

## Vancouver set to lose more gas stations amid boom in real estate

FRANCES BULA >  
VANCOUVER  
SPECIAL TO THE GLOBE AND MAIL  
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Canada's spent \$100,000 for the site, but the project ended up costing \$2.9-billion on-site cleanup and other costs were added in. (John Woods for The Globe and Mail)

# Gasoline Forensics: Determining Sources in Multi-Media

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Property is becoming more valuable. There is ample evidence of empty lots both in urban and rural settings which formerly belonged to service or bulk stations. The reason the lots are empty is because the cost of reclaiming these sites exceeds the commercial value of the property. That scenario is changing as a result of federal, provincial and industry financial aid to support redevelopment.

PROPERTY REPORT

## Life after Corner Gas: The challenges of developing old service stations

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PUBLISHED OCTOBER 3, 2016

Calgary – “we looked at 143 intersections and counted 24 vacant lots – all former gas stations,” she says adding the number is similar today, if not higher

“We do a census of sites across Canada, and the number of stations has gone from more than 20,000 in 1989 to about 12,000,” Mr. Parent says.

IN ADDITION: What about bulk stations – where oil companies are trying to get out of a lease. They cannot unless they determine sources of contamination and develop a mitigation plan. Also determine source of contamination on a development in vicinity of a bulk station and service station.

As value of land increases – reclamation in support of redevelopment is becoming an option – e.g. Vancouver and Edmonton (Whyte avenue).

There is still evidence of former gas station sites, however, the number is shrinking due to redevelopment. Bulk stations are a problem for industry, some of which want to get out of a lease but cannot until sources of hydrocarbons are determined and cleanup initiated. We have sites where multiple bulk stations exist along side other industries which used large amounts of fuel. Imperative to determine sources of the hydrocarbons. This is where forensic science can be of assistance.

## The Problem

- Redevelopment of former service station or bulk station sites is not uncommon but can result in challenges for the developer.
- The discovery of hydrocarbon contamination on the proposed development site may require further investigation resulting in the collection of LNAPL, soil and water samples for testing.
- Aerial photographs may reveal several potential historical sources of hydrocarbons.
- Even though development is observed on aerial photographs this may have been performed prior to regulations demanding evaluation and mitigation, i.e. there truly is more than one source.
- Depending upon the results, off-site sample collection may be warranted.
- It is important to determine sources of hydrocarbons. The information derived may be critical in obtaining building permits and receiving incentives (municipal and provincial) for cleanup and redevelopment.
- Financial support from associated oil and gas companies may be garnered if convincing forensic data reveals their product(s) are implicated.

Aerial photographs can provide surprising information including potential unsuspected sources of hydrocarbons from former service stations which have been masked by development. Forensic analyses may reveal several sources of hydrocarbons not just those associated with a particular service station operator.

**Table A-9. Subsoil Remediation Guideline Values for Commercial Land Use - All Exposure Pathways (BTEX and PHC Only)**

This table must **not** be used for Tier 1 assessment and remediation, unless directed by Section 2.4.3 or 5.1.2. Tier 1 soil guidelines are found in Tables 1, 3 and 4. This table is provided to assist Tier 2 guideline development, using the procedures outlined in the companion Tier 2 document (ESRD 200 as amended 7).

Receptor	Overall Guideline		Human						Ecological					Other		
Pathway			Direct Soil Contact	Vapour Inhalation		Protection of Domestic Use Aquifer		Off-Site Migration	Direct Soil Contact*		Nutrient/Energy Cycling Check	Protection of Freshwater Aquatic Life	Off-Site Migration	Management Limit		
Soil Type	Fine	Coarse	-	Fine	Coarse	Fine	Coarse	-	Fine	Coarse	-	Fine	Coarse	-	Fine	Coarse
Building Type			-	Slab	Slab	-	-	-	-	-	-	-	-	-	-	-
Unit	(mg/kg)	(mg/kg)	(mg/kg)	mg/kg	mg/kg	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Benzene	0.046	0.078	120	11	1.2	0.046	0.078	1,100	620	360	-	7.9	0.17	890	-	-
Toluene	0.52	0.12	980	14,000	1,600	0.52	0.95	9,200	660	500	-	63,000	0.12	2,100	-	-
Ethylbenzene	0.073	0.14	2,500	6,700	760	0.073	0.14	24,000	860	600	-	NGR	540	1,600	-	-
Xylenes	0.99	1.9	720	1,800	210	0.99	1.9	6,900	460	700	-	NGR	41	930	-	-
F1	640	440	19,000	4,700	440	1,100	2,200	30,000	640	640	-	30,000	1300	3,000	800	700
F2	520	520	10,000	24,000	2,400	1,500	2,900	30,000	520	520	-	30,000	520	2,100	1,000	1,000
F3	4,300	3,400	23,000	-	-	-	-	30,000	5,000	3,400	-	-	-	4,300	5,000	3,500
F4	10,000	6,600	30,000	-	-	-	-	30,000	13,200	6,600	-	-	-	30,000	10,000	10,000

Notes:  
 a. Exclusion of the ecological direct soil contact pathway for F1, F2, F3, and F4 is permitted below 3 metres  
 na = exposure pathway not applicable to subsoil  
 NGR - no guideline required, calculated value >1,000,000 mg/kg

Alberta Tier 2 guidelines reveal hydrocarbon concentrations of PHS F1 ranging from 440 – 640 mg/kg and PHC F2 guidelines of 520 mg/kg depending upon the soil type (fine or coarse). These are the trigger values for reclamation.

Table 2. Alberta Tier 1 Groundwater Remediation Guidelines

Soil Type Land Use	Fine				Coarse				Notes
	Natural Area	Agricultural	Residential/ Parkland	Commercial/ Industrial	Natural Area	Agricultural	Residential/ Parkland	Commercial/ Industrial	
Unit	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	
Mercury (total)	0.00005	0.00005	0.00005	0.00005	0.00005	0.00005	0.00005	0.00005	
Nickel	see note 1	see note 2	see note 1	see note 1	see note 1	see note 2	see note 1	see note 1	1,2
Selenium	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	
Silver	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	
Uranium	0.015	0.01	0.015	0.015	0.015	0.01	0.015	0.015	
Zinc	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	
<b>Hydrocarbons</b>									
Benzene	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	
Toluene	0.024	0.024	0.024	0.024	0.021	0.021	0.021	0.021	
Ethylbenzene	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	
Xylenes	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	
Styrene	0.072	0.072	0.072	0.072	0.072	0.072	0.072	0.072	
F1	2.2	2.2	2.2	2.2	2.2	0.81	0.81	2.2	
F2	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	
Acenaphthene	0.0060	0.0060	0.0060	0.0060	0.0058	0.0058	0.0058	0.0058	
Anthracene	0.0034	0.0034	0.0034	0.0034	0.000012	0.000012	0.000012	0.000012	
Fluoranthene	0.24	0.24	0.24	0.86	0.000057	0.000057	0.000057	0.000057	
Fluorene	0.0042	0.0042	0.0042	0.0042	0.003	0.003	0.003	0.003	
Naphthalene	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	
Phenanthrene	0.00086	0.00086	0.00086	0.00086	0.0004	0.0004	0.0004	0.0004	
Pyrene	0.71	0.71	0.71	0.71	0.000092	0.000092	0.000092	0.000092	
Carcinogenic PAHs (as B(a)P TPE)	0.00004	0.00004	0.00004	0.00004	0.00004	0.00004	0.00004	0.00004	3
Benzo[a]anthracene									
Benzo[b]fluoranthene									
Benzo[k]fluoranthene									
Benzo[a,h,i]perylene									
Benzo[a]pyrene	0.0018	0.0018	0.0018	0.0066	0.0018	0.0018	0.0018	0.0066	4
Chrysene									
Dibenzo[a,h]anthracene									
Indeno[1,2,3-c,d]pyrene									

PHC F1 groundwater guidelines range from 0.81 – 2.2 mg/L depending upon the intended use of the proposed development. PHC F2 groundwater guidelines are 1.1 mg/L irrespective of intended land use.

Part XV.1  
Environmental  
Protection Act  
- Ontario

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Depending upon which table is applicable to a subject site, PHC-F1 concentrations between 420 – 750 ug/L and PHC-F2 concentrations of 150 ug/L in groundwater are posted as the criteria.

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Exceedance of either of these values generally requires further delineation followed by remediation or risk assessment

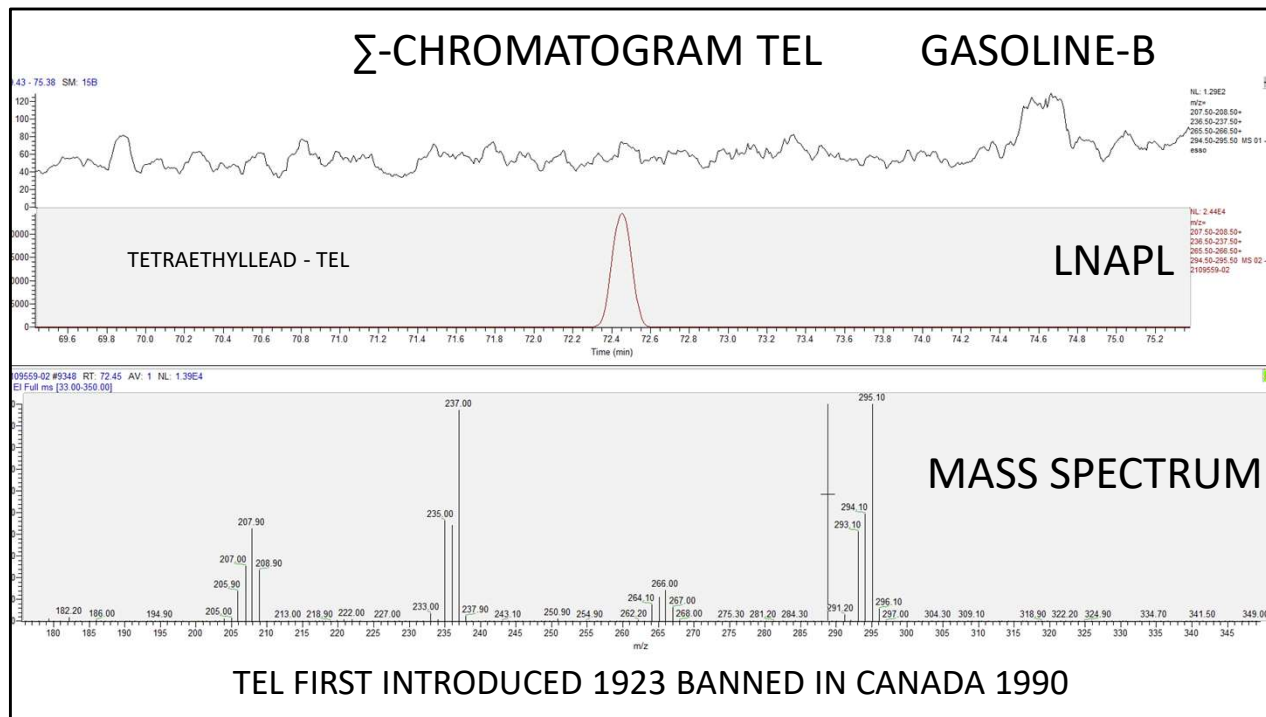
Groundwater guidelines can vary from province to province. For example, work we have conducted in Ontario list reclamation guidelines for groundwater of 420 – 750 ug/L for PHC-F1 and 150 ug/L for PHC F2.

