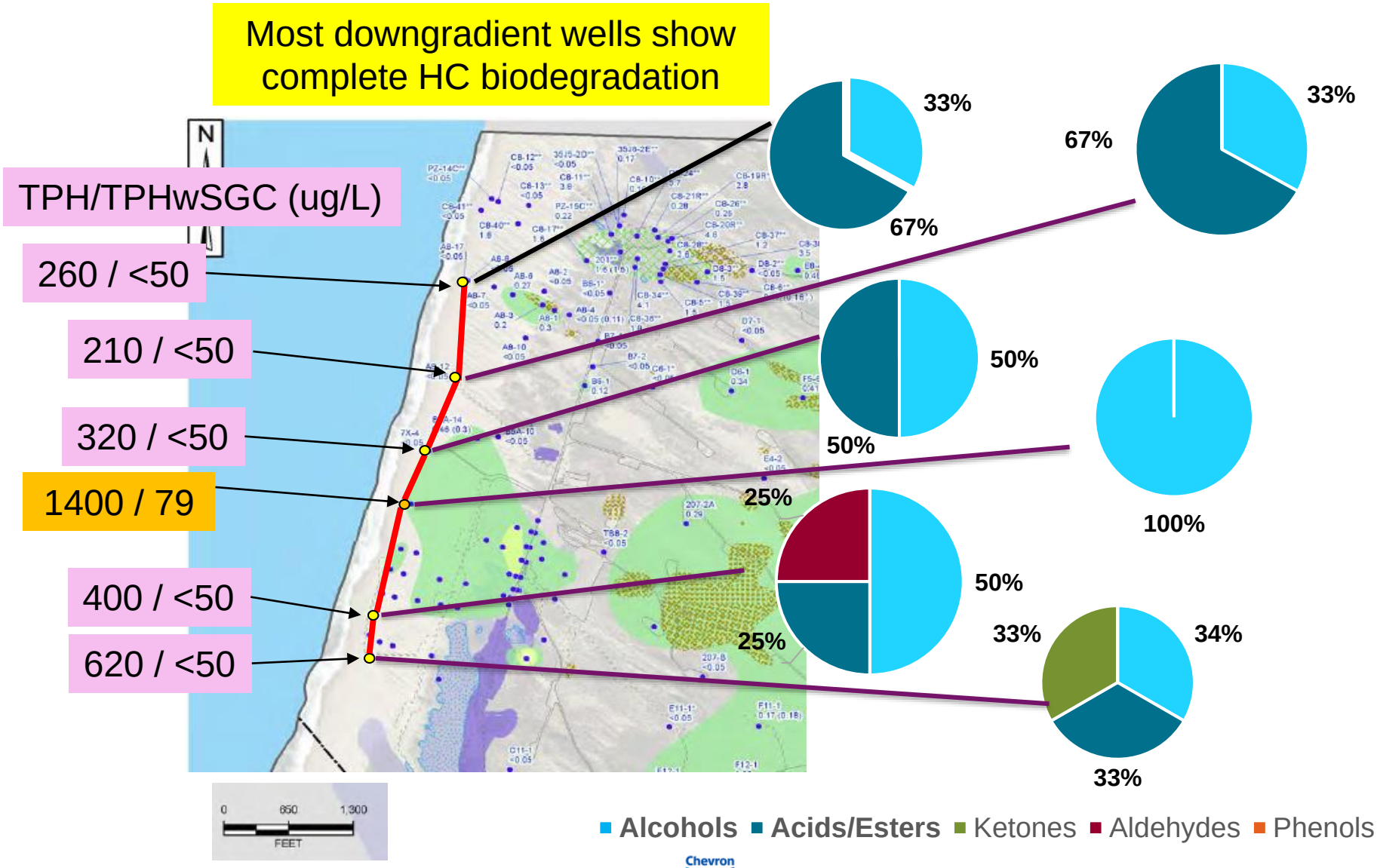


Alcohols | Acids/Esters | Ketones | Aldehydes | Phenols

TPHwSGC – Total Petroleum Hydrocarbons with Silica Gel Cleanup

