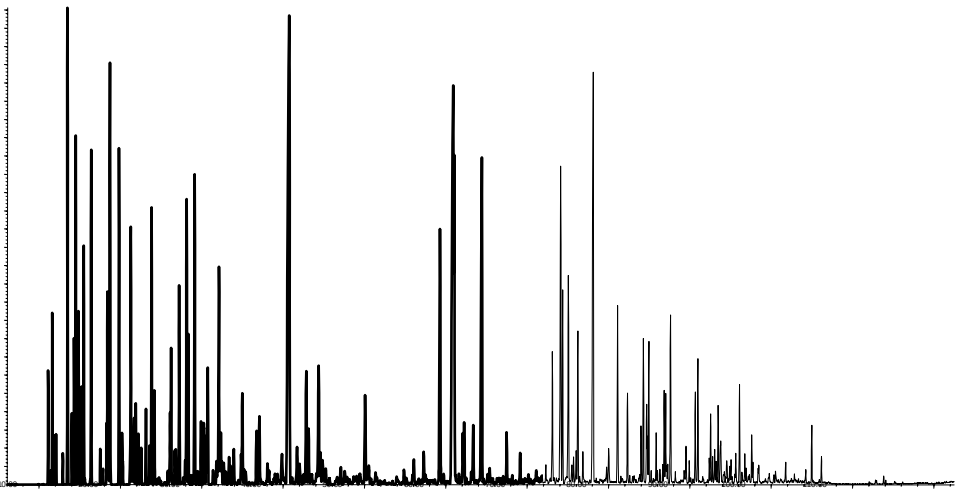
Forensic Environmental Chemistry: differentiatiation of gasoline and their sources

D.A. Birkholz, Enviro-Test Laboratories



Acknowledgments

- Michael Langdeau, ETL - PONA GC/MS analysis
- Tammy Henderson, ETL - data interpretation/reduction
- Jarrod Roberts, ETL - gasoline weathering experiments

Issues

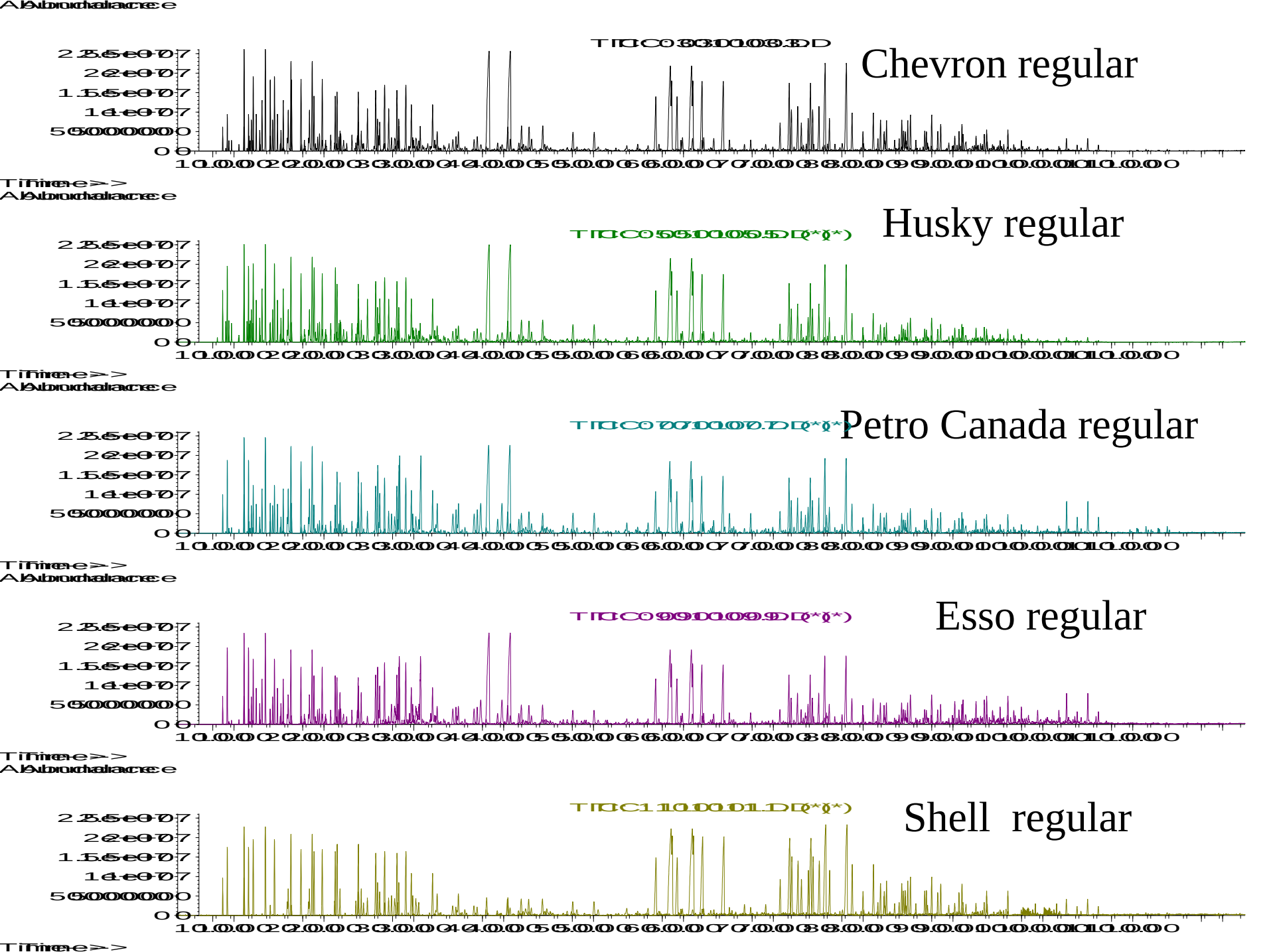
- Contamination of soil, water, sediment and biological samples with petroleum hydrocarbon. Desire to determine source
- Co-mingled plumes leaking to environment, several source. Who is and is not responsible
- Accidental releases from unknown sources. Who is responsible
- Property transactions and issues of liability concerning contamination.
- Properties may exchange hands many times and may be exposed to different activities and petroleum products
- Land lease issues and contamination from past tennants
- Deepest pocket usually deemed responsible

Gasoline

- 965 compounds identified in gasoline - CAN/CGSB-3.0 No. 14.3
- Hydrocarbon constituents generally span a range from C_3 - C_{12}
- Constituents conventionally described in terms of major chemical classes, namely: PIANO
- PIANO: paraffins, isoparaffins, aromatics, naphthenes, and olefins

