Funakoshi Site Investigation: Crude Oil and Soil Extract Characterization using Two-Dimensional Gas Chromatography

dig

Dolan Integration Group

Geochemistry for Energy™

digforenergy.com

303.531.2030

Summary

- Soils at Anadarko's Wattenberg well site (Funakoshi) were contaminated with hydrocarbons. APC decided to investigate the source of contamination using established geochemical methods.

- DIG met with Anadarko and Tasman Geoscience and suggested the use of Comprehensive GCxGC analysis to characterize the crude produced by APC at the Funakoshi site, and extracted hydrocarbons from soils at the site.

- Fieldwork was performed by **Tasman Geoscience**. GCxGC analysis was performed at **Woods Hole Oceanographic Institute**. GCxGC data interpretation was undertaken by **DIG**.

- Results from the extraction process show the most contaminated soils were near the KP Kauffman tank batteries.

- GCxGC results show extracts to be of a different source, and reflect a lower maturity oil relative to the Funakoshi crude. This is concluded from the presence of naphthalenes and isoprenoids in the extract samples.

- Comparison with baseline whole oil GC data of Wattenberg produced oils suggest the extracted hydrocarbons are of Sussex source.

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Hydrocarbon Fingerprinting Using Whole Oil GC

Sampling and Analysis Workflow

Sampling → Extraction → GC Analysis → Oil Characterization → Interpretation

- Sampling of contaminant plume (soil or H_2O), along with potential sources (tank battery, wellhead, bradenhead, etc.). If actual point sources are unavailable, proximal representatives may be used (i.e. nearby well producing same formation)
- Sampling – 1L samples of groundwater collected in glass bottles, soil samples collected in 400ml glass jars, crude oils (for end member characterization) in glass vials.
- Extraction – hydrocarbons extracted from water or soil samples using dichloromethane, which preserves compounds in the C9-C44 semi-volatile range
- GC, GC-MS, GCxGC Analysis performed on soil/water extract and crude oil samples
- Interpretation of analytical data with spatial context

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Extraction Process

Extraction – hydrocarbons extracted from water or soil samples using dichloromethane, which preserves compounds in the **C9-C44 semi-volatile range**.

Focus comparison on C9+ hydrocarbons

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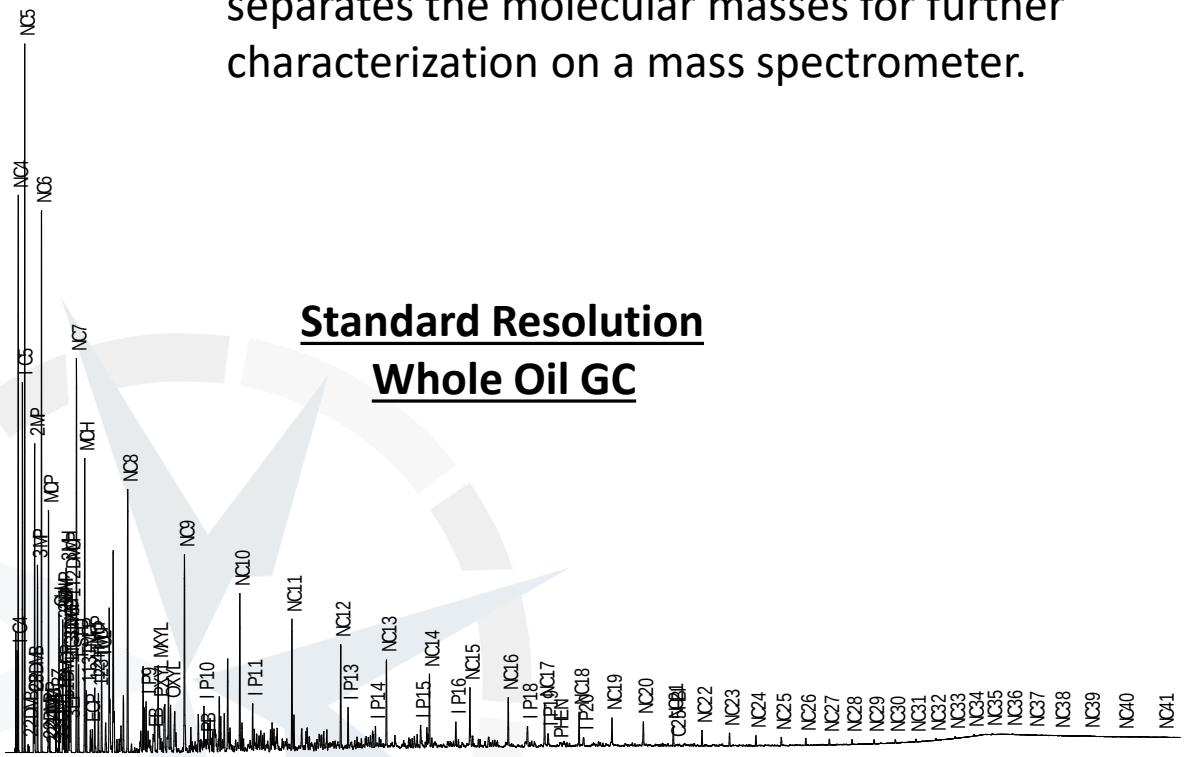
Gas Chromatography

Standard Resolution GC

- The gold standard of hydrocarbon "fingerprinting".
- We all are very familiar with this plot and it has satisfactorily characterized crude oils for decades.
- This has stood the test of time and separates the molecular masses for further characterization on a mass spectrometer.



Standard Resolution Whole Oil GC

What can we derive from these data?

- Paraffin Distribution
- (Paraffin aka, saturated or aliphatic compounds)
- Light HC analysis
- Pristane/Phytane Ratio
- Isoprenoid/Alkane Ratios
- Carbon Preference Index
- Waxy Oil Determination

Make interpretations for:

- Source Depositional environment of the generating source rock(s).
- Level of Biodegradation
- Maturity (qualitative) determination.

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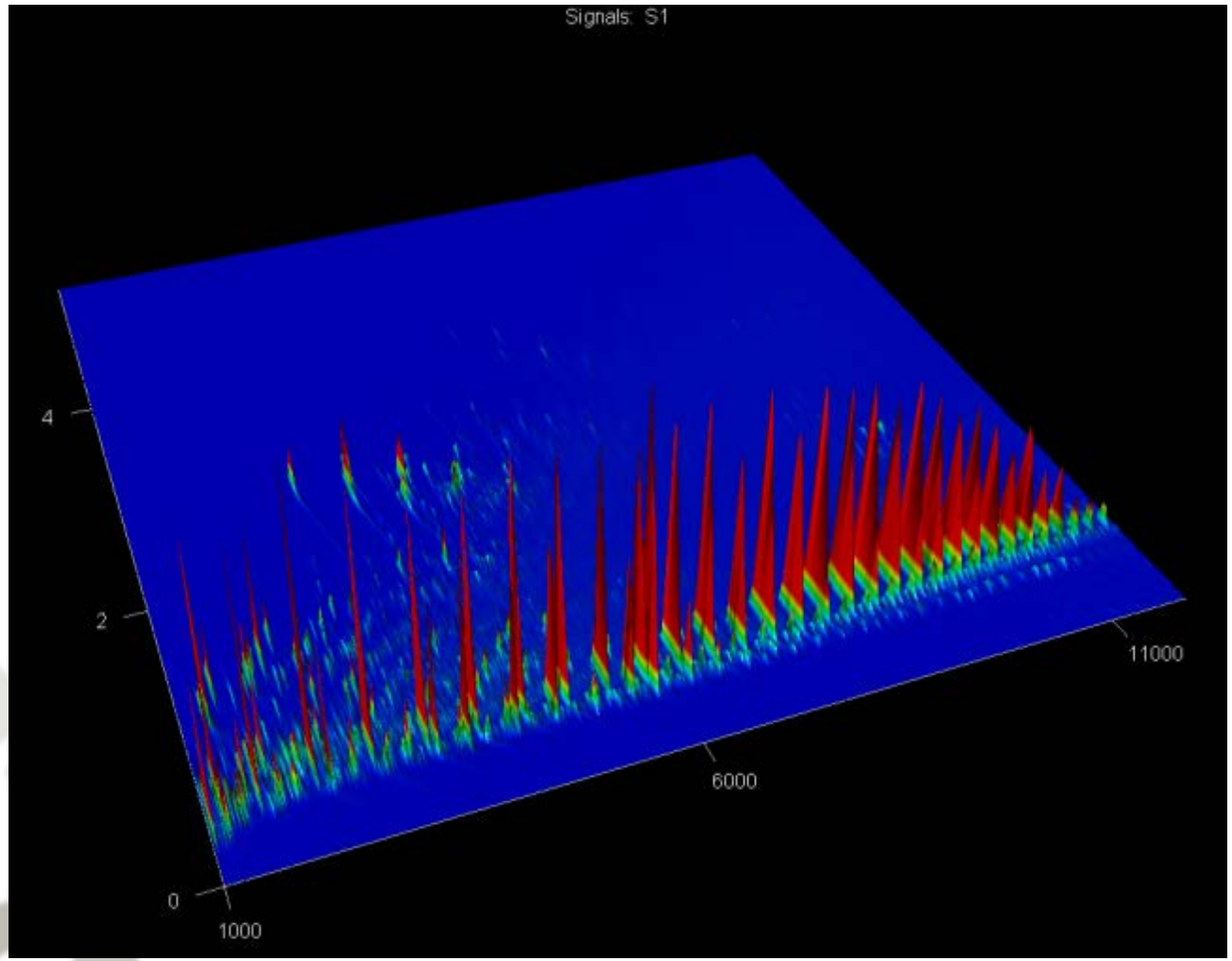
GCxGC Technology Review

Two Dimension GC (GCxGC)

- Adding another dimension of time
- Two columns in one oven
- Once the masses are separated, introduce the molecules to a second column. Further resolve.
- A thermal modulator is used to refocus the effluent to the second column.
- The polar compounds begin to resolve in the 2nd dimension.
- The branched, aromatic alkanes and cyclic alkanes, aka: paraffins, cycloparaffins, aromatics and naphthenes, (fully saturated HCs are better resolved also)

Two Dimension GC Whole Oil GCxGC



GCxGC Technology Review

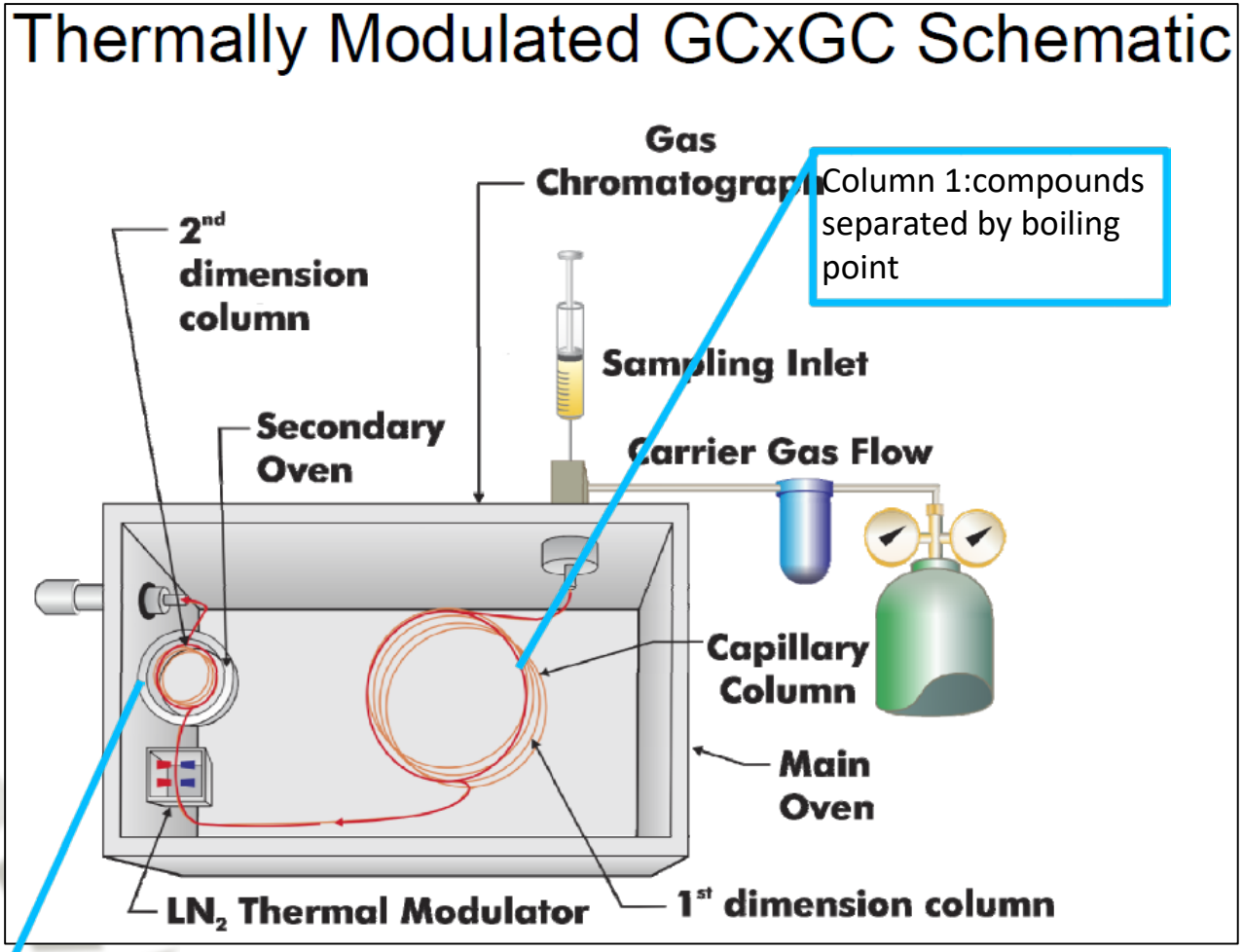
A New Approach

Two-columns interfaced with a thermal modulator

The modulator:

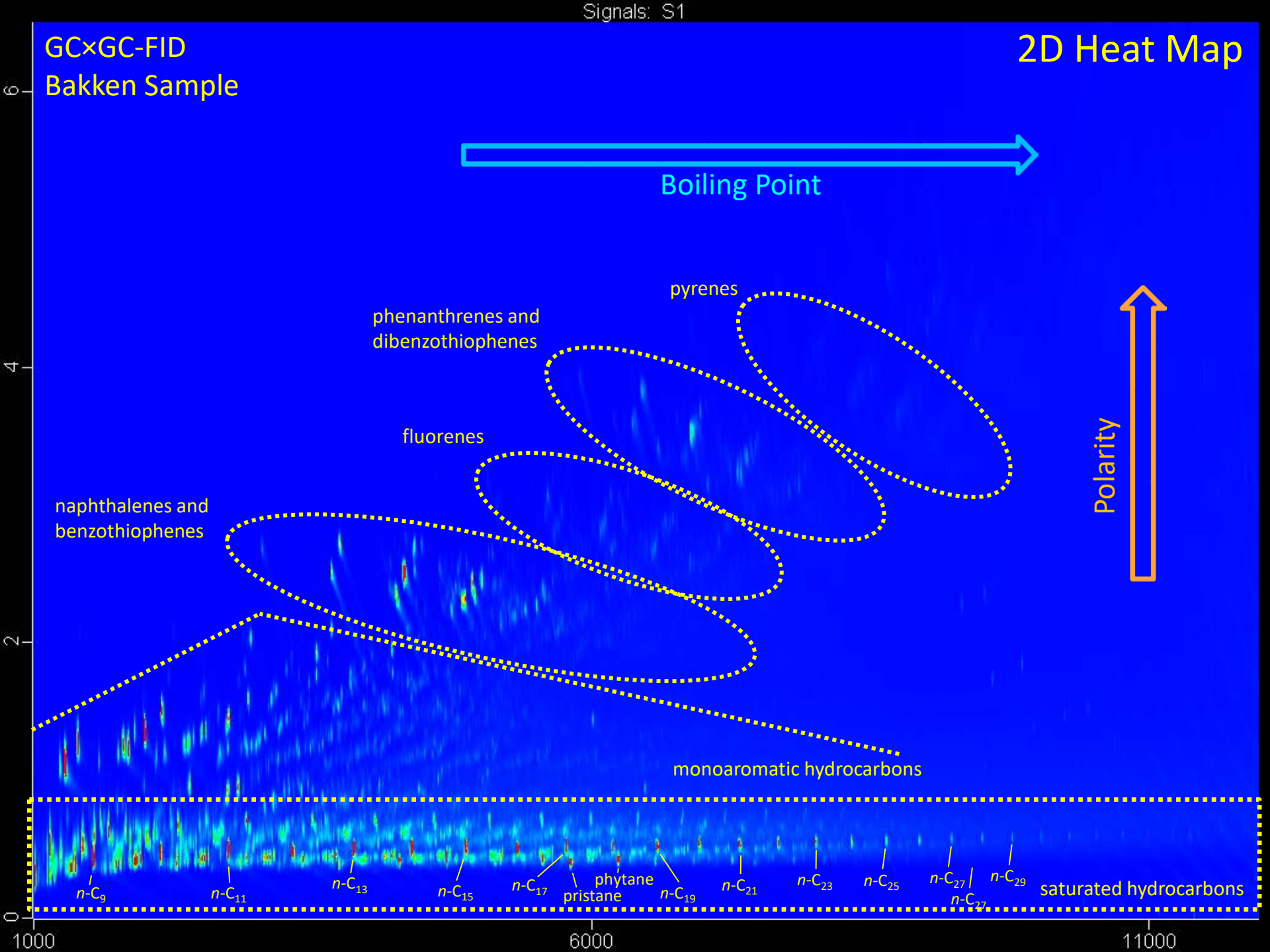
1. Collects and **focuses** volumes of effluent
2. Injects these volumes into the secondary column

Column 2: Compounds separated by polarity



Can be equipped with a Flame Ionization Detector (FID) or Time of Flight Mass Spectrometer (TOFMS) for more comprehensive molecule identification

Images courtesy of Leco Technologies


Signals: S1
GC×GC-FID
Bakken Sample
2D Heat Map
Boiling Point
Polarity
pyrenes
phenanthrenes and
dibenzothiophenes
fluorenes
naphthalenes and
benzothiophenes
monoaromatic hydrocarbons
saturated hydrocarbons
n-C9
n-C11
n-C13
n-C15
n-C17
pristane
phytane
n-C19
n-C21
n-C23
n-C25
n-C27
n-C27
n-C29
0
2
4
6
1000
6000
11000

Sampling and Extraction Results

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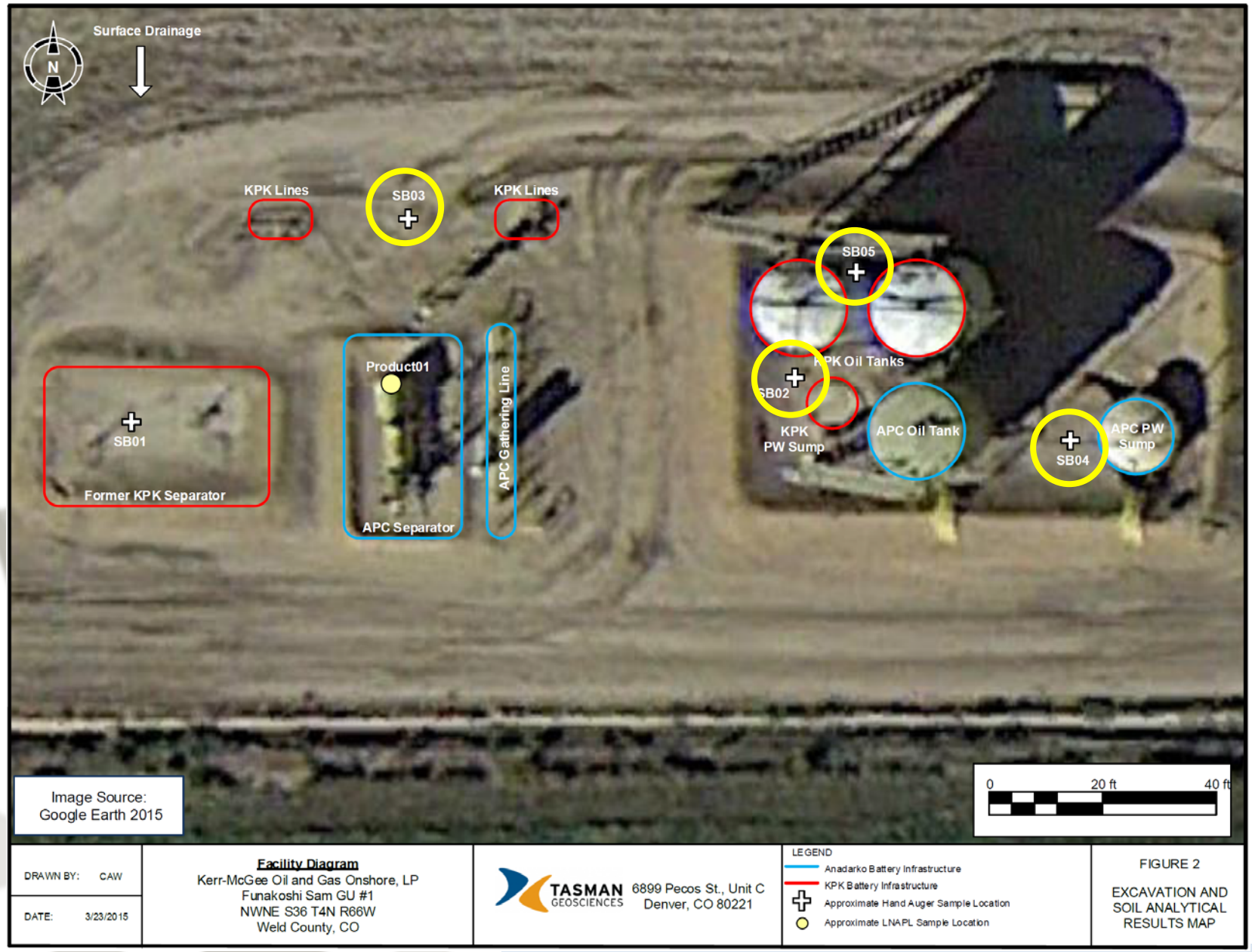
Sampling Location and Site



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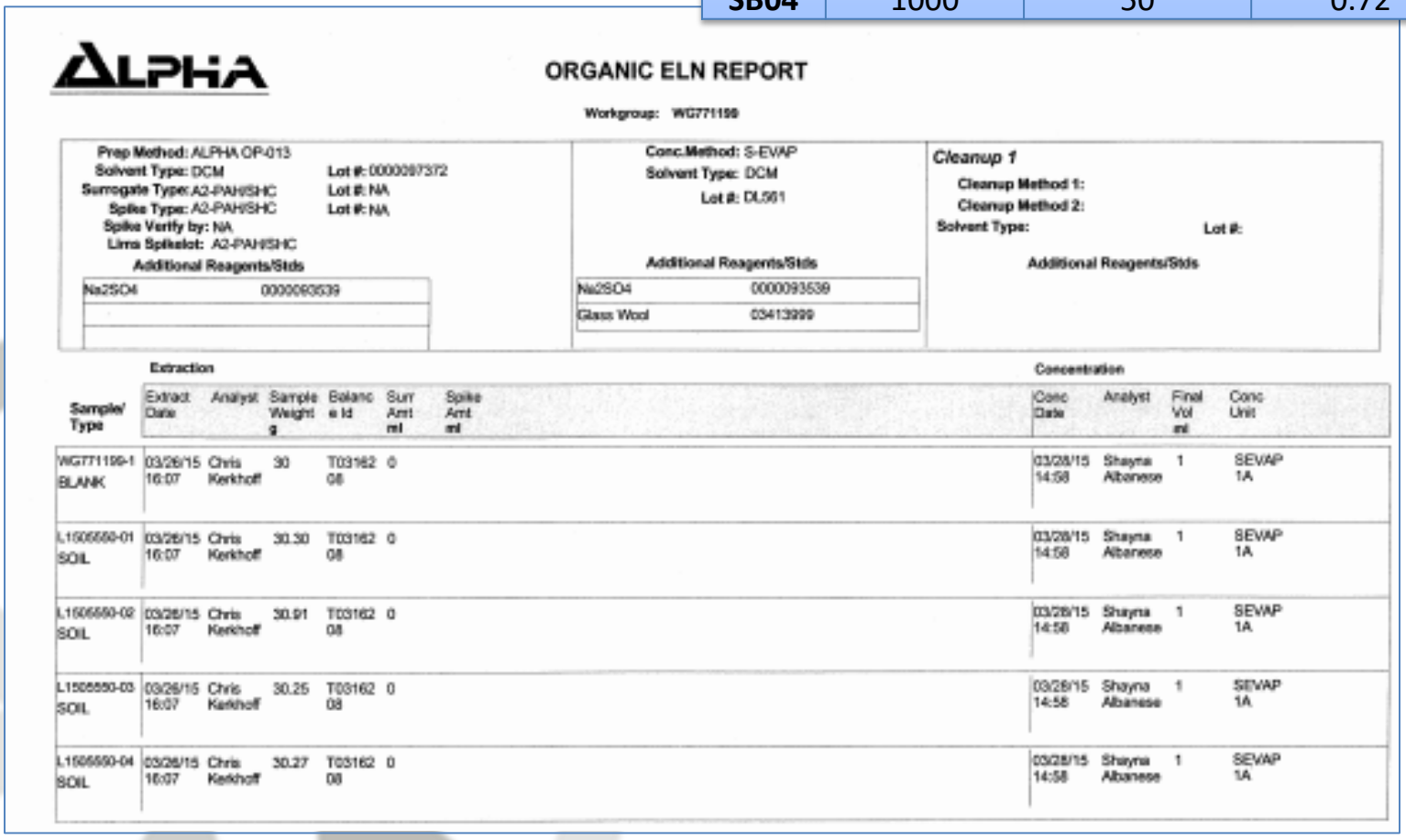
Extraction Results and Procedures

Hydrocarbons extracted from four soil samples using dichloromethane (methylene chloride)

Sample	Extract Volume (ul)	Aliquot Removed (ul)	Aliquot Weight (mg)	Extract Weight (mg)
SB03	1000	50	0.11	2.1
SB02	1000	50	1.47	29.3
SB05	1000	50	1.18	22.94
SB04	1000	50	0.72	14.36



ALPHA

ORGANIC ELN REPORT

Workgroup: WG771159

Prep Method: ALPHA OP-013
Solvent Type: DCM
Surrogate Type: A2-PAH/SHC
Spike Type: A2-PAH/SHC
Spike Verify by: NA
Lims Spikelot: A2-PAH/SHC
Lot #: 0000087372
Lot #: NA
Lot #: NA

