Application of Forensic Chemistry to Environmental Work

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Outline of Presentation:

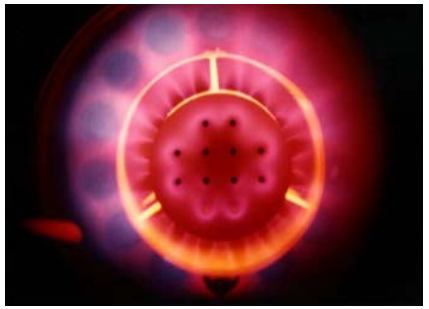
- Introduction to GTI
- Manufactured Gas Plant Operations – an environmental problem
- Introduction to Forensic Chemistry
- Application to a Test Site
- Results
- Conclusion

GAS TECHNOLOGY INSTITUTE

- **Independent, Not-for-Profit R&D Organization**
  - 18-acre campus in Des Plaines, IL
  - 350,000 ft^2 facility
  - Labs, test facilities, library, classrooms
- **Natural Gas Focus**
- **Formed in 1941**
- **7 Centers**

Exploration & Production

Pipeline Materials



Combustion

Gasification

Environmental

Fuel Cells

Distributed Generation

Environmental Science & Forensic Chemistry

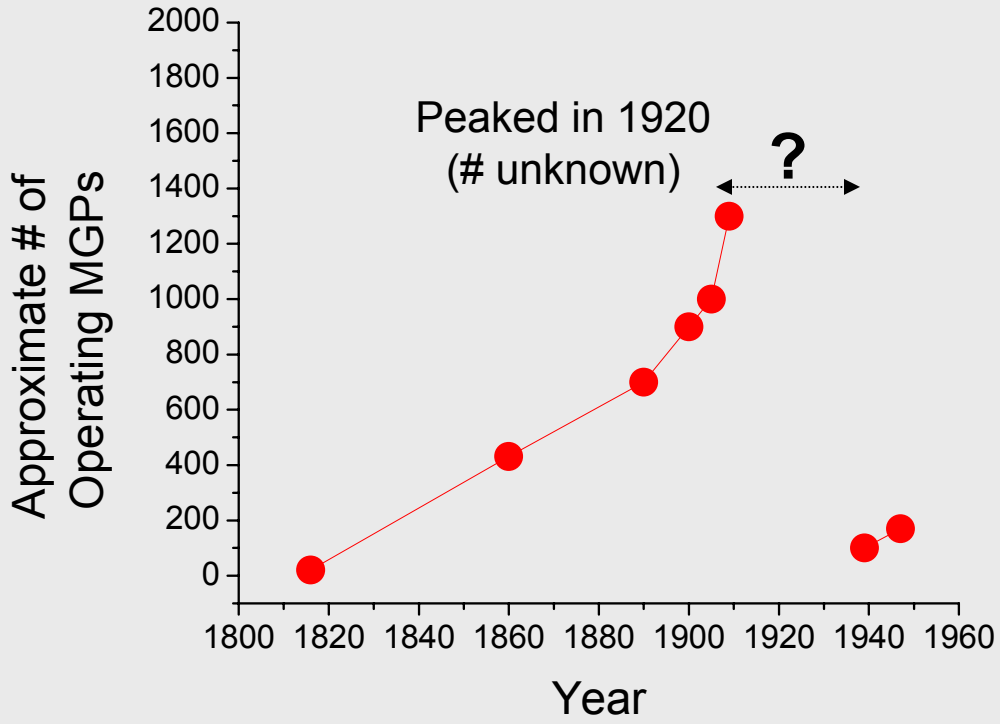
- R&D Laboratory and Services
- Research in:
  - Microbiology/Molecular Biology
  - Chemistry/Geochemistry
  - Phytoremediation
  - Biorefining
  - Remediation Techniques

"Environmental" means many things in the Gas Utilities Industry

- Greenhouse Gas Production/Mitigation
- PCBs associated with Gas Transmission
- Air Quality – Indoor and Outdoor
- Operations – Related: Corrosion
- MGP Site Cleanups and Long-Term Management:
  - Landside
  - Sediments

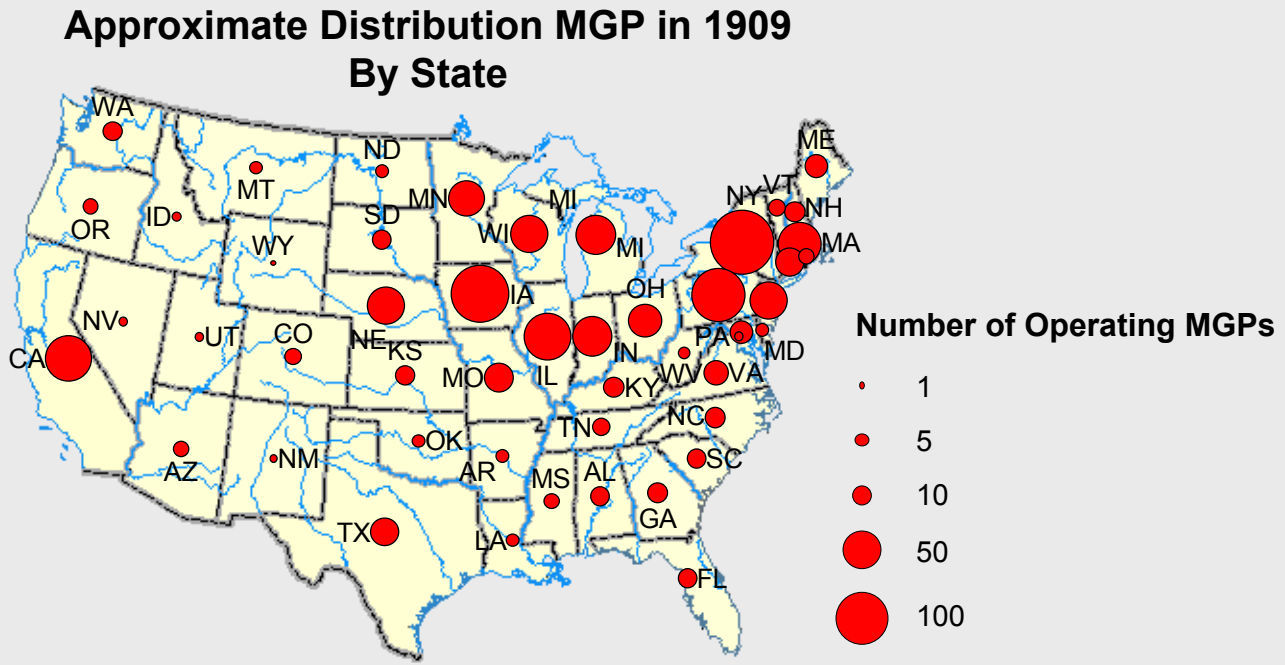
Number of Former MGPs in the United States

- The US EPA and others estimate that from 1815 to 1960 over 1,500 MGPs operated in the USA
- Number operated at a given time -- difficult to say



Location of Former MGPs in the United States

- Former MGPs are found everywhere the US, in small towns and large cities, in industrial zones and in relatively rural settings



Location of Former MGPs

- Some former MGPs are located near waterfronts such as rivers and lakes

Nature of the Problem

- "Town Gas" was produced in North America through combustion of coal/oil – produced "Manufactured Gas"
- The process produced "MGP" waste – mostly pyrogenic PAHs (tar-like materials)
- There are many sources of PAH-material in the environment – some look MGP waste
- Detecting PAHs alone can lead to the conclusion that all tar-like waste is from former MGP site.
- A technique was needed to discern PAH sources in the environment:
  FORENSIC CHEMISTRY

