
# Pyrogenic vs Petrogenic Source Determination:
## Diagnostic PAH ratios

Gordon Nelson
Andrew Garrard

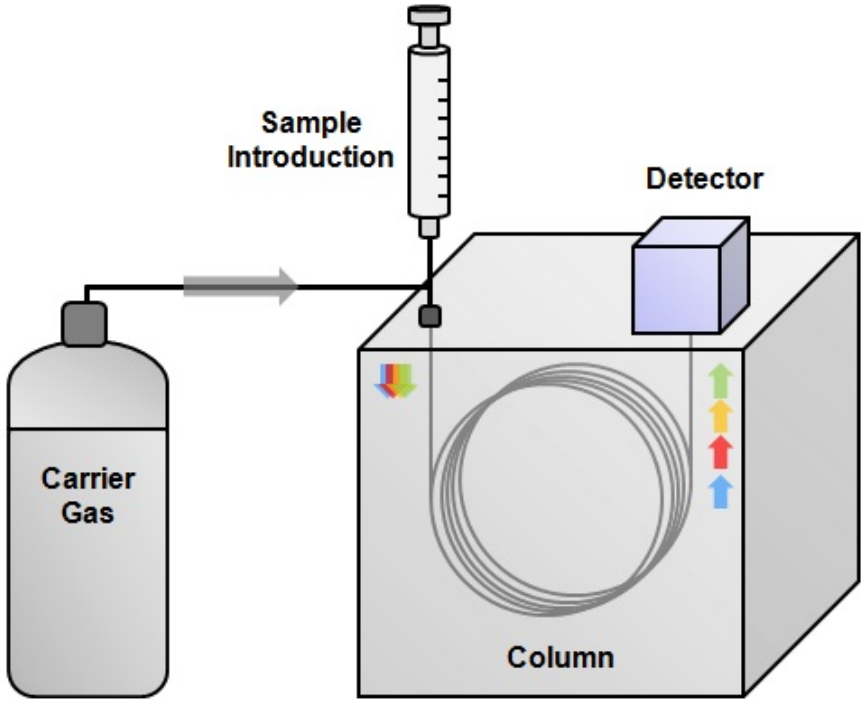
# The Issue

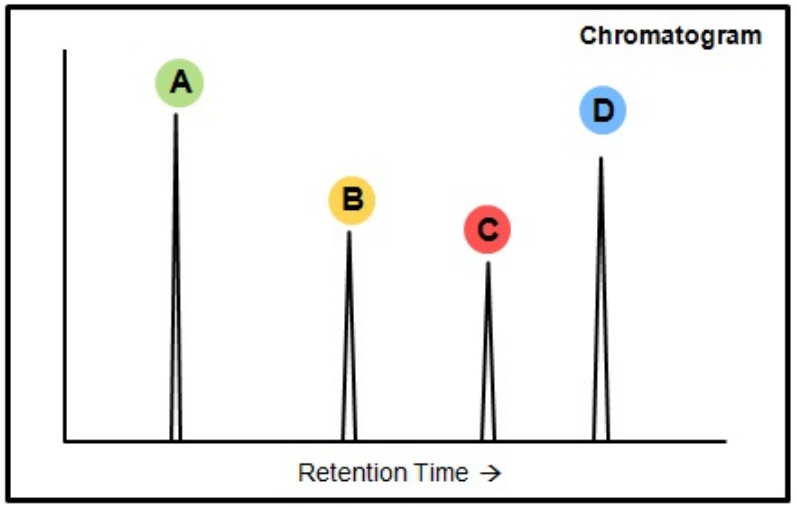
- One of the most common analysis in environmental labs is petroleum hydrocarbon analysis by gas chromatography.

- CCME CWS for PHCs was the starting point for much of what is done in different jurisdictions today.

- Although a common parameter this analysis can sometimes lead to additional interpretation/analysis to clarify the situation

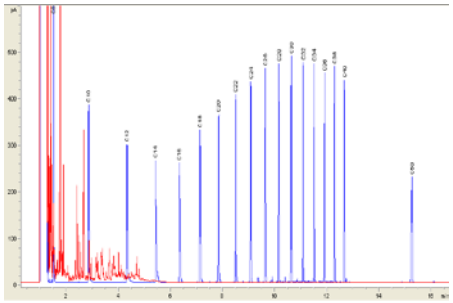
# Gas Chromatography / Flame Ionization Detection



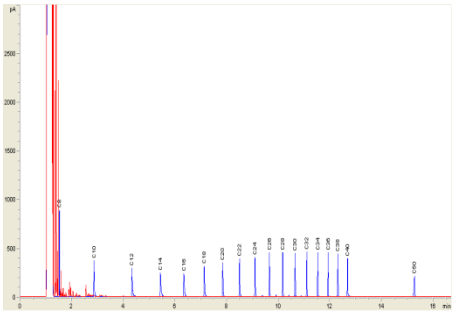
# Identification
## Petroleum Products

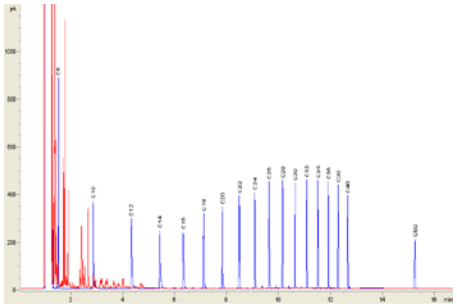
Various



Fresh Gasoline

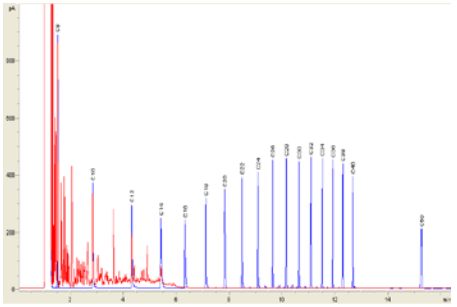
Aviation Gasoline

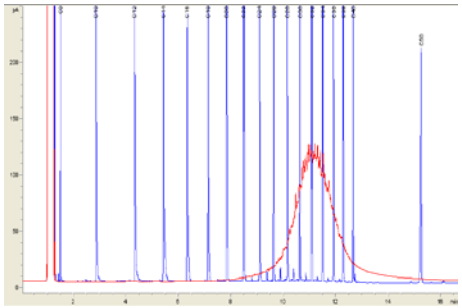




Weathered Gasoline

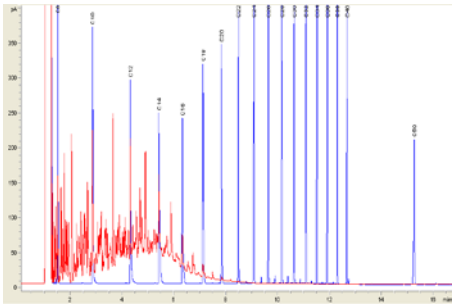
Jet Fuel A



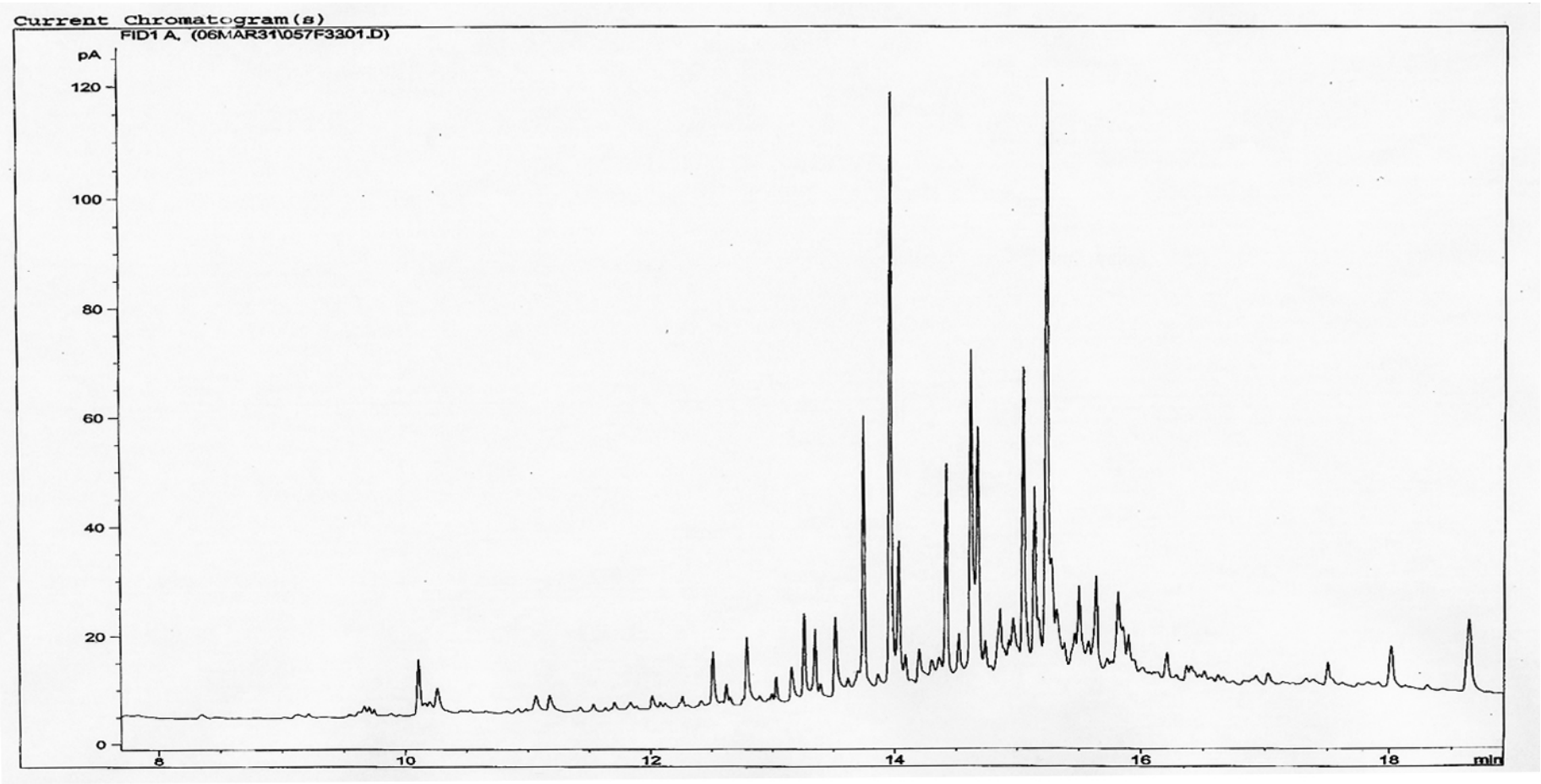


New Motor Oil

Diesel



# Identification
## Biogenic Hydrocarbons




Real sample suspected to be Peat Moss

# Pyrogenic Hits

- Potential co-extractive material could be pyrogenic in nature.
- Combustion by-products won't all be removed by silica gel.
- GC/FID patterns not definitive.
- PAH and extended PAH analysis can be a useful next step.

