# Forensic Fingerprinting and Source Identification of the Lake Temiskaming (Quebec) Mystery Oil Spill (2008)

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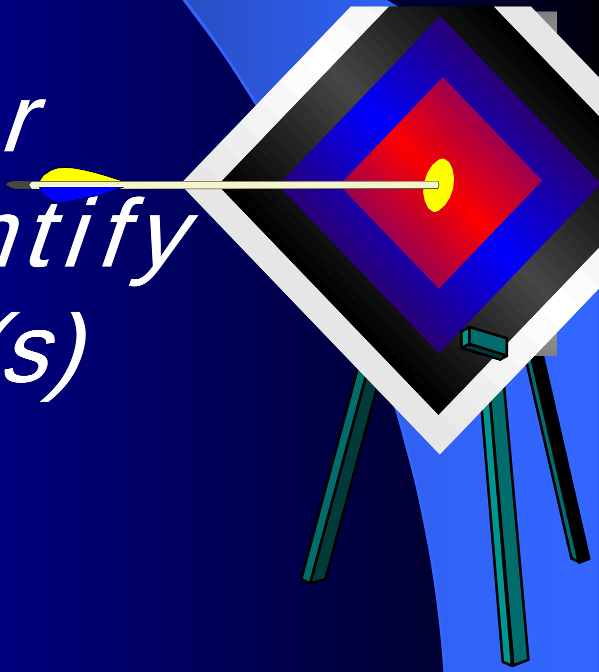
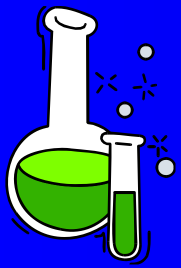
# To Unambiguously Identify Spilled Oils Are Extremely Important and Challenging

- For environmental damage assessment;
- For prediction of the potential long-term fate, behavior, and impact of spilled oils on the environment;
- For selecting appropriate spill response and taking effective clean-up measures;
- Critical for setting disputes related to liability.

This case study illustrates how to use the advanced fingerprinting techniques to characterize complicated spill oil samples mixed with other background HCs and identify the possible spill source(s)





# Background ( I )

- The vessel “Lady Belle” moored on Quebec side of Lake Temiskaming in the spring of 2008.

# Background (I)

- This vessel has some rocky history:
  - sank in the last year, and
  - had been raised and refurbished.
- In the spring of 2008 it was taken to Quebec side apparently up for sale

# Background (II)

- There was a sheen of spilled operating fluid or fuel in the area of the vessel “Lady Belle”.
- It was unknown whether the oil was
  - from leaking of the vessel or
  - from the area of the shoreline which exhibited evidence of possible impact or
  - from other sources.
- Transport Canada Marine Safety inspector collected a soil sample from the shoreline which exhibited evidence of possible impact (a possible source), water samples from the vicinity of the vessel, and water with sorbent from steering flat and sewage of the vessel.
- Samples were submitted to the ESTS oil spill research lab for HC fingerprinting and source identification.

# Five Representative Samples

- Spill Sample #1 (1296):
  - Water (with oil sheen on the surface);
  - Collected from the surrounding area of the Vessel, Port side;
  - Sampling time: May 08, 2008; weight: 83.0 g.
- Spill Sample #2 (1297):
  - Water (with oil sheen on the surface);
  - Collected from the surrounding area of the Vessel, near shore;
  - Sampling time: May 08, 2008; weight: 121 g.
- Sample #3 (1298):
  - Water with sorbent;
  - Collected from steering flat of the Vessel;
  - Sampling time: May 08, 2008; weight: 85.4 g, .

# Five Representative Samples

- Sample #4 (1299):
  - Dirt soil;
  - Collected from from the area of the shoreline which exhibited evidence of possible impact;
  - Sampling time: May 08, 2008; weight: 19.6 g.
- Sample #5 (1230):
  - Water with sorbent;
  - Collected from sewage of the Vessel;
  - Sampling time: May 08, 2008; weight: 59.2 g.

# Sample Preparation (I)

- Prior to use, all glassware were rinsed with DCM 3 times, and proofed to be clean and target-analyte-free;
- Weigh samples
- Sample extraction
- Combine extracts and further dry extracts with anhydrous sodium sulfate
- Concentrate extracts
- Solvent exchange
- Aliquot of extract for TSEM determination
- Silica gel column cleanup and fractionation of extracts

# Sample Preparation (II)

- Soil sample extraction:
  - mixed with anhydrous sodium sulfate
  - Spiked with surrogates
  - Extracted with DCM/C6 (1:1) overnight using Soxhlet apparatus
- Sobent extraction:
  - Removed and separated from water phase
  - Dried overnight in fumehood
  - Spiked with surrogates
  - Extracted with DCM/C6 (1:1) 3 times using ultrasonication
- Water extraction:
  - Spiked with surrogates
  - Extracted with DCM 3 times using L/L extraction

# Column Cleanup and Fractionation

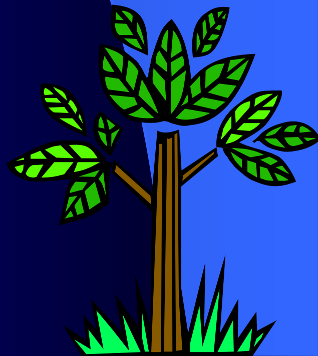
- Aliquots of concentrated extracts were transferred into 3-g silica gel column
- 12 mL of n-C6 and 15 mL of DCM/C6 (1:1) were used to elute the saturated and aromatic hydrocarbons, respectively
- Two fractions (F1 and F2) were concentrated, spiked with IS and adjusted to 1.00 mL for GC-FID and GC-MS analyses
  - F1: for analysis of n-alkanes and biomarker terpanes and steranes
  - F2: for analysis of oil-characteristic alkylated homologous PAHs and other EPA priority PAHs
  - F3 (combined form 100 ul of F1 and F2): for analysis of GC-detectable TPH and UCM
- For QA/QC, the EST reference oil Prudhoe Bay oil (13% weathered) was used as the ref. oil standard, and the deionized water was treated as a normal water sample to monitor method blank.

# *Analytical Approach*

- A tiered multi-criterion approach was used for fingerprinting and identifying the Lake Unknown oil samples:
  - ***Tier1***, determination of hydrocarbon groups in oil residues;
  - ***Tier 2***, product screening and determination of *n*-alkanes and TPH;
  - ***Tier 3***, distribution pattern recognition of target PAHs and biomarker components;
  - ***Tier 4***, determination and comparison of diagnostic ratios of the “source-specific marker” compounds;
  - ***Tier 5***, determination of weathered percentages of the residual oil;
  - *In addition*, the input of pyrogenic PAHs to the spill samples were identified and characterized.

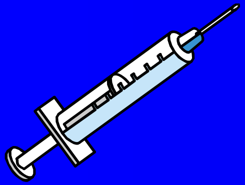
# Target Hydrocarbon Groups

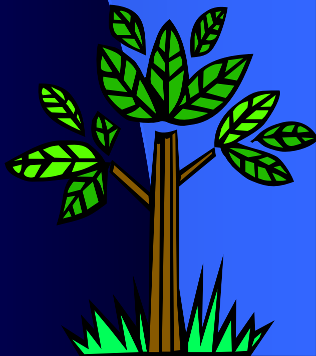
- TSEM: total solvent extractable materials
- GC-TPH (GC detectable - total petroleum hydrocarbon);
- UCM: unresolved complex mixtures, appeared as GC unresolved “humps”;
- Total saturates;
- Total aromatics;
- Total n-alkanes from n-C8 to n-C41



# Instrumentation: GC-FID

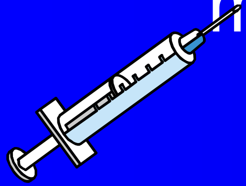
- Agilent 6890 GC-FID: for analyses of *n*-alkane distribution (n-$C_8$ through n-$C_{41}$, pristane and phytane) and TPH
- Columns: the DB-5HT (30 m x 0.32 mm ID, 0.10 μm film thickness) fused silica columns
- Temperature program





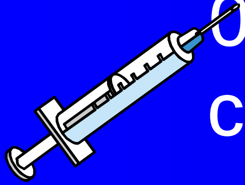
# Determination of TPH

- IS Method
    - RRF = $(A/A_{IS}) \times (C_{IS}/C)$
    - TPH (mg/kg) = $(A_{PHC} \times W_{IS} \times D) / (A_{IS} \times RRF \times W_S)$
- The IS method uses 5-α-androstane (a cyclo-alkane) as the IS for determination of PHC.
- Prior to sample analysis, the instrument is calibrated using a hydrocarbon standard mixture (n-C8 - n-C34).