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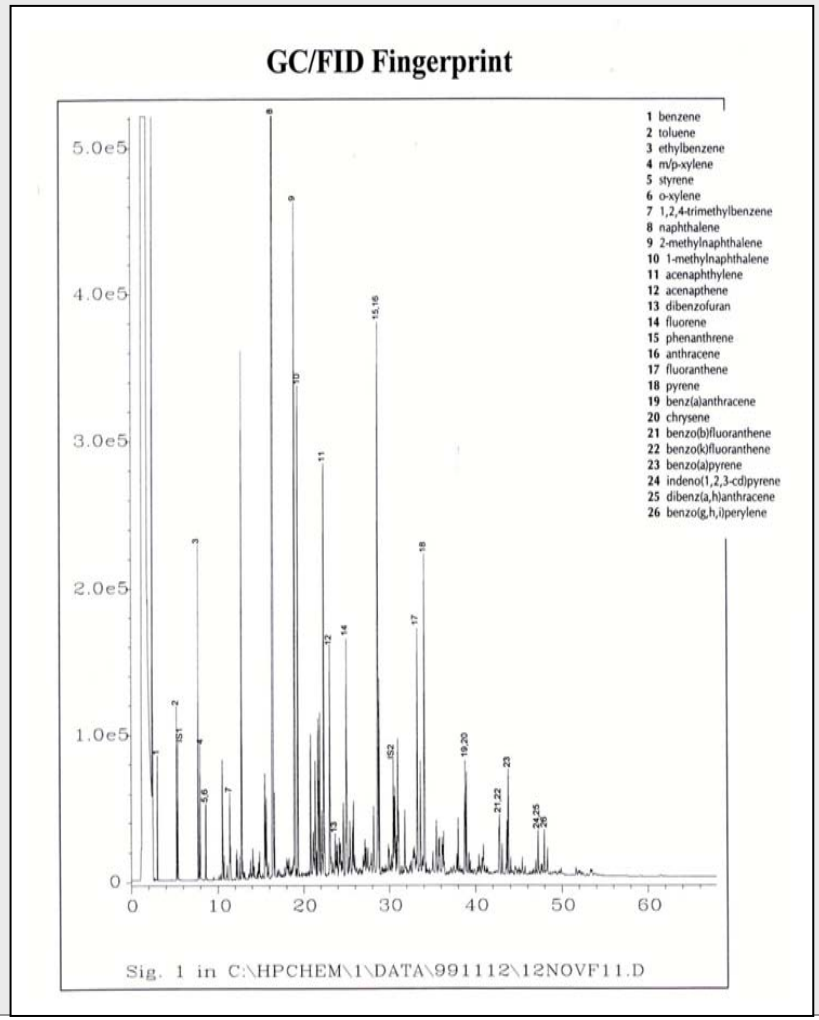
What is “Chemical Fingerprinting”- Forensic Chemistry?

It is the technique of analyzing samples and generating chemical “fingerprints” (chromatograms) which are distinctive to a type of waste.

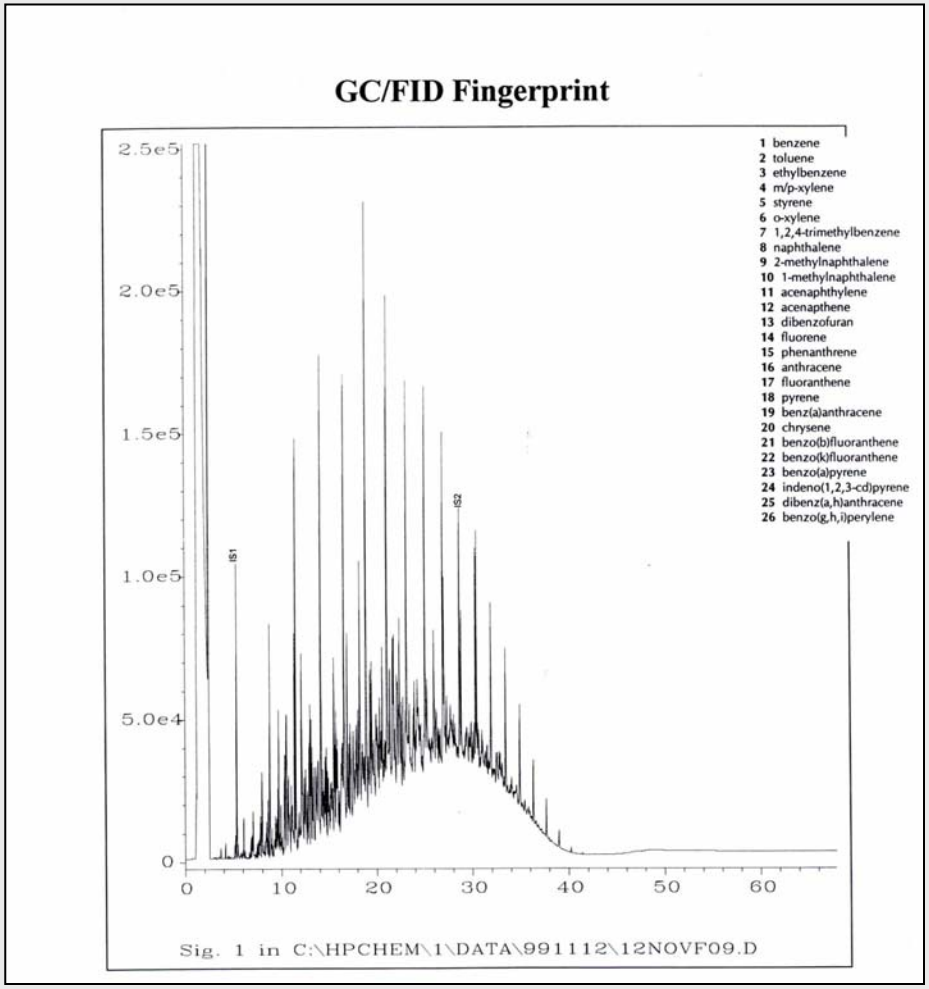
Chemical Fingerprinting Techniques

- GC/FID – gas chromatography with flame ionization detector
- GC/MS – gas chromatography with mass spectrometry

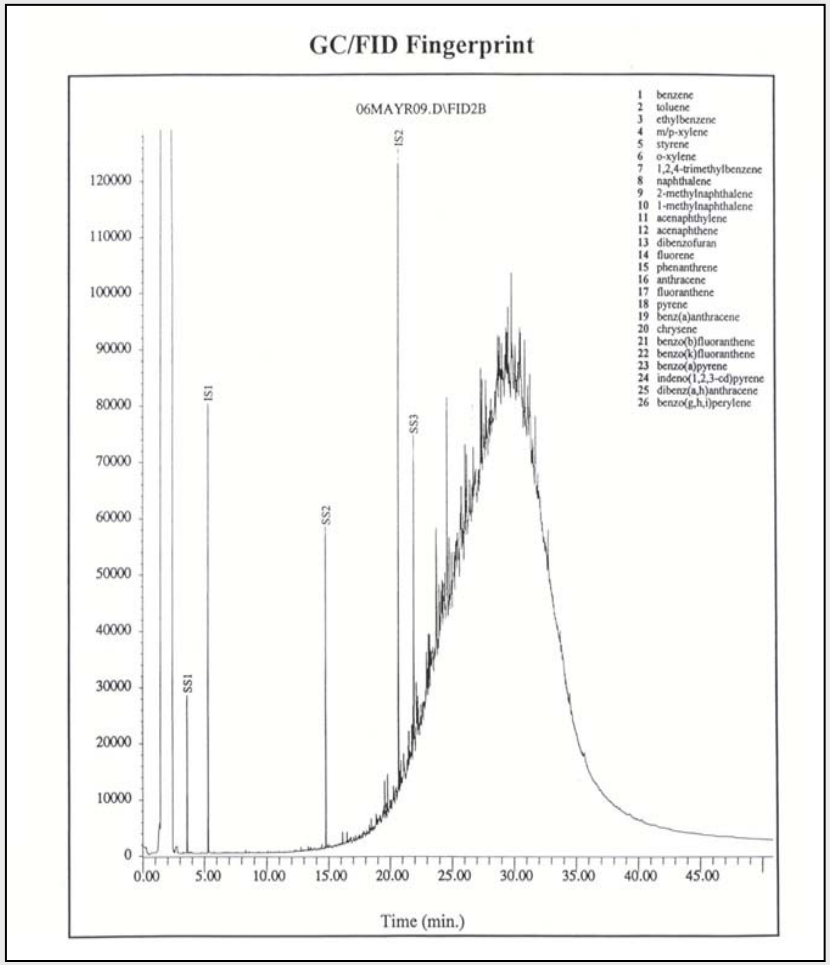
Example of a "Pyrogenic Substance" – MGP-Type Tar