# PAHs

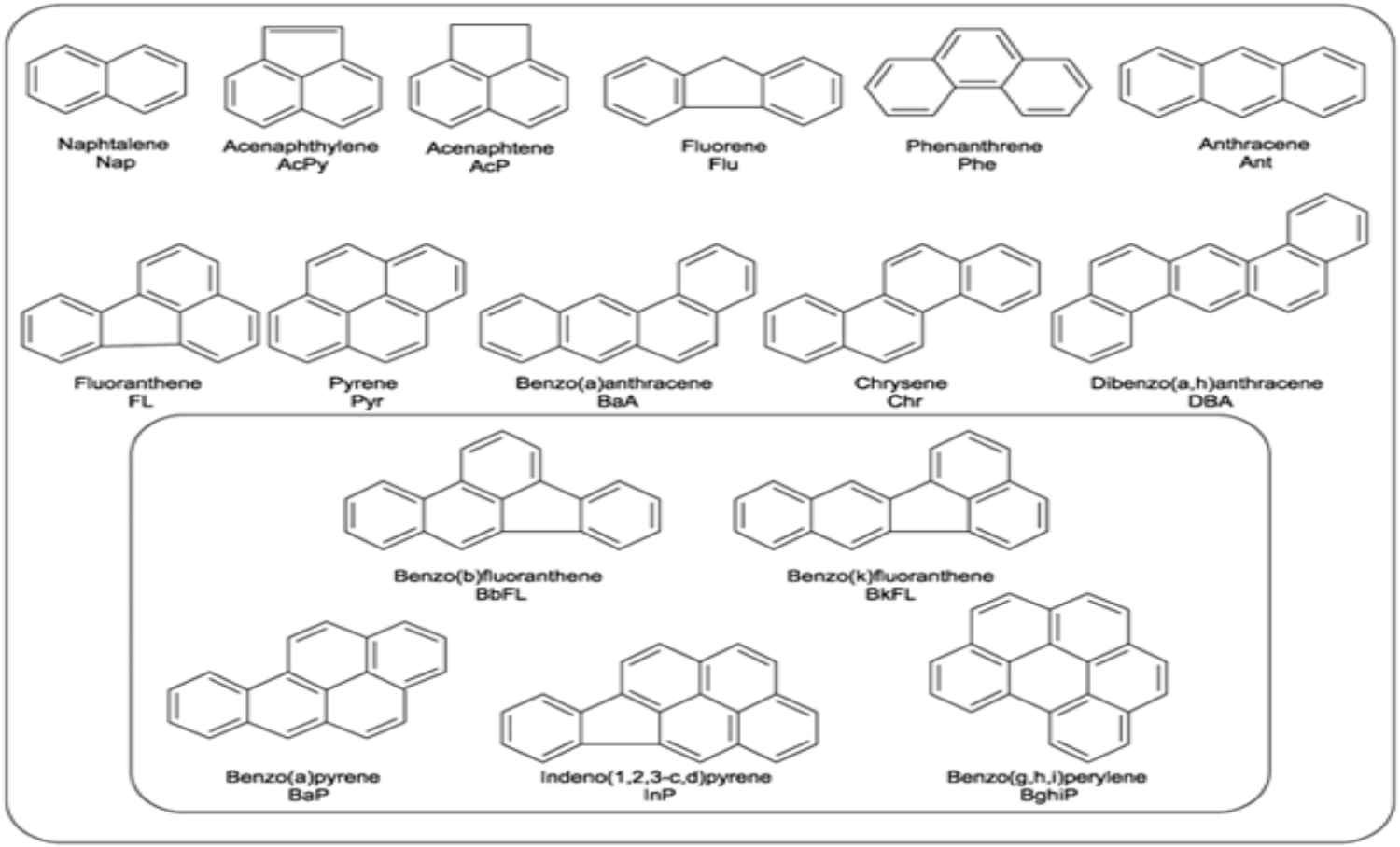



**Figure 1.** Structures of the sixteen PAH studied in this work. The five structures in the small box are the compounds listed in the European Council Directive 98/83/EC. Under each chemical structure are the compound name and its acronym.

# PAH Analysis:

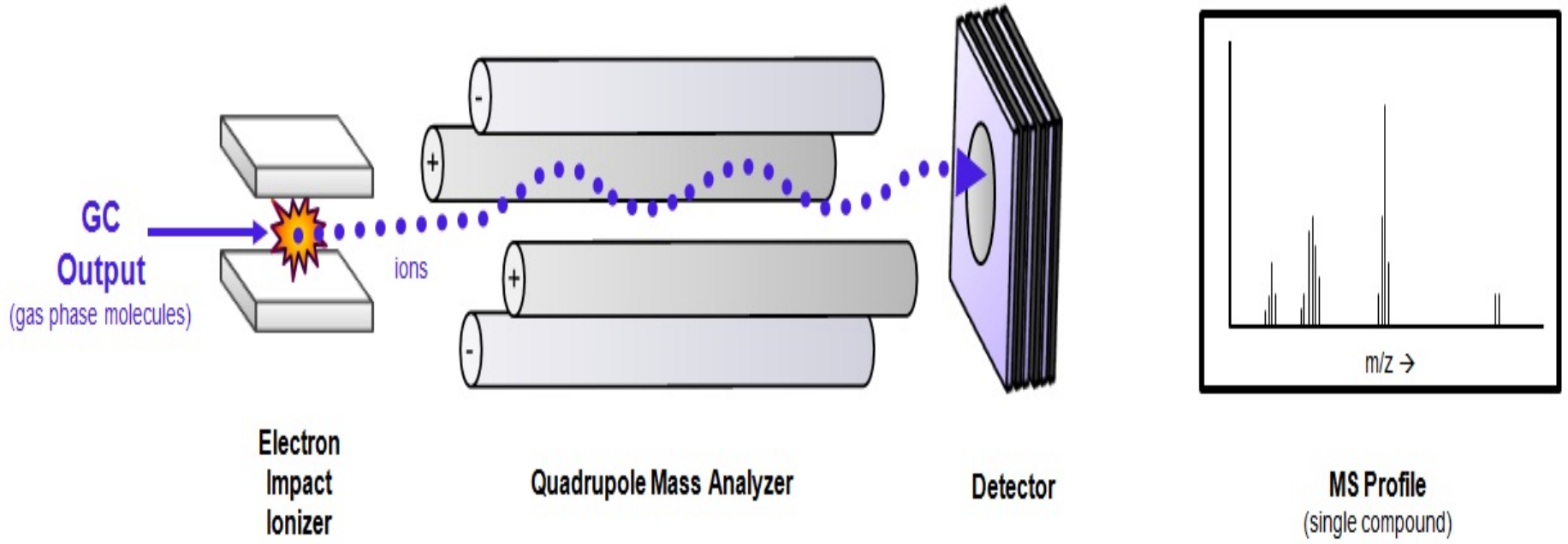
## Extended list

Naphthalene
2-Methylnaphthalene
1-Methylnaphthalene
C2-Naphthalenes
C3-Naphthalenes
C4-Naphthalenes
Biphenyl
C1-Biphenyl
C2-Biphenyl
Acenaphthylene
Acenaphthene
C1-Acenaphthene
Fluorene
C1-Fluorenes
C2-Fluorenes
C3-Fluorenes

Phenanthrene
Anthracene
C1-phenanthrene/ anthracene
C2-phenanthrenes/ anthracenes
C3-phenanthrenes/ anthracenes
C4-phenanthrenes/ anthracenes
Fluoranthene
Pyrene
C1-Fluoranthenes/Pyrenes
C2-Fluoranthenes/Pyrenes
C3-Fluoranthenes/Pyrenes
C4-Fluoranthenes/Pyrenes
Dibenzothiophene
C1-Dibenzothiophene
C2-Dibenzothiophene
C3-Dibenzothiophene
C4-Dibenzothiophene

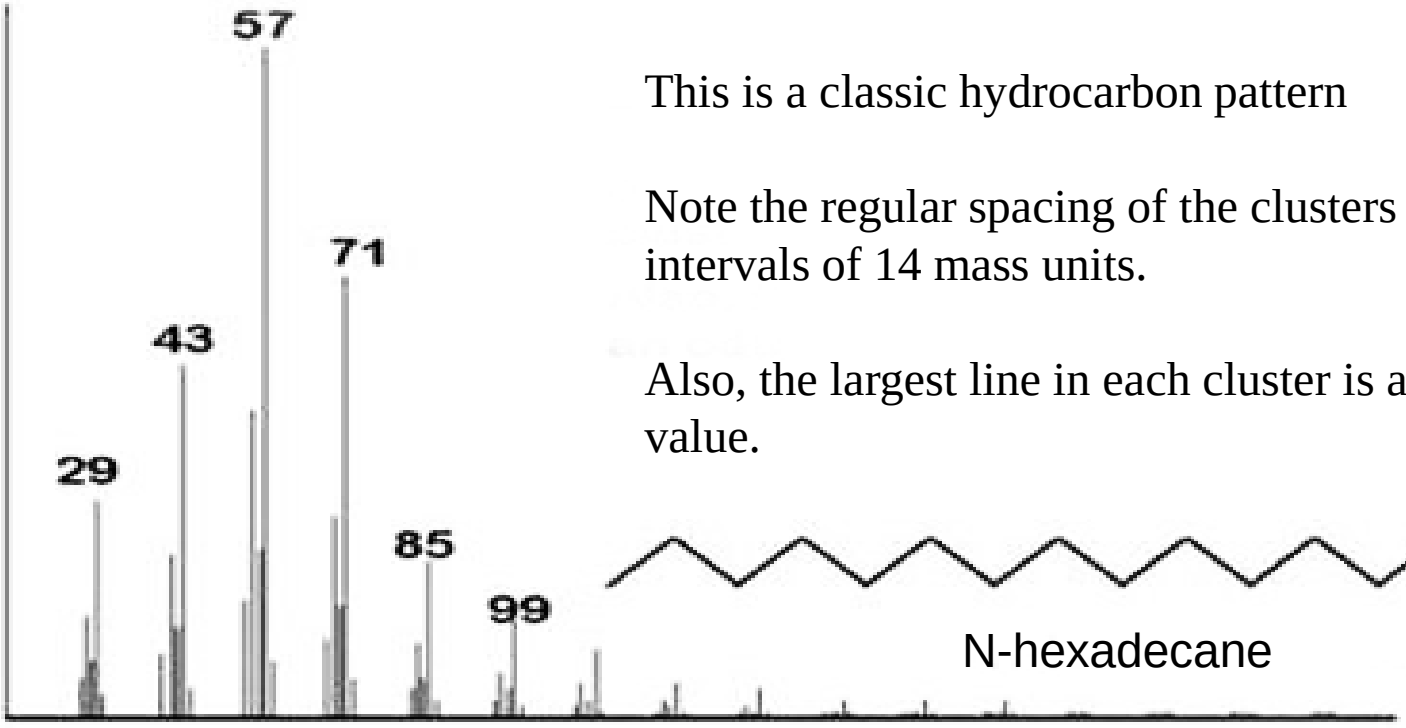
Benzo(a)anthracene
Chrysene
C1-Benz(a)anthracene/Chrysenes
C2-Benz(a)anthracene/Chrysenes
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(e)pyrene
Benzo(a)pyrene
Perylene
C1-Benzofluoranthenes/ benzopyrenes
C2-Benzofluoranthenes/ benzopyrenes
Indeno(1,2,3-cd)pyrene
Dibenzo(ah)anthracene
Benzo(ghi)perylene