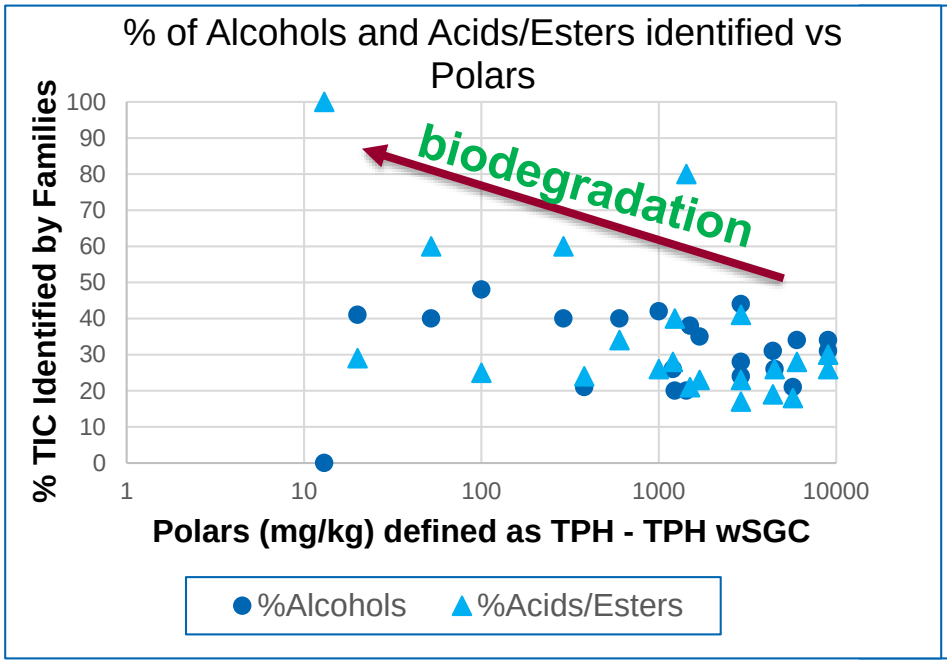
GCXGC data - % TIC in Transect 2

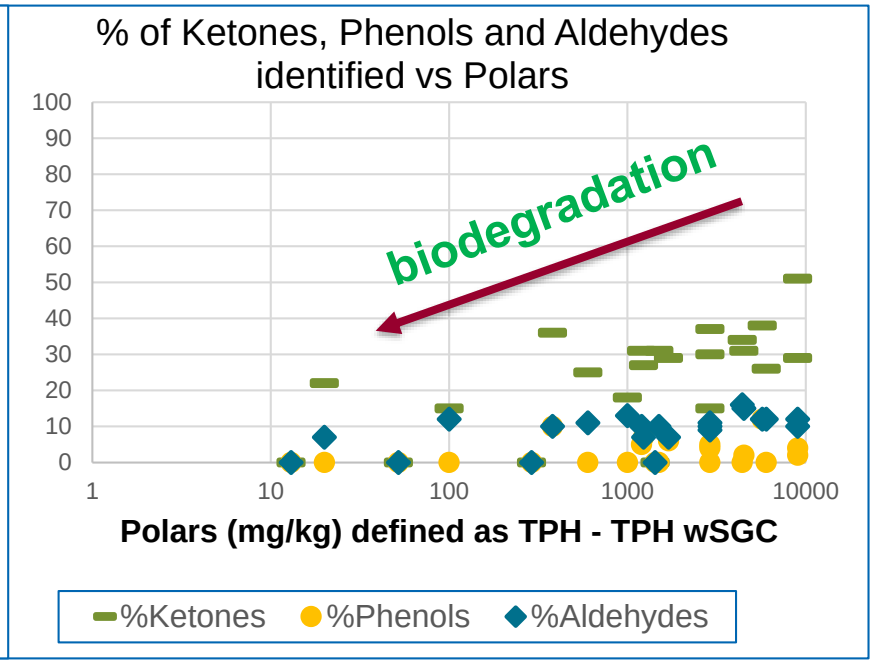
Most downgradient wells show complete HC biodegradation