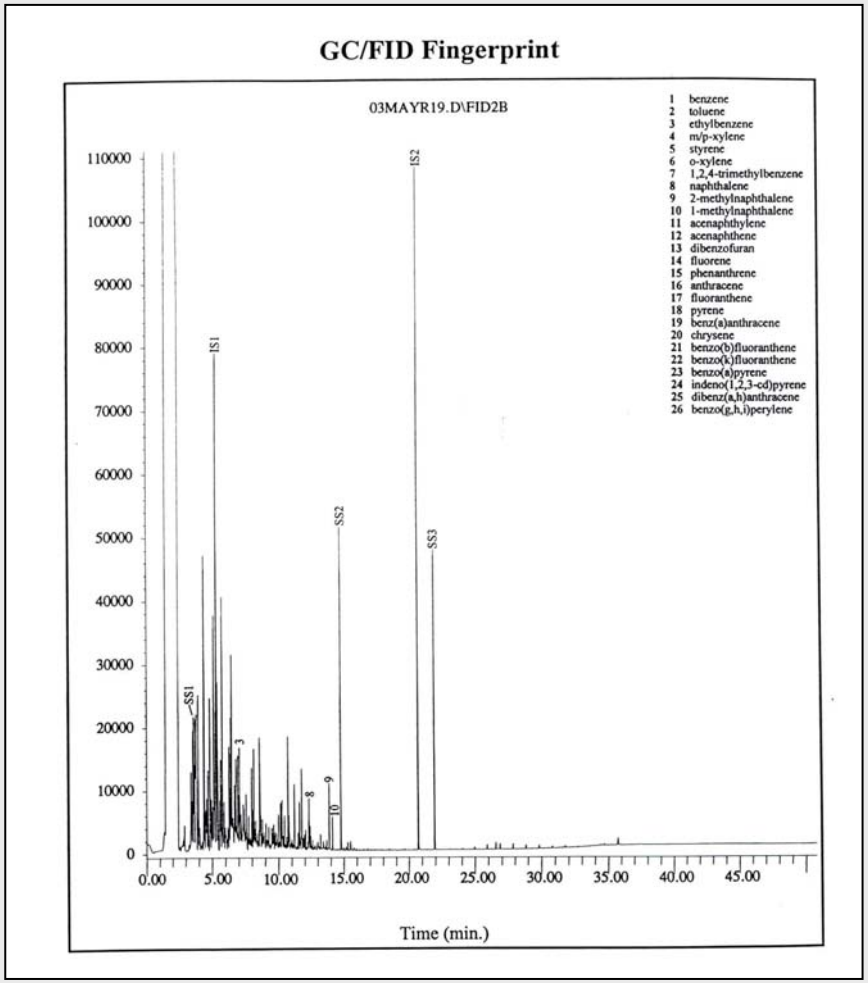
Example of a "Petrogenic Substance" – Diesel Fuel



