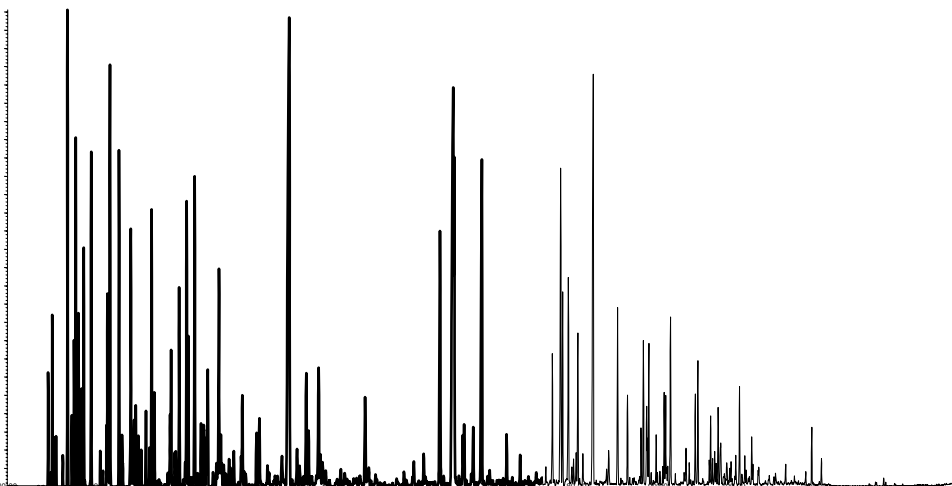


Forensic Environmental Chemistry: differentiation of gasoline and their sources

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 tenants
- Deepest pocket usually deemed responsible

Gasoline



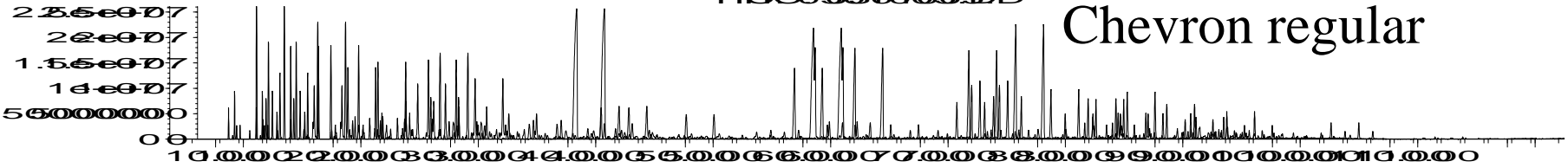
- 965 compounds identified in gasoline - CAN/CGSB-3.0 No. 14.3
- Hydrocarbon constituents generally span a range from C_3 - C_{12}
- Constituents conventionally described in terms of major chemical classes, namely: PIANO
- PIANO: paraffins, isoparaffins, aromatics, naphthenes, and olefins

Gasoline

<i>Gasoline type</i>	<i>Paraffins</i> %	<i>Isoparaffins</i> %	<i>Aromatics</i> %	<i>Naphthenes</i> %	<i>Olefins</i> %
<i>87 Octane</i>	9.59	38.34	38.61	6.10	7.36
<i>89 Octane</i>	9.06	38.13	43.36	3.84	5.60
<i>92 Octane</i>	7.48	39.68	43.36	3.26	6.22

TIC0330108.D

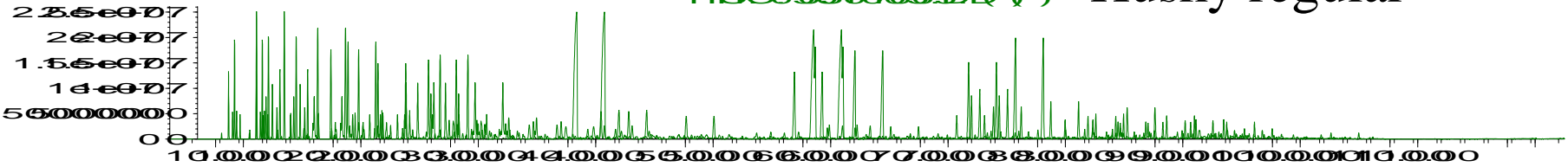
Chevron regular



Time>>
Abundance

TIC0550106.D(*)

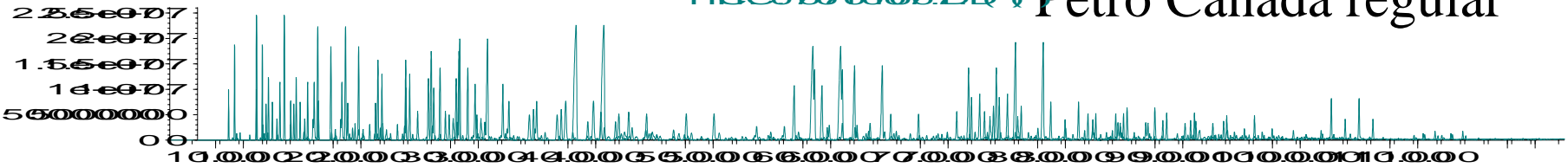
Husky regular



Time>>
Abundance

TIC07070107.D(*)

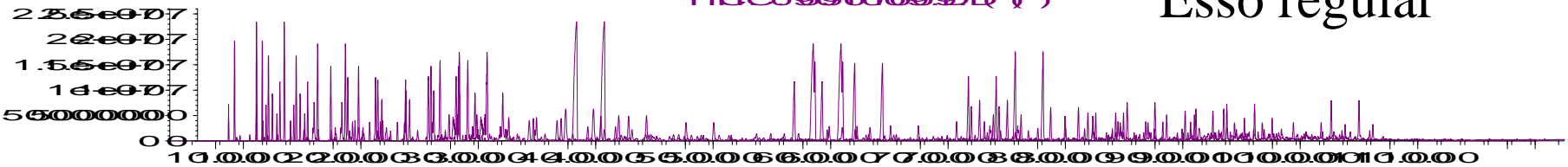
Petro Canada regular



Time>>
Abundance

TIC0990109.D(*)