# Instrumentation: GC-MSD

- Agilent 6890 GC - 5973 MSD: for analyses of target PAH and biomarker compounds, including:
  - 5 alkylated PAH homologous groups
  - other EPA priority PAHs, and
  - biomarker terpanes and steranes.
- G1701 BA MSD ChemStation: for system control and data acquisition.
- Columns: the HP-5MS (30 m x 0.25 mm ID, 0.25 µm film thickness) fused silica columns



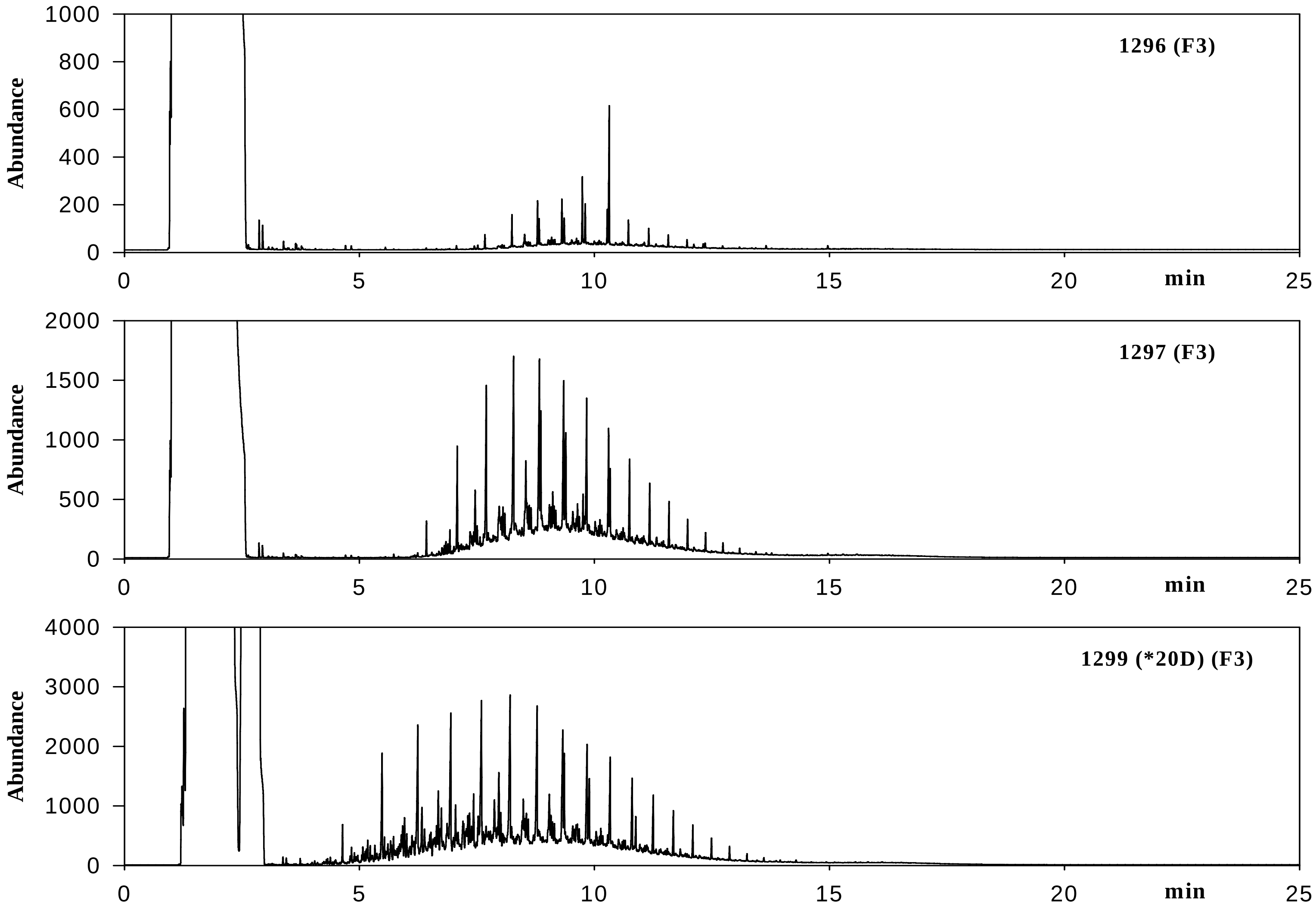


*Fig. 1 GC/FID chromatograms of F1 and F3*

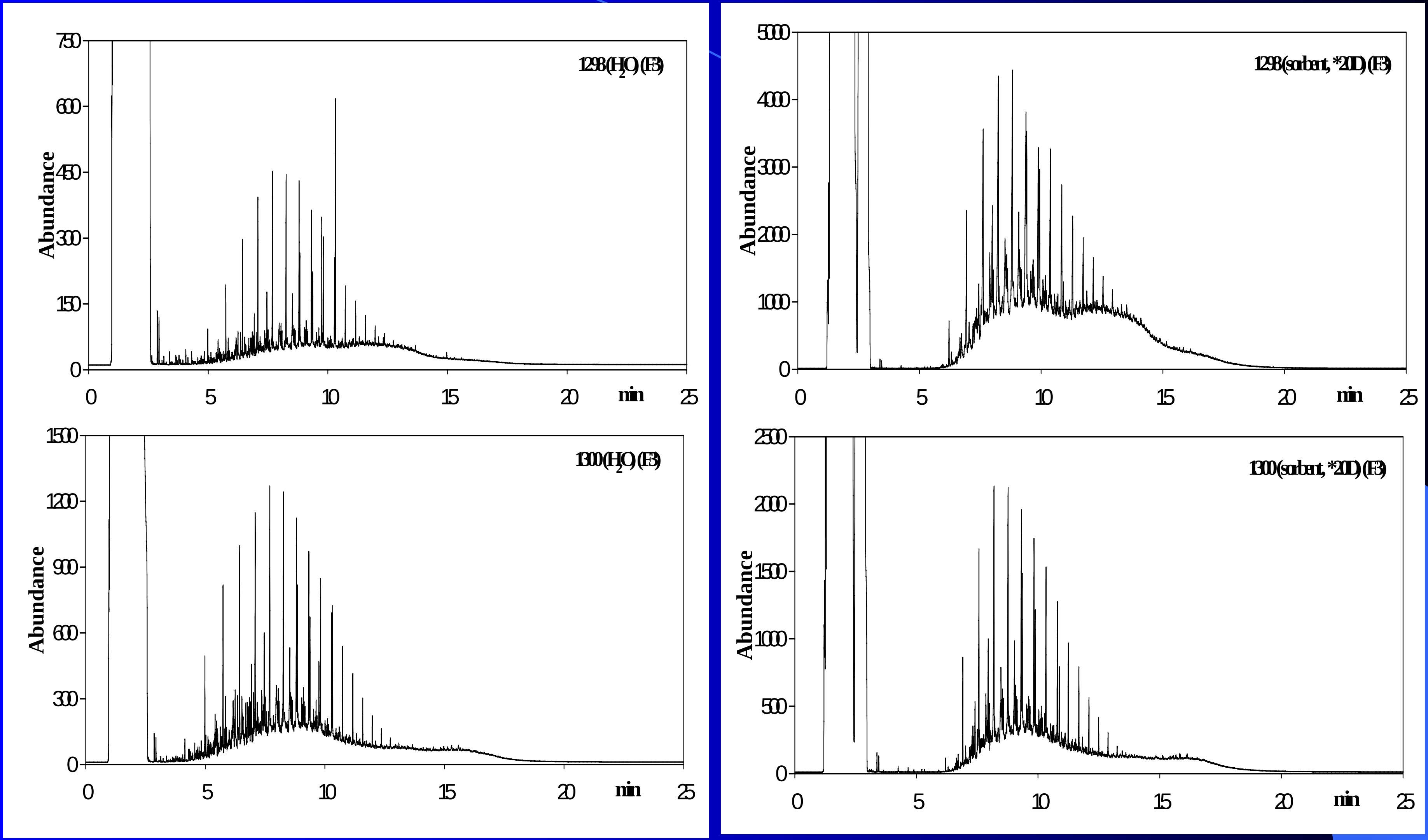
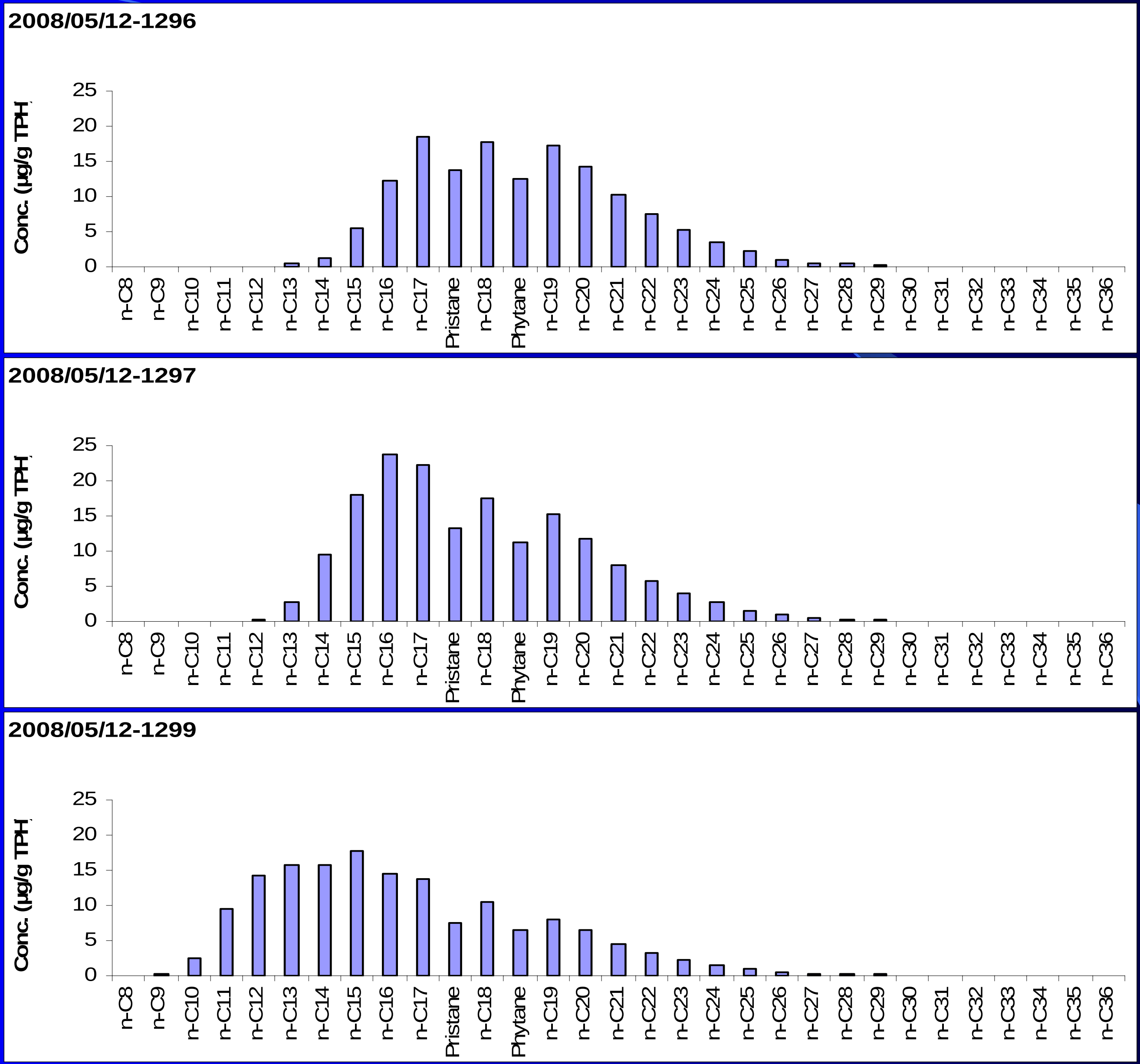