Additional Reagents/Stds

Na2SO4	0000093539

Conc.Method: S-EVAP
Solvent Type: DCM
Lot #: DL561

Additional Reagents/Stds

Na2SO4	0000093539
Glass Wool	03413999

Cleanup 1
Cleanup Method 1:
Cleanup Method 2:
Solvent Type:
Lot #:

Additional Reagents/Stds

Sample/ Type	Extraction: Extract Date	Analyst	Sample Weight g	Balance Id	Surr Amt ml	Spike Amt ml	Concentration: Conc Date	Analyst	Final Vol ml	Conc Unit
WG771159-1 BLANK	03/26/15 16:07	Chris Kerkhoff	30	T03162 08	0		03/28/15 14:58	Shayna Albanese	1	SEVAP 1A
L1506550-01 SOIL	03/26/15 16:07	Chris Kerkhoff	30.30	T03162 08	0		03/28/15 14:58	Shayna Albanese	1	SEVAP 1A
L1506550-02 SOIL	03/26/15 16:07	Chris Kerkhoff	30.91	T03162 08	0		03/28/15 14:58	Shayna Albanese	1	SEVAP 1A
L1506550-03 SOIL	03/26/15 16:07	Chris Kerkhoff	30.25	T03162 08	0		03/28/15 14:58	Shayna Albanese	1	SEVAP 1A
L1506550-04 SOIL	03/26/15 16:07	Chris Kerkhoff	30.27	T03162 08	0		03/28/15 14:58	Shayna Albanese	1	SEVAP 1A

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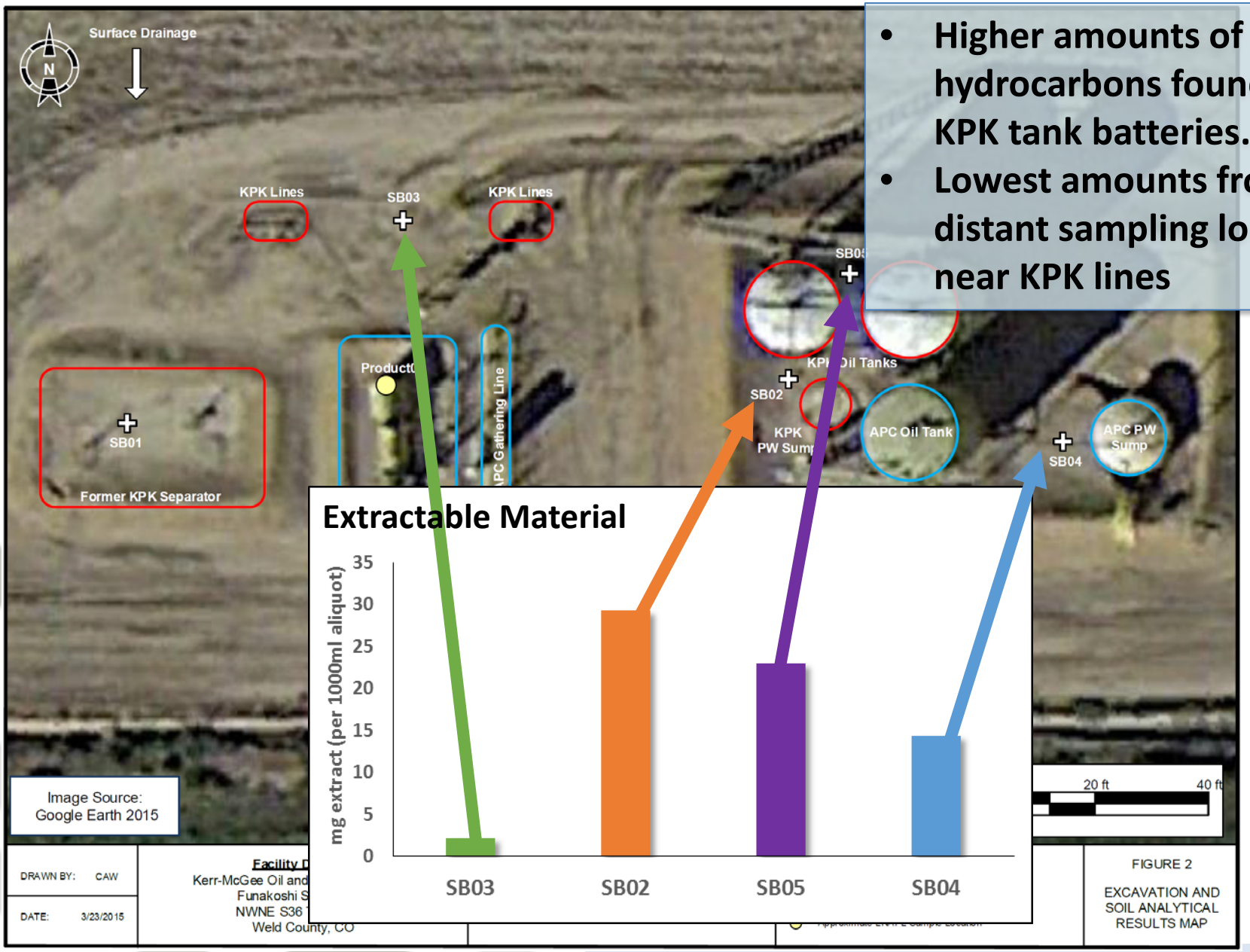
Extraction Results

- Higher amounts of extracted hydrocarbons found near KPK tank batteries.
- Lowest amounts from distant sampling location near KPK lines



GCxGC Results of Soil Extracts

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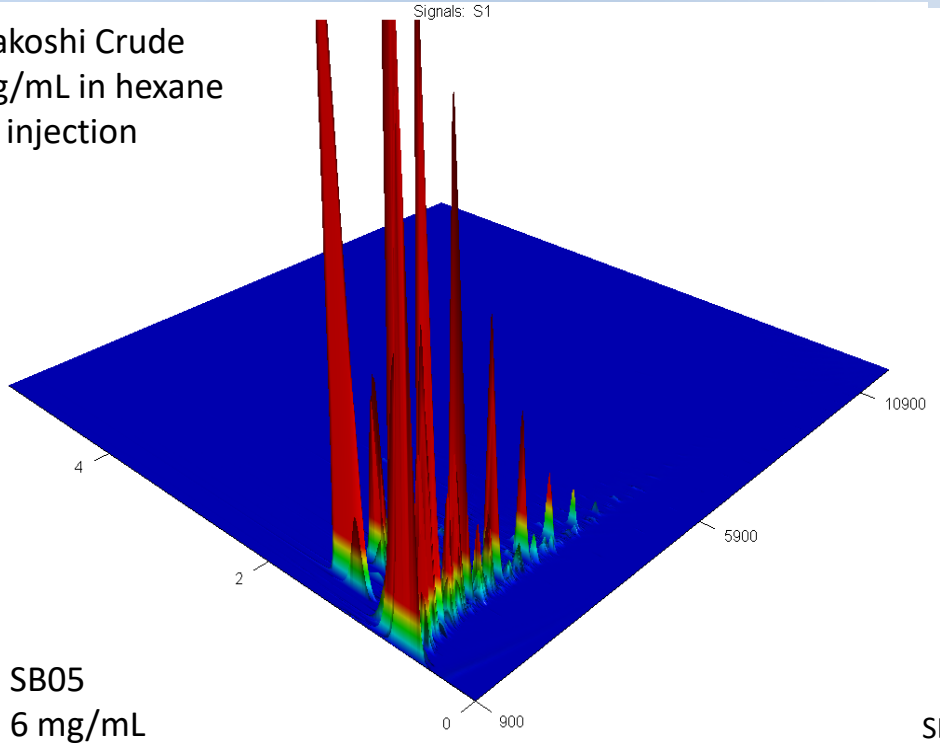
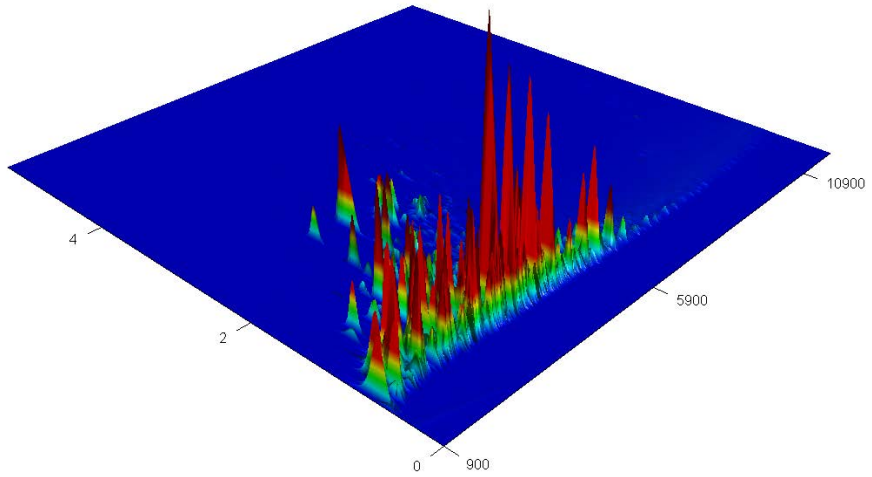
GCxGC Mountain Maps

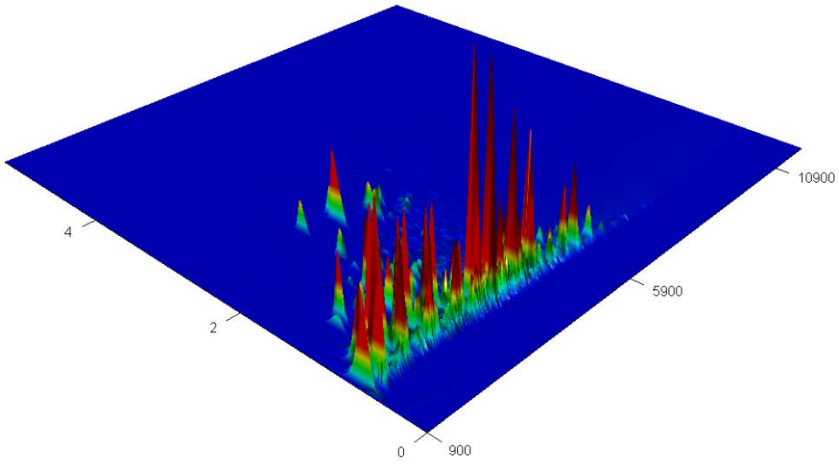
Funakoshi Crude
6 mg/mL in hexane
1 µL injection



