CHEMICAL MARKER STRATEGY FOR EVALUATING FUTURE CONTAMINATION AT A WOOD PRESERVING FACILITY

National Environmental Monitoring Conference 2014
Washington, D.C.

August 4, 2014

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Outline

- Purpose of Investigation
- Assessment Methodology
- Sample Results
- Conclusions
- Wrap up and Q & A

Are your Data Scientifically Valid, Usable, & Meaningful?

How much of a chance are you willing to take that they are not?

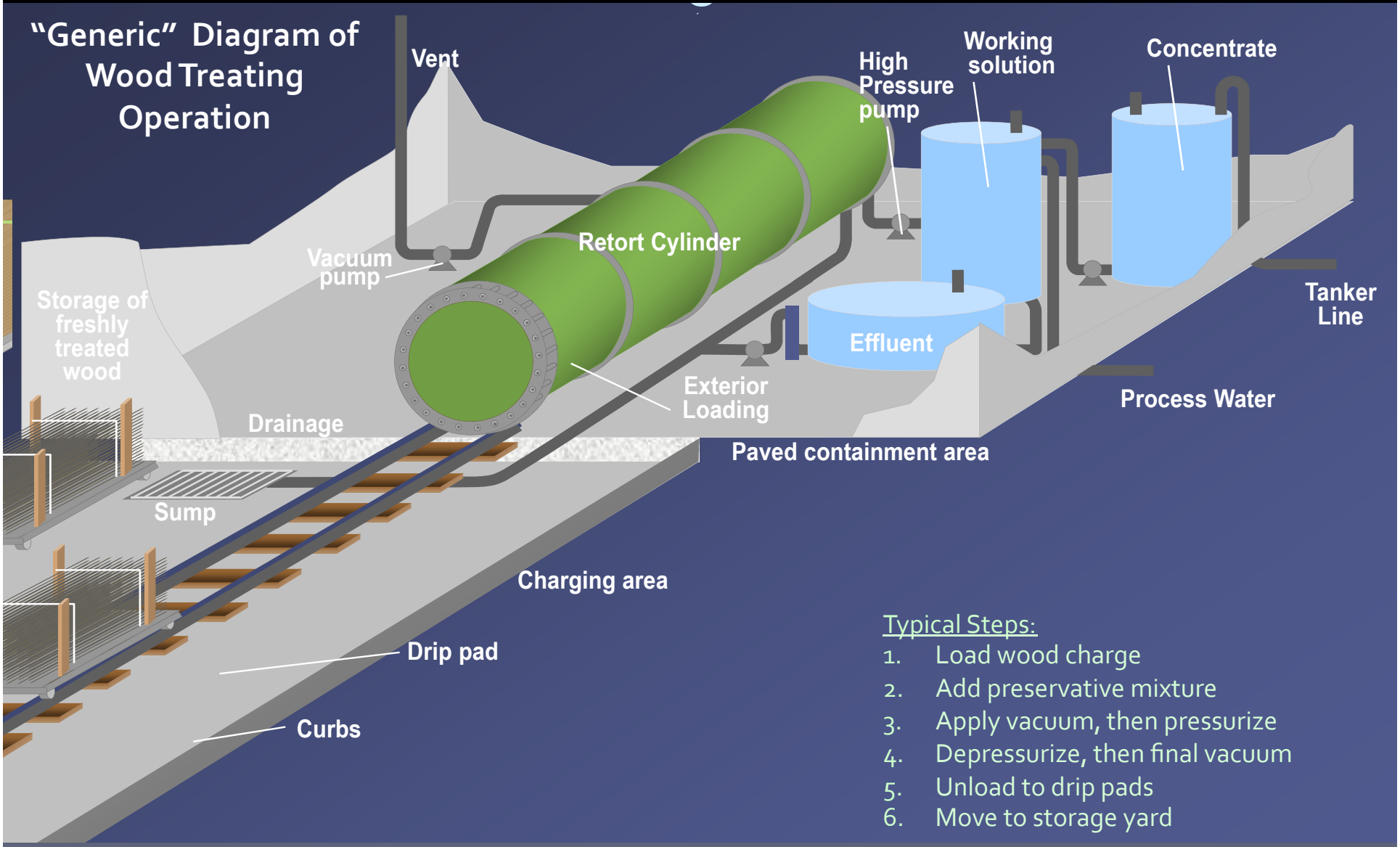
Purpose of Investigation

Differentiate Historical Site COC's from Current-Use PCP Wood Treatment Solution should Future Spill Occur?

Pentachlorophenol (PCP) is one of the primary historical COCs, but need multiple lines-of-evidence to answer question

Purpose of Investigation, cont.

Site historically used for wood treatment (organic and inorganic preservatives)



Typical Steps:

1. Load wood charge
2. Add preservative mixture
3. Apply vacuum, then pressurize
4. Depressurize, then final vacuum
5. Unload to drip pads
6. Move to storage yard

http://www.trainex.org/osc2012/uploads/543/OSC_2012_Ind_Process_01_Wood_Preserving_18Nov11.pdf

Purpose of Investigation, cont.

- Historical contaminants primarily include:
  - DNAPL (primarily creosote)
  - PAHs from creosote, P-9 oil, and other sources (PAH signatures are of petrogenic and pyrogenic)
  - PCP (including other chlorinated phenols)
  - Arsenic, chromium, and copper
  - PCDD/Fs (not fully characterized site-wide)

Purpose of Investigation, cont.

- Former Superfund site with "final" remedy:
  - Underground vertical barrier wall
  - Low-permeability asphalt cap
  - GW extraction system
  - Contaminated ditch surface soils and sediments excavated and disposed at offsite licensed facility

Purpose of Investigation, cont.

- Current ownership also using PCP
- Proactive approach:
  - Conduct "Baseline" Study then "Marker Strategy"
  - Identify and delineate nature and extent of COCs
  - Routine & Advanced Chemical Fingerprinting
  - Differentiate historic from current use COCs
  - Acquire data of documented & known quality
  - Be cost-effective & meet legal agreements

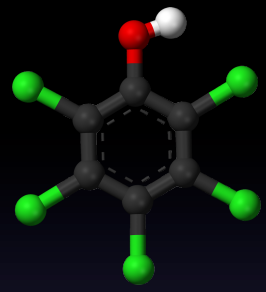
Site Map


Boneyard
Treated Wood Storage Yard
Block Dissolver
Process Area
Kilns
Railcar Shed
White Pole Storage Yard
Treated Wood
Inspection Area
North Tank Farm
Treating Room
Drip Pad
Retorts
Dry Shed
Hazardous Waste Storage
Incisor
Staining
Bldg
Waste Water Treatment System
Approximate Location of Vertical Barrier
South Tank Farm
Peeler
MatCon Cap
Office
Stormwater Treatment System

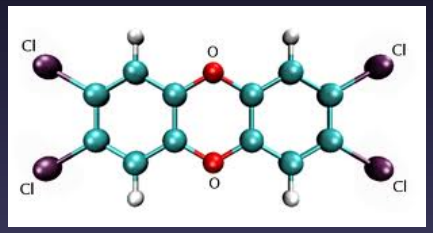
Assessment Methodology

- Reviewed historical data
- Baseline & Marker Strategy Study
  - Collected soil, sediment, & GW
  - Collected PCP treatment solution*