*Fig. 1   GC/FID chromatograms of F3*

# Hydrocarbon Group Analysis Results

| Sample | 1296 | 1297 | 1299 | 1298 (water) | 1300 (water) | 1298 (sorbent) | 1300 (sorbent) |
|---|---|---|---|---|---|---|---|
| TPH (mg) | 0.65 | 5.59 | 328 | 2.27 | 7.19 | 489 | 220 |
| TSH/TPH (%) | 87 | 86 | 91 | 85 | 88 | 94 | 92 |
| Resolved Peaks/ TPH (%) | 29 | 34 | 36 | 24 | 31 | 22 | 27 |
| Total alkanes/TPH (mg/g TPH) | 144 | 170 | 157 | 99 | 115 | 113 | 129 |
| Total PAHs/TPH (ug/g TPH) | 1200 | 4416 | 7061 | 5030 | 6850 | 5040 | 4534 |
| Total biomarkers /TPH (ug/g TPH) | 523 | 414 | 330 | 1171 | 859 | 2647 | 1218 |



2008/05/12-1296

2008/05/12-1297

2008/05/12-1299

*Fig. 3  n-Alkane Distribution (Y axis: mg/g TPH)*

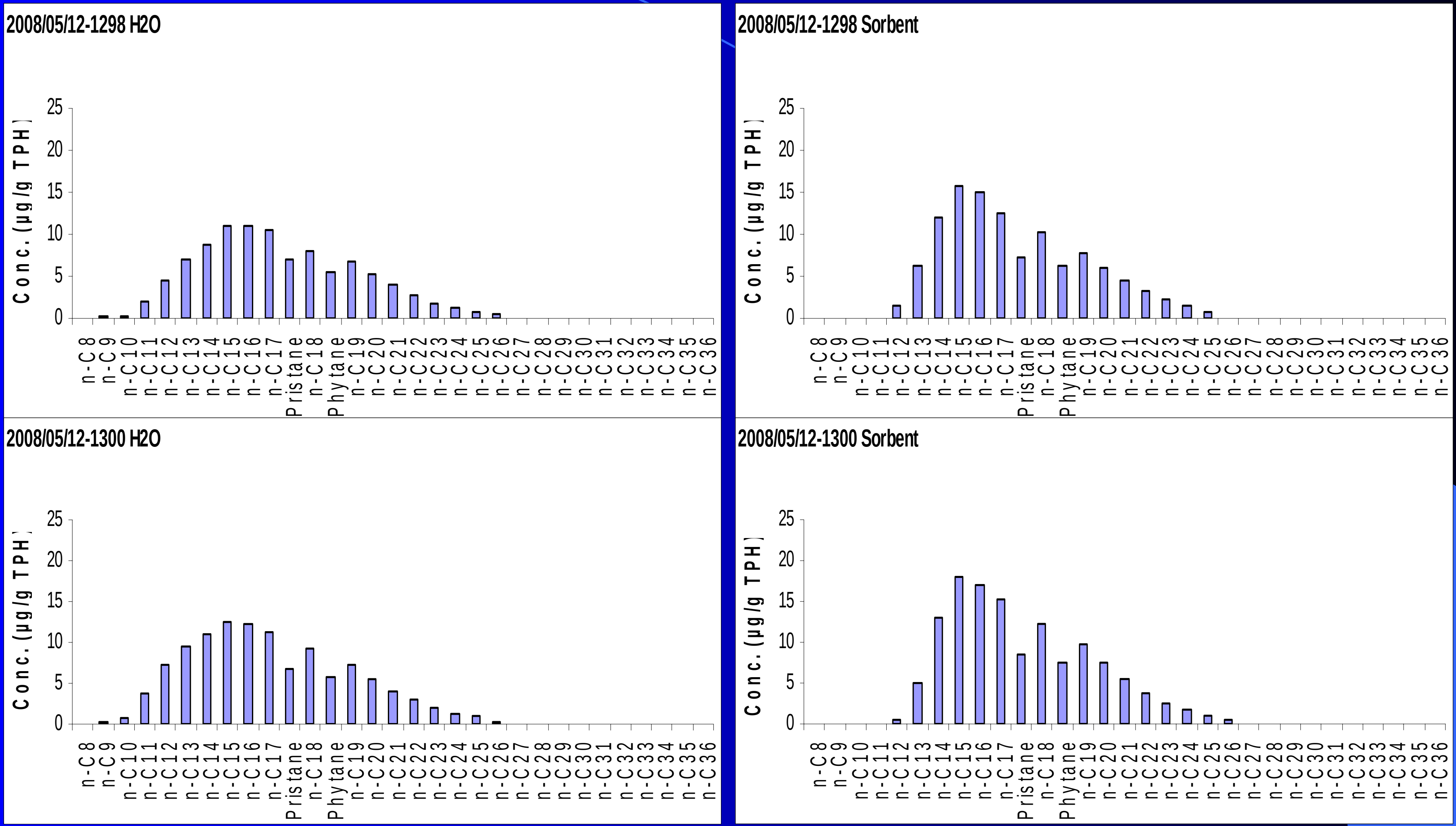
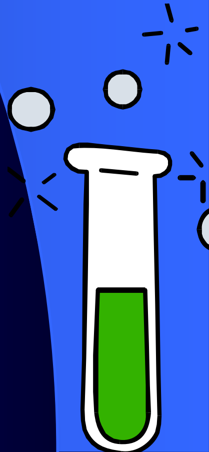
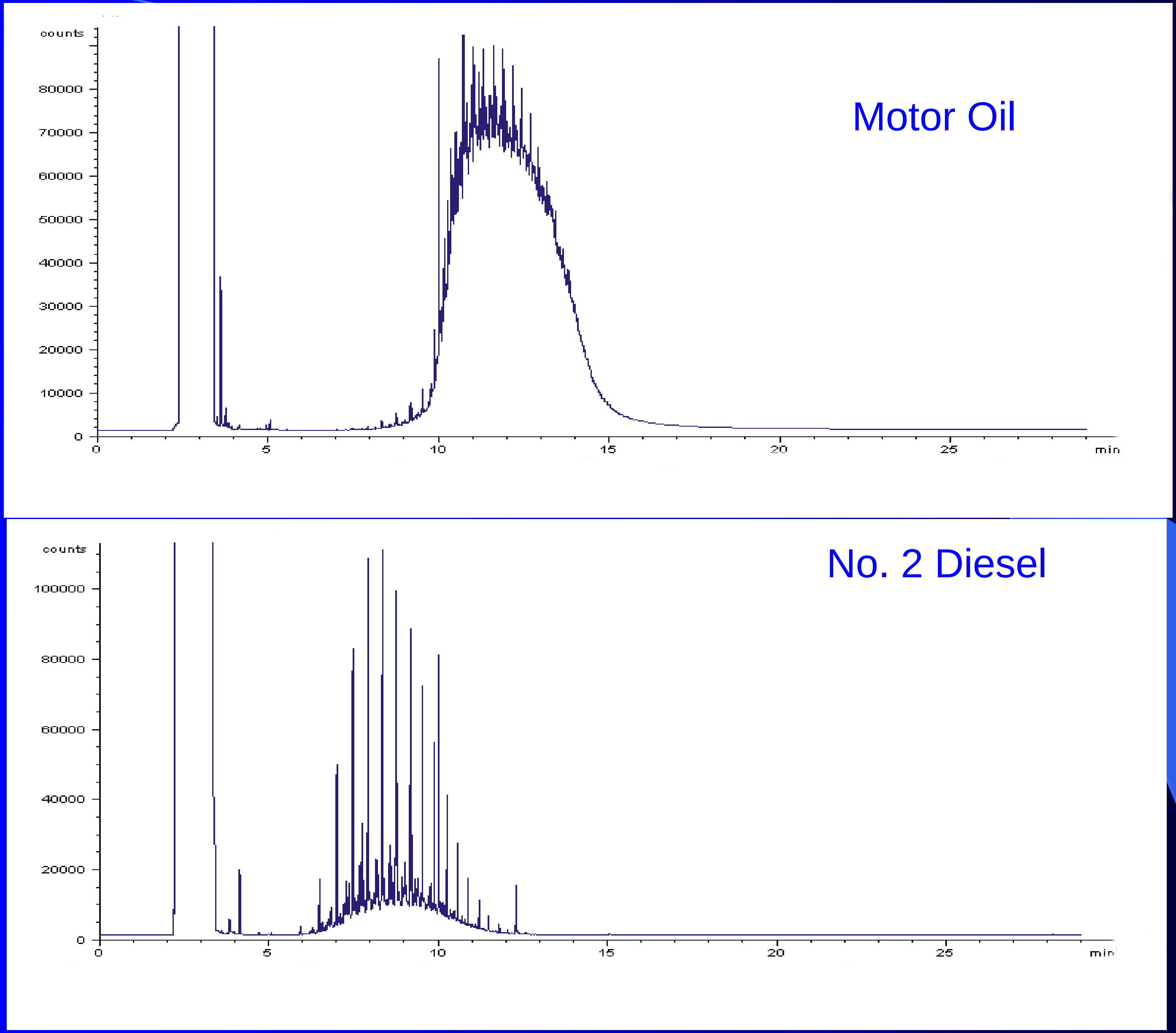


