

Environmental Forensics

DoD-Environmental Monitoring and
Data Quality (EMDQ) Workshop
March 29, 2011

Report Documentation Page

Form Approved
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE 29 MAR 2011	2. REPORT TYPE	3. DATES COVERED 00-00-2011 to 00-00-2011			
4. TITLE AND SUBTITLE Environmental Forensics		5a. CONTRACT NUMBER			
		5b. GRANT NUMBER			
		5c. PROGRAM ELEMENT NUMBER			
6. AUTHOR(S)		5d. PROJECT NUMBER			
		5e. TASK NUMBER			
		5f. WORK UNIT NUMBER			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) NewFields Environmental Forensics Practice, LLC, 300 Ledgewood Place Suite 305, Rockland, MA, 02370		8. PERFORMING ORGANIZATION REPORT NUMBER			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)			
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)			
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES Presented at the 2011 DoD Environmental Monitoring & Data Quality Workshop (EMDQ 2011), 28 Mar ? 1 Apr, Arlington, VA. U.S. Government or Federal Rights License					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 106	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

Presenter

- Stephen Emsbo-Mattingly, M.S.

NewFields Environmental Forensics Practice, LLC

300 Ledgewood Place

Suite 305

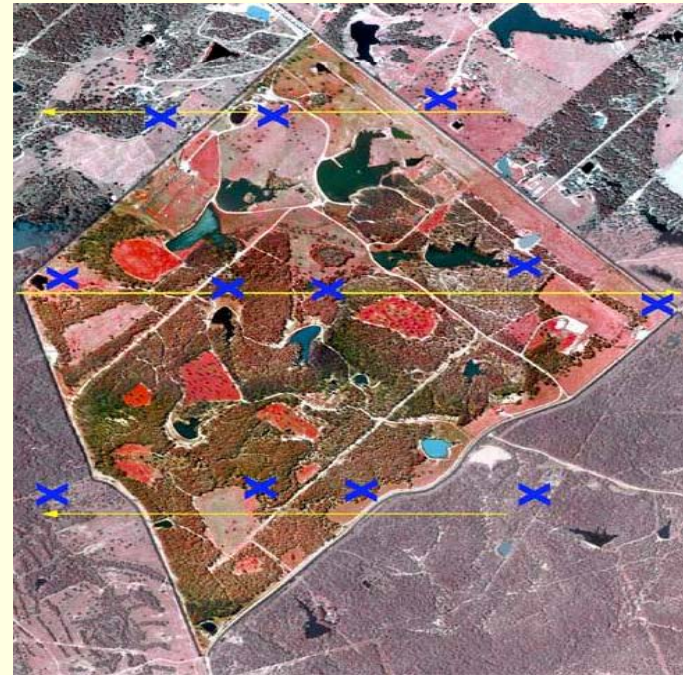
Rockland, MA 02370

(781) 264-7081

smattingly@newfields.com

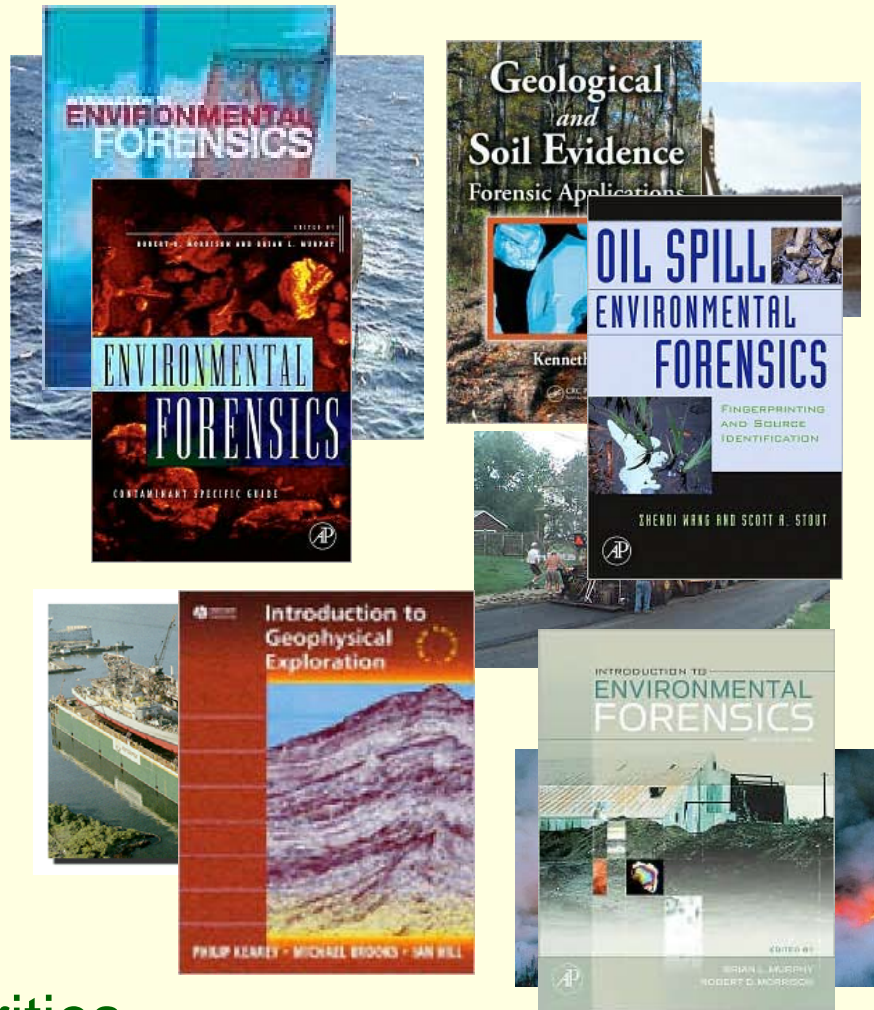
Overview

- Multiple Lines of Evidence
 - Concentration
 - Composition
- Analytes and Media
 - Indoor Air (VOCs)
 - Sediment RI/FS (PCBs)
 - Natural Attenuation (PCBs)
 - Soil and Sediment Background (PAHs)
- Case Studies & Tiered Approaches
- Closing Thoughts



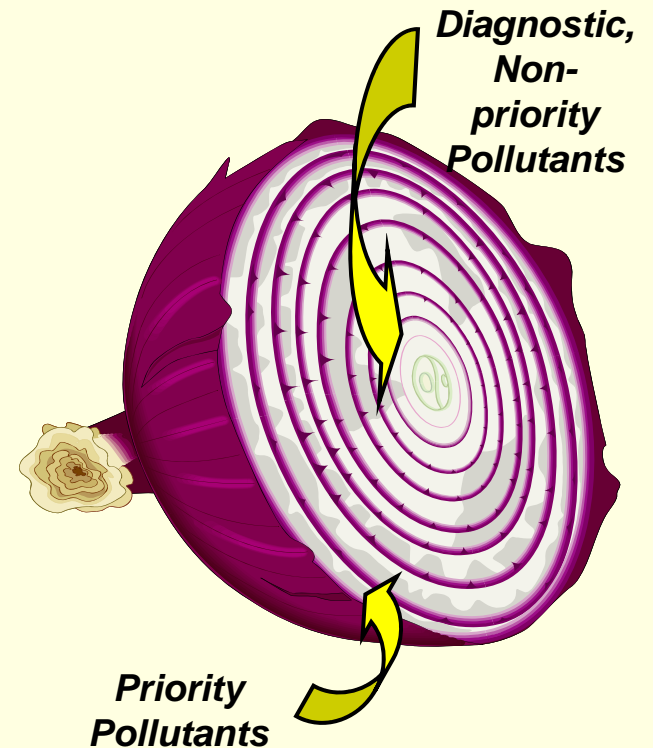
Forensic Applications

- DOD
- US EPA
- NOAA
- NYSDEC
- MADEP
- USDOD/Coast Guard
- XOM Valdez Spill
- UN Gulf War Damage Assessment
- Hurricane Katrina
- NORD Test
- MA, CA, OR Port Authorities



Standard EPA Methods

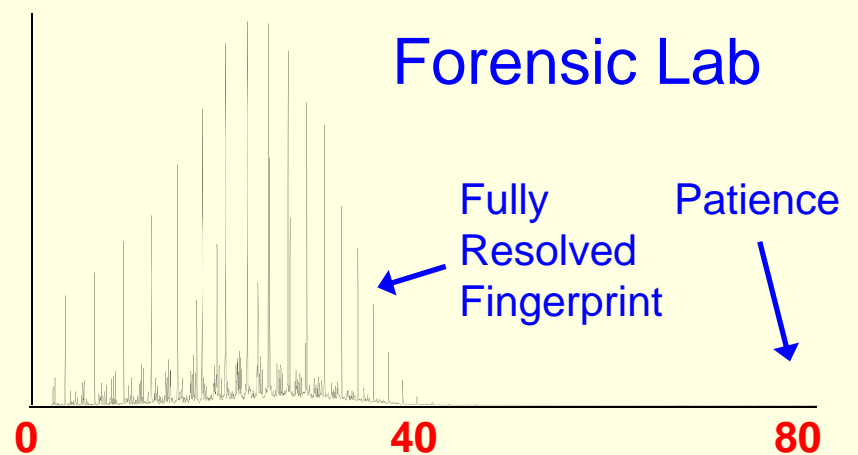
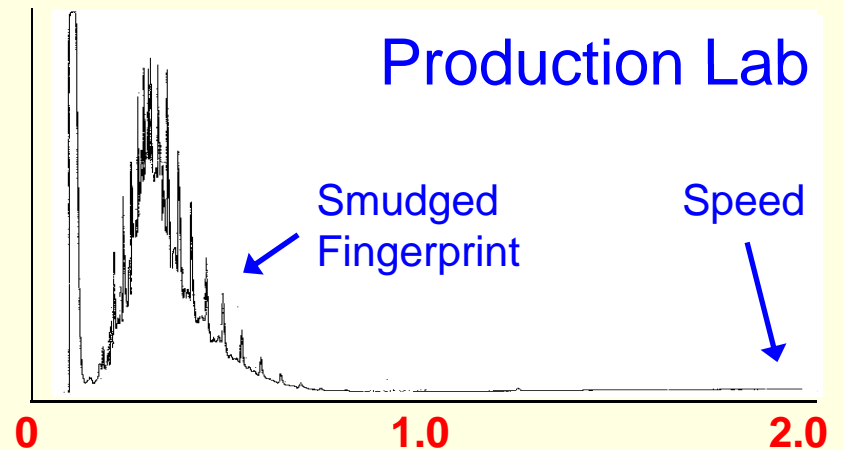
- Standard Methods
 - Nature and Extent
 - Risk Assessment
- Priority Pollutants
 - About 130 chemical indicators of hazardous material
- Chemical Fingerprints
 - Hundreds of chemicals co-occur with Priority Pollutants in source specific patterns



Peel the Onion!

How do Standard EPA Methods Differ from Forensic Methods?

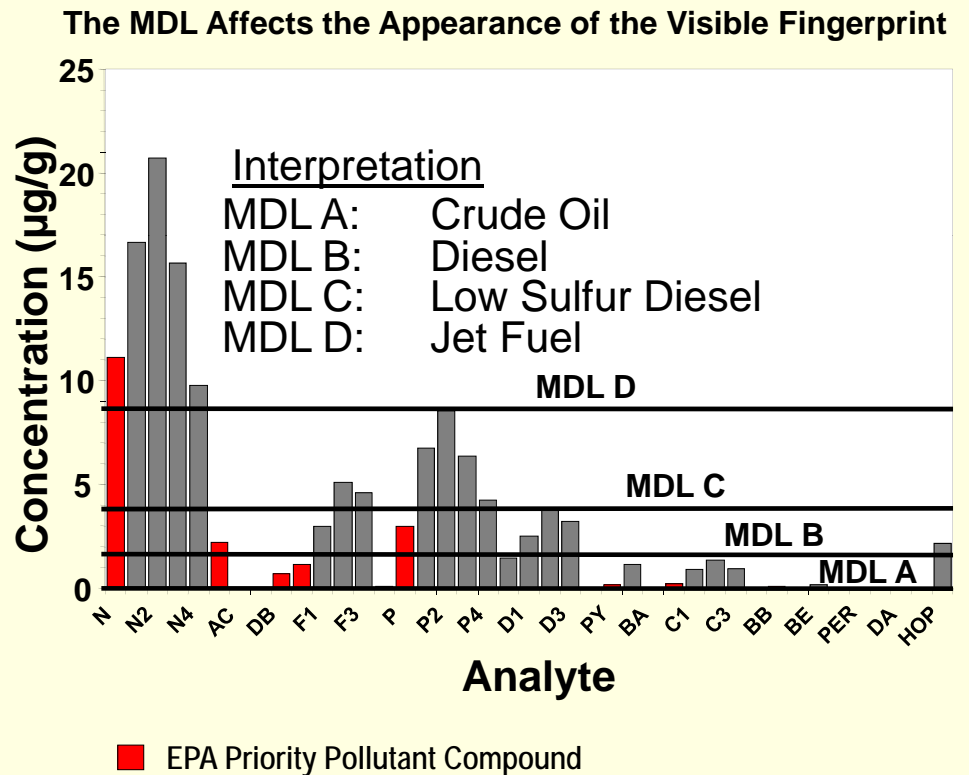
- Production Laboratories
 - Time is money
 - Faster runs mean faster turnaround and higher profits
 - Loss of Forensic value
- Forensic Method Improve Resolution



Retention Time (minutes)⁶

Forensic Methods: Better Sensitivity

- Standard methods only target chemicals above a certain concentration
 - EQL for PAH is 660 µg/kg wet by EPA 8270
 - Chemicals in lower conc. can provide added “forensic” detail about source of higher conc. chemicals



Douglas et al. (2004) *Env. Sci. Technol.* 38:3958-3964

Air: Vapor Intrusion

DoD-Environmental Monitoring and
Data Quality (EMDQ) Workshop
March 29, 2011

Background Contaminants in Indoor Air



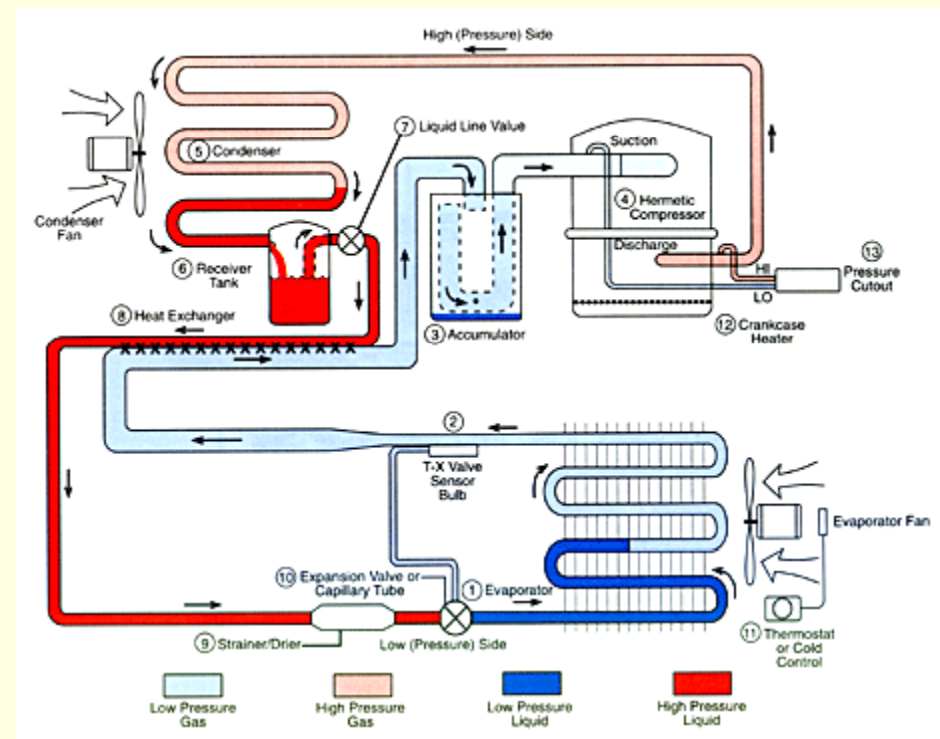
What is air?

Gas	Fraction (ppmv)	Percent
Nitrogen (N ₂)	780,840 ppmv	78.08%
Oxygen (O ₂)	209,476 ppmv	20.95%
Argon (Ar)	9,340 ppmv	0.93%
Carbon dioxide (CO ₂)	383 ppmv	0.038%
Neon (Ne)	18.18 ppmv	0.0018%
Helium (He)	5.24 ppmv	0.00052%
Methane (CH ₄)	1.745 ppmv	0.00017%
Krypton (Kr)	1.14 ppmv	0.00011%
Hydrogen (H ₂)	0.55 ppmv	0.000055%
Nitrous oxide (N ₂ O)	0.3 ppmv	0.000030%
Xenon (Xe)	0.087 ppmv	0.0000870%
Ozone (O ₃)	0.07 ppmv	0.0000070%
Nitrogen dioxide (NO ₂)	0.02 ppmv	0.0000020%
Iodine (I)	0.01 ppmv	0.0000010%
Carbon monoxide (CO)	trace	trace
Ammonia (NH ₃)	trace	trace

What are the principal contaminants in Indoor Air?

■ Refrigerants & Propellants

- Heat Transfer
- Phase Change
- Noncorrosive
- Nonflammable
- Nontoxic
- Odorless
- Colorless



Propellants, Refrigerants, and Chlorinated Solvents

Pre-Freons (< 1930s)

Chloromethane
Sulfur Dioxide
Anhydrous Ammonia
Manufactured Gas
Light Hydrocarbons

Halomethanes

Bromochlorodifluoromethane (Halon1211)
Bromochloromethane (Halon1011)
Bromodifluoromethane (Halon 1201)
Bromomethane (Halon 1001)
Bromotrifluoromethane (Halon1301)
Chlorodifluoromethane (HCFC22)
Chlorofluoromethane (HCFC31)
Chloromethane
Chlorotrifluoromethane (CFC13)
Dibromodifluoromethane (Halon 1202)
Dibromomethane
Dichlorodifluoromethane (CFC12)
Dichlorofluoromethane (Halon 112)
Dichloromethane (DCM)
Difluoromethane (HFC32)
Fluoromethane (HFC41)
Iodomethane (Halon 10001)
Tetrachloromethane (CFC10)
Tetrafluoromethane (PFC14)
Tribromofluoromethane (Halon 1103)
Tribromomethane (Bromoform)
Trichlorofluoromethane (CFC11)
Trichloromethane (Chloroform)
Trifluoroiodomethane (Freon 13T1)
Trifluoromethane (HFC23)

Haloethanes

1,1,1,2-Tetrafluoroethane (HFC-134a)
1,1,1-Trichloro-2,2,2-trifluoroethane (CFC-113a)
1,1,1-Trichloroethane
1,1,2,2,2-Pentafluoroethane (HFC-125)
1,1,2,2-Tetrafluoroethane (HFC-134)
1,1,2-Trichloro-1,2,2-trifluoroethane (CFC-113)
1,1-Dichloro-1-fluoroethane (HCFC-141b)
1,1-Dichloroethane (Freon 150a)
1,1-Difluoroethane (HFC-152a)
1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC-114)
1,2-Dichloroethane (Freon 150)
1-Chloro-1,1,2,2,2-pentafluoroethane (CFC-115)
1-Chloro-1,1-difluoroethane (HCFC-142b)
2-Chloro-1,1,1,2-tetrafluoroethane (HFC-124)
Dibromotetrafluoroethane (Halon 2402)
Hexachloroethane (CFC-110)
Hexafluoroethane (Halon 2600)

Adhesives

- Adhesives
- Liquid or Paste
- Bind Surfaces
- Natural
 - Animal Rendering
 - Egg Whites
 - Plant Extracts
- Synthetic
 - Drying
 - Contact
 - Thermoplastics
 - Pressure



Adhesives in Indoor Air

Water-based Adhesives

Starch
Gums
Albumen
Sodium silicated
Casein
Methyl cellulose
Lignin
Polyvinyl alcohol

Glue Solvents

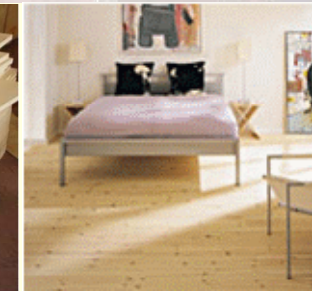
Formaldehyde
Acetone
Vinyl acetate
Ethyl-2-cyanoacrylate
Carbon Tetrachloride
Acrylic acid
Octodecyl alcohol

Adhesive Solvents

Ethyl-2-cyanoacrylate
Methyl ethyl ketone
Acetone
Toluene
Petroleum solvent naphtha
Vinyl acetate
Styrene
Hexane
1,3-Butadiene
1,2,4-Trimethylbenzene
Mineral spirits
Xylene
Cumene
Pentane
Cyclohexane
2,2-dimethylbutane
Carbon Tetrachloride
2-Methylpentane
3-Methylpentane
Cyclohexanone
Butyl alcohol
Butanol
Ethyl ether
Methyl isobutyl ketone

Household Solvents

- Solvents Dissolve Solutes
- Water & Organic
- Natural
 - Ethanol
 - Terpenes
- Petroleum
 - Naphtha
 - Mineral Spirits
- Halogenated
 - Dry Cleaning
 - Cosmetics
 - Plywood
 - Foamed Insulation
 - Furniture & Rugs



Household Solvents in Indoor Air

Paints-Oil Base

Carboxylic Acids
Cycloparaffins
Elastomers
Epoxy resins
Glycerols
Glycols
Melamine alkyds
Pentaerythritols
Phenolic aldehyde resins
Phenolics
Phthalic acids
Polyesters
Polyurethane esters
Resins
Rosins
Silicone alkyds
Styrene polyesters
Urea alkyds

Paints-Water Base

Acrylic resins
Alkyd resins
Carboxylic acids
Cellulose Resins
Chlorofluorocarbons
Epoxy resins
Hydrocarbon resins
Natural oils
Phthalates
Plasticizers
Rubbers
Styrene-butadiene polymers
Vinyl resins

Lacquers

Acrylics
Cellulosics
Natural resins
Natural rubbers
Phosphate alkyds
Phthalates
Shellac
Styrenated alkyds
Synthetic rubbers
Vinyls
Zein lacquers

Household Solvents in Indoor Air

Cologne

Benzaldehyde
Ethyl acetate
Hexane
Methylene Chloride
Ethanol
Benzophenone
Stearyl alcohol
Fragrances

Shampoo

Benzaldehyde
Methylene Chloride
Benzyl alcohol
Stearyl alcohol
Dyes
Fragrances

Perfume

Benzaldehyde
Ethyl acetate
Hexane
Ethanol
Benzophenone
Stearyl alcohol
Fragrances

Lipstick

Glycerin
Benzoic acid
Polyethylene
Polybutene
Parabens
Dyes
Iron Oxides
Waxes

Household Solvents in Indoor Air

Fragrances

Acetaldehydes	Cinnamates	Mercaptans
Acetates	Citrals	Methyl ethyl ketone
Acetic acids	Cresols	Methyl isopropyl ketone
Acetones	Cumins	Natural oils
Alcohols	Cyclohexanes	Nitriles
Aldehydes	Dioxanes	Normal alkanes
Alkyl ketones	Ethers	Phenols
Amines	Formates	Phenones
Benzenes	Furfurals	Phthalides
Benzoates	Glycerols	Pinenes
Benzoic acid	Glycines	Pyridines
Biphenyls	Glycols	Pyrroles
Cadinene	Hydroquinones	Quinolines
Caffeine	Indoles	Resorcinol
Camphene	Isophorones	Salicylates
Camphor	Isopropyl acetate	Sterates
Carboxylic acids	Isopropyl alcohol	Styrene
Carboxylic alcohols	Laurates	Sulfides
Castor oil	Lavandins	Terpenes
Cedranes	Leucine	Thiols
Celluloses	Limonenes	Thiophenes
Cineoles	Menthols	Vanillins

Petroleum Products

- Paraffins
 - Alkanes
- Isoparaffins
 - Isooctane
- Aromatics
 - BTEX
- Naphthenes
 - Cyclohexane
- Olefins
 - 1-Hexene
- Additives
 - MTBE, EtOH



Petroleum Products in Indoor Air

Gasoline

C5 to C12 Hydrocarbons
C6 to C11 Aromatics
Additives
Prominant Constituents:
Butane
Isobutane
Pentane
Isopentane
Hexane
Heptane
Octane
2,2-dimethylbutane
2,2,4-trimethylpentane
1-pentene
2,2,4-trimethyl-1-pentene
Cyclopentane
Methylcyclopentane
Cyclohexane
Benzene
1,2,4-Trimethylbenzene
Toluene
Ethylbenzene
Xylenes
2-Methylpentane
3-Methylpentane
Isopropanol

Kerosene

C8 to C18 Hydrocarbons
C8 to C13 Aromatics
Prominant Constituents:
Nonane
Decane
Undecane
Dodecane
Tridecane
Tetradecane
Pentadecane
Hexadecane
Isoalkanes
Naphthenes
Alkylated Benzenes

Diesel

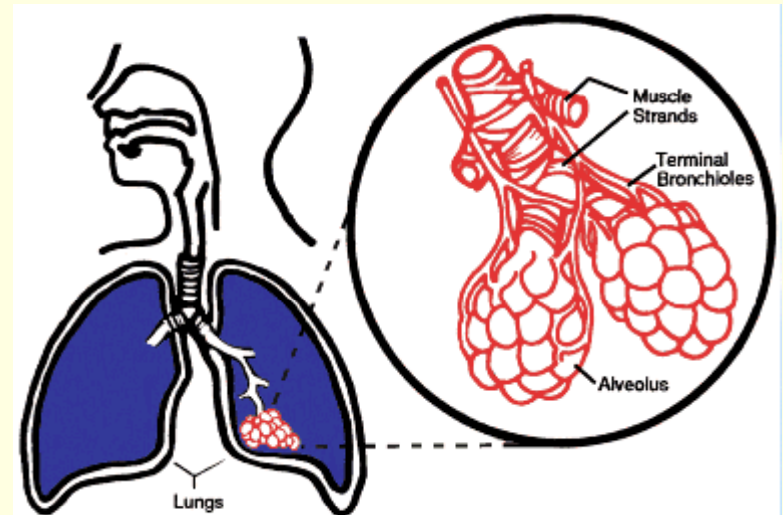
C10 to C28 Hydrocarbons
C9 to C16 Aromatics
Prominant Constituents:
Undecane
Dodecane
Tridecane
Tetradecane
Pentadecane
Hexadecane
Heptadecane
Octadecane
Nonadecane
Eicosane
Heneicosane
Isoparaffins
Naphthenes
Alkylated Benzenes
Naphthalenes

Blended Lubricant (WD40)

Solvent Fraction
C7 to C12 Hydrocarbons
C7 to C10 Aromatics
Prominant Constituents:
Stoddard solvent
Mineral spirits
Petroleum distillates
Methylene chloride
Hexane
Heptane
Octane
Nonane
Polydimethylsiloxanes
Ethanol
Isobutane
o-phenylphenol
Pentane
Isoparaffins
Naphthenes
Alkylated Benzenes

Respiration

- Breathe In, Breathe Out
 - Industrial Workplace
 - Dry Cleaners
 - Print Shop
 - Office
- Metabolic Byproducts
 - Alcoholic Beverages
 - Meat
 - Cigarettes