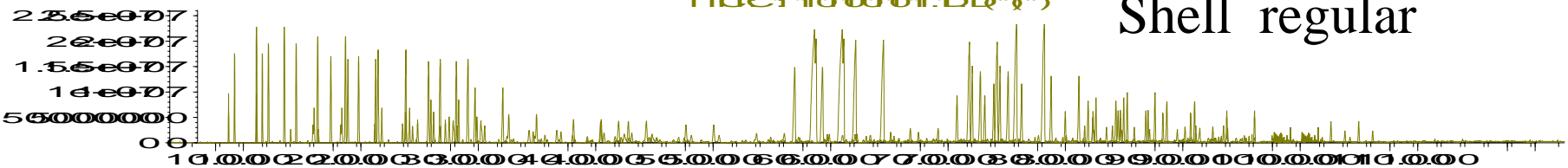
Esso regular



Time>>
Abundance

TIC1100011.D(*)

Shell regular



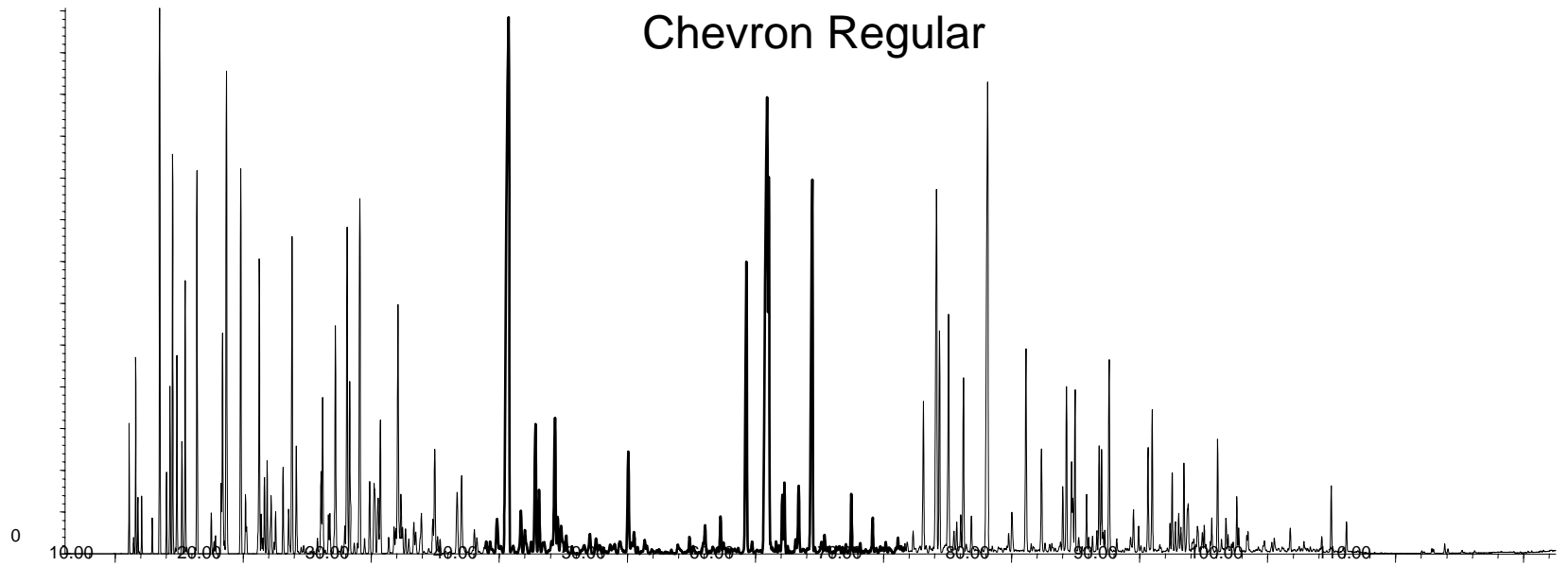
Time>>

Historical Forensic Methods

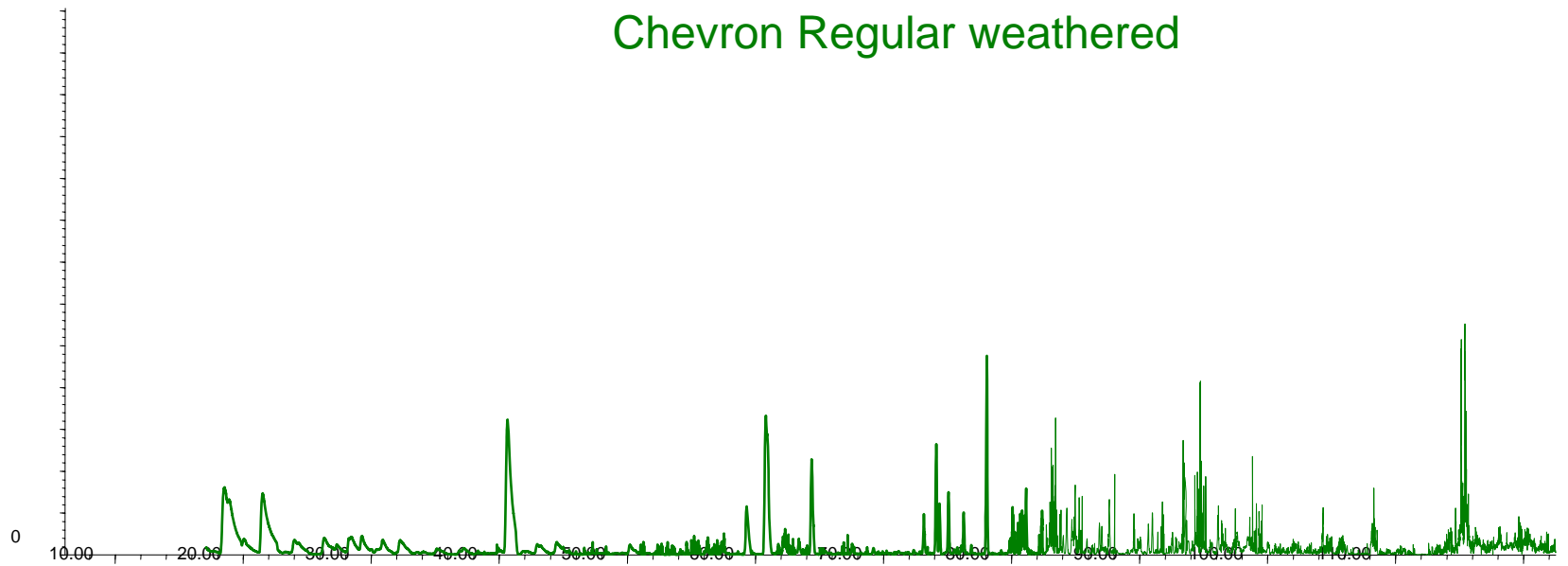


- **Gas chromatographic analyses of samples and petroleum products (TPH)**
- **Method 8015 total extractables**
- **CAN/CGSB - 3.0 No. 14.3**
- **BTEX and total purgeables**
- **Pb, V, Ni**
- **EDCl and EDBr**
- **MtBE**
- **2-component ratios**
- **$R_b = (B+T)/(E+X)$**
- **CCME method for TPH**
- **Oxygenated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