## Gasoline



- 361 compounds identified (Whittmore, 1979)
- > 900 compounds identified by CAN/CGSB – 3.0, No. 14.3 (2016) and ASTM D6730 (2016).
- Bottom line: gasoline is complex. Most of the hydrocarbons occur within five hydrocarbon classes: paraffins, isoparaffins, aromatics, naphthenes, and olefins (referred to as PIANO).
- Hydrocarbon constituents generally span a range from C<sub>3</sub> - C<sub>12</sub>.
- Refineries producing gasoline use different processes. For example simple refineries employ only a few processing steps (e.g. distillation and reformation). Complex refineries have many more processing steps (e.g. cracking, reforming, isomerization, alkylation, polymerization).
- No two refineries are identically engineered or produce refined products that are identical. Armed with this knowledge, chemical fingerprinting of gasolines can be conducted and interpreted more fully (process forensics).
- Production of gasoline categorized as Performance Era (pre-1970) and Regulatory Era (1970 – present). Depending upon the era, process forensics provides a powerful tool to discriminate different gasolines.

Gasoline is a complex mixture of hydrocarbons. In 1979 Whittmore, identified 361 compounds. With modern day equipment over 900 compounds have been identified by the Standards Council of Canada (CAN/CGSB – 3.0, No. 14.3 (2016)). It is likely that the application GC X GC TOF/MS (time of flight mass spectrometry) could identify a larger number of compounds because of increased peak resolution. However, better resolution does not necessarily translate into better data because environmental factors and co-mingling plumes can cloud any conclusions. The oil spill international network of experts (OSINET) formed as part of the Bonn agreement, recognized and developed forensic tools published in 2006, 2012, and 2023. Over two decades of international round robin studies, involving over 46 laboratories throughout the world have been conducted evaluating source and spill relationships. Originally designed for crude oil investigations the latest versions of the OSINET method have incorporated light hydrocarbons. Of particular importance is the use of ratios of chemicals with similar chemical and physical properties. Some of those ratios are provided in this presentation. A mixing model has also been developed to deal with co-mingling plumes.



Understanding refining and blending practices is critical to performing forensic investigations, especially those involving gasoline. The above chromatogram reveals the presence of tetraethyllead in an LNAPL sample which is not present in a suspected source. The Canadian government regulated levels of lead in gasoline as follows:

3 g/US gallon – January, 1976

1.1 g/US gallon – January, 1987

Banned nation wide – December, 1990

TEL was first used in automotive gasolines in 1923. In order to draw a timeline for the above observation important to determine start up date for the industries in question. We do know the TEL found in the gasoline represents a source prior to 1990.

Ref: Stout, et.al., (2006). Automotive Gasoline, In: Environmental Forensics: Contaminant Specific Guide, Eds. R.D. Morrison and B.L. Murphy, Elsevier Science and Technology, pp 465 – 531.

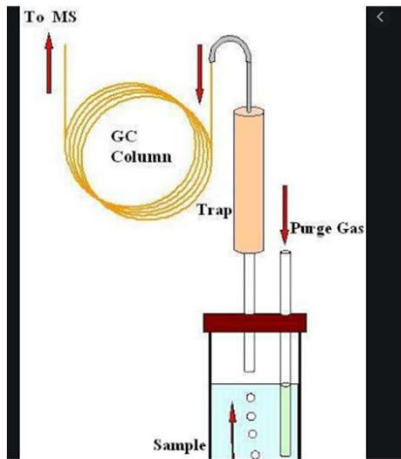


## GOAL

- TO DEVELOP PROCESSES TO DETERMINE SOURCES OF GASOLINE IN
- LNAPL (LIQUID NON-AQUEOUS PHASE LIQUID)
- CONTAMINATED SOIL
- WATER – EXCEEDING GUIDELINES, PARTICULARLY SHEEN
- QUESTION: IS THERE EVIDENCE OF A COMMON SOURCE OR MULTIPLE SOURCES?
- Yes we have LNAPL, contaminated soil and groundwater. Is the contamination derived from a common source? This is what council wants to know.

Slide is self explanatory.

## METHOD RECOMMENDED FOR DETERMINING GASOLINE IN LNAPL, SOIL AND WATER



- Modified US-EPA Method 8260 measures 109 compounds
- Method tested using SRMs which reported 23 analytes
- Four books on hydrocarbon forensics recommend this method for gasoline (2006, 2007, 2016, 2018)
- Several peer reviewed papers including a claims journal.

Ref: Uhler, et. al., (2003). Intern. J. Environ. Anal. Chem., **83**: 1 - 20

Ref: Stout, et. al., (2006). Environmental forensics: contaminant specific guide, Automotive Gasoline, pp 466 - 527

Ref: Stout, et. al., (2016). Standard Handbook Oil Spill Environmental Forensics; Fingerprinting and Source Identification, Chemical fingerprinting of gasoline and distillate fuels, pp. 509-564

Ref: Beall, et.al., Environ. Claims Journal, **14**: 487-506

**In litigation, any method used that deviates will likely be held to this standard**

For LNAPL doubt you will be challenged because ASTM and Standards Council of Canada Methods (ASTM D6730-01 and CAN/CGSB-3.0, No. 14.3

However, soil and water you may be challenged

Litigation experts want to know if gasoline found in groundwater, soil and LNAPL is derived from a common source. In particular a source belonging to their client both on and off their property bounds. Modification of US-EPA Method 8260 was designed to measure 109 compounds found in gasoline. The method has been applied to the analysis of LNAPL, soil and groundwater. US-EPA methods have been accepted by Canadian courts. These methods are also the foundation of many test methods used in provincial jurisdictions to measure pollutants which are regulated. EPA method 8260 suffers from a number of problems which will be discussed. However, any alternative methods employed in the analysis of LNAPL, soil and groundwater will have to demonstrate similar precision to US-EPA Method 8260. As shown in the slide US-EPA Method 8260 is a purge & trap, GC/MS (gas chromatography/mass spectrometry) method.

## Purge and Trap Analyses Analytical Issues

- “Experience with purge-and-trap systems has shown that analysis of highly contaminated samples can potentially contaminate the transfer system: after analysis of such a sample, a reagent water blank should be analyzed to confirm that the system is free from interferences and cross-contamination. If the reagent water blank analysis is not free of interferences, the system must be decontaminated by either a bake-out procedure or through more detailed instrument maintenance. Sample analysis should not resume until a reagent water blank demonstrates that the system is free of interferences”
- Need to screen samples before analyses which takes time and is inefficient
- Reference: Douglas et. al., (2007). Chemical Fingerprinting Methods. In: Introduction to Environmental Forensics, Second Edition, Eds. Brian L. Murphy and Robert D. Morrison, Elsevier Academic Press, pp 351 – 352
- Biggest problem ALS Laboratories had using P&T had was turnaround time for BTEX – F1 analyses because of constant bake out and instrument maintenance. Hydrocarbon contamination of groundwater samples received by lab in Alberta not unusual.
- For that reason, ALS got rid of purge & trap and went to headspace analyses and found the same or better sensitivity
- That is precisely why we opted for passive headspace analyses
- Ontario Labs do not have this problem because they receive primarily “clean water samples”. However, many switched to headspace.

The biggest problem with US-EPA Method 8260 (modified to measure gasoline) is that the concentration range is small. Large concentrations of gasoline can overload the system resulting in extensive cleaning and “baking” of the system in order to eliminate any contaminants. This results in extensive downtime resulting in reporting delays. Many laboratories have abandoned this method and switched to automated headspace GC/MS analyses in order to avoid the problems associated with P&T GC/MS.

## Comparison LNAPL/NEAT samples

- **Purge & Trap Method 8260**
- 20 mg of gasoline diluted with 10 mL methanol (2 mg/mL)
- 50 uL of sample-methanol extract is added to a 40 mL VOA vial containing 20 mL reagent water
- Samples analyzed by purge & trap
- Quantitative data for 109 analytes
- Modified method 8260 (Uhler et.al., 2003)
- Column RTX-1 PONA – 50m X 0.32 mm X 0.5 um film thickness
- Scan mode m/z 35 - 350
- **OUR METHOD**
- Gas chromatography/mass spectrometry – direct injection
- Column: RTX-PONA- 100m X 0.25 mm X 0.5 um film thickness
- Split ratio: 100:1
- 1 ul injection
- Oven: 35°C, hold 5 min, 1.5°C/min to 50°C, hold 5 min, 2°C/min to 200°C, hold 20 min.
- Scan mode: m/z 35 - 350

This slide compares the P&T GC/MS method used to analyze LNAPL and neat gasoline with direct injection high resolution GC/MS as advocated by ASTM and the Standards Council of Canada (ASTM D6730-01 and CAN/CGSB-3.0, No. 14.3)

## Comparison of Soil Samples

- **Purge & Trap**
- A 1 - 5 g aliquot of the sample is added to 10 mL HPLC grade methanol and then gently mixed, allowing the methanol to extract target analytes from the soil samples. A 50–100 mL aliquot (dependent on the expected level of contamination) is then removed from the methanol extract and added to a 40 mL VOA vial containing 10 mL of reagent water. This vial is then placed onto the autosampler tray, with the instrument fortifying the sample with the necessary surrogate RIS–SIS solution. The analytical sequence is then initiated.
- Modified method 8260 (Uhler et.al., 2003)
- **Passive headspace analysis**
- 100 uL of gasoline or LNAPL added to a Kimwipe as reference
- Placed in a 1-quart paint can
- Surrogates and Carbon strip added
- Paint can sealed and heated at 80 degrees Celsius for 16h
- Paint can cooled to room temperature and carbon strip retrieved
- Carbon strip added to carbon disulphide containing ISTD and analyzed by GC/MS
- Aliquot of soil added to 1-quart paint cans (usually 40 – 50g). **PHC data used as a guide.**
- Surrogates and Carbon strip added
- Heated and analyzed as per above

This slide compares the P&T GC/MS method (modified US-EPA Method 8260) to the use of passive headspace (PHS) analysis for the analyses of soil samples. The PHS method has been used extensively in arson investigations. Many peer reviewed manuscripts and text books have presented this method.