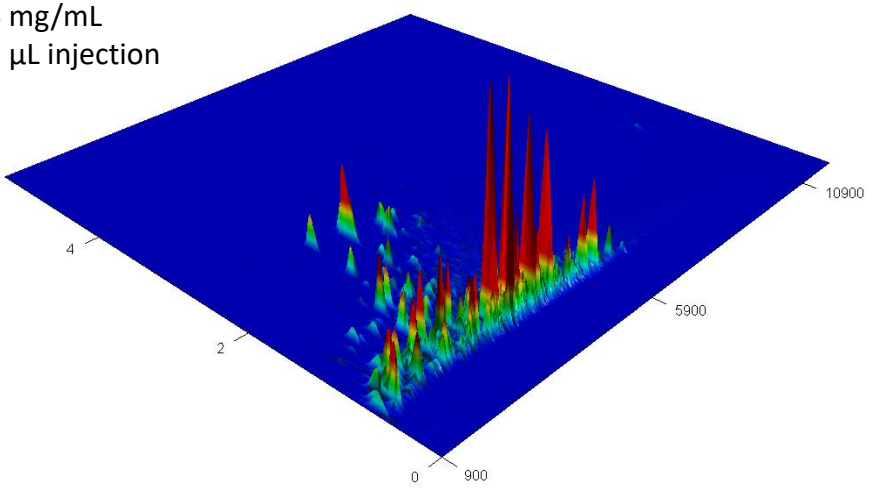
SB02
6 mg/mL
1 µL injection



SB05
6 mg/mL
1 µL injection



SB04
6 mg/mL
1 µL injection



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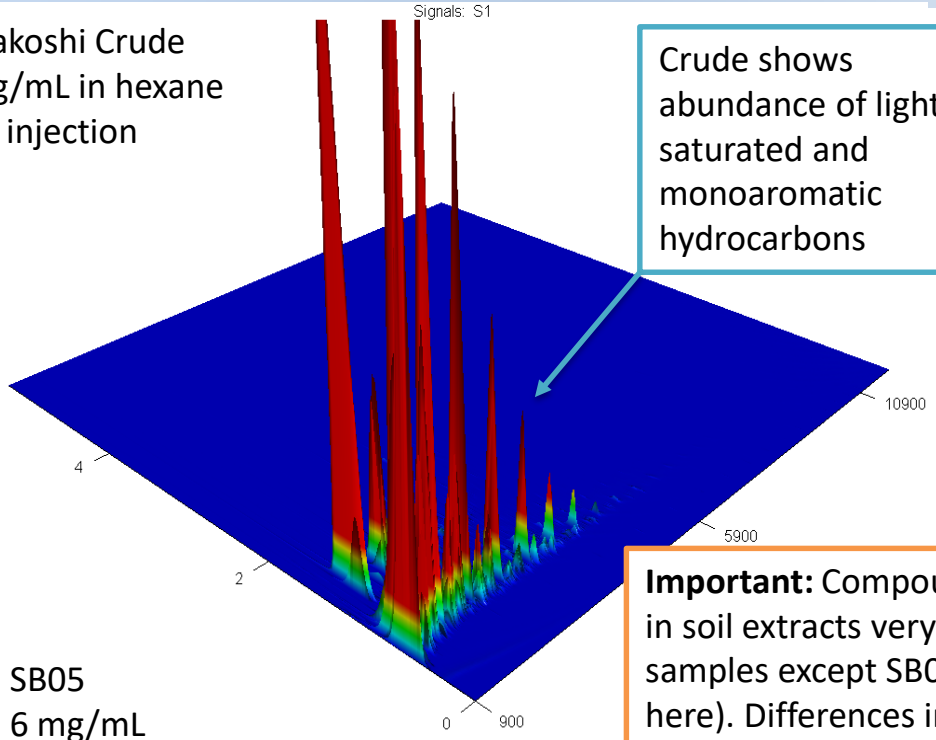
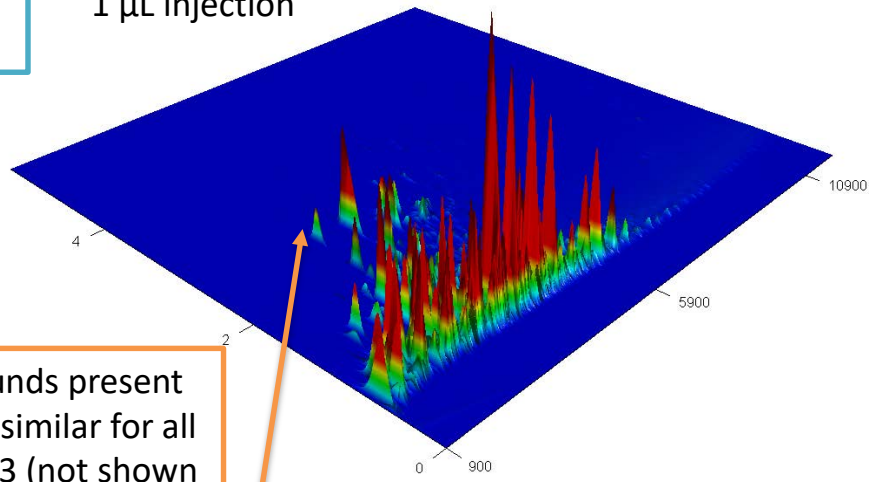
GCxGC Mountain Maps

Funakoshi Crude
6 mg/mL in hexane
1 µL injection

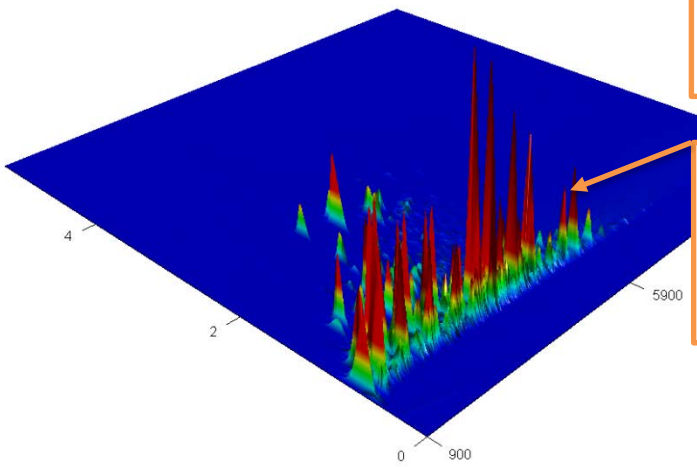


Crude shows abundance of light saturated and monoaromatic hydrocarbons

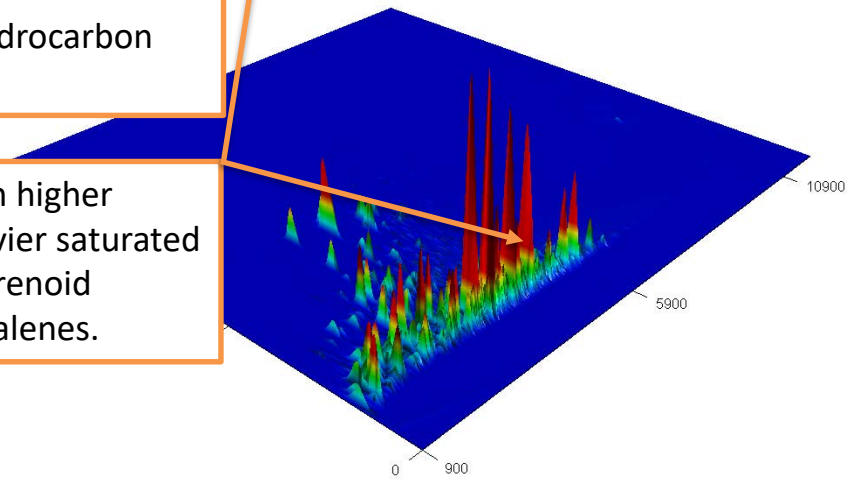
SB02
6 mg/mL
1 µL injection



SB05
6 mg/mL
1 µL injection



Important: Compounds present in soil extracts very similar for all samples except SB03 (not shown here). Differences in relative peak heights reflect concentration of hydrocarbon contaminant in soil.



Soil extracts contain higher abundances of heavier saturated hydrocarbons (isoprenoid range), and naphthalenes.

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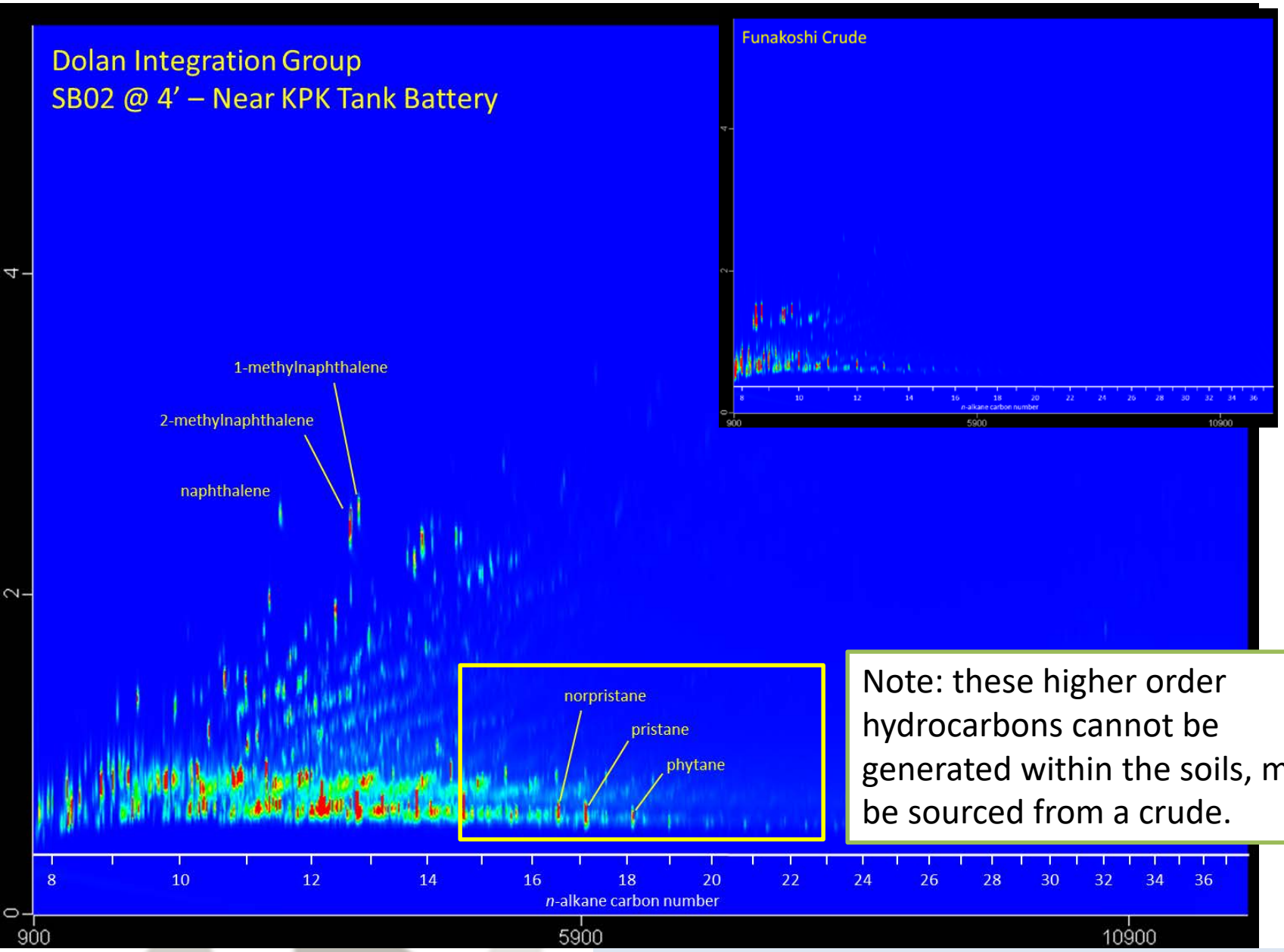
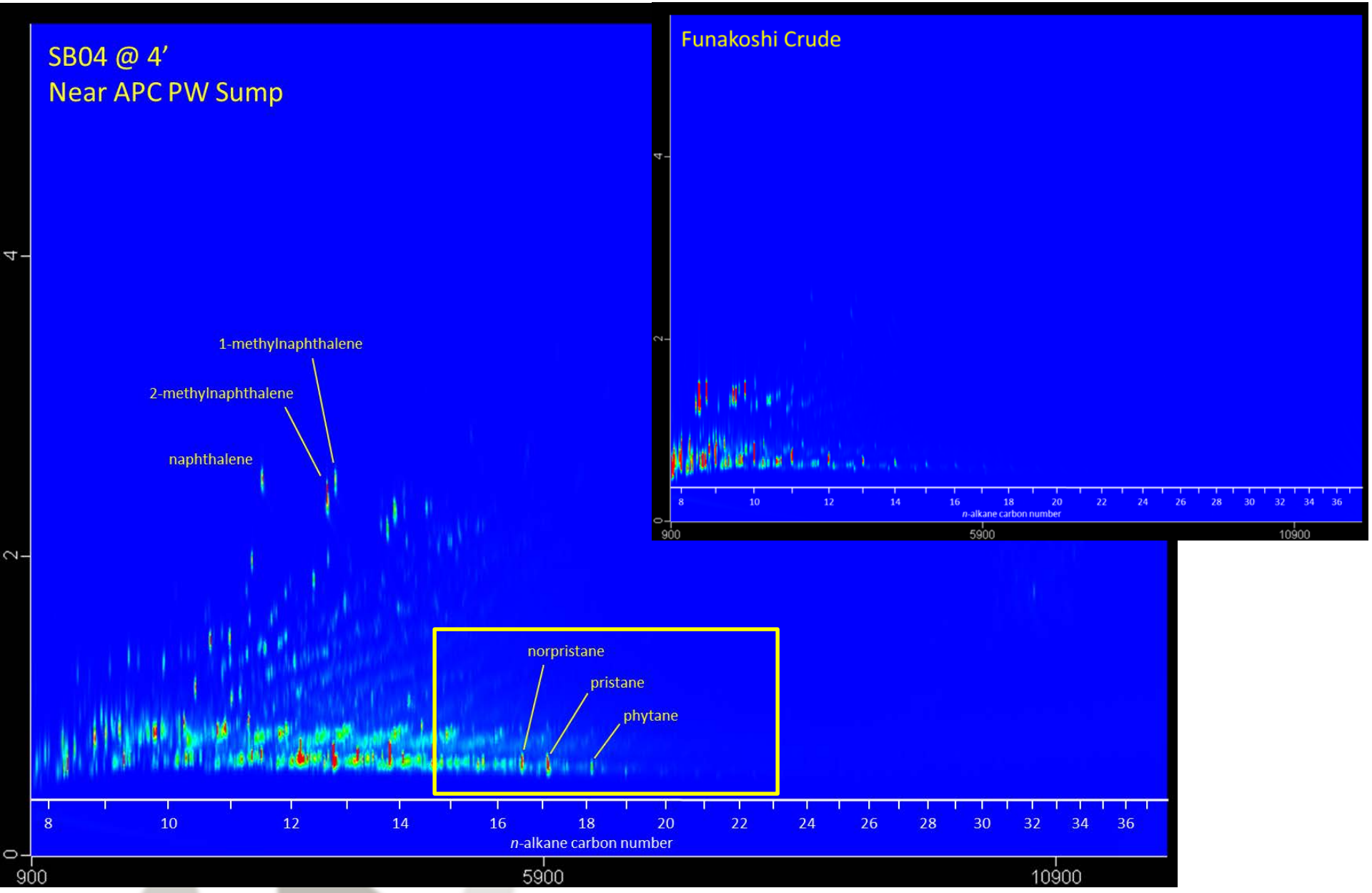
GCxGC Heat Maps (Plan View)

