Analyzing PCBs in Source Materials and Environmental Media: Soil, Water and Air

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Agenda

- Background Information
- Analytical Methodology
- Options for Analytical Support
- Media and Methods
- Building Materials
- TSCA, MCP, CT RCP, & NY considerations
- Conclusion

Background on PCBs

Aroclors

Homolog

Congener

Total PCB

Aroclors

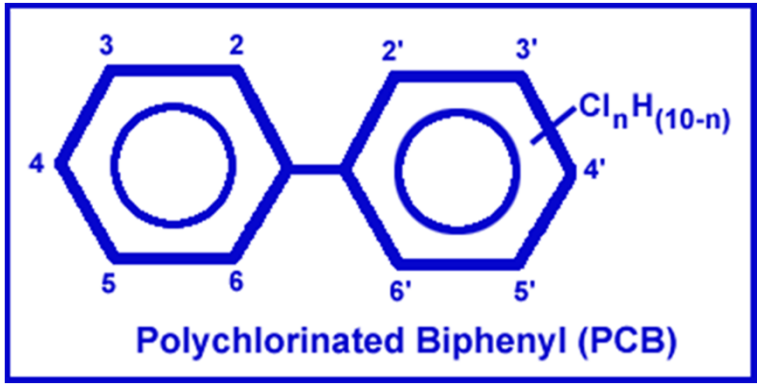
- PCBs were produced as mixtures of PCB Congeners and various impurities under a variety of trade names.
- Aroclors are technical grade mixtures that are identified by the 4 digit numbering code in which the last two digits indicate the chlorine content by weight percent (except for Aroclor 1016).

Aroclor Designation	**Chlorination % Level**	**US Production**
Aroclor 1016	41%	12.88%
Aroclor 1221	21%	0.96%
Aroclor 1232	32%	0.24%
Aroclor 1242	42%	51.76%
Aroclor 1248	48%	6.67%
Aroclor 1254	54%	15.73%
Aroclor 1260	60%	10.61%
Aroclor 1262	62%	0.83%
Aroclor 1268	68%	0.33%

Source: Brown EST 28(13):2295-2305 1994

Congener

- Each PCB molecule contains 1 to 10 chlorine atoms attached to a biphenyl structure, allowing for 209 possible arrangements.
- Each of these **209** arrangements is called a congener.



- Examples of PCB Congener

2,2'dichlorobiphenyl

2,2',3,3',4,4'5,5'6,6' Decachlorobiphenyl

Congeners

- Many researchers have found that the full chemical names of these PCB congeners unwieldy. Therefore they have developed multiple shorthand nomenclature.
- BZ Numbers - Ballschmitter & Zell is the original shorthand system which has been modified numerous times since its appeared in 1983.

For Example: **Congener**	**BZ/ IUPAC**	
2-MoCB	BZ 1	PCB 1
2,2',3,3',4,4'5,5'6,6' DeCB	BZ 209	PCB 209

- IUPAC Numbers do not exist as a unique set. Corrections to the BZ system, when rooted in IUPAC rules for numbering substitutions, have been incorrectly labeled as IUPAC Numbers.
- **There is no authoritative shorthand for congeners. All existing list reflect a snapshot in time.** Recommendation is to select structures alone or Chemical Abstract Service (CAS) Registry numbers.

Homolog

- When PCBs are subdivided by degree of chlorination the term homolog (or homologue) is used.
- There are 10 homologs.

Homolog		**Number of Chlorines**
Monochlorobiphenyl	MCB	One Chlorine
Diclorobiphenyls	DiCB	Two Chlorines
Trichlorobiphenyls	TrCB	Three Chlorines
Tetrachlorobiphenyls	TeCB	Four Chlorines
Pentachlorobiphenyls	PeCB	Five Chlorines
Hexachlorobiphenyls	HxCB	Six Chlorines
Heptachlorobiphenyls	HpCB	Seven Chlorines
Octachlorobiphenyls	OCB	Eight Chlorines
Nonachlorobiphenyls	NCB	Nine Chlorines
Decachlorobiphenyls	DCB	Ten Chlorines