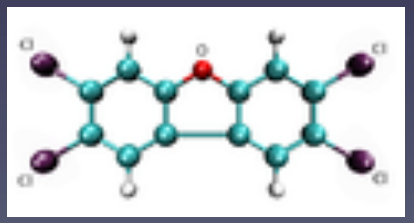
    *mixture of 6% PCP + co-solvent + Diesel #2
  - Completed Analyses for:
    - SVOCs & PCP
    - PCDD/Fs
    - Hydrocarbons by Full scan GC/MS



http://commons.wikimedia.org/wiki File:Pentachlorophenol-3D-balls.png



http://commons.wikimedia.org/wiki/File:Dioxine_pcdd.png



http://commons.wikimedia.org/wiki/File:Furane_pcdf.png

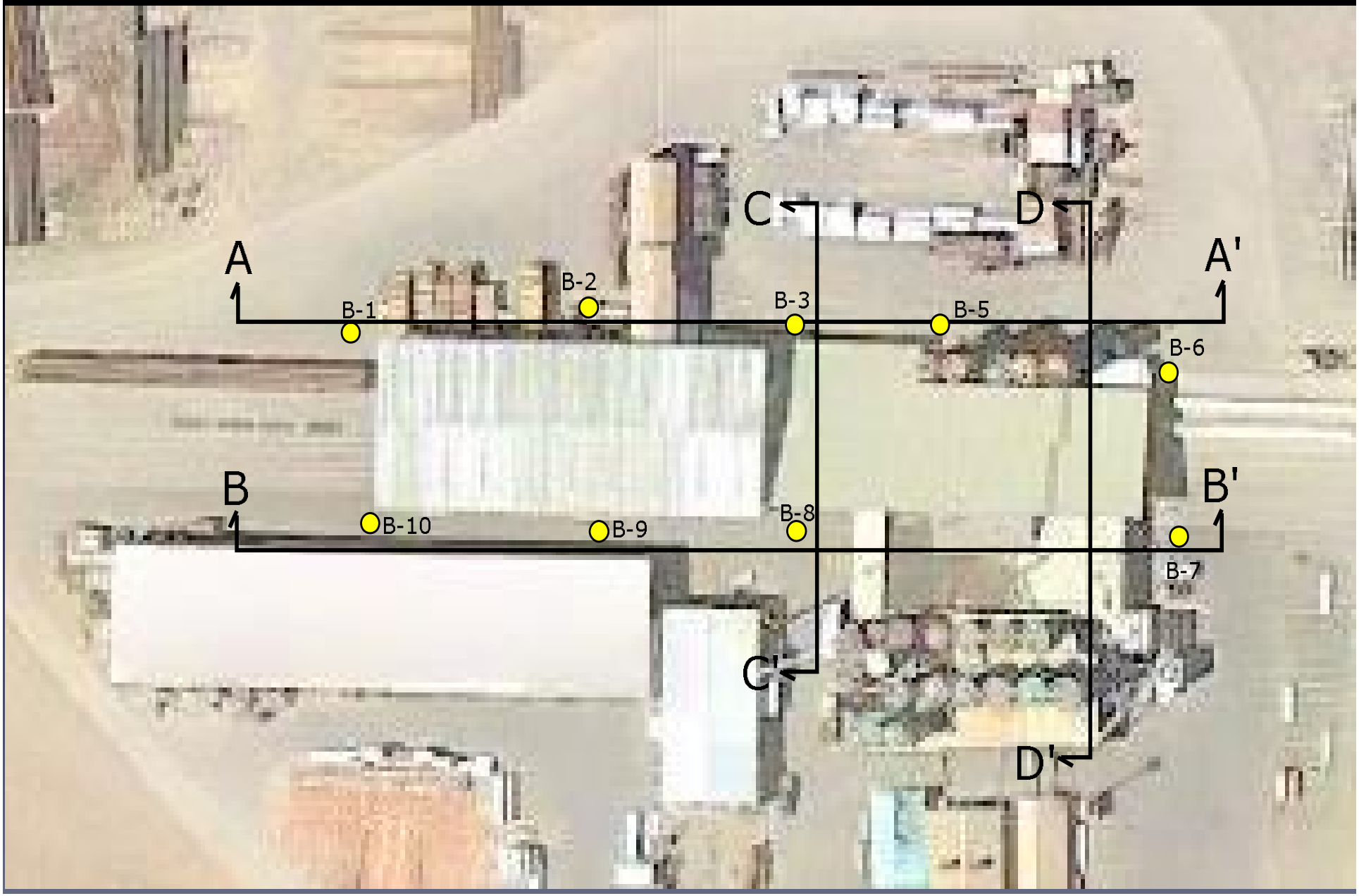
Assessment Methodology, continued

Data acquired for petroleum-related compounds included following:

- Full-scan GC/MS - Tentatively Identified Compounds
- m/z 85 and m/z 113: *n*-Alkanes & Iso-Alkanes + Isoprenoids
- m/z 83 : Alkylcyclohexanes
- m/z 134 : C_4-Alkylbenzenes
- m/z 123: Bicyclanes (i.e., Bicyclic Sesquiterpanes)
- m/z 191: Tri-, Tetra-, and Pentacyclic Terpanes (i.e., Sesquiterpanes)
- m/z 127: Steranes
- Histogram for selected alkylbenzenes, alkylated PAHs, alkylated biphenyls, alkylated biphenyls/dibenzofurans, alkylated benzothiophenes, and steranes

“S”, “D”, & “WP” Sampling Locations Locations

Treatment Plant Boring ("B") Locations



Assessment Methodology, cont.

- Completed data verification, validation, & DQA
- PCP primary COC (past and present)
- PCP not necessarily a good "marker"
- Historical contamination is problematic

Assessment Methodology, cont.

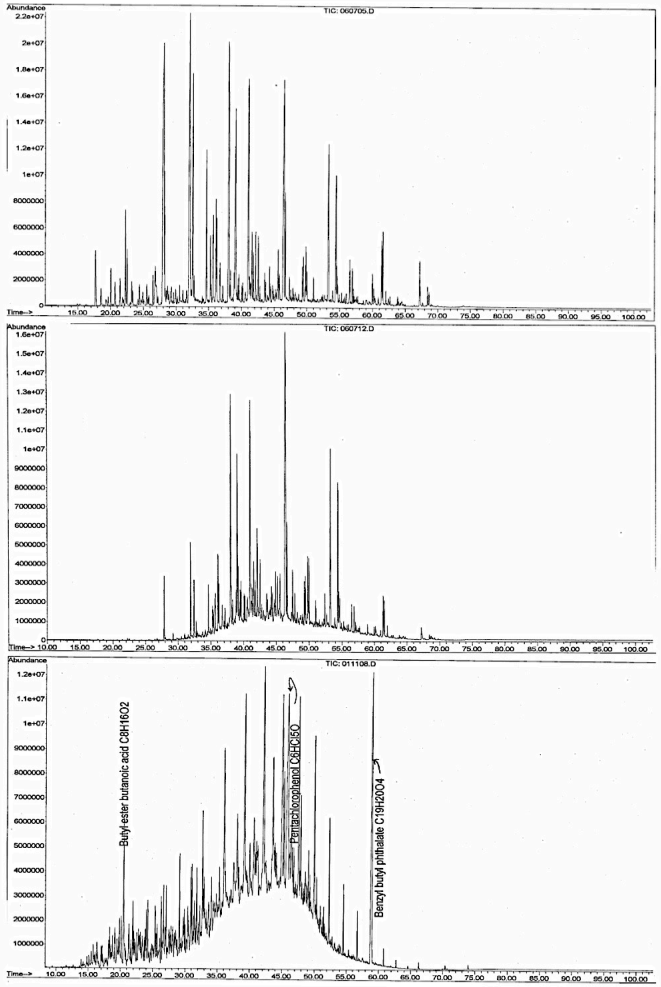
- Multiple lines-of-evidence needed:
  - Differentiate historical vs. possible future COCs
  - Any unique "marker" compounds present?
  - Compared PCDD/Fs results
  - Reviewed SICPs, mass chromatograms, etc.
  - Confirmed absence/presence of co-solvent (i.e., BBP) with PCP