## Comparison of water samples (sheens)

- **Purge & Trap**
  - Sheen extracted with Teflon net
  - Net extracted with methanol.
  - Aliquot of methanol subjected to P&T analyses
  - Ref: Stout et.al., (2016). Standard Handbook Oil Spill Environmental Forensics, Fingerprinting and Source Identification, pp 509-564
- **ETFE or hydrophobic pad extraction followed by PHS**
  - 100 uL of gasoline or LNAPL added to a Kimwipe as **reference**
  - Placed in a 1-quart paint can
  - Surrogates and Carbon strip added
  - Paint can sealed and heated at 80 degrees Celsius for 16h
  - Paint can cooled to room temperature and carbon strip retrieved
  - Carbon strip added to carbon disulphide containing ISTD and analyzed by GC/MS
  - Water collected in 1-gallon paint can (usually 4 bailors) and shipped to lab. **Field extraction not recommended.**
  - Sample is added to a large aluminum pan (disposable turkey broiler pan)
  - Extracted with ETFE netting or hydrophobic pad.
  - ETFE netting or pad subjected to passive headspace analysis, i.e. placed in a 1-quart paint can, etc. etc.
  - Ref: V. Totten and J. Willis (2020). Forensic Science International, 312: 110309

The analyses of sheens observed on the surface of water presents an analytical challenge. Routine chemistry labs would consider solvent extraction, concentration followed by GC/MS direct injection of the extract. However, this approach will result in the loss of many important analytes critical to forensic analyses. The use of ETFE (ethylene tetrafluoro ethylene) nets as well as hydrophobic pads is recommended. ETFE netting and Hydrophobic pad are subject to PHS analysis.

Ref: Totten, V. and J. Willis (2020). Forensic Science International, 312: 110309

Ref: Stout et.al., (2016). In: Handbook Oil Spill Environmental Forensics, Elsevier, pp. 509 - 564

## Purge and Trap – Gasoline Samples

- The accuracy of the modified EPA Method 8260 is demonstrated through the comparison of the published NIST SRM certified and reference values and the concentrations determined by the modified EPA 8260 method
- **23 analytes out of 109 reported**
- ***The RPD between the NIST and modified EPA Method results are shown to be less than 15% for most compounds.***
- RPD not to exceed 25%
- Highest RPDs are evident in compounds present at low concentrations.
- **NOTE PAPER REPORTS INDIVIDUAL COMPOUNDS**
- **WE ARE REPORTING RATIOS SO DIFFERING COMPOUNDS WITH DIFFERING RPDS MAY BE COMPARED**

In order to determine the precision and accuracy of modified US-EPA Method 8260, four reference gasolines were obtained from NIST (National Institute of Standards & Technology). These include SRM (standard reference material) 2294 – 2297. Twenty-three (23) analytes were reported out of the 109 that were measured (21%). It should be noted that modified US-EPA Method 8260 is a quantitative method and that values obtained were compared to those published by NIST for the SRMs analyzed. Of particular interest is the relative percent difference defined as  $(\text{difference}/\text{mean} * 100)$ . Our interest is semi-quantitative, i.e. analytes are determined and specific ratios are calculated. However, the RPD is critical. Based upon modified method US-EPA 8260, RPDs of less than 15% - 25% are acceptable. The large range is due to concentration differences, i.e. lower concentrations result in more variability.

Ref: Uhler, et.al., (2003). Molecular fingerprinting of gasoline by modified EPA 8260 Gas Chromatography – Mass Spectrometry Method. International Journal of Environmental & Analytical Chemistry, 83: 1-20

## Precision of Purge & Trap for Soil

- Six replicates analyzed of spiked soil with SRM 2290 at 20 mg/kg
- The % RSD was generally less than 20%
- Total number analytes reported was 109 compounds measured.

This slide is self explanatory



NEAT GASOLINE			
RATIO	ESSO	COSTCO	PIONEER
	RSD%	RSD%	RSD%
toluene/n-C8	10.75	9.37	14.03
1M3PB/1M4PB	1.00	2.22	3.24
1M2EB/1M3EB	2.20	1.52	3.85
224-TMP/MCH	6.90	10.15	2.12
isopentane/pentane	6.58	15.09	14.13
KI = 2MH + 23 DMP/3MH + 24 DMP	1.08	1.15	0.99
2-MN/1-MN	3.11	4.00	2.76
pentenes/pentane	14.87	8.78	4.72
octane index	8.49	5.81	4.07
135TMB/124TMB	2.73	4.14	6.58
1M3PB/1M4PB	0.96	2.09	3.19
1M2EB/1M3EB	2.43	3.68	3.85
1M3EB/1M4EB	2.23	1.74	4.03
1M2EB/1M4EB	1.70	2.08	0.41
1M2EB/123TMB	1.86	2.95	6.80
123-TMB/124TMB	3.61	7.90	12.21
1M2EB/124-TMB	3.64	5.08	6.05
1M3EB/124-TMB	1.34	1.58	2.30
	ALL RATIOS < 15%		
	MOST MEET EN2020 < 5%		

This slide shows the chemical analyses of three neat gasoline samples analyzed in triplicate. Ratios are presented to compare the samples. These are common ratios to determine differences in process as well as ratios of compounds with similar physical and chemical properties which is important to deal with environmental weathering. All ratios revealed relative standard deviations (RSDs) of less than 15%. Most revealed RSDs of less than 5% which is an OSINET requirement.

The differences in ratios clearly show that the three gasoline samples are different, i.e. refined and blended in differing ways.

## PROCESS FORENSICS

NEAT GASOLINE							
	Esso	Costco Premium	Pionner	Comment	Esso	Costco	Pioneer
					RSD%		
toluene/n-C8	19.62 ± 2.11	33.38 ± 3.12	9.55 ± 1.34	Amount of reformate blended	10.75	9.37	14.03
1M3PB/1M4PB	2.00 ± 0.02	1.80 ± 0.04	1.85 ± 0.06	Reforming conditions	1.00	2.22	3.24
1M2EB/1M3EB	2.27 ± 0.05	1.98 ± 0.03	2.08 ± 0.08	Reforming conditions	2.20	1.52	3.85
224-TMP/MCH	8.12 ± 0.56	11.72 ± 1.19	2.83 ± 0.06	Amount of alkylate blended	6.90	10.15	2.12
isopentane/pentane	0.76 ± 0.05	1.59 ± 0.24	0.92 ± 0.13	Amount of isomerate blended	6.58	15.09	14.13
KI = 2MH + 23 DMP/3MH + 24 DMP	0.93 ± 0.01	0.87 ± 0.01	1.01 ± 0.01	Amount of straight run gasoline	1.08	1.15	0.99
2-MN/1-MN	1.93 ± 0.06	2.00 ± 0.08	2.17 ± 0.06	Reforming conditions	3.11	4.00	2.76
pentenes/pentane	13.65 ± 2.03	8.31 ± 0.73	9.54 ± 0.45	Amount of FCC gasoline	14.87	8.78	4.72
octane index	10.96 ± 0.93	15.50 ± 0.90	4.92 ± 0.20	Index relates to octane rating	8.49	5.81	4.07
					Red = RSD% > 10		
					Green = RSD% < 5 , i.e. meet EN 2020		
					Black - RSD% < 10		
Octane index = (2,2,4-TMP + Toluene)/(n-C <sub>7</sub> + n-C <sub>8</sub> )							

The ratios presented for neat gasoline reflect upon refinery processes, namely reformation, alkylation, isomerization, fluidized cracking, etc. Many ratios reveal relative standard deviations (RSDs) of less than 5% and all are less than 15%. Higher variability is a function of concentration. Differing blending processes can result in lower concentrations for some analytes resulting in higher variance of the data.

The process forensic investigation provided makes it clear that the three gasolines are clearly different, i.e. differing refining and blending processes.

	ESSO PHS		COSTCO PHS		PIONEER PHS		
	MEAN	RPD	MEAN	RPD	MEAN	RPD	
<b>M/Z 105</b>							
EB/MPX	0.07	0.00	0.12	0.00	0.06	15.38	
135TMB/124TMB	0.34	8.96	0.34	5.88	0.30	19.35	
1M3PB/1M4PB	1.90	3.66	1.90	6.90	1.88	4.28	
1M2EB/1M3EB	0.43	14.29	0.49	6.19	0.34	22.22	←
1M3EB/1M4EB	1.96	11.00	1.69	12.17	2.15	18.27	
1M2EB/1M4EB	0.84	2.38	0.82	7.23	0.73	5.41	
1M2EB/123TMB	0.98	2.02	1.16	2.60	1.12	0.00	
123-TMB/124TMB	0.32	16.39	0.30	6.67	0.23	21.28	
1M2EB/124-TMB	0.31	13.33	0.35	8.70	0.26	18.87	
1M3EB/124-TMB	0.72	1.40	0.72	1.40	0.74	4.08	
<b>M/Z 119</b>	mean	RPD	mean	RPD	mean	RPD	
123TMB/124TMB	0.54	9.26	0.42	11.36	0.42	11.36	
124TMB/123TMB	1.85	9.04	2.37	11.16	2.37	11.16	
14M2EB/12M4EB	0.58	3.45	0.54	3.70	0.54	3.70	
1245/1235	0.68	1.47	0.65	1.52	0.65	1.52	
13M5E/1M4E	33.65	4.04	10.67	24.10	10.67	24.10	
<b>M/Z 128/43,57,71,85</b>							
Napthalene/Dodecane	MEAN	RPD	MEAN	RPD	MEAN	RPD	
	0.34	30.56	22.11	18.99	3.59	5.79	←
<b>M/Z 141/142</b>							
DR-2MN/1-MN	MEAN	RPD	MEAN	RPD	MEAN	RPD	
	2.02	3.98	1.95	0.51	2.18	5.09	←
<b>M/Z 141/156</b>							
2-EN/26 + 27-DMN	0.48	4.17	0.56	12.07	0.56	3.57	
16-DMN/13 + 17-DMN	0.50	6.00	0.42	9.30	0.48	0.00	
DR-B/2-EN	0.76	6.58	0.92	4.35	0.25	3.85	←
	MEAN	RPD	MEAN	RPD	MEAN	RPD	
137-TMN/136-TMN	1.08	15.32	0.84	18.29	0.85	1.16	
METHOD 8260 RPDS FOR SOIL < 20%							
the %RSD tends to increase with decreasing concentration							

<b>NEAT RATIOS</b>
toluene/n-C8
224-TMP/MCH
isopentane/pentane
KI = 2MH + 23 DMP/3MH + 24 DMP
pentenes/pentane
octane index

SOIL

Analyses of soil samples presents differing challenges. Some process ratios identified in analyzing neat samples may not be an option for consideration, due to weathering (evaporation, water dissolution and biodegradation). Duplicate analyses, are required as part of the OSINET method. The majority of relative percent differences are well below 20% listed for P&T GC/MS (modified US EPA Method 8260). Some ratios are profoundly different revealing differing refining and blending practices (red arrows). We presented duplicate analyses because we follow OSINET protocol, i.e. all samples are analyzed in duplicate.