Aroclor GC Patterns

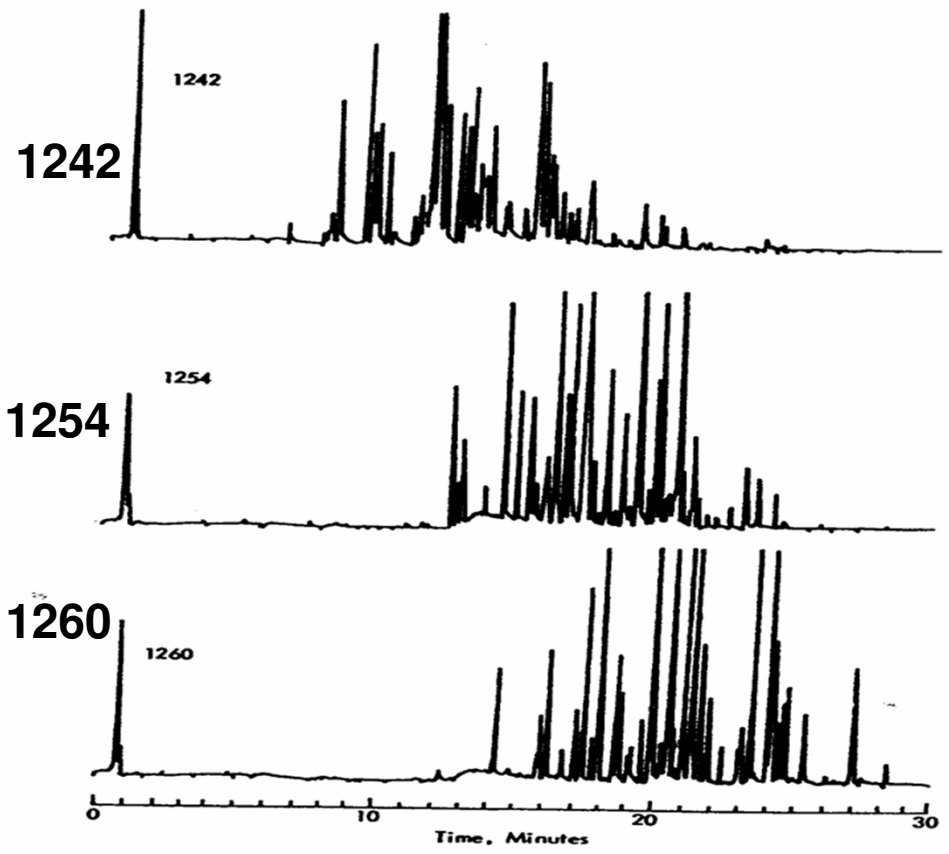
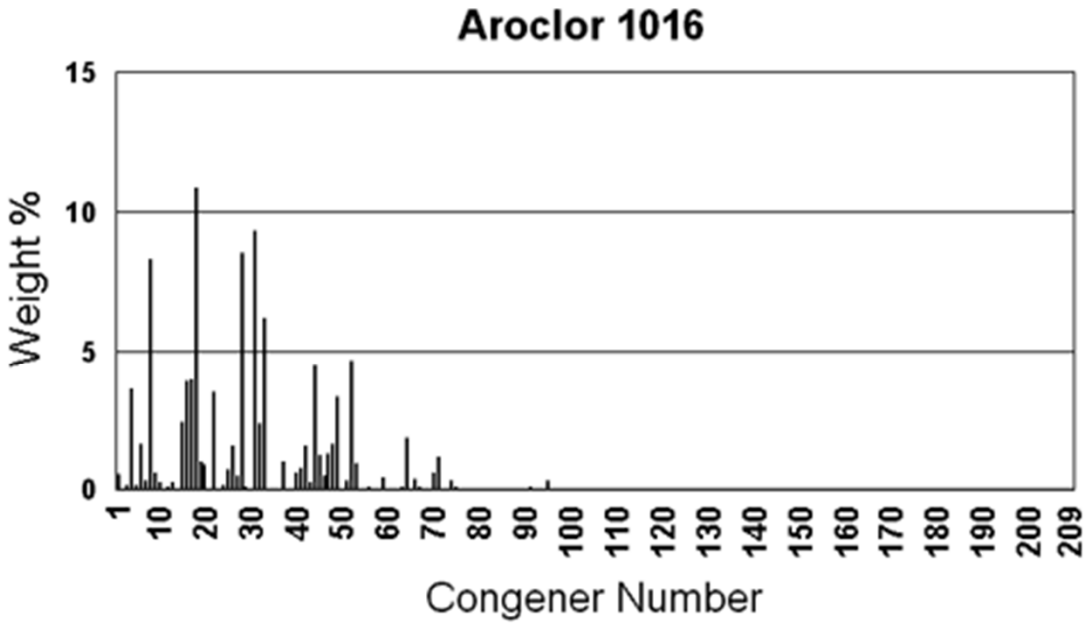