*Fig. 3  n-Alkane Distribution (Y axis: mg/g TPH)*

# Product Type Screening and Determination of HC Groups (I)

- Assessment of chemical composition features and degradation trends of the samples can be illustrated by qualitative and quantitative examination of their GC traces:
  - The major oil components, n-alkanes, are distributed in a carbon range for C8-C28 with the maximum being around C14-C19 range. No obvious n-alkanes greater than C30 were detected.
  - The TPH were determined in the range of 0.6-7.2 mg for water samples (water sample 1296 and 1297; and water phases of samples 1298 and 1300). But the TPH were determined to be as high as 489 and 220 mg for sorbent of samples 1298 and 1300, clearly indicating that most oils in samples 1298 and 1300 were absorbed on sorbents.
  - The ratios of total saturates (TSH) to TPH were determined to be in a range of 85-94% range, much greater than the ratios of total aromatics (TAH) to TPH, indicating the oil hydrocarbons were dominated by the saturated hydrocarbons.





# *GC Chromatograms of Pure Motor Oil and Diesel*

# Product Type Screening and Determination of HC Groups (II)

- Water samples 1296 & 1297 show very similar GC chromatographic features (similar carbon range, hydrocarbon distribution profiles, and one Gaussian-shape UCM) with that of soil sample 1299.
- In comparison, samples 1298-water & 1298-sorbent and samples 1300-water & 1300-sorbent demonstrated significantly different chromatographic profiles (two significant "humps") from the water samples 1296, 1297, and soil sample 1299.
- The chromatographic features that
  - the oil in water samples 1296 and 1297, and in soil sample 1299 are ***heavier diesel type fuel***;
  - the oils in samples 1298 and 1300 are very likely ***mixture of heavier diesel fuel and lube oil***.

# Product Type Screening and Determination of HC Groups (III)

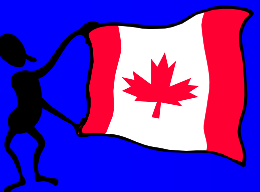
- For comparison on a same foot, the concentrations of total n-alkanes are expressed as concentrations of total n-alkanes relative to TPH, that is in mg/g TPH.
- The total n-alkanes for 1296, 1297 and 1299: in a range of 144-170 mg/g TPH, which are typical n-alkane values in diesel type fuels.
- The total n-alkanes for 1298 and 1300: 99 and 113 mg/g TPH for the water phases, and 114 and 129 mg/g TPH for the sorbent phases. These a-alkanes were mostly from the heavier diesel portion of the samples 1298 and 1300. They are significantly lower than the concentrations in 1296, 1297 and 1299.

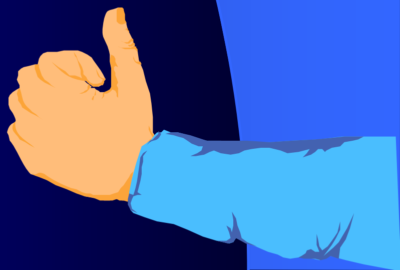
# Product Type Screening and Determination of HC Groups (IV)

- The hydrocarbons in 1296 and 1297 were more weathered than samples 1298, 1299 and 1300, indicated by more loss of lower molecular weight n-alkanes (C9-C13).
- In general, two water samples (1296 and 1297) and the soil samples (1299) show very similar GC chromatographic profiles, n-alkane distribution patterns, and smaller UCM, suggesting the oil in the water samples and the soil sample may come from the same source.

# Questions which must be answered:

- *Do these three oils really come from the same source?*
- *Is there any input of other hydrocarbons into samples?*
- In order to unambiguously answer these questions, the multi-criterion approach must be adopted, analyses of more than one suite of analytes must be performed.