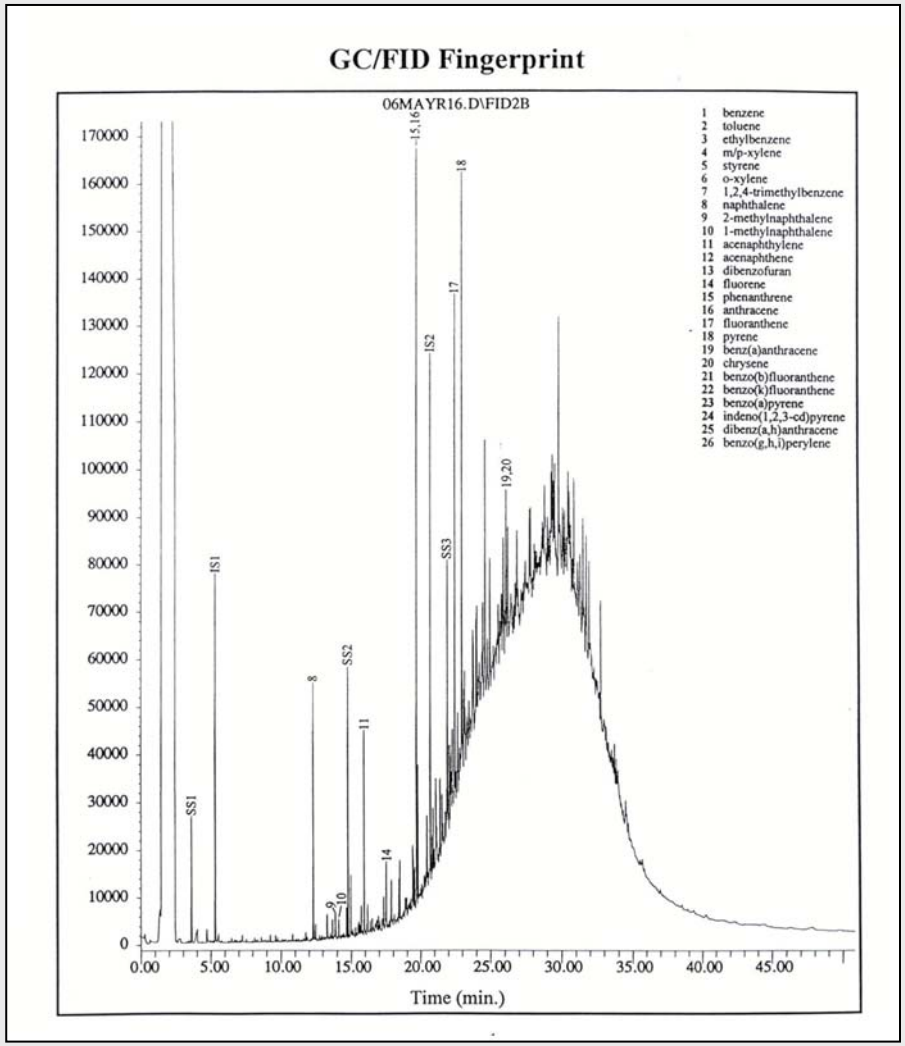
Example of Asphalt-Tar



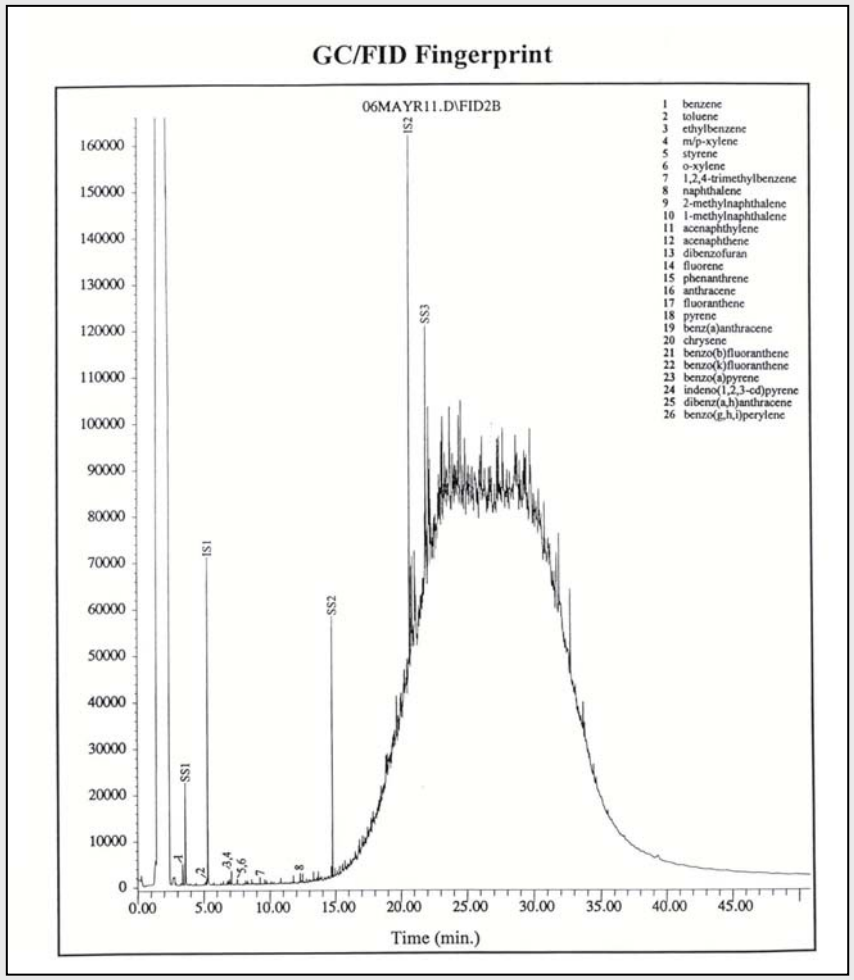
Example of Gasoline – No Tar Present



Example of Both MGP-Type Tar & Asphalt Like Tar



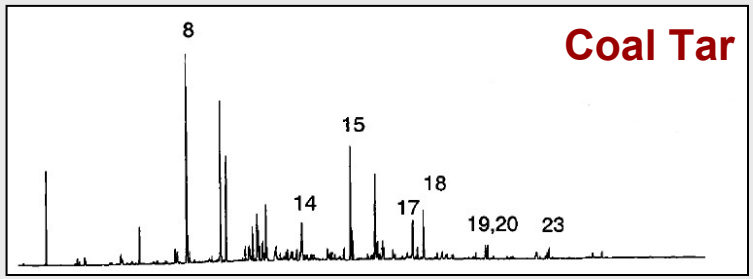
Example of Asphalt-Like Tar & Gasoline

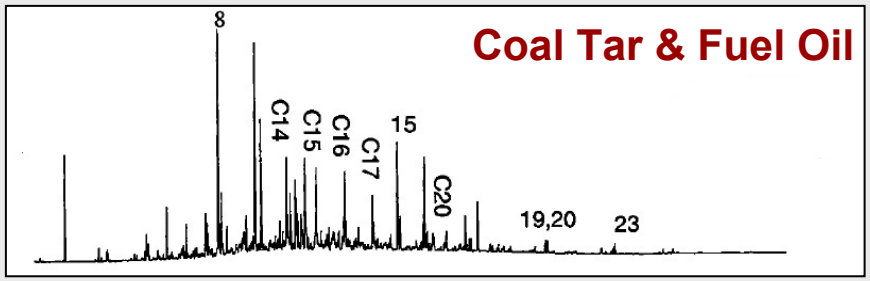


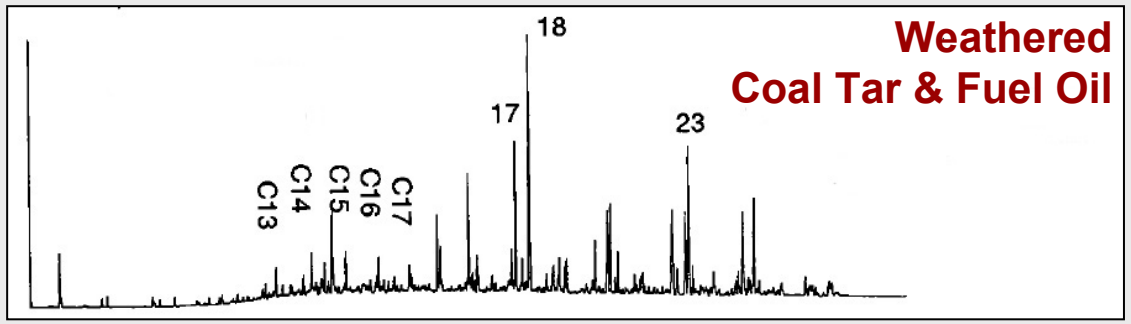
Difficult Conditions

Limitations of GC/FID & GC/MS

- Reliability decreases for:
  - A sample with multiple sources
  - Extensively weathered samples
  - *Low-levels of contamination (< 50 ppm)*







What is *Background* for PAHs?
The definitions vary!

- Natural background
- Anthropogenic background
- Regulatory background
- Area background
- *Urban background*

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Urban Background PAHs

- Natural background
  - Pre-existing and naturally produced
- Atmospheric fallout
  - Transportation, heating systems, power generation, industries
- Fill
  - Building materials
  - Debris, ash, trash
- Spills and sprays

***** sometimes higher than MGP PAHs *****

Isotope Analysis


Finnigan Delta + XL

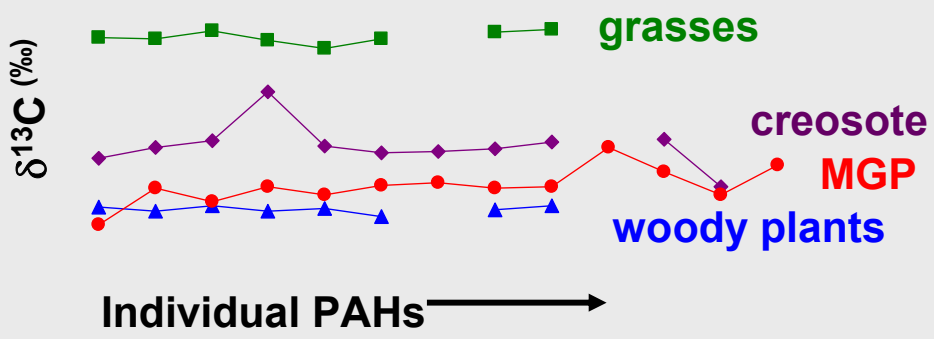
- Gas chromatography with isotope ratio mass spectrometry (GC/IRMS)
- Measure the stable isotope ratios of individual compounds in complex mixtures (e.g., C, H, S, O)
- Carbon isotope
  - Two stable isotopes of carbon: ^{12}C & ^{13}C
  - Naturally occurring ratio of $^{12}C/^{13}C \approx 99:1$

Compound Specific Carbon Isotope Ratios (CSIRs)

- CSIRs are reported relative to a standard carbon source (in ‰)

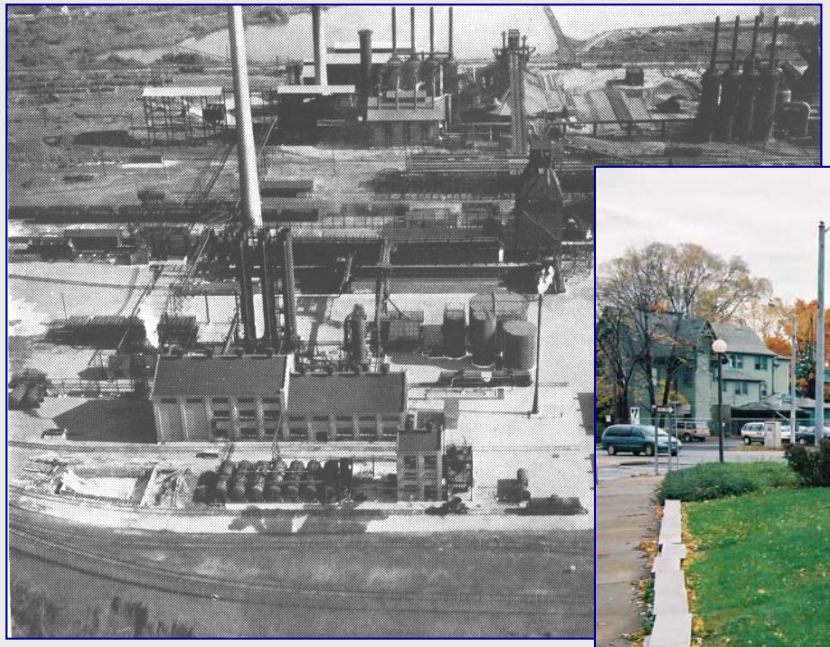
$$\delta\,{}^{13}C = \left[\frac{({}^{13}C/{}^{12}C)_{spl} - ({}^{13}C/{}^{12}C)_{std}}{({}^{13}C/{}^{12}C)_{std}} \right] \times 1000$$

- Carbon isotope ratios of PAHs from different hydrocarbon sources are often different