Sample Results

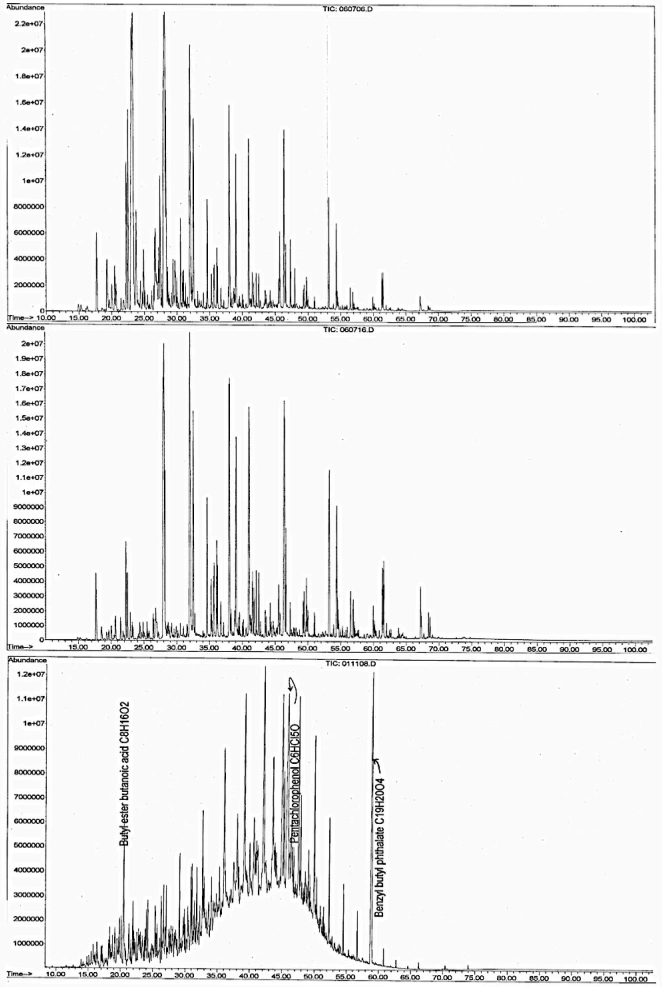
- Results of the hydrocarbon and PCDD/F data
- Time constraints, so few examples shown
- Data from two borings taken by retorts and drip pads are illustrated for example
- Co-located GW sample & soil sample are compared to the PCP working solution

Sample Results: Full Scan GC/MS (TIC's)

Full GC/MS Scan: TLC-B3 Aqueous, TLC-B3 Soil, and Working Solution

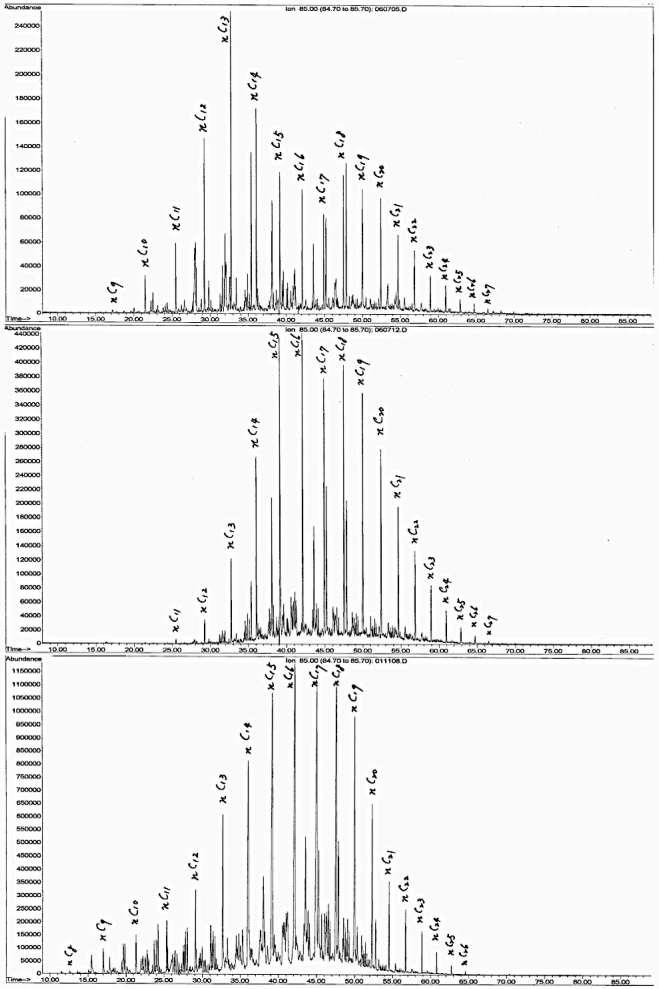


Full GC/MS Scan: TLC-B8 Aqueous, TLC-B8 Soil, and Working Solution

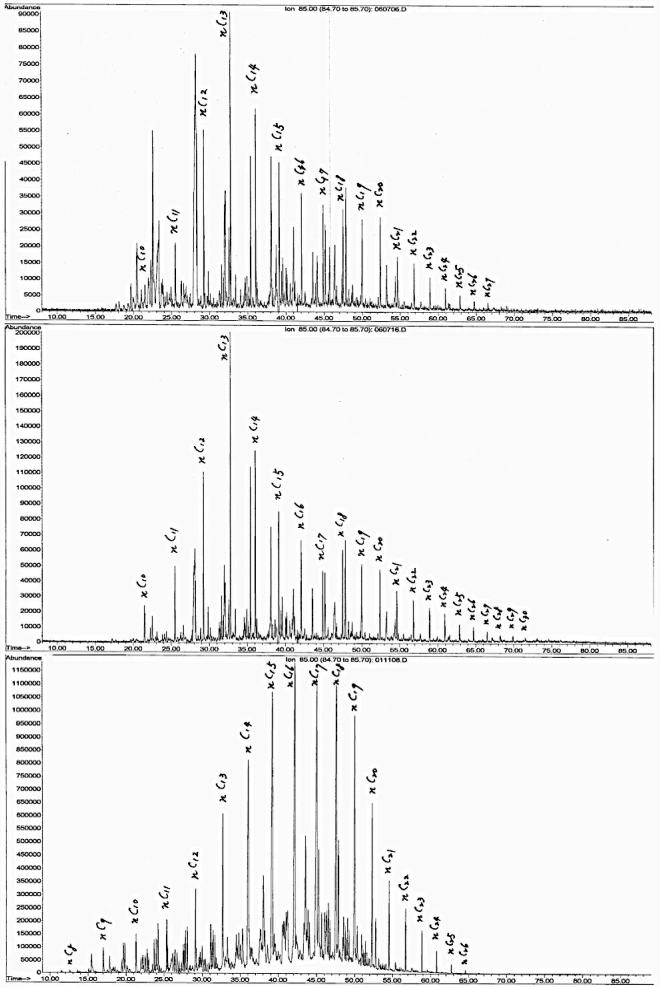


Sample Results: m/z 85 (n-Alkanes)

Part 1: m/z 85 Paraffins and Isoparaffins: TLC-B3 Aqueous, TLC-B3 Soil, and Working Solution

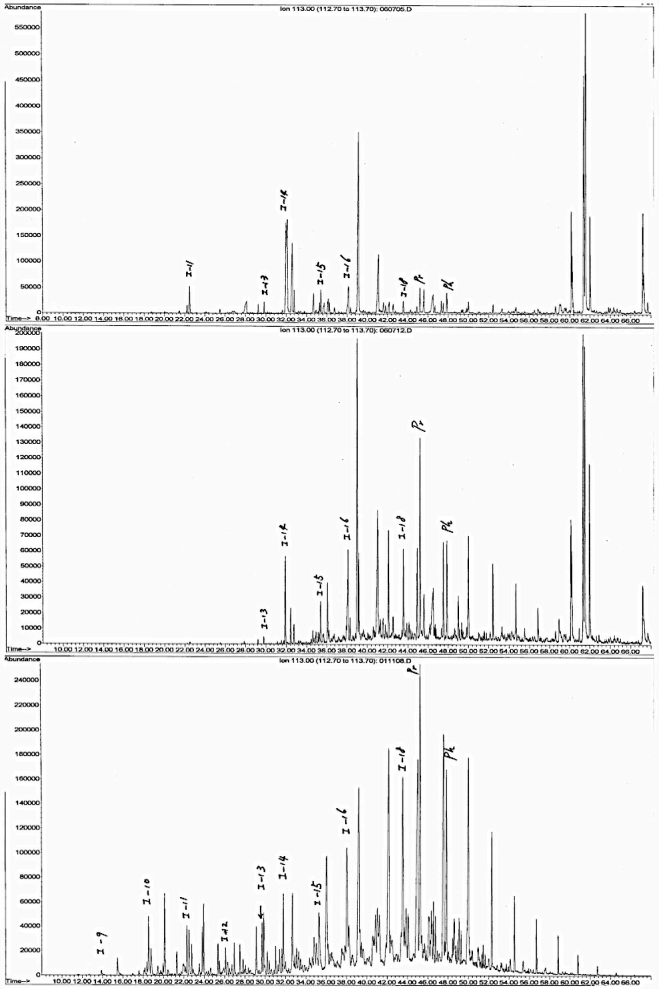


Part 1: m/z 85 Paraffins and Isoparaffins: TLC-B8 Aqueous, TLC-B8 Soil, and Working Solution