Chevron Regular



Chevron Regular weathered



Weathering



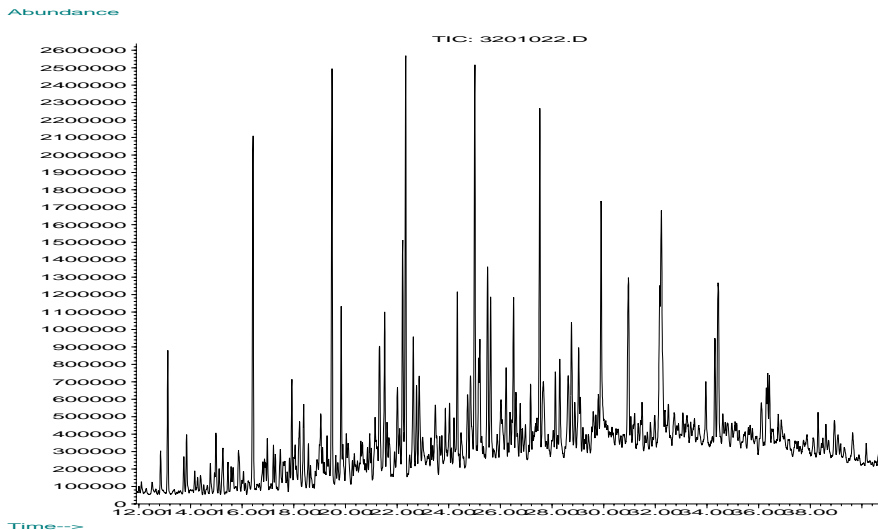
- Light molecules evaporate
- Some molecules removed by dissolution into groundwater
- Biodegradation: depends on 1) presence of microbiota with the metabolic capacity to degrade components; 2) the recalcitrance of the compounds in the oil mixture; and 3) growth and activity factors that influence the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

Fingerprinting weathered gasoline

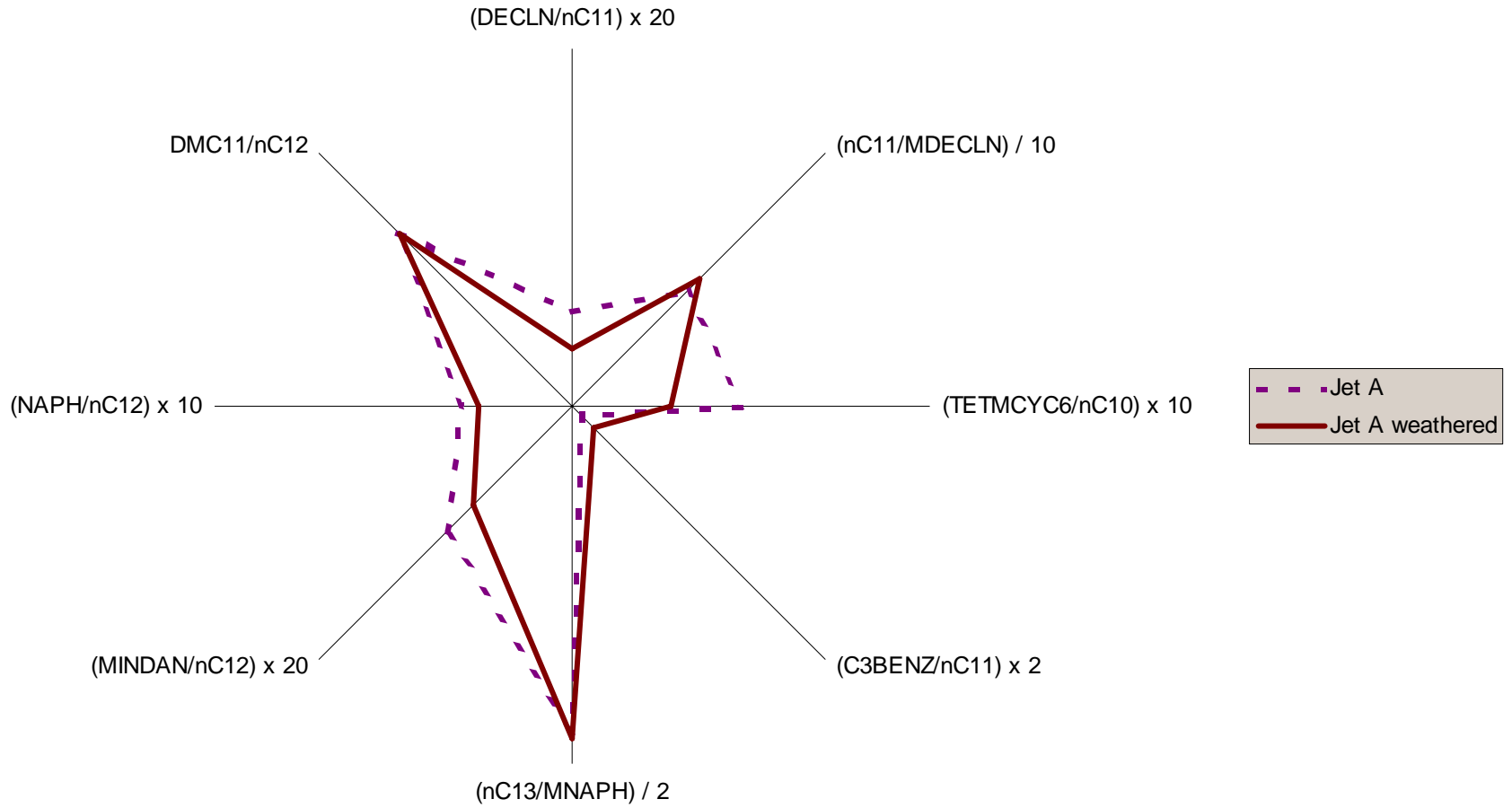
- Aromatic compounds strongly concentrated in the groundwater and soil and to a lesser extent in the free product, relative to the naphthenes, paraffins and isoparaffins.
- Isotopic ratios
- PIANO fingerprinting and diagnostic pairing of compounds with similar water solubility. Plotting of ratios (Sauer and Costa, Environmental Forensics, 4: 319-329, 2003)
- Alkylbenzenes and alkyl naphthalenes resistant to biodegradation
- C₀ - C₃ - naphthalenes via GC/MS followed by PCA (Sandercock and Pasquier, Forensic Science Intl 140: 43-59, 2004)
- Octane index = Iso + T/nC₇ + nC₈ (Schmidt et al, Environmental Forensics, 4: 75-80, 2003)
- Two-dimensional GC (Frysiner et al, J. Forensic Sci. 47: 471-482, 2002)