<http://www.niehs.nih.gov/oc/factsheets/ozone/ithurts.htm>

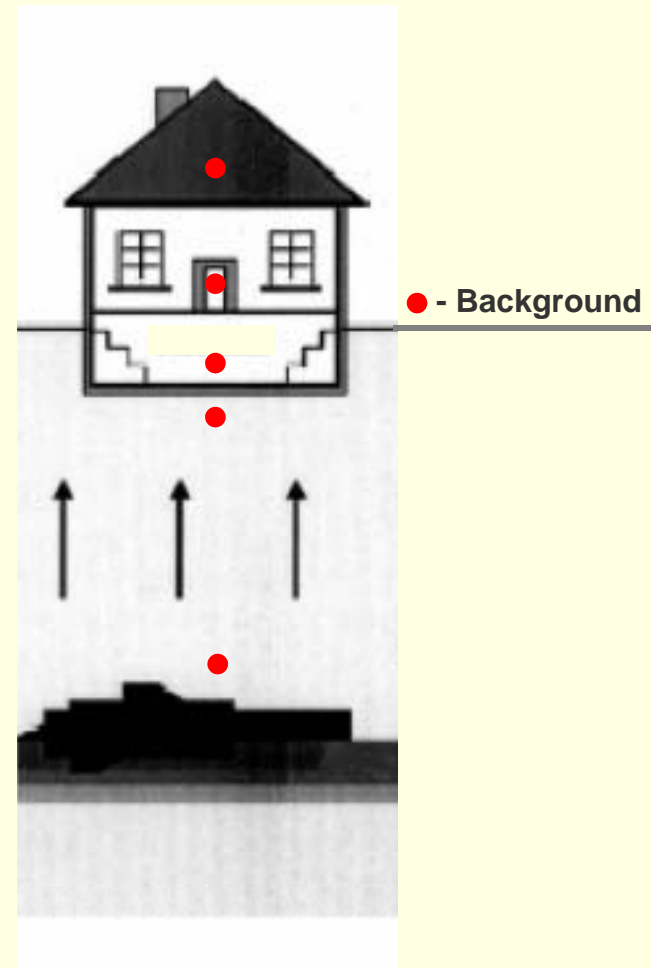
Respired Indoor Air Contaminants

Common Chemicals in Cigarette Smoke

Aldehydes	Lead
Acetone	Methanol
Acrolein	Methyl Ethyl Ketone
Acrylonitrile	Naphthalenes
Ammonia	Nickel
Benzene	Nicotine
Benzo(a)pyrene	Nitric Oxide
1,3-Butadiene	NNN (N-nitrosornicotine)
Butane	NNK (4-Methylnitrosamino- 1-3-Pyridyl-1-Butanone)
Cadmium	NAT (N'-Nitrosoanatabine)
Carbon Monoxide	Phenol
Catechol	Pyridine
Chromium	Quinoline
Chrysene	Resorcinol
Cresol	Styrene
Ethanol	Toluene
Hydrogen Cyanide	Vinyl chloride
Isoprene	

Case Study

- Up Gradient
 - MGP (1913-52)
 - Svc Station (1957-87)
- Down Gradient
 - Res. Neighborhood
- Monitoring (2 yr)
 - Outdoor
 - Indoor
 - Subslab
 - Source Soil Gas



Traditional TO-15 Analytes

Chlorine

Chloromethane (CM)
Vinyl chloride (VC)
Chloroethane (CE)
1,1-Dichloroethene (11DCE)
Methylene chloride (DCM)
3-Chloropropene (3CP)
trans-1,2-Dichloroethene (T12DCE)
1,1-Dichloroethane (11DCA)
cis-1,2-Dichloroethene (C12DCE)
Chloroform (CF)
1,1,1-Trichloroethane (111TCA)
Carbon tetrachloride (CT)
1,2-Dichloropropane (12DCP)
Trichloroethene (TCE)
cis-1,3-Dichloropropene (C13DCP)
trans-1,3-Dichloropropene (T13DCP)
1,1,2-Trichloroethane (112TCA)
Tetrachloroethene (PCE)
Chlorobenzene (CB)
1,1,2,2-Tetrachloroethane (1122PCA)
2-Chlorotoluene (2CT)
1,3-Dichlorobenzene (13DCB)
1,4-Dichlorobenzene (14DCB)
1,2-Dichlorobenzene (12DCB)
1,2,4-Trichlorobenzene (124TCB)
Hexachlorobutadiene (HCBD)

Fluorine

Dichlorodifluoromethane (DCFM)
Freon-114 (F114)
Trichlorofluoromethane (TCTFM)
Freon-113 (F113)

Bromine

Bromomethane (BM)
Vinyl bromide (VB)
Bromodichloromethane (BDCM)
Dibromochloromethane (DBCM)
Bromoform (BF)

Oxygen

Acetaldehyde (ACT)
1,3-Butadiene (13B)
Ethanol (EOH)
Acrolein (ACL)
Acetone (ACE)
Isopropyl Alcohol (IPOH)
Tertiary butyl Alcohol (TBA)
2-Butanone (2B)
1,4-Dioxane (14D)
4-Methyl-2-pentanone (MIBK)
2-Hexanone (MBK)

Traditional TO-15 Analytes (cont)

Sulfur

Carbon disulfide (CD)

Aliphatics

Butane (C4)
Pentane (C5)
Hexane (C6)
Heptane (C7)
Octane (C8)
Nonane (C9)
Decane (C10)
Undecane (C11)
Dodecane (C12)
2,2,4-Trimethylpentane (224TMP)
Cyclohexane (CH)

Aromatics

Benzene (B)
Toluene (T)
Ethylbenzene (E)
p+m-Xylene (mpX)
Styrene (STY)
o-Xylene (oX)
4-Ethyl toluene (4ET)
1,3,5-Trimethylbenzene (135TMB)
1,2,4-Trimethylbenzene (124TMB)
1,2,3-Trimethylbenzene (123TMB)
Indan (IN)
Indene (INE)
1,2,4,5-Tetramethylbenzene (1245TMP)
Naphthalene (NO)
2-Methylnaphthalene (2MN)
1-Methylnaphthalene (1MN)

Fuel Additives

MTBE (MTBE)
1,2-Dichloroethane (12DCA)
1,2-Dibromoethane (12DBE)

Forensic TO-15 Analytes

Paraffins

Pentane (C5)
Hexane (C6)
Heptane (C7)
Octane (C8)
Nonane (C9)
Decane (C10)
Undecane (C11)
Dodecane (C12)
Tridecane (C13)

Isoparaffins

Isopentane (IP)
2,3-Dimethylbutane (23DMB)
2-Methylpentane (2MP)
3-Methylpentane (3MP)
2,2-Dimethylpentane (22DMP)
2,4-Dimethylpentane (24DMP)
2-Methylhexane (2MH)
2,3-Dimethylpentane (23DMP)
3-Methylhexane (3MH)
Isooctane (ISO)
2,5-Dimethylhexane (25DMH)
2,4-Dimethylhexane
2,2,3-TMP (24DMH/223TMP)
2,3,4-Trimethylpentane (234TMP)
2,3,3-Trimethylpentane (233TMP)
2,3-Dimethylhexane (23DMH)
3-Ethylhexane (3EH)
2-Methylheptane (2MHEP)
3-Methylheptane (3MHEP)

Aromatics

Benzene (B)
Toluene (T)
Ethylbenzene (E)
p+m-Xylene (mpX)
Styrene (STY)
o-Xylene (oX)
Isopropylbenzene (IPB)
n-Propylbenzene (PROPB)
1-Methyl-3-ethylbenzene (1M3EB)
1-Methyl-4-ethylbenzene (1M4EB)
1,3,5-Trimethylbenzene (135TMB)
1-Methyl-2-ethylbenzene (1M2EB)
1,2,4-Trimethylbenzene (124TMB)
sec-Butylbenzene (SECBUT)
1-Methyl-3-isopropylbenzene (1M3IPB)
1-Methyl-4-isopropylbenzene (1M4IPB)
1-Methyl-2-isopropylbenzene (1M2IPB)
Indan (IN)
Indene (INE)

Aromatics (cont)

1-Methyl-3-propylbenzene (1M3PB)
1-Methyl-4-propylbenzene (1M4PB)
n-Butylbenzene (BUTB)
1,2-Dimethyl-4-ethylbenzene (12DM4EB)
1,2-Diethylbenzene (12DEB)
1-Methyl-2-propylbenzene (1M2PB)
1,4-Dimethyl-2-ethylbenzene (14DM2EB)
1,3-Dimethyl-4-ethylbenzene (13DM4EB)
1,3-Dimethyl-5-ethylbenzene (13DM5EB)
1,3-Dimethyl-2-ethylbenzene (13DM2EB)
1,2-Dimethyl-3-ethylbenzene (12DM3EB)
1,2,4,5-Tetramethylbenzene (1245TMP)
Pentylbenzene (PENTB)
Naphthalene (N0)
2-Methylnaphthalene (2MN)
1-Methylnaphthalene (1MN)

Forensic TO-15 Analytes (cont)

Naphthenes

Cyclopentane (CYP)
Methylcyclopentane (MCYP)
Cyclohexane (CH)
Methylcyclohexane (MCYH)
1-Ethyl-1-methylcyclopentane (1E1MCP)

Olefins

1,3-Butadiene (13B)
1-Pentene (1P)
2-Methyl-1-butene (2M1B)
2-Pentene (trans) (T2P)
2-Pentene (cis) (C2P)
1-Hexene (1HEX)
1-Heptene (1H)
1-Octene (1O)
1-Nonene (1N)
1-Decene (1D)

Sulfur

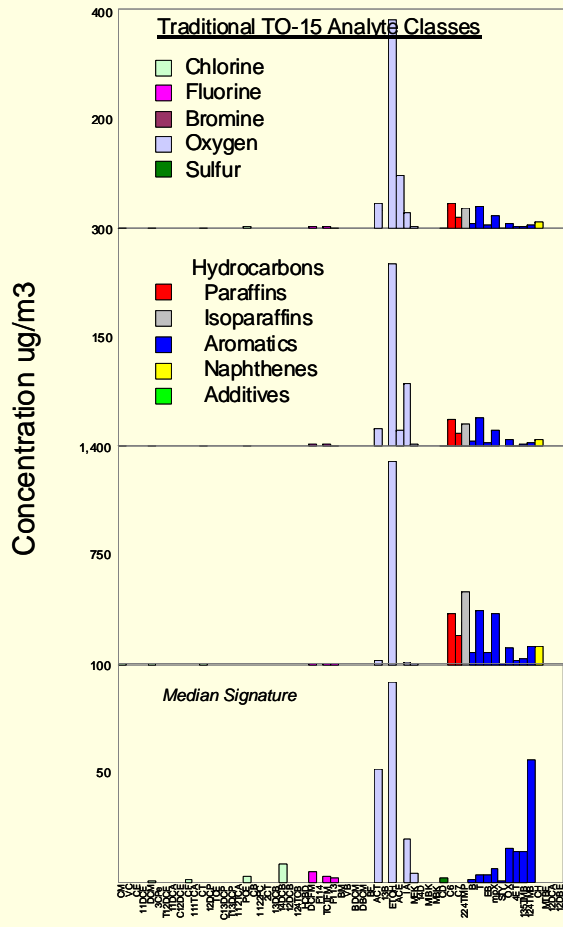
Thiophene (THIO)
2-Methylthiophene (2MTHIO)
3-Methylthiophene (3MTHIO)
2-Ethylthiophene (2ETHIO)
Benzothiophene (BT0)

Additives

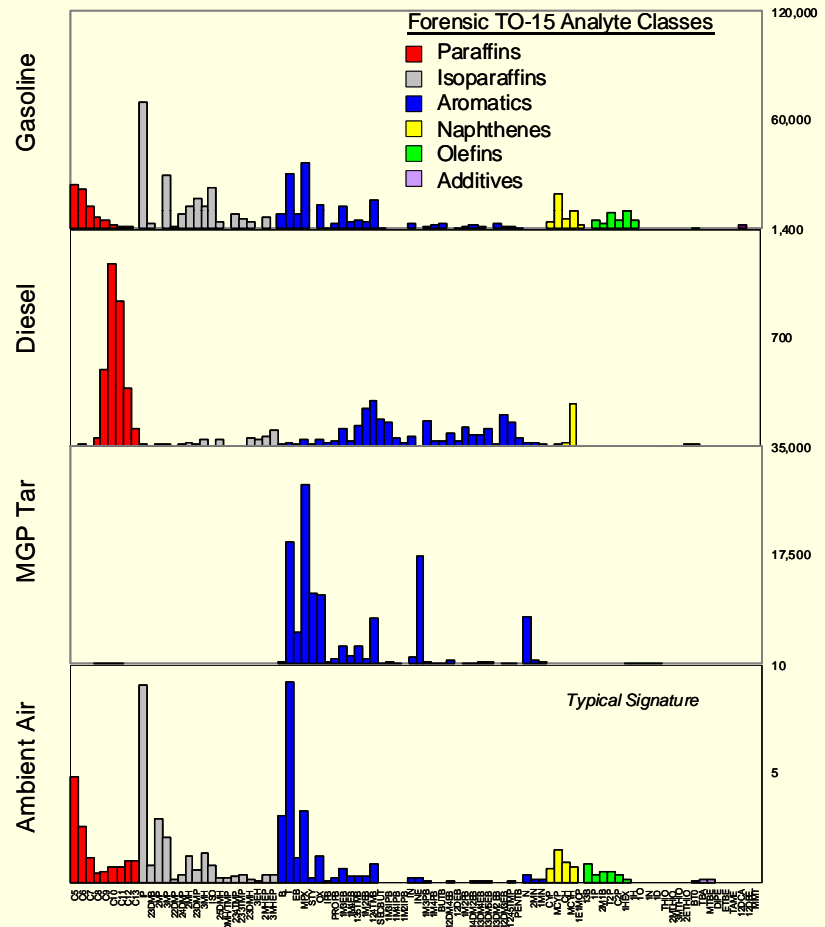
Tertiary butyl Alcohol (TBA)
MTBE (MTBE)
Diisopropyl Ether (DIPE) (DIPE)
Ethyl Tertiary Butyl Ether (ETBE) (ETBE)
TAME (TAME)
1,2-Dichloroethane (12DCA)
1,2-Dibromoethane (12DBE)
MMT (MMT)

Source Signature Results

Traditional TO-15 Results

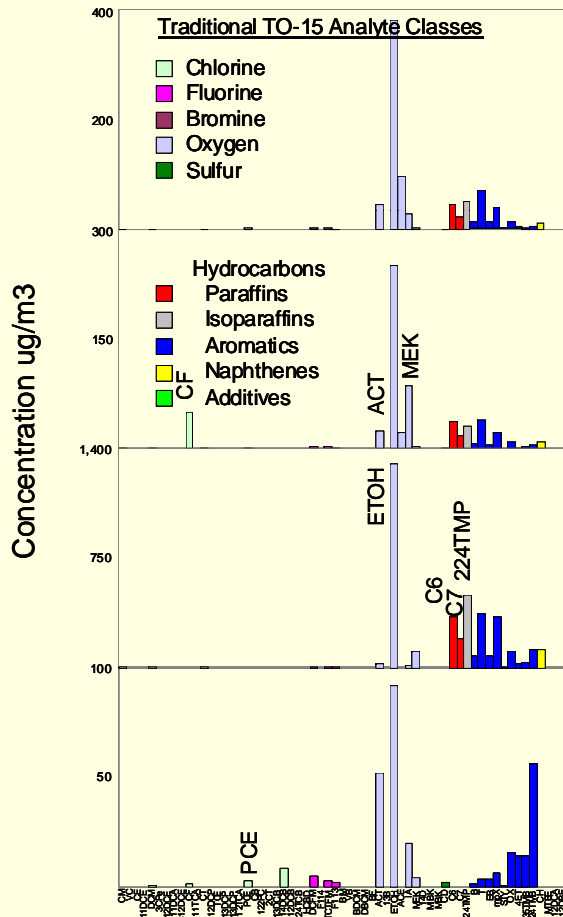


Forensic TO-15 Results

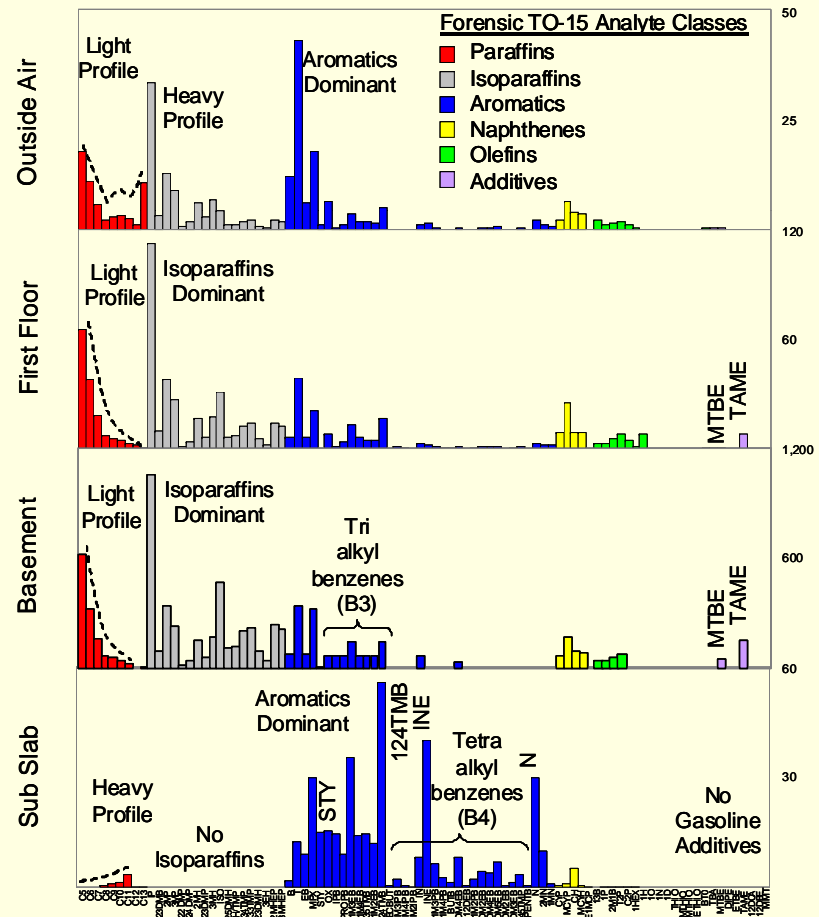


Residential Results Results

Traditional TO-15 Results



Forensic TO-15 Results



Indoor Air Summary

- Concentration
 - Variable
 - Screen
 - Regulatory Limits
 - Literature
- Composition
 - Traditional TO15
 - Forensic TO15
- Multiple Lines of Evidence

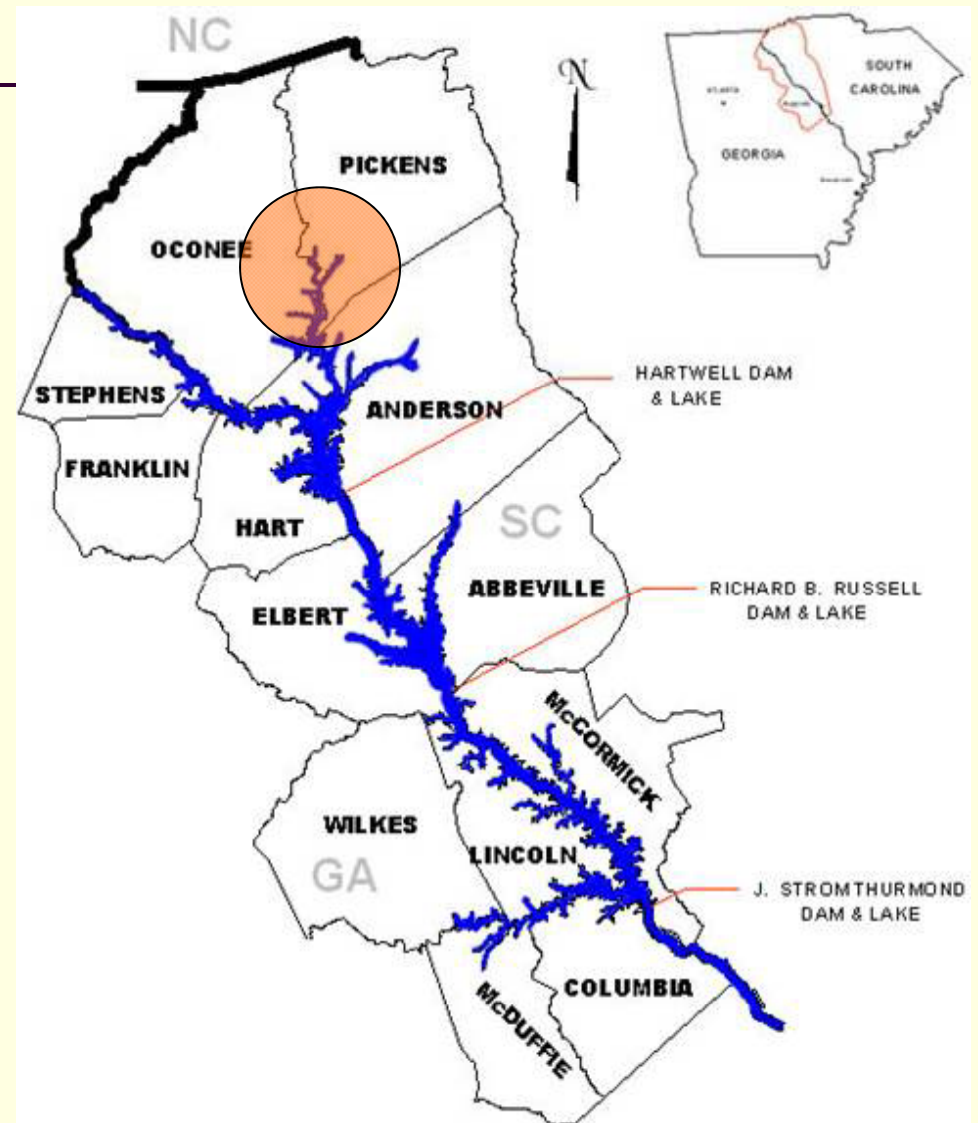


PCBs in Sediment: Natural Attenuation

DoD-Environmental Monitoring and
Data Quality (EMDQ) Workshop
March 29, 2011

Lake Hartwell Site

- Fresh water lake
- Sangamo-Weston Capacitor Manufacturing (1955 – 1978)
- Aroclors used: 1016, 1242, 1254
- Terrestrial sources removed in mid-90s
- MNR selected by Region 4 (1995 ROD)



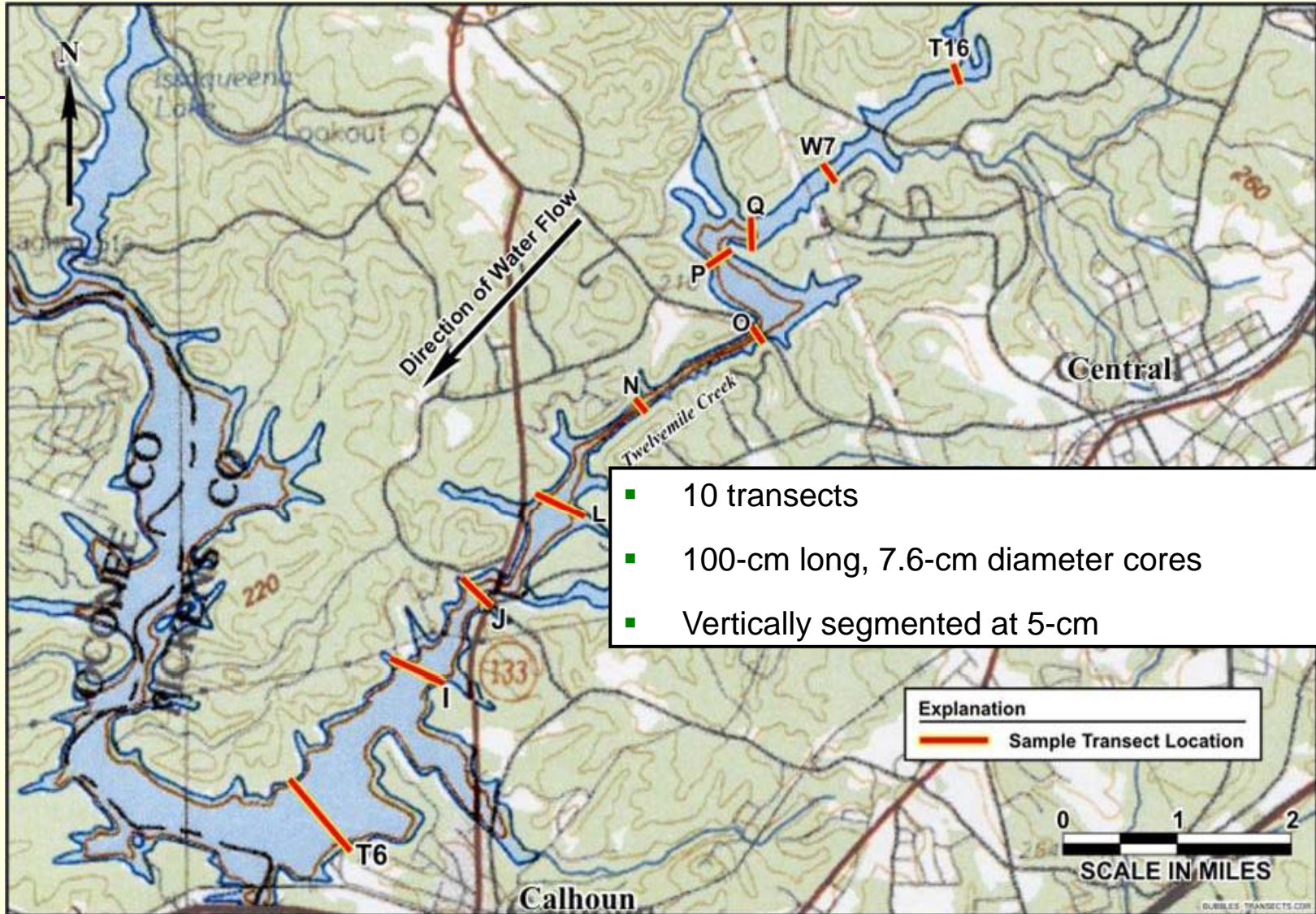
U.S. EPA Objectives

- Improve our understanding of natural alteration mechanisms that contribute to the recovery of PCB-contaminated sediments
- Apply a range of forensics techniques to better understand the fate and transport of PCBs at Lake Hartwell
- Characterize source and transformation end member patterns
- Examine PCB biological transport pathways and patterns

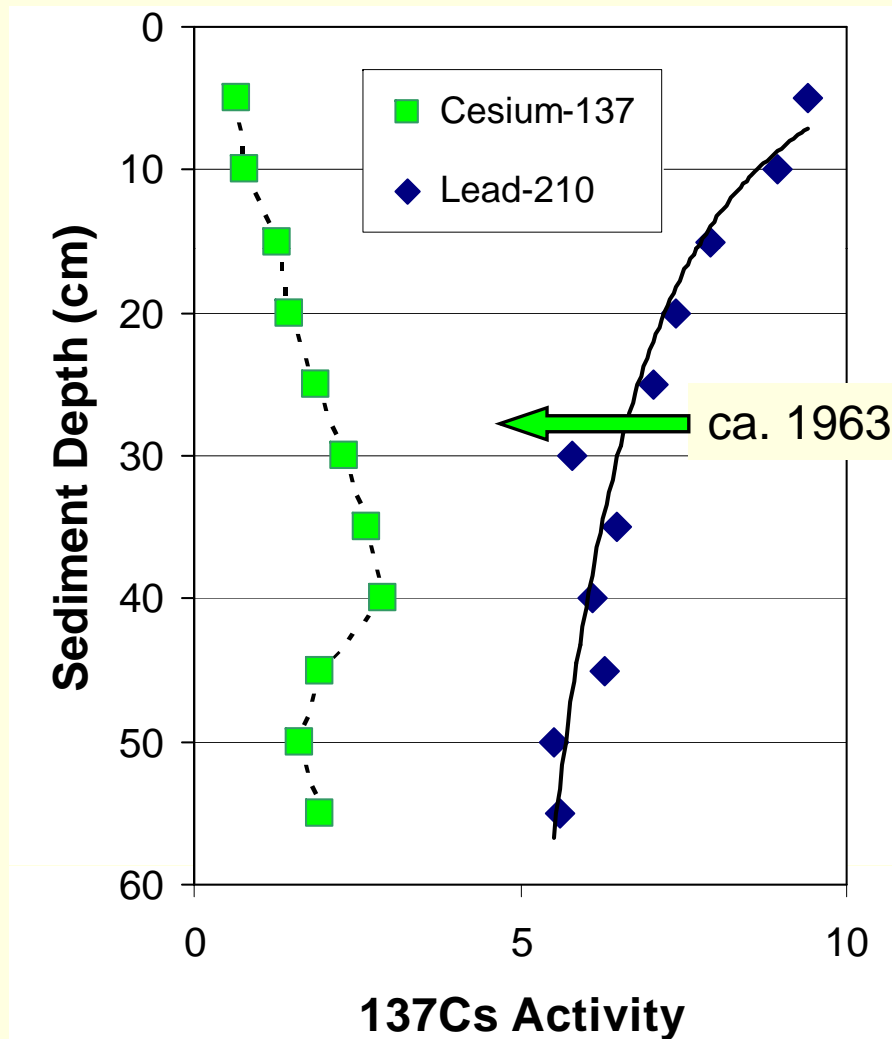
Water and Sediment Characterization (2000 & 2001)