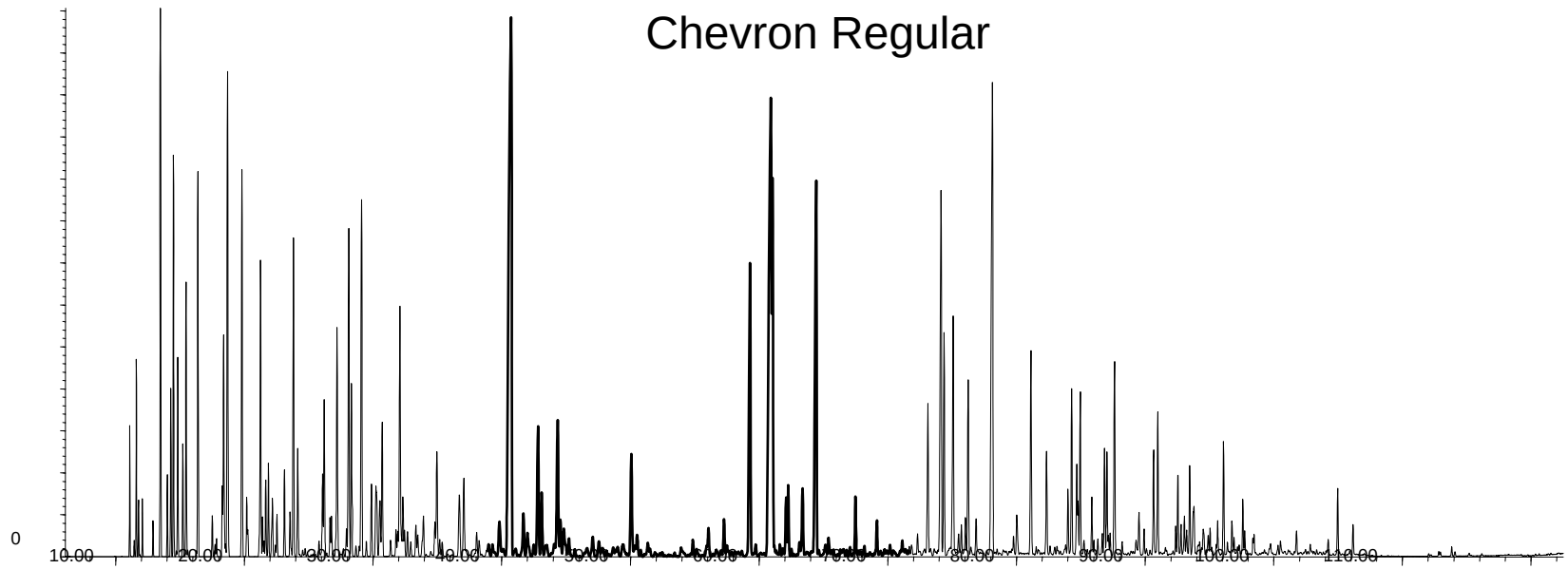
Gasoline

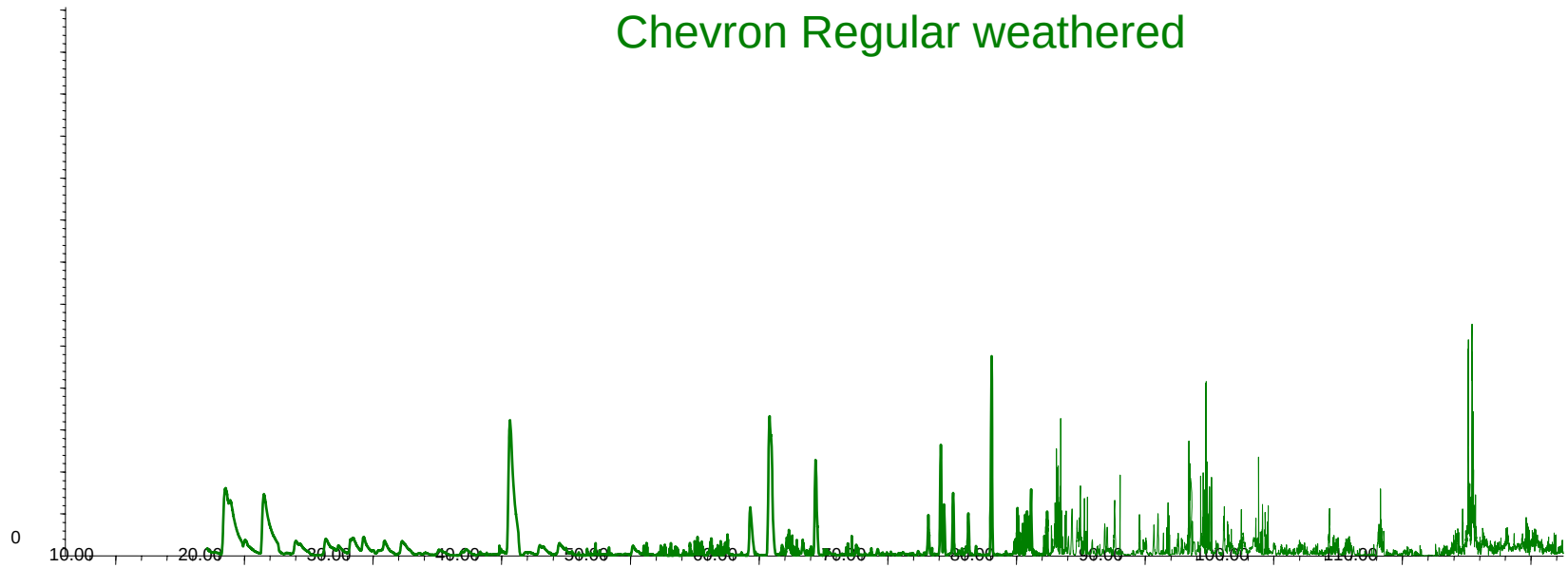
Gasoline type	*Paraffins %*	*Isoparrafins %*	*Aromatics %*	*Naphthenes %*	*Olefins %*
87 Octane	9.59	38.34	38.61	6.10	7.36
89 Octane	9.06	38.13	43.36	3.84	5.60
92 Octane	7.48	39.68	43.36	3.26	6.22


Chevron regular
Husky regular
Petro Canada regular
Esso regular
Shell regular

Historical Forensic Methods

- Gas chromatographic analyses of samples and petroleum products (TPH)
- Method 8015 total extractables
- CAN/CGSB - 3.0 No. 14.3
- BTEX and total purgeables
- Pb, V, Ni
- EDCl and EDBr
- MtBE
- 2-component ratios
- Rb = (B+T)/(E+X)
- CCME method for TPH
- Oxygenated blending agents (alcohols and ethers) by GC/FID
- Dye additives
- Diphenyl disulphides
- Isotopic ratios $^{13}C/^{12}C$, D/H, $^{34}S/^{32}S$ does not change to same extent as the molecular composition during the physical and biological process


Chevron Regular
0
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
110.00


Chevron Regular weathered
0
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
110.00