WATER SHEENS									
ETFE Nets Followed by PHS									
m/z 105	ESSO			COSTCO			PIONEER		
	mean	std dev	RSD%	mean	std dev	RSD%	mean	std dev	RSD%
135TMB/124TMB	0.18	0.02	12.45	0.19	0.03	17.95	0.18	0.02	12.09
1M3PB/1M4PB	1.92	0.05	2.64	1.75	0.04	2.46	1.79	0.05	2.66
1M2EB/1M3EB	0.67	0.12	17.68	0.58	0.02	3.97	0.62	0.03	4.75
1M3EB/1M4EB	2.38	0.08	3.17	2.05	0.05	2.25	2.16	0.09	4.01
1M2EB/1M4EB	1.61	0.32	19.78	1.18	0.06	4.80	1.34	0.05	3.51
1M2EB/123TMB	0.29	0.06	19.69	0.45	0.09	20.36	0.33	0.06	16.69
123-TMB/124TMB	0.48	0.03	7.18	0.39	0.05	13.01	0.41	0.04	9.03
1M2EB/124-TMB	0.14	0.02	14.46	0.17	0.04	21.09	0.13	0.02	15.07
1M3EB/124-TMB	0.21	0.06	30.10	0.30	0.07	21.59	0.22	0.03	12.11
m/z 119	ESSO			COSTCO			PIONEER		
	mean	std dev	RSD%	mean	std dev	RSD%	mean	std dev	RSD%
123TMB/124TMB	0.86	0.06	6.70	0.69	0.11	15.86	0.87	0.16	18.02
124TMB/123TMB	1.16	0.08	7.08	1.47	0.26	17.58	1.18	0.23	19.05
14M2EB/12M4EB	0.54	0.08	15.17	0.49	0.03	5.54	0.49	0.06	11.70
1245/1235	0.60	0.09	15.38	0.63	0.03	4.91	0.63	0.04	5.66
DR-NAPHTHALENE/ISTD	ESSO			COSTCO			PIONEER		
	mean	std dev	RSD%	mean	std dev	RSD%	mean	std dev	RSD%
DR-2MN/1-MN	1.81	0.07	3.61	1.86	0.03	1.78	2.00	0.04	2.15
2-EN/26 + 27-DMN	0.46	0.03	6.74	0.51	0.01	2.47	0.50	0.00	0.26
16-DMN/13 + 17-DMN	0.47	0.03	6.13	0.43	0.01	2.30	0.48	0.01	3.02
DR-B/2-EN	0.81	0.03	4.05	0.87	0.02	1.90	0.24	0.01	3.97
137-TMN/136-TMN	0.90	0.05	5.19	0.88	0.04	4.12	0.94	0.01	0.99
Average RSDs			11.14	9.72			8.70		
GREEN MEET OSINET STANDARD VARIANCE									
YELLOW DISTINCT DIFFERENCES BETWEEN ALL GASOLINES									

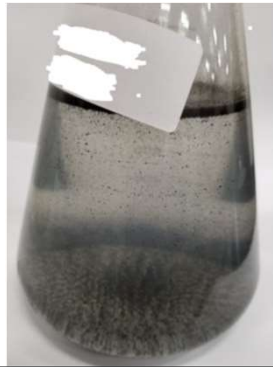
NEAT RATIOS
toluene/n-C8
224-TMP/MCH
isopentane/pentane
KI = 2MH + 23 DMP/3MH + 24 DMP
pentenes/pentane
octane index

Sheen sampling involves collection of groundwater and extraction using hydrophobic pads or ETFE nets. The pads or nets are subjected to passive headspace analysis using 1 quart paint cans and carbon strips (Albrayco Technologies, Cromwell, Connecticut). The nets/pads are added to a 1 quart paint can, surrogates are added, along with a carbon strip. The cans are sealed with a lid and heated at 80°C overnight. Upon heating, the cans are cooled to room temperature and the carbon strips retrieved. The strips are added to 1 mL of carbon disulphide containing an internal standard and analyzed using GC/MS with the aid of a PONA column.

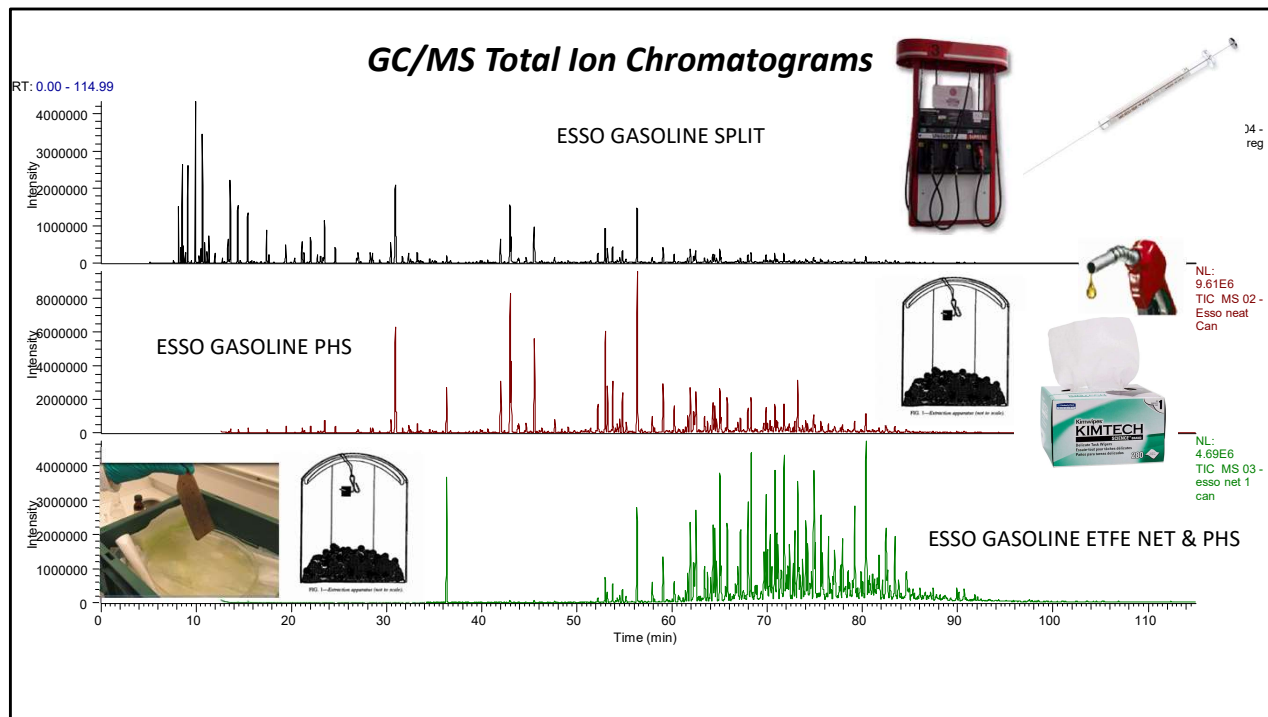
From the above slide ratios incorporated for neat gasoline are not employed because of weathering. The ratios used are largely dominated by alkylated benzenes and naphthalenes which appear in the “tail end” of gasoline. Most ratios are less than 20% RSD, however, many meet OSINET guidelines of < 5%. Average RSDs are 8.7 – 11.14% (n = 19). Ratios highlighted in yellow reveal obvious differences between the samples analyzed.

WE NOW HAVE THE TOOLS TO DEAL WITH  
GASOLINE FORENSIC INVESTIGATIONS  
INVOLVING LNAPL, SOIL AND GROUNDWATER

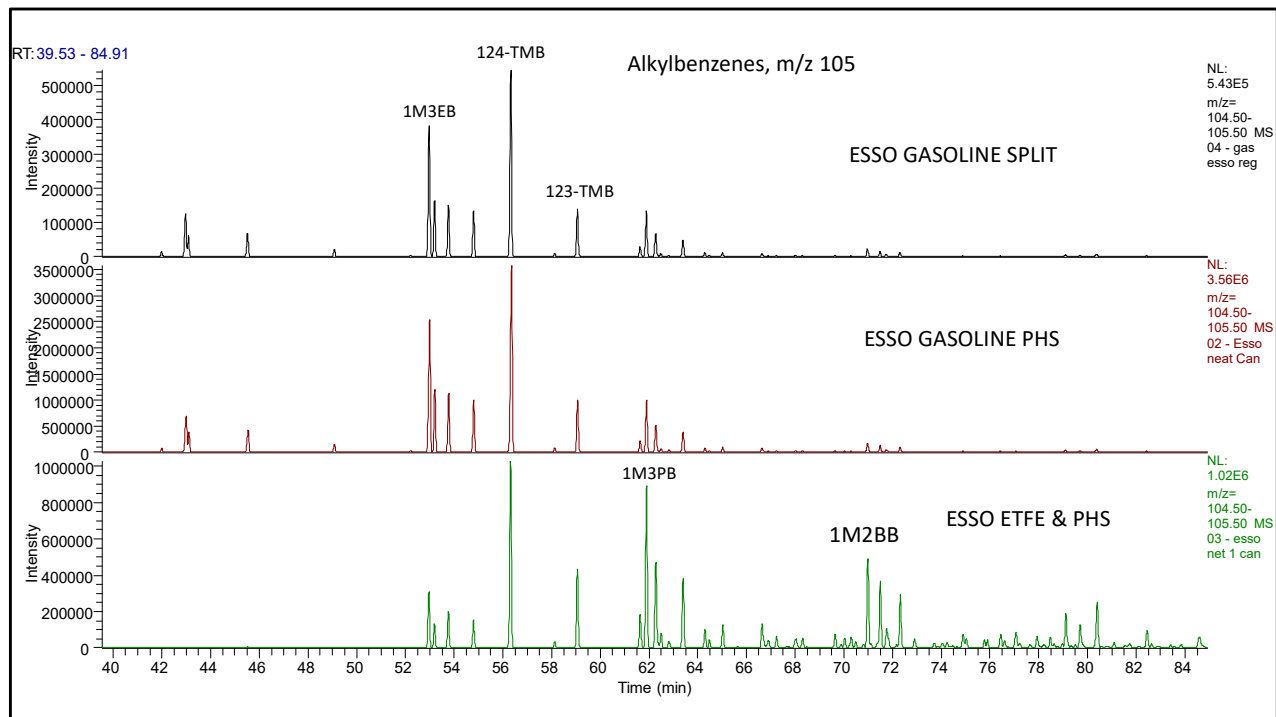
- LNAPL – DIRECT INJECTION GC/MS
- SOIL – PHS FOLLOWED BY GC/MS
- WATER – ETFE NET OR HYDROPHOBIC PAD EXTRACTION FOLLOWED BY PHS AND GC/MS
- PRECISION IN KEEPING WITH MODIFIED METHOD 8260