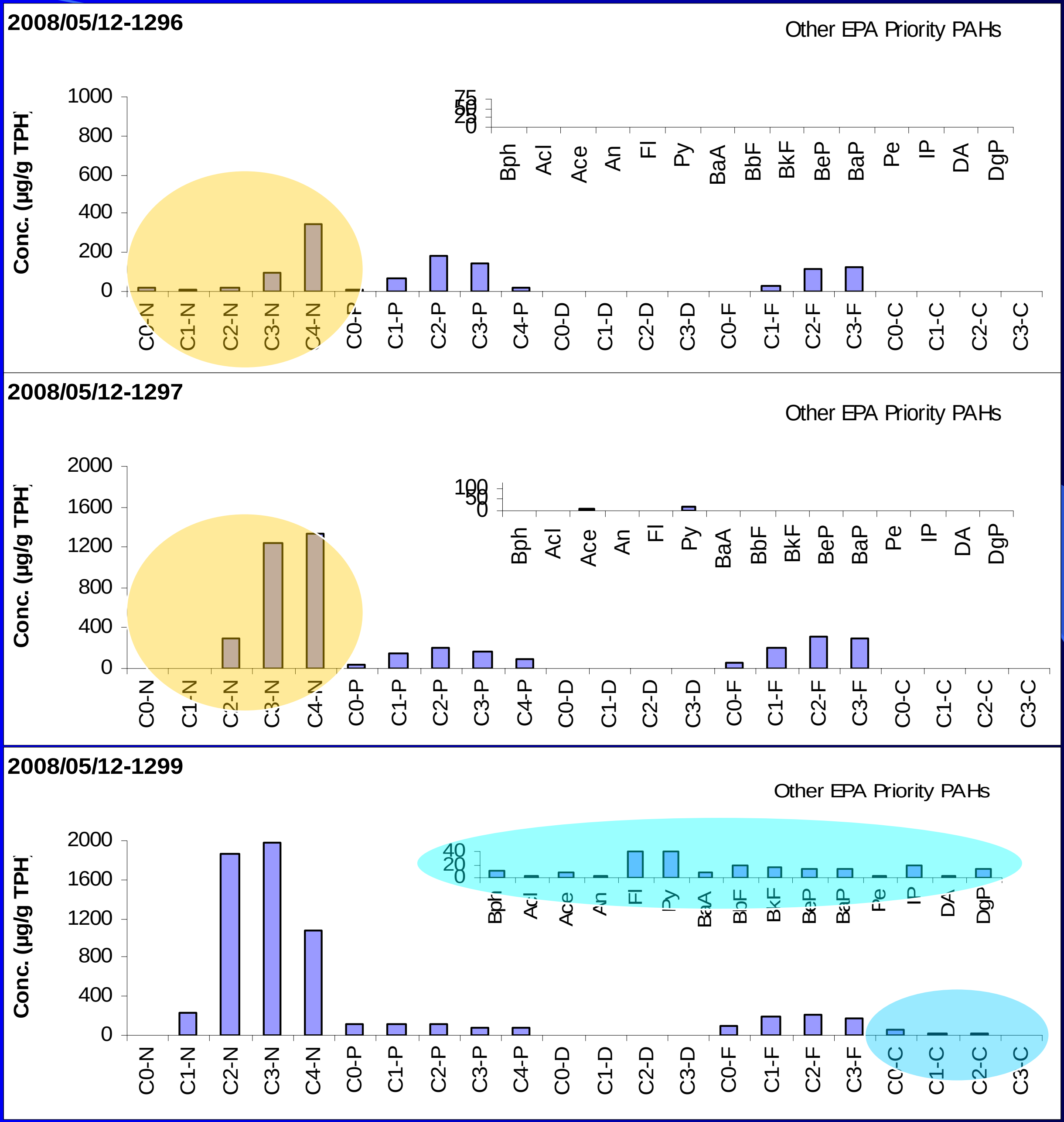


Fig. 4 Distribution of Target PAHs

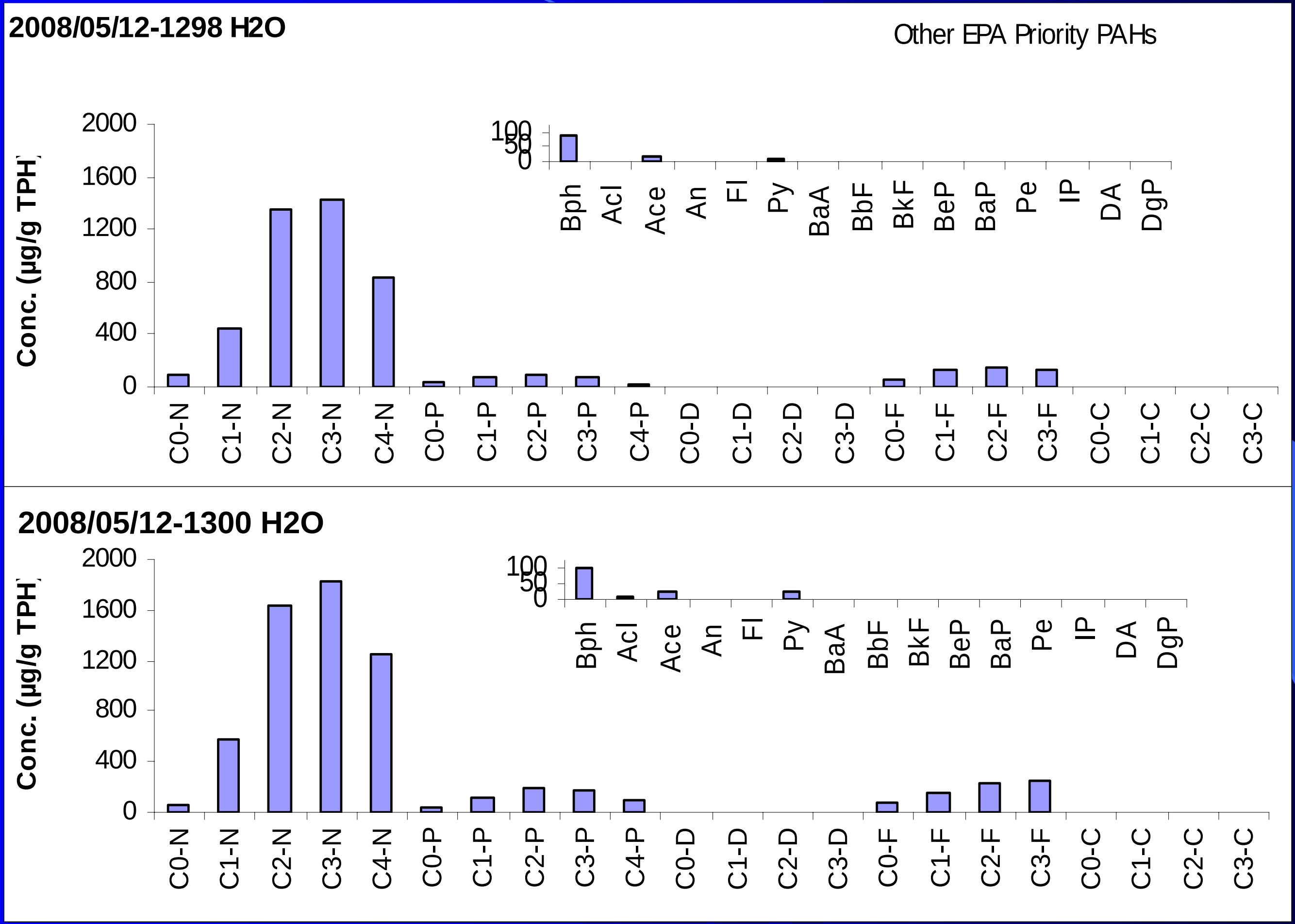


*Fig. 4 Distribution of Target PAHs*

# PAH Analysis Results

| **Alkylated PAHs** | **1296 (ug)** | **1297 (ug)** | **1299 (ug)** | **1298-water (ug)** | **1300-water (ug)** |
|---|---|---|---|---|---|
| Naphs (C0-C4) | 0.32 | 16.0 | 1698 | 9.42 | 38.4 |
| Phens (C0-C4) | 0.28 | 3.64 | 170 | 0.68 | 4.47 |
| Dibens (C0-C3) | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Fluos (C0-C3) | 0.18 | 4.86 | 211 | 1.03 | 5.23 |
| Chrys (C0-C3) | 0.00 | 0.00 | 29.2 | 0.00 | 0.00 |
| ***Sum*** | ***0.78*** | 24.5 | ***2108*** | ***11.1*** | ***48.1*** |
| ***Other EPA PAHs*** | ***0.00*** | ***0.17*** | ***209*** | ***0.30*** | ***1.13*** |
| ***Total PAHs (ug/g TPH)*** | ***1200*** | ***4416*** | ***7061*** | ***5030*** | ***6850*** |

# Distribution of Target Alkylated PAHs (I)

- Dominance of alkylated naphthalenes;
- No detection of the high MW alkylated chrysenes in all samples (except for the soil sample 1299);
- This is typical features in the chemical composition of alkylated PAHs for diesel type fuels.
- The relative distribution patterns of alkylated PAHs are very much the same for spilled samples 1296 and 1297;
- Lube oils only contain trace amount of alkylated PAHs, while PAH concentrations are high in diesels.
- Therefore, it can be expected that the portion of lube oil in a mixture of diesel/lube oil would only have minimum effects on the PAH distribution pattern and profile.

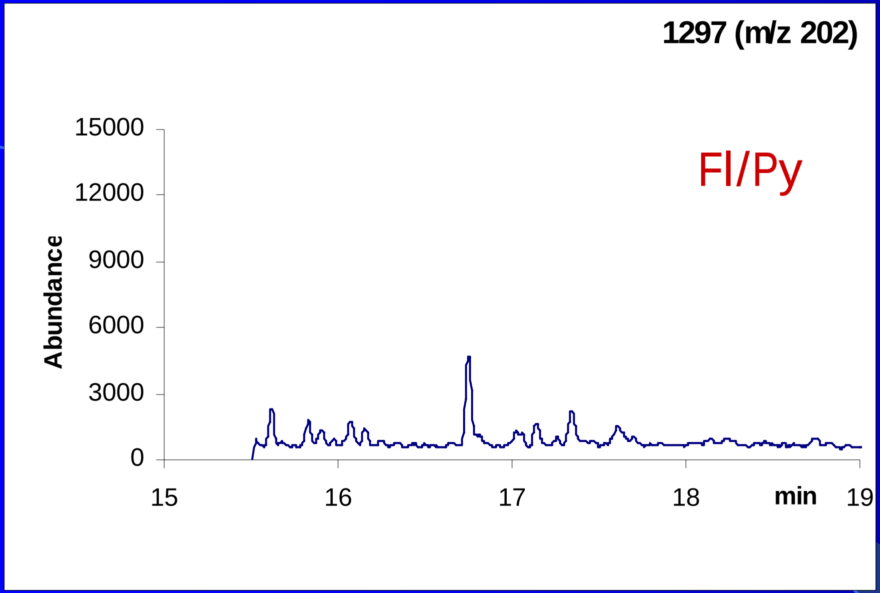
# Distribution of Target Alkylated PAHs (II)

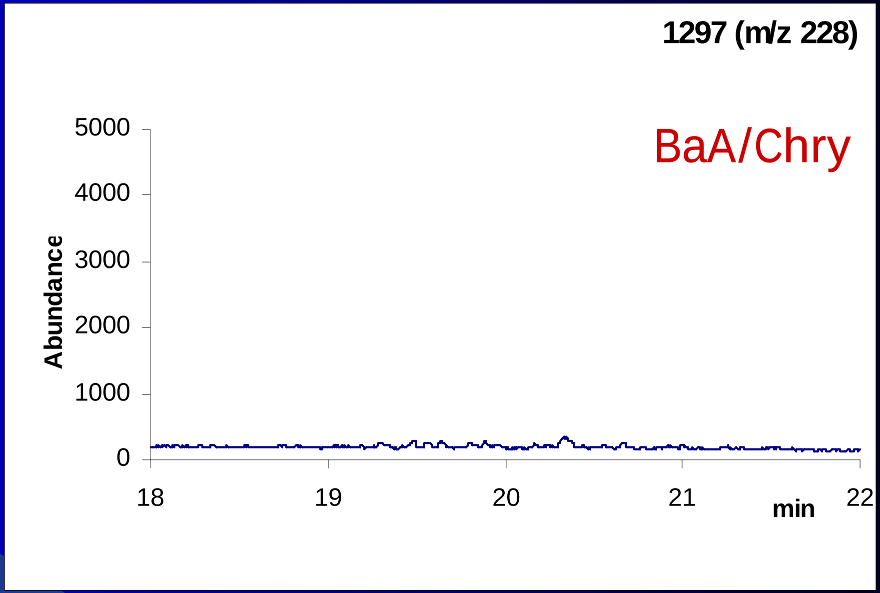
- No sulfur-containing alkylated dibenzothiophenes were detected in all samples, indicating the spilled fuel was a heavier diesel fuel of very low-sulfur content;
- The loss of lower MW alkylated naphthalenes was obvious for samples 1296 and 1297, resulting in development of the relative distribution of C0-N < C1-N < C2-N < C3-N < C4-N.
- This indicates that PAHs in samples 1296 and 1297 had been significantly weathered after the oil spill accident.
- For all samples except to the soil sample 1299, only those 2-4 ring other EPA priority PAHs were detected in relatively low concentrations, and no high MW 5- and 6-ring EPA priority PAHs were detected;
- This is another chemical composition feature in PAHs for most diesel type fuels.

