

Environmental Forensics

A Closer Look

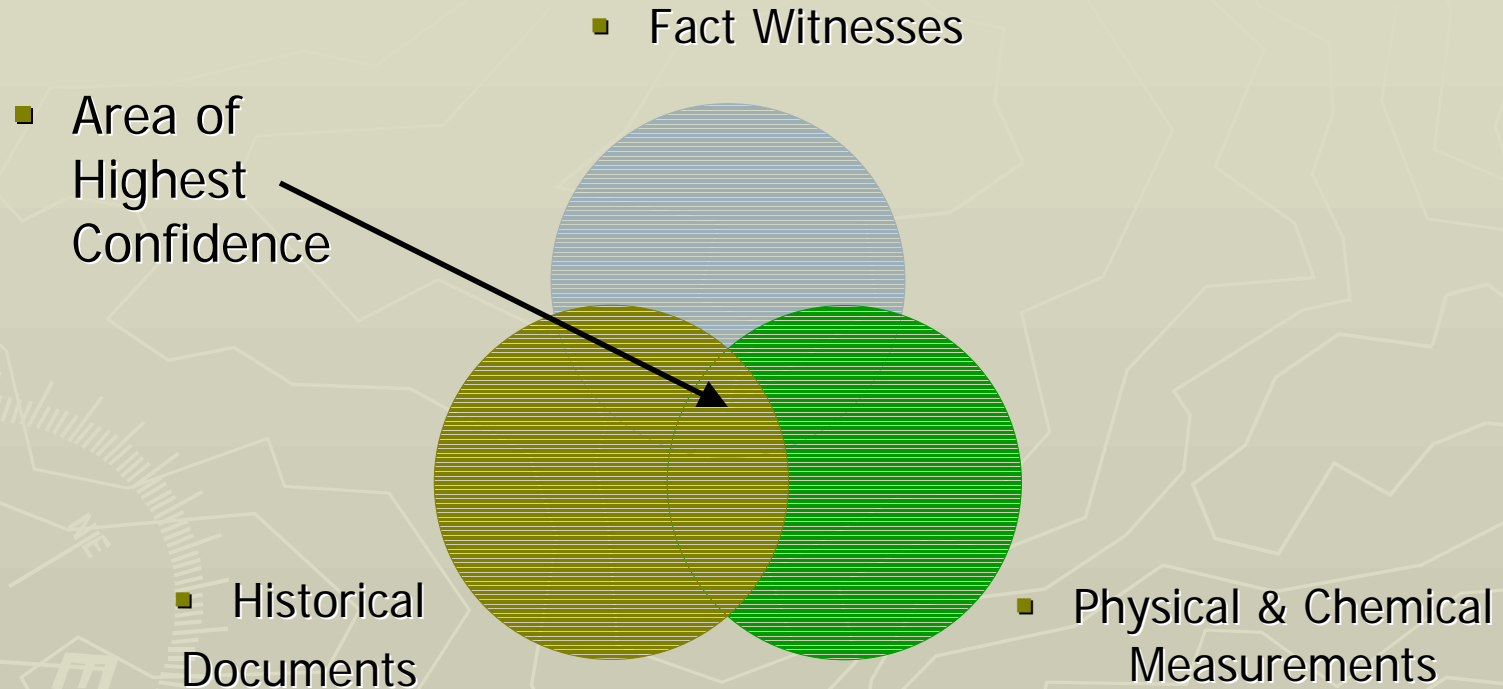
The Who, What, and When of
Environmental Investigations



Forensics

- ❖ Whereas classic site investigation is primarily concerned with “what” and “where” relative to the question of risk, forensics is primarily concerned with “who” and “when” relative to the question of responsibility.
- ❖ Forensic investigations tend to be “holistic”, involving multiple disciplines, a variety of old tools (used in new ways), and new tools.

Holistic Development of Facts



The Daubert Factors

- ❖ US Supreme Court ruling on admissibility of scientific theory and evidence
 - Testable hypotheses
 - Peer review
 - Defined error rates and methods of control
 - Generally accepted

- ❖ USEPA guidance documents, if applied correctly, will result in conclusions that meet the Daubert standards.