- Detailed PCB chromatography (107 congeners) provided information on vertical and horizontal PCB distributions
- Sediment isotope analyses (^{210}Pb and ^{137}Cs) were used to age dating sediments and calculate sedimentation rates
- Detailed chemical fingerprinting identified dechlorination patterns in sediment and biota

Sediment Core Locations



Sediment Age Dating



■ ^{210}Pb

■ 22.3-year half life

■ Peak at surface

■ Decays with depth

■ ^{137}Cs

■ 30-year half life

■ Peak ca. 1963

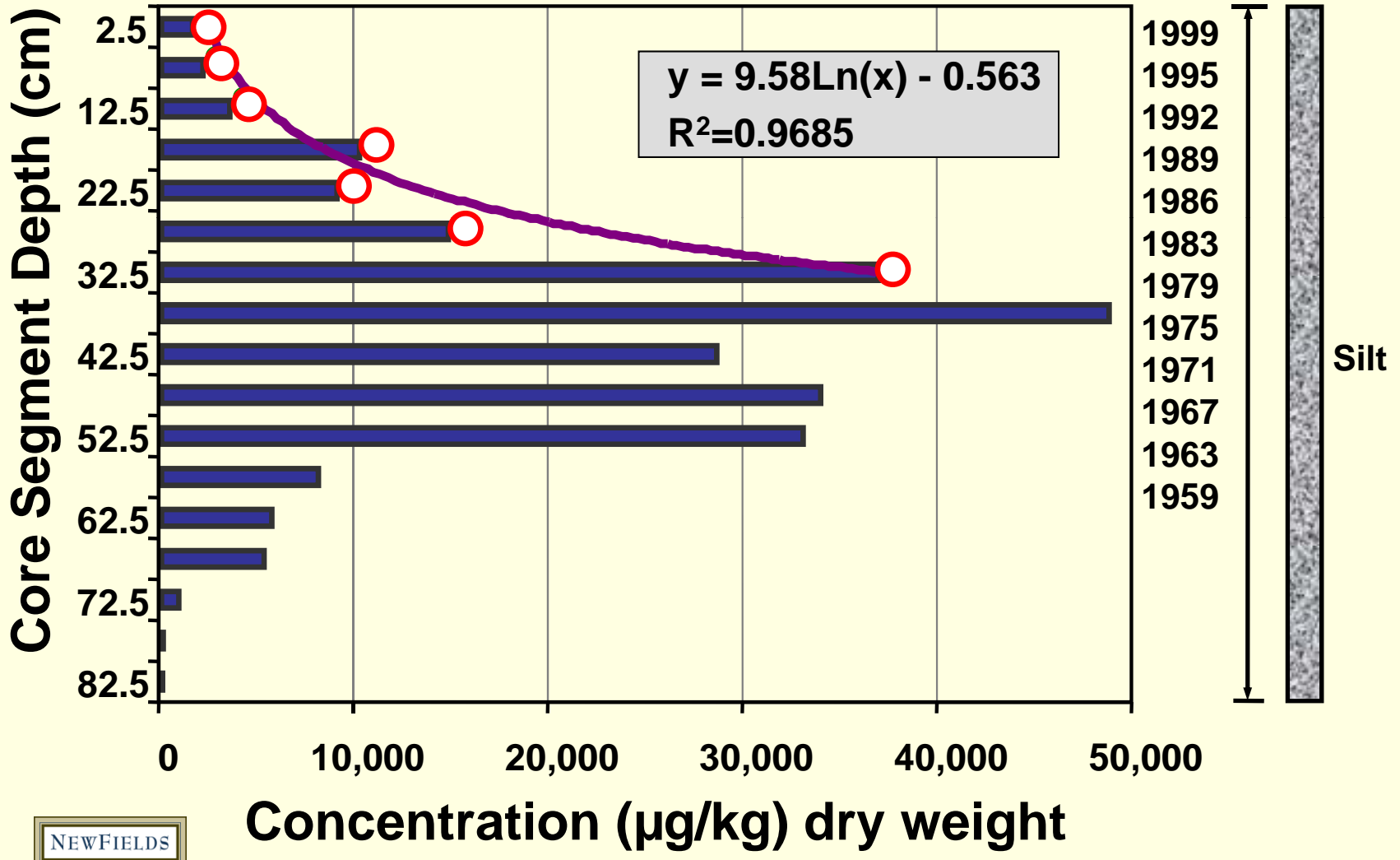
■ First appears ca. 1957

■ Decays toward surface

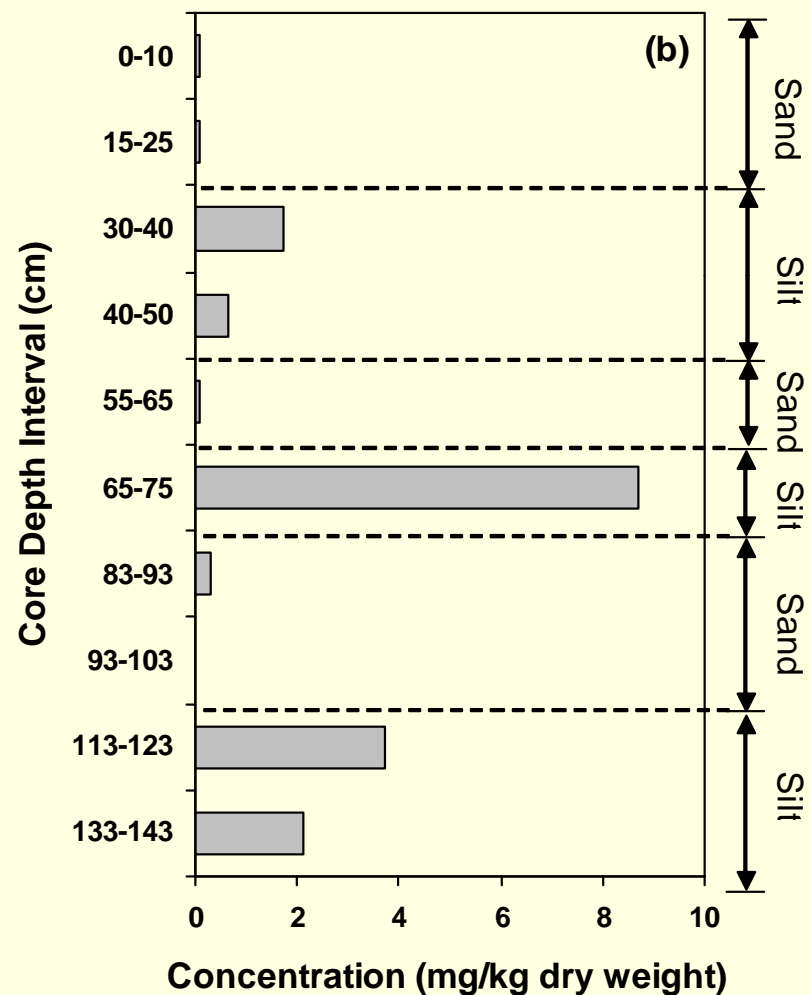
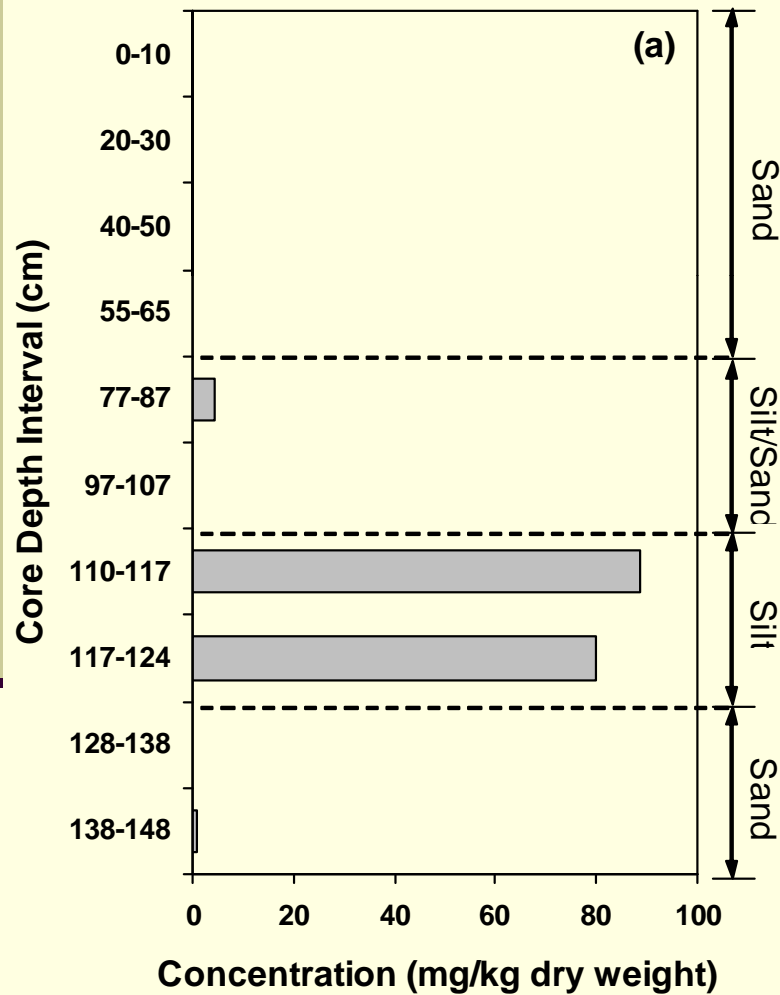
■ Lake Hartwell

Deposition ~ 1 cm/yr

Sediment Deposition and Contaminant Burial



Variability in Core Profiles (Upstream Cores at Lake Hartwell)

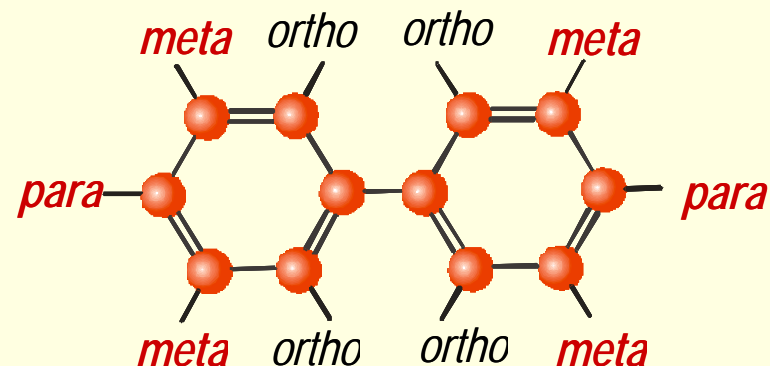


Fingerprinting PCB Source and Transformation Processes

- Sorption/Sequestration
- Physical transport
 - Longitudinal transport redistributes source signatures and molar concentrations
 - Vertical transport (burial) conserves molar concentrations
- Dissolution/volatilization
 - Loss of lower molecular weight congeners
- Dechlorination
 - Loss of higher molecular weight congeners
 - Accumulation of lower molecular weight congeners

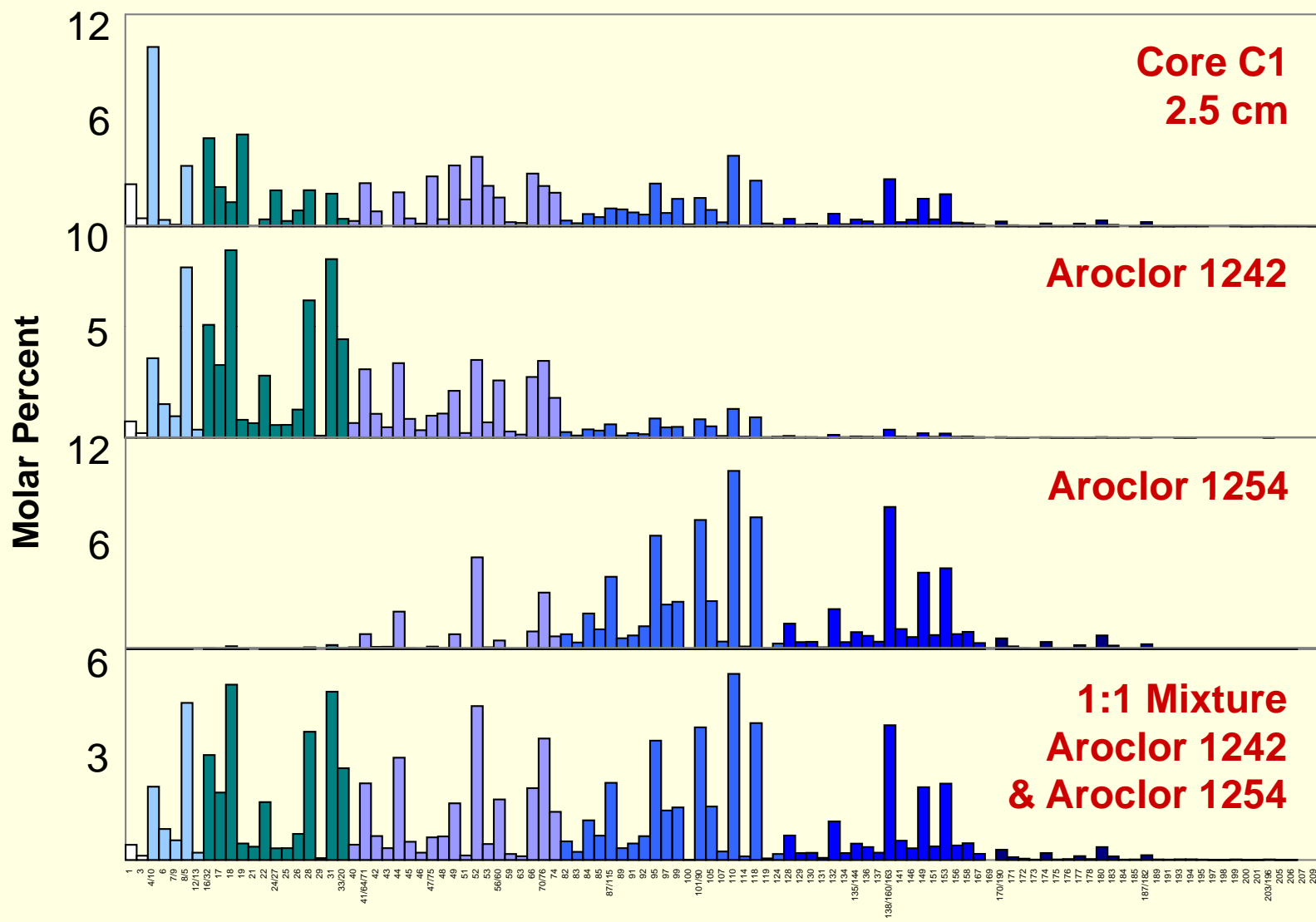
PCB Weathering

Increased chlorination increases molecular weight and hydrophobicity, decreases solubility and mobility

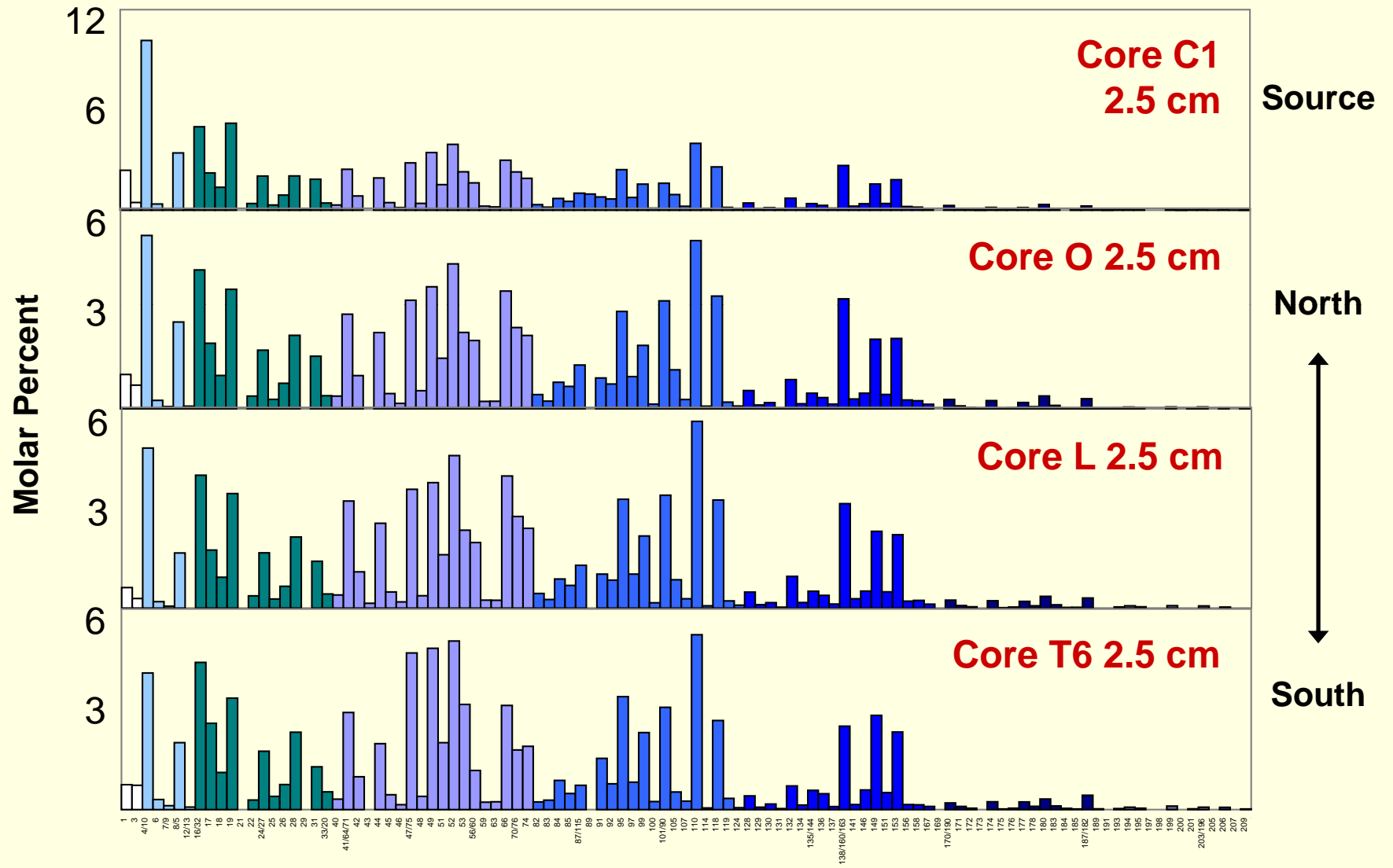


Mechanism	Relative Kinetics	Level of Chlorination
Solubility, Dissolution, Volatilization	Low Cl > High Cl	Impacts primarily mono, di, tri-Cl BP
Biological oxidation	Low Cl > High Cl	Impacts primarily mono-, di-, tri-Cl BP
Reductive dechlorination	High Cl > Low Cl	Impacts primarily tri- through deca-Cl BP
Toxicity	High Cl > Low Cl	coplanar increases, <i>meta/para</i> > <i>ortho</i>

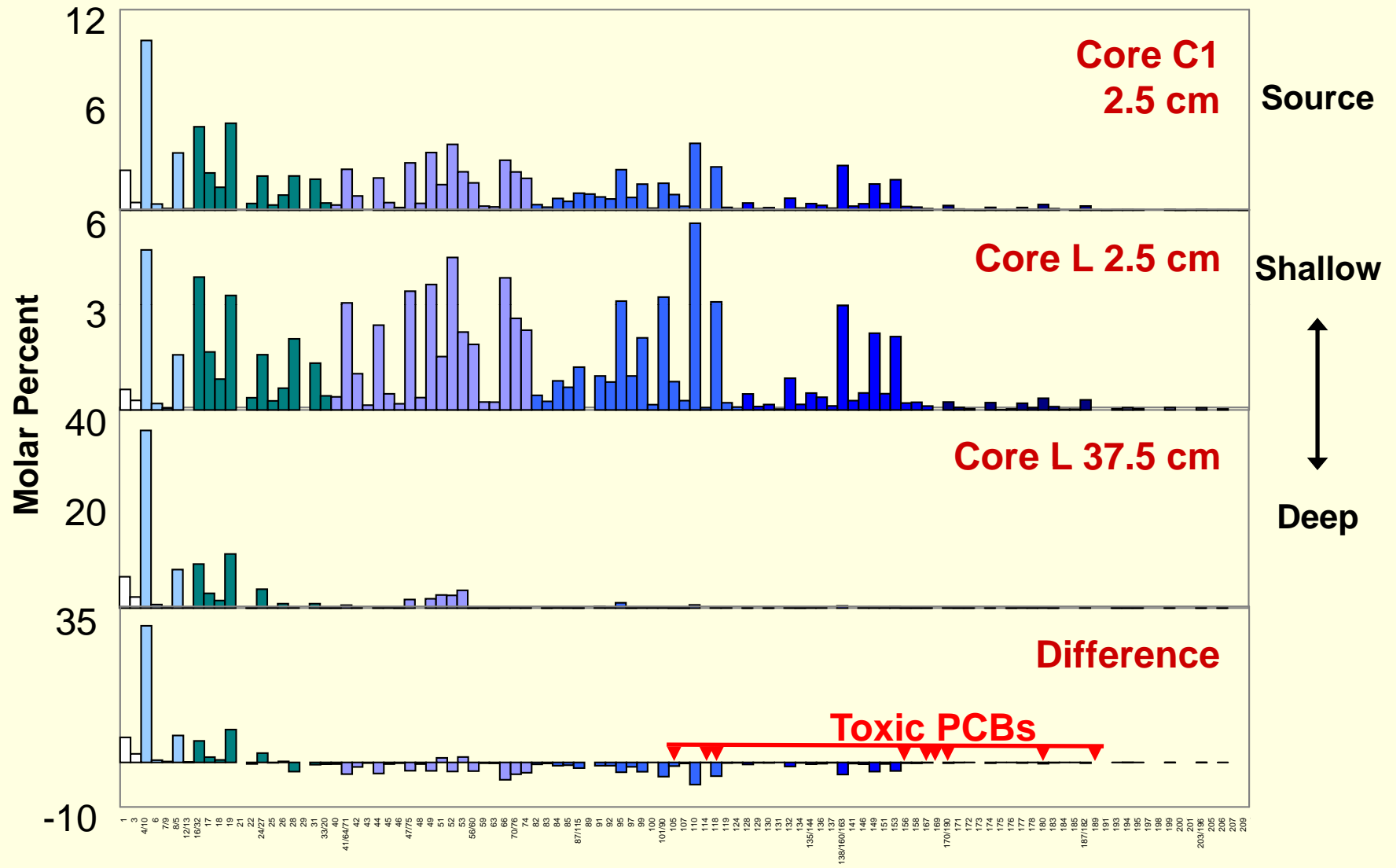
Aroclor Source Signature



Spatial Homogeneity



Vertical Heterogeneity



Lake Hartwell Core L

Major Congener Shifts

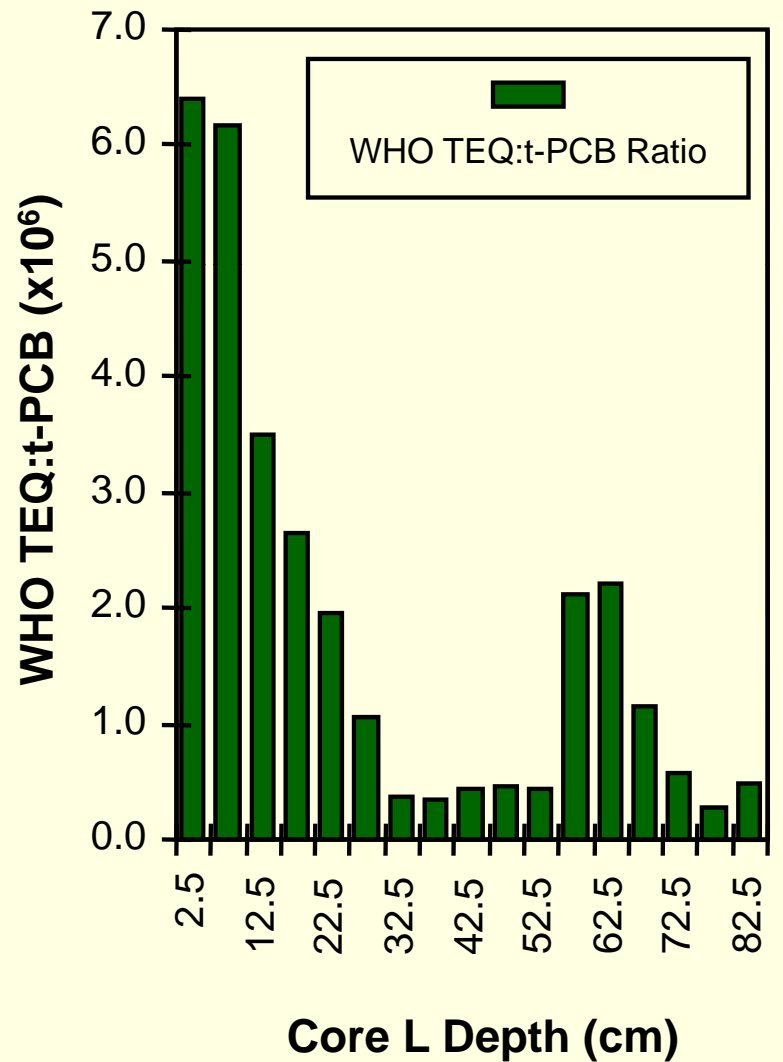
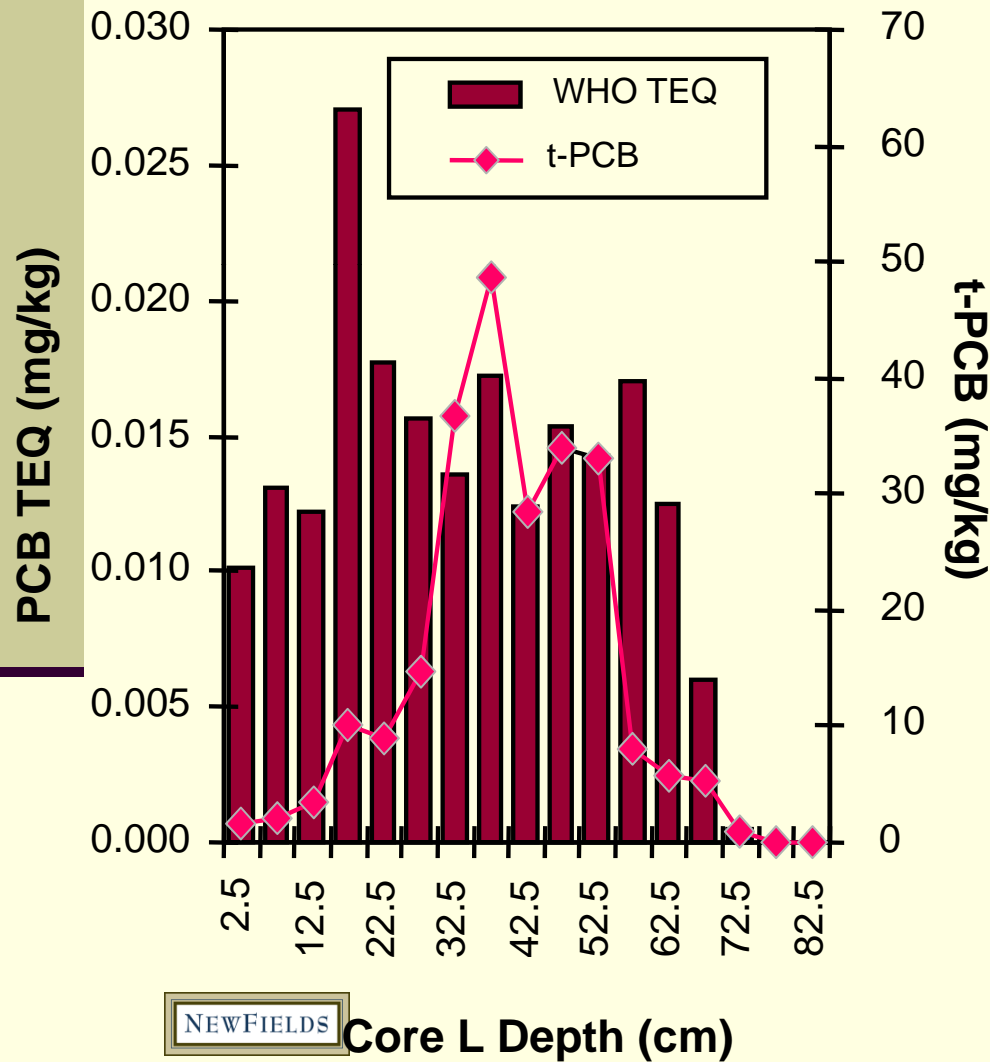
IUPAC No.	Congener Name	Percent Change
PCB 1	2-chlorobiphenyl	4.4
PCB 4/10	2,2'/2,6-dichlorobiphenyls	29
PCB 8/5	2,4'/2,3-dichlorobiphenyls	5.8
PCB 16/32	2,2',3/2,4',6-trichlorobiphenyls	5.8
PCB 19	2,2',6-trichlorobiphenyl	8.4
PCB 24/27	2,3,6/2,3',6-trichlorobiphenyls	2.5
PCB 66 -156	tetra- through hexachlorobiphenyls	-45