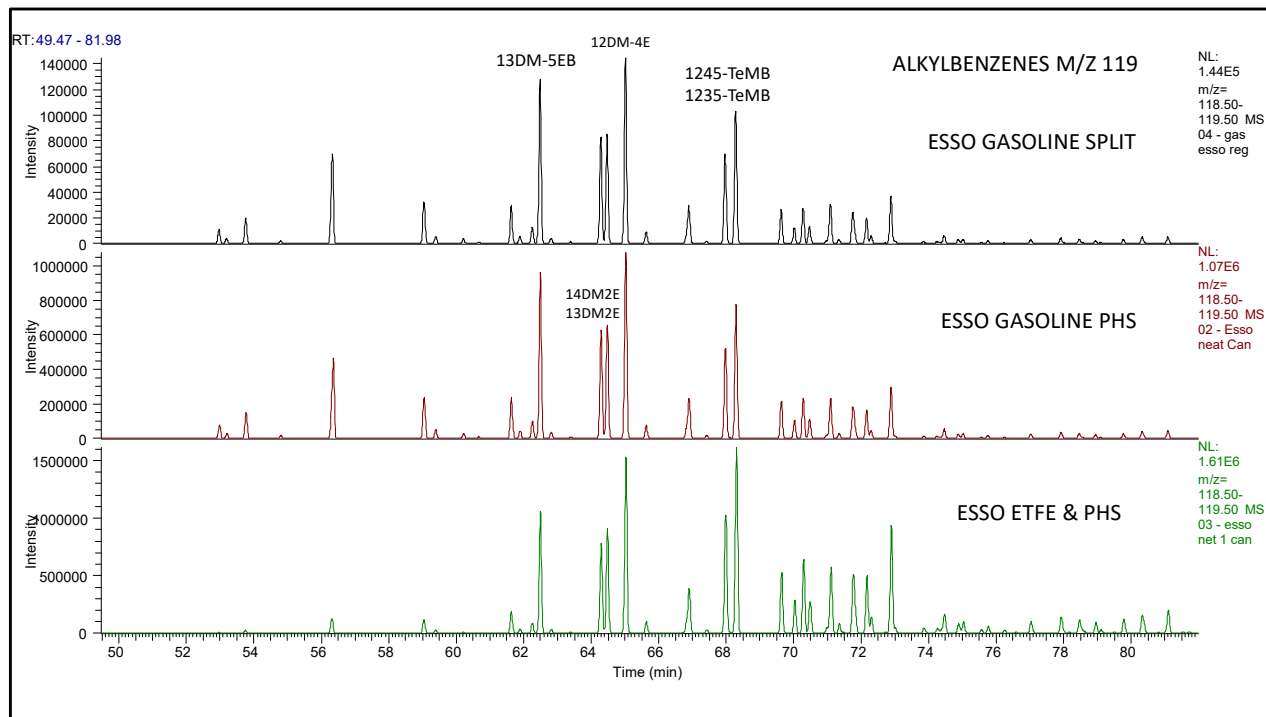
This slide is self explanatory.



This slide reveals GC/MS total ion chromatograms obtained for Esso gasoline analyzed neat, employing passive headspace analyses and ETFE extraction followed by PHS analyses. It is observed that PHS analyses concentrates the “tail end” components of gasoline. This is especially true for the application of sheen sampling (ETFE net followed by PHS). These “tail end” components tend to be more recalcitrant to weathering.

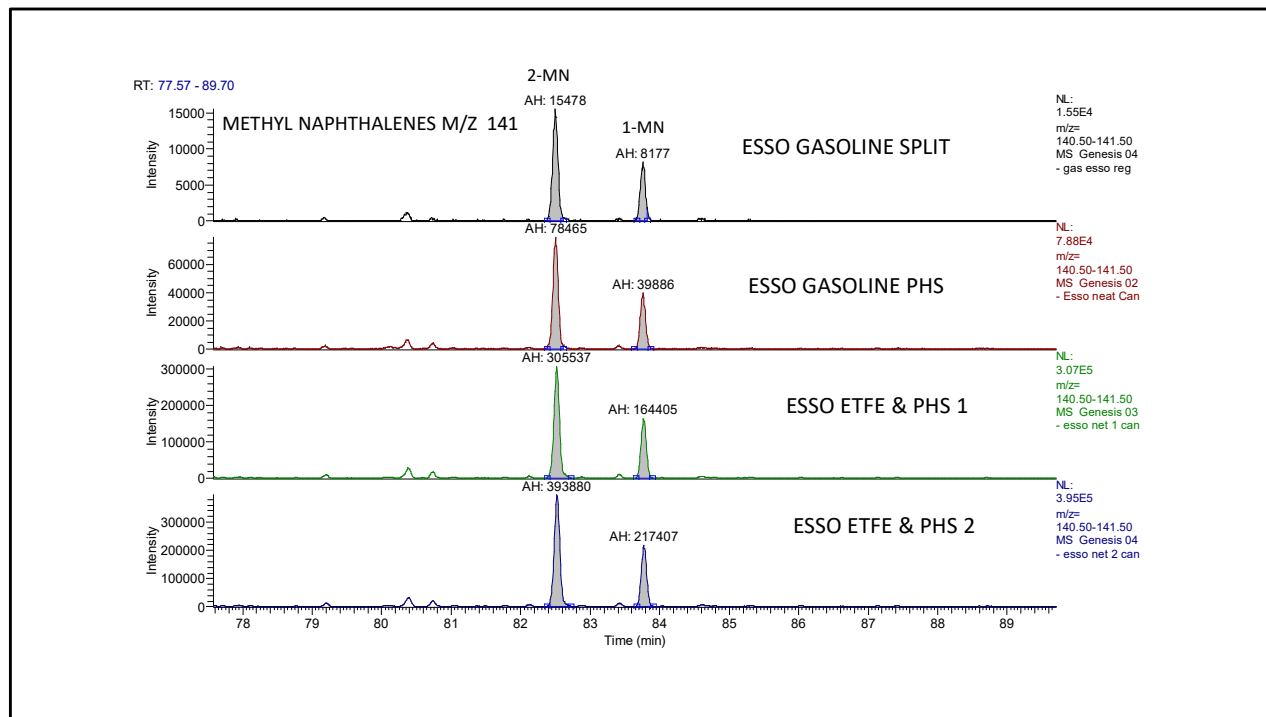


This slide reveals an extracted ion-current profile for m/z 105 obtained using GC/MS analyses. These are profiles for C<sub>3</sub>-benzenes and are obtained for Esso gasoline analyzed neat, employing PHS analyses as well as ETFE net extraction followed by PHS. From this slide it is observed that PHS results in higher responses (2 – 7-fold) over the analysis of neat gasoline. Higher responses for “tail end” alkylbenzenes are observed following ETFE extraction followed by PHS analyses.



This slide shows a GC/MS extracted ion-current profile for m/z 119 which is characteristic of C<sub>4</sub>-benzenes. Higher responses are observed for the analyses of gasoline analyzed using PHS and ETFE extraction followed by PHS. It should be emphasized that the responses observed of PHS depends upon concentrations of gasoline in soil and in water (i.e. sheen).