Examples of Forensic Studies

- ❖ Cost allocations
 - Establish responsibility for wastes
 - Contribution to total cost of remedy
- ❖ Property transfers
 - Establish “reserves”
 - Identify contributors
- ❖ Insurance Litigation
 - Triggering release date
 - Character relative to contract (expected vs accidental)
 - Equity of allocation
- ❖ Toxic Tort
 - Probability of harm
 - Equivalence of “harm” and “risk”

Tools

❖ Documentary

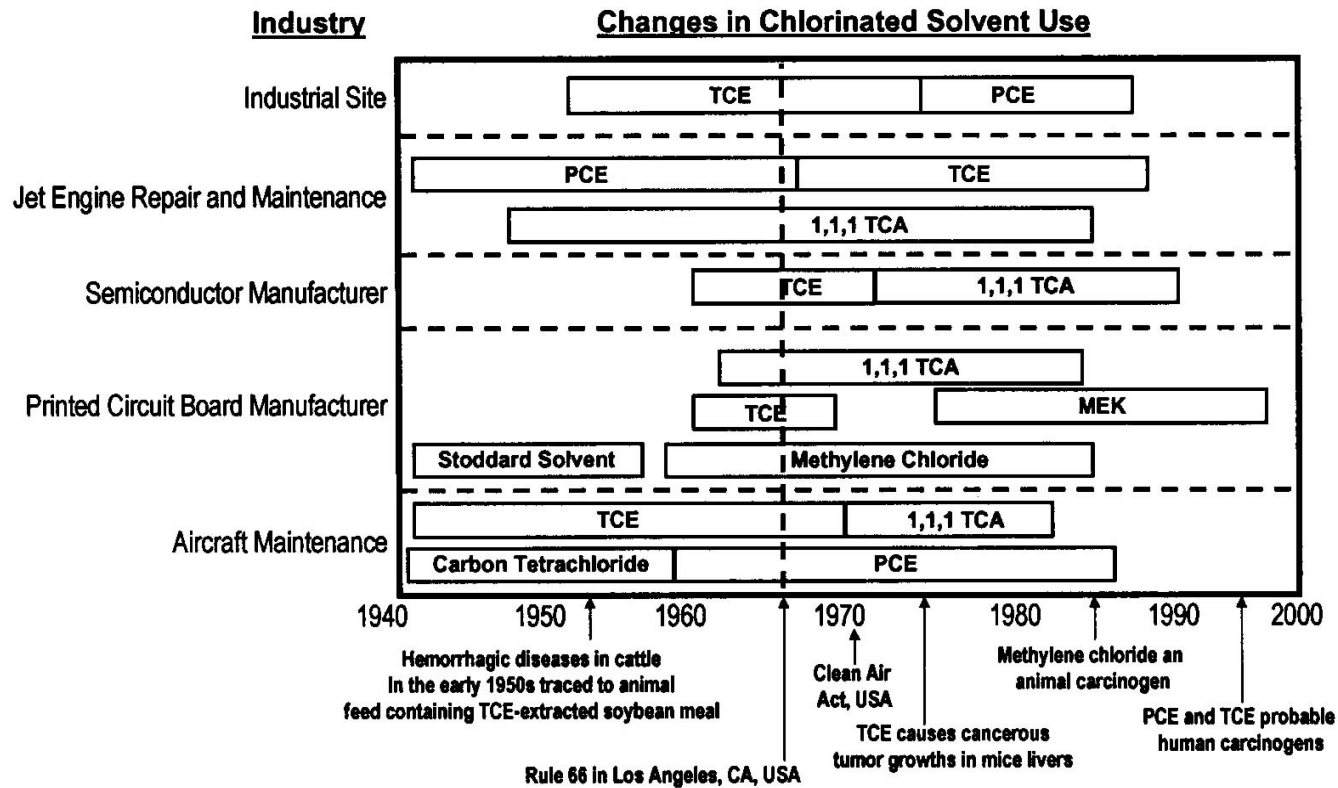
- Identification of Releases
- Age Dating Releases

❖ Data Types

- Availability data- What was available from who, when
- Formulation data – Additives and combinations
- Application data – Used in what industries for what purposes
- Physical and chemical property data – Fate & Transport
- Business records – Purchasing, Process Design, Shipping