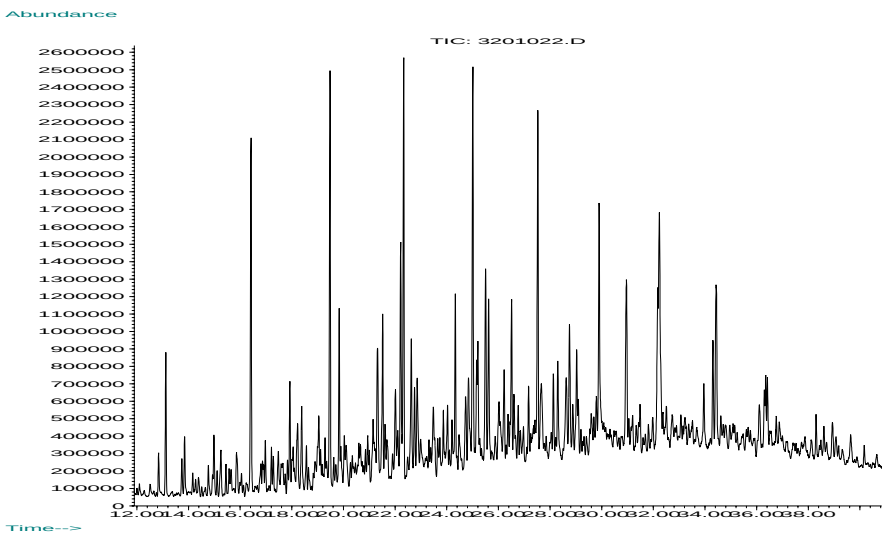
Weathering

- Light molecules evaporate
- Some molecules removed by dissolution into groundwater
- Biodegradation: depends on 1) presence of microbiota with the metabolic capacity to degrade components; 2) the recalcitrance of the compounds in the oil mixture; and 3)growth and activity factors that incluence the microbial population dynamics

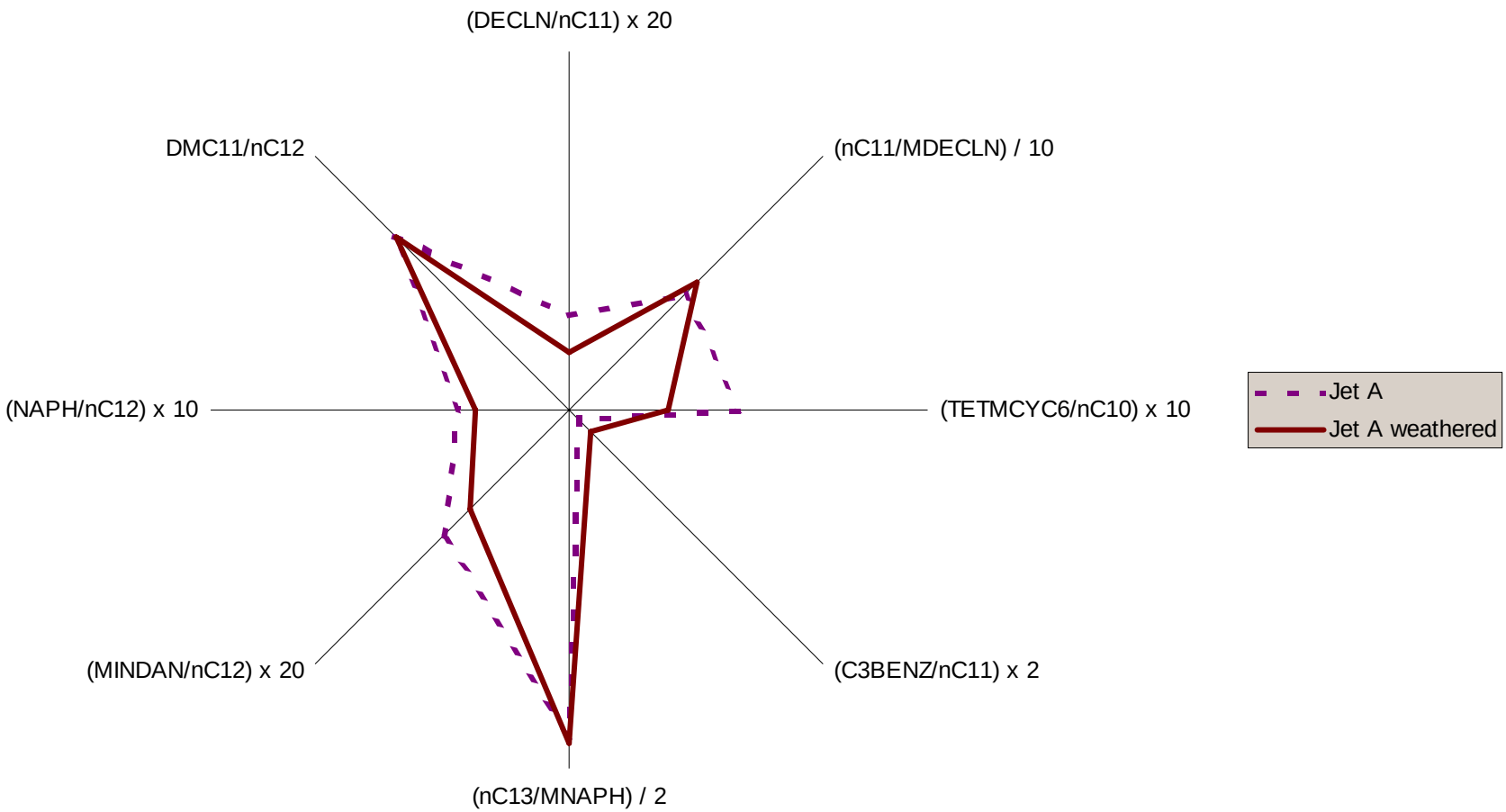
Fingerprinting weathered gasoline

- Aromatic compounds strongly concentrated in the groundwater and soil and to a lesser extent in the free product, relative to the naphthenes, paraffins and isoparraffins.
- Isotopic ratios
- PIANO fingerprinting and diagnostic pairing of compounds with similar water solubility. Plotting of ratios (Sauer and Costa, Environmental Forensics, 4: 319-329, 2003
- Alkylbenzenes and alkylnapthalenes resistent to biodegradation
- C_0 - C_3 - naphthalenes via GC/MS followed by PCA (Sandercok and Pasquier, Forensic Science Intl 140: 43-59, 2004
- Octane index = Iso + T/nC_7 + nC_8 (Schmidt et al, Enviromental Forensics, 4: 75-80, 2003
- Two-dimensional GC (Frysinger et al, J. Forensic Sci. 47: 471-482, 2002