Technical Objective

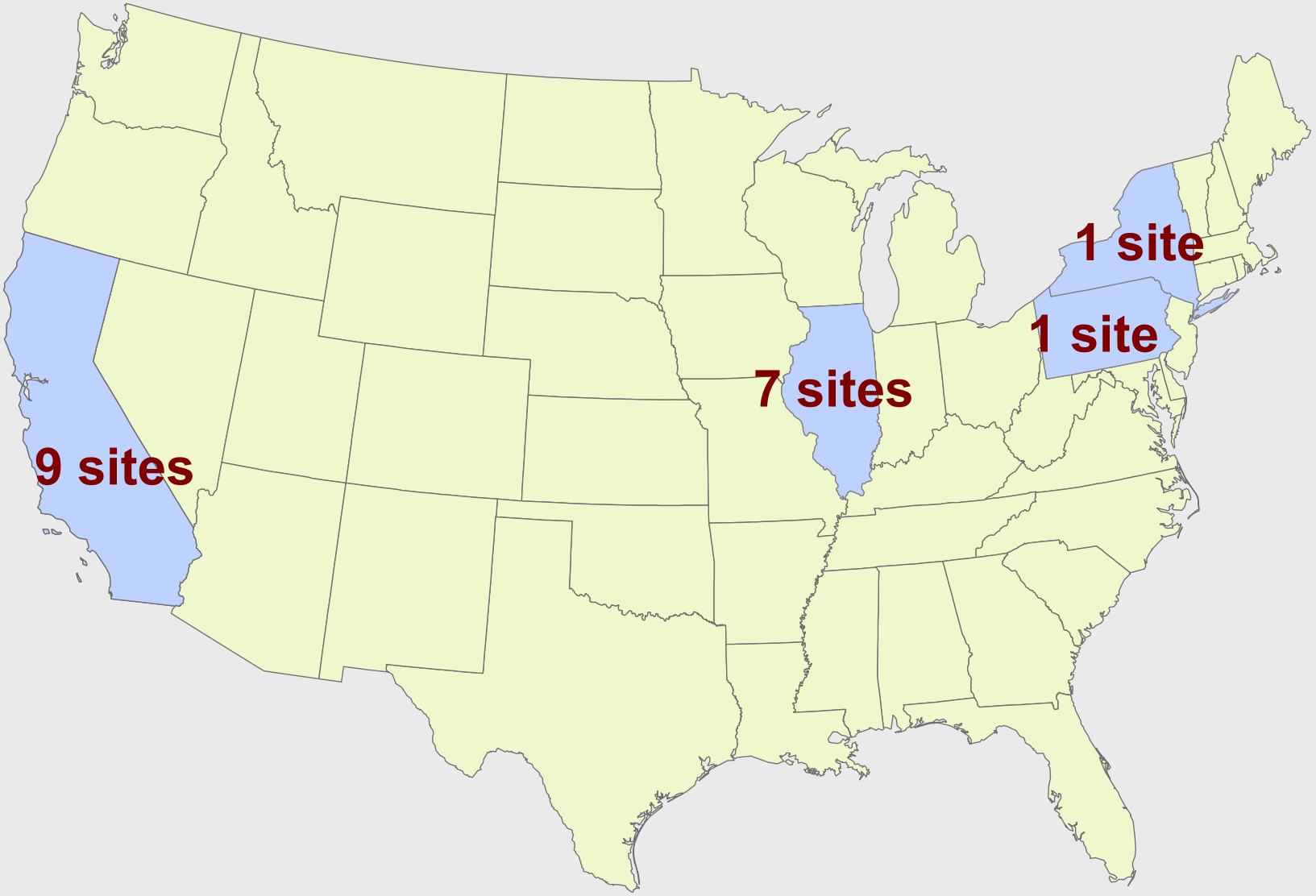
MGP versus urban background using GC/IRMS



Background Sampling Design

- Select cities or towns
  - List and number all populated areas
  - Use a random number generator to select areas
- Grid placed over a map of each city or town to randomly select sampling sites
- Sites scouted and described
- Soil samples collected 0-6”
- *NAPLs from MGP sites in each city or town collected*

Sampling Sites



Site Selection Criteria

- Sampling sites included:
  - Parks and playgrounds
  - Schools
  - Roadway medians
  - Parking lot landscaping
  - Grounds of government buildings
  - Utility properties
  - Commercial properties
  - Residential properties
- All sites were free of any visual contamination and known PAH sources

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RESULTS: 3 Cities in Midwest US

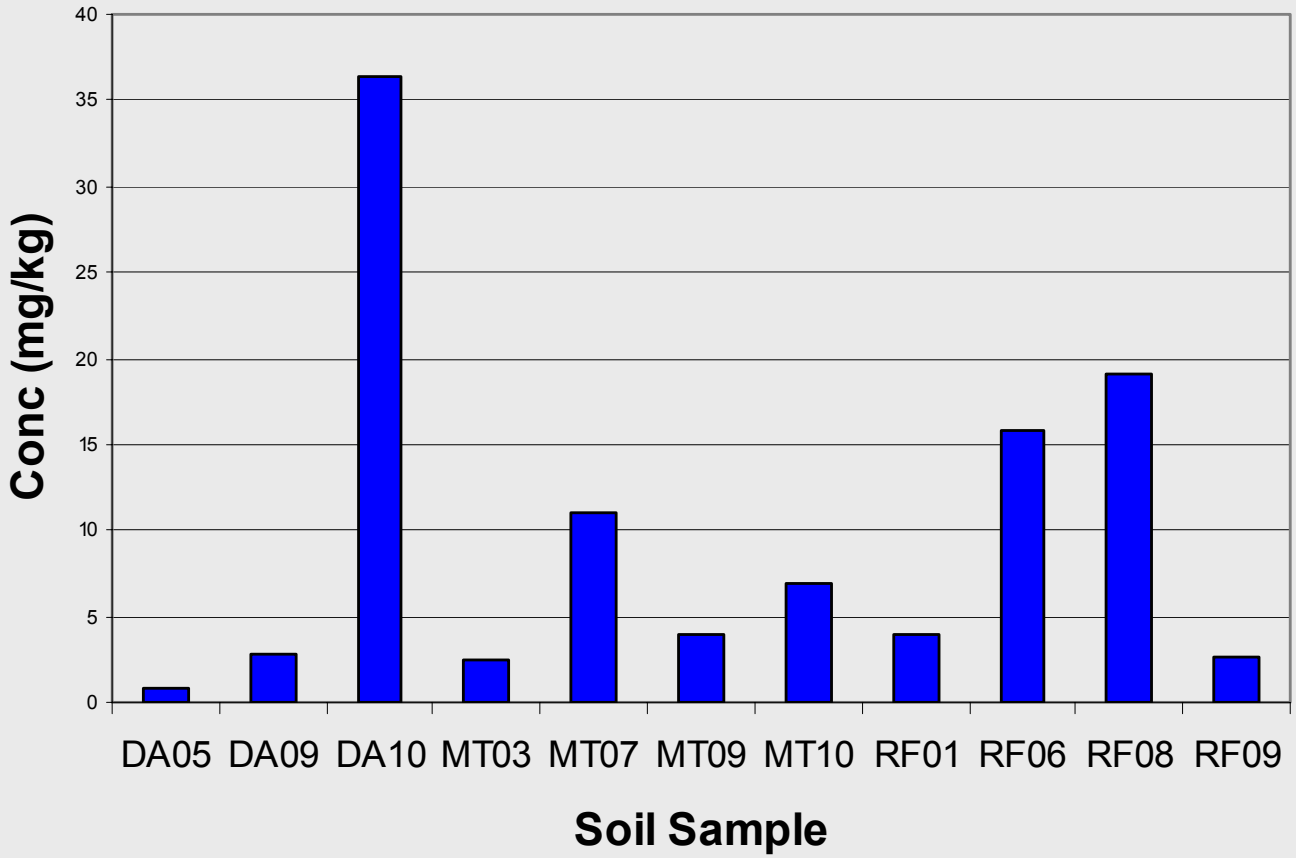
Background Soils and Tar Reference Samples

Soil	NAPL	Soil	NAPL
MT03 MT07 MT09 MT10	T282	RF01 RF06 RF08 RF09	T283
DA05 DA09 DA10	T284		
T185	Crude tar from a steel mill coke plant		