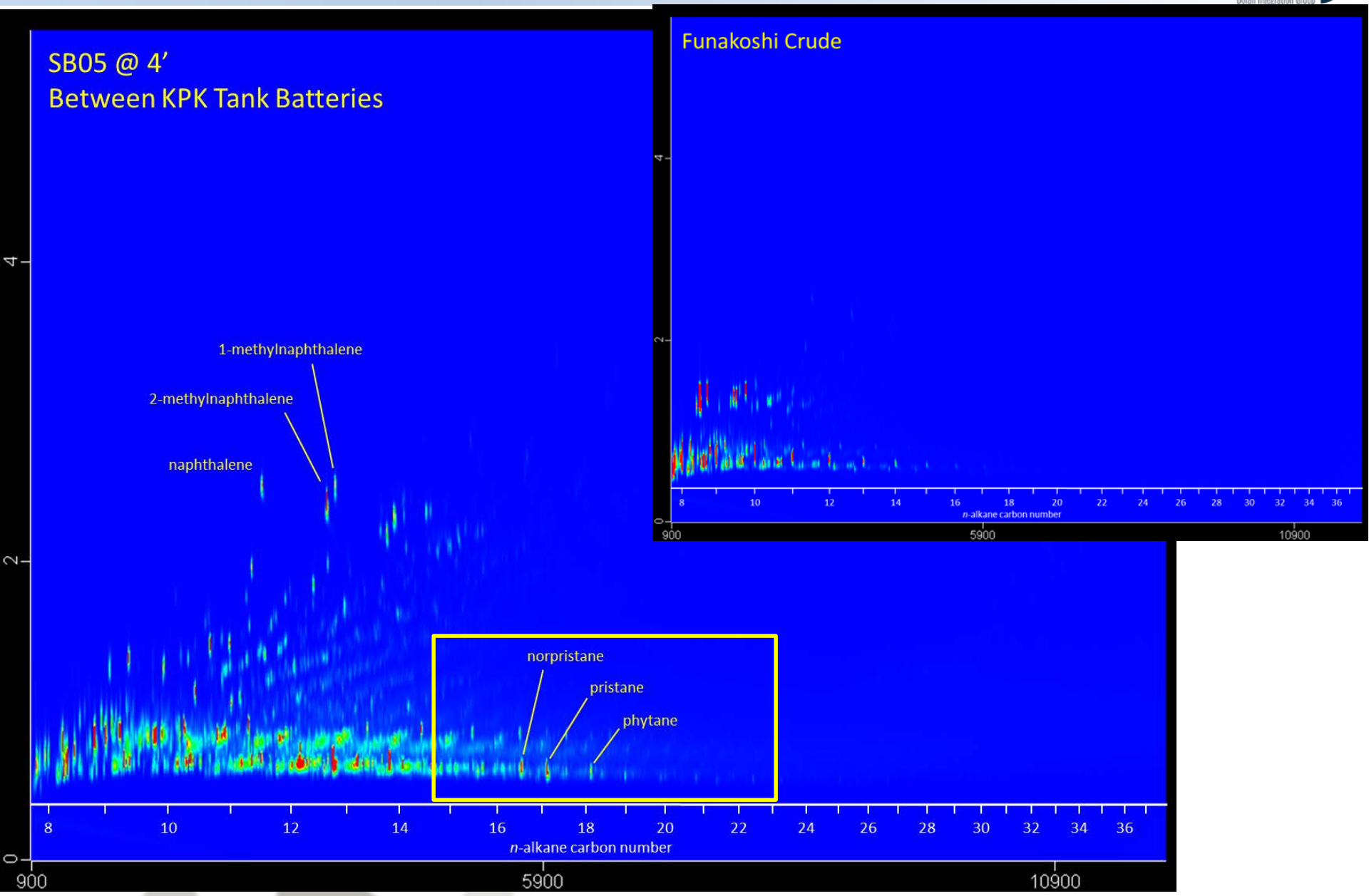


Note: these higher order hydrocarbons cannot be generated within the soils, must be sourced from a crude.

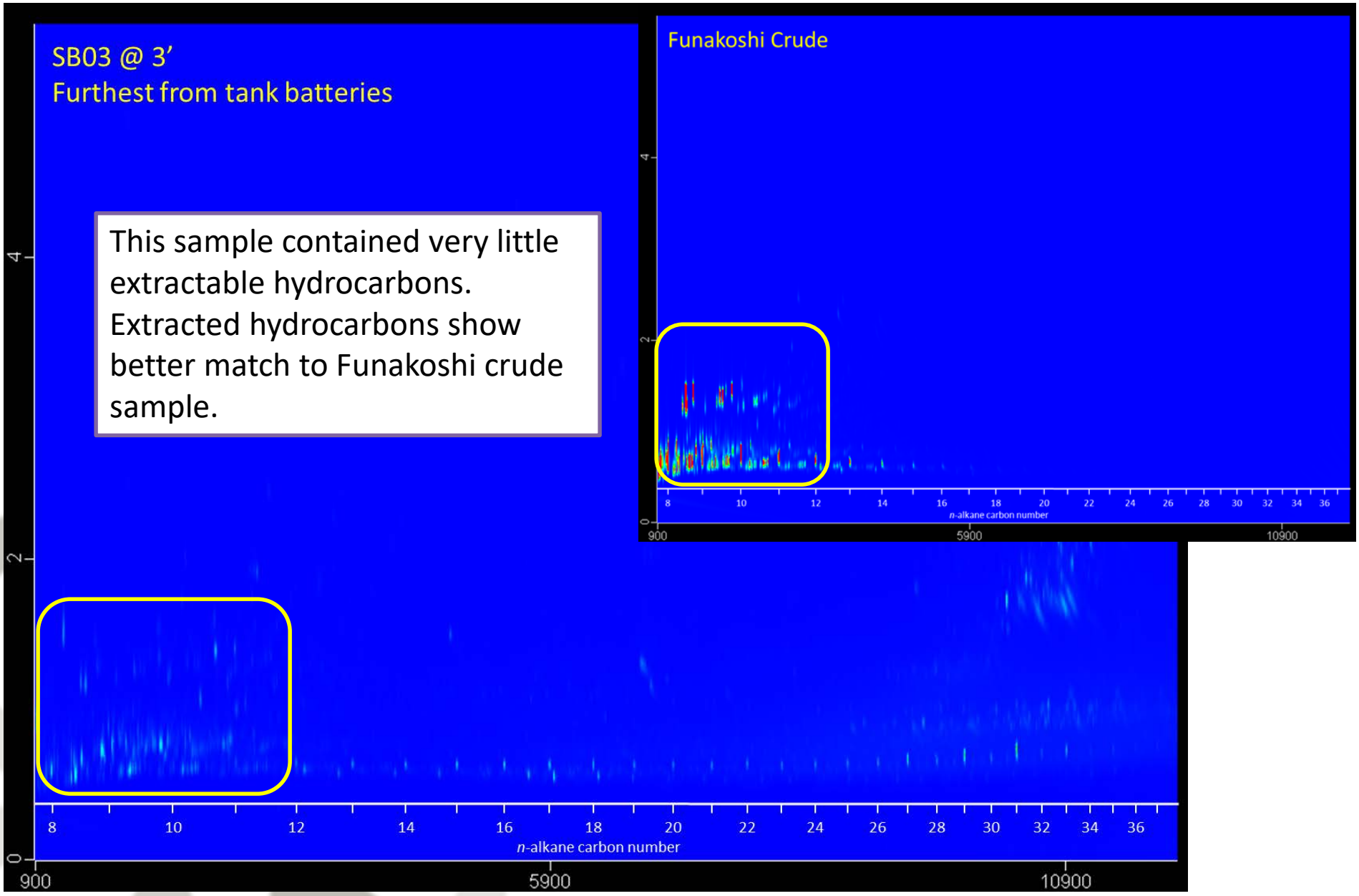
GCxGC Heat Maps (Plan View)



GCxGC Heat Maps (Plan View)



GCxGC Heat Maps (Plan View)



GCxGC Heat Maps (Plan View)

Zoomed in to the C8-C12 range, we can see several shared compound (or compound groups) between this soil extract and crude.

Comparison with Baseline Oil Dataset

The following slides compare soil extract and Funakoshi crude GCxGC results with whole oil GC data from Denver Basin Oils.

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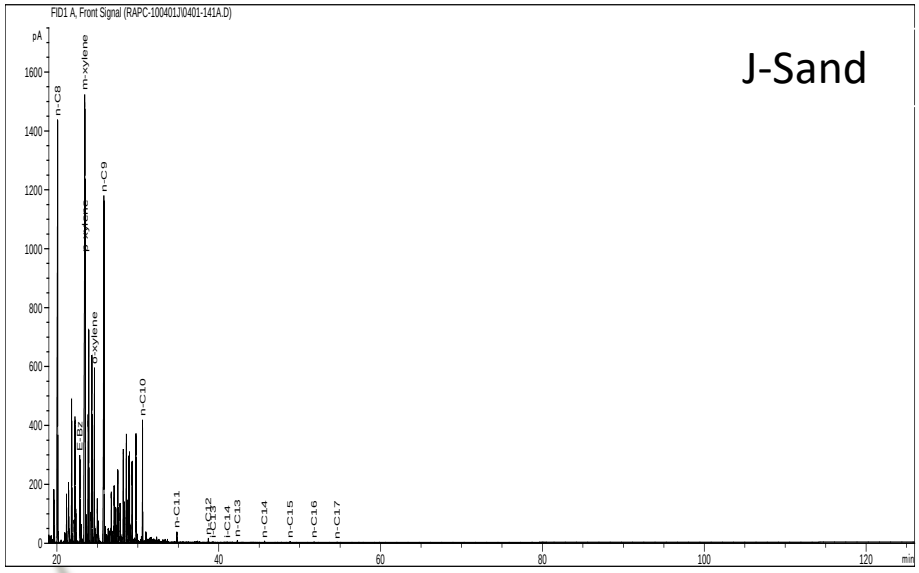
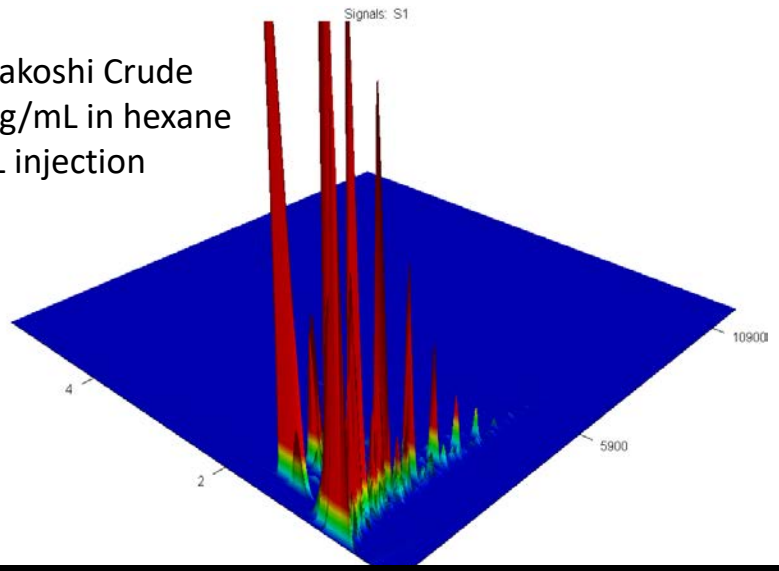
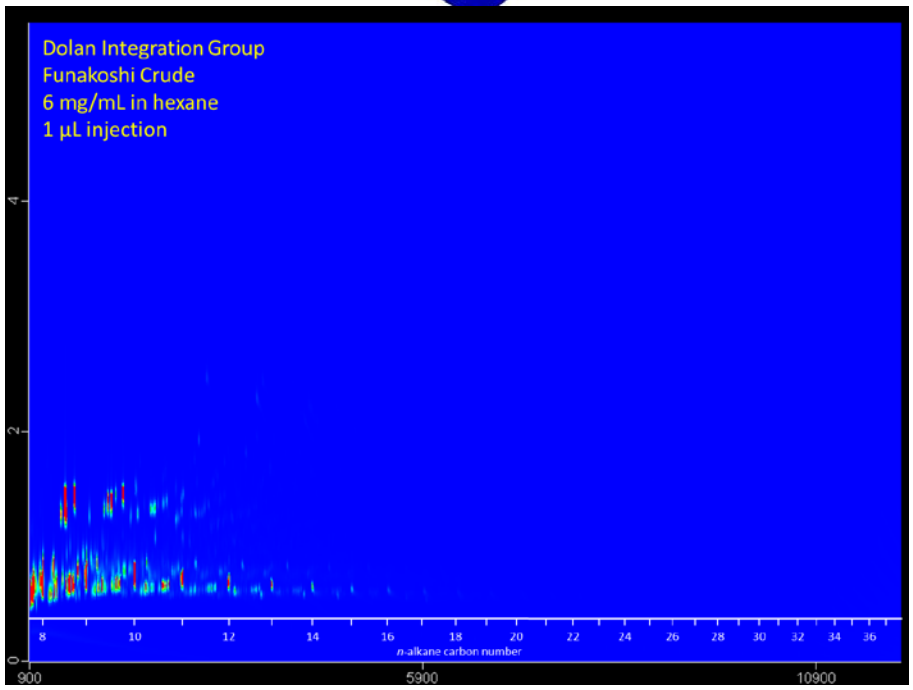
Comparison with Baseline Data



J-Sand

Funakoshi Crude
6 mg/mL in hexane
1 µL injection

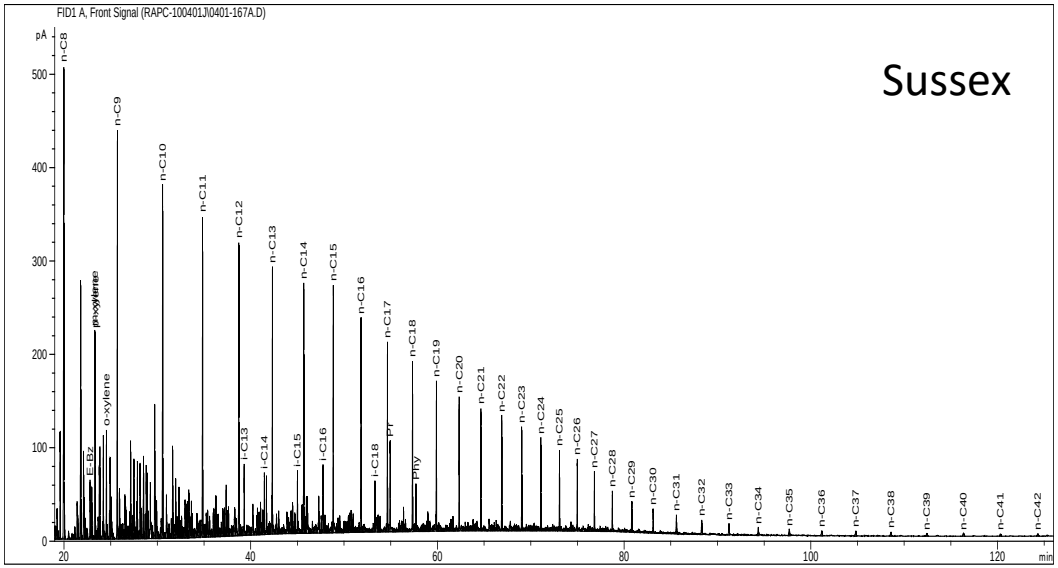




The Funakoshi crude compares well with a J-Sand source from nearby in the Wattenberg (approx. three miles distance)

Note the lack of C16+ Alkanes in both samples and abundance of hydrocarbons in the C8 to C12 range.