Soil Biodegradation

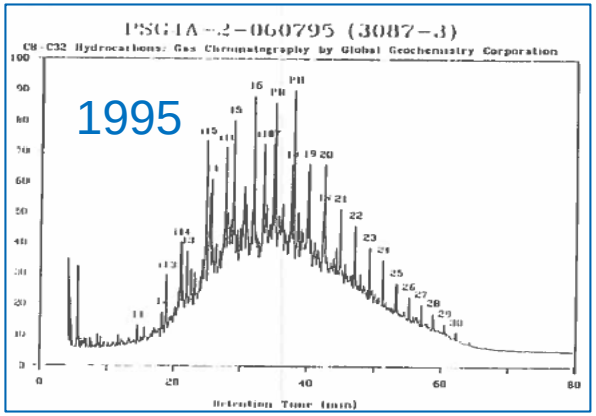
- Results from 24 soil samples show samples with higher % Polars have a higher % of less biodegraded metabolite classes

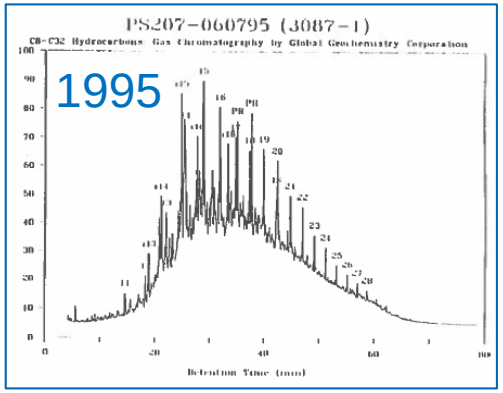


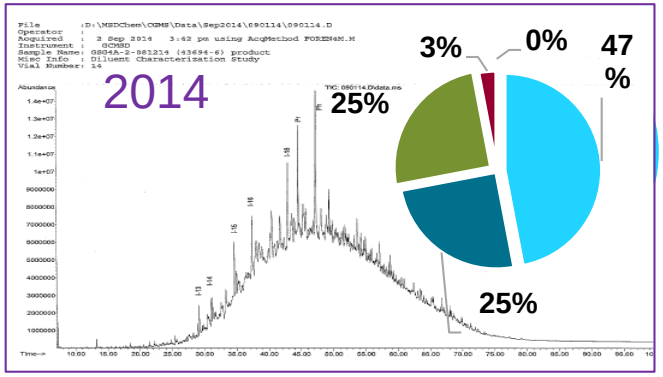


Interior LNAPL attenuation

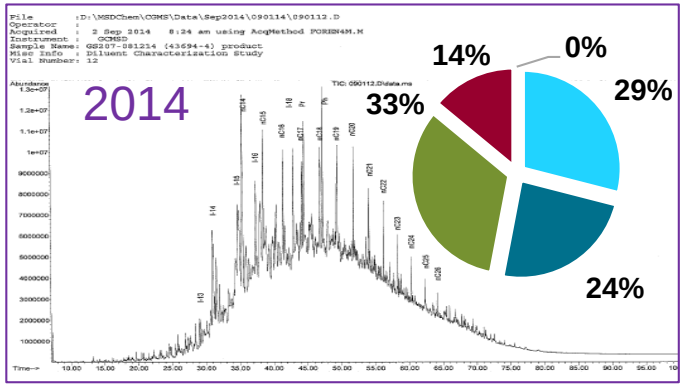
- **3 out of 4 samples** - The n-alkanes have been completely removed, and only the isoprenoids remain as resolvable peaks.
- **1 out of 4 samples** - The 2014 sample has lost the C11-C13 n-alkanes; and the nC17/Pristane and nC18/Phytane ratios are slightly lower than in 1995.







- %Alcohols
- %Acids/Esters
- %Ketones
- %Aldehydes
- %Phenols



Note – Chromatograms and GCXGC results by % TIC detections after Zemo, 2016

Conclusions

- **Biodegradation of petroleum hydrocarbons occurs in groundwater, soil and LNAPL phases**. GCXGC-TOF-MS is a tool that can show natural attenuation/biodegradation.
  - GCXGC-TOF-MS can provide family and structural class information relevant for toxicity evaluation
- **Biodegradation indicators are useful:** Biodegradation indicators (higher presence of acids/esters and alcohols) are present in LNAPL and are more prevalent in the outer edges of the plume (metabolite plume vs. source zone).
- **SGC can help evaluate natural attenuation:**
  - The difference between TPH without SGC and TPH with SGC is a good indicator of polars (non-hydrocarbons) load in soil and groundwater.
  - SGC can serve to evaluate naturally occurring organics and background and lab/sampling contamination.

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Thank you

Questions?

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