World Health Organization (WHO) Toxic Equivalency Factors (TEF)

IUPAC No.	Chlorine Substitutions	2,3,7,8-TCDD TEF
WHO Congeners Included in PCB Analyses		
PCB105	mono- <i>ortho</i> substituted	0.00010
PCB114	mono- <i>ortho</i> substituted	0.00050
PCB118	mono- <i>ortho</i> substituted	0.00010
PCB156	mono- <i>ortho</i> substituted	0.00050
PCB167	mono- <i>ortho</i> substituted	0.00001
PCB169	non- <i>ortho</i> substituted (coplanar)	0.01000
PCB170	di- <i>ortho</i> substituted	0.00010
PCB180	di- <i>ortho</i> substituted	0.00001
PCB189	mono- <i>ortho</i> substituted	0.00010
WHO Congeners Not Included in PCB Analyses ^(a)		
PCB77	non- <i>ortho</i> substituted (coplanar)	0.00050
PCB123	mono- <i>ortho</i> substituted	0.00010
PCB126	non- <i>ortho</i> substituted (coplanar)	0.10000
PCB157	mono- <i>ortho</i> substituted	0.00050

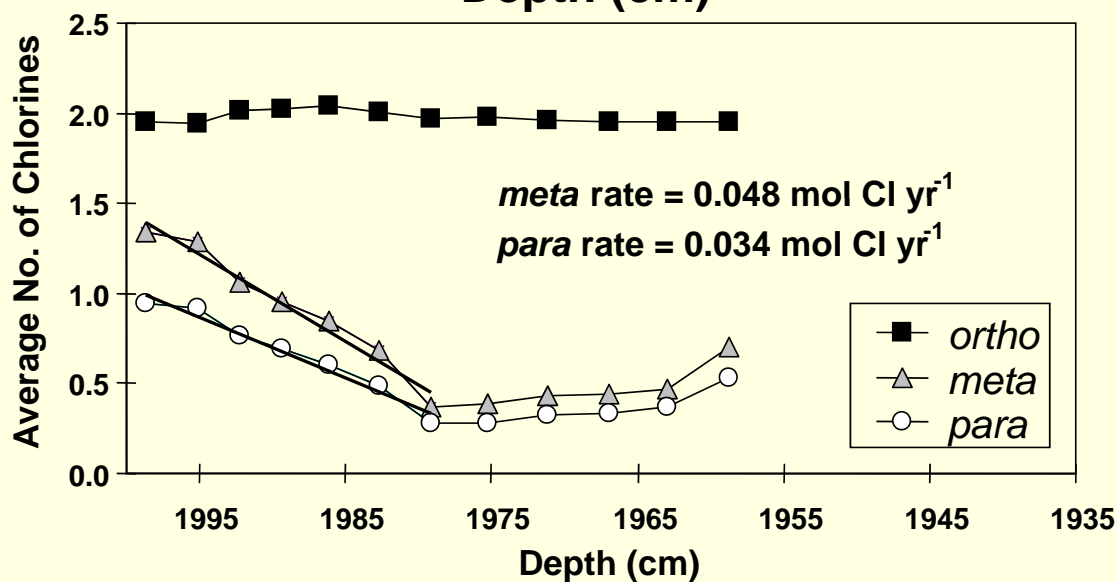
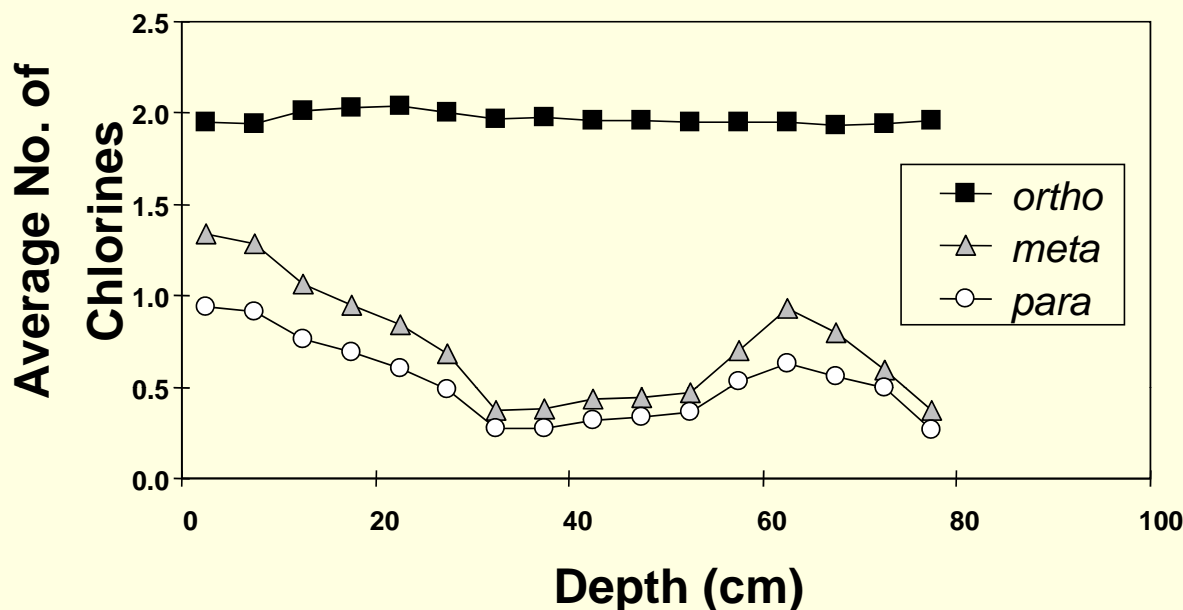
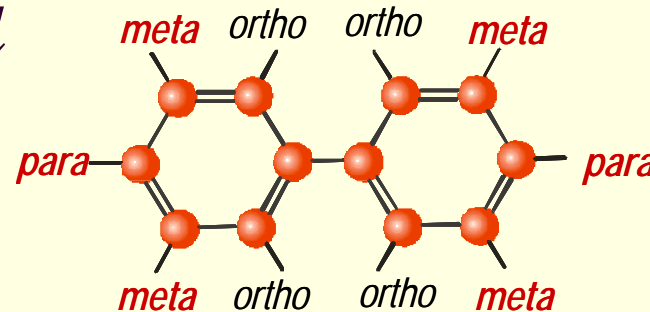
(a) Congeners require EPA Method 1668

Lake Hartwell t-PCB TEQs



NEWFIELDS

ortho, meta, and para Dechlorination



Average Rates (n = 11)

$$meta = 0.053 \pm 0.04$$

$$para = 0.037 \pm 0.03$$

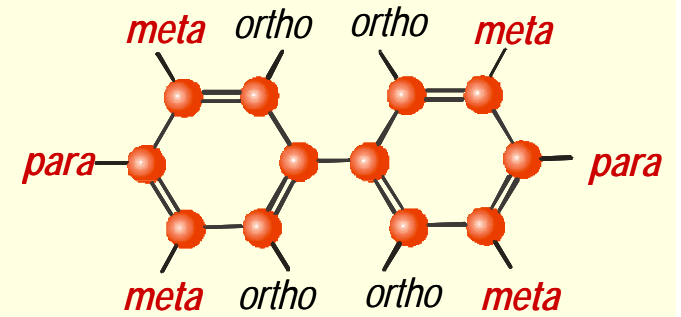
18 yr per *meta* Cl

27 yr per *para* Cl

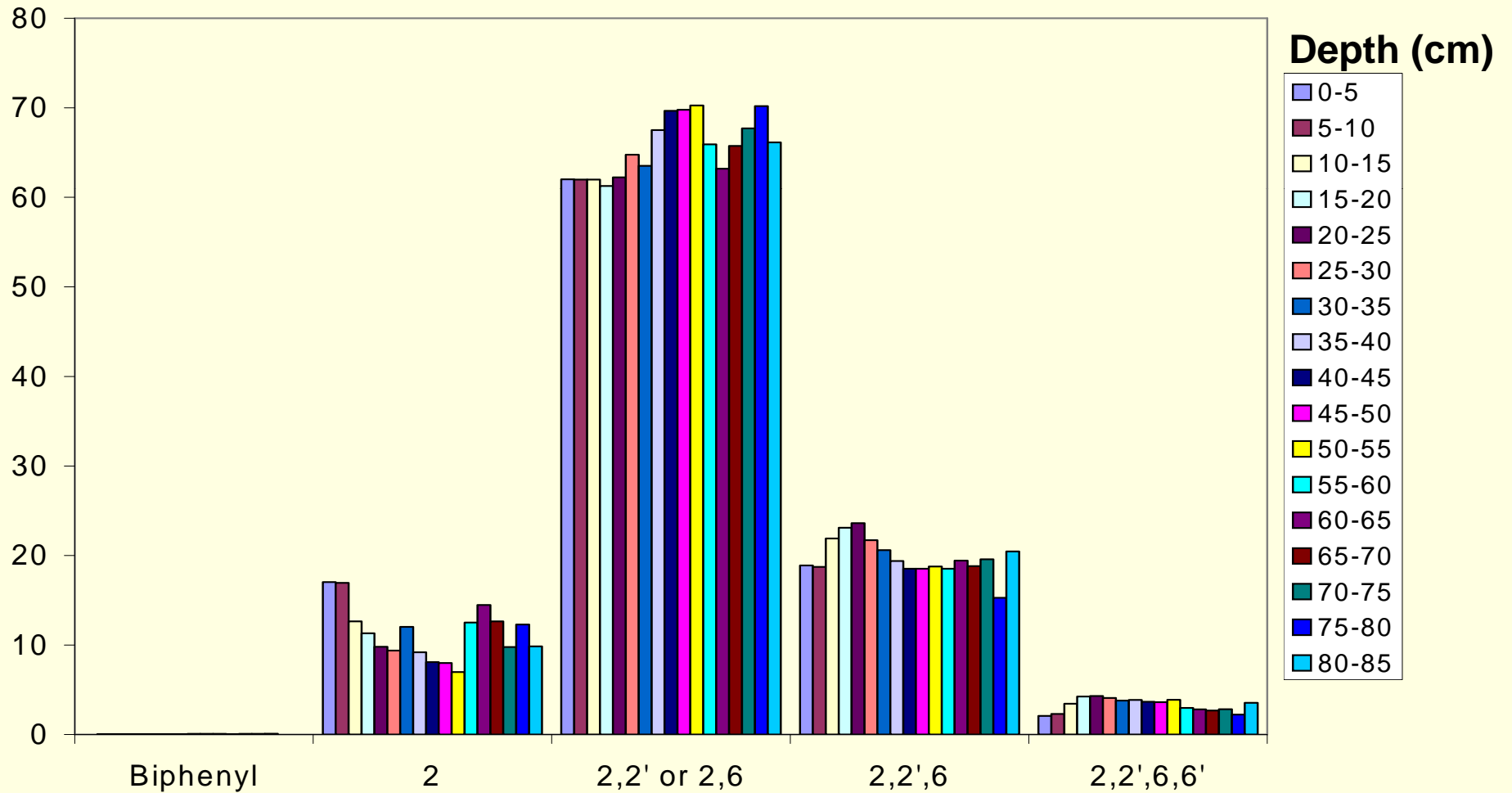
Magar et al., *ES&T* 39(10):3538-3547, *ES&T* 39(10):3548-3554

Ortho Signatures

Core L

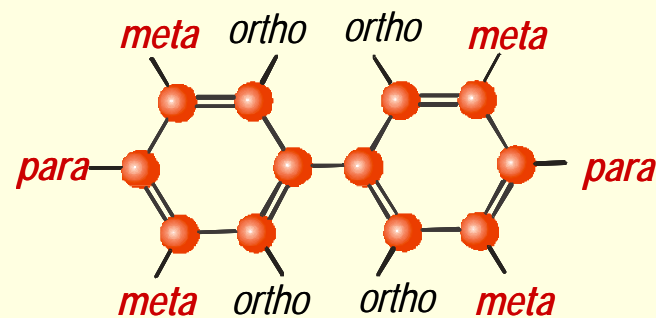


Molar Percent

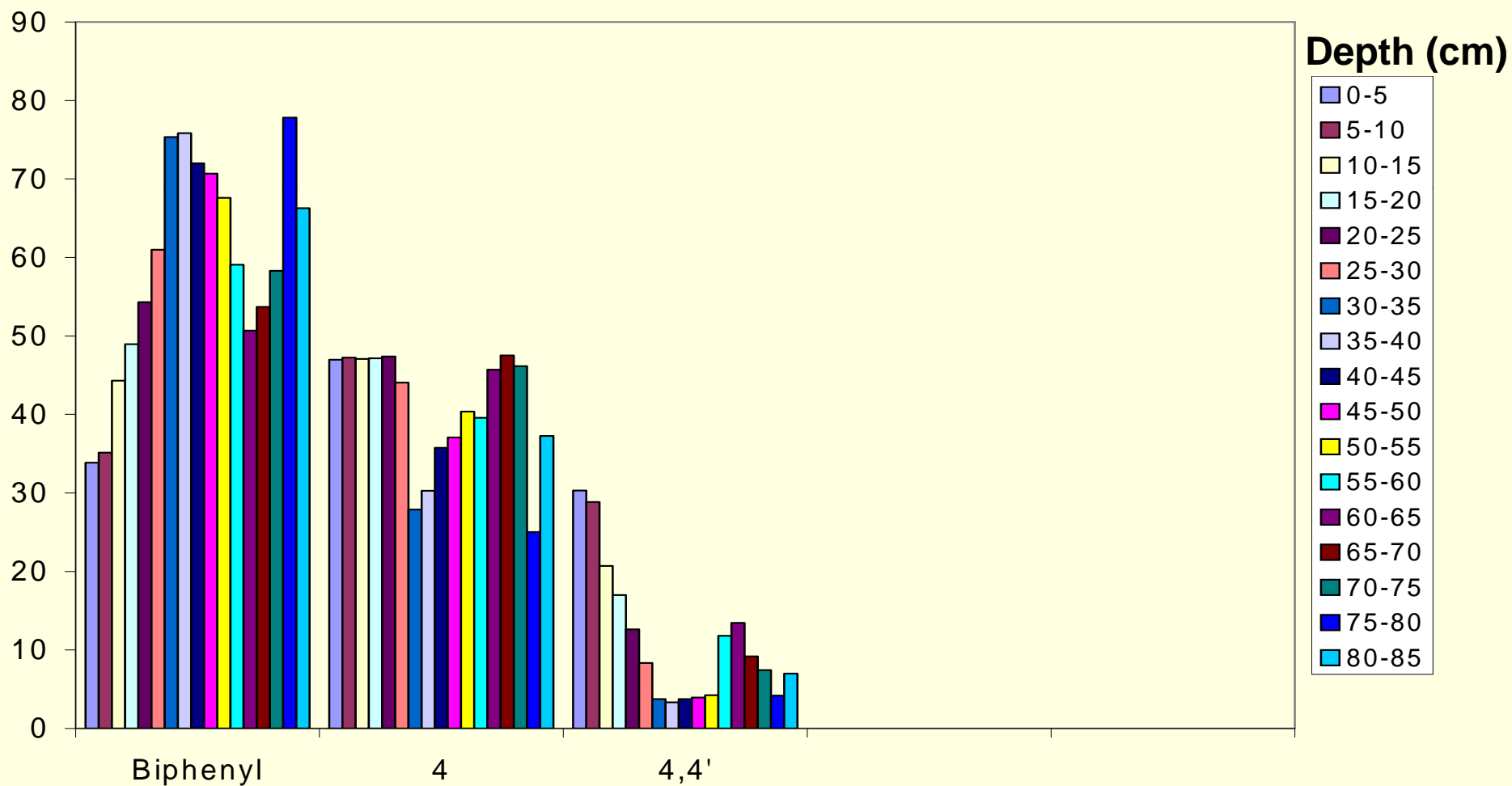


Para Signatures

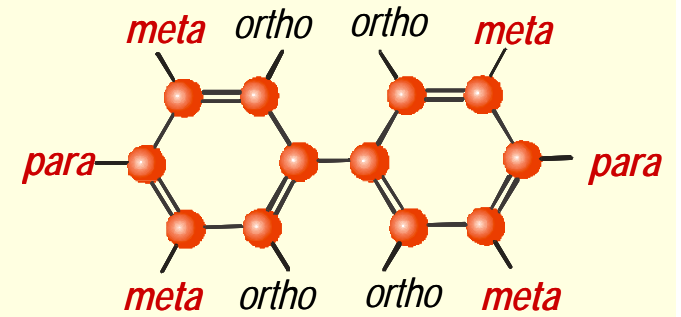
Core L



Molar Percent

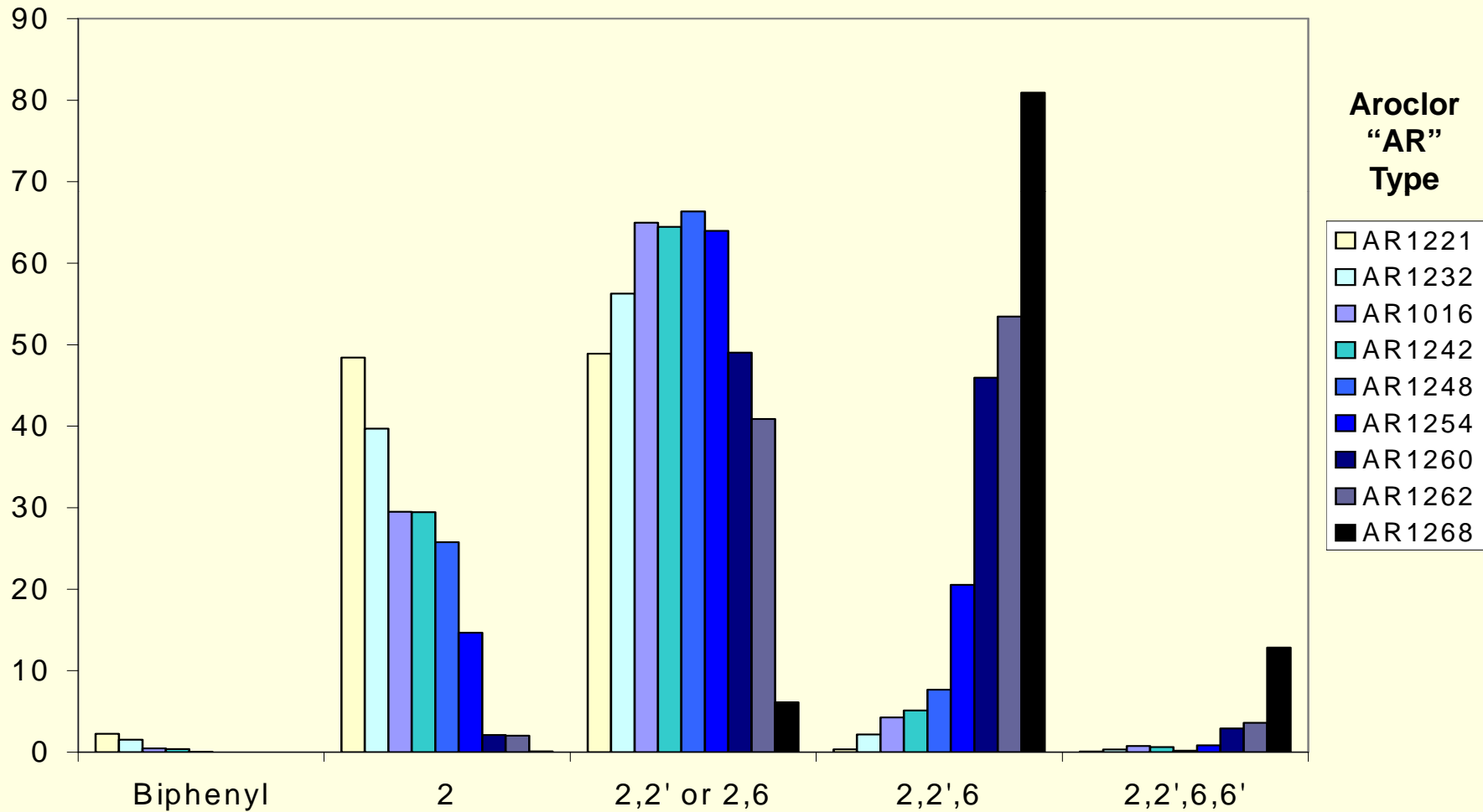


Ortho Signatures



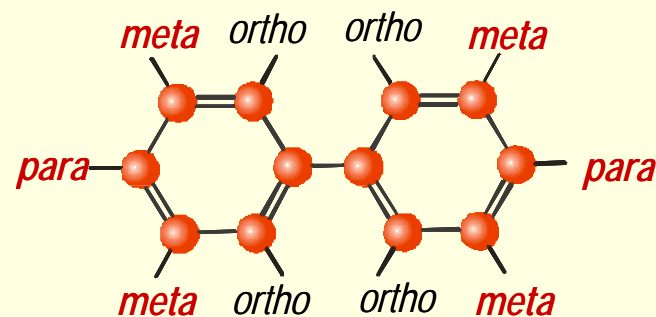
Aroclor Standards

Molar Percent

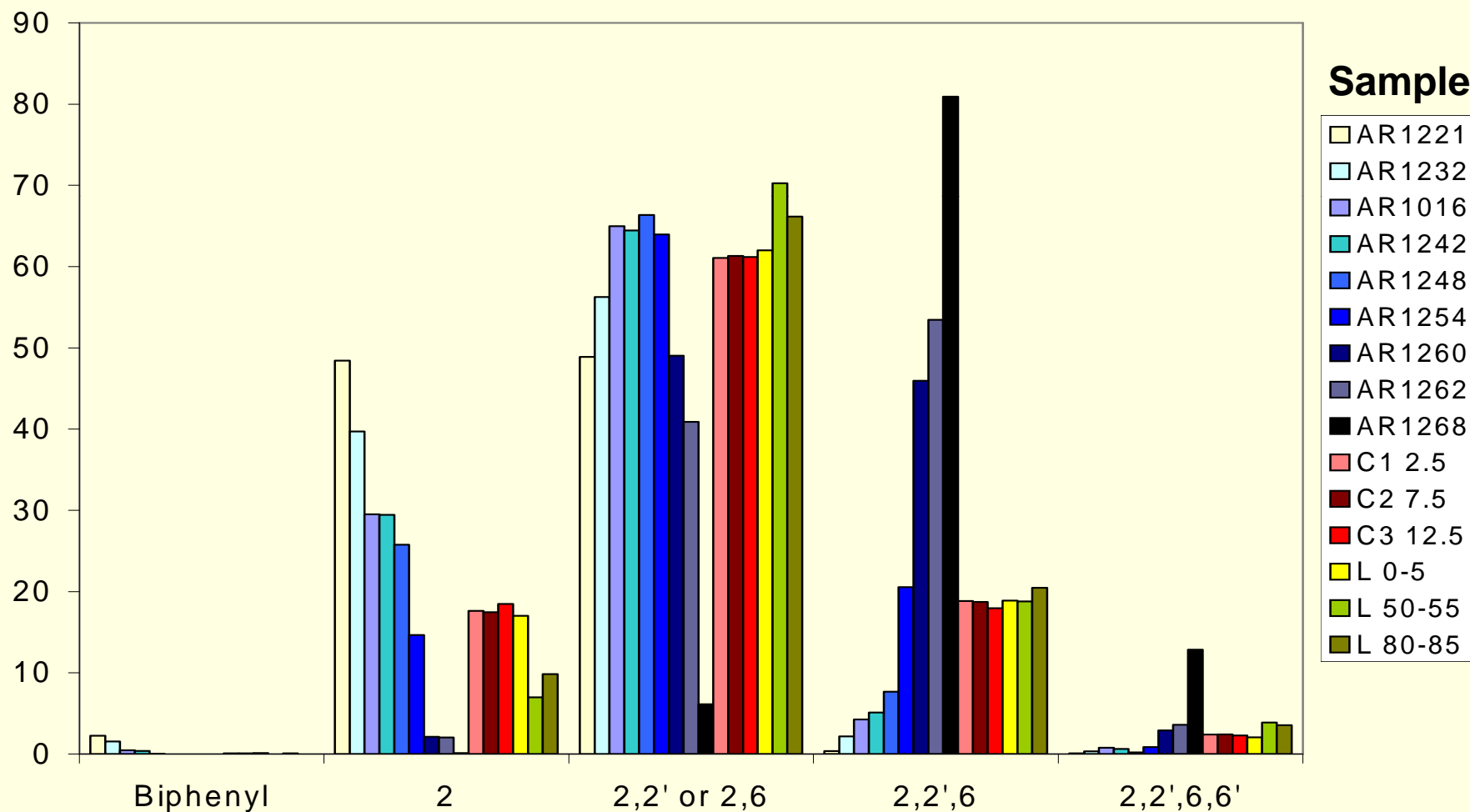


Meta Signatures

Core L



Molar Percent



Results

- Highest PCB concentrations associated with silt/clay
- Surface sediment PCBs at or approaching 1.0 mg/kg
- Time to achieve surface sediment concentrations
 - *0 to 5 yr to achieve 1.0 mg/kg*
 - *2 to 10 yr to achieve 0.4 mg/kg*
 - *10 to 30 yr to achieve 0.05 mg/kg*
- Homologue shifts with depth and time
 - *Cl4/Cl5/Cl6 congeners reduced from 80% to 20% t-PCB*
 - *Cl1/Cl2/Cl3 congeners increased from 20% to 80% t-PCB*
- Significant accumulation of ortho chlorinated congeners
- Potential detoxification, based on WHO TEQ analysis