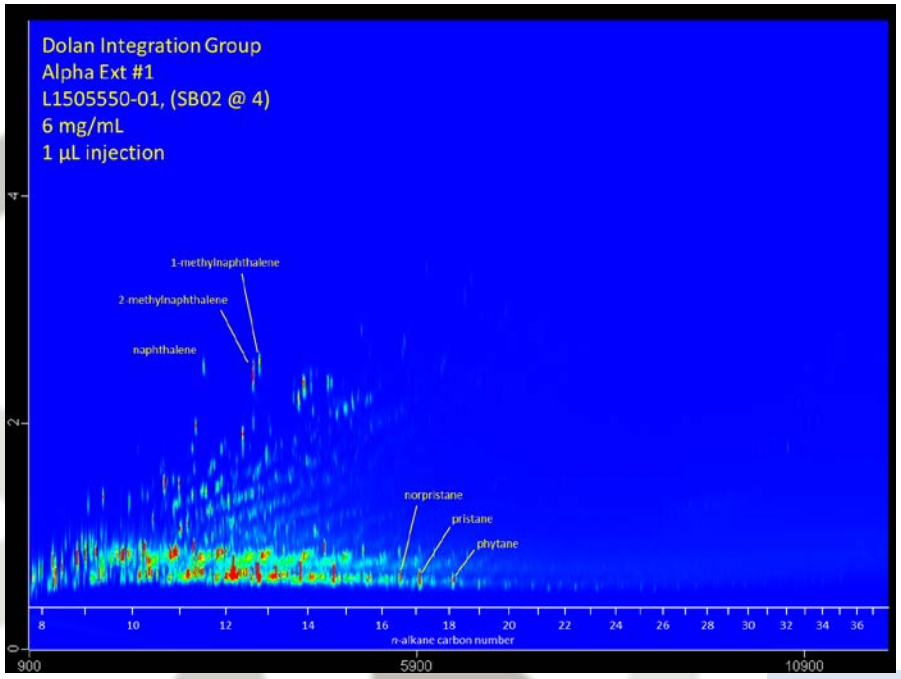
Comparison with Baseline Data

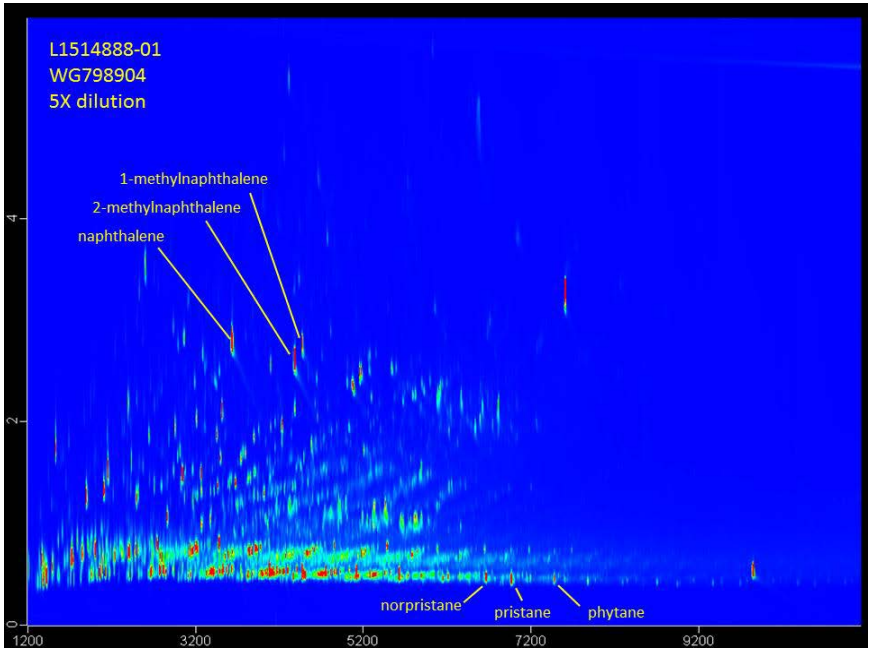


Sussex

The oil extracts compare well with a Sussex crude (from approx. 20 miles away)

Soil and Groundwater extracts show abundances of hydrocarbons up to C25



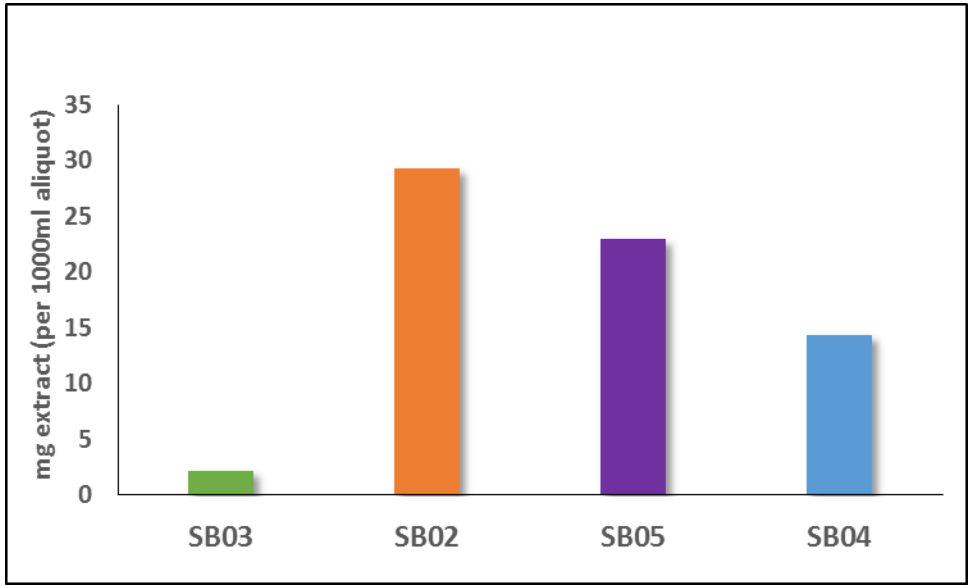


Pristane/Phytane Comparison

The abundances of Pristane and Phytane (Pr/Ph) are commonly used in oil correlations. Low-wax marine-source oils are known to have ratios between 1-3. The value is initially reflective of the source kerogen, but then can gradually increase with thermal maturation.

Pristane and Phytane were found in SB02, SB04, and SB05 samples.

Source	Pristane/Phytane
Sussex Baseline	1.79
SB02 @ 4’	1.79
SB04 @ 4’	2.11*
SB05 @ 4’	1.65*
GW-03	2.4*
J-Sand Baseline	n/a
Funakoshi Crude	n/a



*Changes in Pr/Ph values may be a result of in evaporation, biodegradation, and/or other weathering processes in the soil (Wang et al., 2005). The SB02 sample, containing the most hydrocarbons and likely closest to the point source of leakage, would be the most trustworthy value.

Soil Extract Conclusions

1. Extraction results indicate highest amount of contamination near KPK tank batteries, low extractable amounts found furthest from KPK Tank Batteries.
2. These soil extracts are compositionally different than the Funakoshi crude.
    1. The extracts are not as enriched in lighter saturate fractions (C8-C12)
    2. The extracts contain isoprenoids and naphthalenes not present in the Funakoshi crude.
3. Comparison with baseline GC data suggest contaminating hydrocarbons are of a Sussex oil, whereas the Funakoshi crude more closely matches a more mature J-Sand oil.
4. The Pristane/Phytane ratio of the most contaminated soil (nearest to the point source) matches the value of a Sussex produced oil.
    1. No Pristane or Phytane contained in the Funakoshi Crude
5. Soil sample SB03, furthest from the KPK Tank batteries, shows a signature unlike the other extracts. It does have some characteristic peaks that compare well with the Funakoshi crude, and is possibly a mixture of various sources.

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Overview of Groundwater Project

Project Overview

1. Groundwater samples collected following excavation of site
2. Groundwaters analyzed for BTEX and extracted hydrocarbons
3. Extracts analyzed using GCxGC

Results

1. First groundwater sample showed very little hydrocarbons, this could be due to the location of the monitoring well, or the short time after excavation was finished
2. The second water sample showed abundant hydrocarbons – GCxGC results indicate the groundwater was contaminated by same crude that contaminated soil

	Sample 1	Sample 2
B	173 µg/L	208 µg/L
T	1,390 µg/L	< 4.0 µg/L
E	174 µg/L	14.7 µg/L
X	2,840 µg/L	< 4.0 µg/L