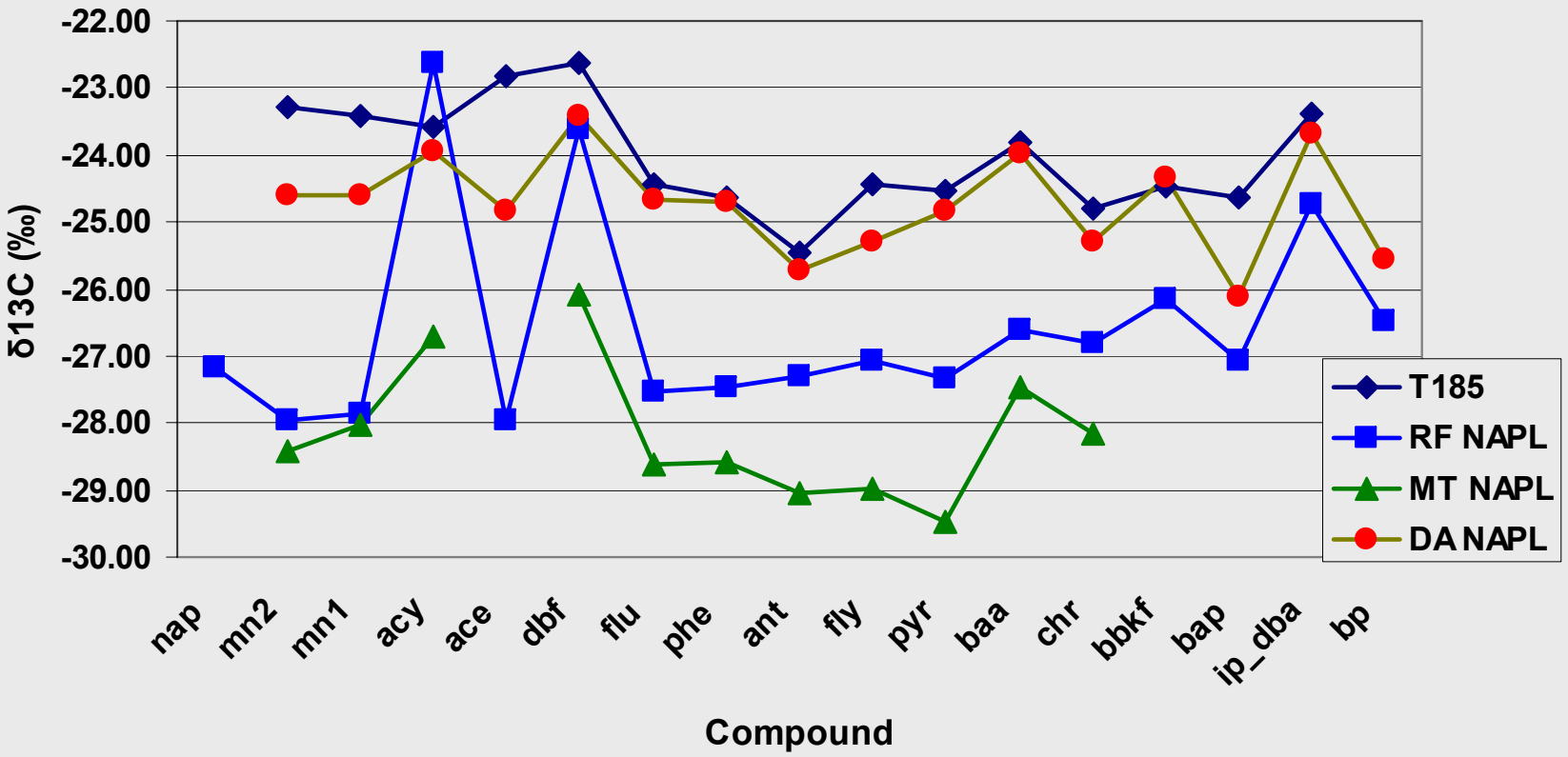
Soil (µg/kg) and NAPL (mg/kg) Concentrations

Sample ID	BAP	NAP	Total PAHs	TOC (%)
DA05	68.8	11.5	834	2.7
DA09	279	16.4	2,880	1.5
DA10	3260	304	36,300	3.6
MT03	193	14.9	2,510	3.7
MT07	900	253	11,100	6.7
MT09	247	365	3,880	4.5
MT10	572	79.1	6,940	4.5
RF01	372	37.7	3,970	2.8
RF06	1760	23.1	15,800	17.0
RF08	1500	67	19,100	4.2
RF09	240	3.88	2,620	2.4
RF NAPL	1970	29900	90400	
MT NAPL	1220	33500	89400	
DA NAPL	1350	16000	52500	
T185	8260	98300	288000	