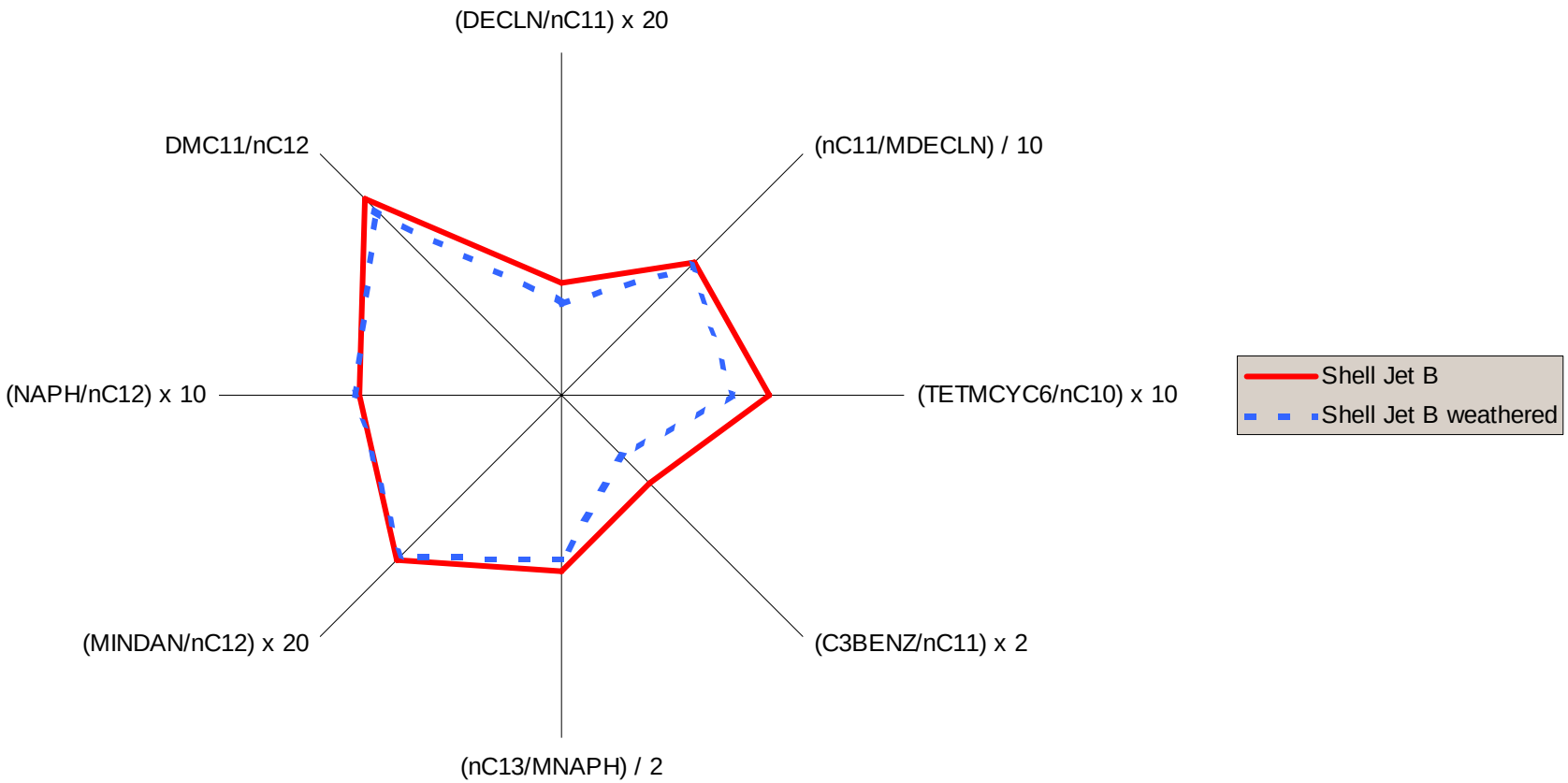
Forensic Chemical Analyses of Petroleum Products
- D.A. Birkholz, Enviro-Test Laboratories
ETL Feb 5, 2001 seminar and SETAC, Nov 11, 2001



Jet A vs Weathered Jet A



Shell Jet B, weathered and unweathered



Methods

Reference gasoline samples obtained as follows:

Chevron, Vancouver, regular and premium

Husky, Prince George, regular and premium

Petro Canada, Edmonton, regular and premium

ESSO, Edmonton, regular and premium

Shell, Edmonton, regular and premium

Weathering

- 2 mL gasoline added to 10 mL tapwater
- Vortex/sonication
- 5 mL of water carefully removed
- transfer to 15 mL centrifuge tube add 2 mL pentane
- vortex/sonication
- pentane removed and analyzed

GC/MS Analysis

- 100m x 0.25mm Petrocol DH column
- Agilent 5973 GC/MS
- Split injection (gasoline)
- Splitless injection (weathered gasoline)
- Peak identification via reference PIANO mix and mass spectra
- Peak selection primarily C4-alkyl benzenes, heavier alkanes (C10 - C12), Indane, naphthalene and methyl naphthalenes