PCB Weathering and Dechlorination Summary

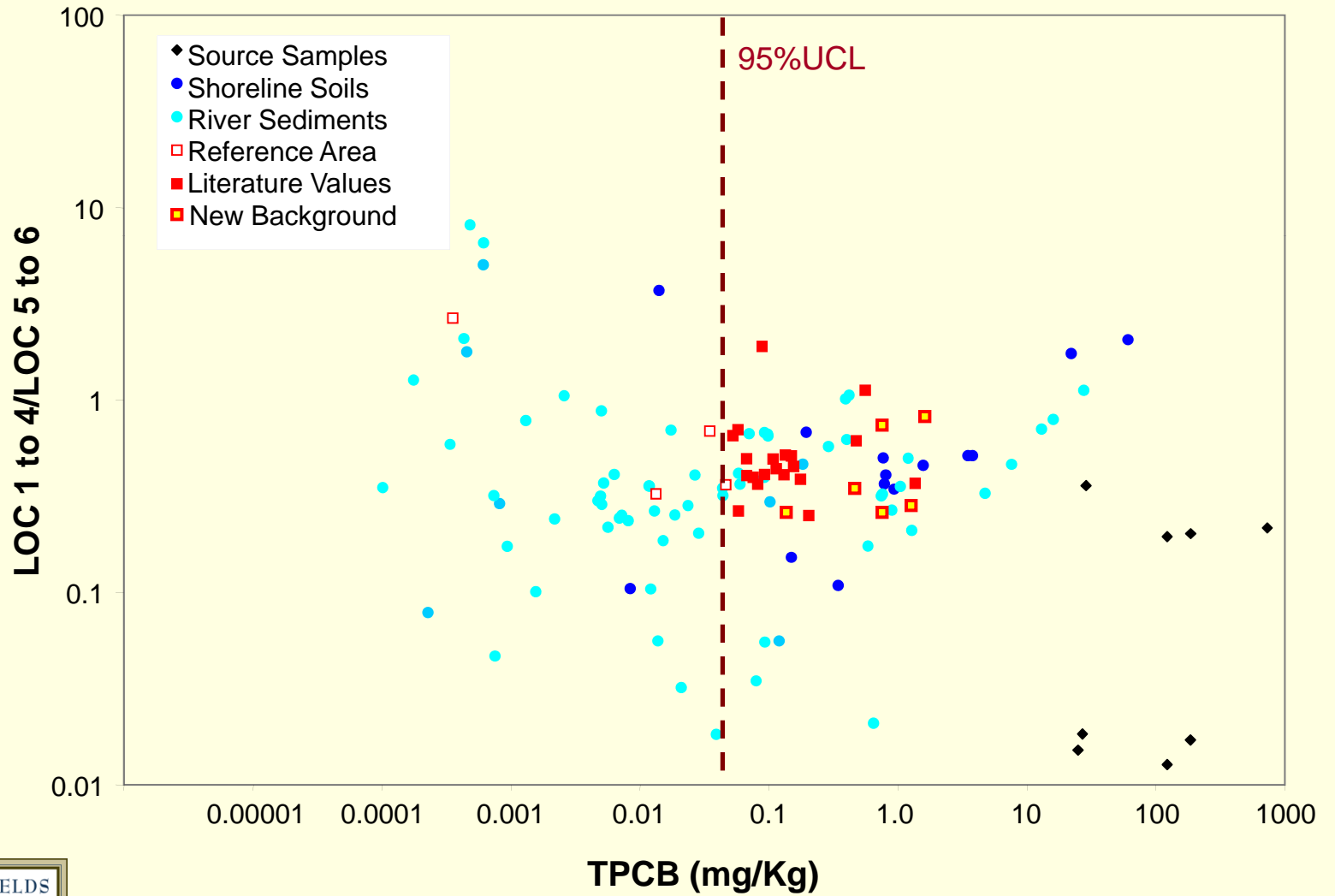
- Dechlorination processes
 - Tetra-deca PBPs transformed to mono-tri PBP
 - *Ortho*-chlorines (least toxic) were conserved
- Toxicity reduction
 - Dechlorination reduces toxicity (fewer chlorines and reduced coplanar congeners)
 - Dechlorination is a progressive process, generally increasing with depth and time
- Heterogeneity
 - Variability within individual cores
 - Variability from core to core



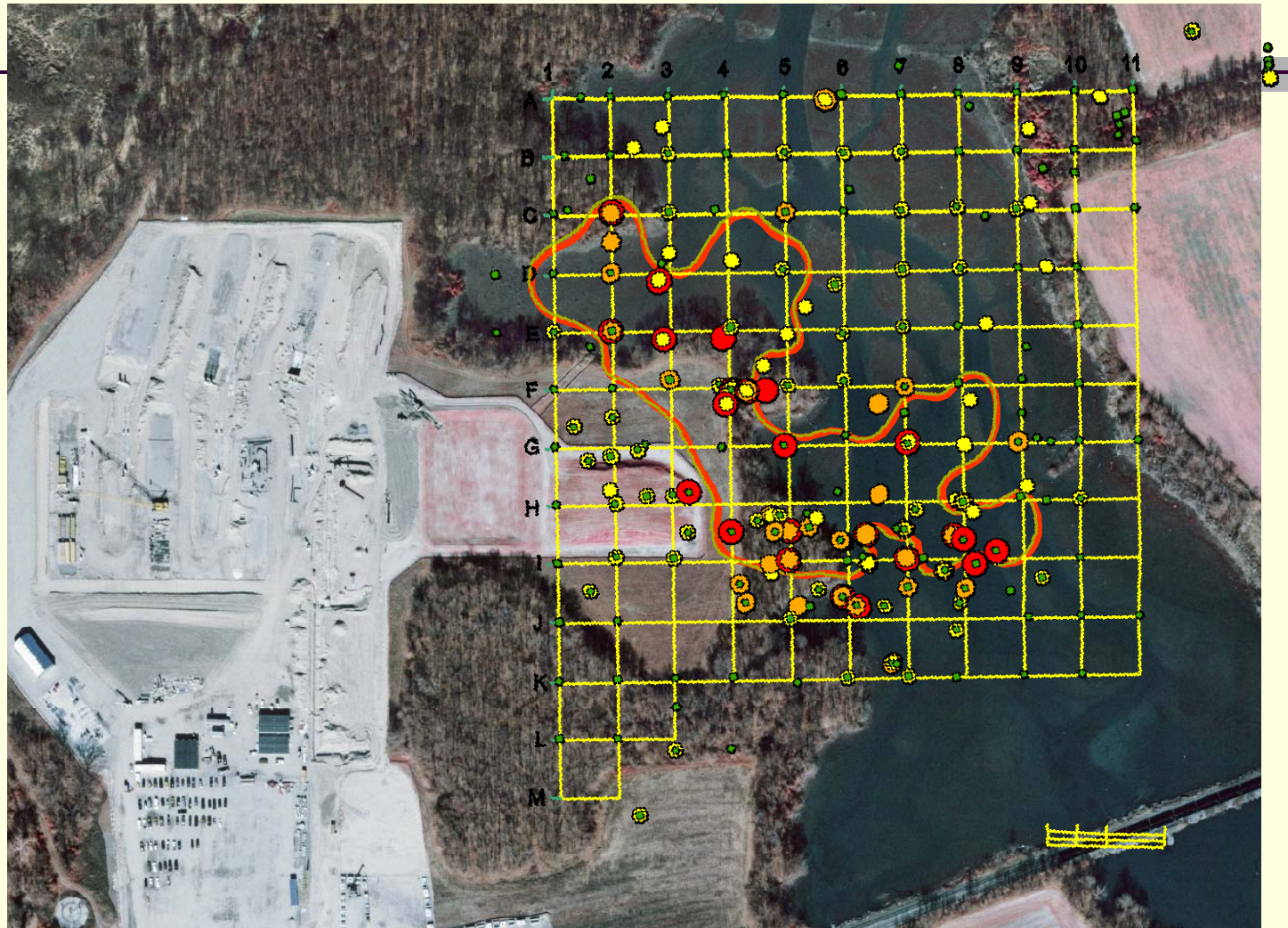
PCBs in Sediment: Forensics Assists RI/FS

DoD-Environmental Monitoring and
Data Quality (EMDQ) Workshop
March 29, 2011

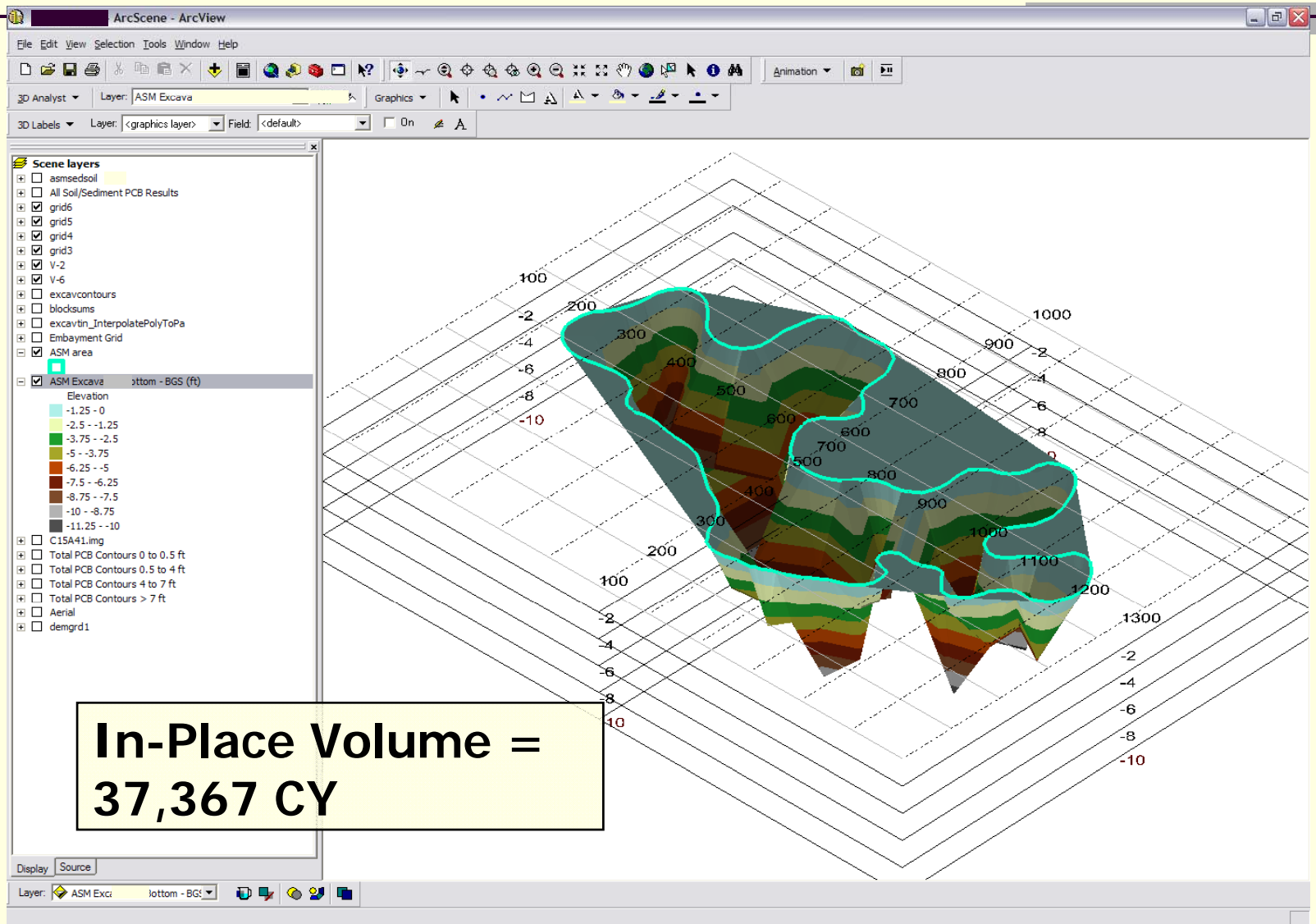
Background PCBs



Source Footprint

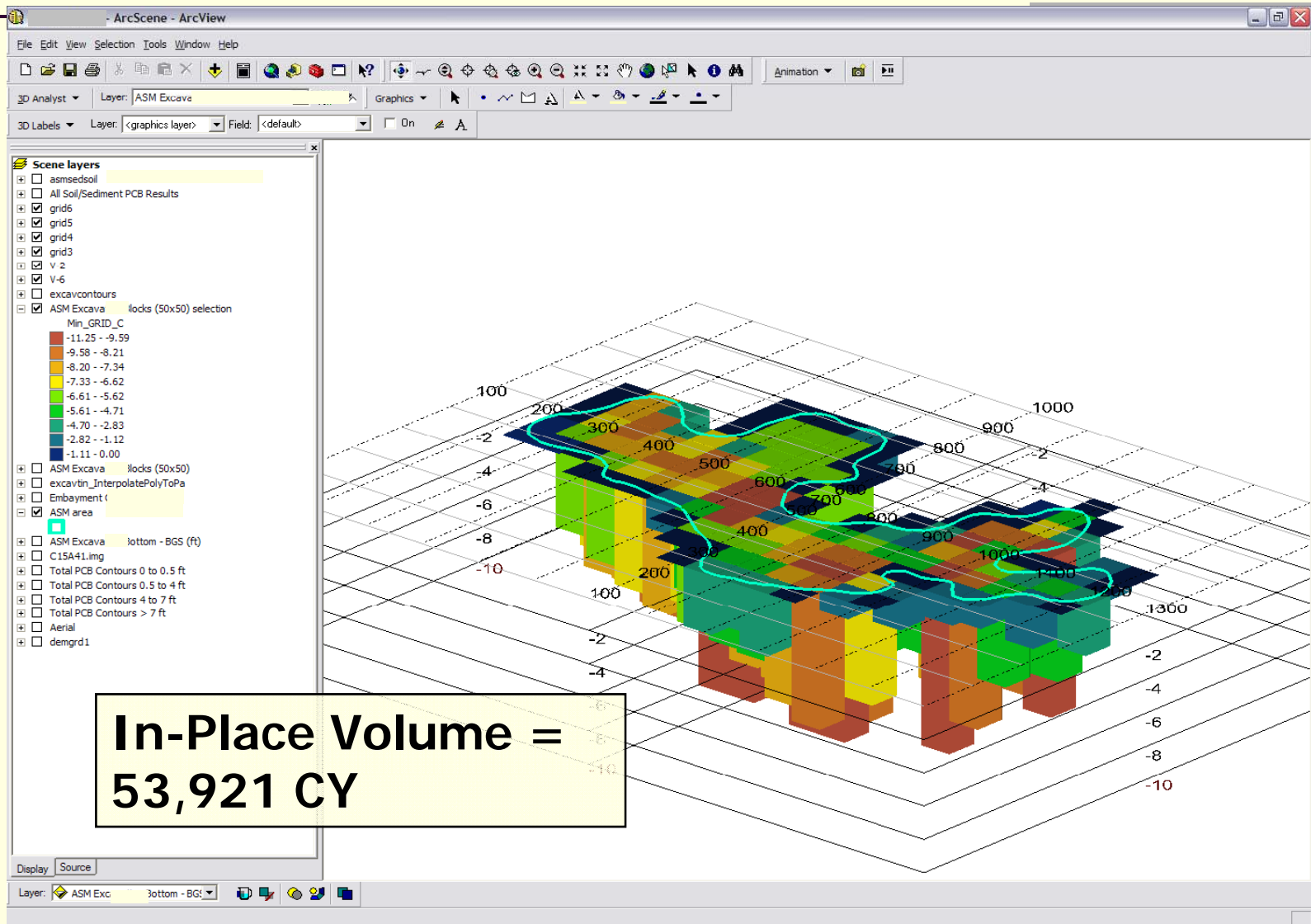


3D Contour of Sediments > 1 ppm Oblique View



3D Block Excavation

Oblique View



Hydrocarbons and PAHs: Background Soils and Sediments

DoD-Environmental Monitoring and
Data Quality (EMDQ) Workshop
March 29, 2011

Hydrocarbon Sources

- Petroleum Industry

- oil and pipeline spills
- terminal releases
- UST and AST leaks
- pavement products



- Tar Products

- manufactured gas plants
- tar refineries
- wood treaters
- building products



Hydrocarbon Sources

- Natural Background

- natural fires
- oil seeps
- eroded coals/shales
- early diagenetic processes



- Anthropogenic Background

- stormwater/surface runoff
- atmospheric deposition (soot)
- non-point/mobile sources
- residential coal and ash



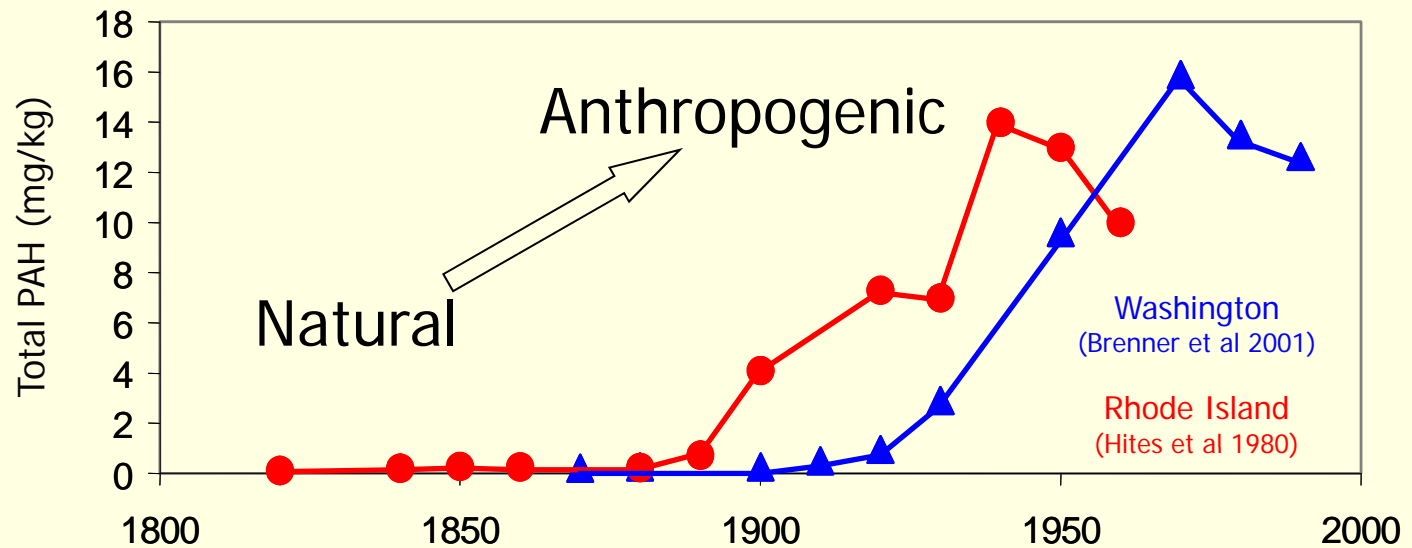
Hydrocarbon Sources

- Natural Background

- natural fires
- oil seeps
- eroded coals/shales
- early diagenetic processes

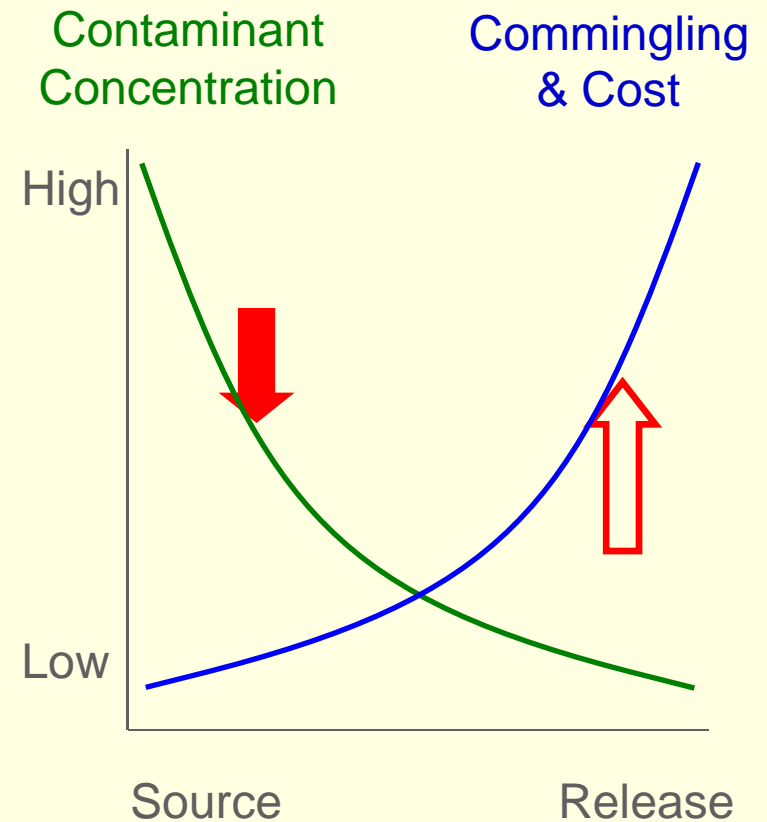
- Anthropogenic Background

- stormwater/surface runoff
- atmospheric deposition (soot)
- non-point/mobile sources
- residential coal and ash



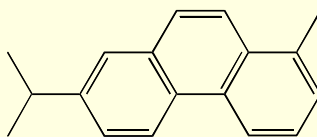
Environmental Challenge

- Migration from the Source
 - Decreases Concentrations
 - Increases Commingling
 - Increases Cost
- Regulatory Limits for PAH
 - Steady or
 - Falling
- Help Needed
 - Separate On vs. Off Site
 - Delineating Remediation Zones
 - Prioritizing Remedial Action
 - Allocating Cleanup Costs

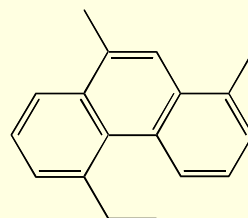


Forensic Methods: Source Specific Compounds and Patterns

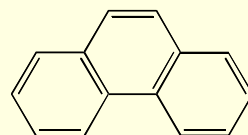
- Diagenic
 - Biologically Mediated
 - Natural
- Petrogenic
 - Petrogenesis
 - Refining
- Pyrogenic
 - Partial Combustion
 - Carbonization
 - Pyrolysis
 - Pyrosynthesis