Forensic Chemical Analyses of Petroleum Products

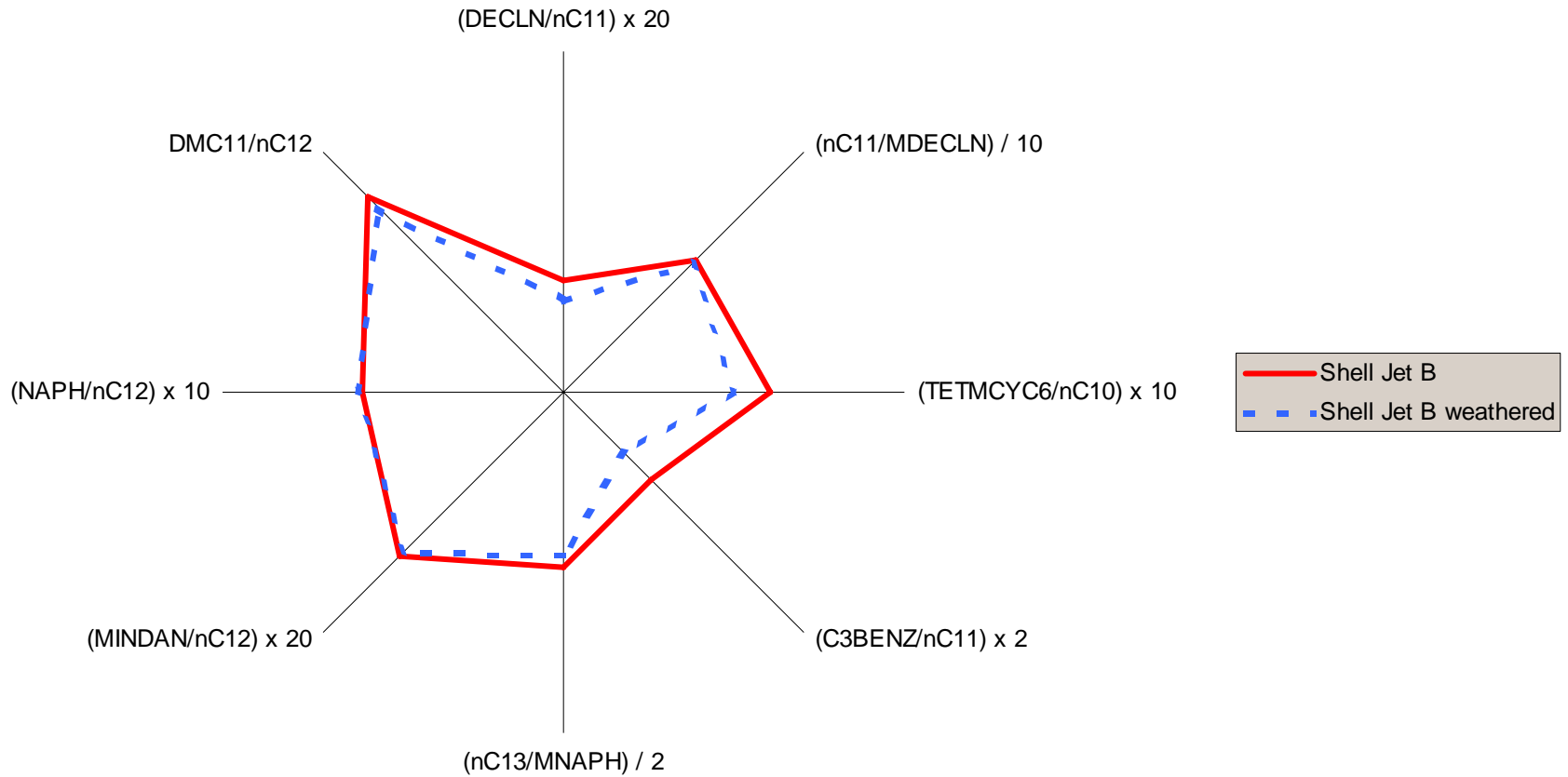
- D.A. Birkholz, Enviro-Test Laboratories
ETL Feb 5, 2001 seminar and SETAC, Nov 11, 2001