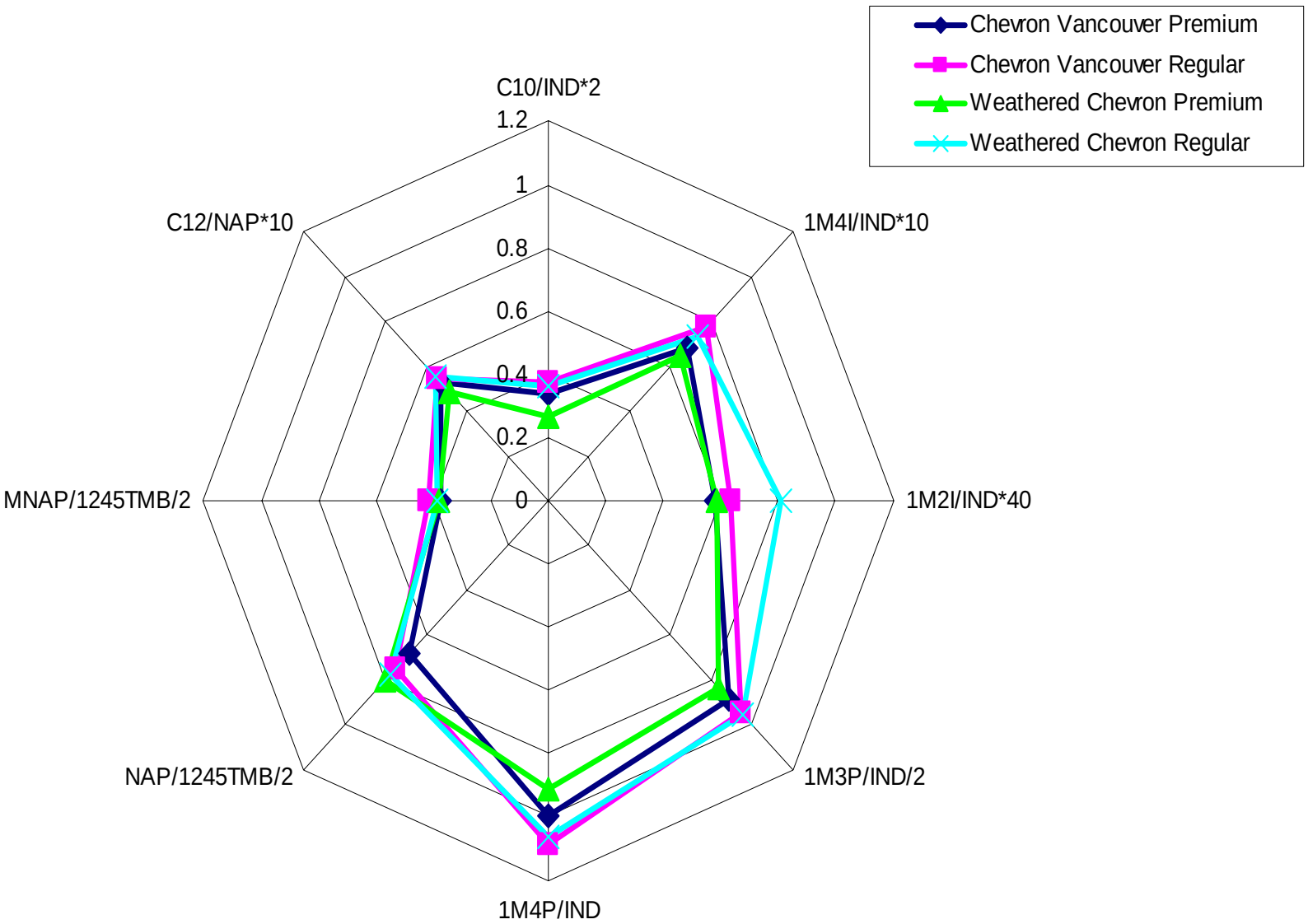
Compound Selection

Name of compound	*Abbreviation*
Decane	C10
1-Methyl-4-Isopropylbenzene	1M4I
Indane	IND
1-Methyl-2-isopropylbenzene	1M2I
1-Methyl-3-n-propylbenzene	1M3P
1-Methyl-4-n-propylbenzene	1M4P
1,2,4,5-Tetramethylbenzene	1245TMB
Naphthalene	NAPH
Dodecane	C12
2-Methylnaphthalene	2MNAP
1-Methylnaphthalene	1MNAP

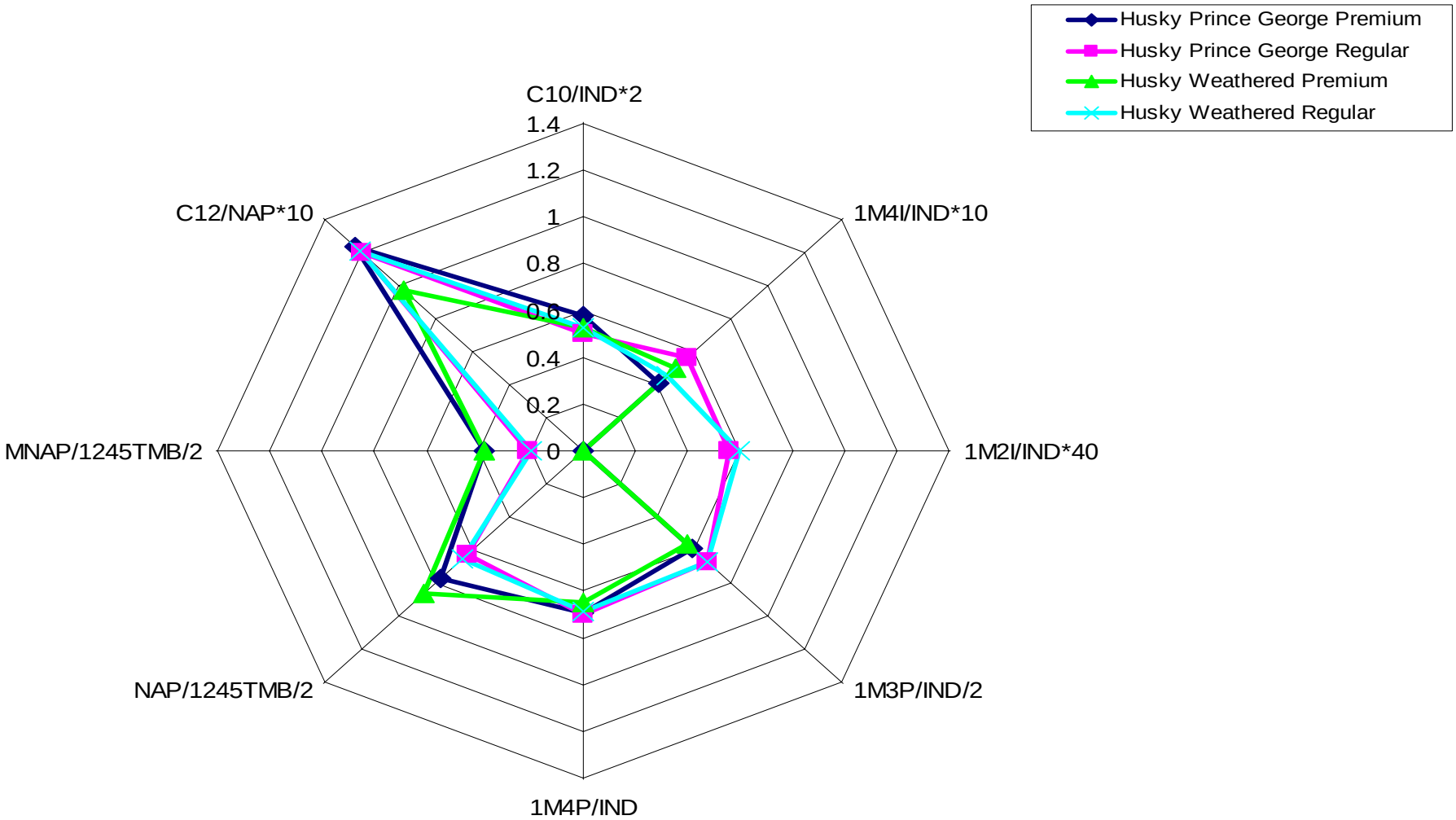
Peak Ratio Selection

Compound Ratio	*Ions monitored*
C10/IND * 2	57/117
1M4I/IND * 10	119/117
1M2I/IND * 40	119/117
1M3P/IND * 2	105/117
1M4P/IND/2	105/117
NAPH/1245TMB/2	128/119
ΣMNAP/1245TMB/2	142/119
C12/NAPH * 10	57/128