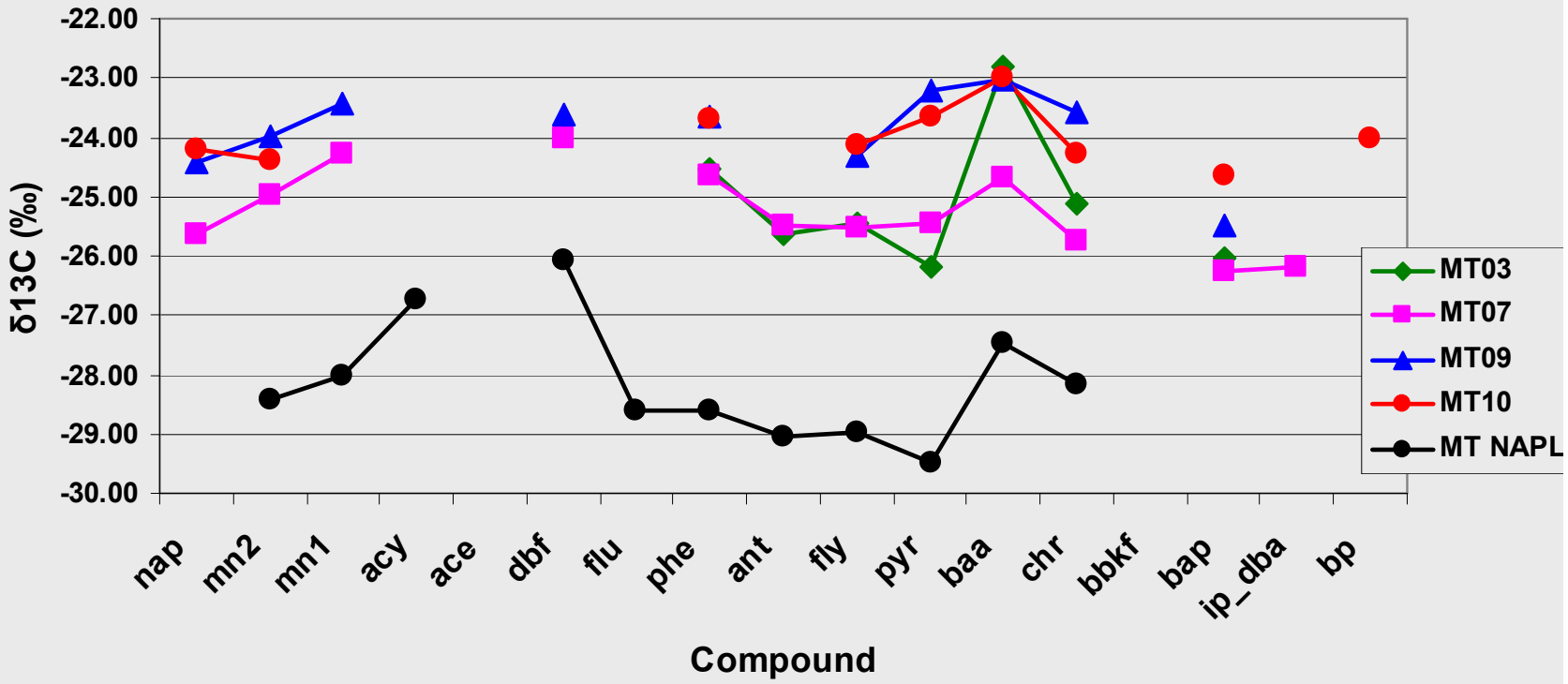
Background Soil Concentrations



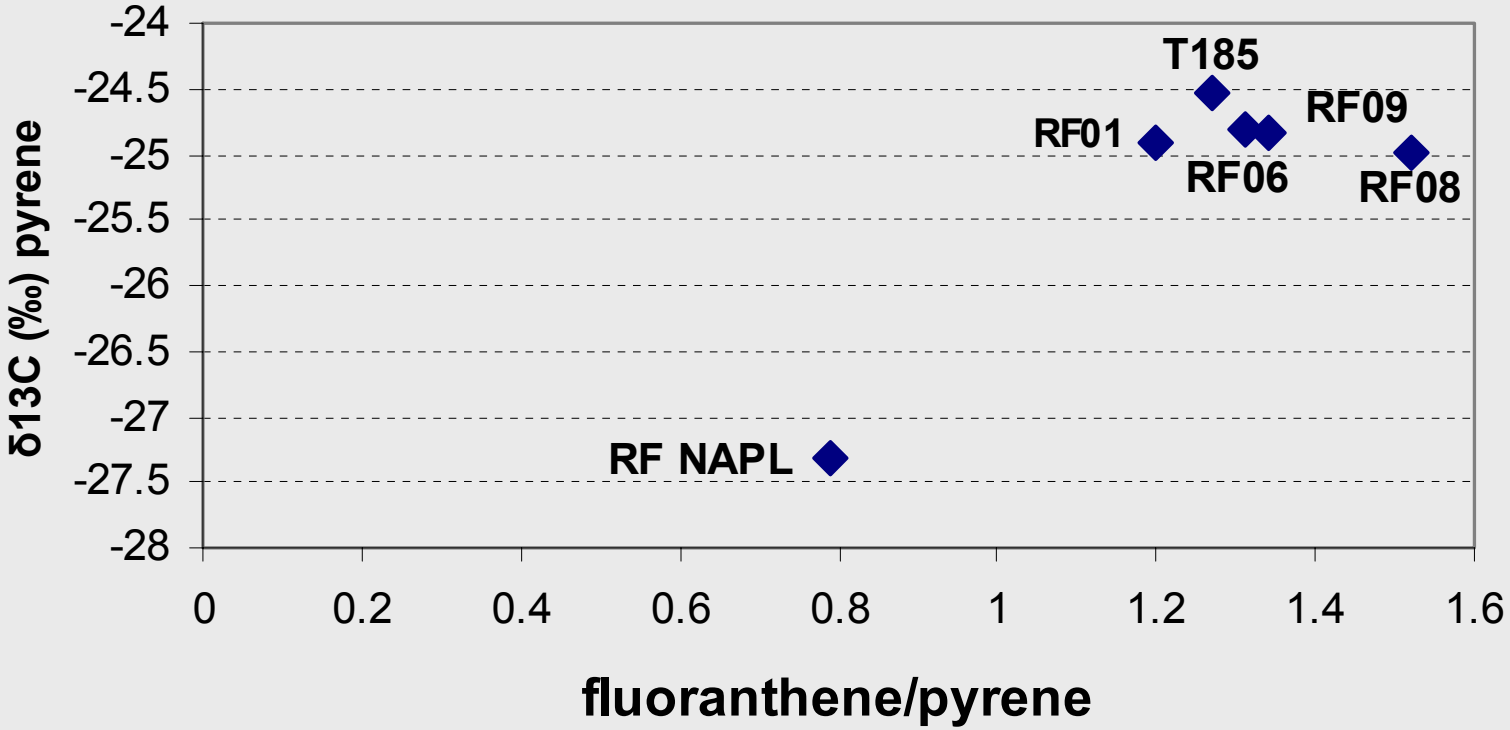
Comparison of CSIRs of NAPL Samples



Comparison of MT Soil and NAPL CSIR Results



Correlation of PAH Patterns to CSIRs



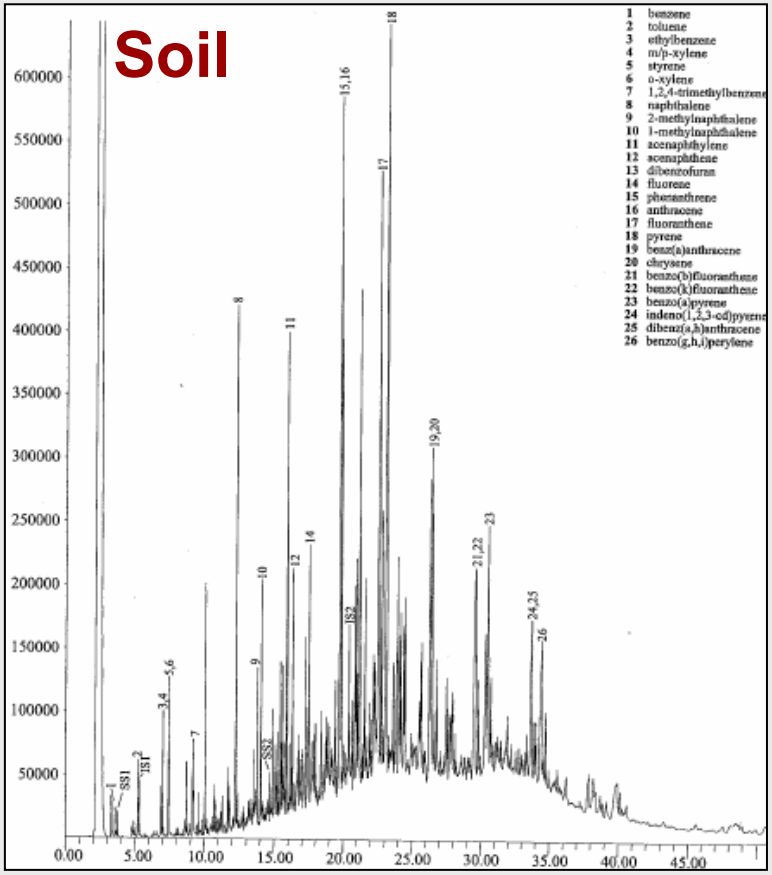
Application to a Site

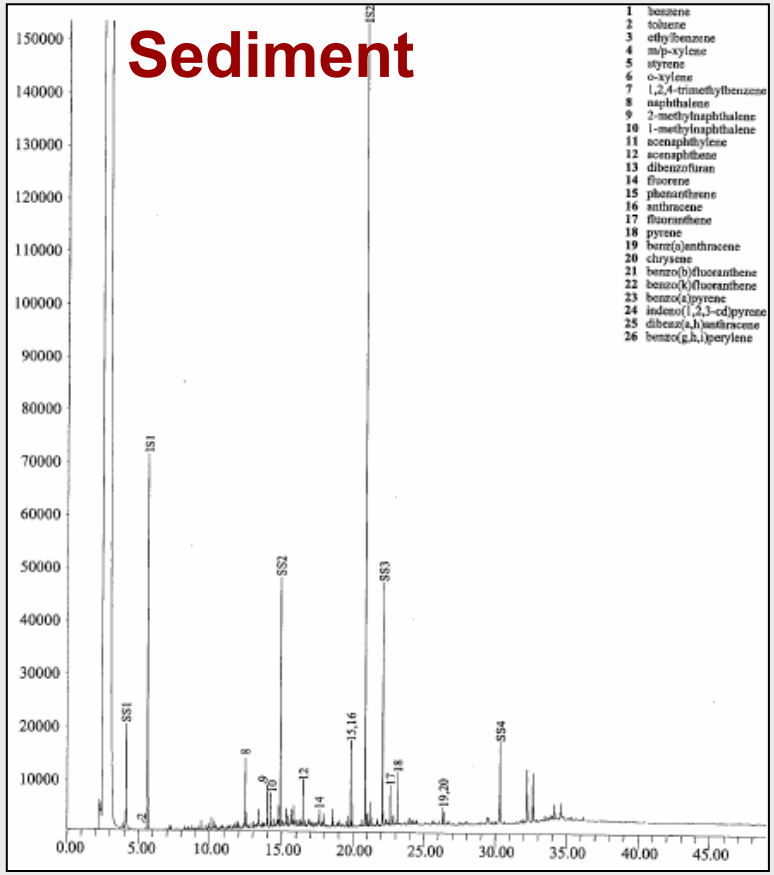
- Former water gas MGP Site near a major lake
- Areas surrounding the properties consist of:
  - Industrial land
  - Wastewater treatment plant
  - Former coal dock with large aboveground fuel oil storage tanks
  - Commercial/residential properties
- Soil consists of a few feet of fill overlying native red clay

Study Design

- 8 soil samples from site (Soils 1-8)
- 5 sediment samples from the major lake near the site (Sediments 1-5)
- Analyses
  - GC/FID
  - GC/MS
  - GC/IRMS