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



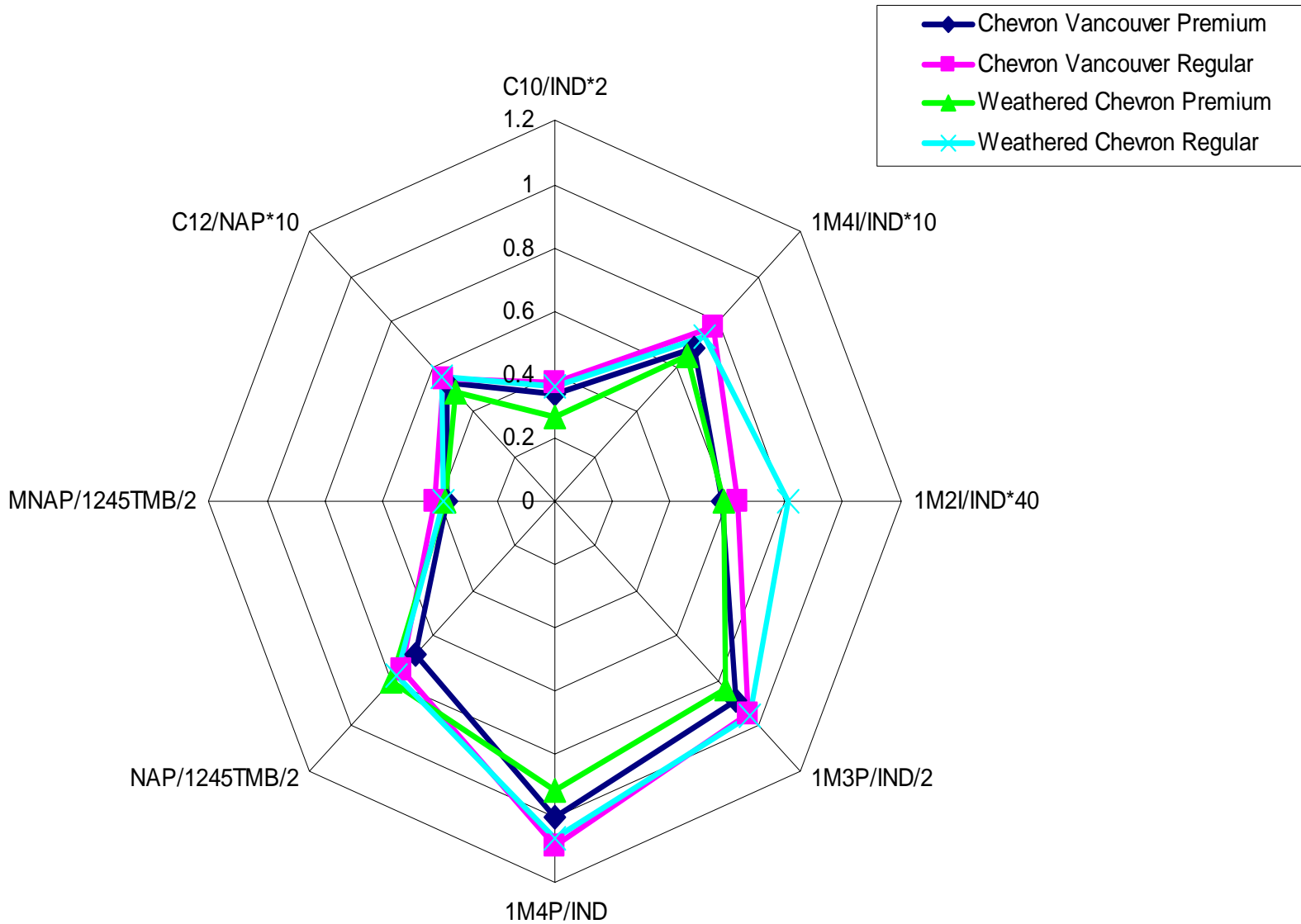
Compound Selection

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

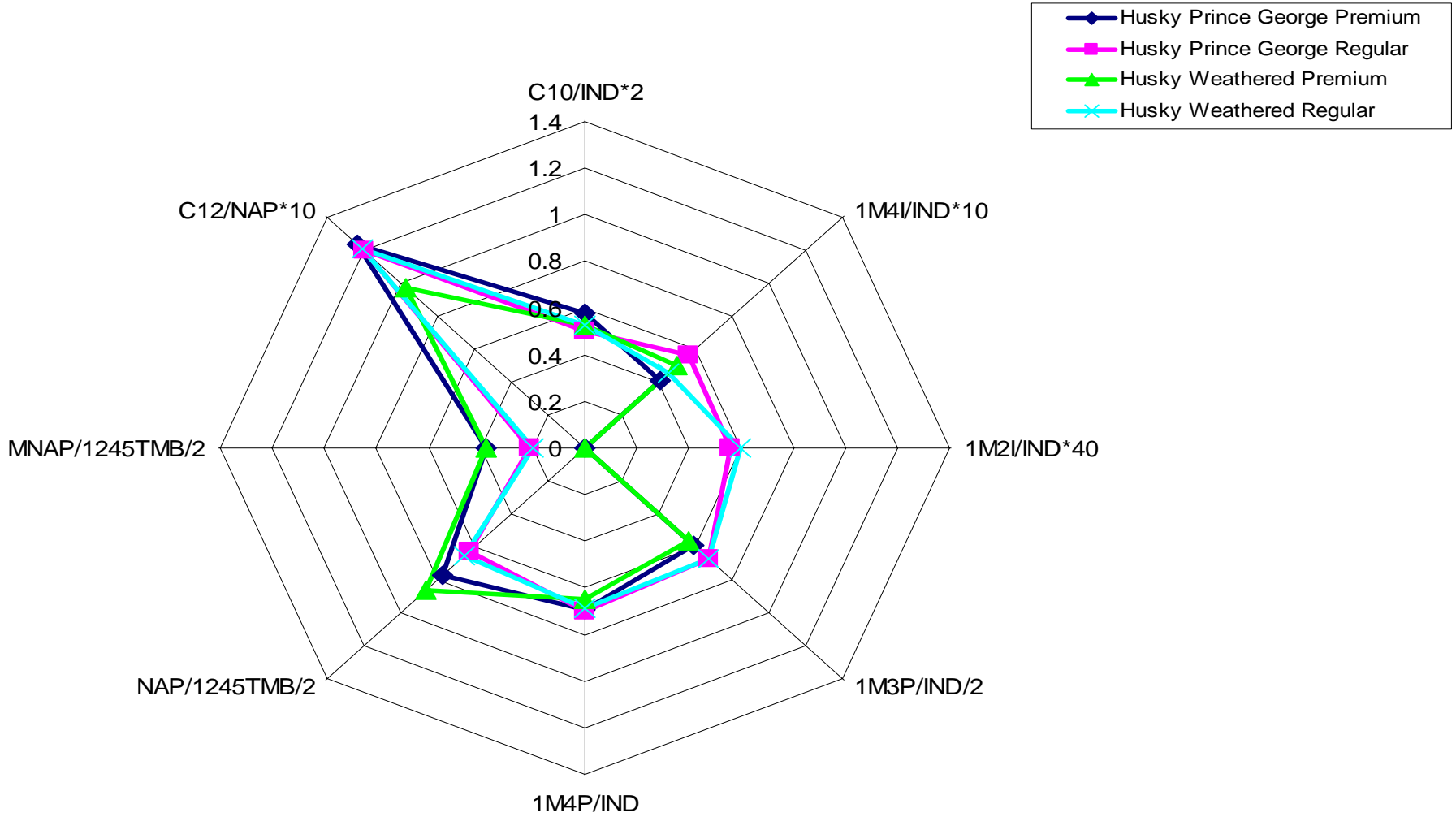