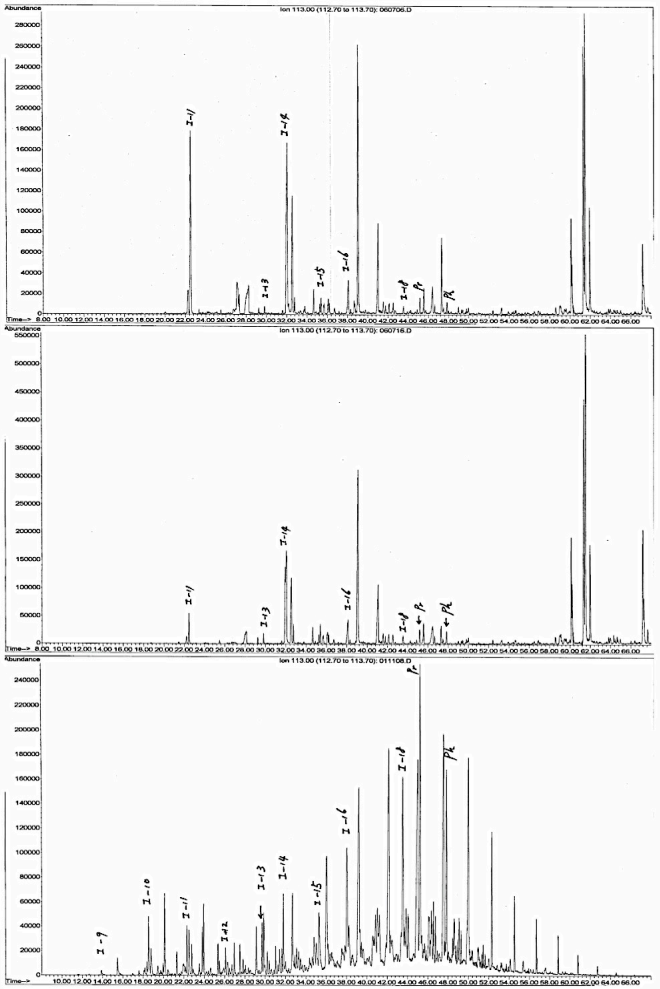


Sample Results: m/z 113 (Isoalkanes & Isoprenoids)

Part 2: m/z 113 Paraffins and Isoparaffins: TLC-B3 Aqueous, TLC-B3 Soil, and Working Solution

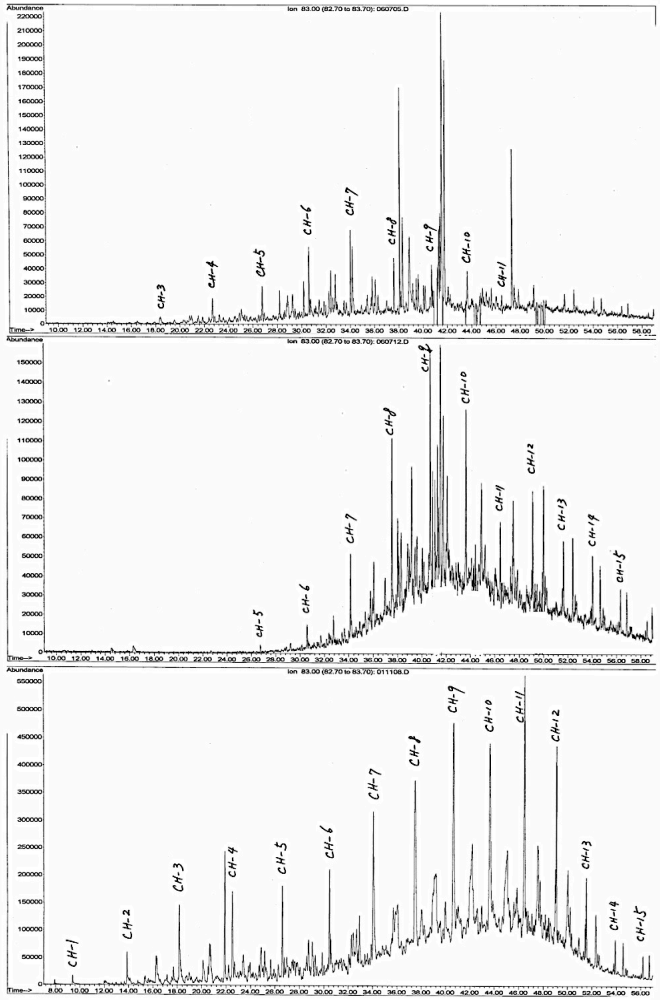


Part 2: m/z 113 Paraffins and Isoparaffins: TLC-B8 Aqueous, TLC-B8 Soil, and Working Solution

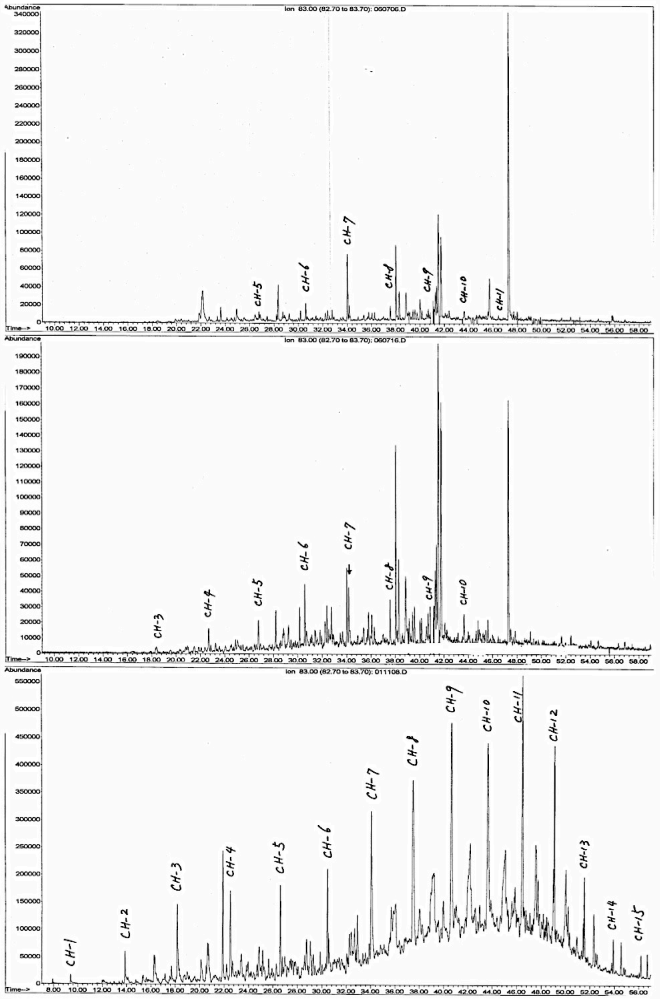


Sample Results: m/z 83 (Alkylcyclohexanes)