Retene



1,9-Dimethyl-7-ethyl phenanthrene



Phenanthrene

Example: PAH Signature Richness

Petrogenic

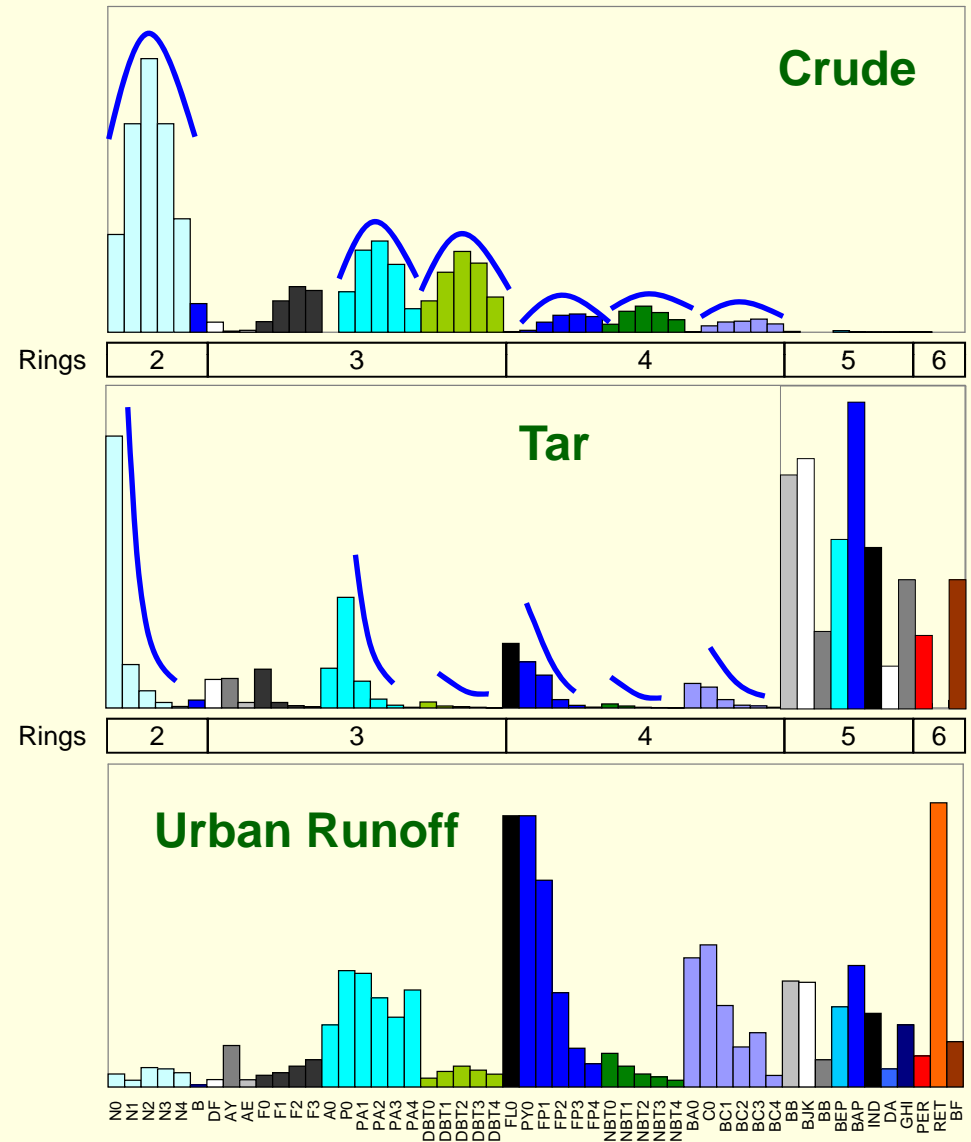
- Alkyl > Parent
- Little 4 to 6 Ring

Pyrogenic I

- Alkyl < Parent
- High 2 and 3 Ring

Pyrogenic II

- Alkyl < Parent
- High 4 to 6 Ring



EPAPAHs v Extended PAHs

Petrogenic

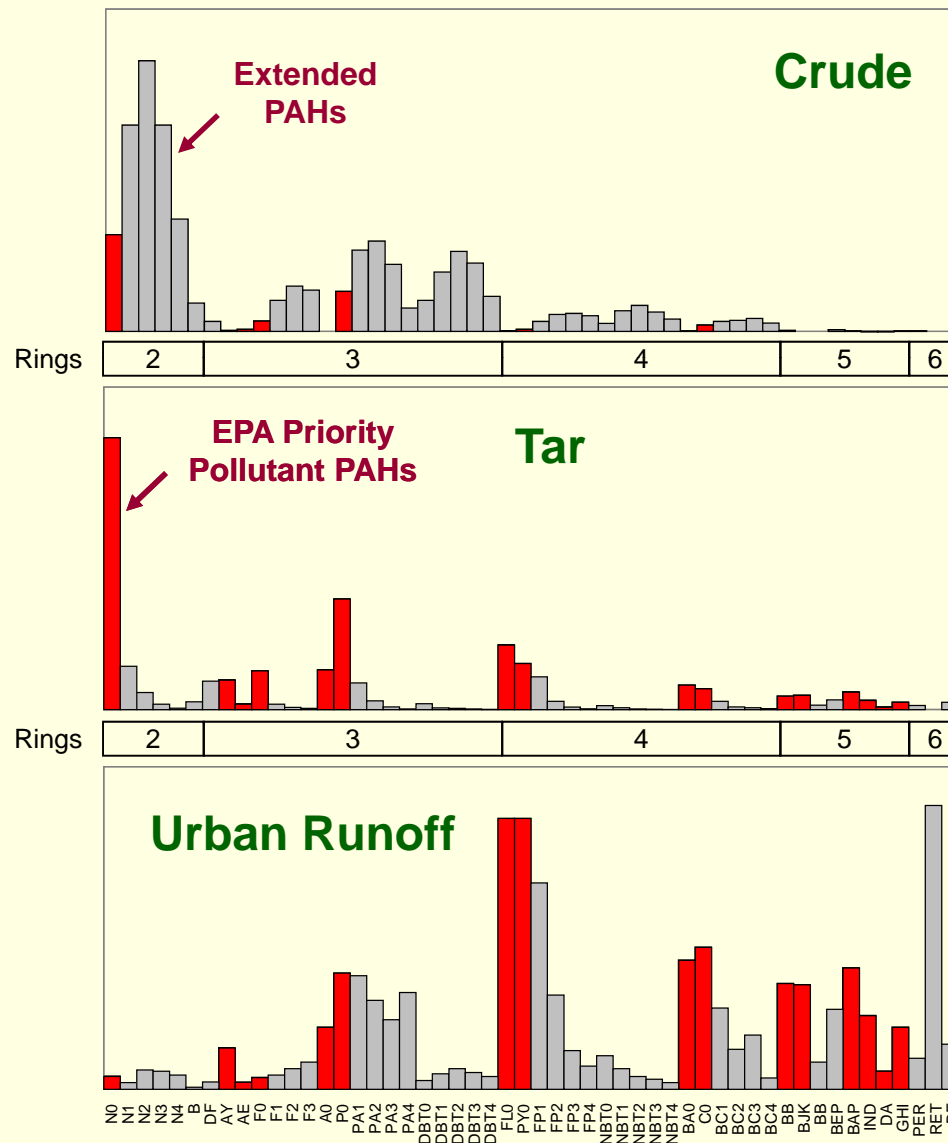
- Alkyl > Parent
- Little 4 to 6 Ring

Pyrogenic I

- Alkyl < Parent
- High 2 and 3 Ring

Pyrogenic II

- Alkyl < Parent
- High 4 to 6 Ring



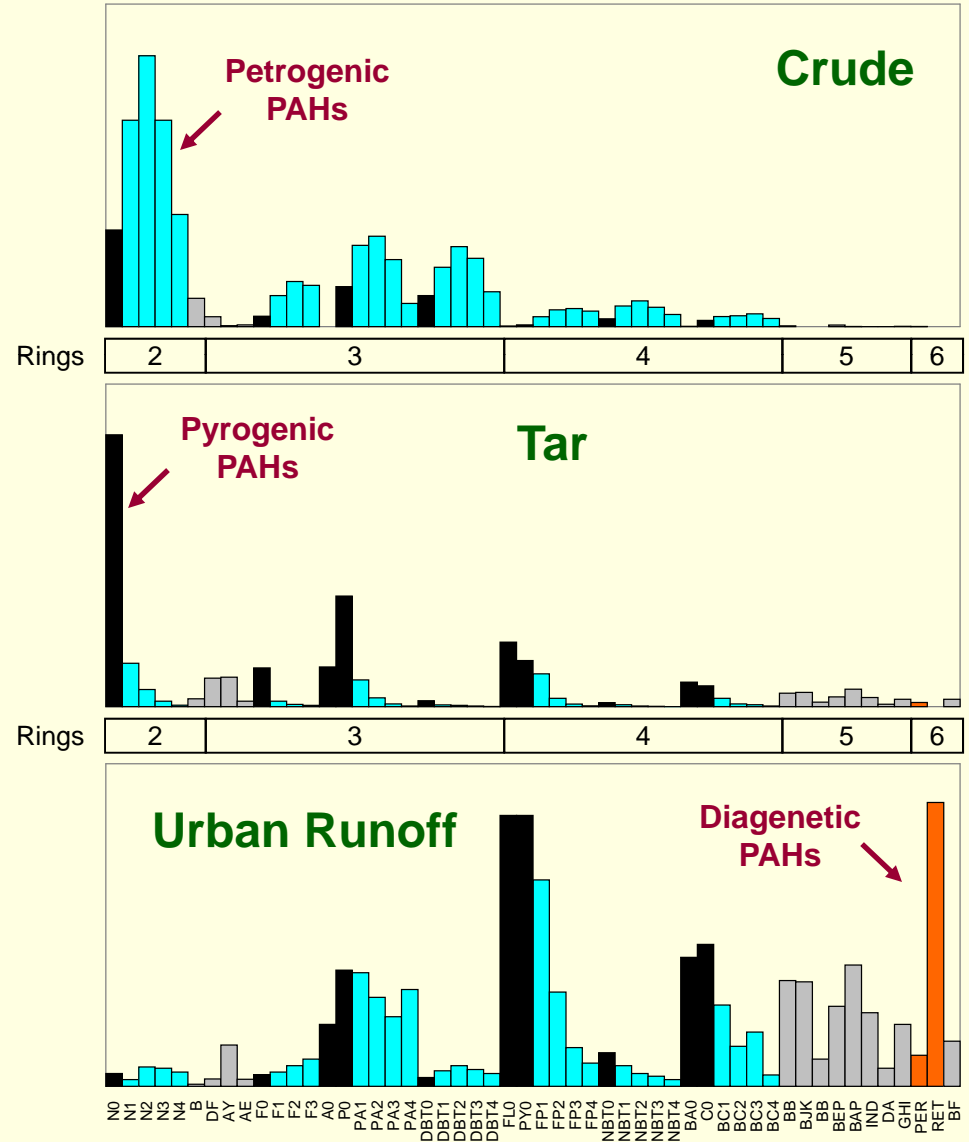
Petrogenic v Pyrogenic

Ratio

$$\frac{\text{Petrogenic}}{\text{Pyrogenic}} = 8.2$$

$$\frac{\text{Petrogenic}}{\text{Pyrogenic}} = 0.3$$

$$\frac{\text{Petrogenic}}{\text{Pyrogenic}} = 1.1$$



Environmental Forensics: Technical Approach for Hydrocarbons

Sample Collection

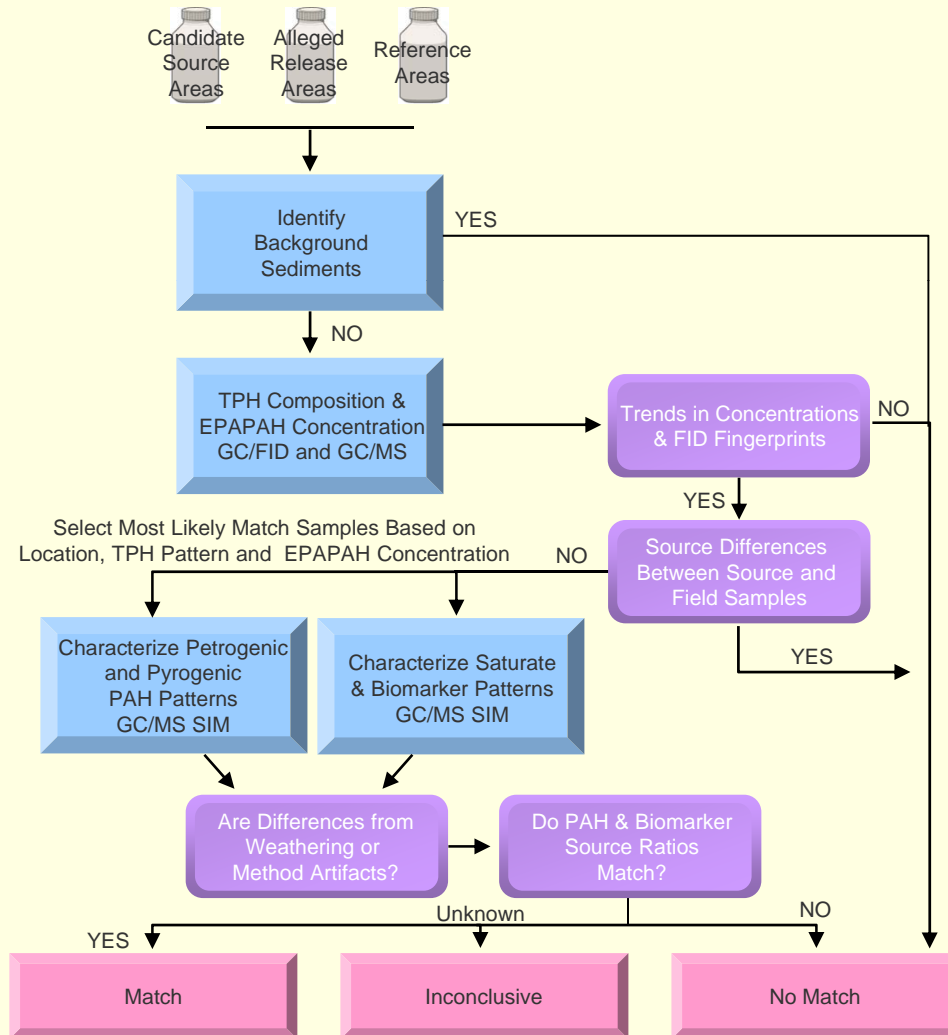
Tier 1

Tier 2

Tier 3

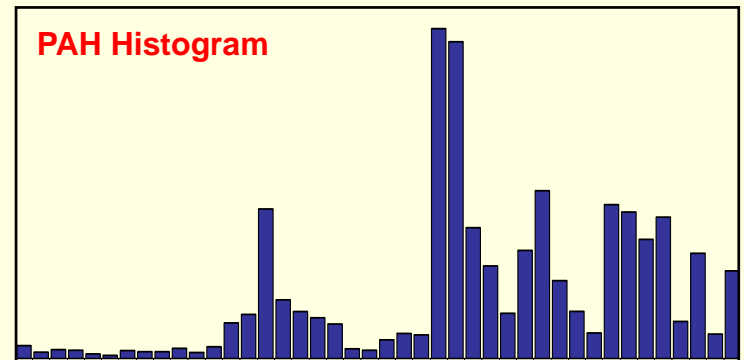
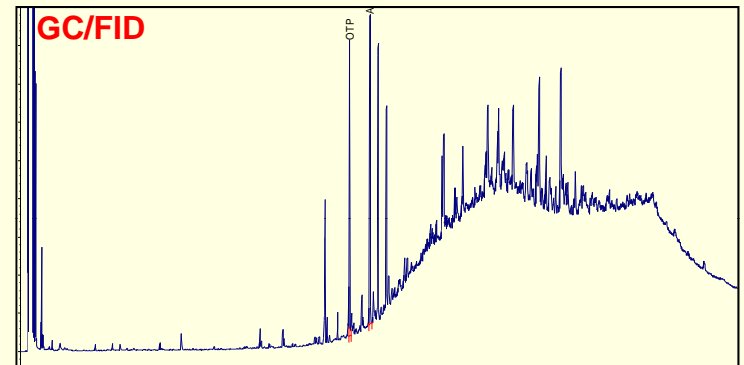
Conclusion

NEWFIELDS



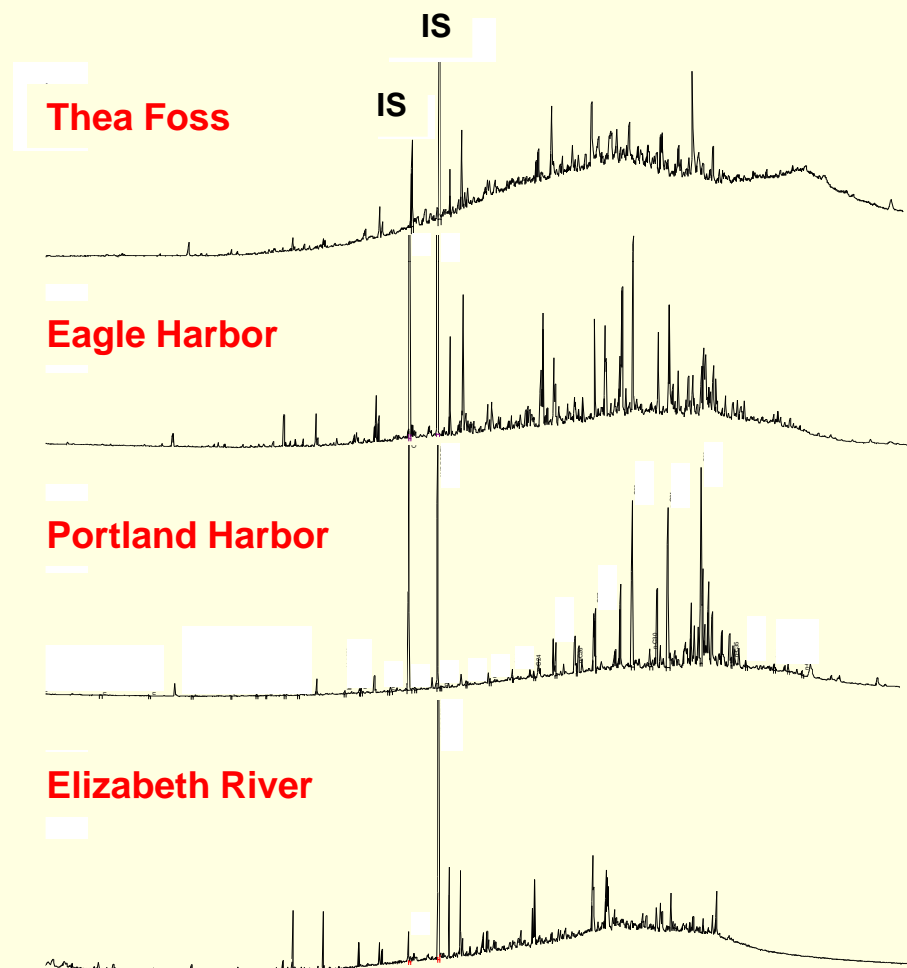
Coastal Background Sediments: National Survey

- 0-10 cm depth composites
- Analytical Methods (EPA SW-846)
 - Sediment Extraction (EPA 3550)
 - Remove Polars (EPA 3611)
 - Remove Sulfur (EPA 3660)
 - GC/FID (EPA 8015M)
 - Total extractable hydrocarbons (C₈-C₄₄ THC)
 - High-resolution 'fingerprints' (90 minute run)
 - GC/MS/SIM (EPA 8270M)
 - 43 PAH analytes (2-6 rings) for most datasets
 - Selected C₀-C₄ alkylated PAH groups (2-4 rings)



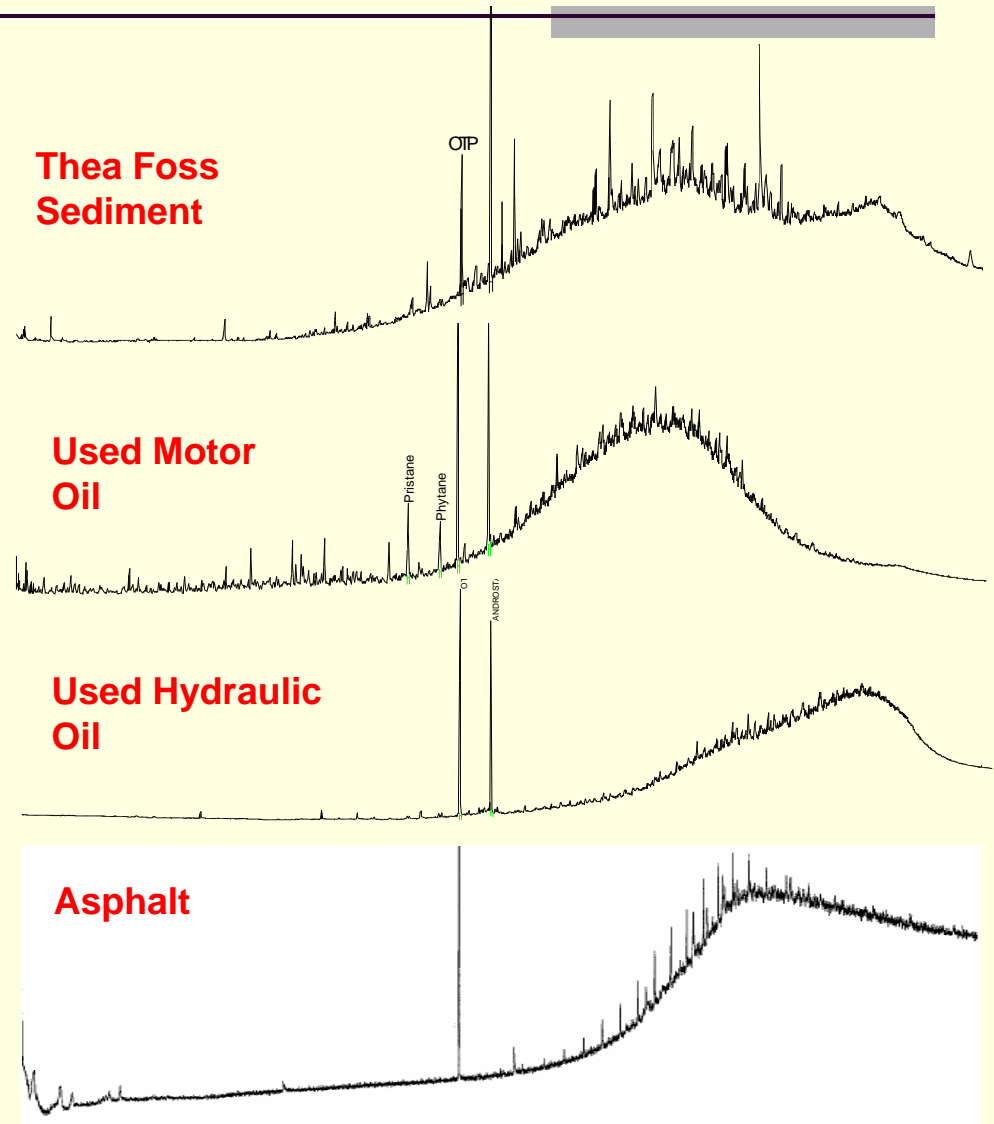
Chromatographic Character of THC

- Overall similar fingerprint of THC in sediments from different urban waterways
- Three predominant features
 - Unresolved complex mixture (UCM) - RRO
 - Resolved parent HPAH
 - Biogenic HC's sometimes evident

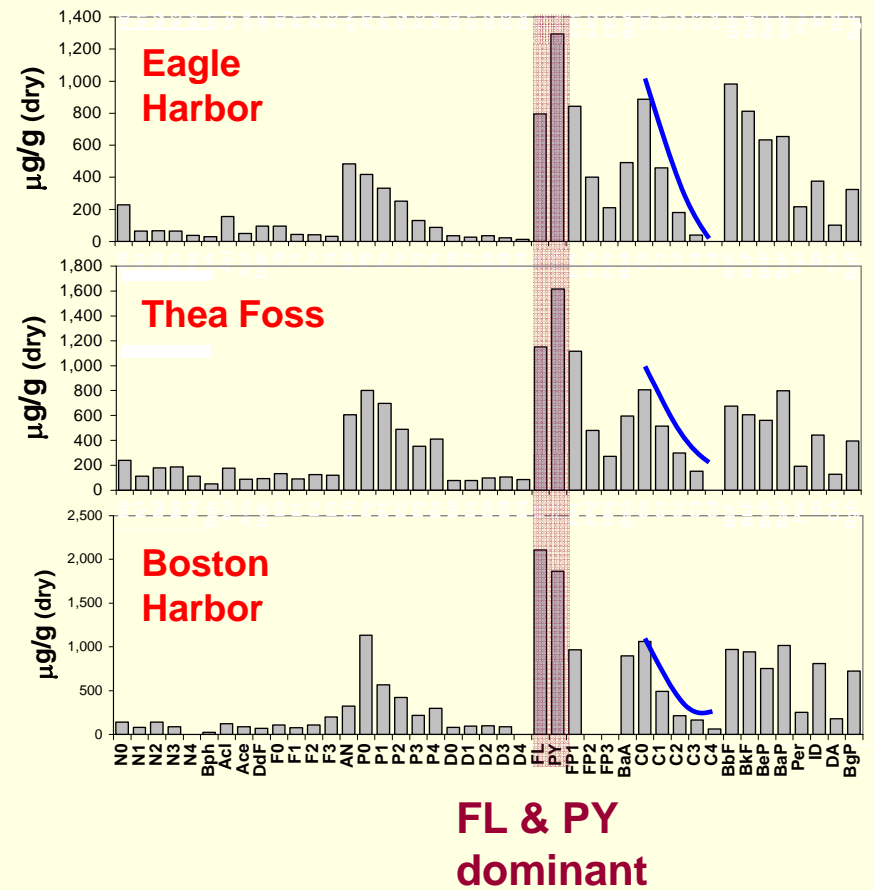
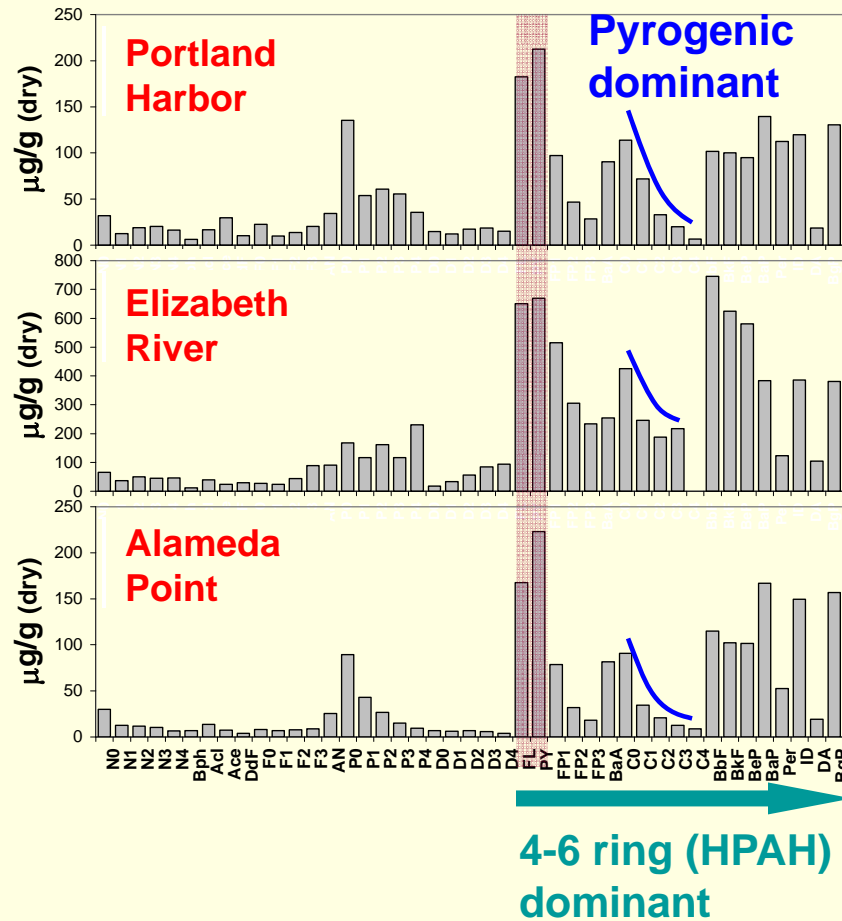


Predominant Contributors to THC

- UCM largely attributable to residual range petroleum products found in urban runoff
- UCM comprises the most significant mass of extractable HC's

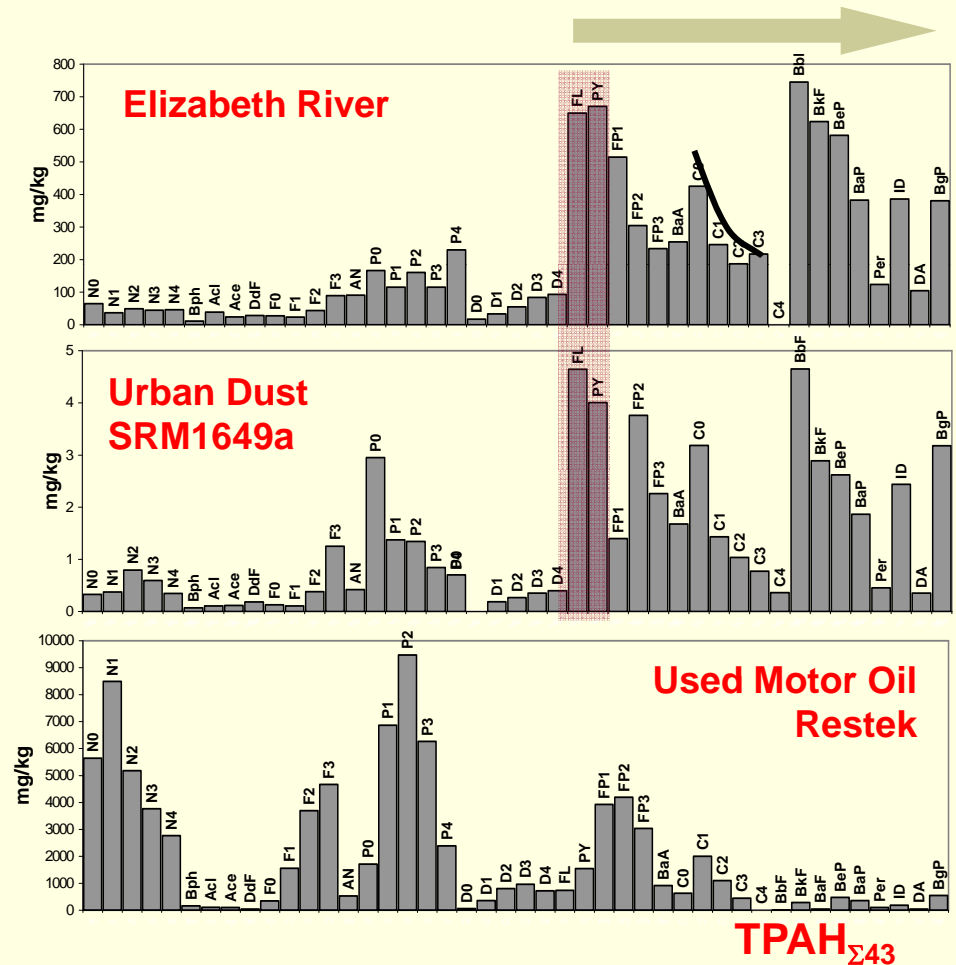


Typical Distributions of PAHs



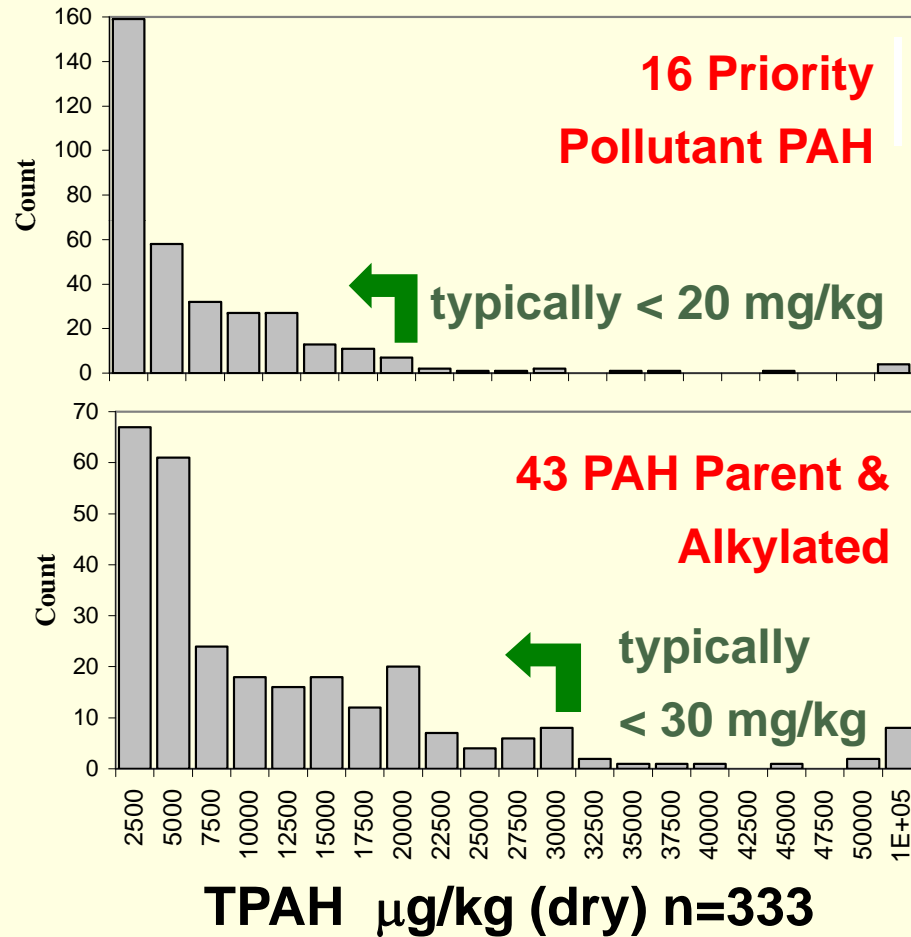
Typical Contributors to PAH

- PAH fingerprint generally consistent with urban dust (soot)
 - soot variability is unknown but likely to vary with local source(s)
- Residual petroleum contribution appears limited