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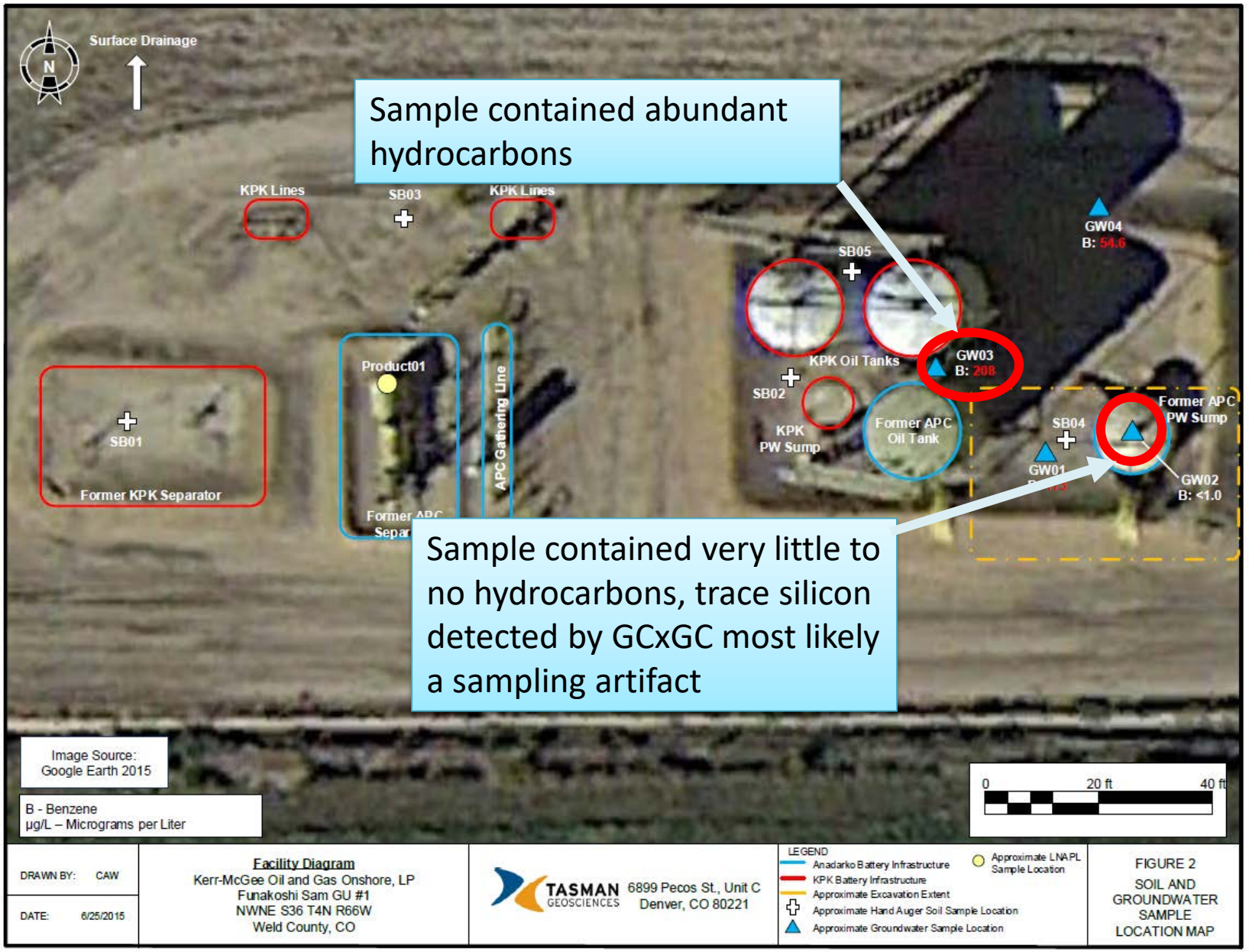
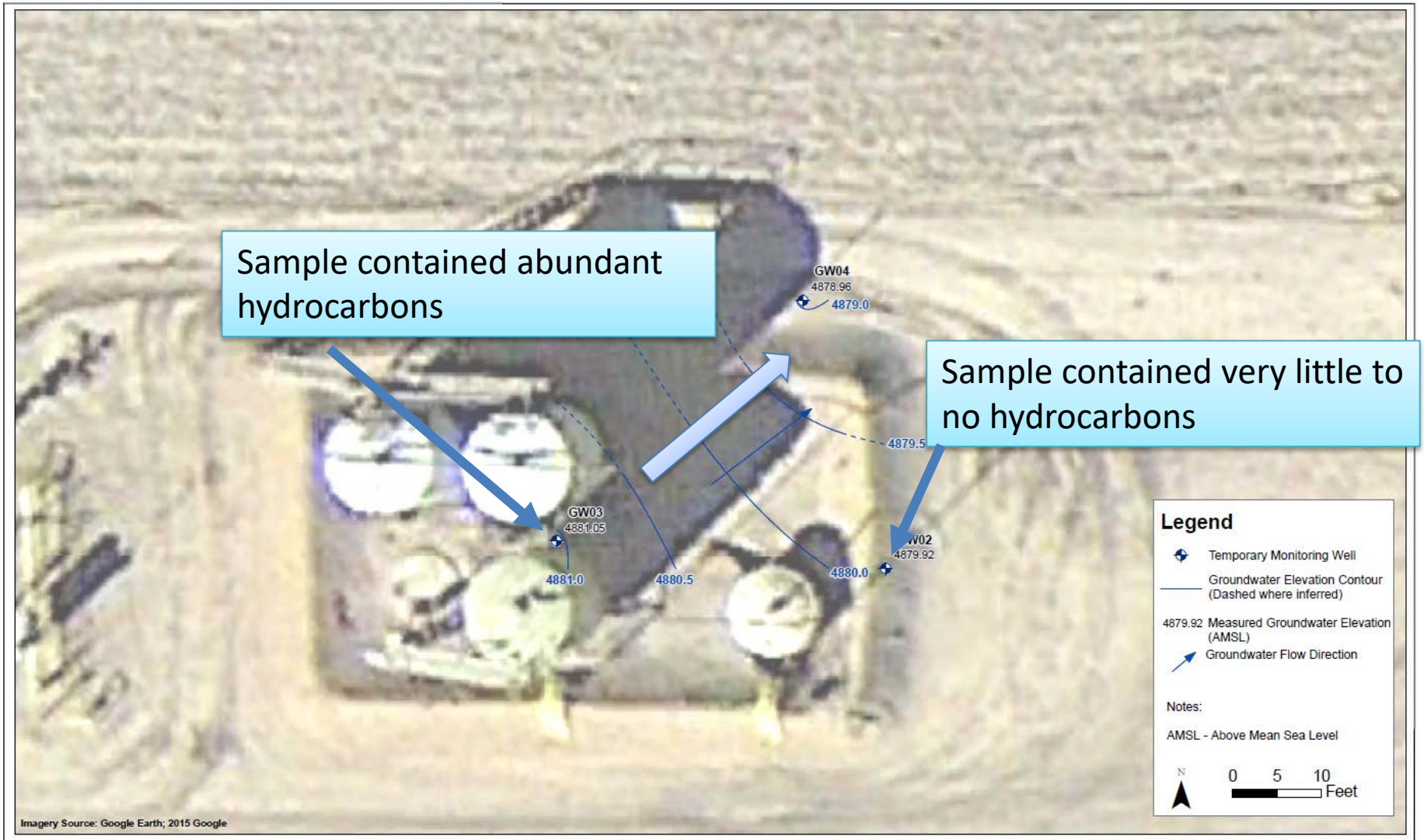
Groundwater Samples

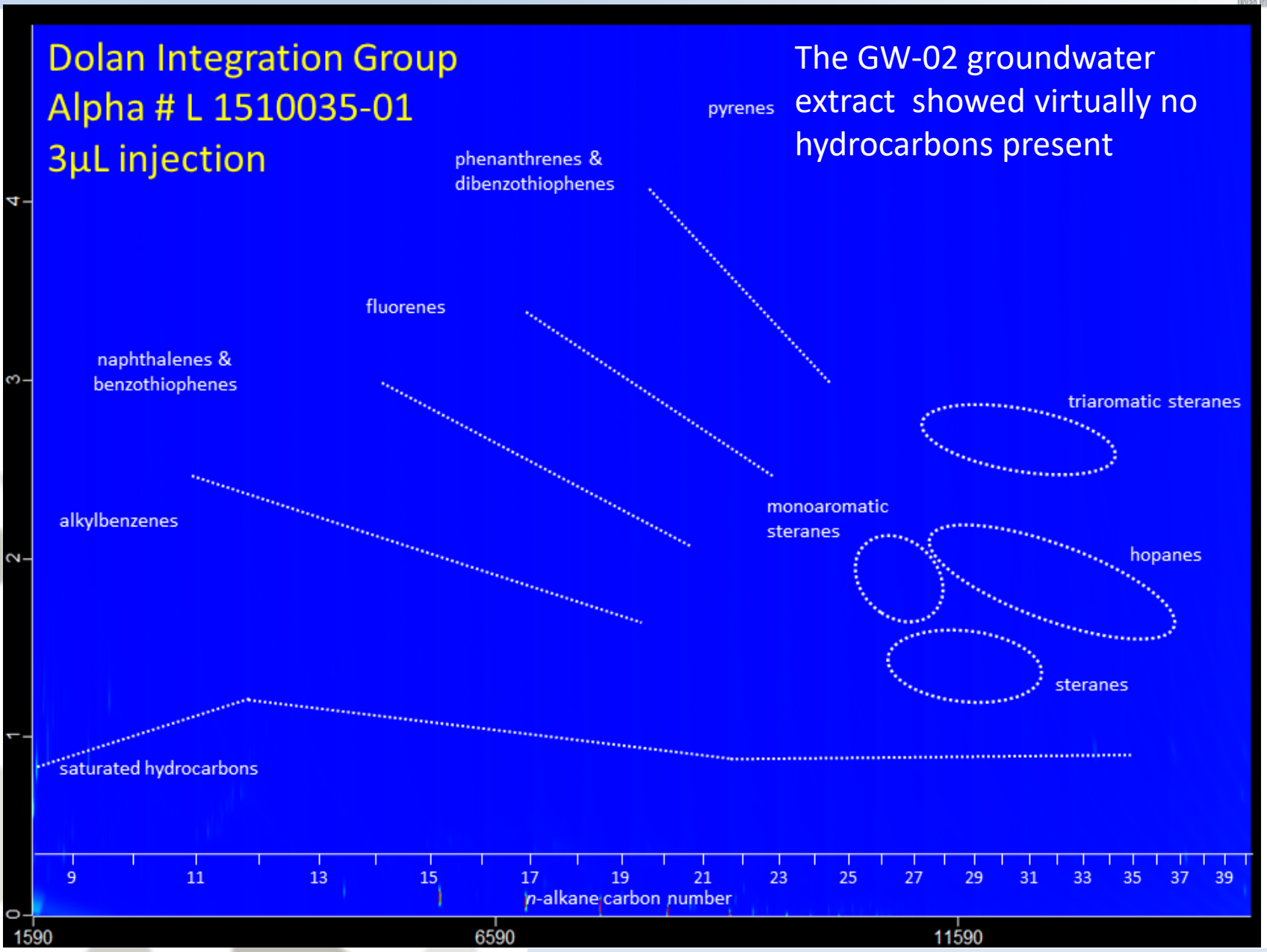


Groundwater Flow

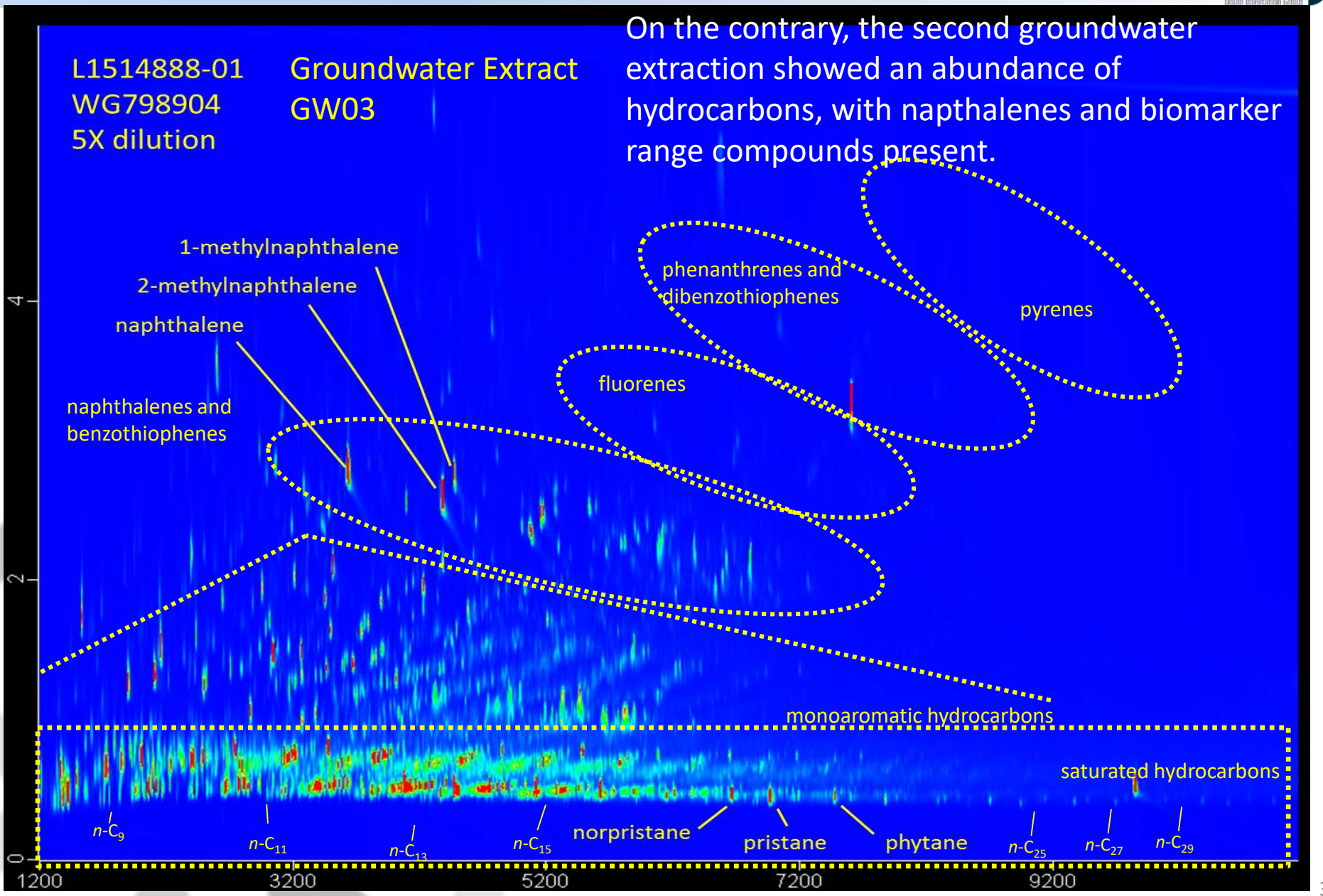


DATE: July 2015 DESIGNED BY: C. Wasko DRAWN BY: D. Arnold	TASMAN GEOSCIENCES Tasman Geosciences, Inc. 6899 Pecos Street - Unit C Denver, CO 80221	Kerr-McGee Oil and Gas Onshore, LLC Funakoshi Sam Gas Unit #1 NWNE S36 T2N R67W Weld County, CO	Groundwater Elevation Contour Map (July 7, 2015)	Figure 3