# GC/MS Analysis



# Mass Spectrometry

## Saturated Hydrocarbons




This is a classic hydrocarbon pattern

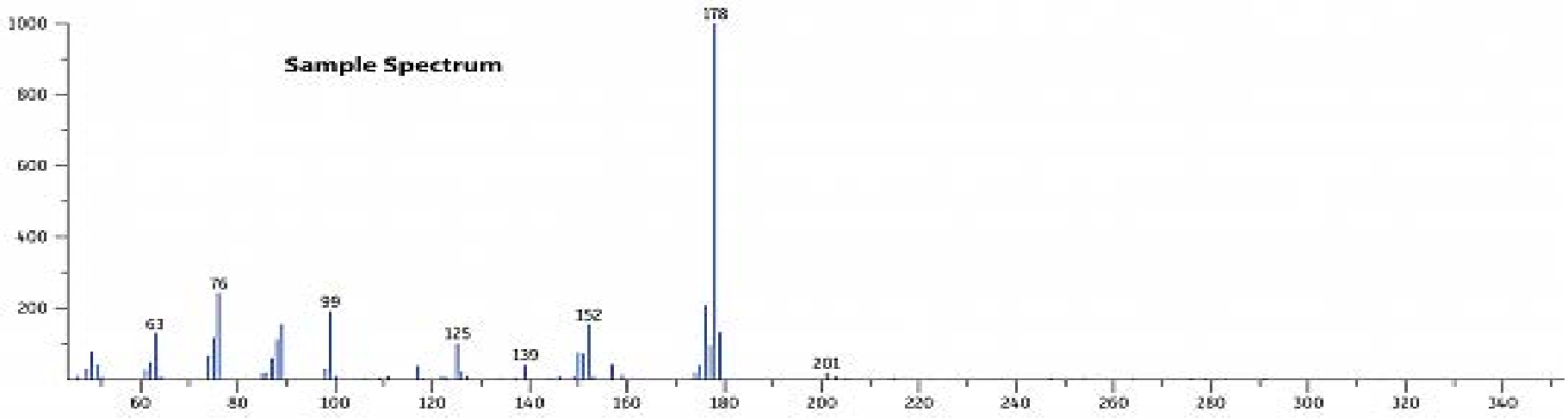
Note the regular spacing of the clusters at intervals of 14 mass units.

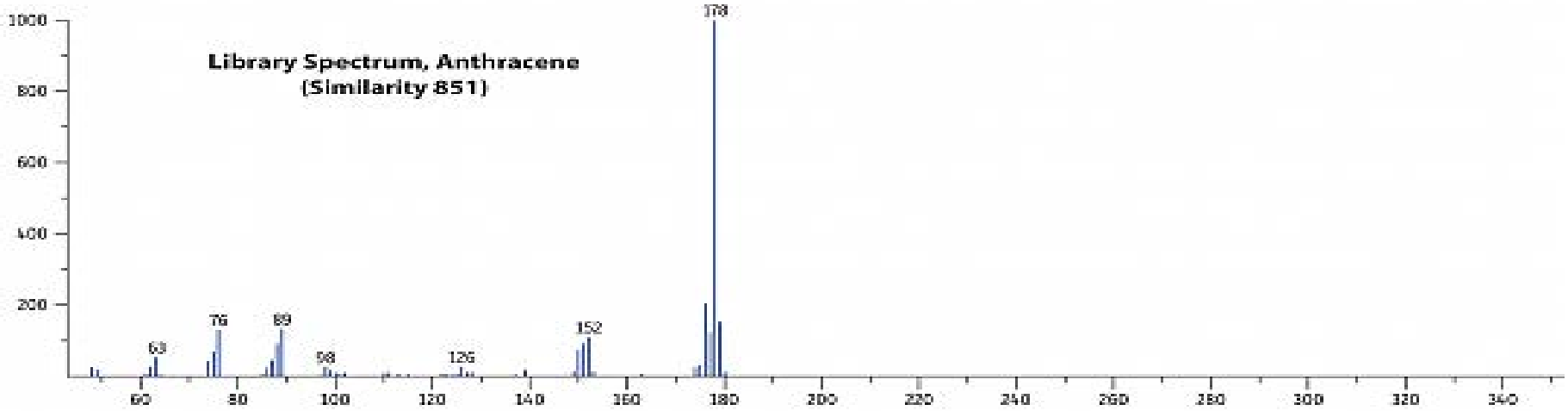
Also, the largest line in each cluster is an odd value.



N-hexadecane

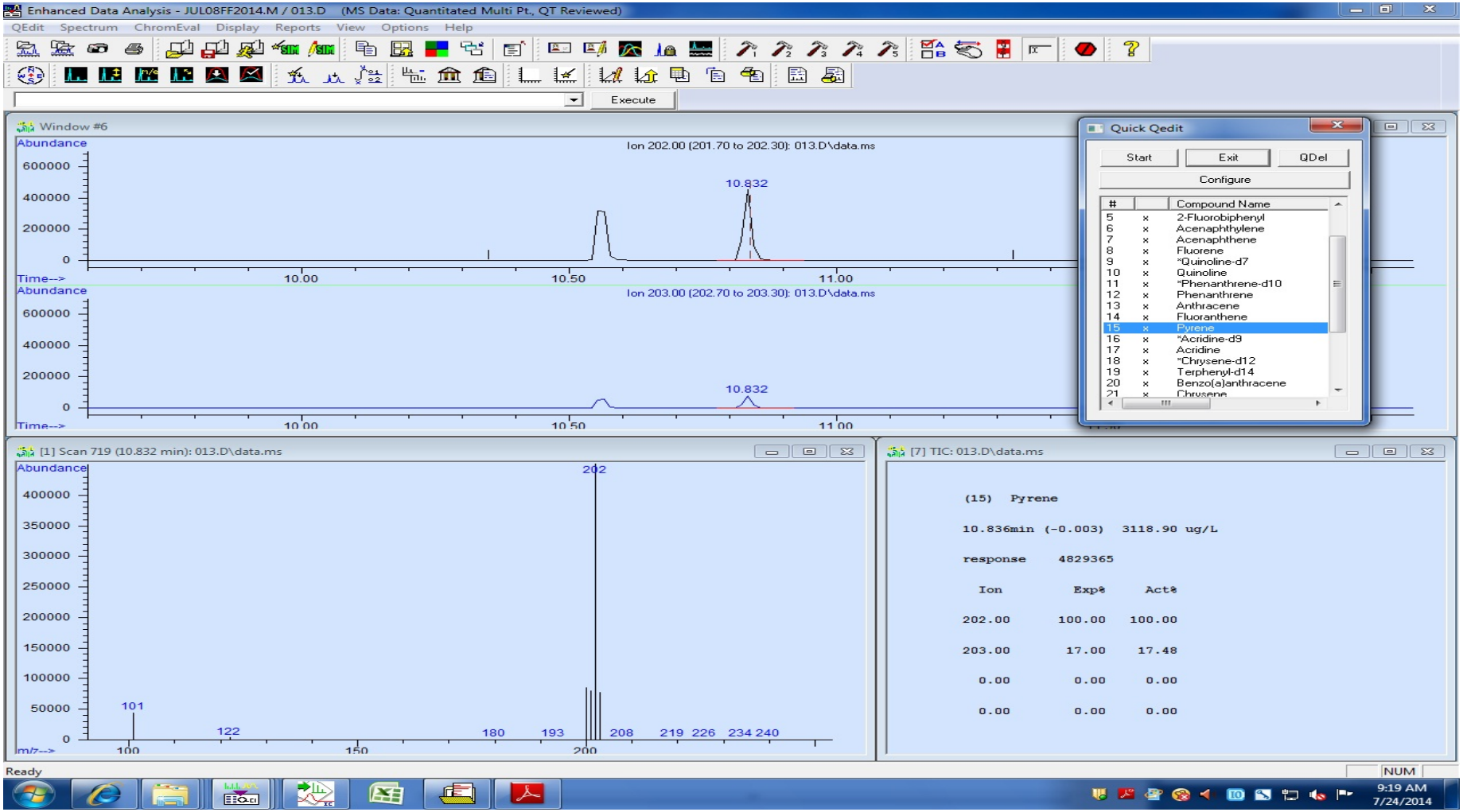
# Mass Spectrometry



# PAH Analysis:

## Extracted Ion Profile



# Diagnostic Ratios

- Certain PAHs compounds will be preferentially formed in either pyrogenic or petrogenic situations.

- Calculation of Diagnostic ratios between PAHs.

- Phenanthrene/Anthracene

- Fluoranthene/Pyrene

- (Fl+Py)/(Fl+Py+C2C4Ph)

- Pyrogenic Index: Zhendi Wang et al: Environmental Science and Technology Centre, Environment Canada.