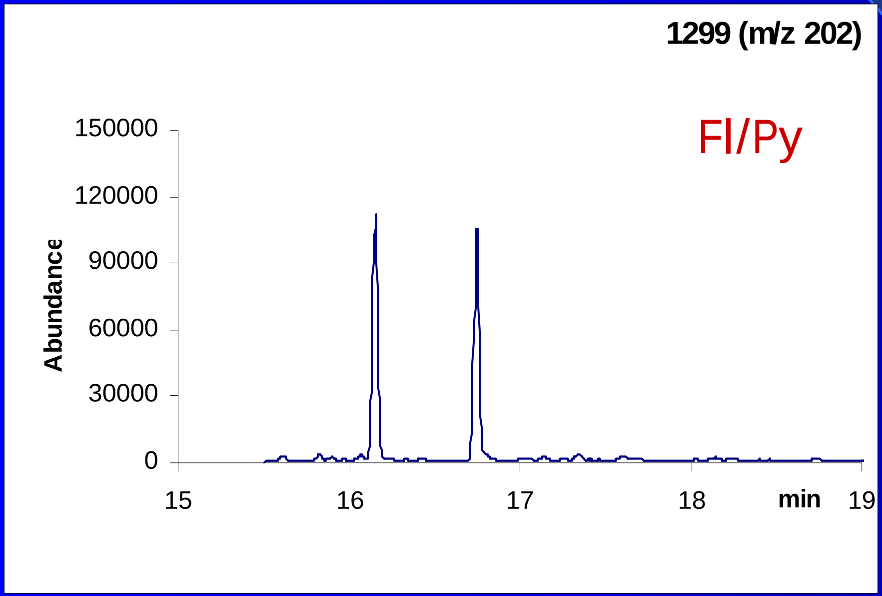
# Diagnostic Ratios of Target PAHs

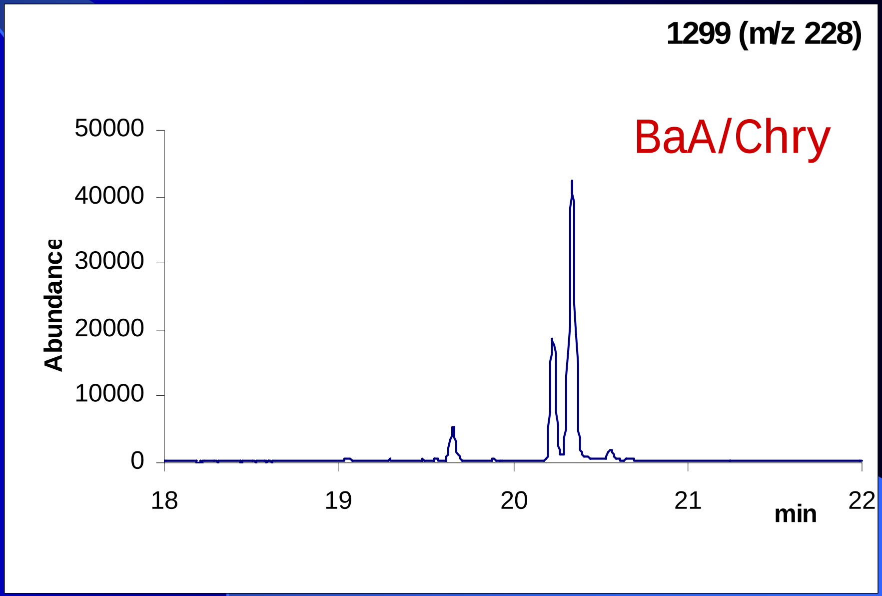
| **Diagnostic Ratio** | **1296 (ug)** | **1297 (ug)** | **1299 (ug)** | **1298-water (ug)** | **1300-water (ug)** |
|---|---|---|---|---|---|
| 3-m-N:1-m-N (m/z 142) | NA | NA | 0.79 | 1.24 | 1.45 |
| (3+2-m-P)/(4/9+1-m-P) (m/z 192) | 1.40 | 1.40 | 1.49 | 1.36 | 1.27 |
| BaA/Chrysene (m/z 228) | NA | NA | 0.45 | NA | NA |
| Fl/Py (m/z 202) | NA | NA | 1.06 | NA | NA |
| IP/BgP (m/z 276) | NA | NA | 1.42 | NA | NA |
| Pyrogenic Index | NA | 0.01 | **0.10** | 0.03 | 0.02 |

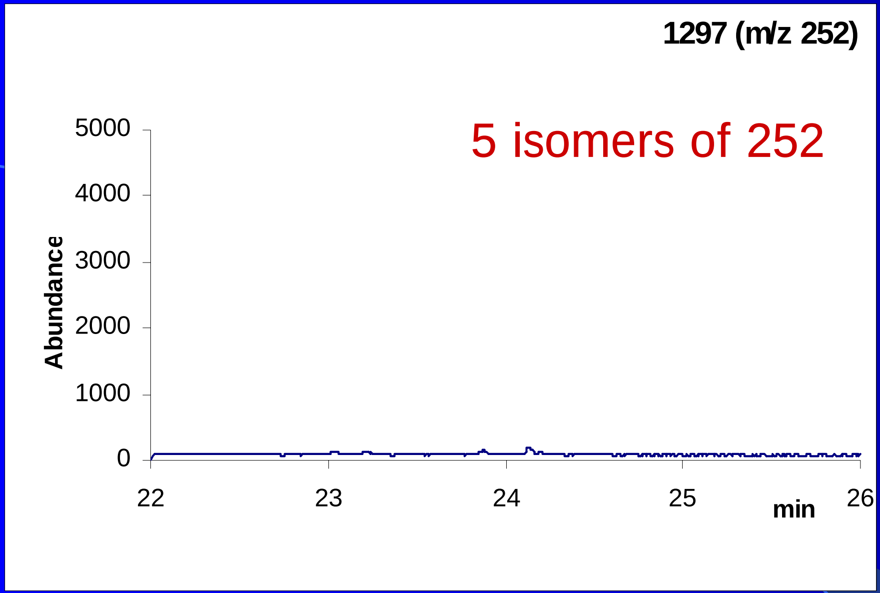
# Comparison of target PAHs in 1297 and 1299





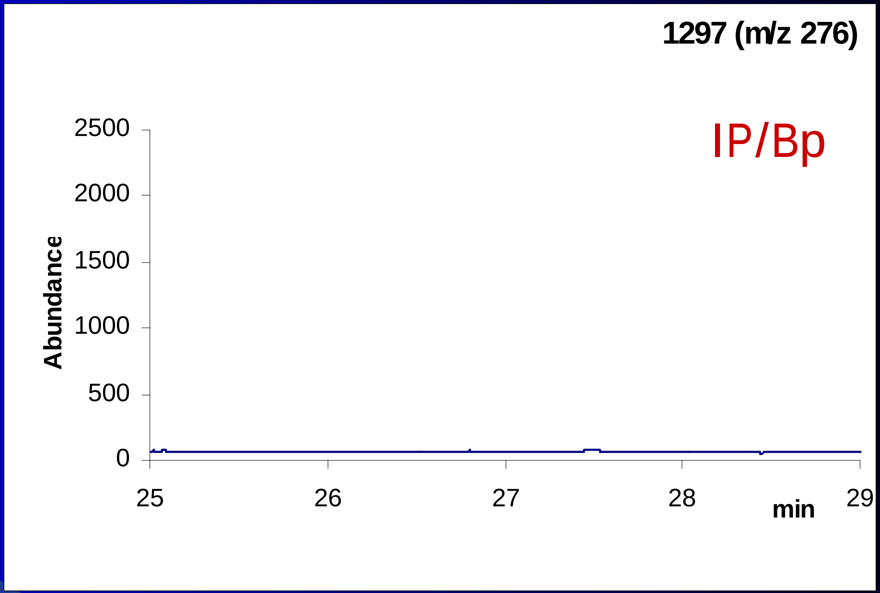






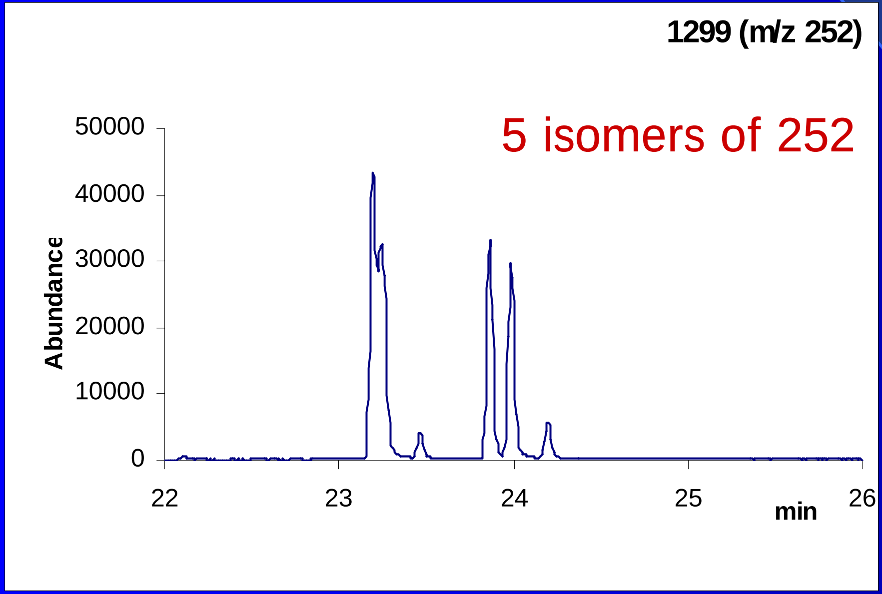
1297 (m/z 252)

5 isomers of 252



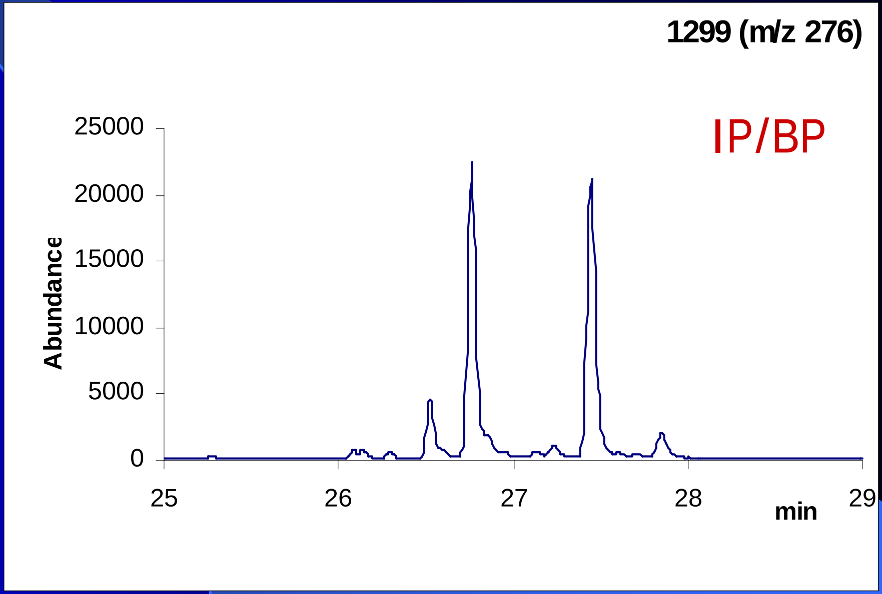
1297 (m/z 276)