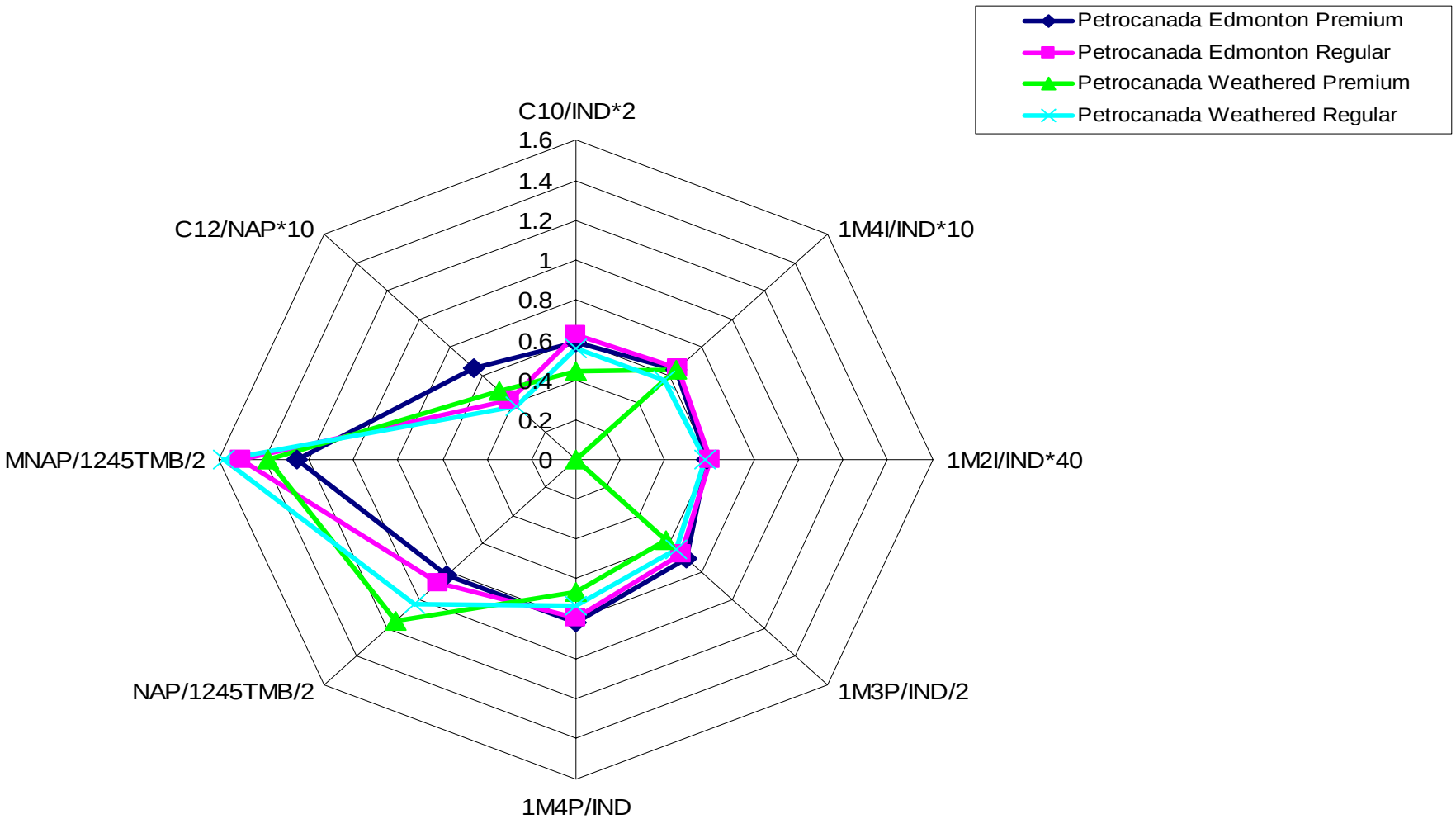
Chevron Vancouver



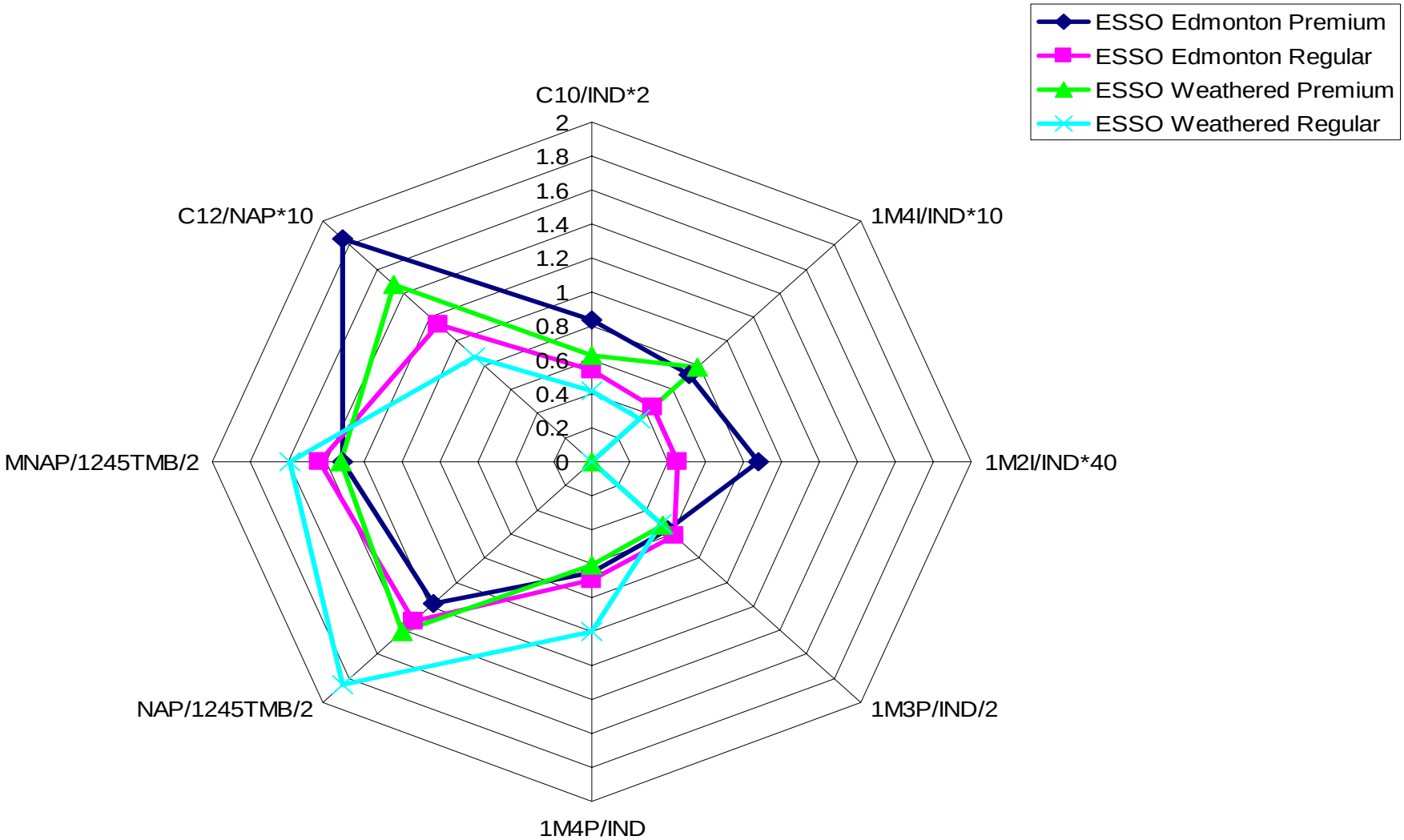
Husky Prince George



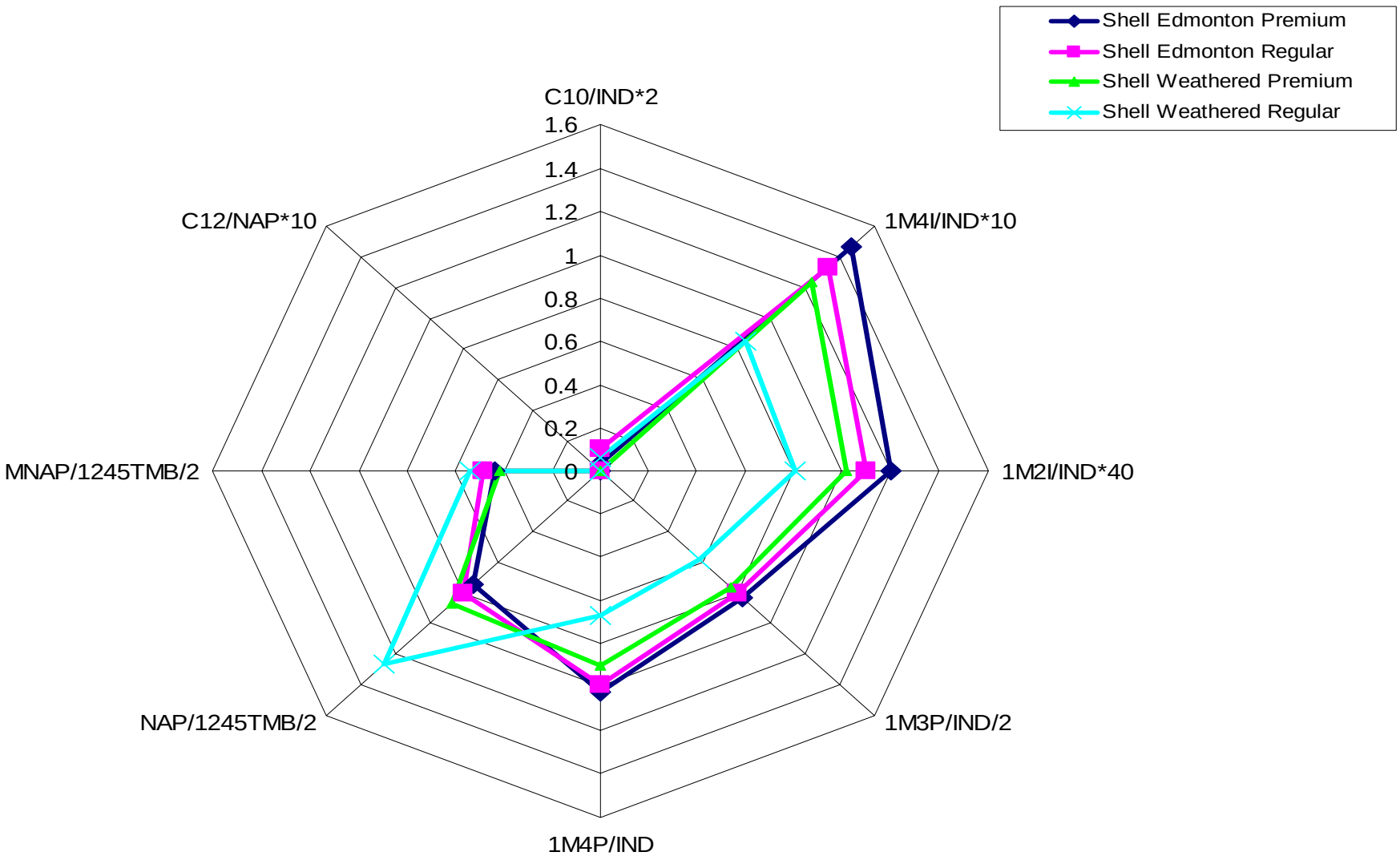
Petrocanada Edmonton



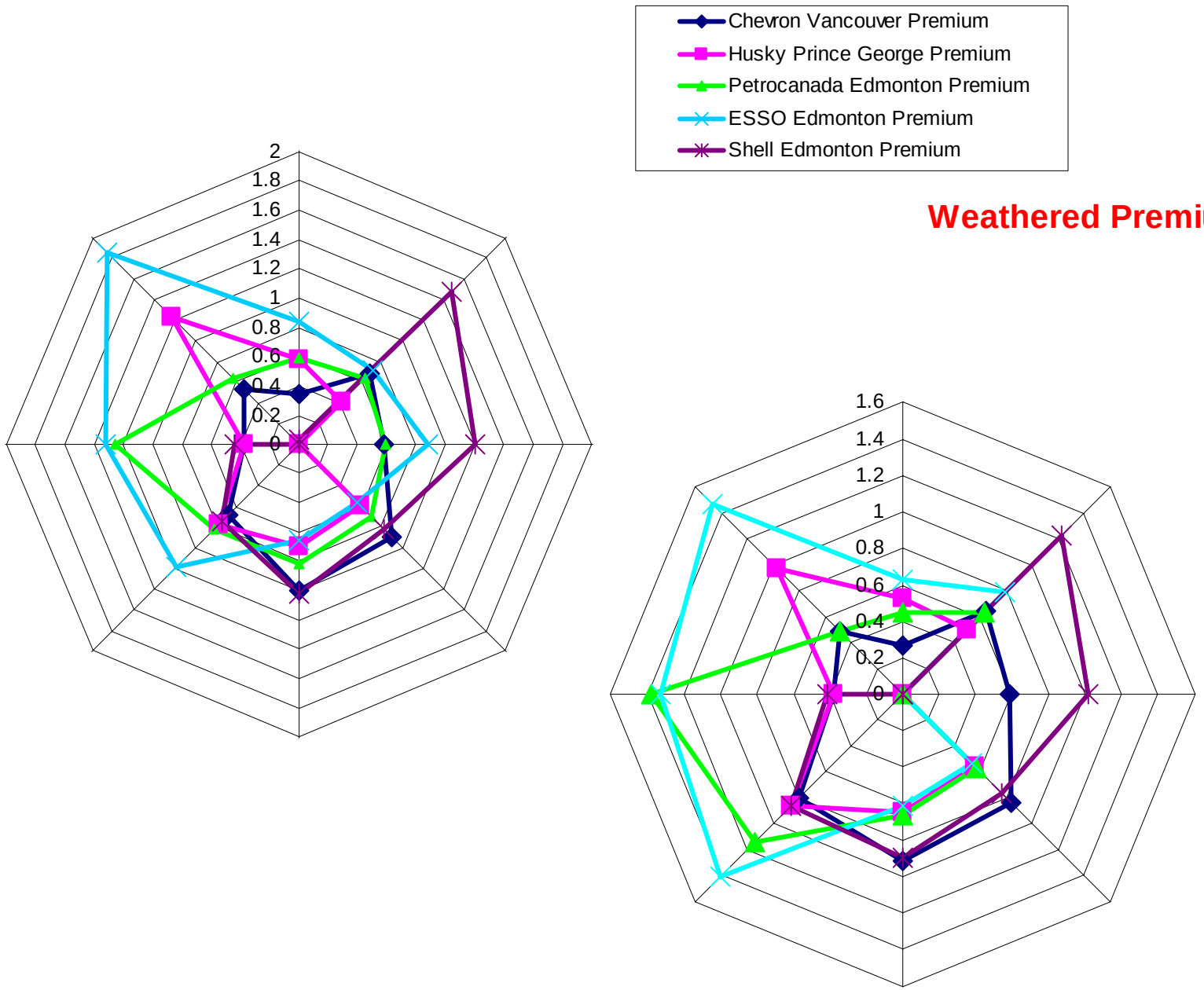
ESSO Edmonton



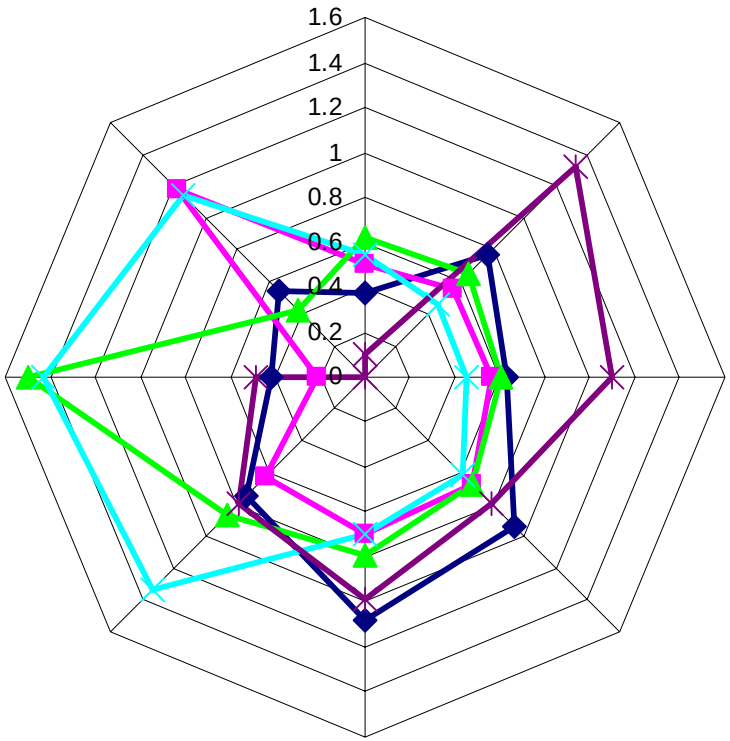
Shell Edmonton



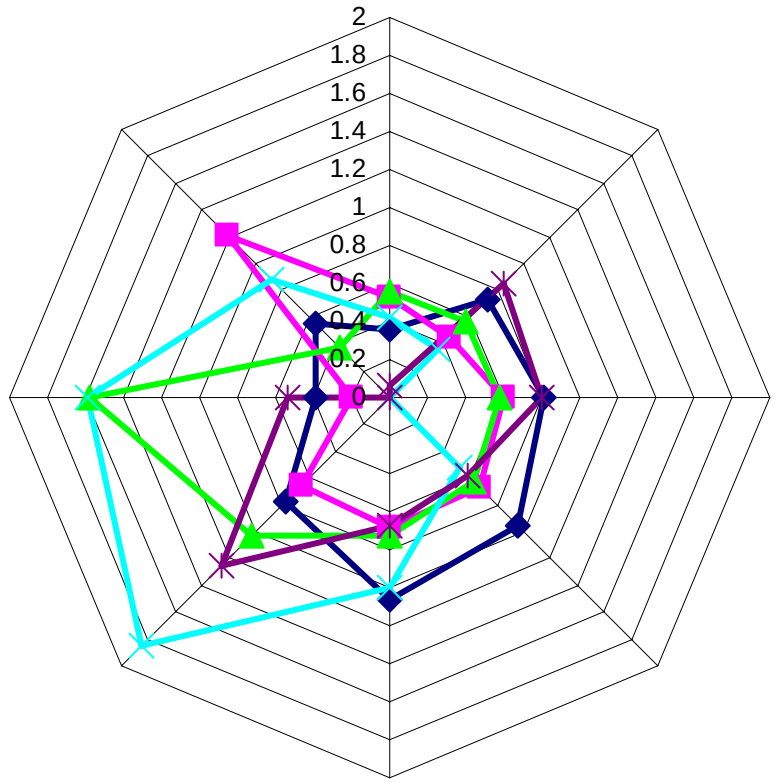
Premium Gasoline



Regular Gasoline



Weathered Regular



Conclusions

- PONA GC/MS analysis followed by selection of select hydrocarbons (saturates, alkylated benzenes, and naphthalenes), followed by specific ratio plots using Excel radar, resulted in unique plots for gasoline obtained from the five Western refineries.
- Using this technique, free product could be referenced to a refinery source. Distinctive plots are observed for each refinery
- Weathered gasoline, i.e. water soluble fraction gave rise to distinctive radar plots showing that environmental samples could be delineated as similar or different, e.g. pieziometer - gasoline contaminated groundwater samples
- Weathered gasoline - although some differences in radar plots were observed relative to fresh gasoline, the profiles were generally similar to allow for product source identification.

Future Directions

- Soil percolation studies followed by analysis of the soil and leachate
- Plots using differing compounds and generating differing ratios to see if we can make weathered and unweathered samples look more similar
- Collection of more gasoline samples to determine if differing refinery dates impact the plots

Acknowledgements

- Funding for this research provided by Enviro-Test Laboratories