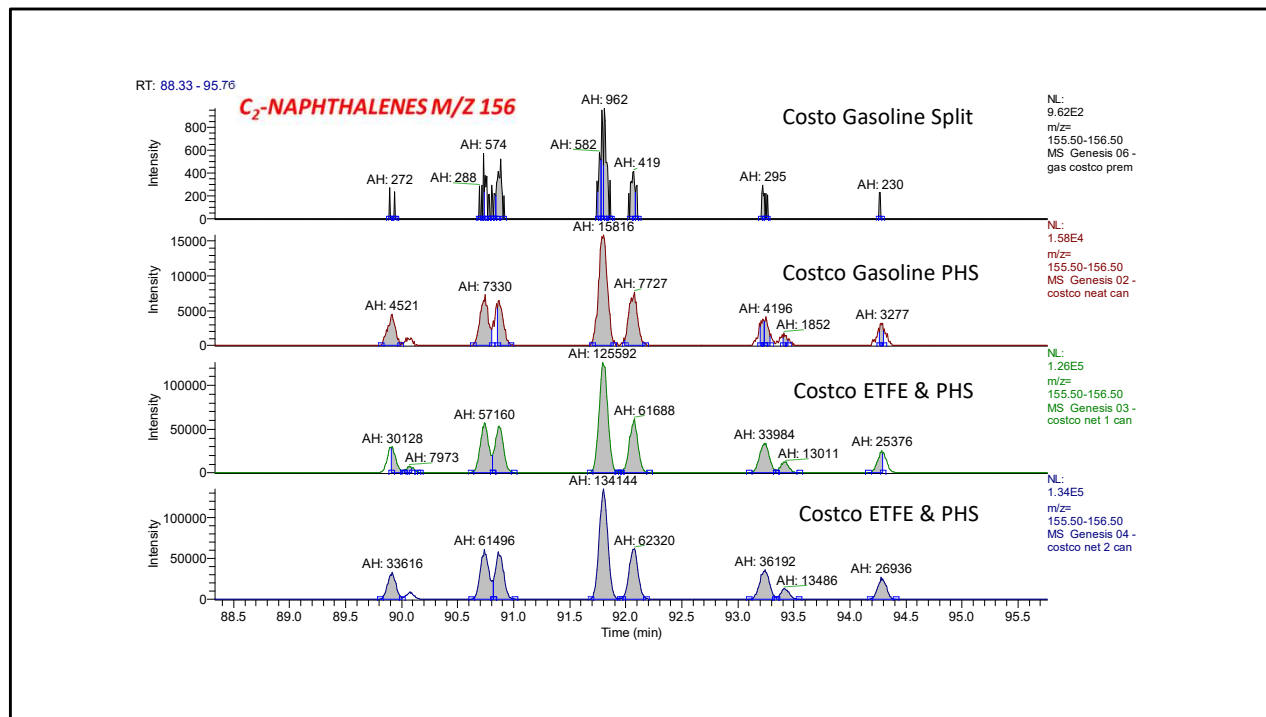




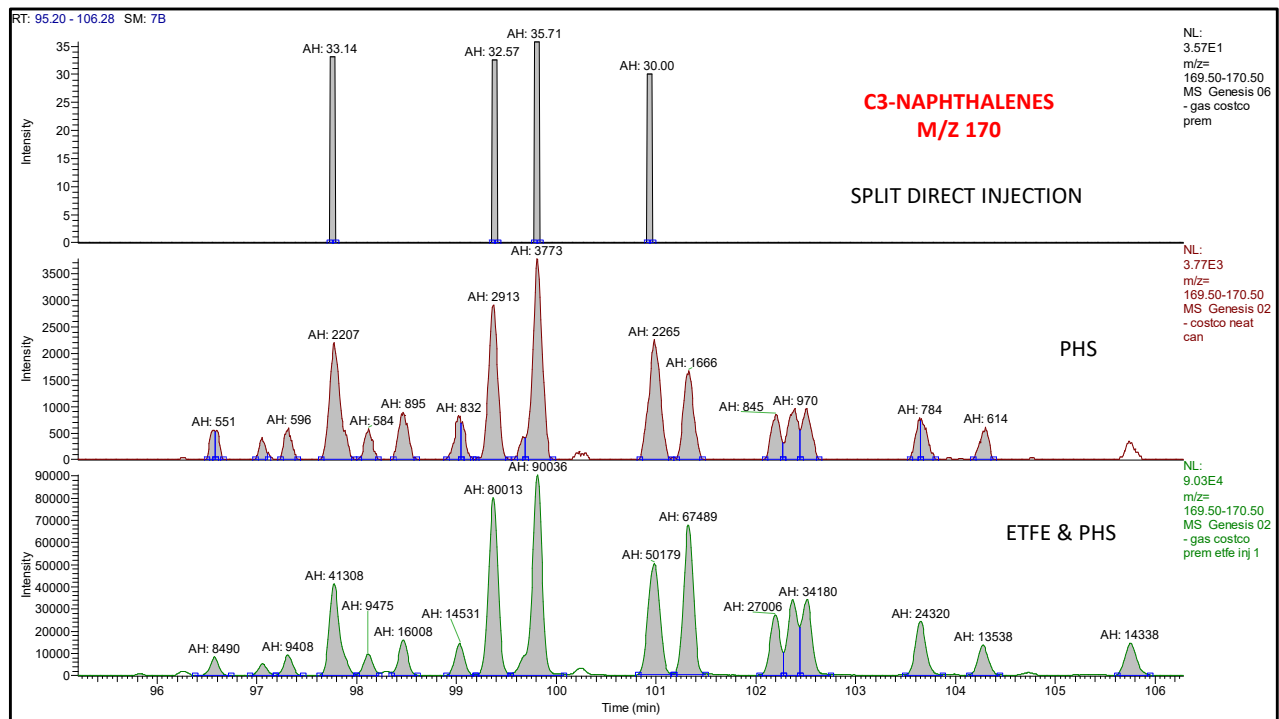
The use of C<sub>0</sub> to C<sub>2</sub>-naphthalenes to determine sources of gasoline have been demonstrated (Sandercock and Pasquier, 2003a, 2004a, and 2004b). This slide reveals a GC/MS extracted ion-current profile for m/z 141 characteristic of methyl naphthalene. Highest area counts are observed for gasoline extracted with ETFE netting followed by PHS analysis. Again this is very much controlled by how much gasoline is present in sheen samples.

#### References:

1. Sandercock, P.M.L. and E. Du Pasquier (2003). Chemical fingerprinting of unevaporated automotive gasoline samples. Forensic Science International, **134**: 1-10
2. Sandercock, P.M.L. and E. Du Pasquier (2004). Chemical fingerprinting of gasoline 2. Comparison of unevaporated and evaporated automotive gasoline samples. Forensic Science International, **140**: 43-59
3. Sandercock, P.M.L. and E. Du Pasquier (2004). Chemical fingerprinting of gasoline. Part 3. Comparison of unevaporated automotive gasoline samples from Australia and New Zealand. Forensic Science International, **140**: 71-7
4. EN 15522-2:2023. Oil spill identification – Petroleum and petroleum related products – Part 2: Analytical method and interpretation of results based on GC/FID and GC-low resolution-MS analyses. Available European Committee for Standardization, CEN-CENELEC Management Centre, Rue de la Science, 23, B1040 Brussels.



This slide shows a GC/MS extracted ion-current profile for m/z 156 which is characteristic of C<sub>2</sub>-naphthalenes. Again we observe higher responses for these chemicals following extraction of gasoline from water with ETFE netting followed by PHS analyses. Responses observed following PHS analyses (employed with soils) and ETFE/PHS (employed for sheens) depends upon concentrations of gasoline present in these sample matrices.

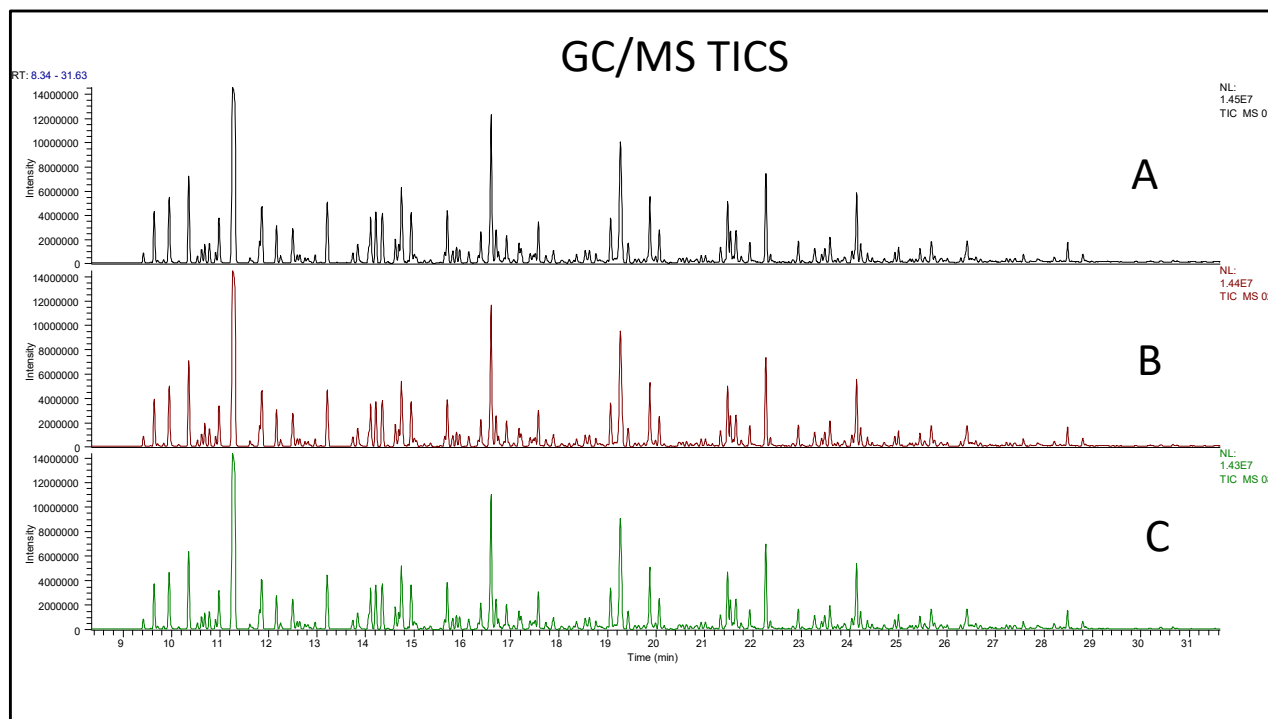


This slide is an extracted ion-current profile for  $m/z$  170 characteristic of  $C_3$ -naphthalenes. We observe higher responses following analyses of gasoline following PHS and ETFE extraction followed by PHS. Again these responses will depend on gasoline concentrations in soil and in water (sheen).