IP/Bp



1299 (m/z 252)

5 isomers of 252



1299 (m/z 276)

IP/BP

# Input of Pyrogenic PAHs

- For 1299, parent PAH phenanthrene and chrysene are the most abundant among their alkylated homologous series;
- C0-C > C1-C > C2-C > C3-C distribution pattern;
- In comparison with crude oils and refined products, 1299 shows extremely high ratios of BaA/chrysene (0.45), BeP/BaP (0.94), and IP/BP (1.42);
- The "Pyrogenic Index" were determined to be as high as 0.10, significantly higher than the corresponding values for crude oils and refined products (<0.05);
- All these facts clearly indicate the formation and input of pyrogenic PAHs.

# Pyrogenic Index

- “Pyrogenic Index (PI)” is defined as

$$PI = \Sigma\ [\text{other (3-6) ring PAHs}]\ /\ \Sigma\ [\text{5 alkylated PAHs}]$$

  - Light oils and lighter oil products: < 0.01;
  - Heavy oils and fuels: <0.03;
  - Bunker C and tarballs: < 0.05;
  - As for weathered and biodegraded oils, the ratios are slightly higher than that of their corresponding original oils;
  - Combustion soot samples: greater than 0.05

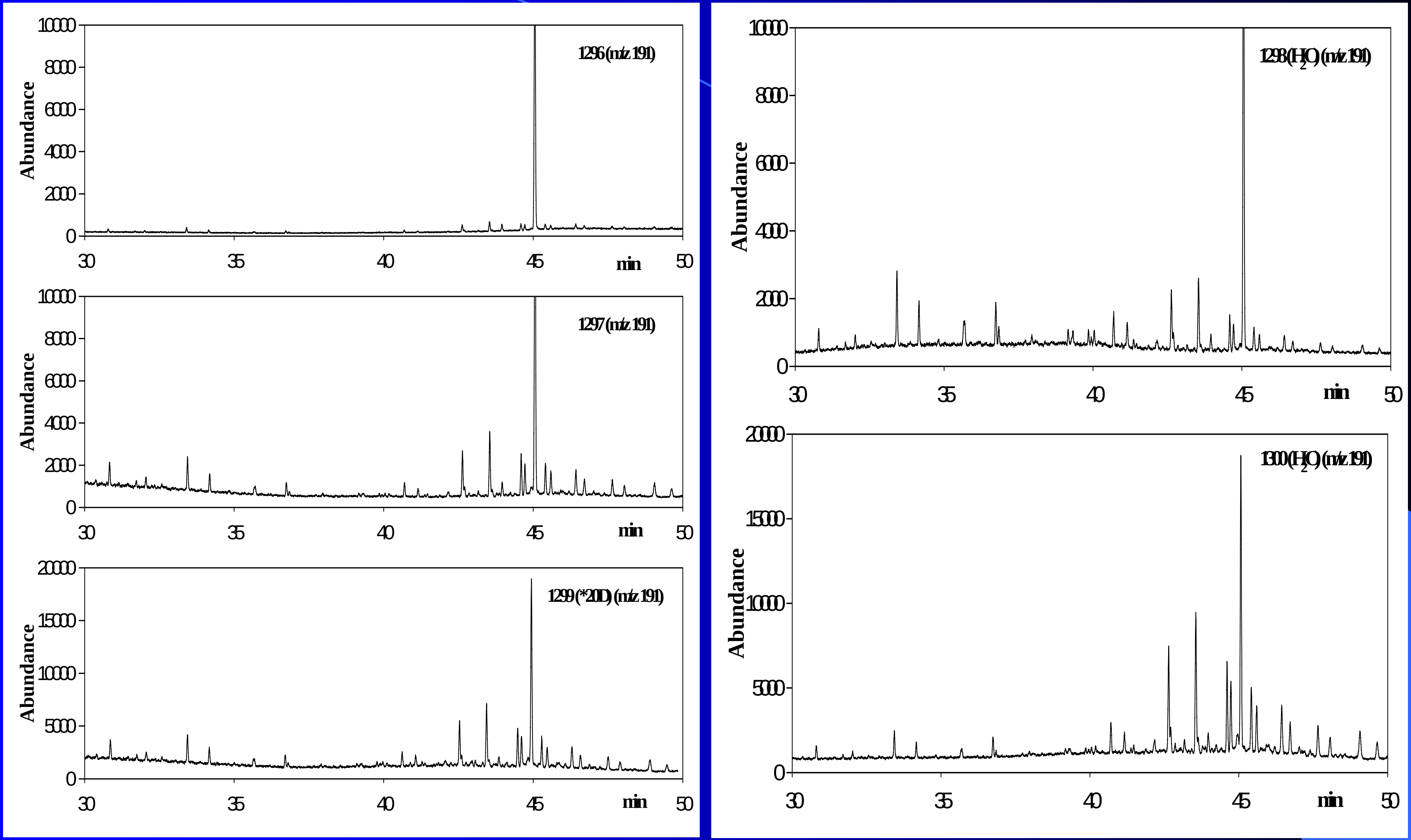


*Fig. 5 Comparison of Biomarker Distribution (m/z 191)*

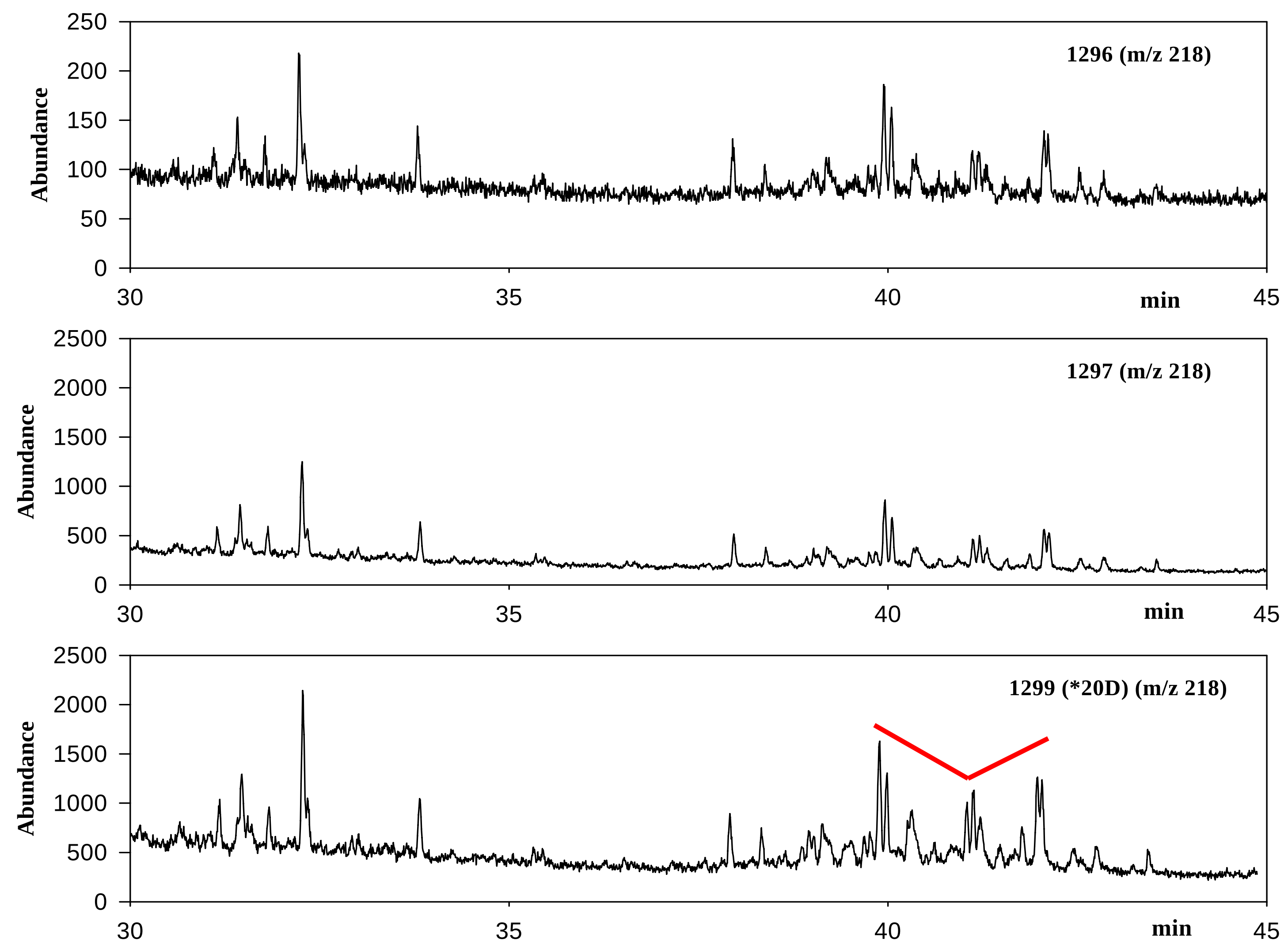
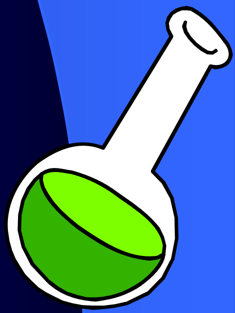