Peak Ratio Selection

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

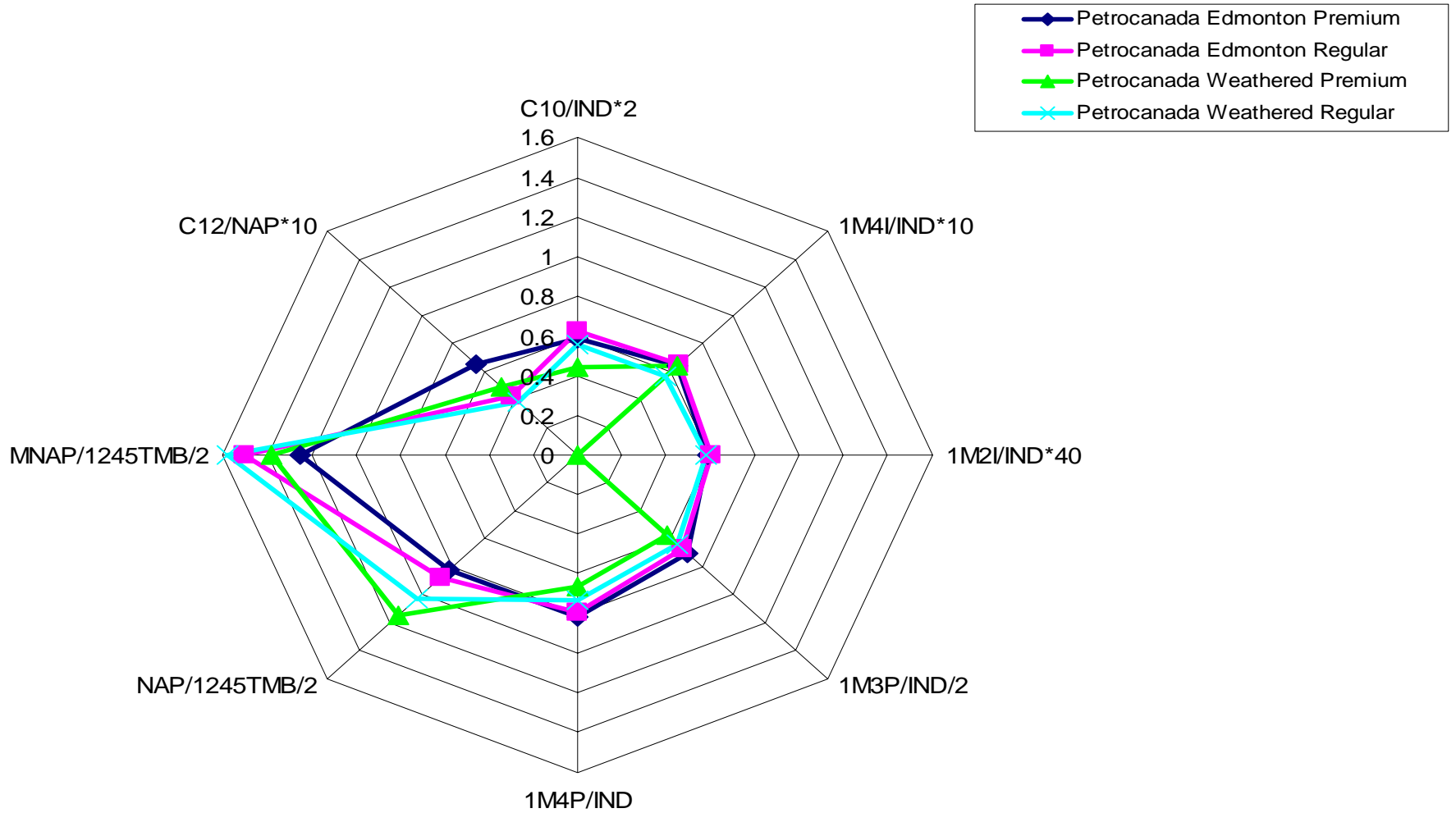
Chevron Vancouver



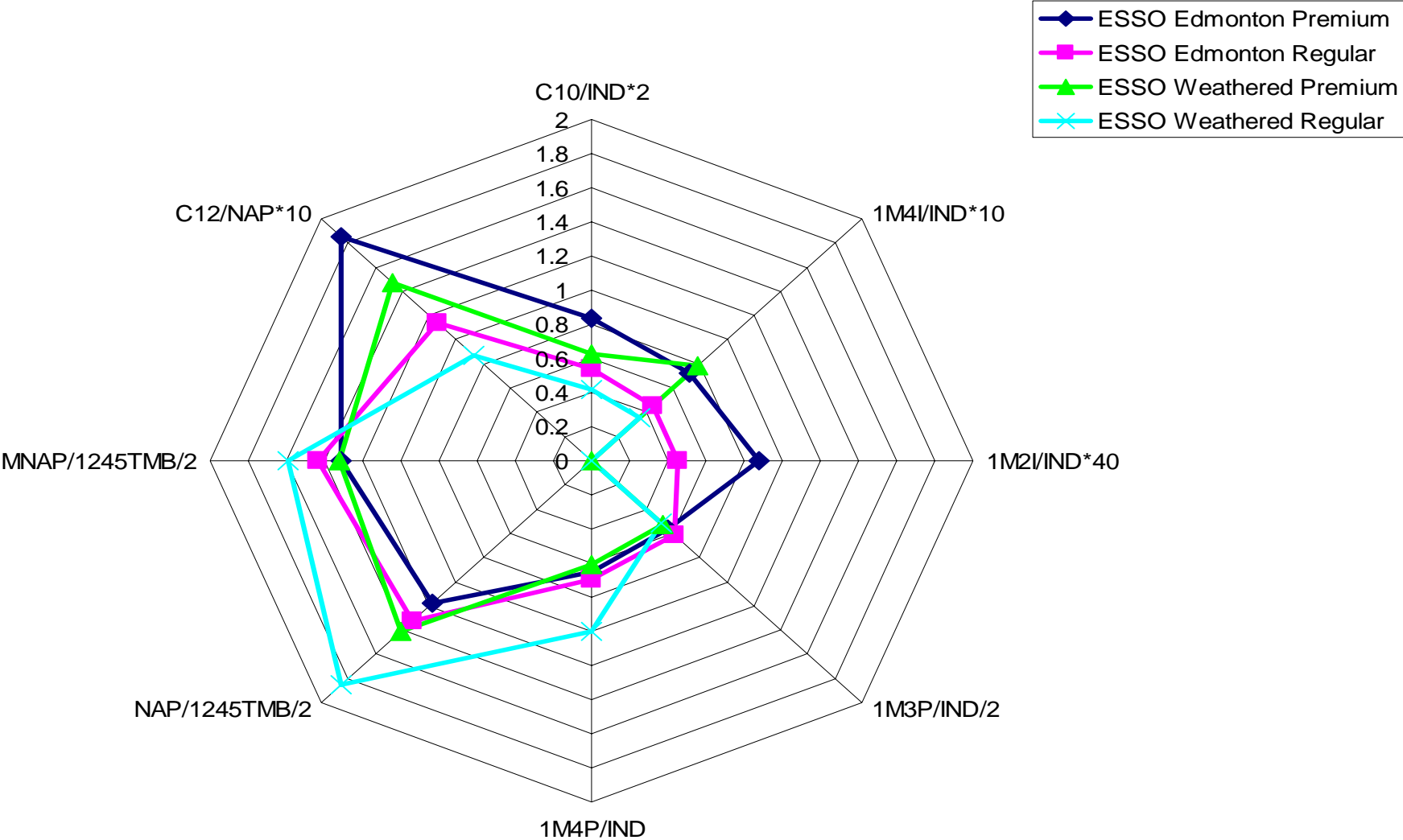