Solvent Usage History

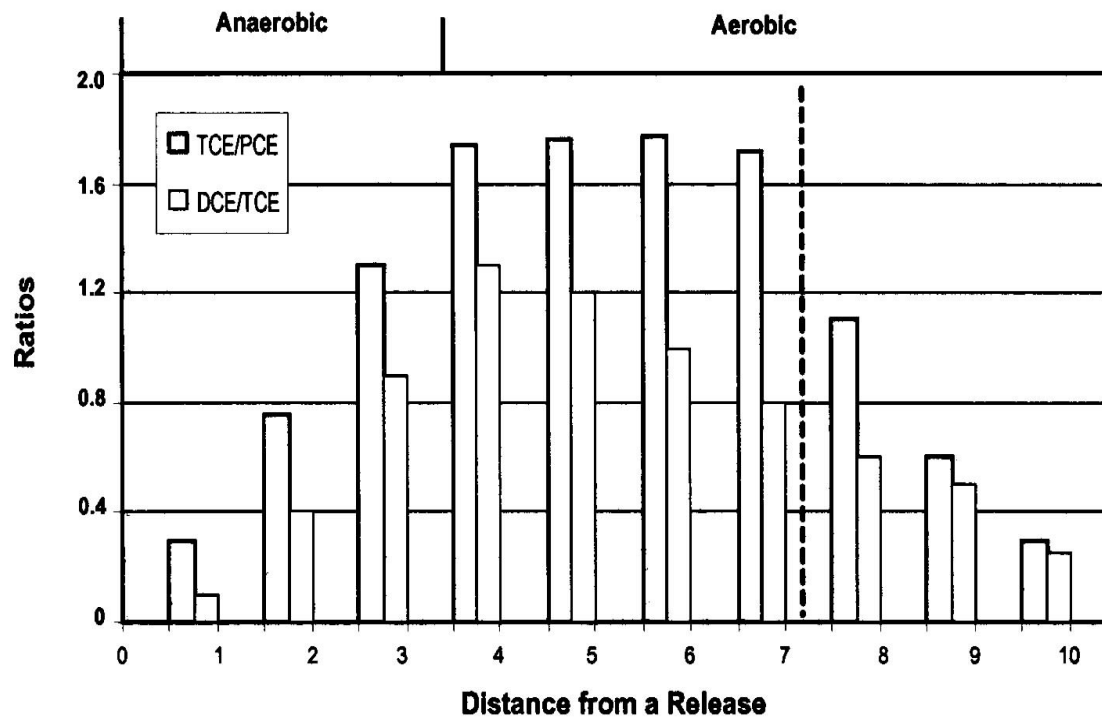
Chlorinated Solvent Usage at Four Industry-Specific Facilities



From: Morrison, 2003

Solvent Formulations

Commercial Formulations and Ratios



From: Morrison, 2003

Tools

❖ Aerial Photography

- Age dating releases
- Identification of sources and pathways

❖ Multi-spectral Surveys – Remote Sensing

- Identify ecological stresses and stressors
- Contaminant identification
- Summary distribution of contaminants

Tools

❖ Laboratory Analysis

- Identification
- Source identification
- Cost allocation

❖ Types

- GC with various detectors
- Spectrophotometric at various wavelengths
- Radiochemistry
- Electrochemical
- Microscopy
- Crystallography
- Physical and chemical properties
- Toxicological

Tools

❖ Unique Identifiers

- Congener analysis
- Biomarkers
- Isotopic ratios
- Additives
- Fingerprinting
- Speciation



TPH Problems

Matrix	TPH – G (ppm)	TPH – D (ppm)
Spinach	<10	60
Carrots	<10	10
Orange Juice	300	<10
Cedar Tree	1400	2200
Pine Tree	450	400
Dandelion	<10	140
Daisy	40	40
Moss	<10	<10

A Closer Look

❖ Isotopic analysis

- Use both stable and radioactive isotopes for dating and identification
 - Radioisotopes are commonly used for dating
 - Stable isotopes are commonly used for identification

❖ Chemical fingerprinting

- A tiered approach is employed
 - Bulk
 - Component ratios
 - Additives
 - Age and weathering effects

Rayleigh Distillation Model

- ❖ Describes isotopic enrichment or depletion during various processes
 - Evaporation
 - Degradation
 - Production (as in methane)
- ❖ Mass balance approach can be used to allocate between multiple sources.