# Pyrogenic Index

PI = £[other(3-6) ring PAHs] /  £[5 alkylated PAHs]

# Pyrogenic Index

| Source Material | PI |
|---|---|
| Light refined products | <0.01 |
| Heavier refined products | <0.03 |
| Heavy oils/crudes | <0.05 |
| Pyrogenic materials | >0.05 |

Weathering will cause a slight increase in PI values

# Experimental Design

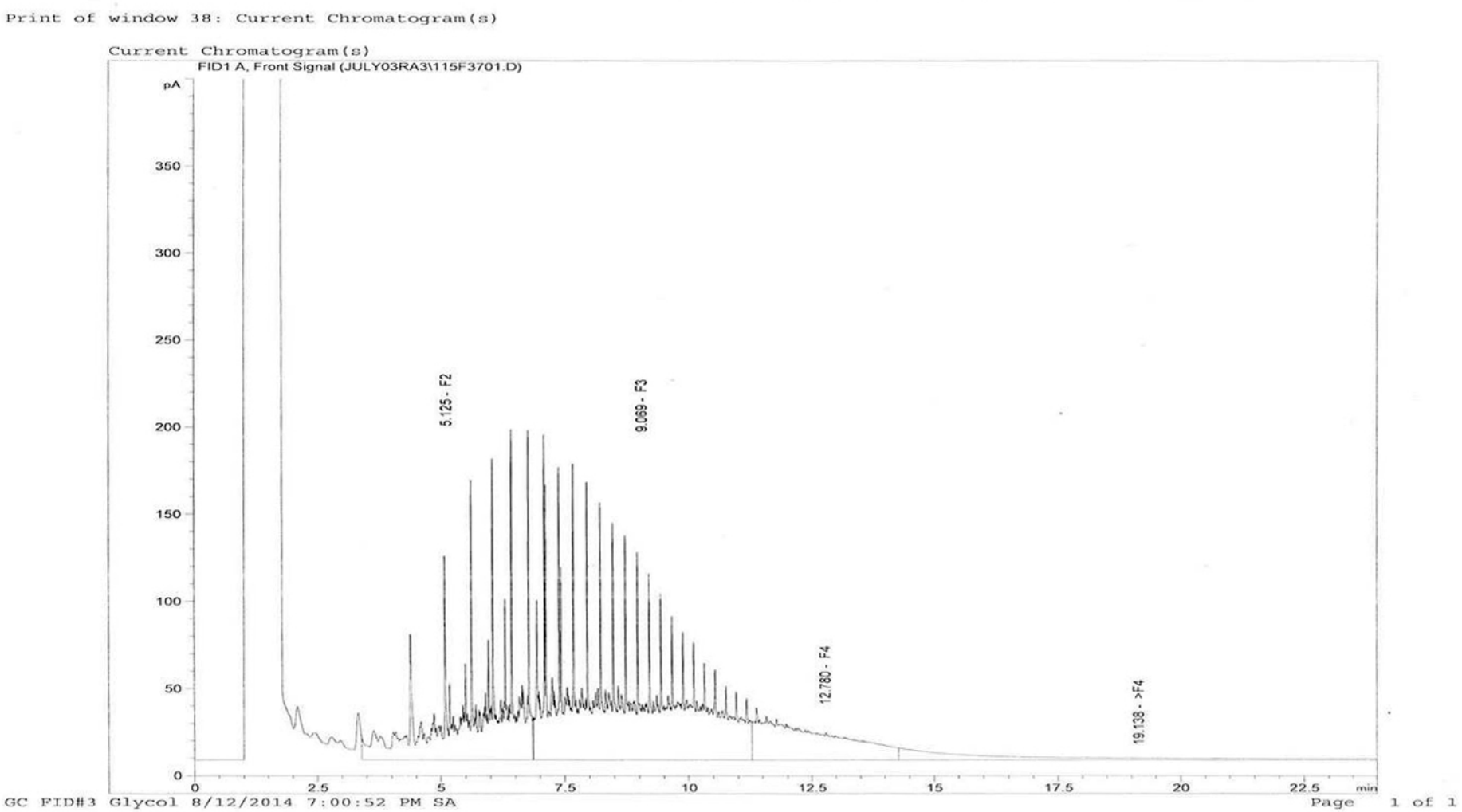
- Clean control soils.
- Clean control soils spiked with  petrogenic source materials.
- Clean control spiked with pyrogenic source material.
- Randomly selected real world samples with positive F2-F4 results.
- Analysis
  - F2-F4 PHC determination by GC/FID
  - Alkylated and parent PAH analysis by GC/MS/SIM

# F2-F4 Results

| Sample | F2 | F3 | F4 |
|---|---|---|---|
| High moisture plus crude | 3250 | 6460 | 1910 |
| High moisture plus motor oil | 34 | 4200 | 316 |
| Low plus crude | 3210 | 6270 | 1790 |
| Low plus motor oil | 35 | 4180 | 303 |
| BBQ Sample | 20 | 63 | 243 |
| Fire pit sample | 41 | 2120 | 589 |

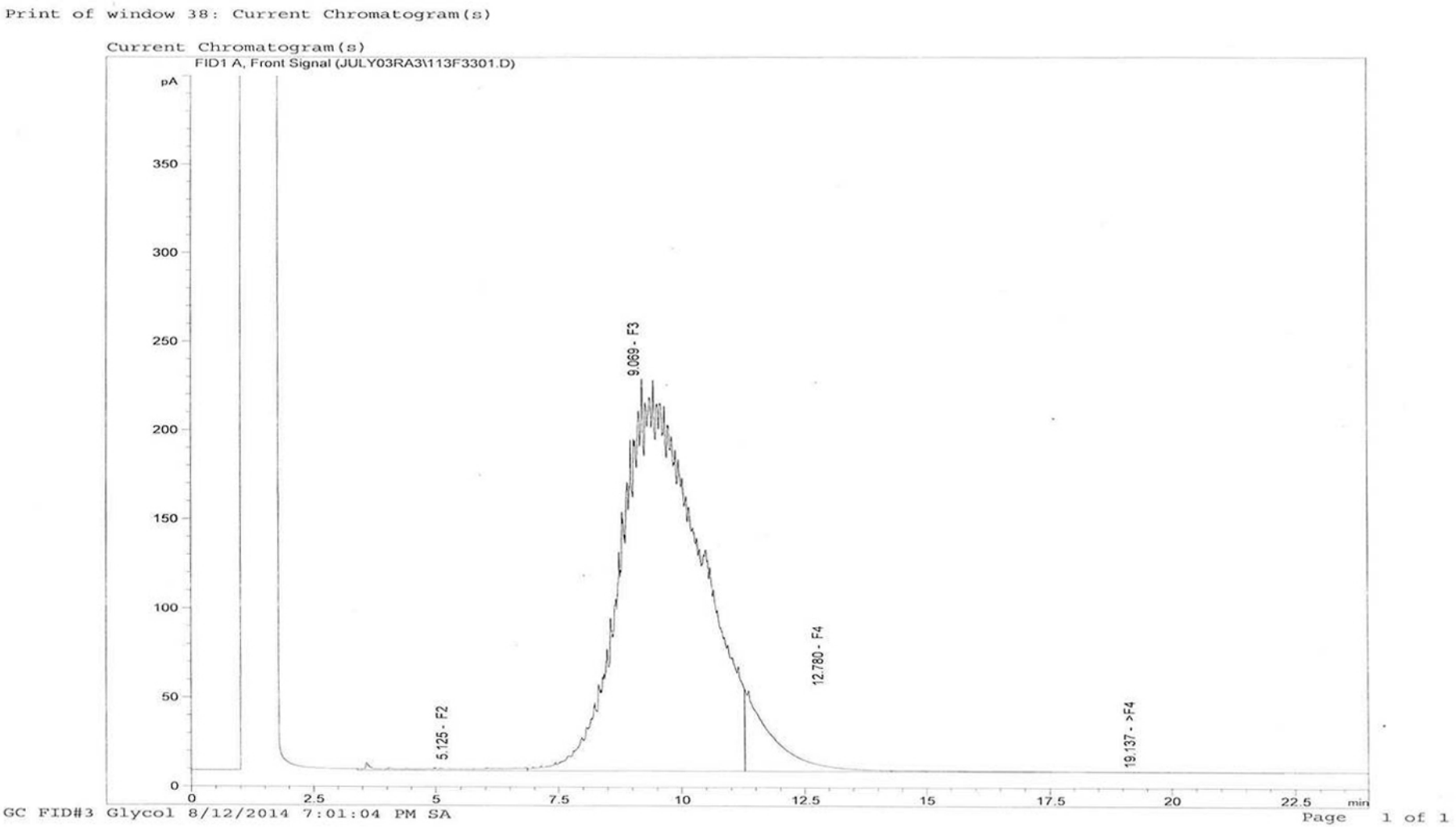
# F2-F4 Chrom:

## Crude Example



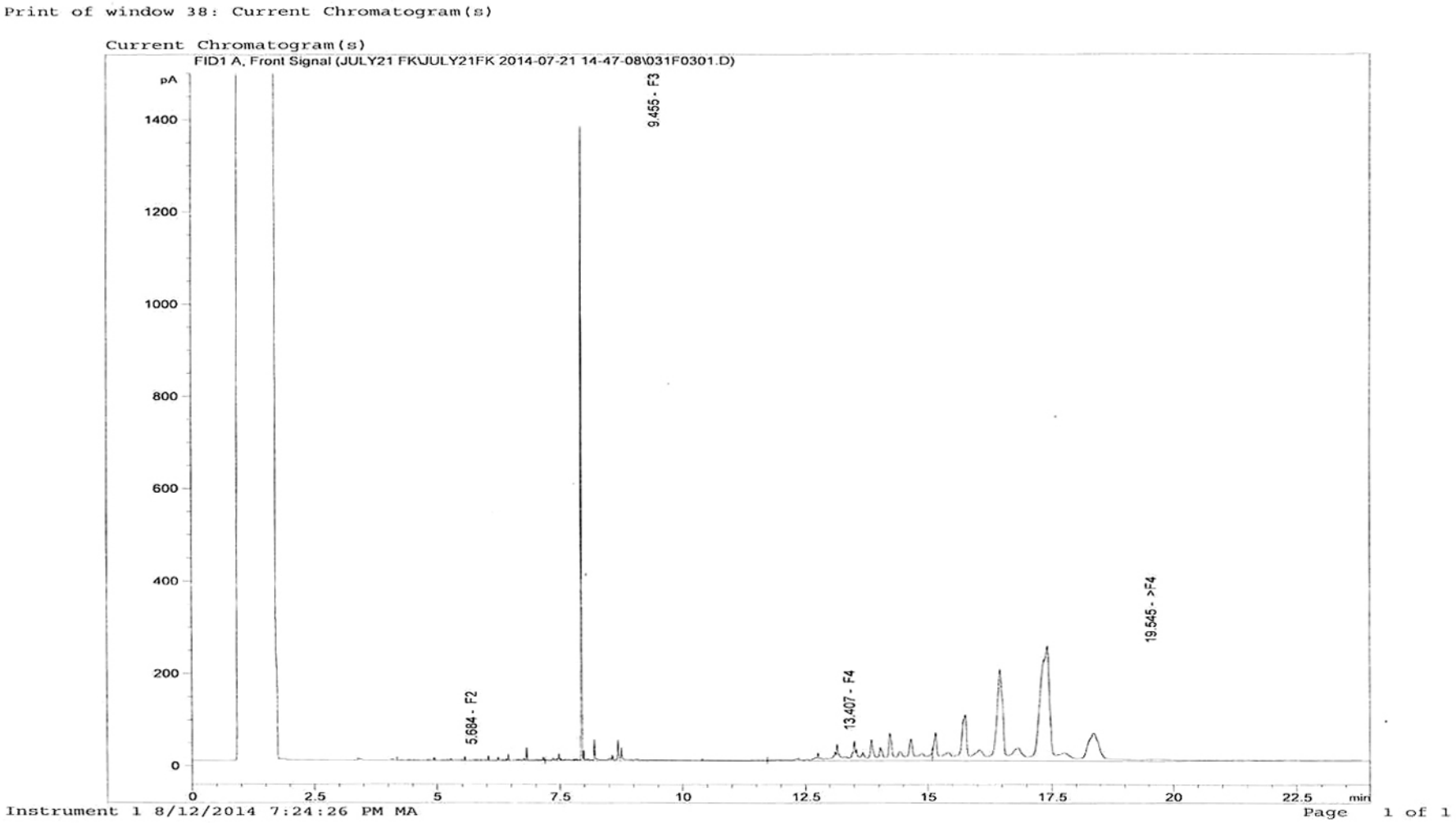
# F2-F4 Chrom:

## Motor Oil Example



# F2-F4 Chrom:

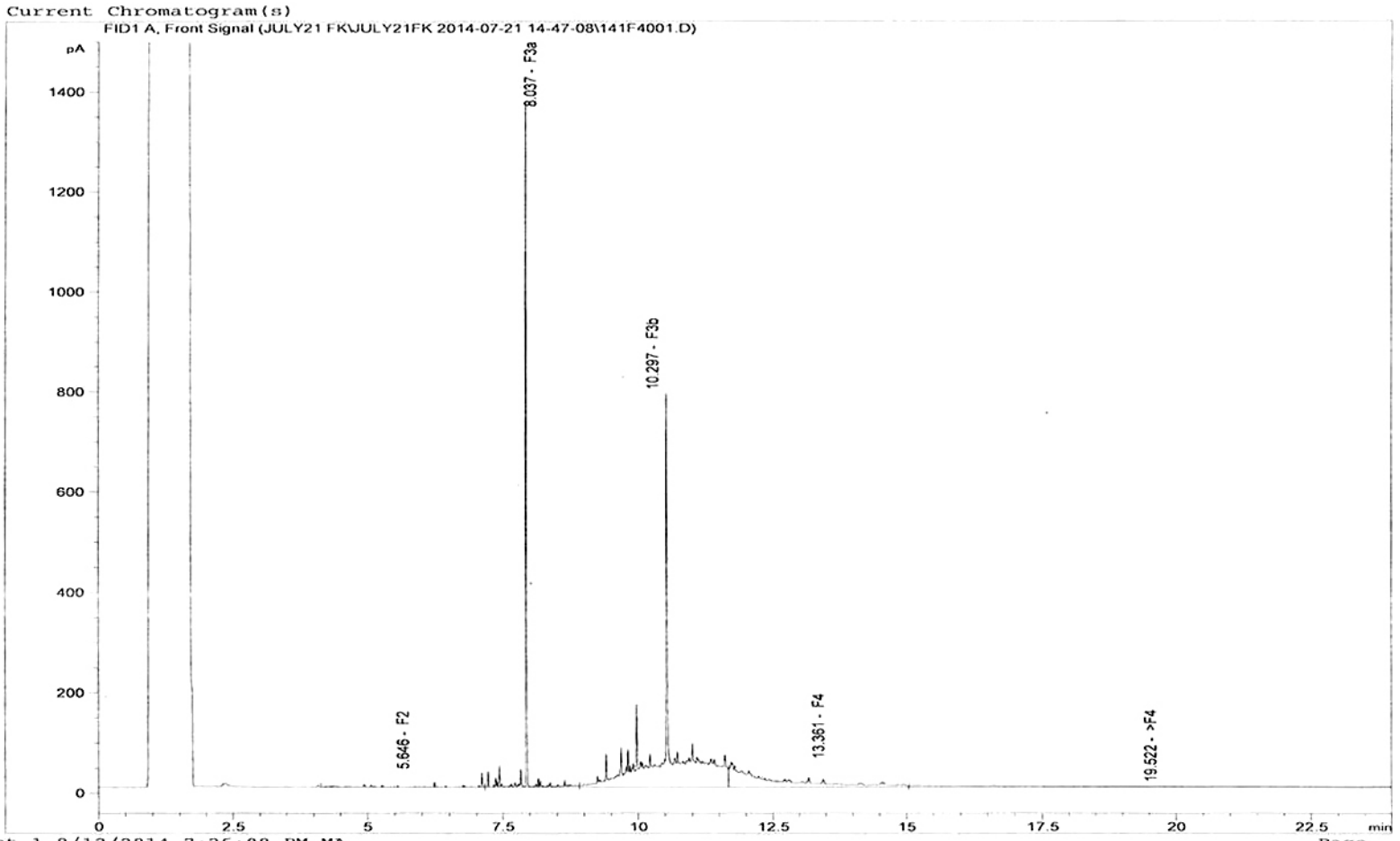
BBQ



# F2-F4 Chrom:

## Fire Pit

Print of window 38: Current Chromatogram(s)




Instrument 1 8/12/2014 7:26:08 PM MA

Page 1 of 1

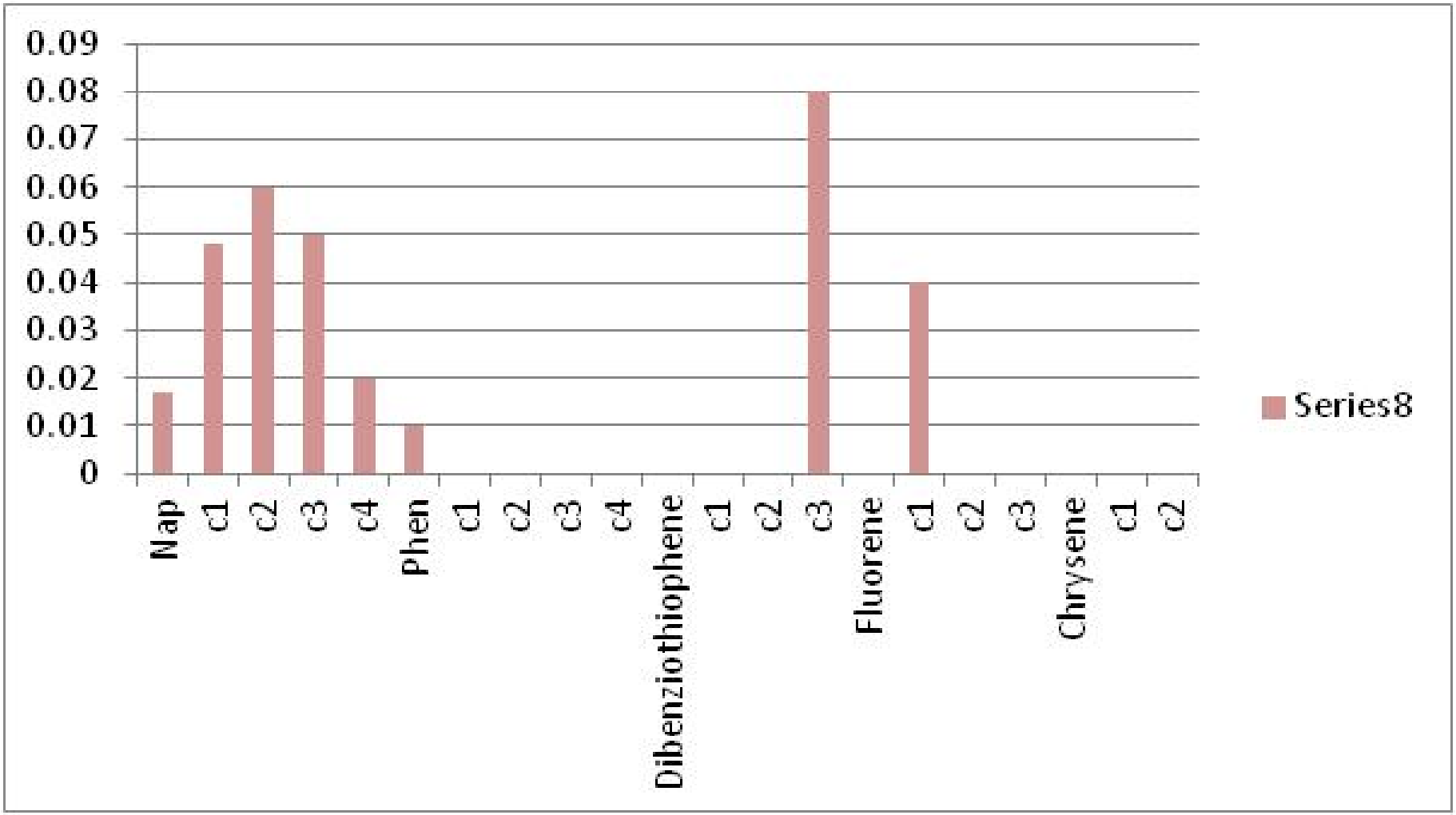
# Control Diagnostic Ratios

| Sample | Phen/Anth | Fluor/Pry | (Fl+Py)/(Fl+Py+C2C4Ph) | MPHE/PHE | PI |
|---|---|---|---|---|---|
| High moisture plus crude | **1.53** | 0.81 | 0.03 | 3.2 | 0.014 |
| High moisture plus motor oil | N.A. | N.A. | N.A. | 0 | 0 |
| Low plus crude | **2.34** | 0.23 | 0.04 | 2.1 | 0.025 |
| Low plus motor oil | N.A. | N.A. | N.A. | N.A. | 0 |
| BBQ Sample | 93 | **2.0** | **0.20** | **0.4** | **0.13** |
| Fire pit sample | N.A. | N.A. | **1.0** | **0** | **0.48** |

- Ph/An for Pyrogenic <10
- Fluor/Pyr for pyrogenic >1
- PI for pyrogenic >0.05
- (Fl+Py)/(Fl+Py+C2C4Ph) >0.2 for Pyro