Husky Prince George



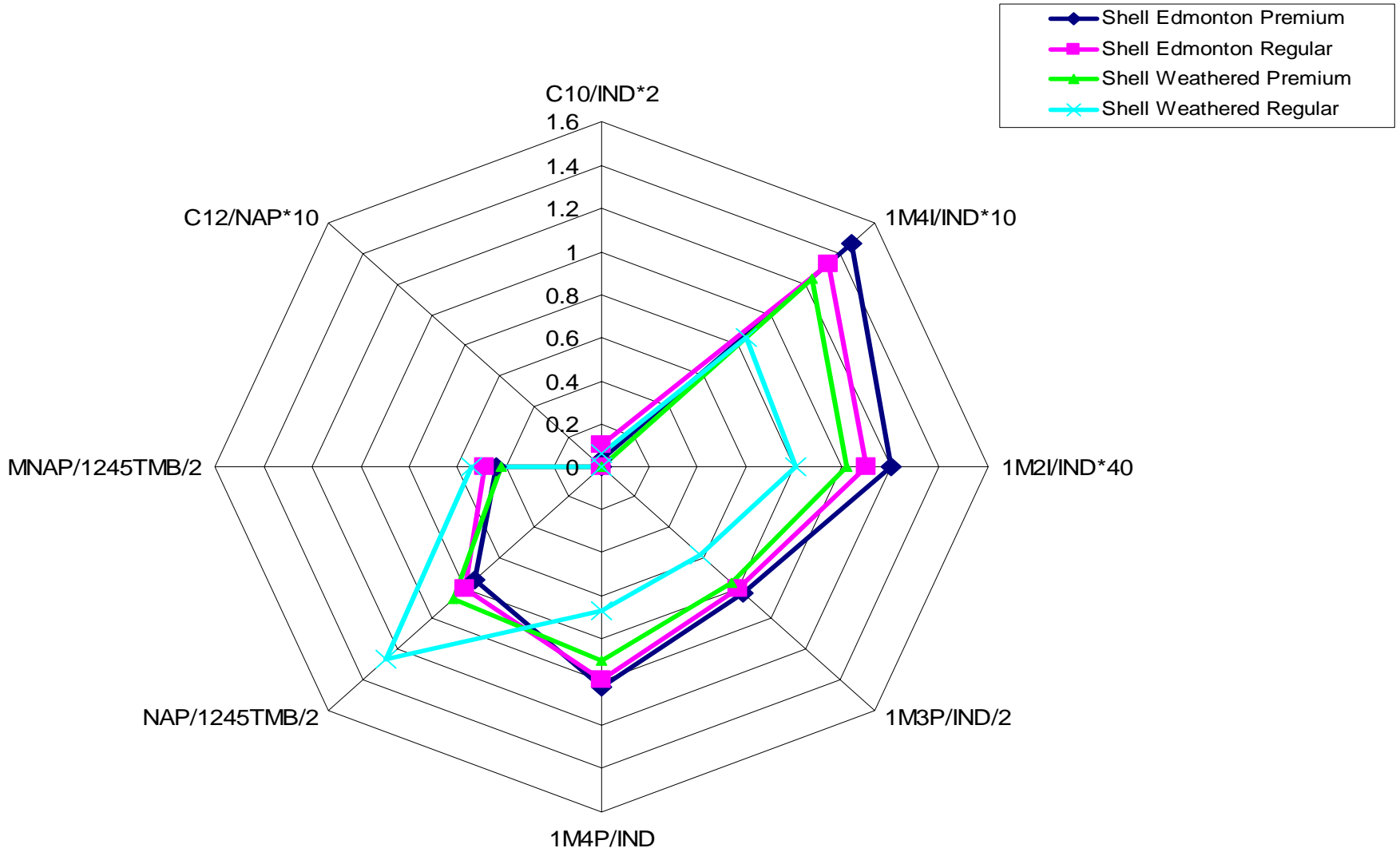
Petrocanada Edmonton



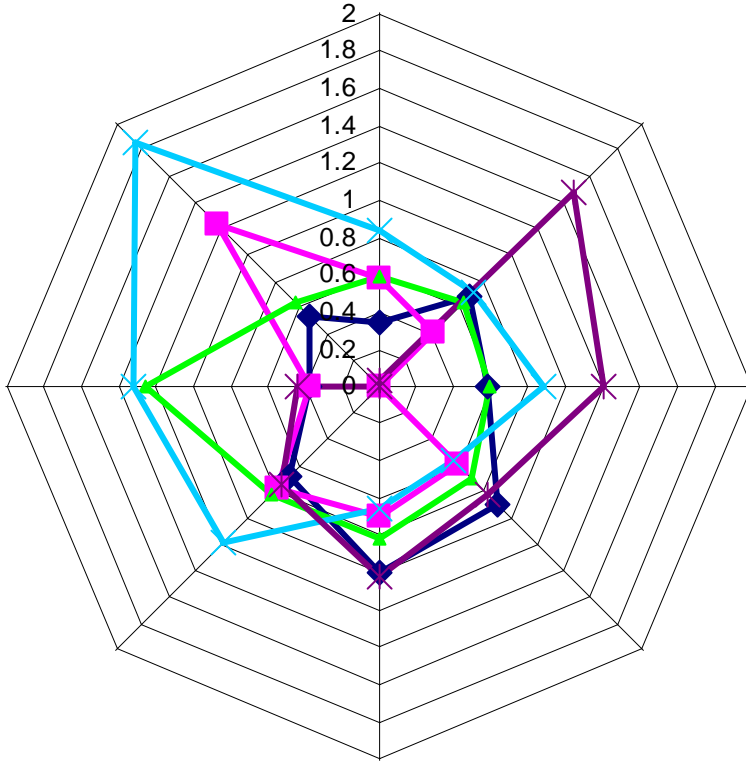
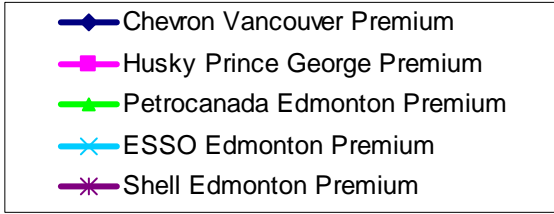
ESSO Edmonton