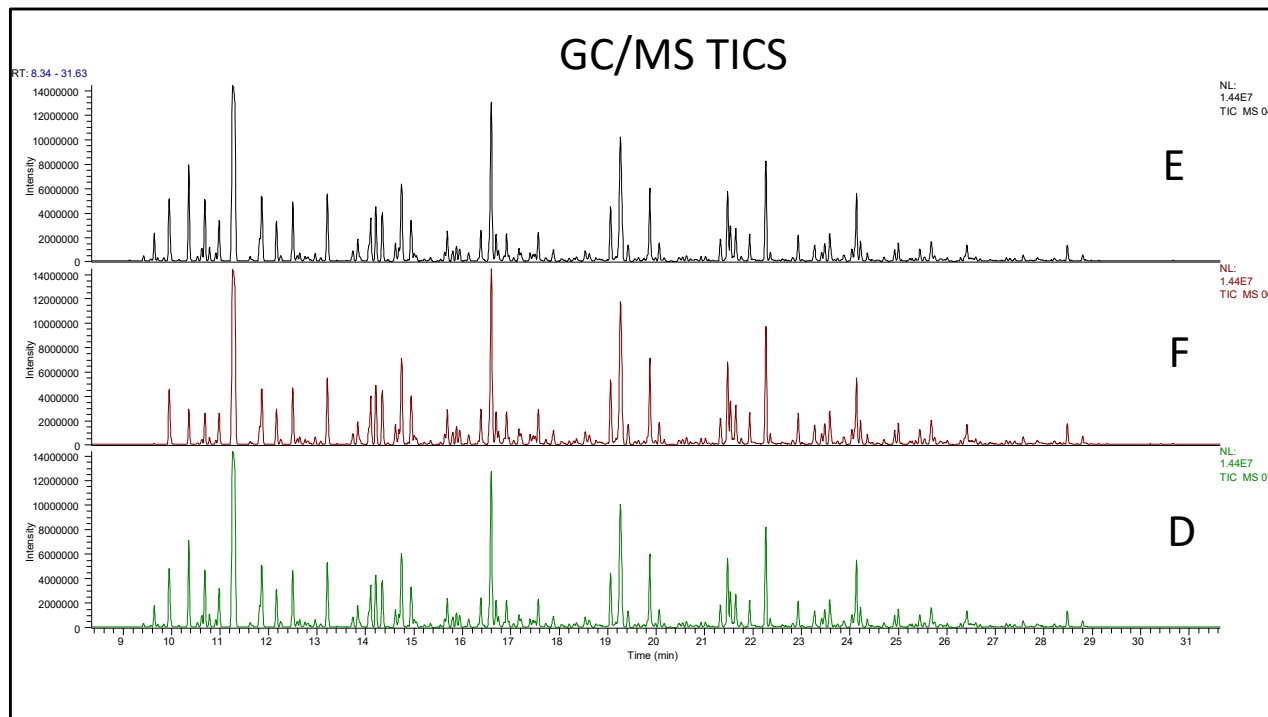
## LETS TEST ON MORE GASOLINE



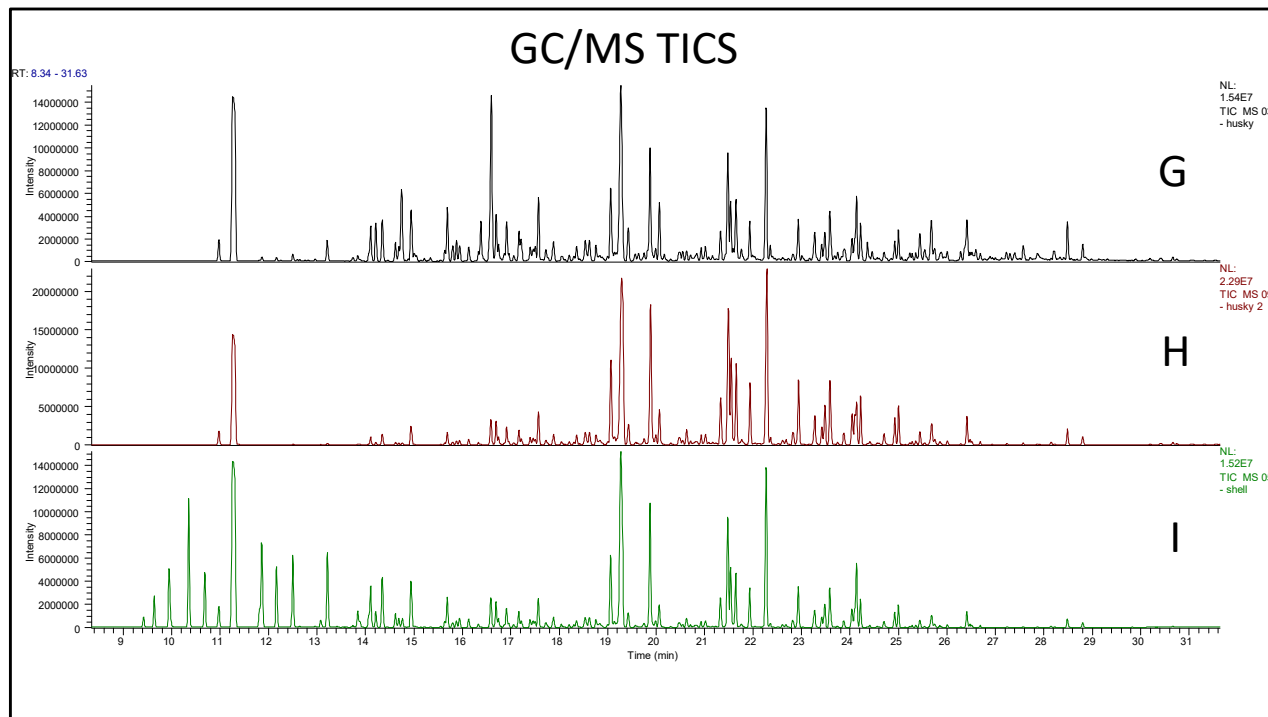
Analyses of three differing gasoline samples provides little weight of evidence. We provide additional data for consideration. We provide data for nine gasolines collected in Alberta.



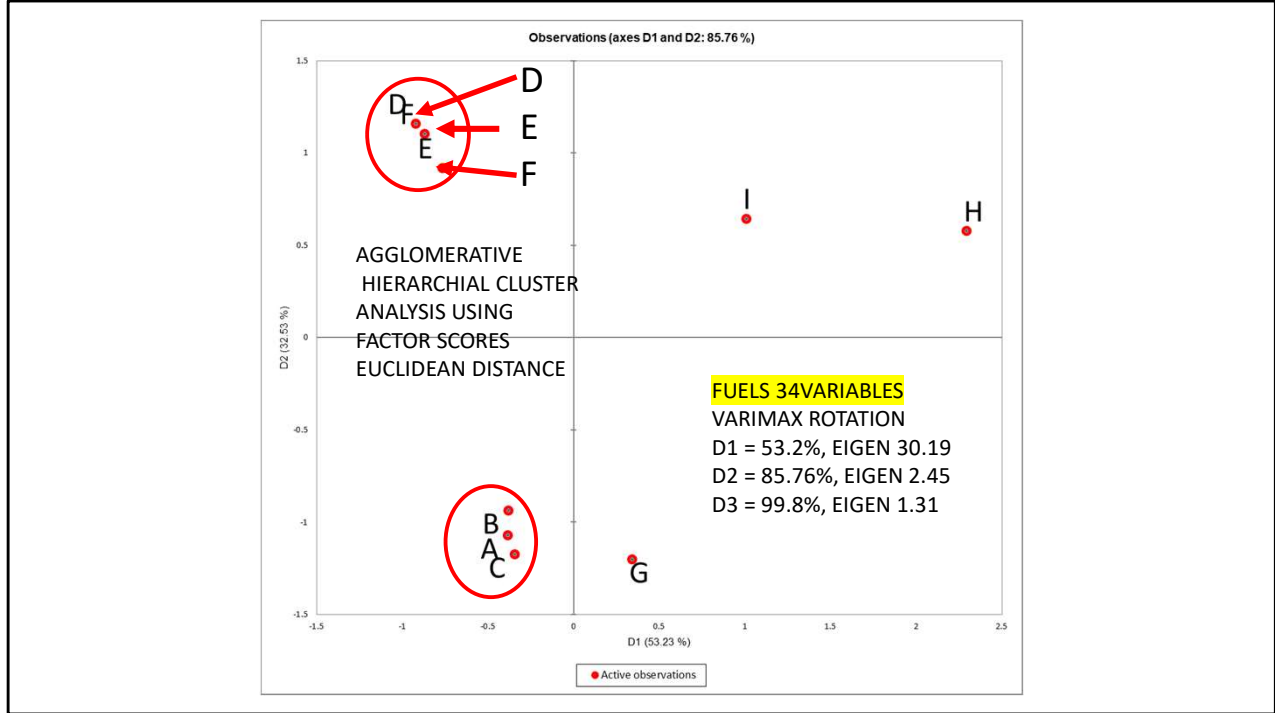
These three samples of gasoline were obtained from three differing retailers. Comparison of GC/MS total ion chromatograms (TIC) reveal similar profiles indicating these are derived from a common bulk station or “jobber”.



These three samples were collected from different retailers. GC/MS TICs reveal that sample D and E are similar. Sample F reveals a similar profile however there are slight difference in the front end of the chromatogram (retention time 9 – 11 min). Samples D and E were derived from a common “jobber”. Sample F may also be derived from the same jobber and the slight difference observed in the front end chromatogram may be explained by further investigation.

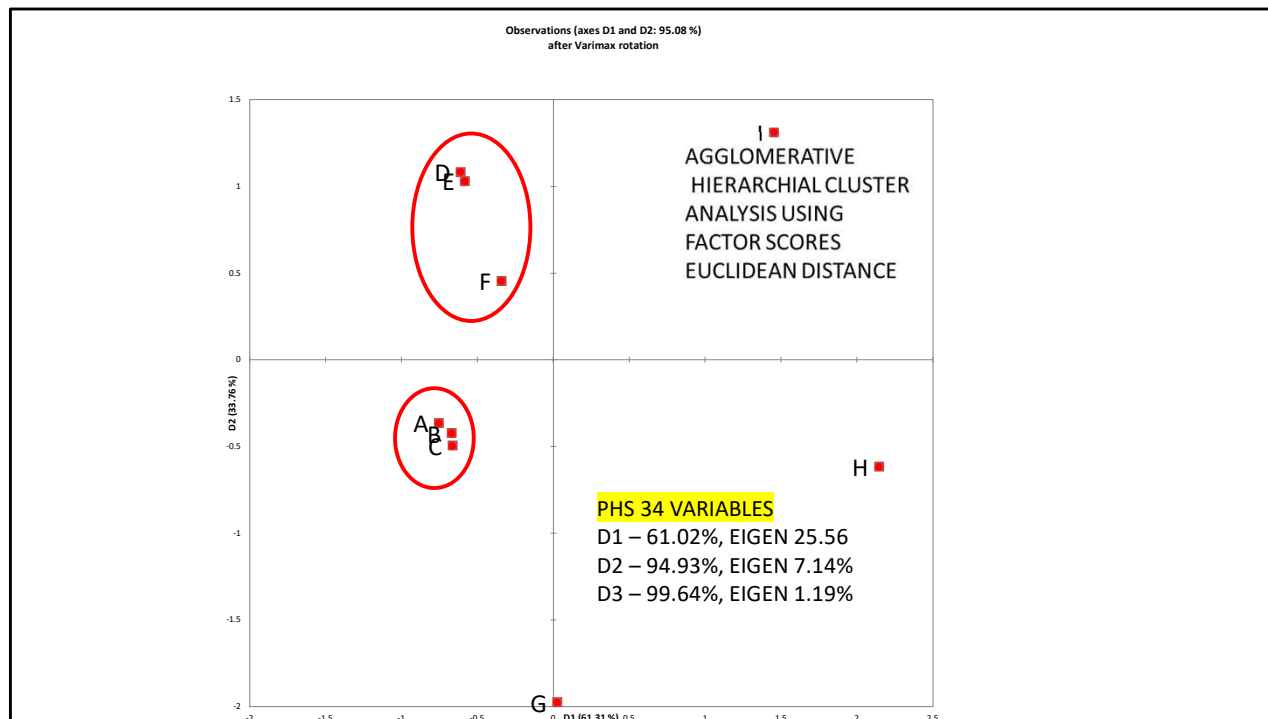


These gasoline samples were obtained from different retailers in Alberta. Review of the GC/MS TICs reveal no similarity indicating differing sources.



Principal components analyses was performed using alkylated benzene data. Thirty-four data points were employed. Following PCA analysis using varimax rotation, factor scores were subjected to hierarchical cluster analyses. These results suggest that samples A,B,C are derived from a common bulk fuel facility or “jobber”. Samples D,E,F are also derived from a common, but different bulk fuel facility. Sample F is slightly different than D and E. Samples G,H, and I are derived from different sources. PCA analyses performed using total ion chromatograms (54 analytes) revealed similar results.