Examples of Useful Isotopes

Isotope	Uses
2H/1H	Identification of landfill gas and leachate
37Cl/35Cl	Distinguish manufacturers of chlorinated solvents
204Pb/206Pb/207Pb/208Pb 205Pb (effectively stable)	Age dating gasoline spills Identify sources of lead in blood
13C/12C	Distinguish crude oils, distinguish BTEX sources, Monitor biodegradation
15N/14N	Distinguish natural from anthropogenic nitrate
18O/16O	Identify water sources
34S/32S	Trace SO ₂ sources

New and Modified Methods

❖ GCMS-

- Extended resolution
- MS/MS
- SIM
- FT-ICR
- TOF

❖ GC/GC

❖ Microbiological

❖ Gravimetrics

❖ Microtaggants

❖ Electron Microscopy

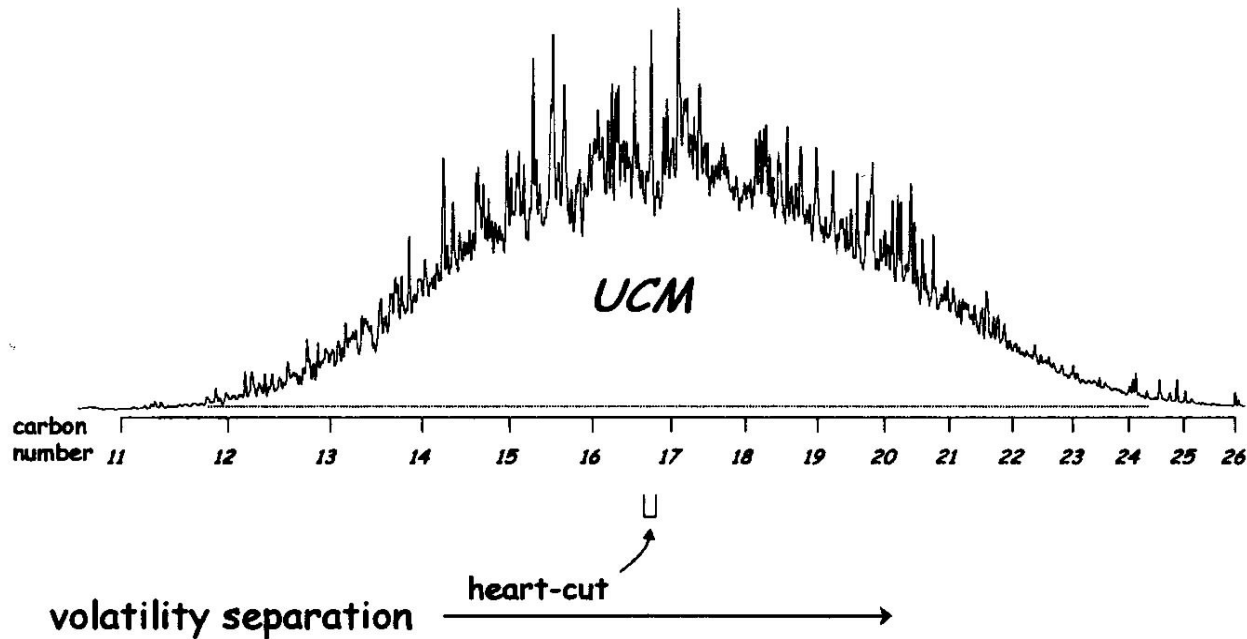
- SEM
- TEM
- XRF
- SEI/BEI

❖ Paper Chromatography

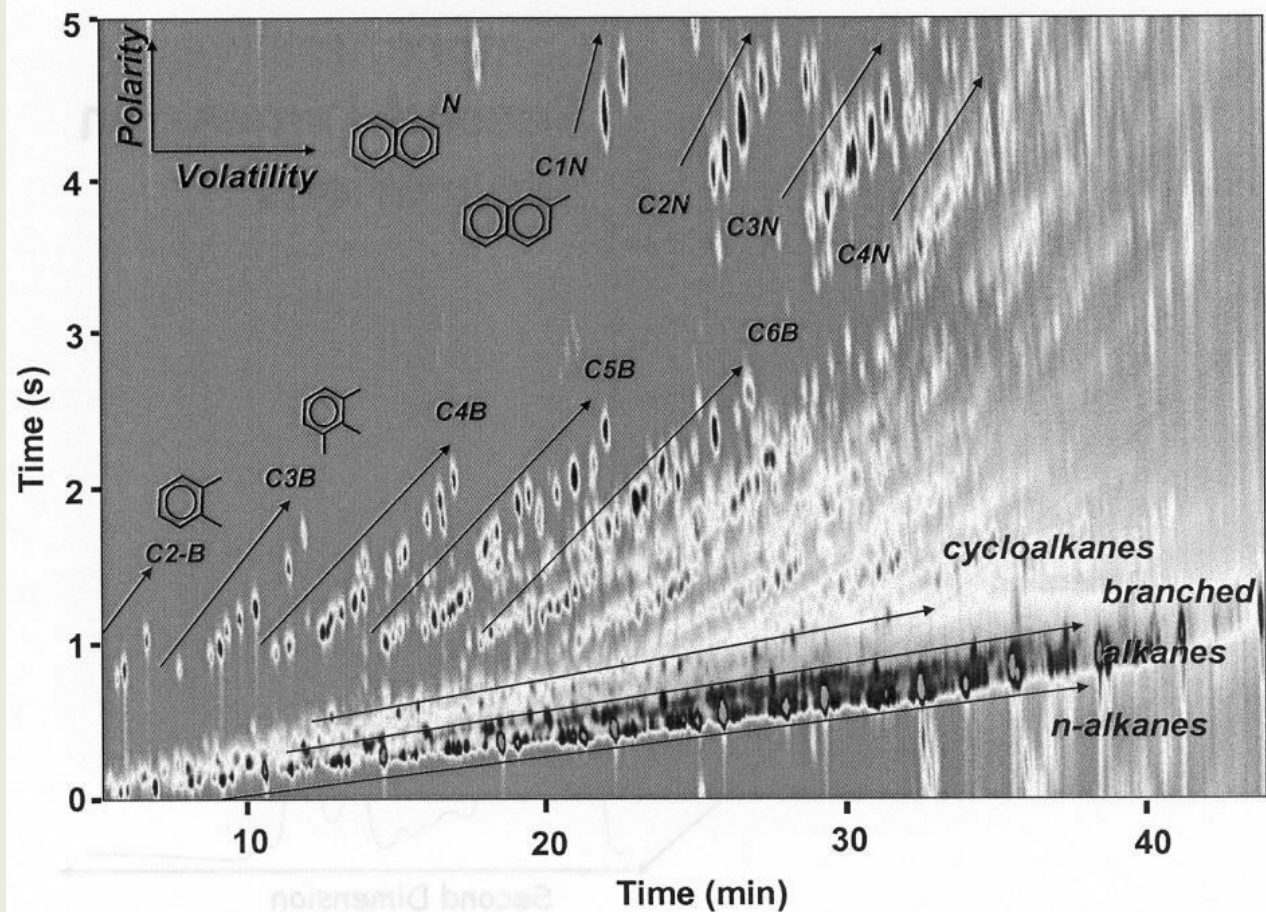
❖ Electrophoresis

Low Resolution Analysis