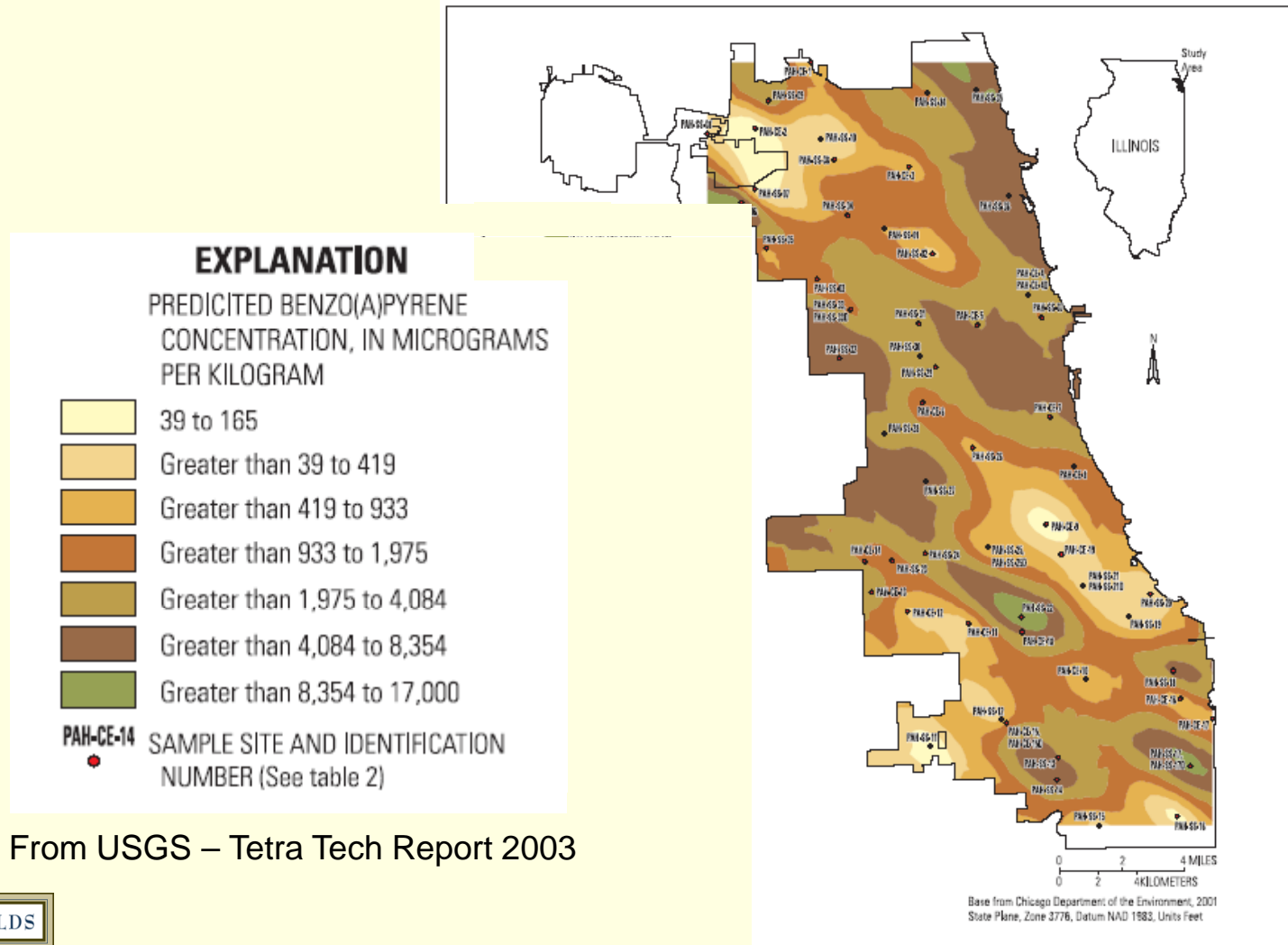


Urban Background - Sediment PAHs -

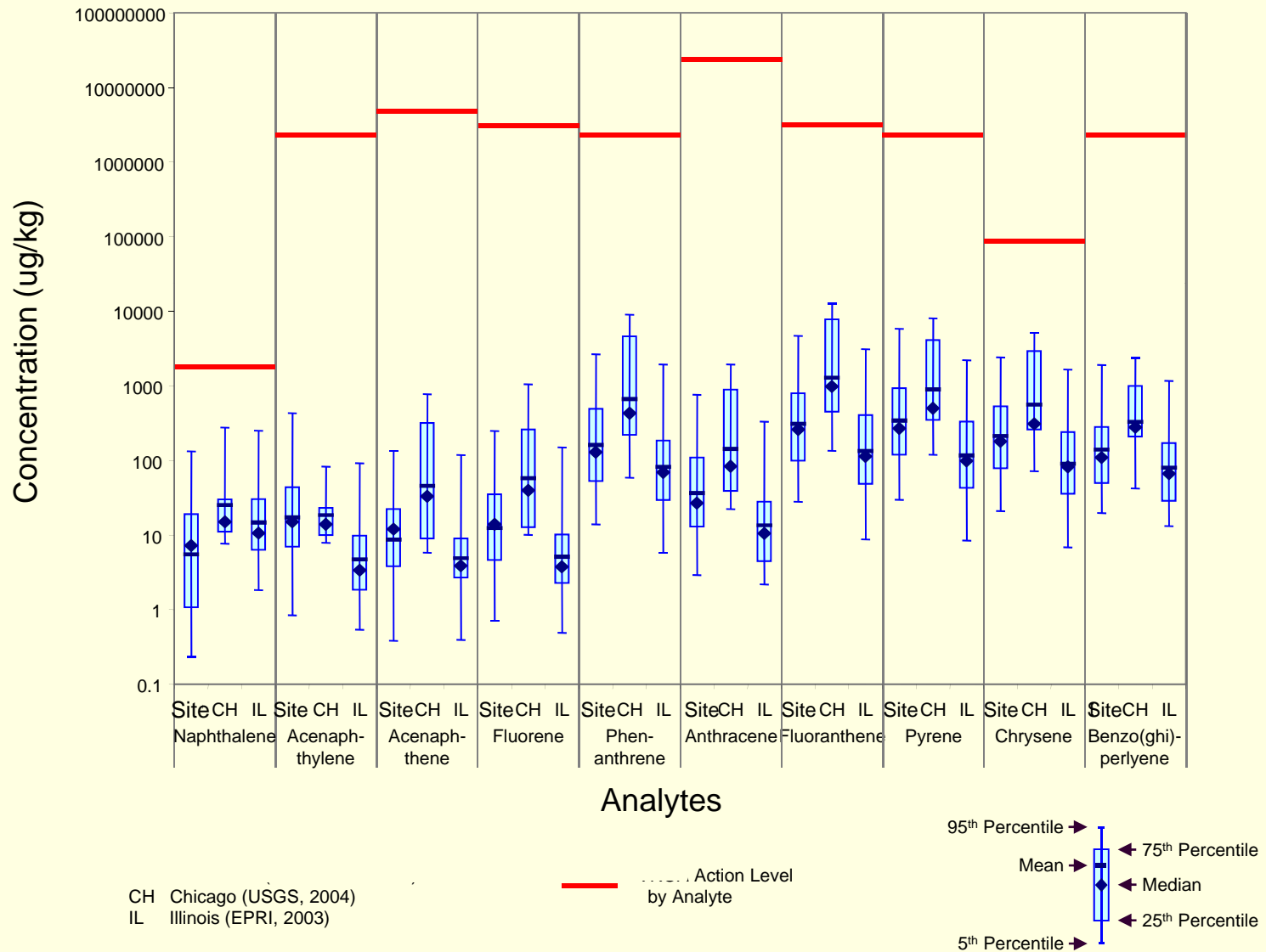
- **Priority Pollutant**
 - median: 3.1 mg/kg
 - 25-75th: 0.9-8.4 mg/kg
 - 10-90th: 0.2-14.9 mg/kg
- **43 PAHs**
 - median: 6.4 mg/kg
 - 25-75th: 2.8-16.1 mg/kg
- **Percent 43 PAH as PP PAH**
 - median: 66%
 - mean: 65 +/- 6.7%



Urban Background - Soil PAHs -

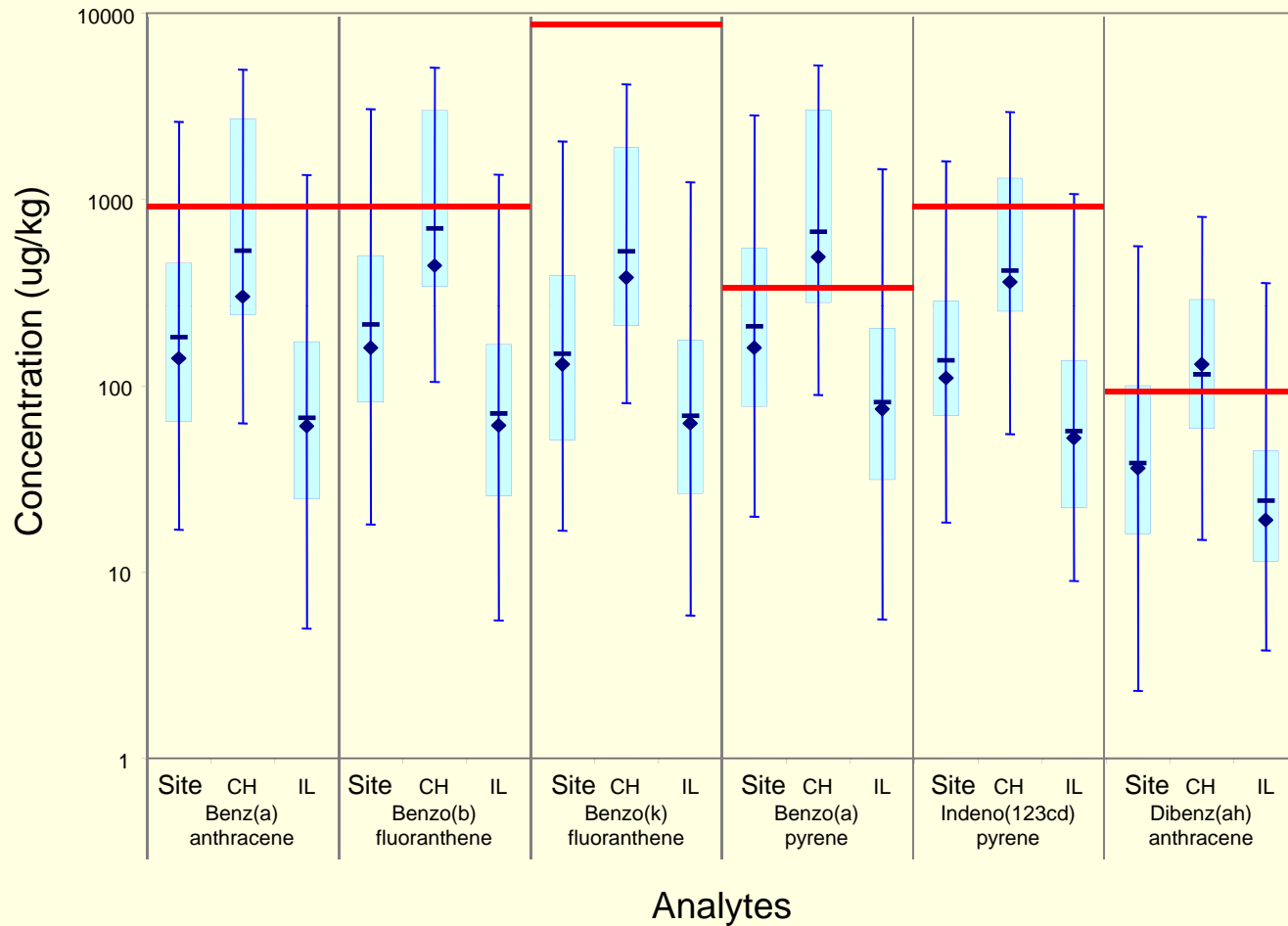


Urban Background - Soil PAHs -



“IL” Data Source: EPRI (2003) “PAHs in Surface Soils in Illinois”
“CH” Data Source: USGS Water Resources Investigation Report 03-4105

Urban Background - Soil PAHs -



BP Barrie Park (Utilities Database)
 CC Cooks County (USGS, 2004)
 IL Illinois (EPRI, 2003)

— VROA Action Level
 by Analyte

95th Percentile →
 ← 75th Percentile
 Mean →
 ← Median
 ← 25th Percentile
 5th Percentile →

“IL” Data Source: EPRI (2003) “PAHs in Surface Soils in Illinois”
 “CH” Data Source: USGS Water Resources Investigation Report 03-4105

Background PAH Origins

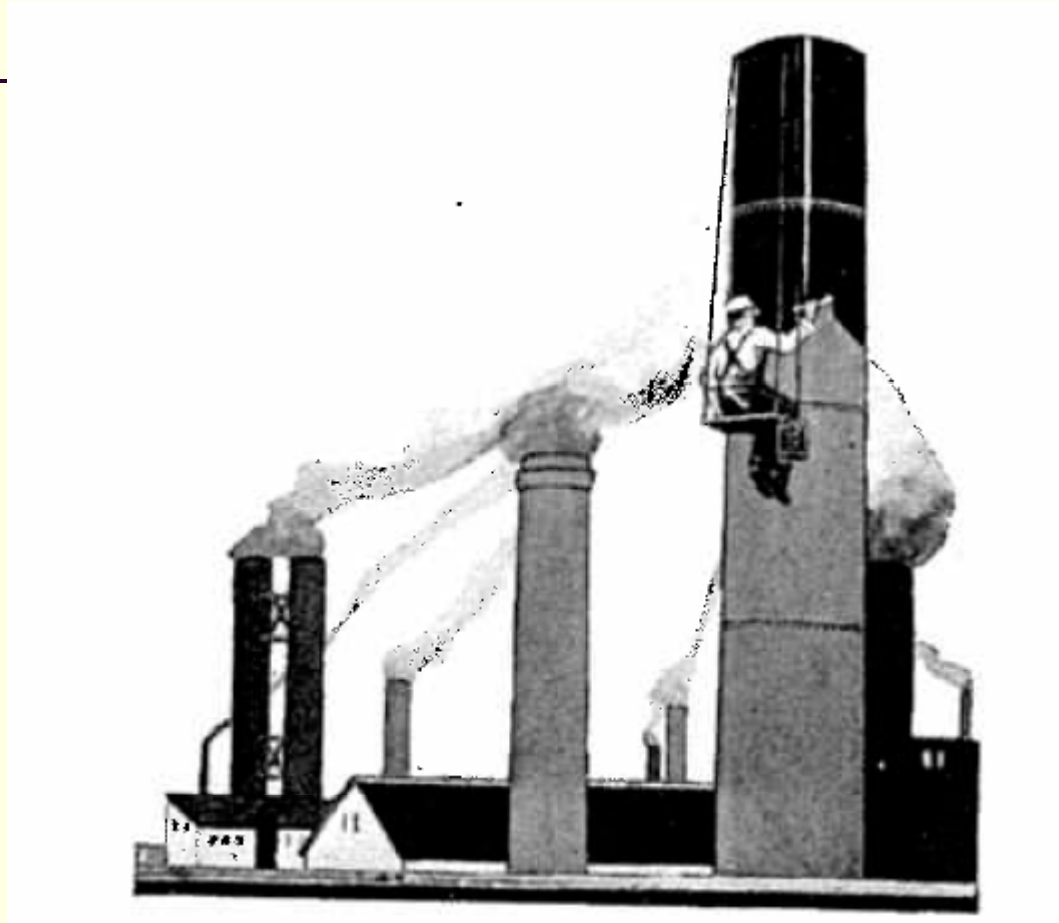
- Paints -

- Resists Acid and Alkaline Solutions
- Prevents Rust on Metals
- Contains Pitch
- Many Applications
 - Wood
 - Masonry
 - Metal



Background PAH Origins

- Paints -

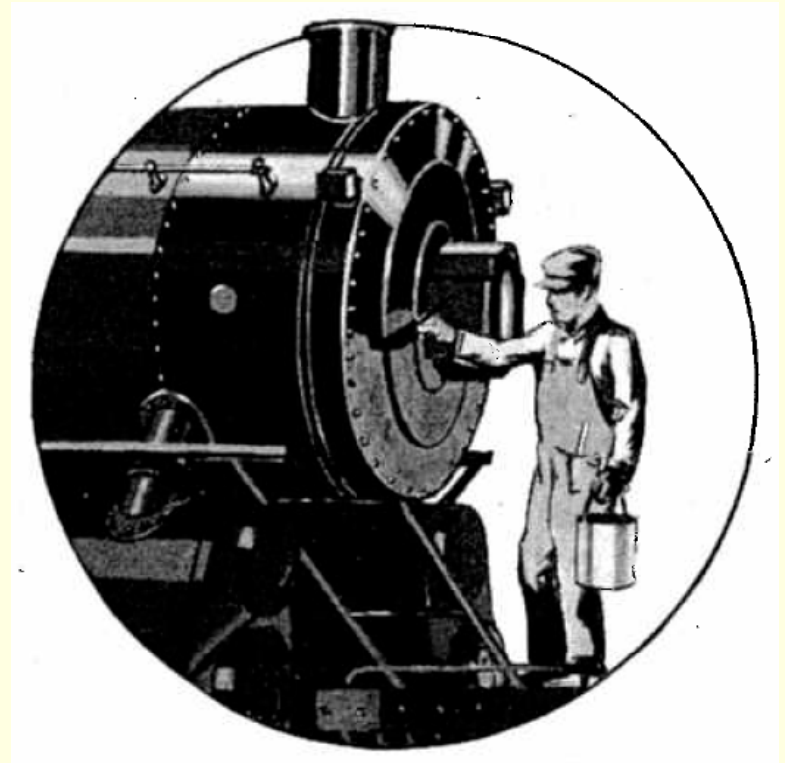


“Everjet Paint Proves its Value by Reducing Repair and Replacement Costs Around Factories.”

Background PAH Origins

- Heavy Equipment -

- Industrial Coatings
- Pitch Based
- Primary Applications
 - Metal
- Resists Degradation
 - Acids
 - Bases
 - Oxidations (Rust)



Background PAH Origins

- Roofs -

- Roofing Materials
- Drains
- Exposed Equipment
- House Insulation
- Freight Cars

- *Full Tar Saturation*
 - *Weather Seal*
 - *Wind Seal*



Background PAH Origins

- Applied as Liquids or Rolls -



“The poured top coat of Spec Roof means just as much pitch on the surface As an ordinary built-up roof.”

Background PAH Origins

- Specialized Roof Products -

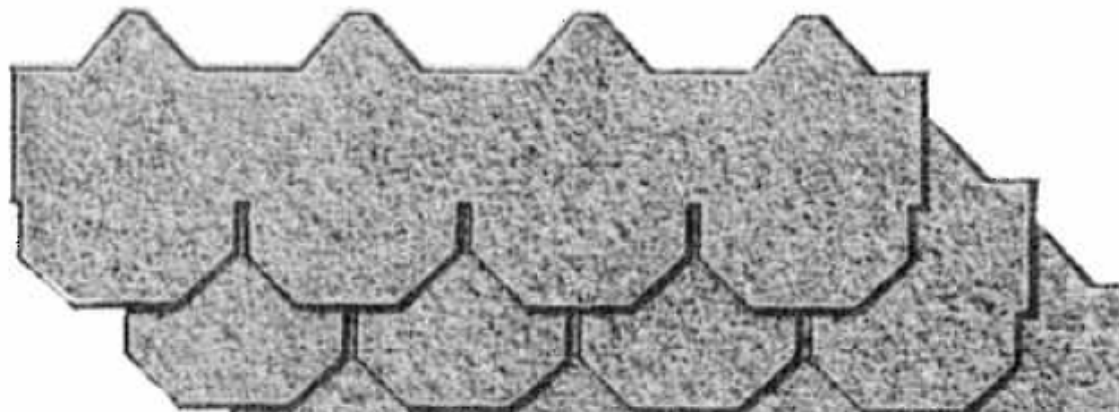
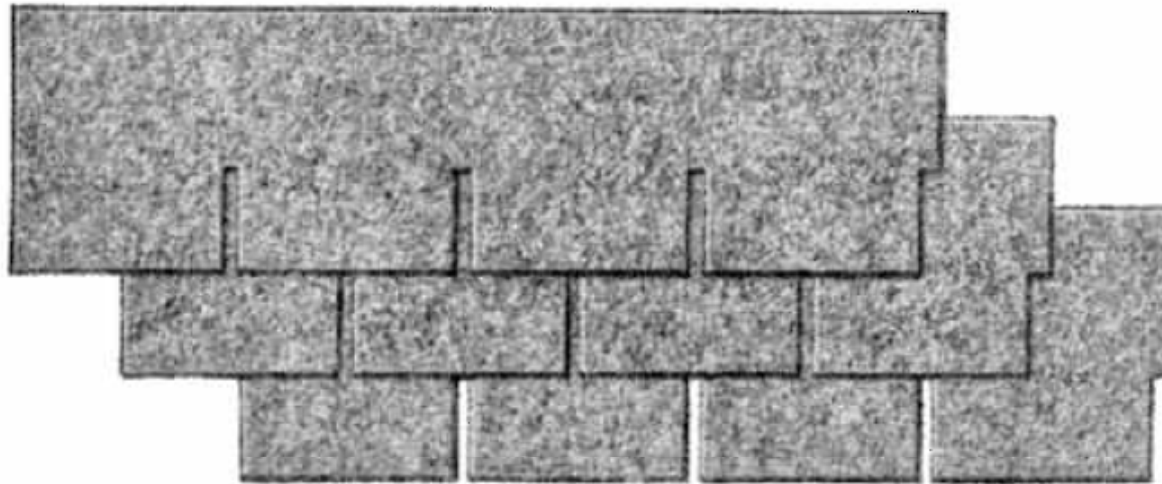
New Roof Decks



Re-Roofing Over
Old Wood Shingles

Background PAH Origins

- Roofs -



Background PAH Origins

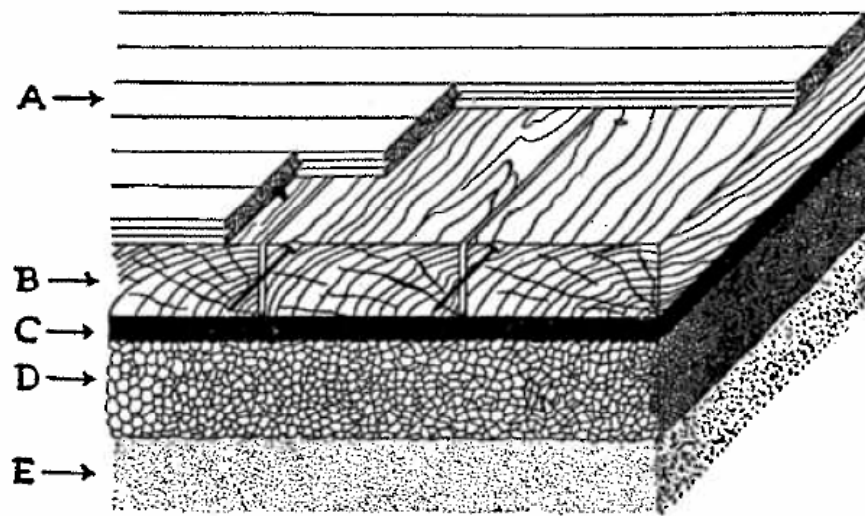
- Floors -



Installing damp-proof course Tar-Rok
First Floor, St. Joseph's School
Cleveland, Ohio

Background PAH Origins

- Floors -



TAR-ROK SUB-FLOOR OVER EARTH

- A—1" hardwood*
- B—3" Carbosoted plank*
- C—1" Tar-Rok damp-proof course*
- D—4" Tar-Rok base*
- E—Earth*

APPLICATION

Where floors are applied over earth, No. 5 Tar is mixed with crushed stone and spread to a thickness of 4". No. 7 Tar is mixed with sand and spread to a thickness of 1". Where concrete foundation is provided, just the sand cushion is used. Heavy plank is set in sand cushion and finished flooring applied over it. Specification covering complete operations furnished on request.

Background PAH Origins

- Tar Distillates -

- Fence Posts
- Farm Buildings
- Silos
- Wooden Bridges
- Mill Rood Docks
- Mine Timbers
- Roadway Guard Rails
- Building Construction in Contact with Ground



Background PAH Origins

- Tar Distillates -



“Fence posts treated with Carbasota
do not rot or decay”

Background PAH Origins

- Solvents -

- Paint Thinner
- Standard Solvent
- *Light Coal Tar*



Background PAH Origins

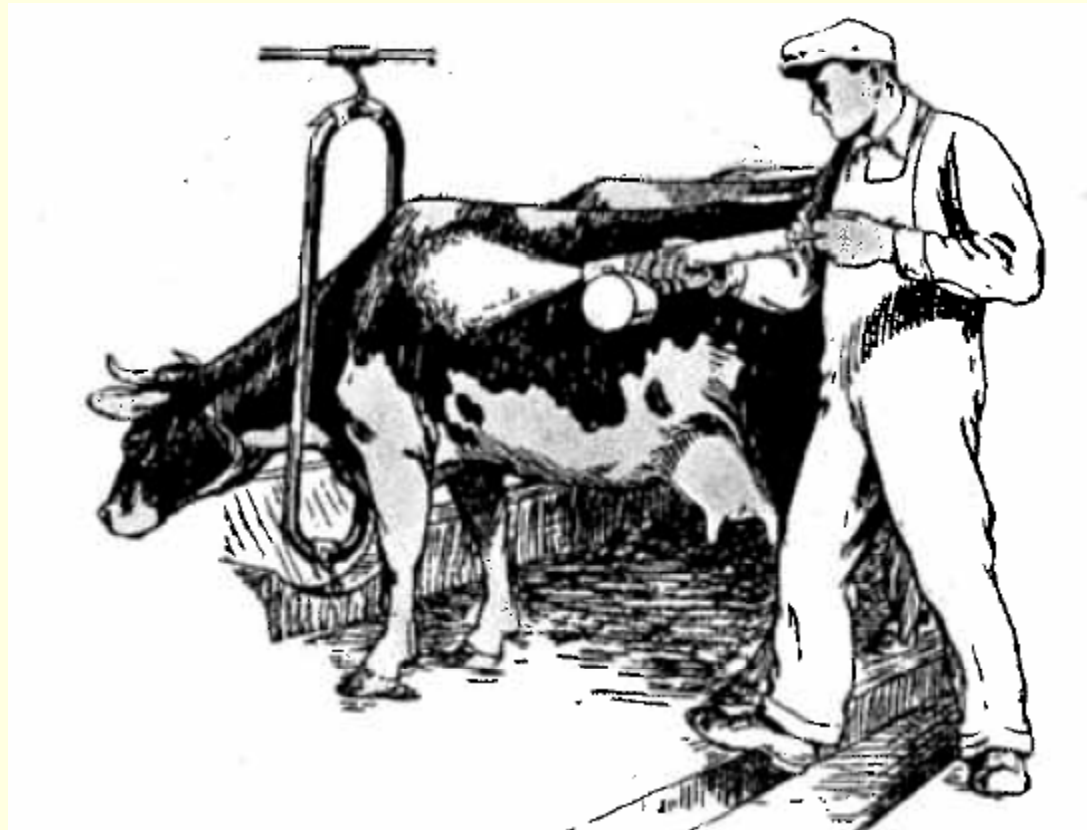
- Farms -



“Spray hen houses with Creonoid
to eliminate chicken mites.”