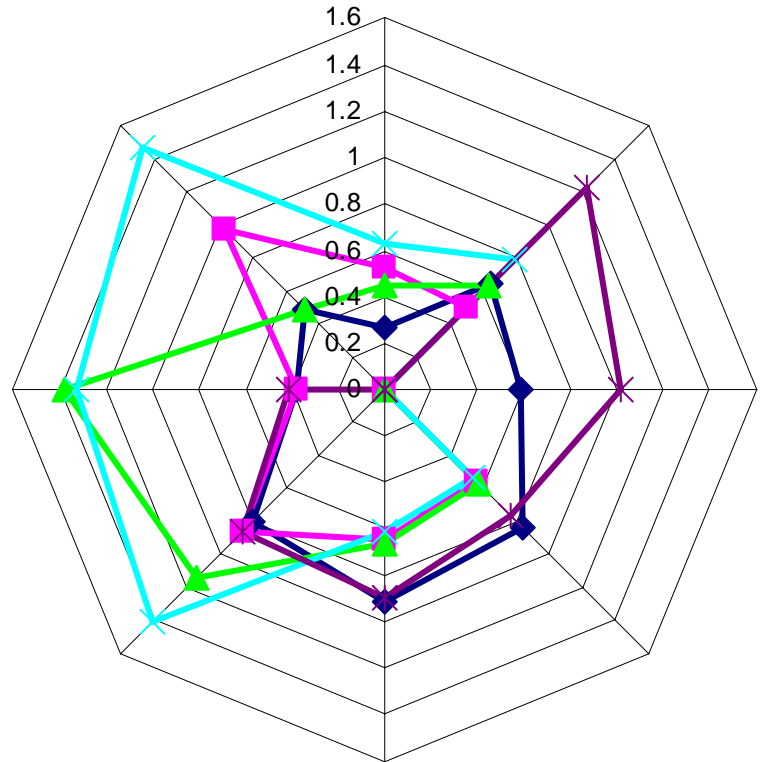
Shell Edmonton



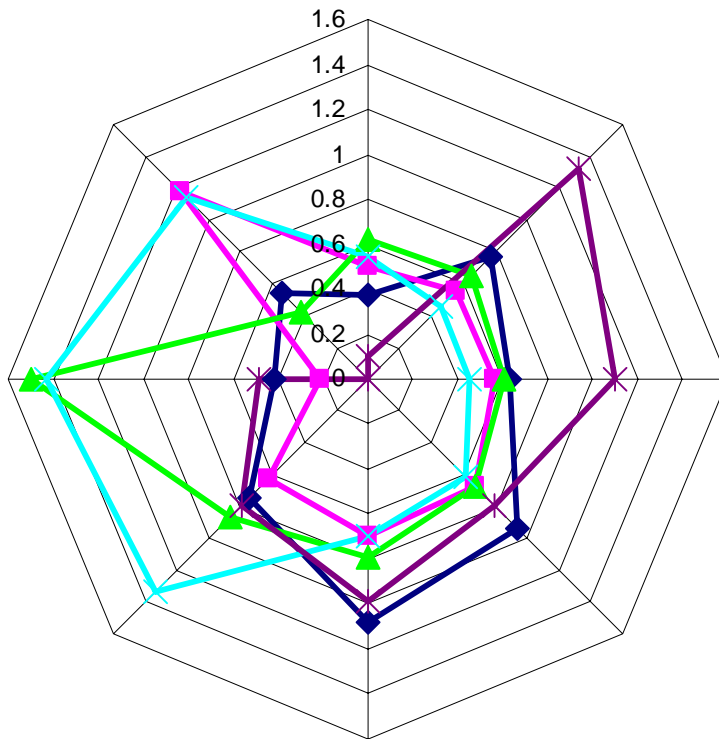
Premium Gasoline



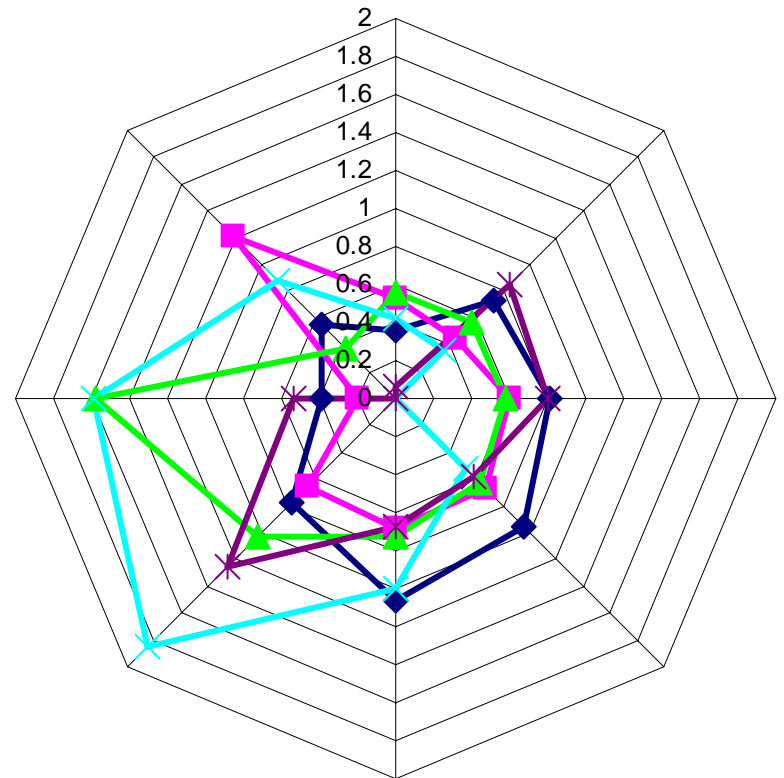
Weathered Premium



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. piezometer - 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