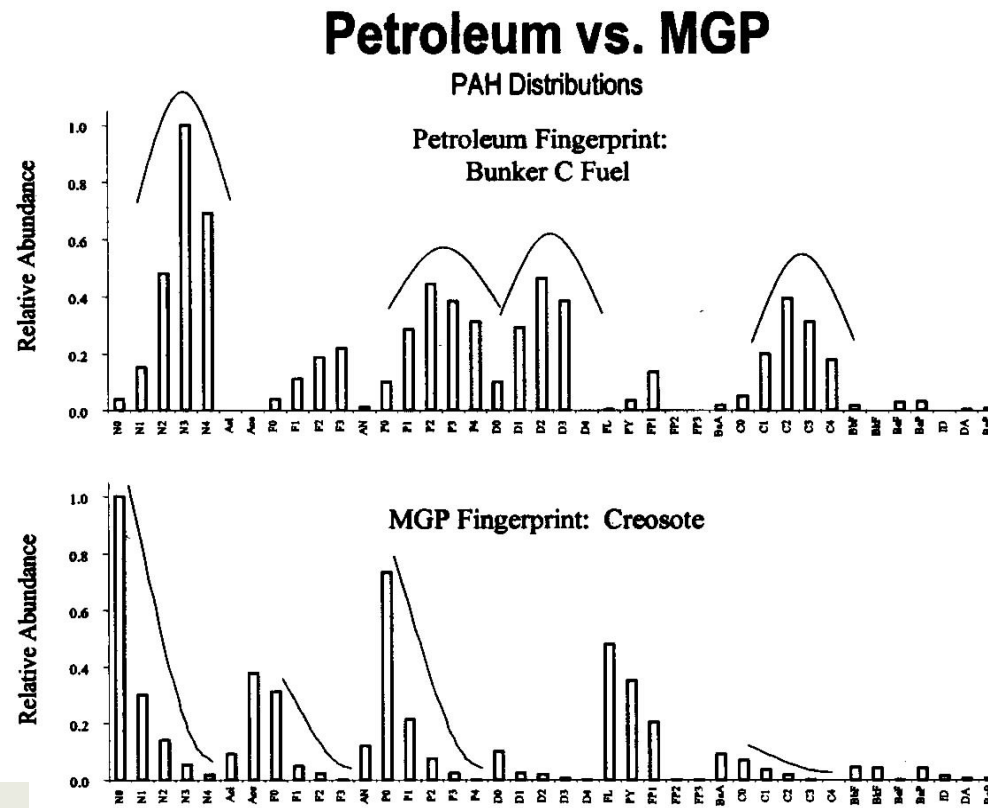
Unresolved Complex Mixture



High Resolution Analysis

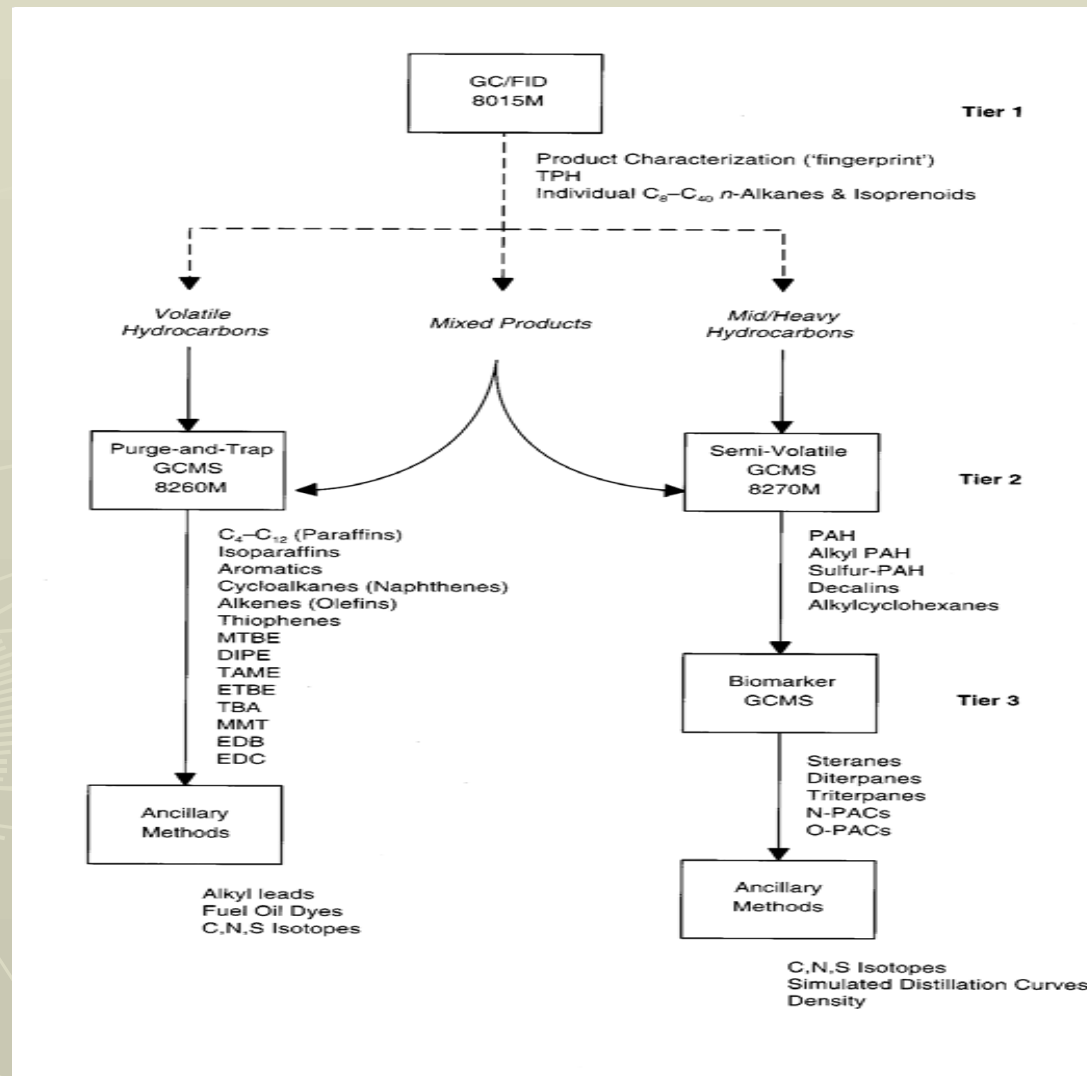


Petrogenic/Pyrogenic



From: Haddad, et al, 2003

Fingerprinting Flowchart



From: Environmental Forensics, Murphy and Morrison, 2002

Biomarkers

❖ Molecular fossils

- Terpanes
- Steranes
- Low Boiling



Tools

❖ Modeling

- Source Identification
- Cost Allocation

❖ Types

- Fate and transport
 - Atmospheric
 - Groundwater
 - Surface water
 - Diatom tracing
- Degradation
- Corrosion

Tools

❖ Statistics

- Analysis of diagnostic ratios
- Principle Component Analysis (PCA)
- Polytopic Vector Analysis (PVA)
- Source Apportionment Factors Explicit Restrictions (SAFER)
- Geostatistical analysis
- Analytical solution and regression methods
- Analysis of variance

Case Study