Alkylcyclohexanes at m/z 83: TLC-B3 Aqueous, TLC-B3 Soil, and Working Solution

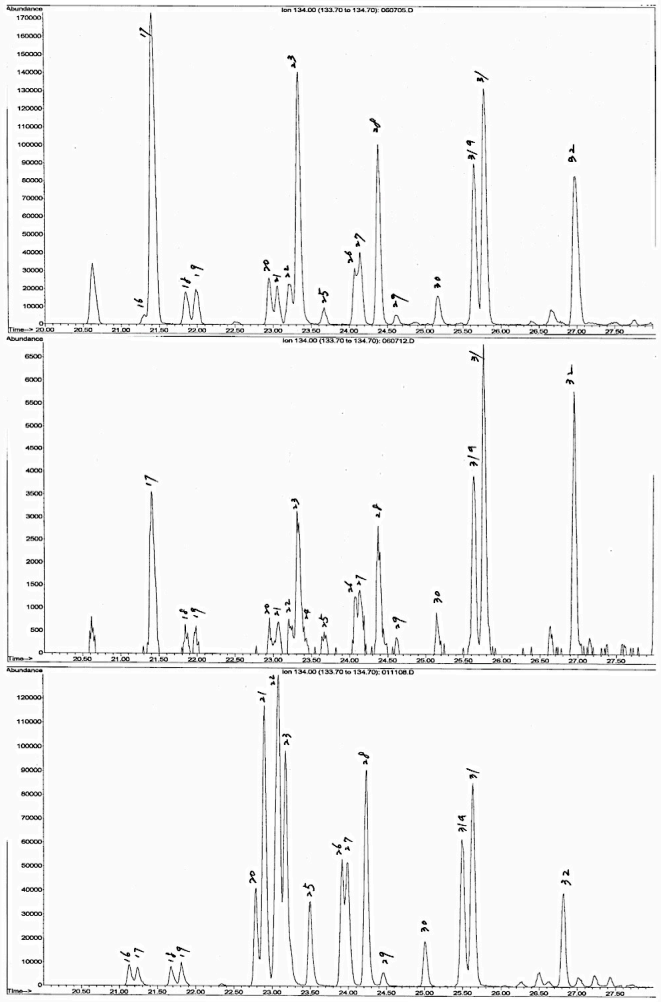


Alkylcyclohexanes at m/z 83: TLC-B8 Aqueous, TLC-B8 Soil, and Working Solution

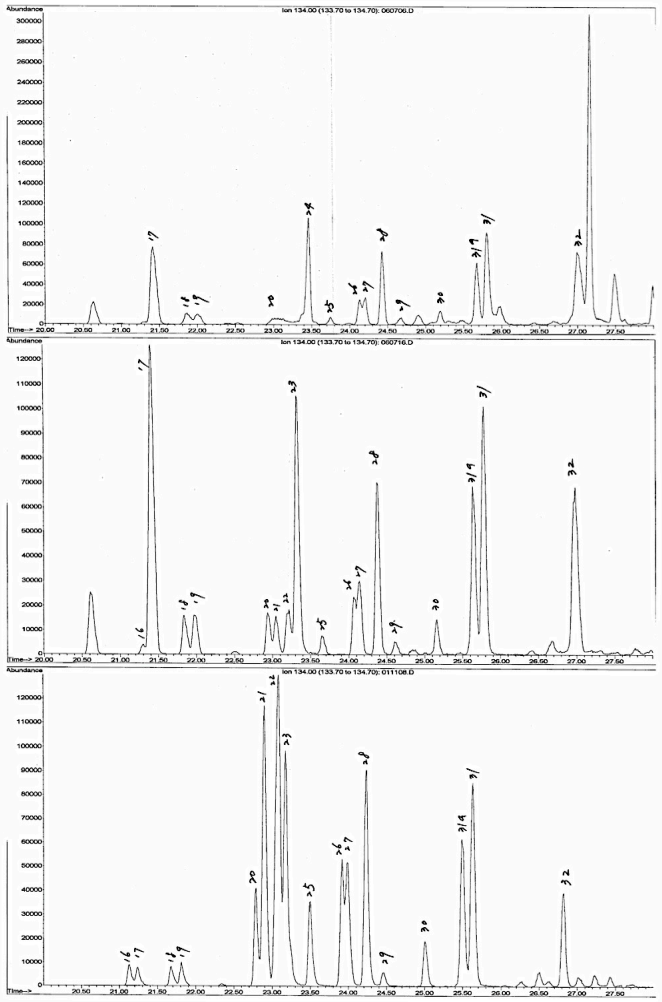


Sample Results: m/z 134 (C-4 Alkylbenzenes)

C_4 Alkylbenzenes at m/z 134: TLC-B3 Aqueous, TLC-B3 Soil, and Working Solution

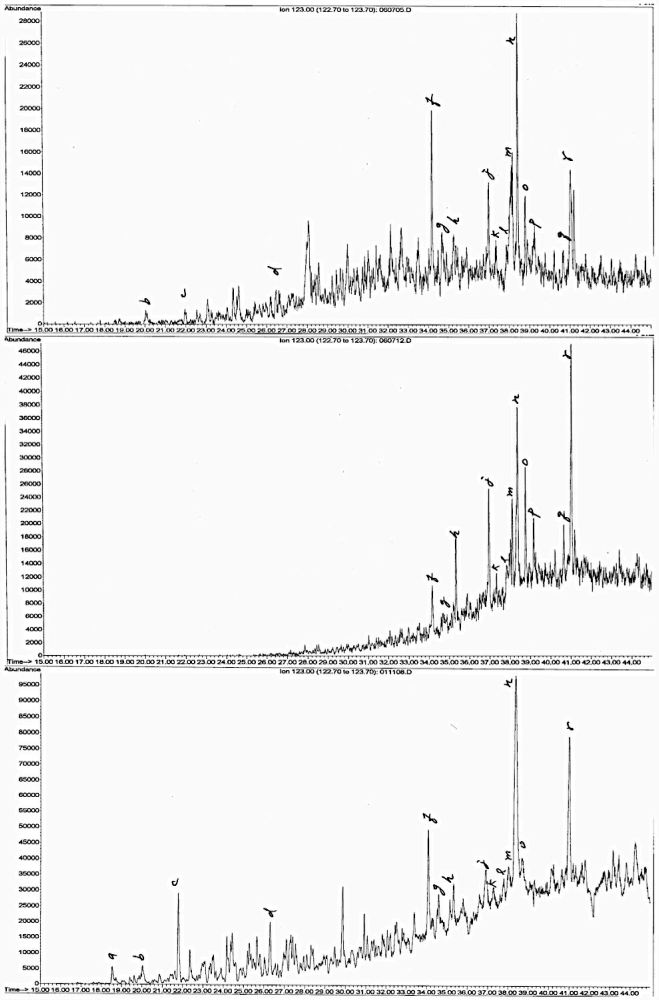


C_4 Alkylbenzenes at m/z 134: TLC-B8 Aqueous, TLC-B8 Soil, and Working Solution

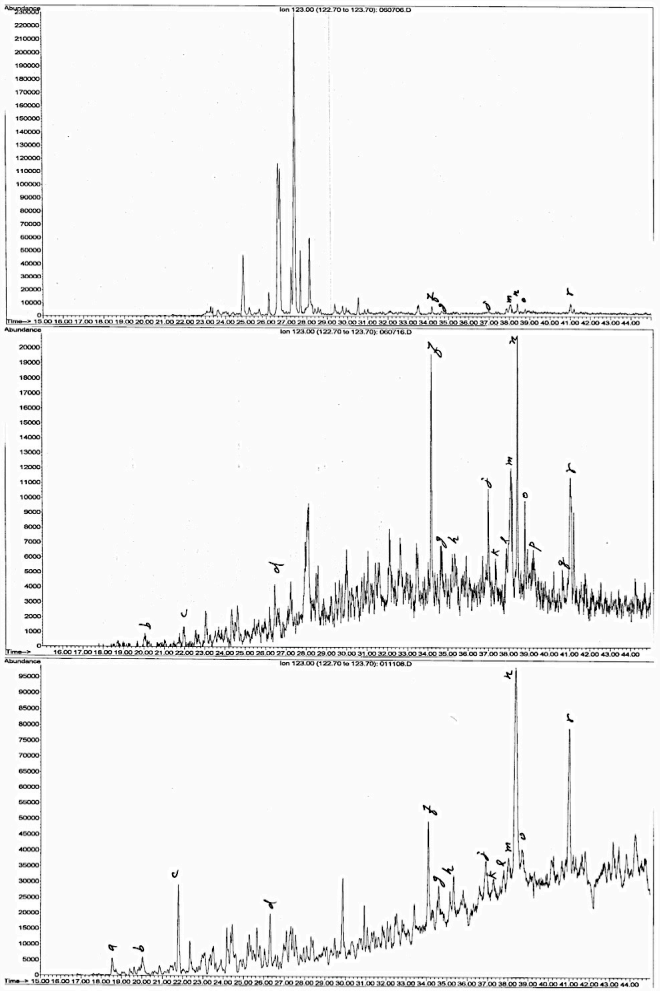


Sample Results: m/z 123 (Bicyclanes)