Similar results are obtained using PHS analysis samples A,B,C derived from a common source and D,E,F are derived from another source. However, sample F is slightly different than D and E. Data obtained using 34 alkylated benzenes

				OCTANE	ISOPENTANE			
SOURCE	MCH/ISTD	TOL/MCH	ISO/MCH	INDEX	INDEX	TOL/n-C8	NAPH/nc12	2-MN/1-MN
A	49.54	2.84	1.46	2.46	0.82	3.61	23	2.48
B	44.2	3.03	1.4	2.55	0.79	3.91	24.6	2.46
C	44.84	2.87	1.35	2.44	0.83	3.62	21.6	2.45
D	26.96	5.38	2.53	3.39	0.6	5.6	86.1	2.64
E	27.23	5.35	2.6	3.41	0.61	5.61	86.7	2.63
F	32.7	5.08	2.51	3.16	0.53	5.07	84.5	2.6
G	52.84	3.09	1.34	2.06	0	2.6	27.3	2.43
H	19.29	1.94	0.17	0.52	0	0.75	242	1.97
I	29.7	0.98	0.31	0.52	0	1.02	251	1.96
PROCESS	SRG/HSRG	REFORMATE	ISOOCTANE	OCTANE RATING	ISOMERATE	REFORMATE	REFORMATE	REFORMATE

These ratios, obtained for neat gasoline reflect refining processes including reformation, isooctane blending, octane index and isomerization (isopentane index).

The responses reflect the PCA results which were obtained using alkylated benzene and total ion data. Samples A,B,C are derived from a common source and ratios obtained are similar for all samples. Samples D,E,F are also derived from a common – although gasoline F is slightly different which is also shown in the PCA. Sample G,H, and I are derived from different sources.

SOURCE	2,3-DM-pentane/2,4-DM-pentane	
	SPILL	PHS
A	1.24	2.79
B	1.22	2.67
C	1.24	2.78
D	1.34	2.88
E	1.32	2.9
F	1.39	3.25
G	1.32	4.1
H	3.14	3.12
I	0.77	1.57
GENERIC FEATURE OF ALKYLATE		

This ratio is known as the “KI ratio”. Alkylate is typically enriched in 2,3-dimethylpentane relative to 2,4-dimethylpentane. Thus the addition of alkylate to gasoline has resulted in an increase in the KI ratio. The results reflect the clustering observed in the PCA analyses.

Ref: Stout, et.al., (2006). Automotive Gasoline, In: Environmental Forensics: Contaminant Specific Guide, Eds. R.D. Morrison and B.L. Murphy, Elsevier Science and Technology, pp 465 – 531.

SOURCE	Split	PHS	Split	PHS	Split	PHS
	Toluene/MCH	Toluene/MCH	iso/mch	iso/mch	Naph/n-C <sub>12</sub>	Naph/n-C <sub>12</sub>
A	2.84	14.06	1.46	1.26	23	17.6
B	3.03	15.54	1.4	1.25	24.6	18.4
C	2.87	15.22	1.35	1.14	21.6	16.8
D	5.38	24.65	2.54	2.51	86.1	66.5
E	5.35	25.79	2.6	2.57	86.7	62.8
F	5.08	31.56	2.51	2.42	84.5	65
G	3.09	21.1	1.34	0.98	27.3	21.7
H	1.98	7.6	0.16	0.13	242	230
I	0.98	3.89	0.29	0.2	251	248
	REFORMATE		ALKYLATE		REFORMATE	

Ratios associated with the blending reformat and alkylate provide information on how gasoline is refined. Here we compare results obtained for neat gasoline (“split”) and passive headspace used for soils. The results clearly show that gasolines A,B,C are obtained from a common source. Samples D,E,F are obtained from a common source but F is slightly different. Samples G,H,I are derived from differing source. Although the ratios obtained differ for gasoline analyzed neat and using PHS differ, the clustering remains the same as observed following PCA analyses.

SOURCE	Split	PHS	Split	PHS	Split	PHS
	1M3EB/1M4EB		1M2EB/123TMB		1M2EB/1M3EB	
A	2.26	2.2	1.05	0.98	0.33	0.37
B	2.29	2.22	1.06	0.96	0.34	0.39
C	2.27	2.18	1.06	0.96	0.34	0.38
D	2.16	2.03	1.13	1.08	0.38	0.44
E	2.1	2	1.12	1	0.39	0.45
F	2.14	1.98	1.14	1.07	0.39	0.44
G	2.07	2.12	1.04	0.82	0.36	0.45
H	1.57	1.54	1.08	0.82	0.47	0.58
I	1.86	1.83	1.07	0.96	0.36	0.47
PROCESS FCC and REFORMATE						

Ratios obtained for C3-benzenes can be impacted by reformate production as well as fluidized cracking. Again clustering results are similar to those obtained using PCA. Ratios were obtained for neat gasoline as well as gasoline analyzed using PHS.

SOURCE	Split	PHS	Split	PHS
	2-MN/1-MN		2-EN/26+27-DMN	
A	2.48	2.38	0.36	0.57
B	2.46	2.4	0.36	0.57
C	2.45	2.4	0.35	0.57
D	2.64	2.58	0.46	0.71
E	2.63	2.55	0.47	0.72
F	2.6	2.55	0.47	0.74
G	2.43	2.37	0.35	0.55
H	1.97	1.89	0.23	0.36
I	1.96	1.9	0.23	0.34

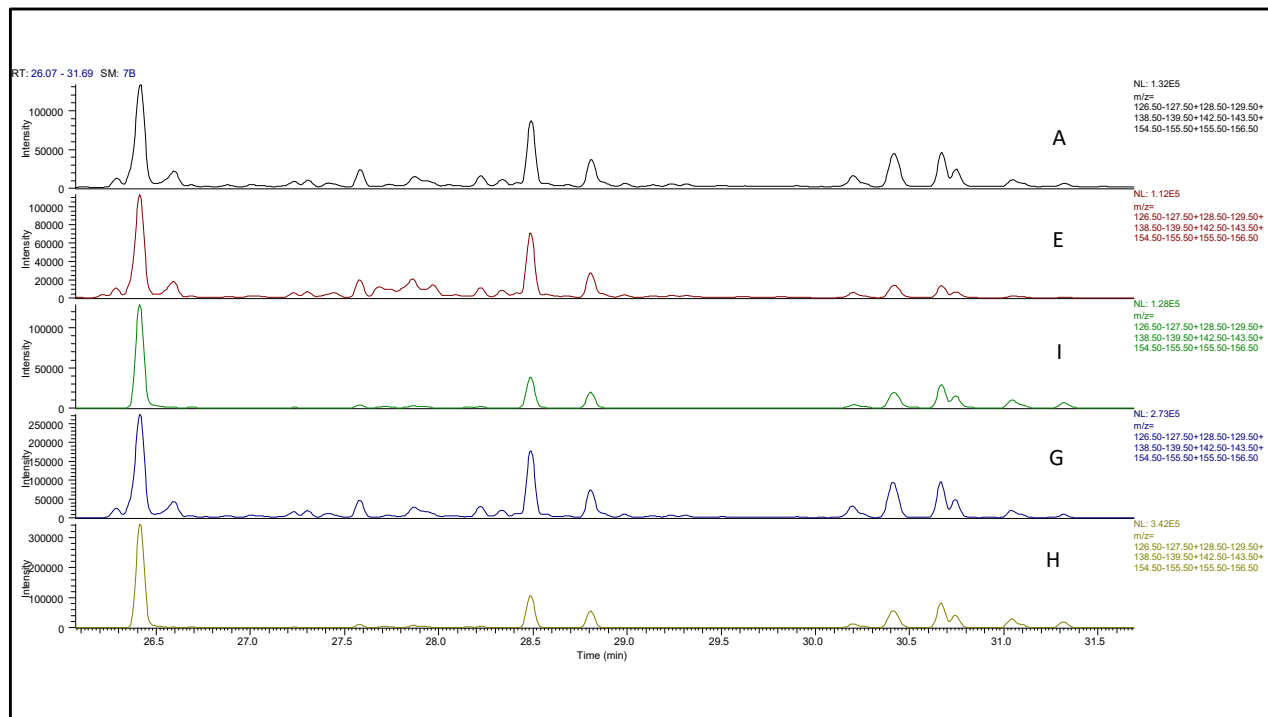
Ratios of alkylated naphthalenes have been used to determine sources of gasoline. Ratios are provided for both neat gasoline as well as analyses conducted using PHS (i.e. soil). Similar clustering is observed for that obtained using PCA.

#### References:

1. Sandercock, P.M.L and E. Du Pasquier (2003). Chemical fingerprinting of unevaporated automotive gasoline samples. Forensic Science International, 134: 1-10
2. Sandercock, P.M.L. and E. Du Pasquier (2004). Chemical fingerprinting of gasoline 2. Comparison of unevaporated and evaporated automotive gasoline samples. Forensic Science International, 140: 43-59
3. Sandercock, P.M.L. and E. Du Pasquier (2004). Chemical fingerprinting of gasoline. Part 3. Comparison of unevaporated automotive gasoline samples from Australia and New Zealand. Forensic Science International, 140: 71-77.
4. EN 15522-2:2023. Oil spill identification – Petroleum and petroleum related products – Part 2: Analytical method and interpretation of results based on GC-FID and GC-low resolution –MS analyses. Available European Committee for Standardization, CEN-CENELEC Management Centre, Rue de la Science 23, B1040 Brussels.

MCH CHARACTERISTIC OF SRG, HSRG, OR NAPHTHA	SOURCE	MCH/ISTD
	A	49.54
	B	44.2
	C	44.84
	D	26.96
	E	27.23
	F	32.7
	G	52.84
	H	19.29
	I	29.7

Straight run gasoline (SRG), heavy straight run gasoline (HSRG) and naphtha contain methyl cyclohexane (MCH). The amount of MCH is indicative of how much is blended to form gasoline. Here MCH is quantitated relative to an internal standard. The ratio of MCH/ISTD generates clusters similar to that observed using PCA.



This is an extracted ion-current chromatogram obtained for naphthalenes ( $C_0$ ,  $C_1$ , and  $C_2$ ). Profiles and intensities reveal differences between sample A, E, I, G, and H.



## CONCLUSIONS

- When performing a site assessment LNAPL is the gold standard to make comparisons.
- This will be used as reference material for any soil and sheen sampling that may be required.
- Use GC/MS PONA for LNAPL
- Use PHS followed by GC/MS PONA for soil
- Use ETFE netting or hydrophobic pads for sheens followed by PHS followed by GC/MS PONA.
- The precision is as good or better than P&T GC/MS and less cumbersome (i.e. getting the concentrations right and avoiding equipment contamination).

This slide is self explanatory.

**Detlef (Deib) Birkholz**

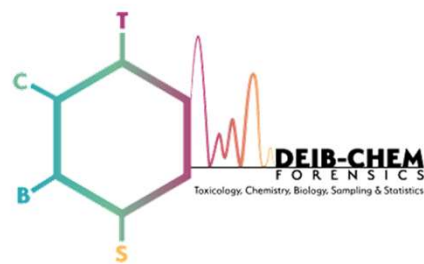
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Forensic services in toxicology (T), chemistry (C)  
biology (B), sampling and statistics (S)



Contact information