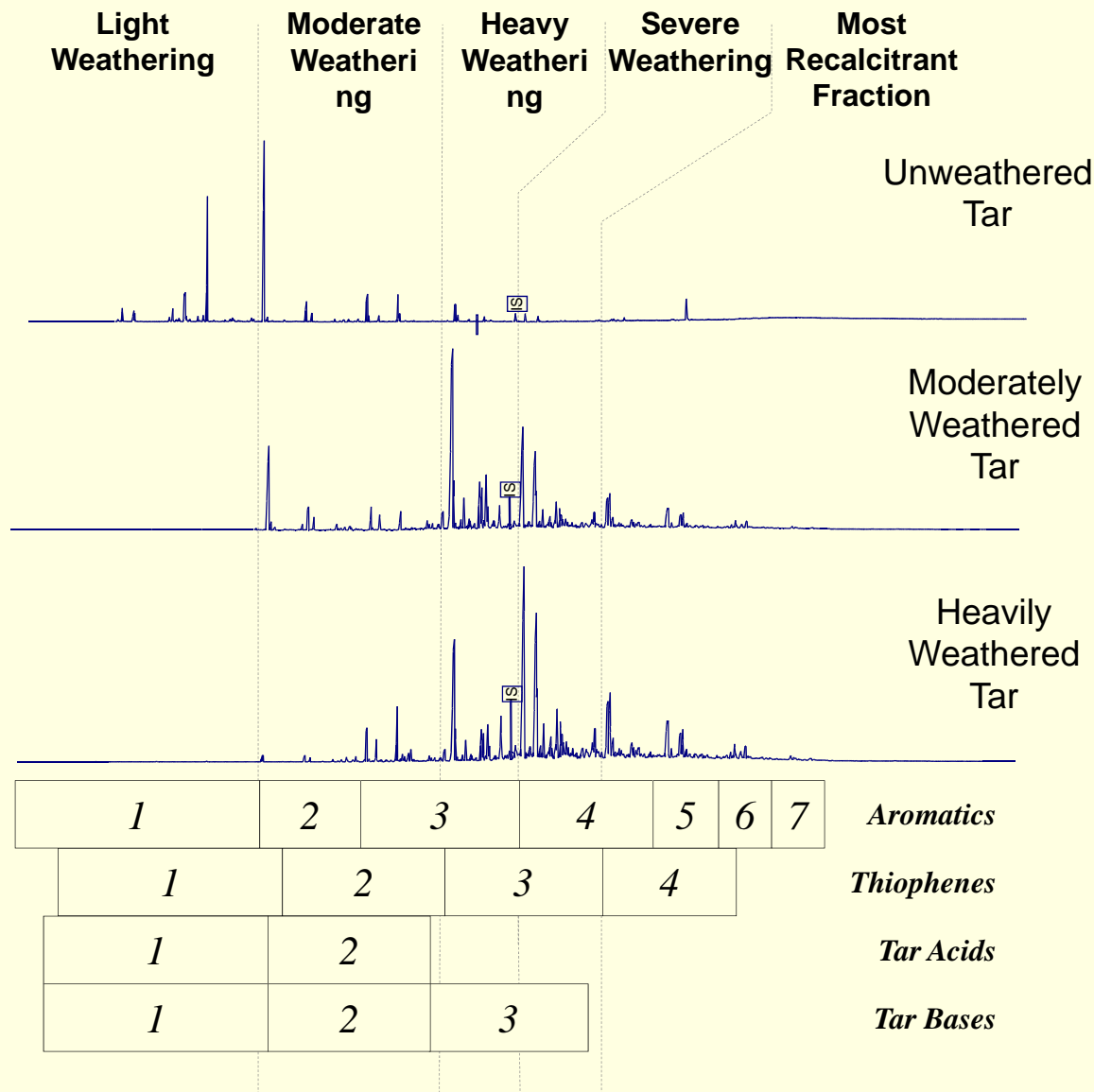
Background PAH Origins

- Farms -



The loss where Horn fly is abundant is considerable, showing reduced vitality, lack of growth, less milk production

After Weathering ... Tar Products can Appear Similar



Background PAH Origins - Heavy Oils -



Applying Tarvia Re-Tread

Background PAH Origins - Heavy Oils -



Applying Seal Coat

Background PAHs

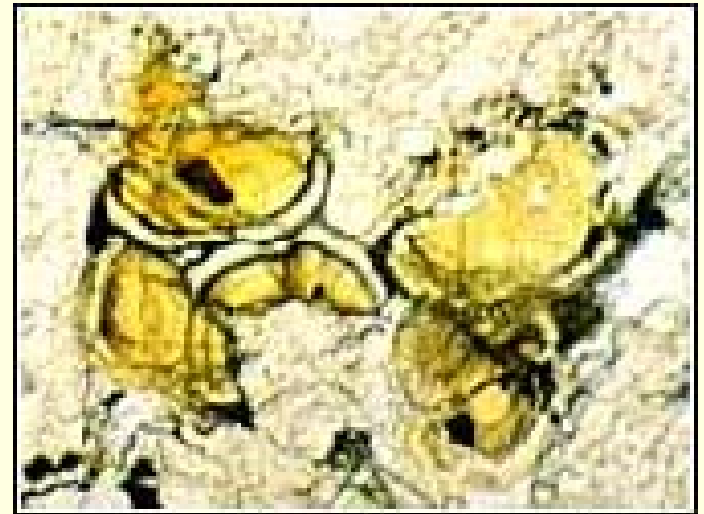
- Galactic ? ... Not a Far Out Idea -



Background PAH Origins

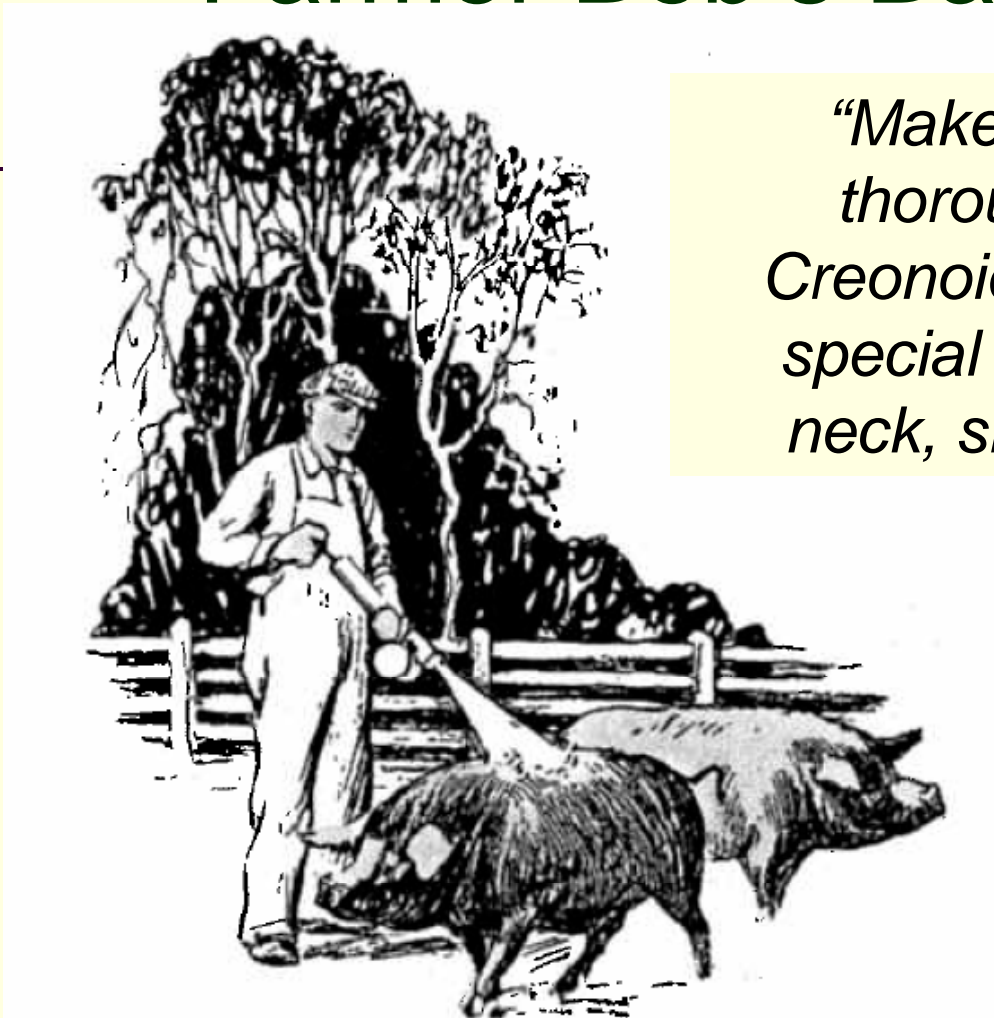
- Martian Meteor -

- Life in Space?
 - Dead microbes degrade into PAHs
 - Found PAHs near Carbonate Minerals
 - Fossilized Organics
- PAHs Exhibited a Unique Meteor Signature
 - Little Naphthalene



Potato Meteor (4.5 lb)
from Mars (ALH84001)

Farmer Bob's Barbeque?



“Make sure the animal is thoroughly sprayed with Creonoid to kill Hog Lice with special attention to the belly neck, shoulders and flank...”

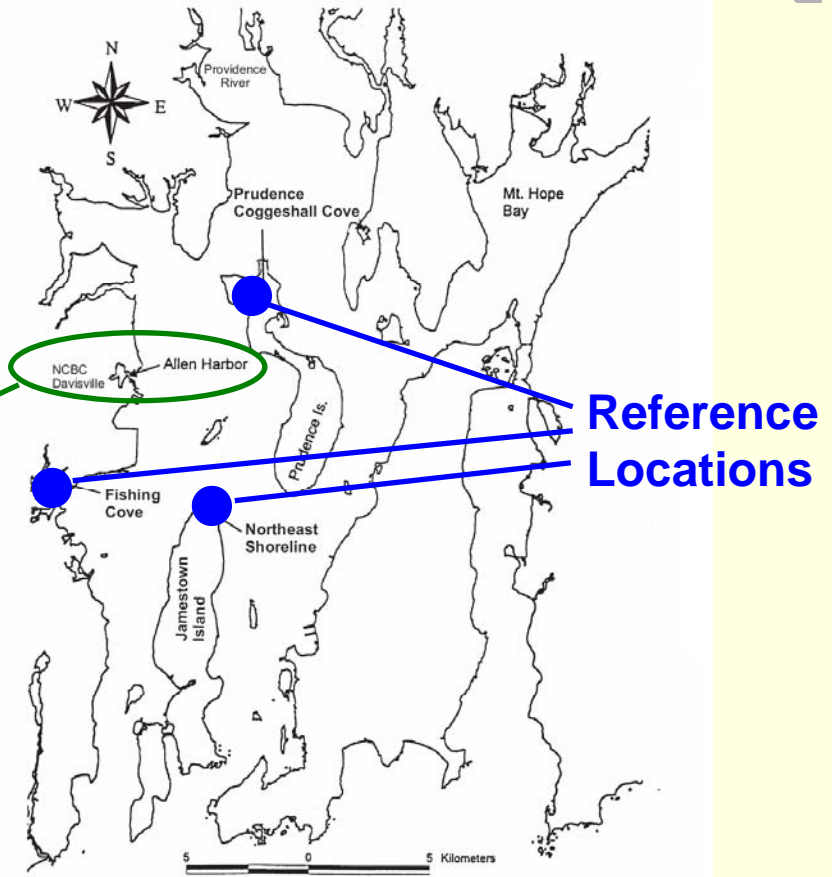
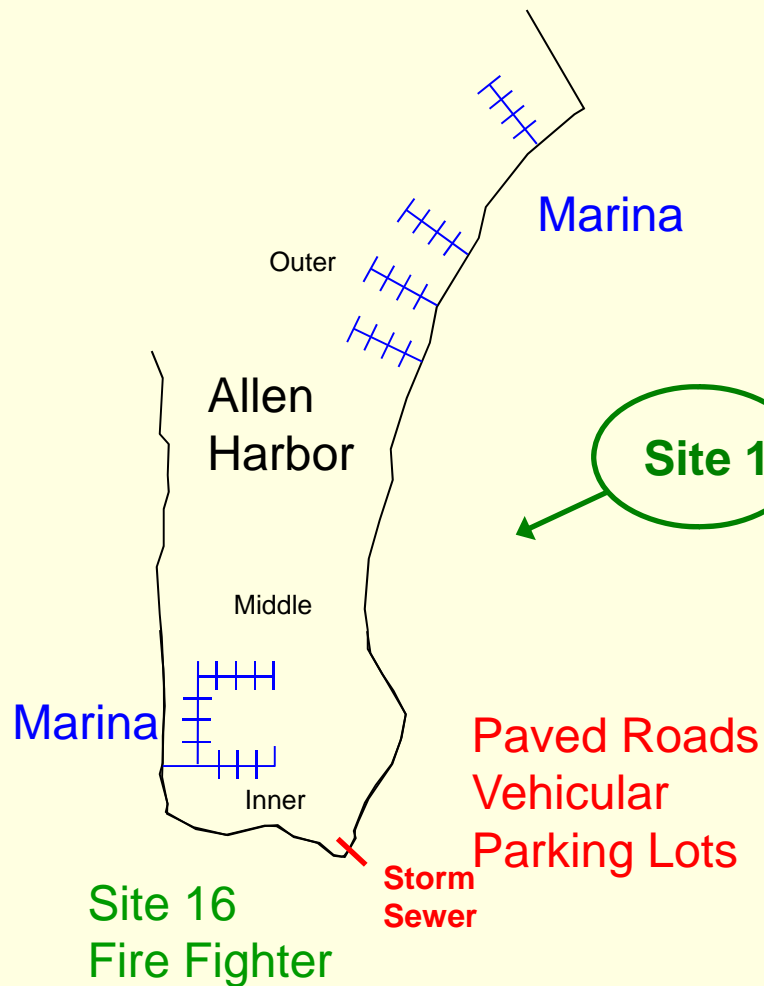
Also spray hog houses and pens thoroughly to kill lice that dropped off the animal.”

Hogs fatten more rapidly when protected against parasites

Hydrocarbons and PAHs: Site 16 - Fire Fighter Training Area

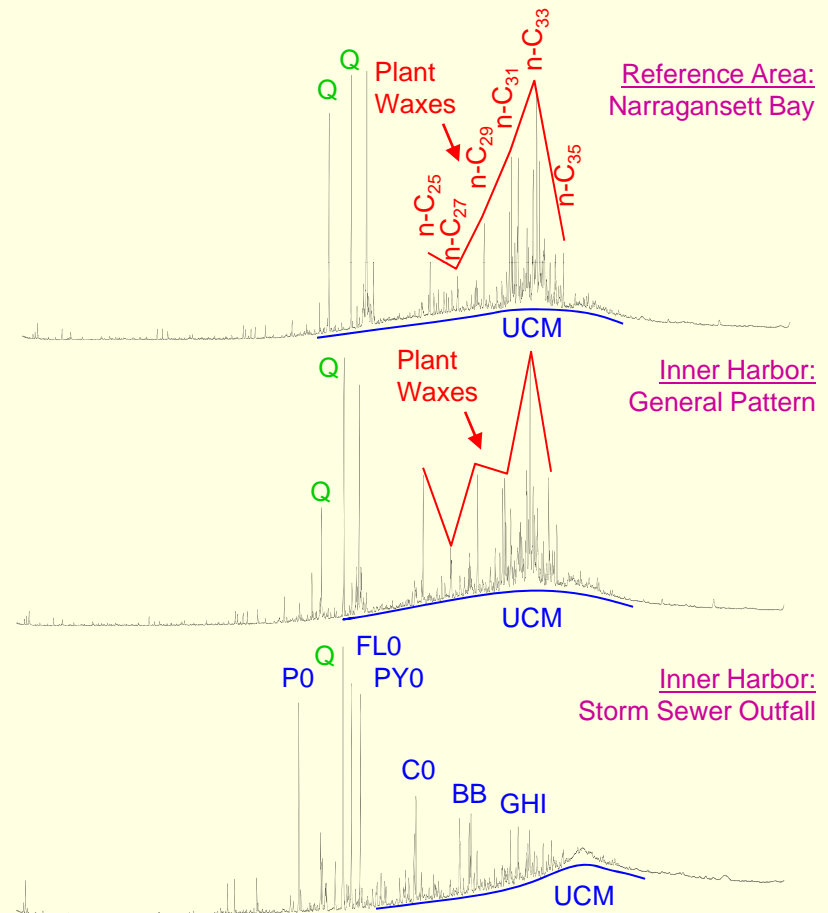
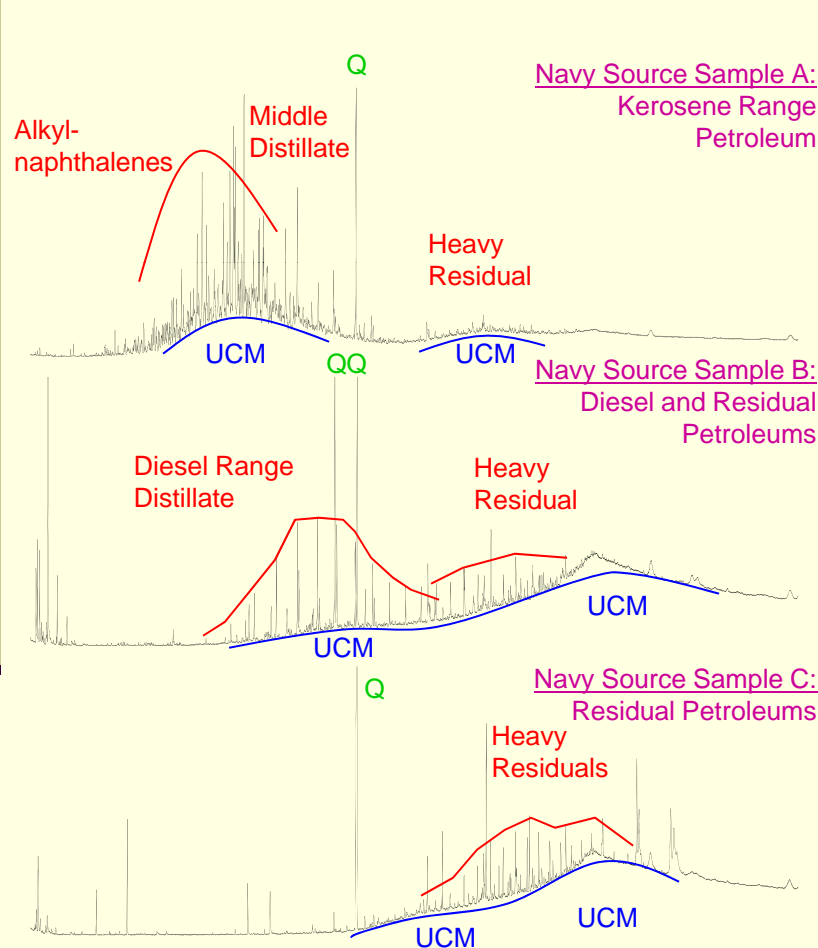
DoD-Environmental Monitoring and
Data Quality (EMDQ) Workshop
March 29, 2011

Case Study: Site 16 – North Kingstown, RI Fire Fighter Training Area & Sediment Impact Study



Case Study: Fire Fighter Training Area

High Resolution Hydrocarbon Fingerprinting (GC/FID)



Q Quality Control Compound
UCM Unresolved Complex Mixture

P0 Phenanthrene
A0 Anthracene

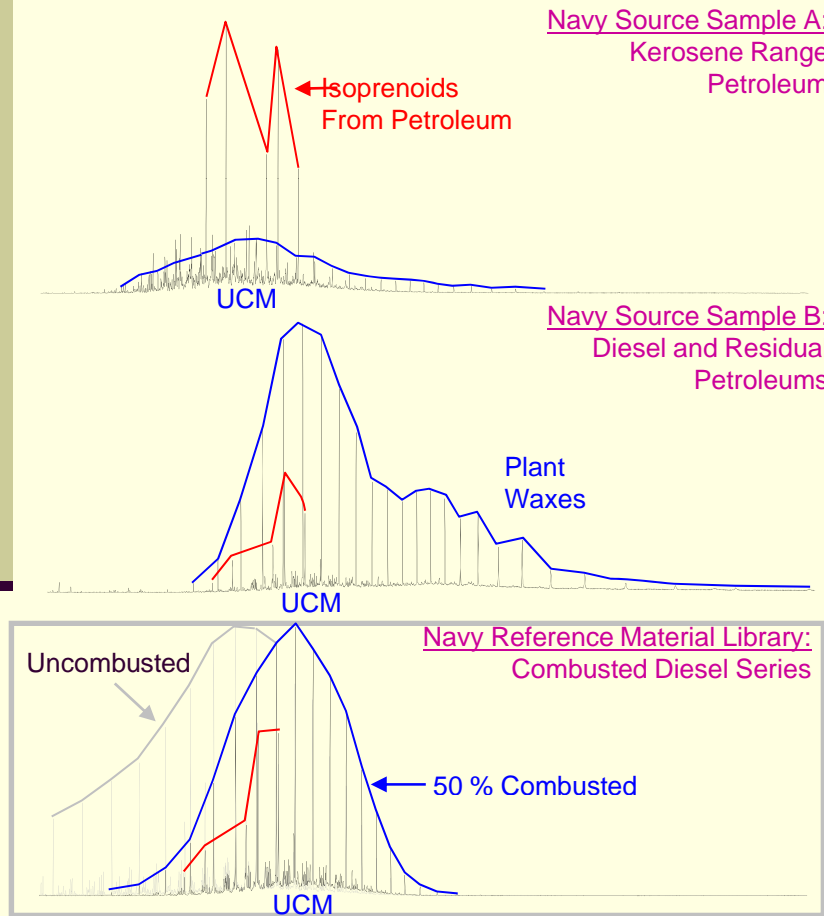
FL0 Fluoranthene
PY0 Pyrene

C0 Chrysene
BB Benzo(b)fluoranthene

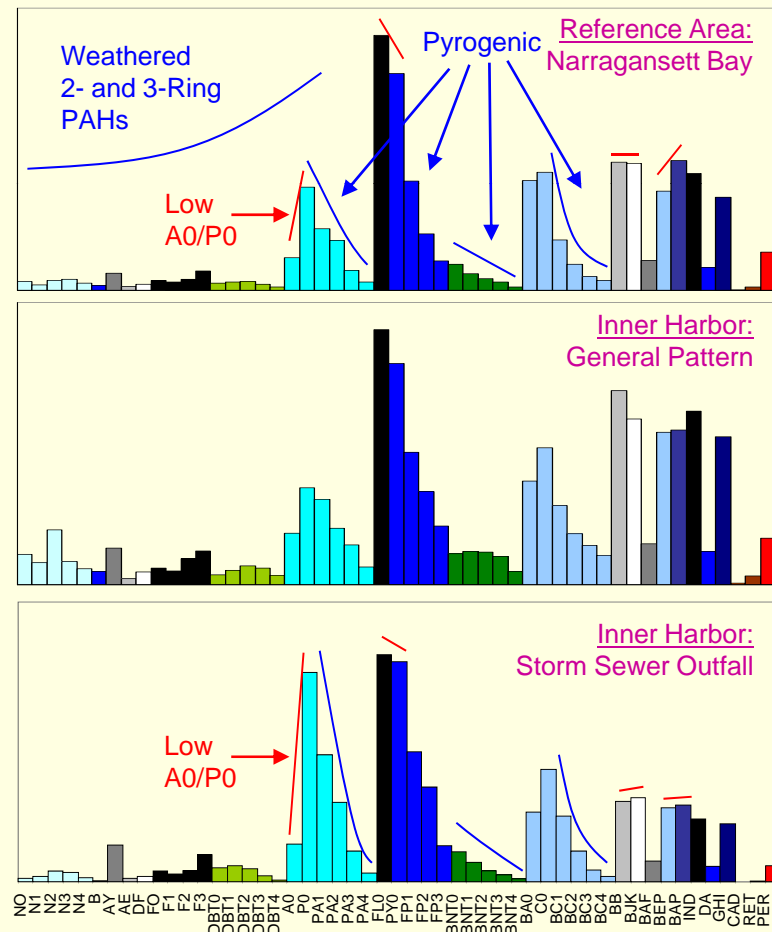
GHI Benzo(ghi)perylene

Case Study: Fire Fighter Training Area Advanced Confirmatory Analyses

Saturates

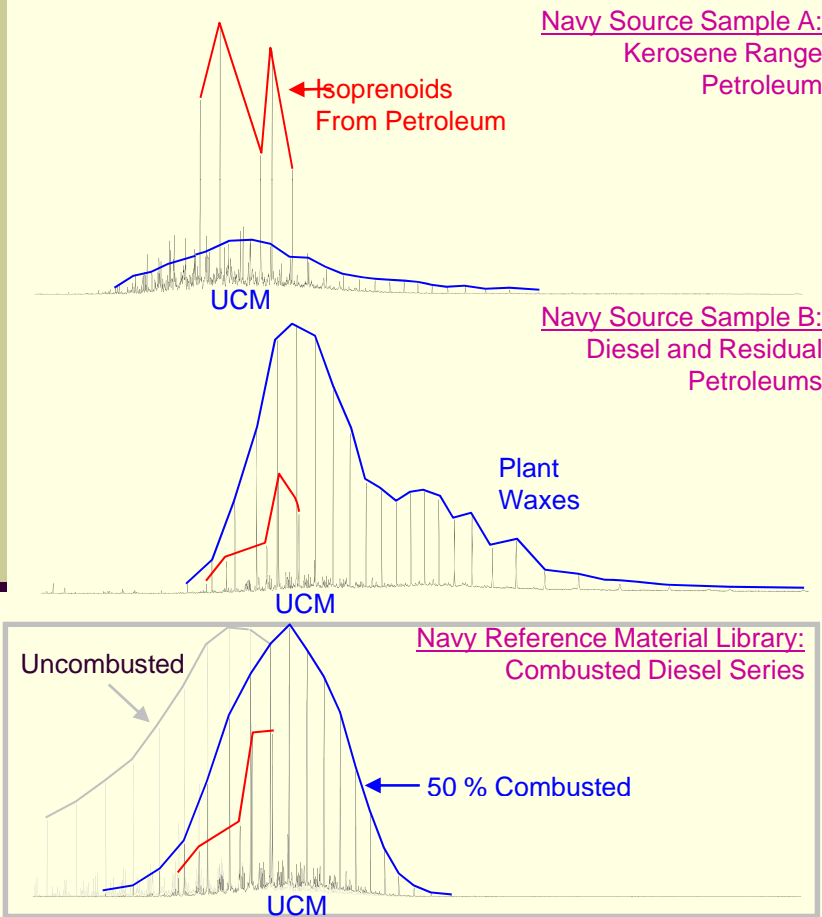


Alkylated PAHs

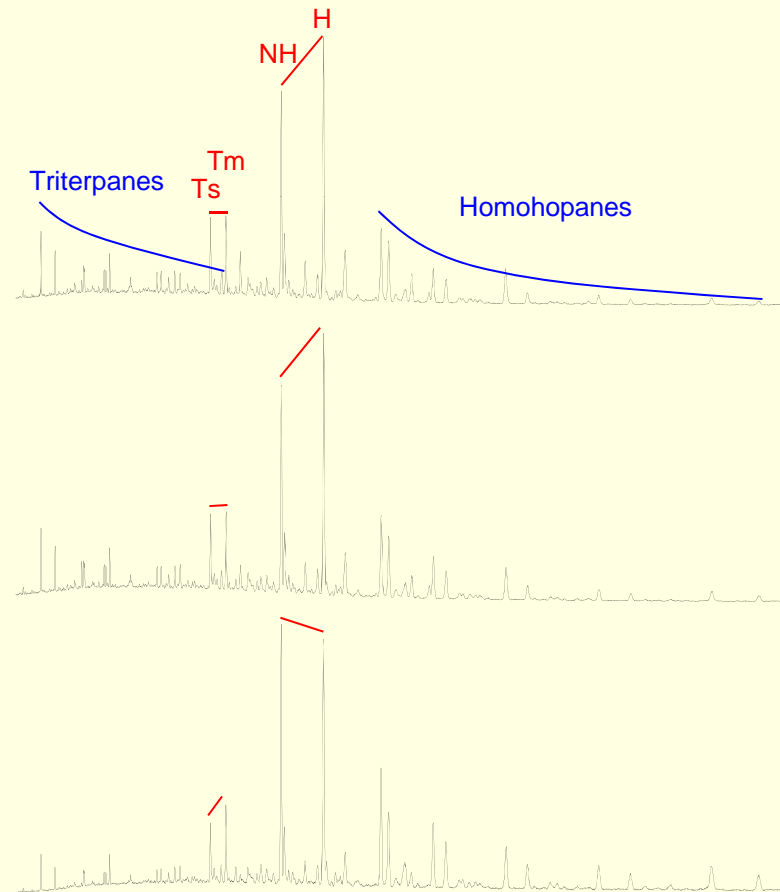


Case Study: Fire Fighter Training Area Advanced Confirmatory Analyses

Saturates



Biomarkers



Case Study: Fire Fighter Training Area

Conclusions

- Navy Used Multiple Petroleum Types at Site 16
 - Kerosene
 - Diesel (~50% Combusted from Library)
 - Crude or Bunker C
- Heavy Petroleum Matched Background
 - Reference Areas
 - Storm Sewers
- PAH Patterns Matched non-Site 16 Sources
 - Background Reference Areas
 - Marina Pilings
- Current Status of Findings
 - Accepted by Navy
 - Under review by regulators

Take Away

- Multiple Lines of Evidence

- Concentration
- Composition

- Forensic Methods

- EPA Method Enhancements
- Broad Applications
- Multimedia
(Air, Soil, Sediment, Water, Tissue)

- Applications

- On-Site vs. Off-Site vs. Background/Fill
- Allocate Commingled Plumes
- Natural Attenuation