Bicyclanes at m/z 123: TLC-B3 Aqueous, TLC-B3 Soil, and Working Solution

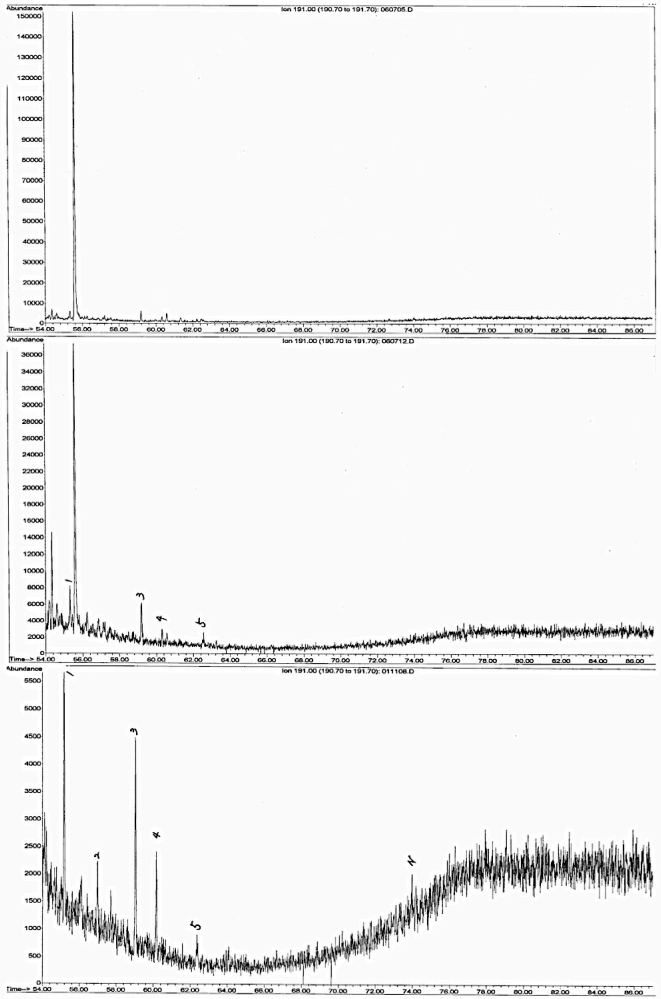


Bicyclanes at m/z 123: TLC-B8 Aqueous, TLC-B8 Soil, and Working Solution

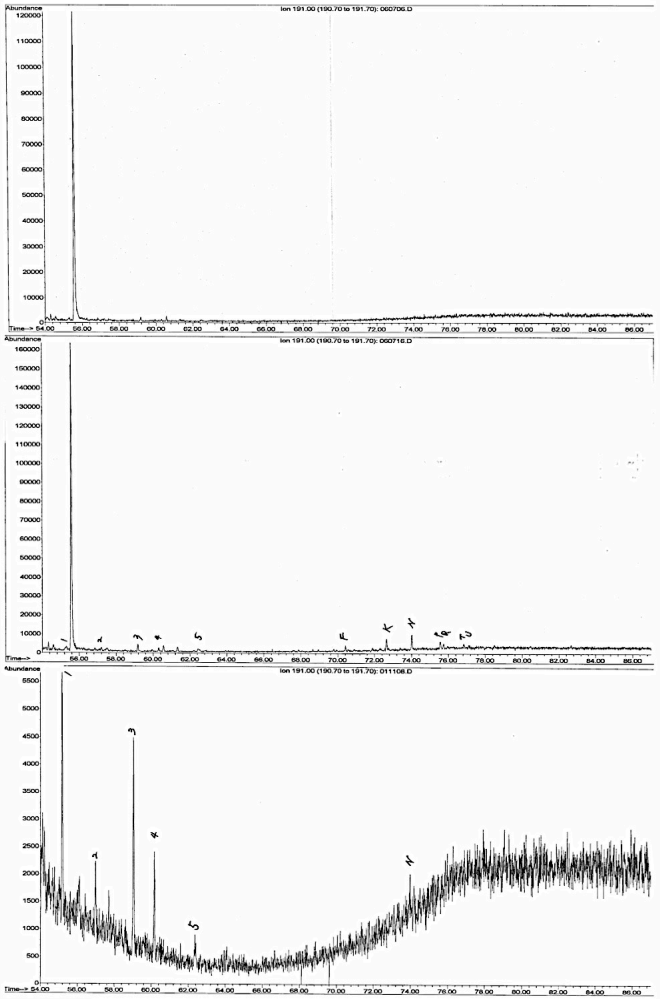


Sample Results: m/z 191 (Terpanes)

Terpanes at m/z 191: TLC-B3 Aqueous, TLC-B3 Soil, and Working Solution

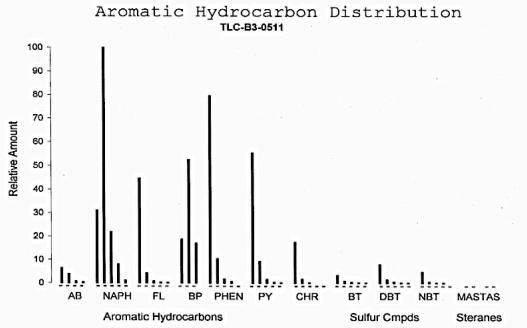


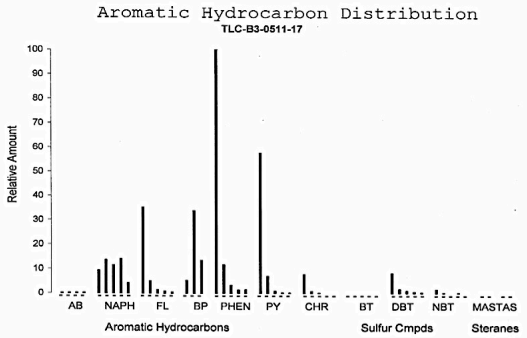
Terpanes at m/z 191: TLC-B8 Aqueous, TLC-B8 Soil, and Working Solution

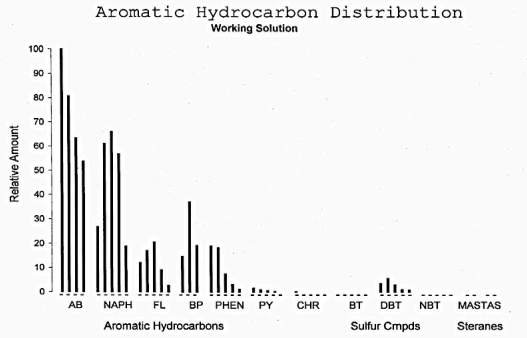


Sample Results: Plots of Aromatic Hydrocarbons

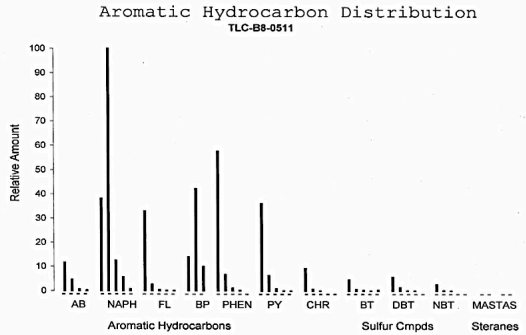
Aromatic Hydrocarbon Distribution: TLC-B3 Aqueous, TLC-B3 Soil, and Working Solution