Chemical Fingerprinting





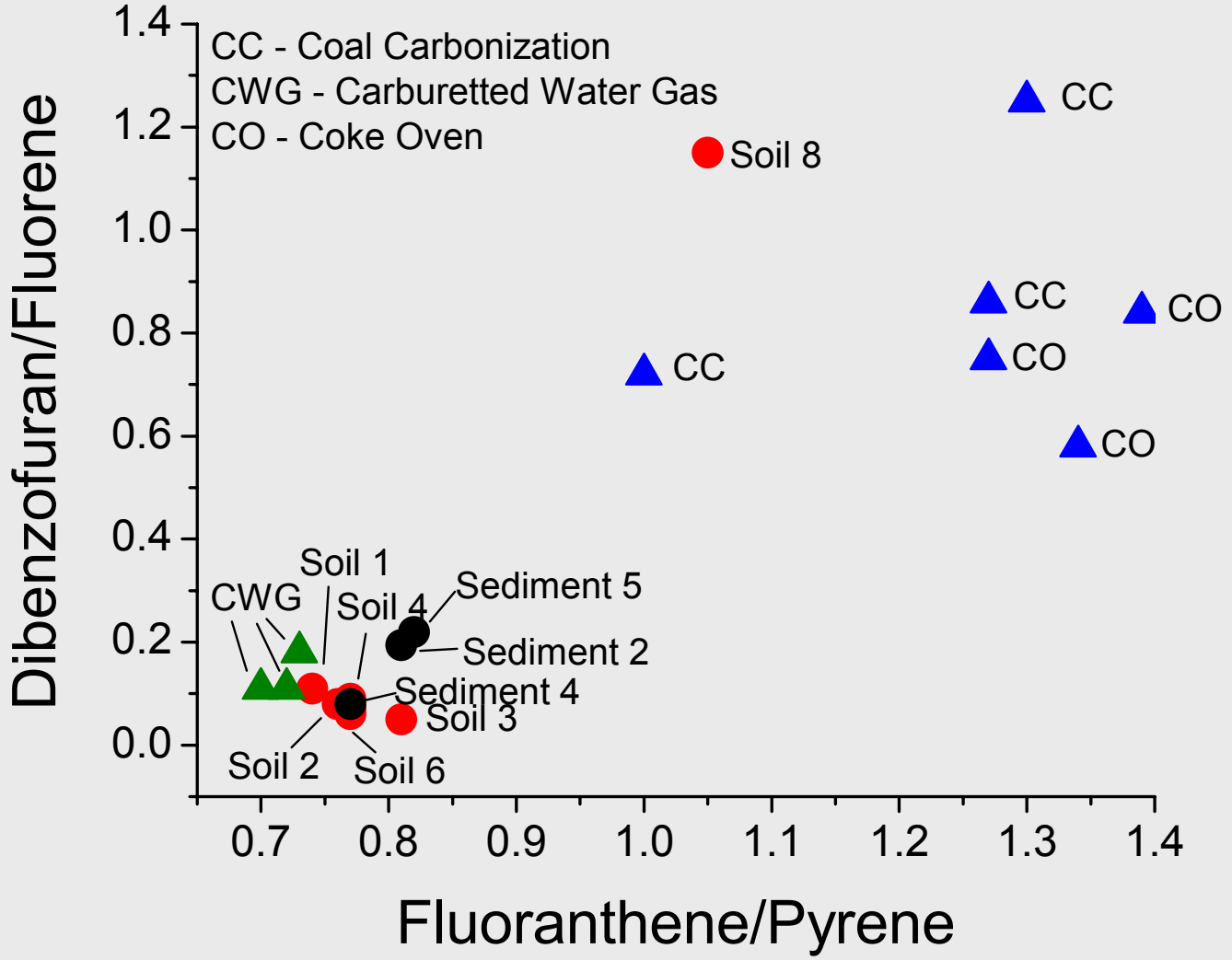
- Soils & Sediments: both pyrogenic & petrogenic sources
- But [PAHs] much lower in sediment samples

Chemical Concentrations: mg/kg

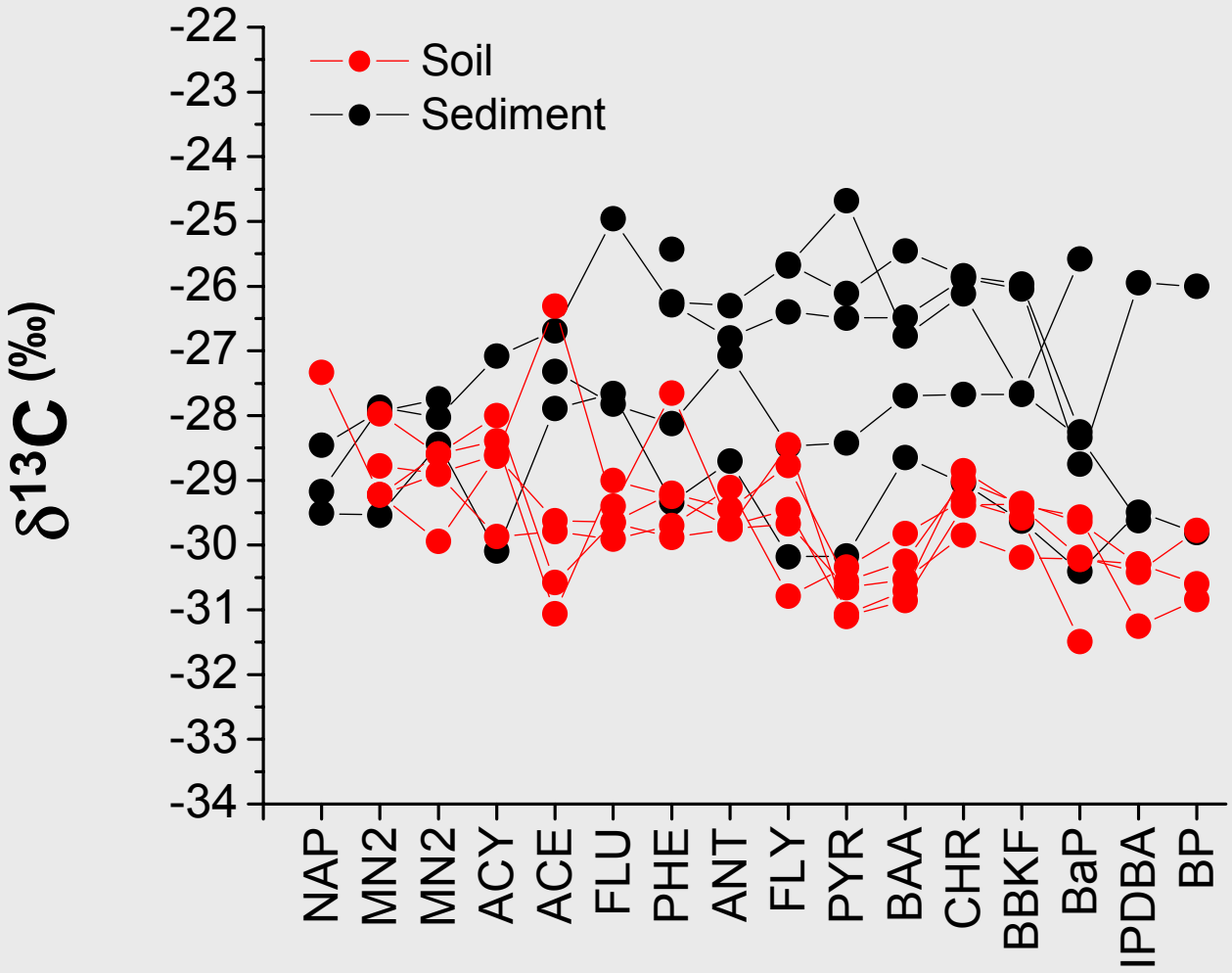
Compounds	Soil	Sediment
Benzene	42.3	0.3
Toluene	116	0.35
Ethylbenzene	78.8	0.14
m/p-Xylenes	185	0.2
Styrene	241	ND
o-Xylene	156	0.05
1,2,4-Trimethylbenzene	138	ND
Naphthalene	1260	0.52
2-Methylnaphthalene	360	0.24
1-Methylnaphthalene	554	0.23
Acenaphthylene	1160	0.09
Acenaphthene	590	0.28
Dibenzofuran	56.2	ND
Fluorene	793	0.15

Compounds	Soil	Sediment
Phenanthrene	2670	0.81
Anthracene	803	0.22
Fluoranthene	1410	0.6
Pyrene	1820	0.77
Benz[a]anthracene	533	0.32
Chrysene	518	0.34
Benzo[b]fluoranthene	305	0.21
Benzo[k]fluoranthene	453	0.22
Benzo(e)pyrene	447	0.24
Benzo[a]pyrene	637	0.37
Perylene	112	0.09
Indeno[1,2,3-cd]pyrene	511	0.16
Dibenz[a,h]anthracene	147	0.07
Benzo[g,h,i]perylene	951	0.45

Selected Source Ratios



CSIRs


Soil
Sediment
δ13C (‰)
-22
-23
-24
-25
-26
-27
-28
-29
-30
-31
-32
-33
-34
NAP
MN2
MN2
ACY
ACE
FLU
PHE
ANT
FLY
PYR
BAA
CHR
BBKF
BaP
IPDBA
BP

Overall Project Results

- Chemical fingerprints show that soils on the site & sediments near the site possess both pyrogenic & petrogenic sources
- Although selected source ratios suggest that pyrogenic substances in the soils & sediments are from CWG tar, the concentrations of PAHs in the sediments are much lower than those of the soils
- CSIRs show that PAH source(s) of the sediments are, in fact, different than those of the soils (e.g., urban runoff)

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Conclusion

- Chemical fingerprinting is a powerful tool for environmental work.
- Forensic chemistry has been used for conclusive waste ownership in soils
- Forensic chemistry has applications for waste ownership in sediments
- GC/IRMS techniques are powerful for background PAH identification
- GC/IRMS has application in waste dating, indoor air quality work, compound fate and transport, weathering, bioavailability and many others

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For further questions, please contact me. Thank you for your attention.

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