▶ Montclair, New Jersey

- Problem: Identify Contaminant
- Tools: Laboratory analysis
- Observations: LNAPL found in drinking water; IR trace used to compare suspect materials with various oils; trace best matches cooking oil
- Conclusion: No harm

Case Studies

❖ Weldon Springs, Missouri

- Problem: Identify source of impact
- Tools: Isotopic ratios (H and O); thermodynamic trend analysis; diatom tracing; mixing model
- Observations: H and O isotopic ratios are atypical for local karst springs; unusually high turbidity and undersaturation with limestone components; comparison to locally available alternatives matches Prairie Lake; diatom tracing and mixing model confirm.
- Conclusion: Prairie Lake is source.

Case Studies

❖ Shawnee, Oklahoma

- Problem: Identify additional responsible parties
- Tools: Groundwater flow mapping; degradation modeling; fate and transport modeling
- Observations: DCE concentrations do not mass balance with suggested TCE source; groundwater traces north east to southwest; highest concentrations DCE are cross-gradient to flow direction; models suggest source in southeast.
- Conclusion: Mixed plume with the largest component, DCE, arising from neighboring property.

Case Studies

❖ Spokane, Washington

- Problem: Allocate costs
- Tools: Laboratory analysis –biomarker to component ratios; multivariate statistical analysis - principle component analysis
- Observations: Qualitative fingerprinting narrows the field of suspect parties; biomarker indices are assessed for influence of weathering and reproducibility; PCA limits the field further
- Conclusion: Multiple PRPs identified.