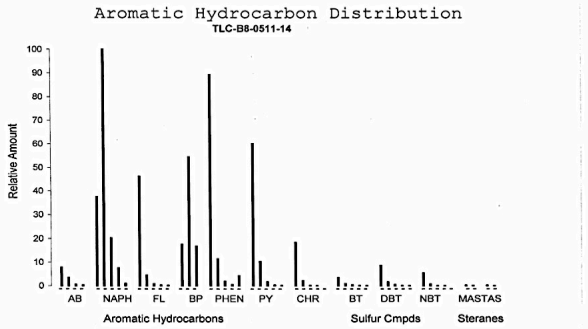


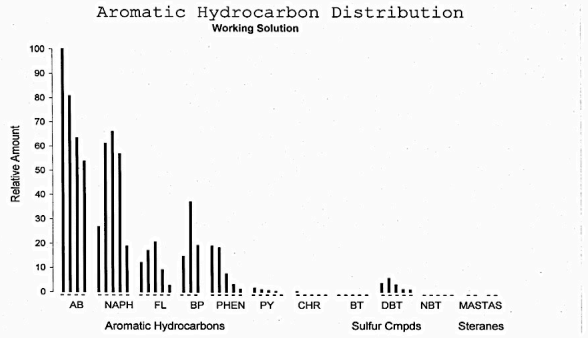




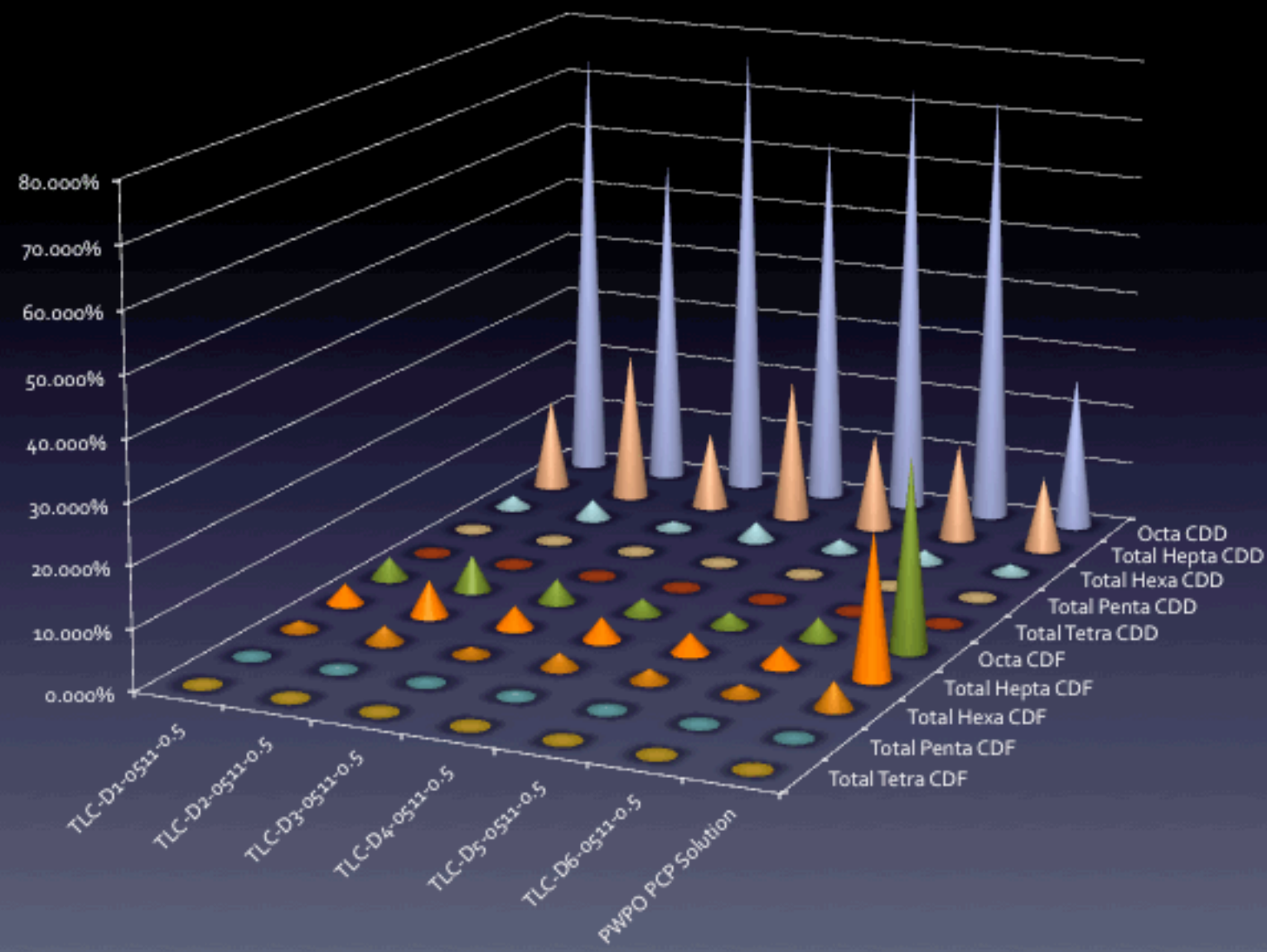
Aromatic Hydrocarbon Distribution: TLC-B8 Aqueous, TLC-B8 Soil, and Working Solution