*Fig. 7 Comparison of Biomarker Distribution (m/z 218)*

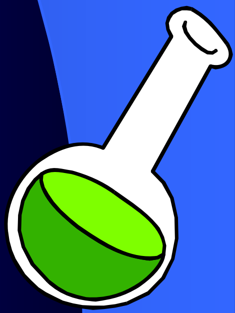
# Analysis of Biomarker Compounds

- The biomarker concentrations of samples 1296, 1297 and 1299: 523, 410 and 336 µg/g TPH respectively, which are in a very much close concentration level.
- The total concentrations of target biomarkers in samples 1296, 1297, and 1299 are much lower than in samples 1298 and 1300 (860-2650 µg/g TPH ).
- 1296 and 1297 and the soil sample 1299 demonstrate nearly identical distribution patterns of terpanes (m/z 191) and steranes (m/z 218):
  - A wide range of terpanes in relatively lower abundances were present in these samples from C19 to C35;
  - As for steranes, the dominance of C27, C28 and C29 20S/20R steranes in a “V” shape distribution with the C27 and C29 being more abundant than C28 sterane series is obvious



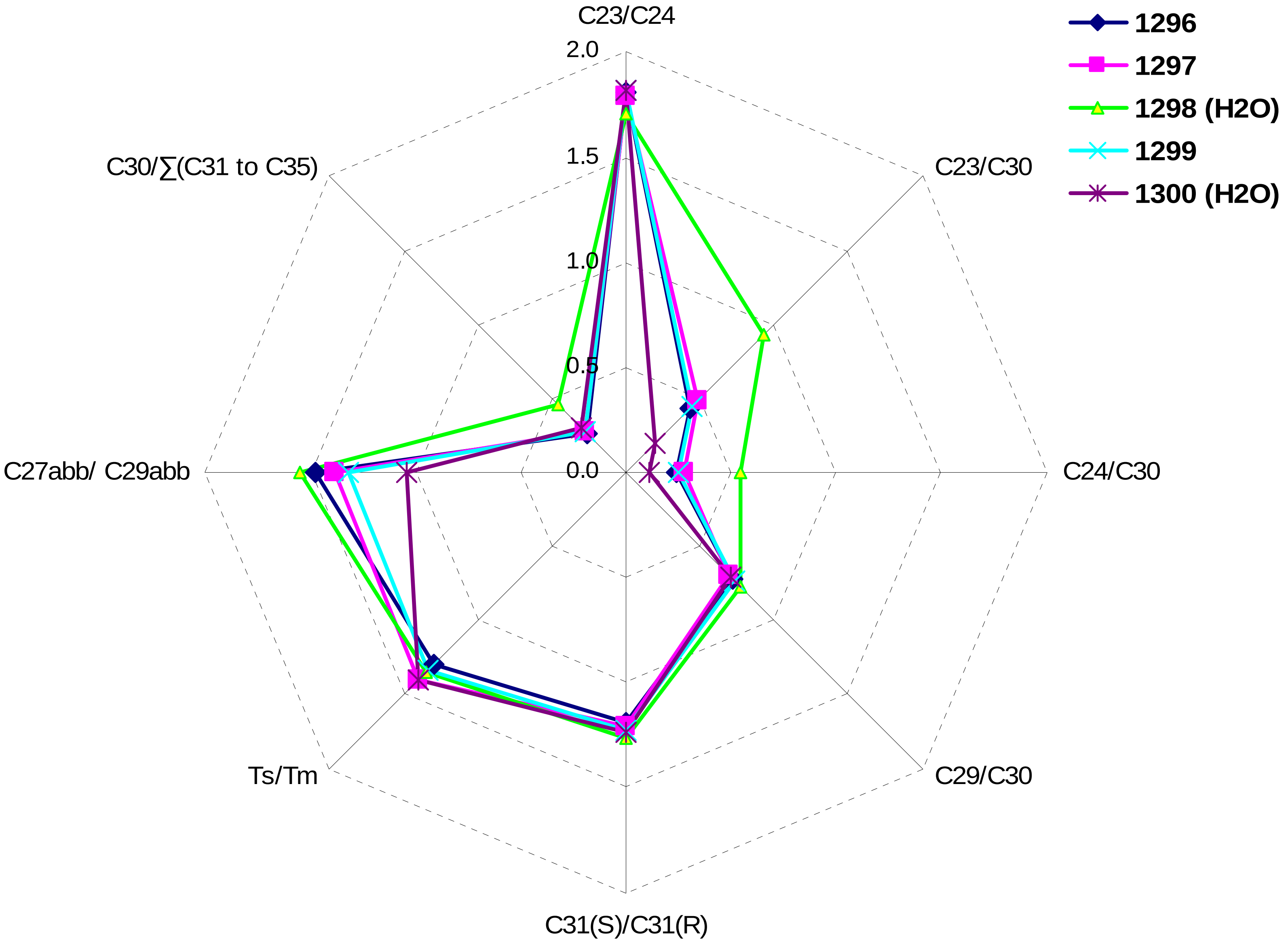
# Analysis of Biomarker Compounds

- The steering flat sample 1298 and the sewage sample 1300 (both water/sorbent phase) show distribution patters of biomakers different from other 3 samples.
- For sample 1298:
  - C23 and C24 terpanes, C29 and C30 hopanes, and C31 to C35 homohopanes are quite abundant;
  - C27 αββ steranes are in much high abundances than C28 and C29 sterane series;
  - This mixed biomarker fingerprints were from both the heavier diesel fuel and the lube oil portions of the sample 1298.
- For sample 1300:
  - the dominance of C29 and C30 hopanes and C31 to C35 homohopanes over smaller terpanes is pronounced;
  - C23 and 24 terpanes are significantly less abundant, and
  - C27 and C29 αββ steranes are much abundant than C28 sterane series.



# Diagnostic Ratios of Biomarkers

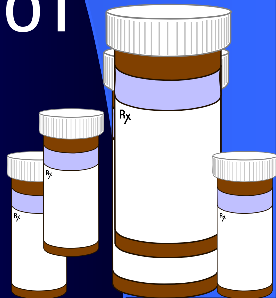
| **Diagnostic ratios** | **1296** | **1297** | **1299** | **1298-water** | **1300-water** |
|---|---|---|---|---|---|
| C23/C24 | 1.81 | 1.79 | 1.82 | 1.71 | 1.82 |
| C23/C30 | 0.43 | 0.49 | 0.45 | 0.92 | 0.19 |
| C24/C30 | 0.24 | 0.27 | 0.25 | 0.54 | 0.11 |
| C29/C30 | 0.72 | 0.69 | 0.73 | 0.77 | 0.70 |
| C31(S)/C31(R) | 1.18 | 1.21 | 1.22 | 1.27 | 1.24 |
| ***C30/(C31 to C35)*** | 0.26 | 0.27 | 0.28 | 0.45 | 0.30 |
| ***Ts/Tm*** | 1.29 | 1.39 | 1.33 | 1.35 | 1.40 |
| ***C27/C29 αββ-steranes*** | 1.38 | 1.39 | 1.32 | 1.55 | 1.04 |
| ***Total biomarkers/TPH (ug/g TPH)*** | ***523*** | ***412*** | ***328*** | ***1196*** | ***855*** |



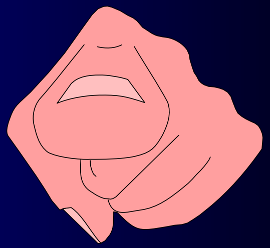
# Radar chart of biomarker diagnostic ratios

# Diagnostic Ratios of Biomarkers

- The diagnostic ratios of target biomarkers are very much the same for samples 1296, 1297 and 1299;
- Sample 1298 (both water and sorbent phase) shows much higher ratios of C23/C30 and C24/C30, and C30/(C31+C32+C33+C34+C35);
- While sample 1300 (both water and sorbent phase) shows much lower ratios of C23/C30 and C24/C30.

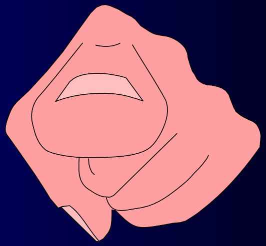


# *Conclusions ( I )*



- Water samples 1296, 1297 and the soil sample 1299 were contaminated by a heavier diesel type fuel.
- The oil hydrocarbon fingerprints are matching each other for these three samples and those minor differences in their fingerprints can be explained by weathering effects and input of pyrogenic PAH.
- The oil hydrocarbons in these 3 samples were most probably from the same source.
- The oil in the steering flat sample 1298 is a mixture of a heavier diesel fuel and a lube oil; while the oil in the sewage sample 1300 is largely from a heavier diesel fuel with smaller contribution of a lube oil.

# Conclusions ( I I )



- The HCs in samples 1296 and 1297 were more weathered than samples 1298, 1299 and 1300, evidenced by more loss of lower molecular weight n-alkanes (C9-C13) and lower alkylated naphthalene series, and by development of the relative distribution of C0-N < C1-N < C2-N < C3-N < C4-N.
- In addition of petrogenic PAHs, the soil sample 1299 also contains small portion of pyrogenic PAHs. These pyrogenic PAHs were most probably generated from some pyrogenic processes.

# Thank you