GW-02 Chromatogram



GW-03 Chromatogram



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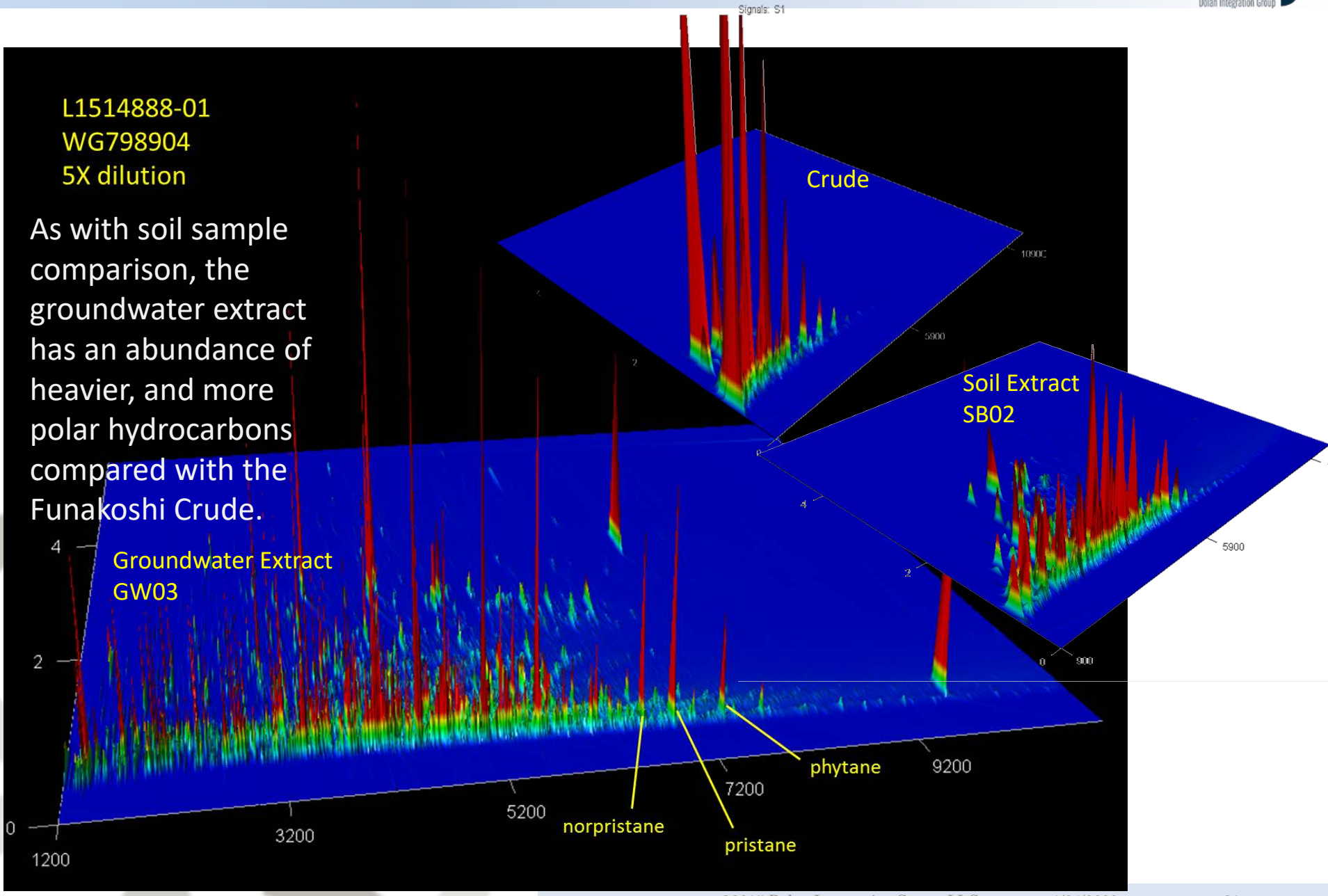
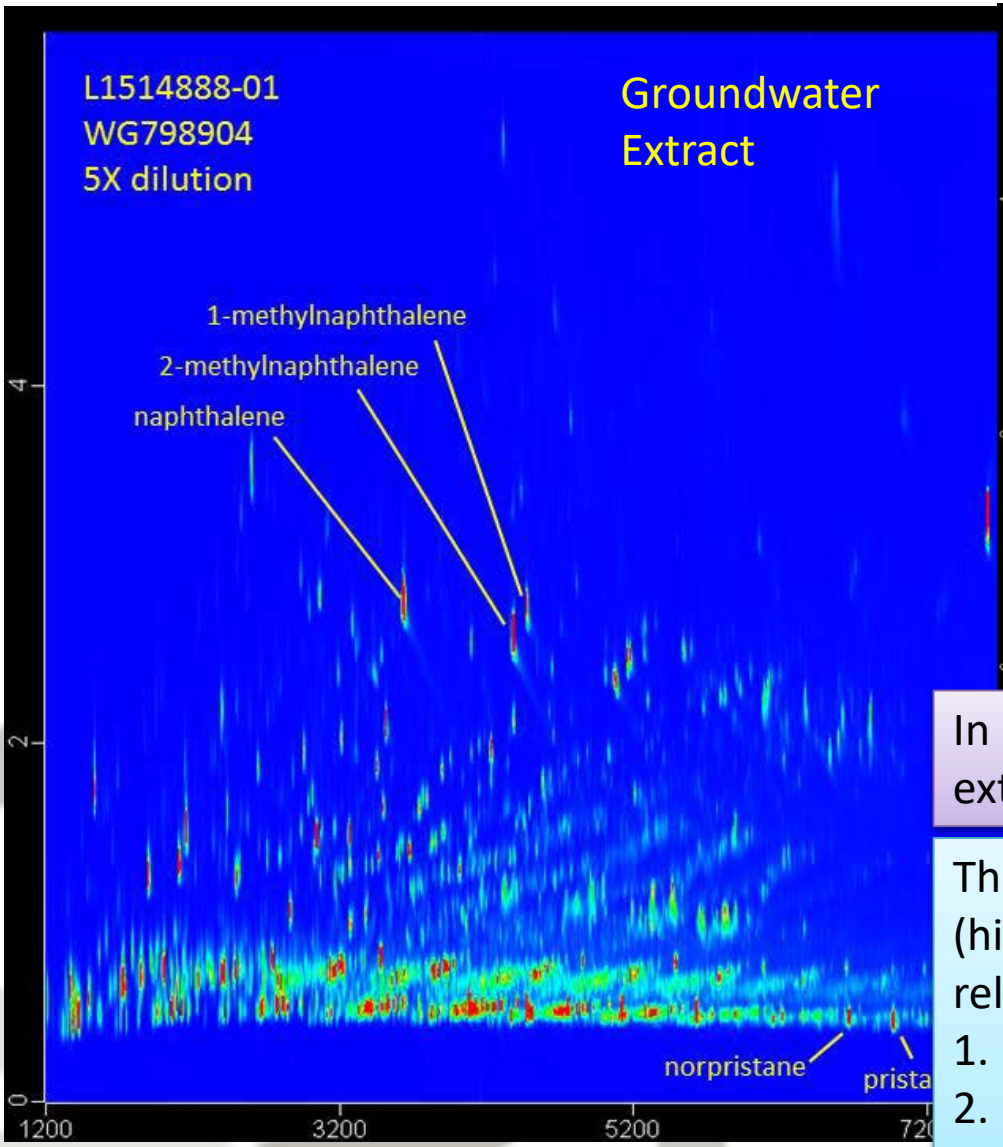
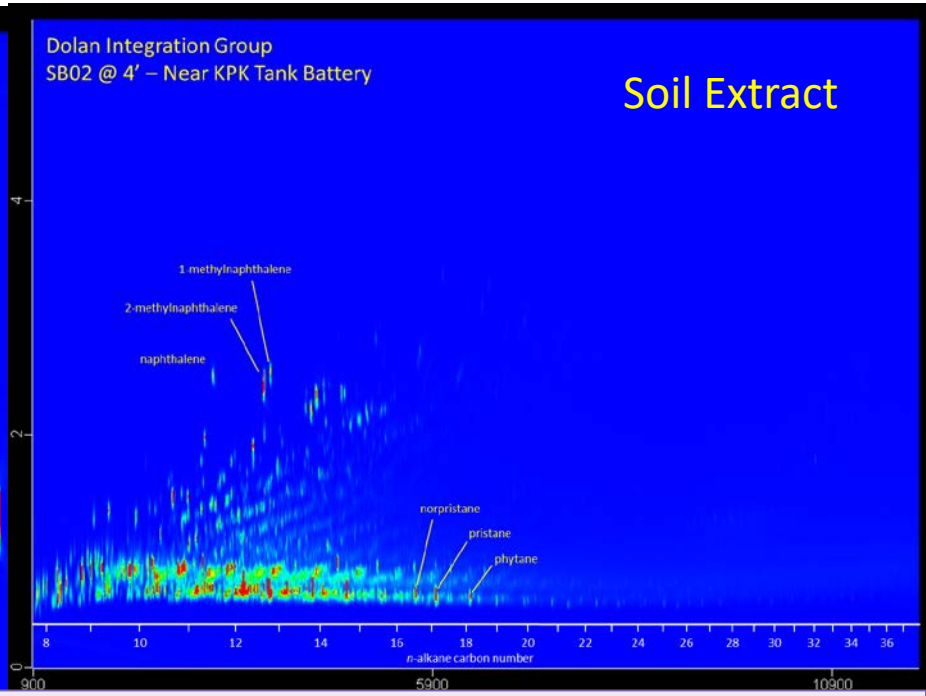
GW-03 Results







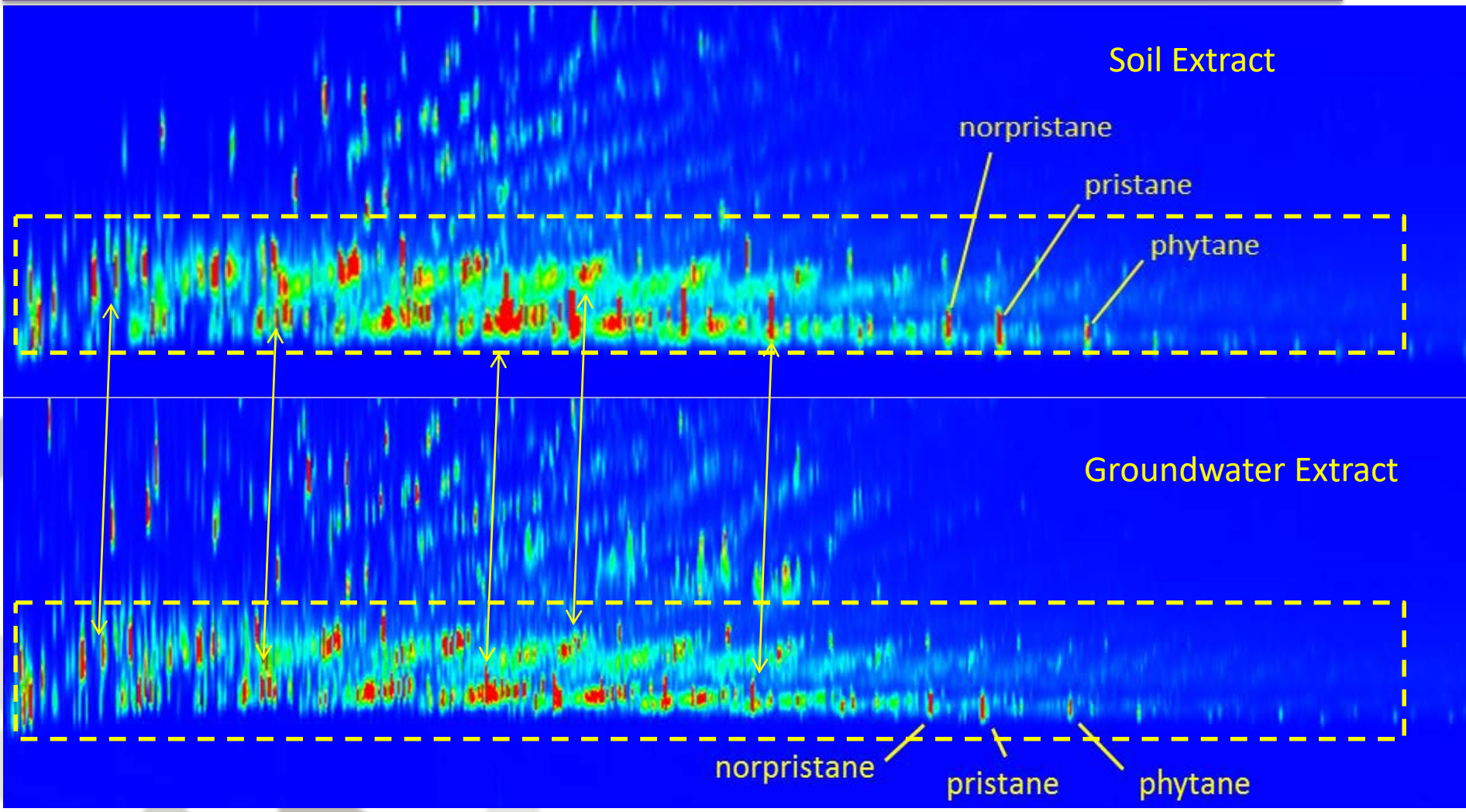
In plan view, the similarities between these extracts becomes much more noticeable.

The abundance of more polar hydrocarbons (higher on Y-axis) in the groundwater is likely related to:

1. Enhanced solubility in the groundwater
2. Reduced degradative effects in groundwater relative to soil (Peters et al. 2005)
3. Different injected mass into the GCxGC.

Comparison with Soil Extract - Alkanes

Comparing the abundances of the less water soluble alkanes suggests the hydrocarbons contaminating the soil and groundwater are from the same source.



Overall Summary

Soils and Groundwater

1. Extraction results indicate highest amount of soil contamination near KPK tank batteries, low extractable amounts found furthest from KPK Tank Batteries.
2. Groundwater contamination apparent following excavation
3. The **soil and groundwater** extracts are compositionally different than the Funakoshi crude.
    1. The extracts are not as enriched in lighter saturate fractions (C8-C12)
    2. The extracts contain isoprenoids and naphthalenes not present in the Funakoshi crude.
4. The Pristane/Phytane ratio of the most contaminated soil (nearest to the point source) matches the value of a Sussex produced oil.
    1. No Pristane or Phytane contained in the Funakoshi Crude
    2. Pristane/Phytane of more distal soil and groundwater extracts may be affected by transport/degradation
5. GCxGC results show distinctive similarities between groundwater and soil extracts, which identify as a lower maturity oil (relative to J-Sand) of probable Sussex origin.