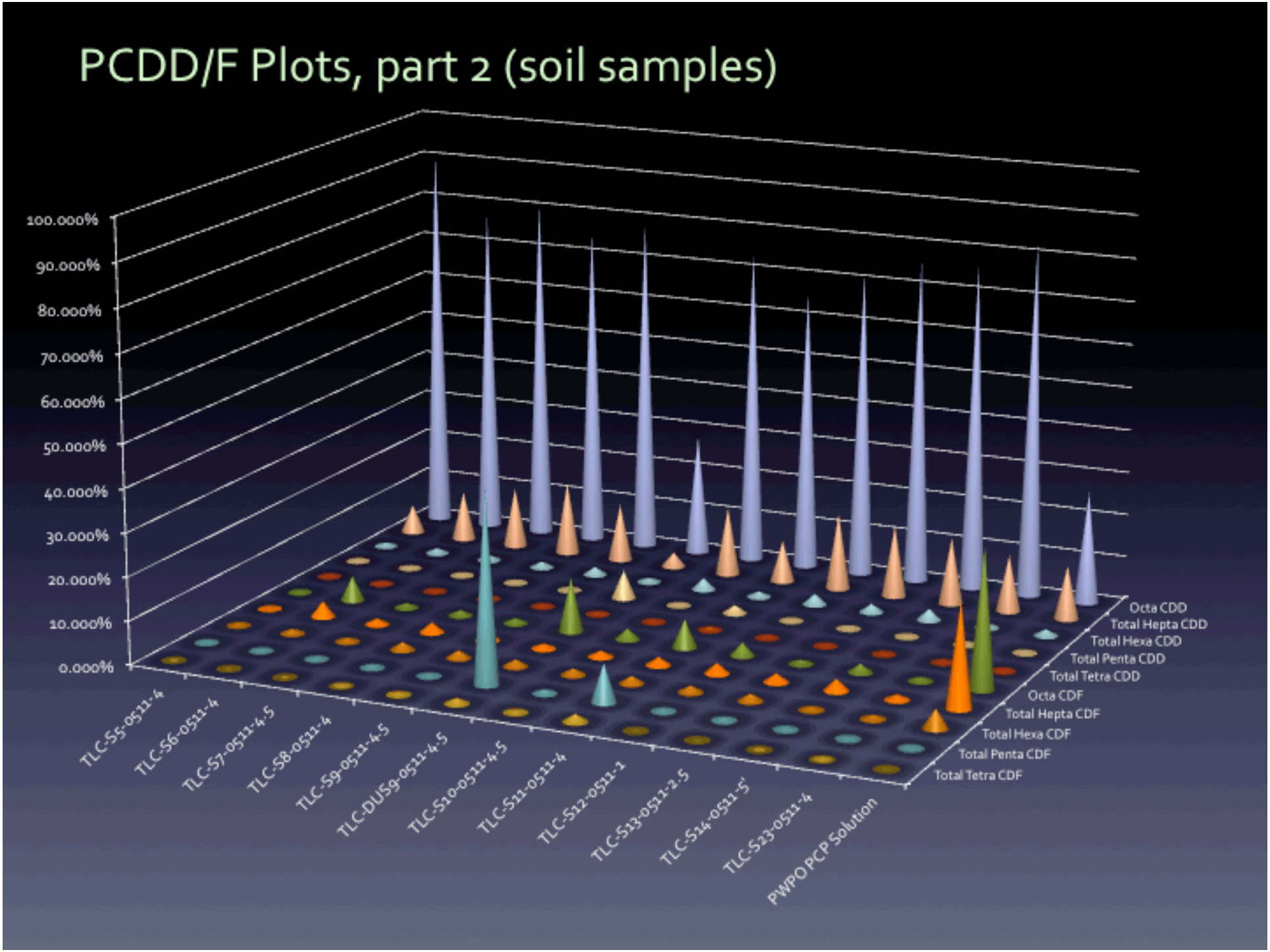




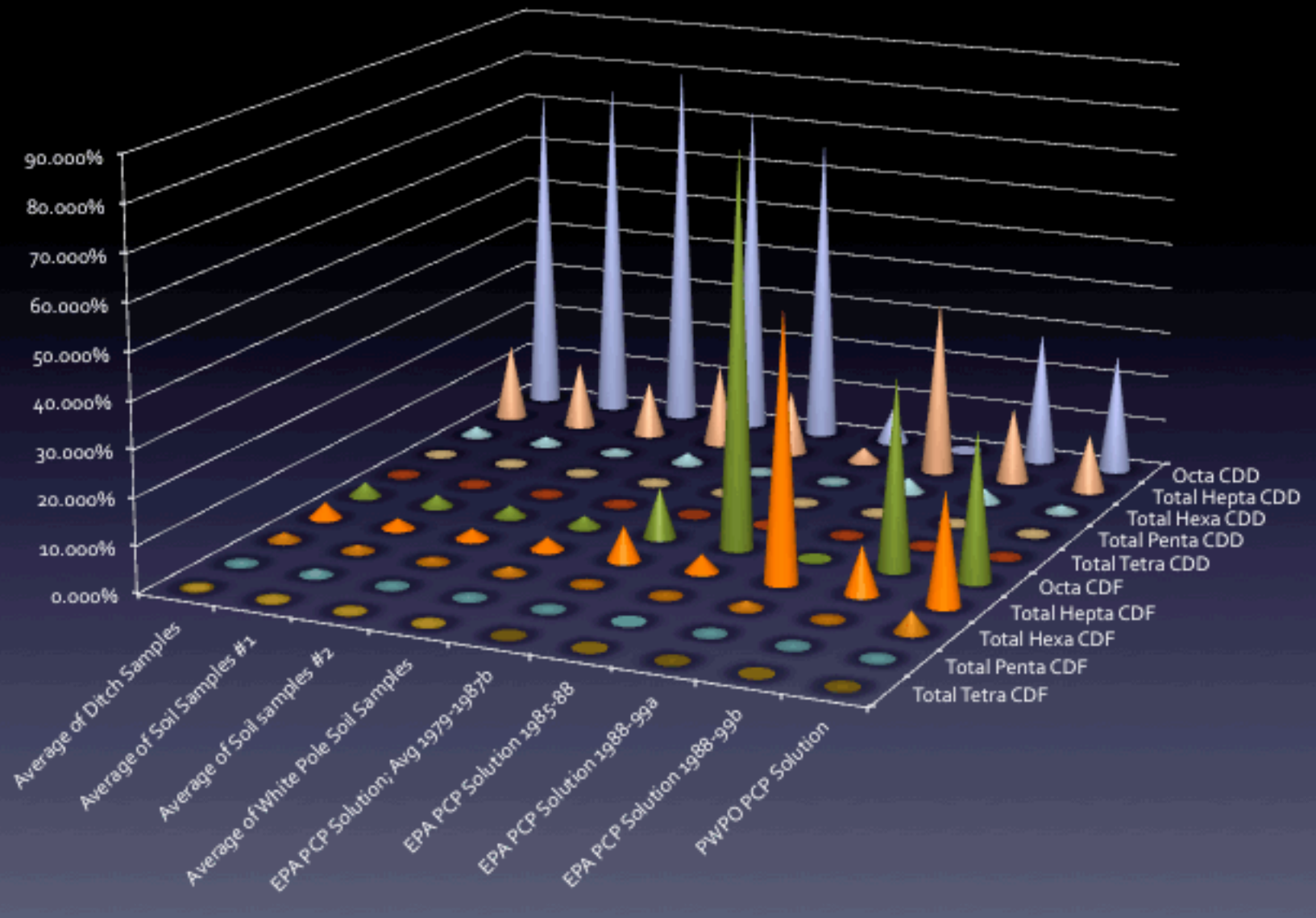
PCDD/F Plots, part 1 (ditch sediments)



PCDD/F Plots, part 2 (soil samples)



PCDD/F Plots, part 3 (average all matrices)



Conclusions

- Source determination is a often a very difficult question to answer
- No single test provides a "silver bullet" when it comes to characterizing the nature, age, and source of contamination
- Multiple "lines-of-evidence" are needed in order to answer the question(s)

Conclusions, cont.

- The "marker strategy" approach found:
  - Can differentiate existing site contamination from a potential future release of current working solution
  - BBP may be a very unique "chemical marker"
  - The PAC & PCCD/F profiles may be most useful data

Conclusions, cont.

- Some thoughts we all should remember:
  - The data and information must be considered in its proper context to draw meaningful conclusions
  - Sometimes the evaluation of the data may be inconclusive
  - Additional detailed analyses may be required
  - All "tools" should be considered to provide a reasonable interpretation about "source"

“An Interested Mind Brooks No Delay”

A quote by ”Cameca” to Dr. Who
The Aztecs (original airdate: May 23, 1964)
Episode 2, Garden of Peace

Acronyms

- BBP – Butyl Benzyl Phthalate
- COCs – Chemicals (or constituents) of concern
- DNAPL – Dense Non-Aqueous Phase Liquid
- DQA – Data Quality Assessment
- GC – Gas Chromatography
- GC/MS – Gas Chromatography/Mass Spectrometry
- m/z – mass-to-charge
- PACs – Polycyclic Aromatic Compounds
- PAHS – Polycyclic Aromatic Hydrocarbons
- PCA – Principal Component Analysis
- PCP – Pentachlorophenol
- PHCs – Petroleum Hydrocarbons
- PCDD – Polychlorinated dibenzo-*p*-dioxin
- PCDF – Polychlorinated dibenzofuran
- SICP – Selected ion current profile
- SIM – Selected Ion Monitoring
- SVOCs – Semivolatile Organic Compounds
- USEPA – U.S. Environmental Protection Agency

Acknowledgements

- NEMC and TNI
- You, the audience for you patience and attention
- The client (needs to remain confidential)
- Terrence E. Belunes, RG, LHG (the Project Manager)
- Kent Patton (Director of Technical Services) and Apex Laboratories LLC
- Alan Jeffrey, Ph.D. and DPRA/Zymax Forensics (now part of PACE)
- Maxxam Analytics International

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- The information presented herein is only an example on how multiple lines-of-evidence for analyses performed can be used in multiple ways to meet data quality objectives.
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Thank You!

Any Questions?

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