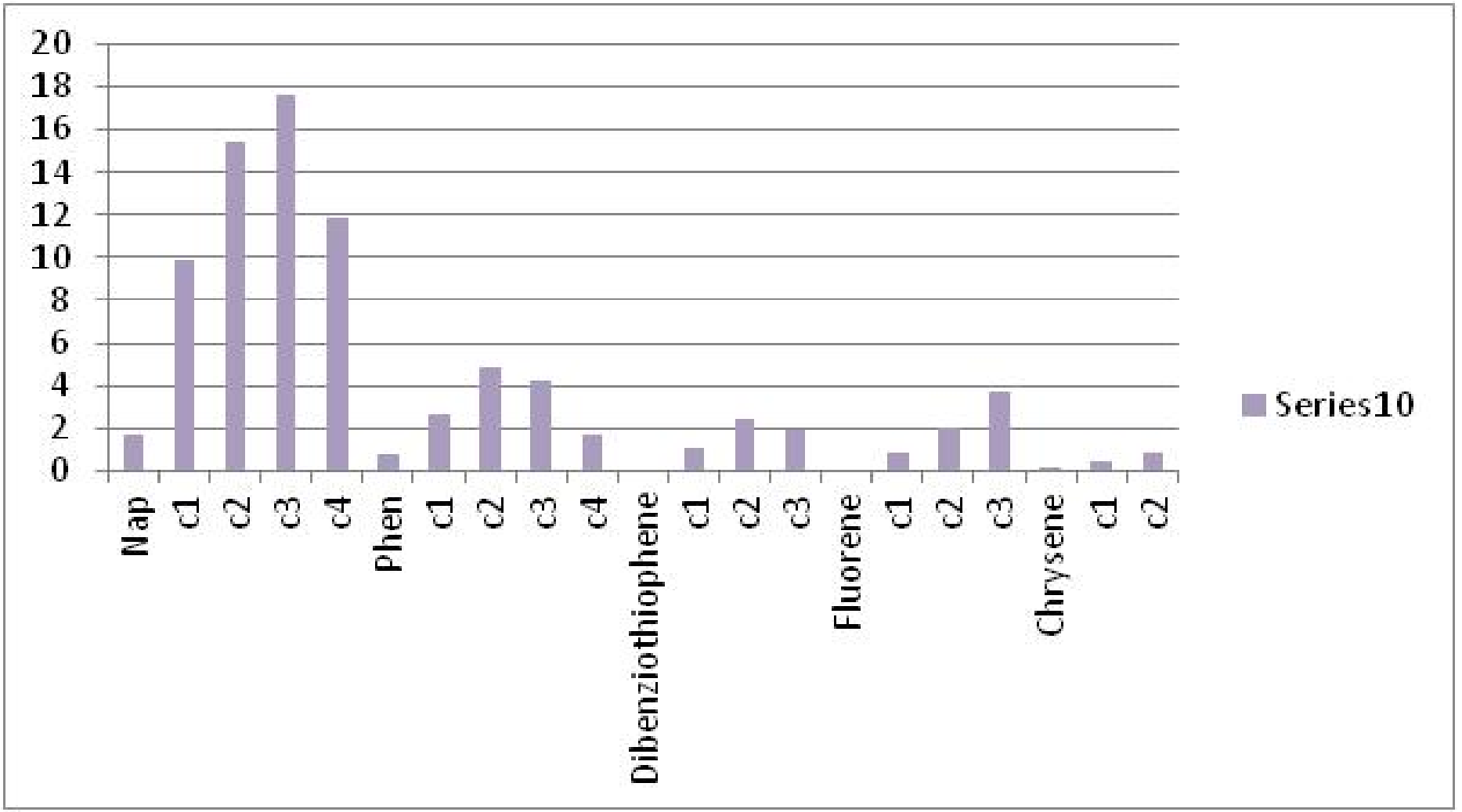
# Subt'd PAH Distribution:

## Motor Oil



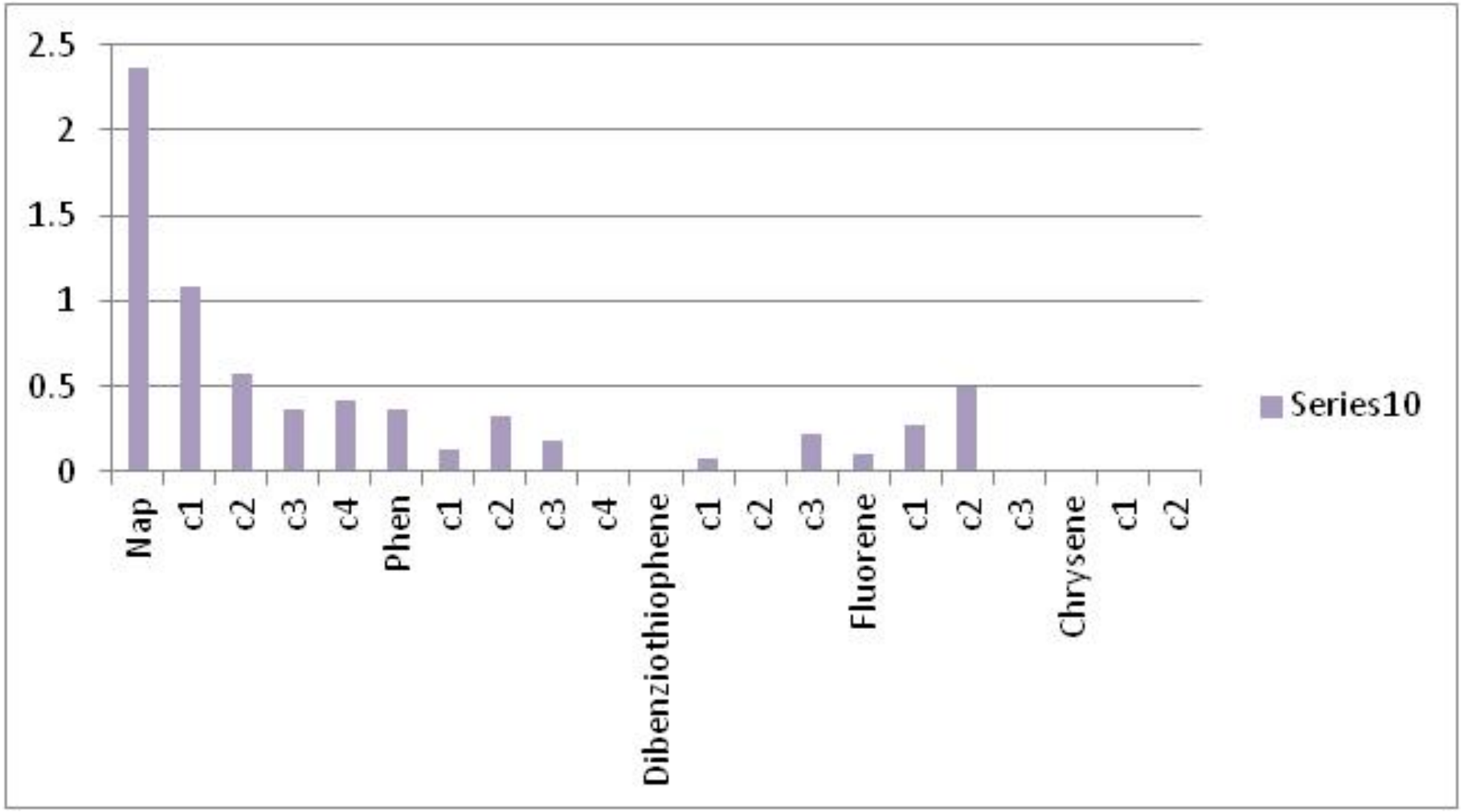
# Subt'd PAH distribution:

## Crude Oil



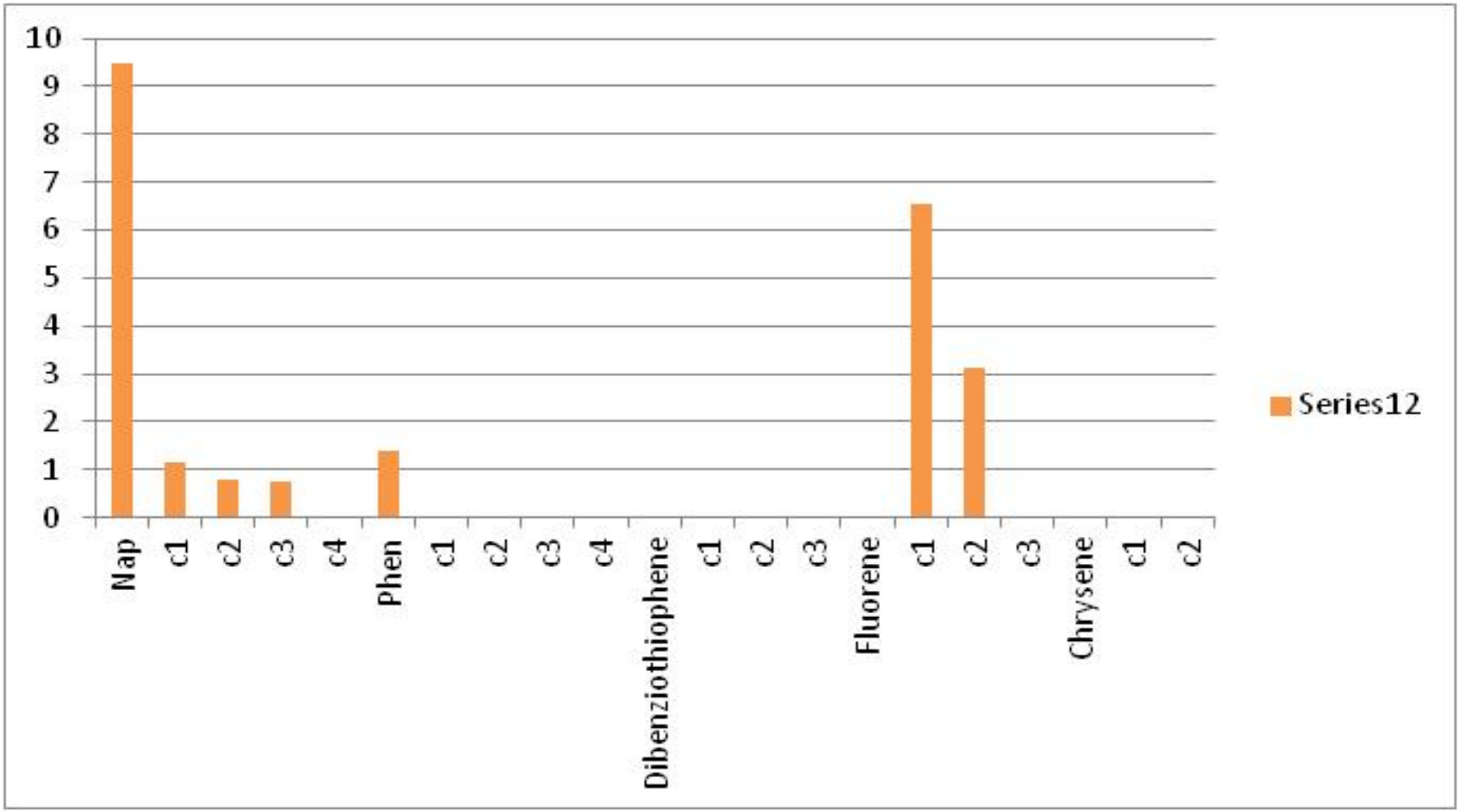
# Subt'd PAH Distribution:

BBQ



# Subt'd PAH Distribution:

## Fire Pit



# F2-F4 Results:

## Real World Samples

| Sample | F2 | F3 | F4 |
|---|---|---|---|
| Sample #1 | 11600 | 34900 | 146 |
| Sample #2 | 741 | 3040 | 1300 |
| Sample #3 | 1580 | 6580 | 2240 |
| Sample #4 | 2700 | 4940 | 1330 |

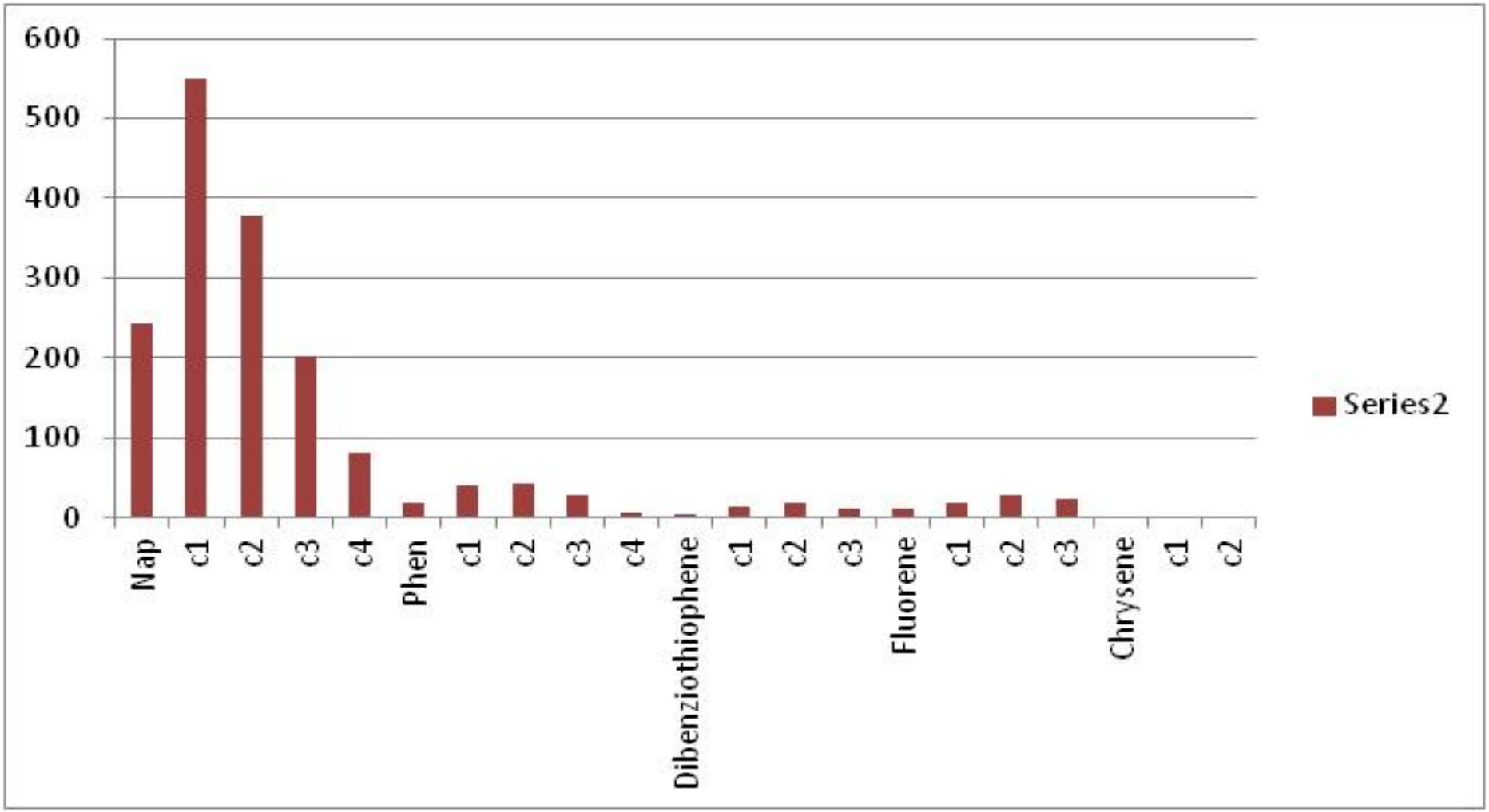
# Real World Sample Diagnostic Ratios

| Sample | Phen/Anth | Fluor/Pry | (Fl+Py)/(Fl+Py+C2C4Ph) | MPHE/ PHE | PI |
|---|---|---|---|---|---|
| Sample #1 | **6.9** | 0 | 0.007 | 2.1 | 0.002 |
| Sample #2 | **1.2** | 0 | 0.033 | 5 | 0.029 |
| Sample #3 | **0.6** | 0.11 | 0.05 | 6 | 0.048 |
| Sample #4 | **0.56** | 0.88 | 0.02 | 2.5 | 0.032 |

- Ph/An for Pyrogenic <10
- Fluor/Pyr for Pyrogenic >1
- (Fl+Py)/(Fl+Py+C2C4Ph) >0.2 for Pyro
- MPHE/PHE 0.5-1 for Pyro
- PI for Pyrogenic >0.05

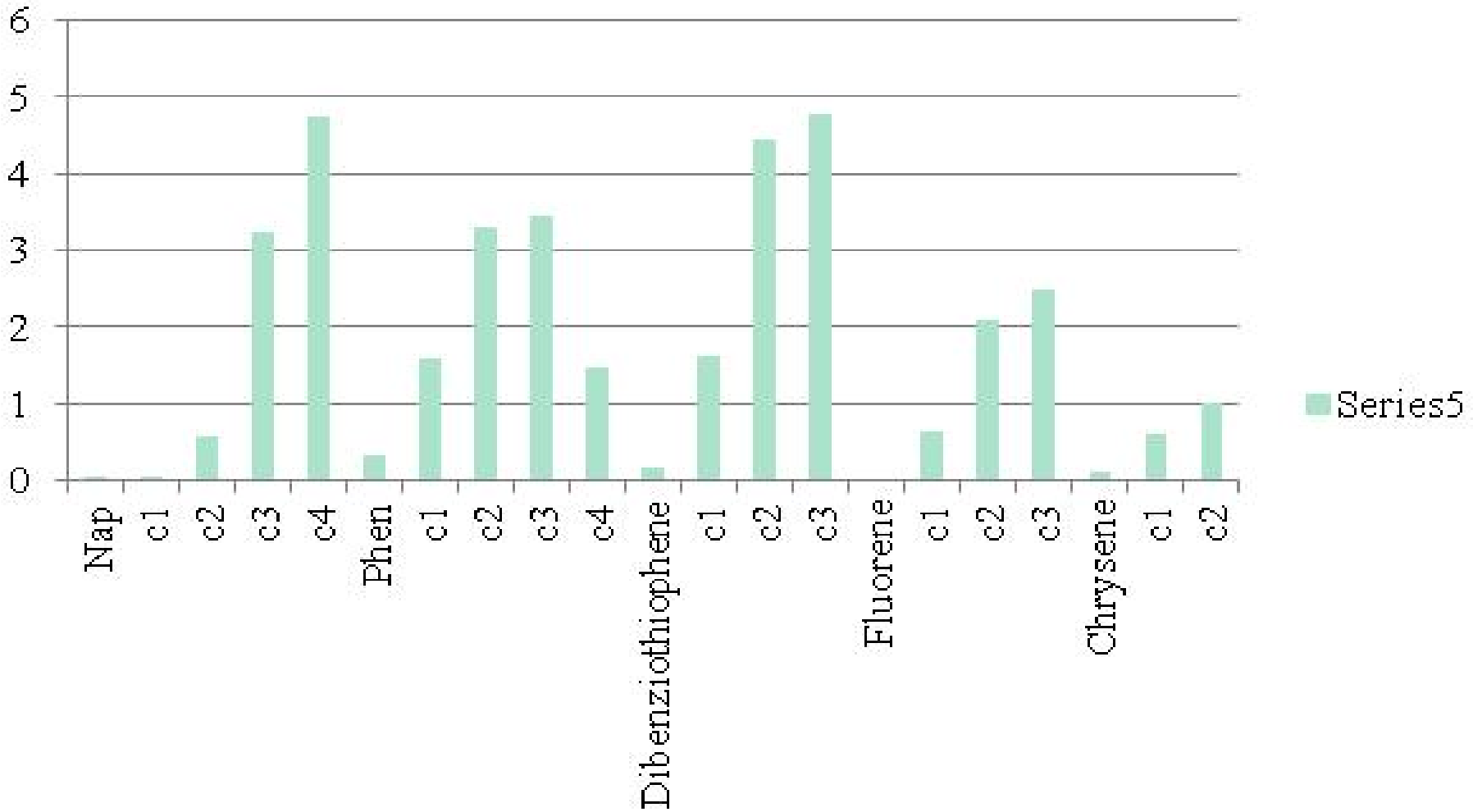
# Subt'd PAH Distribution:

## Sample 1



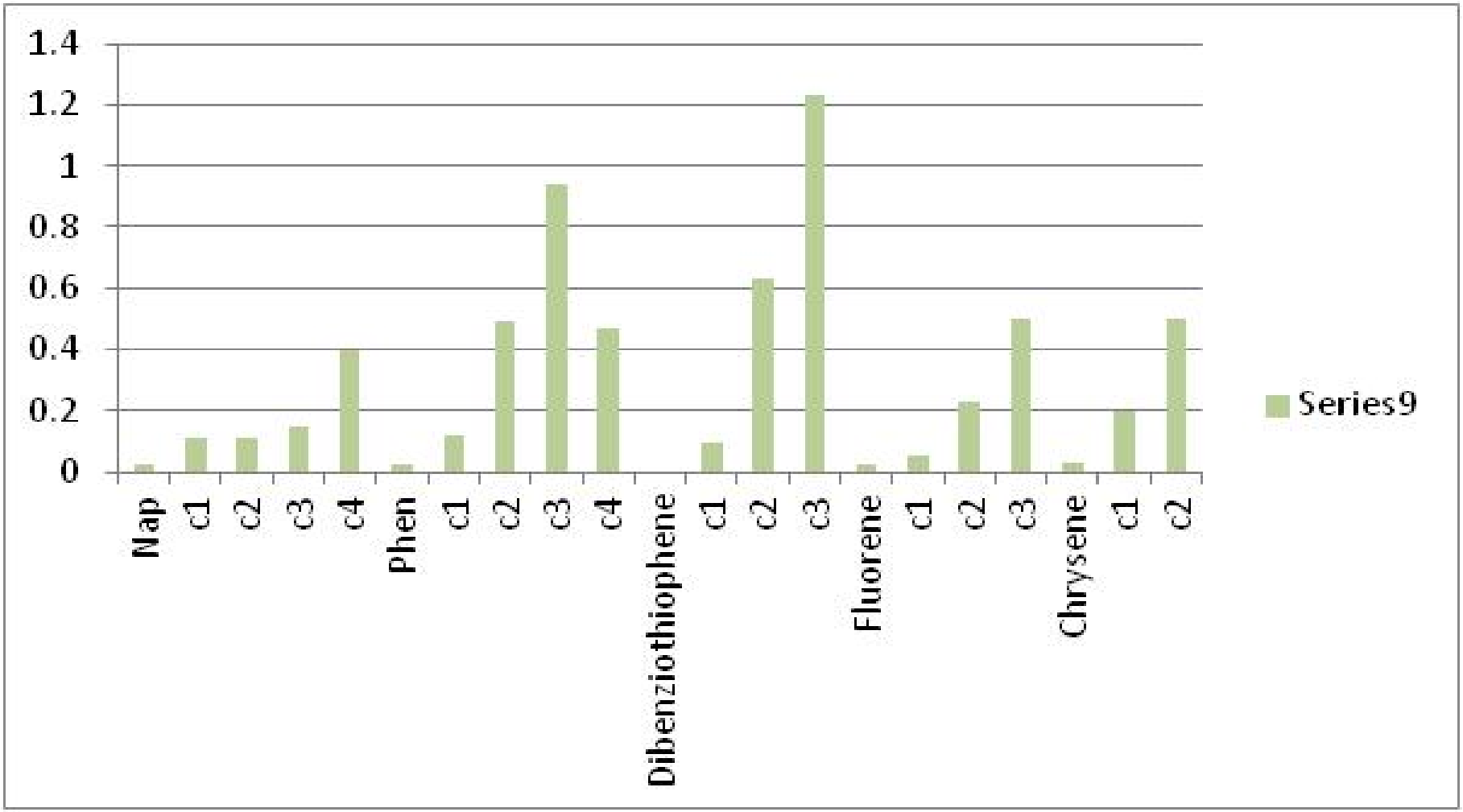
# Subt'd PAH Distribution:

## Sample 2



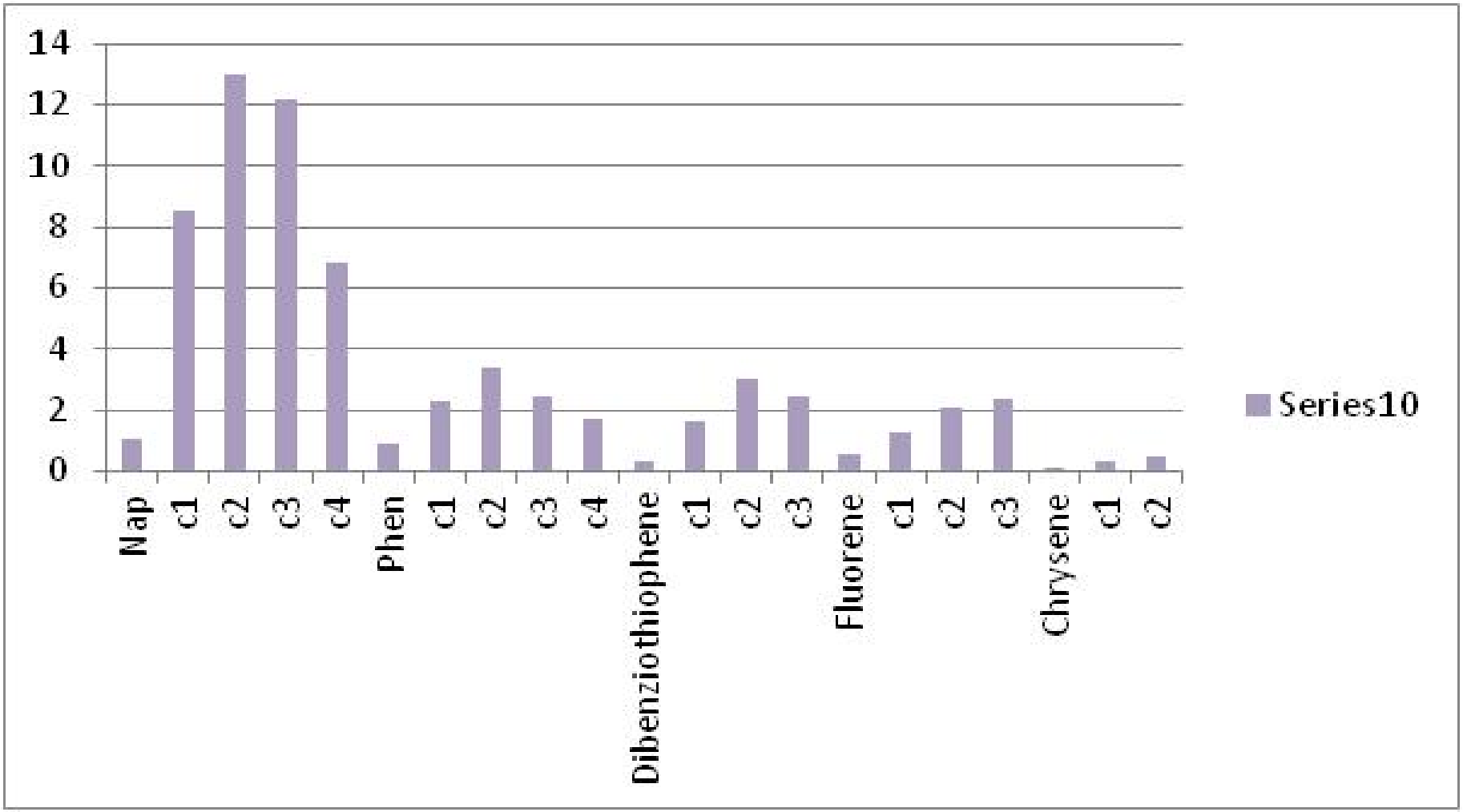
# Subt'd PAH Distribution:

## Sample 3



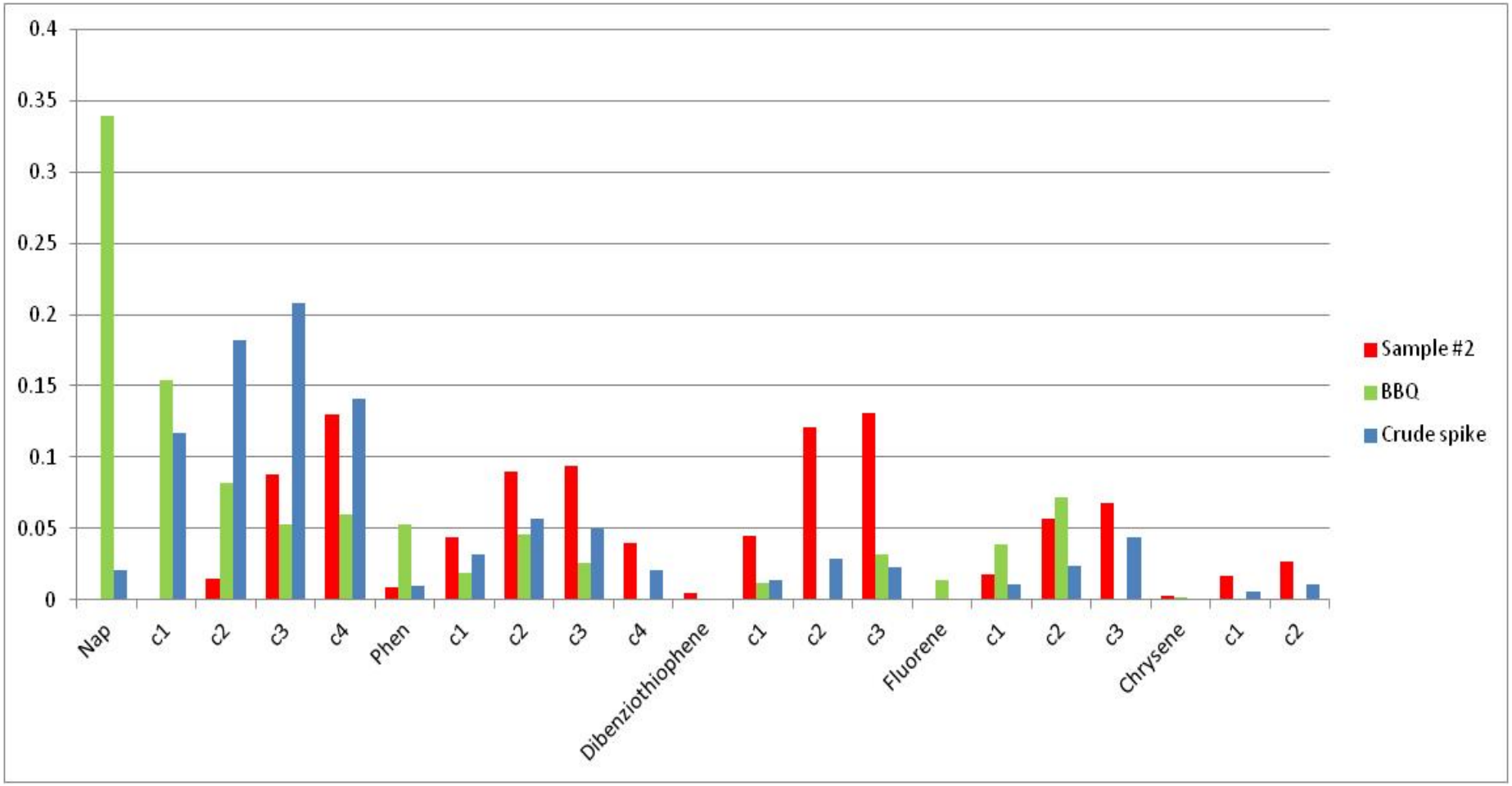
# Subt'd PAH Distribution:

Sample 4



# Subt'd PAH Distribution:

## Sample vs Crude Spike vs Pyrogenic



# Summary

- Phenanthrene/Anthracene: least reliable.
- Fluoranthene/Pyrene: decent
- (Fl+Py)(Fl+Py+C2C4Ph) : better
- Mphe/Phe :  mixed
- PI:  most conclusive
- Distinctive patterns were noticed from alkyl PAH plots

# Conclusions

- The more compounds utilized in the ratios the better.

- Useful ratios:
  - (Fl+Py)(Fl+Py+C2C4Ph)
  - Mphe/Phe
  - PI

- These in combination with visual inspection of the alkyl PAH plots can be used as diagnostic tools in determining pyrogenic sources in cases of potential wood based combustion byproducts.


# QUESTIONS AND DISCUSSION

Thank you