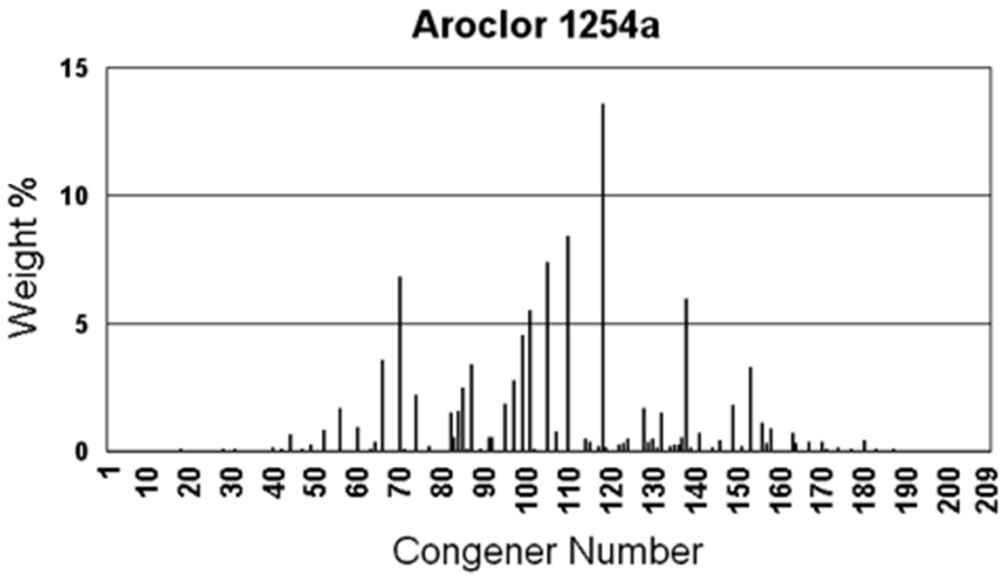
Figure 7-6 HRGC/ECD chromatograms of Aroclors 1242, 1254, and 1260 on a 0.29 mm i.d. × 20 m Apiezon L column. The column temperature was 70°C, programmed at 10°C/min to 130°C, then at 4°C/min to 230°C, with a 10-min hold. Samples (2 µL) were injected using splitless injection. (From Bush, B., et al., *J. Assoc. Off. Anal. Chem.*, 65(3):555, 1982. With permission.)

M.Erickson. Analytical Chemistry of PCBs Second Edition.

Composition of Aroclor Mixtures

http://www.epa.gov/toxteam/pcbid/aroclor_comp.htm





PCB's - Molecular Formulas, Name, Number of Congeners, IUPAC Number and % Chlorine

Molecular Formula	Chlorobiphenyl	Number of Congeners	IUPAC-No.	% Chlorine
$C_{12}H_9Cl$	Mono	3	1 to 3	18.79
$C_{12}H_8Cl_2$	Di	12	4 to 15	31.77
$C_{12}H_7Cl_3$	Tri	24	16 to 39	41.30
$C_{12}H_6Cl_4$	Tetra	42	40 to 81	48.65
$C_{12}H_5Cl_5$	Penta	46	82 to127	54.30
$C_{12}H_4Cl_6$	Hexa	42	128 to 169	58.93
$C_{12}H_3Cl_7$	Hepta	24	170 to 193	62.77
$C_{12}H_2Cl_8$	Octa	12	194 to 205	65.98
$C_{12}HCl_9$	Nona	3	206 to 208	68.73
$C_{12}Cl_{10}$	Deca	1	209	71.10

Data Reporting ‘Opportunities’

- Data can be reported as Aroclors, as individual [co-eluting] congeners, or as homologs; depending on the method chosen
- Weathering of PCBs Aroclors
- Total PCBs
  - Addition
  - How are the ND values used this calculation?
    - ND = RL, ½ RL or 0?
- Polychlorinated Terphenyls [PCTs] & Polychlorinated Naphthalenes [PCNs]
- Aroclor data can not be used to calculate congeners/homologs, nor can congener /homolog data be used to calculate Aroclor data as a routine service offering [without the use of a environmental forensic chemist]

Analytical Methodologies

Summary of PCB Methods

Source of Methods	Applications of Methods
EPA 505, 508, 525, 508A, 525.2	Drinking Water
EPA 608, 625, 680, 1668, 1668A, 1668B, 1668C	Clean Water Act, Groundwater, Surface Water, NPDES, Waste Water
CLP various statements of work	Soil, Water
SW 846 8080, 8080A, 8082, 8082A, 8250, 8270, 4020 Immunoassay, 9078, 9079	Soil, Water, Sediment
Compendium of Method TO-4, TO-9A	Ambient Air
0010/3542/1668A	Source Air
NIOSH 8004	Industrial Hygiene
EPA Oil Method	Oil
Custom methods	Project Specific Application

Analysis of PCBs

- **Preparative Methods**
  - Extraction
    - Clean-up
    - Concentration
- **Determinative Methods**
  - Instrumental analysis
    - GC/ ECD
    - GC/MS
    - HRGC/HRMS

Common PCB Methods Used

- EPA SW-846 8082- Analysis of Aroclors and select Congeners by GC-ECD
- EPA Method 680/EPA Method 8270M- Analysis of PCB congeners and homologs by LRMS
- EPA 1668, 1668A,1668B or 1668C- Analysis of PCB congeners and/or homologs by HRMS

PCB Aroclor Method

- PCB have been historically analyzed to meet TSCA requirements.

- Historically for environmental samples, PCB concentration have been quantified by a comparison to Aroclor standards
- Data report as:
  - Aroclor 1016
  - Aroclor 1221
  - Aroclor 1232
  - Aroclor 1242
  - Aroclor 1248
  - Aroclor 1254
  - Aroclor 1260
  - additionally Aroclors 1262 and 1268

Various Extraction Techniques Available

- Soxhlet (method 3540)
- Sonication (method 3550)
- Waste Dilution (method 3580)
- Other (automated soxhlet, microwave, ASE)

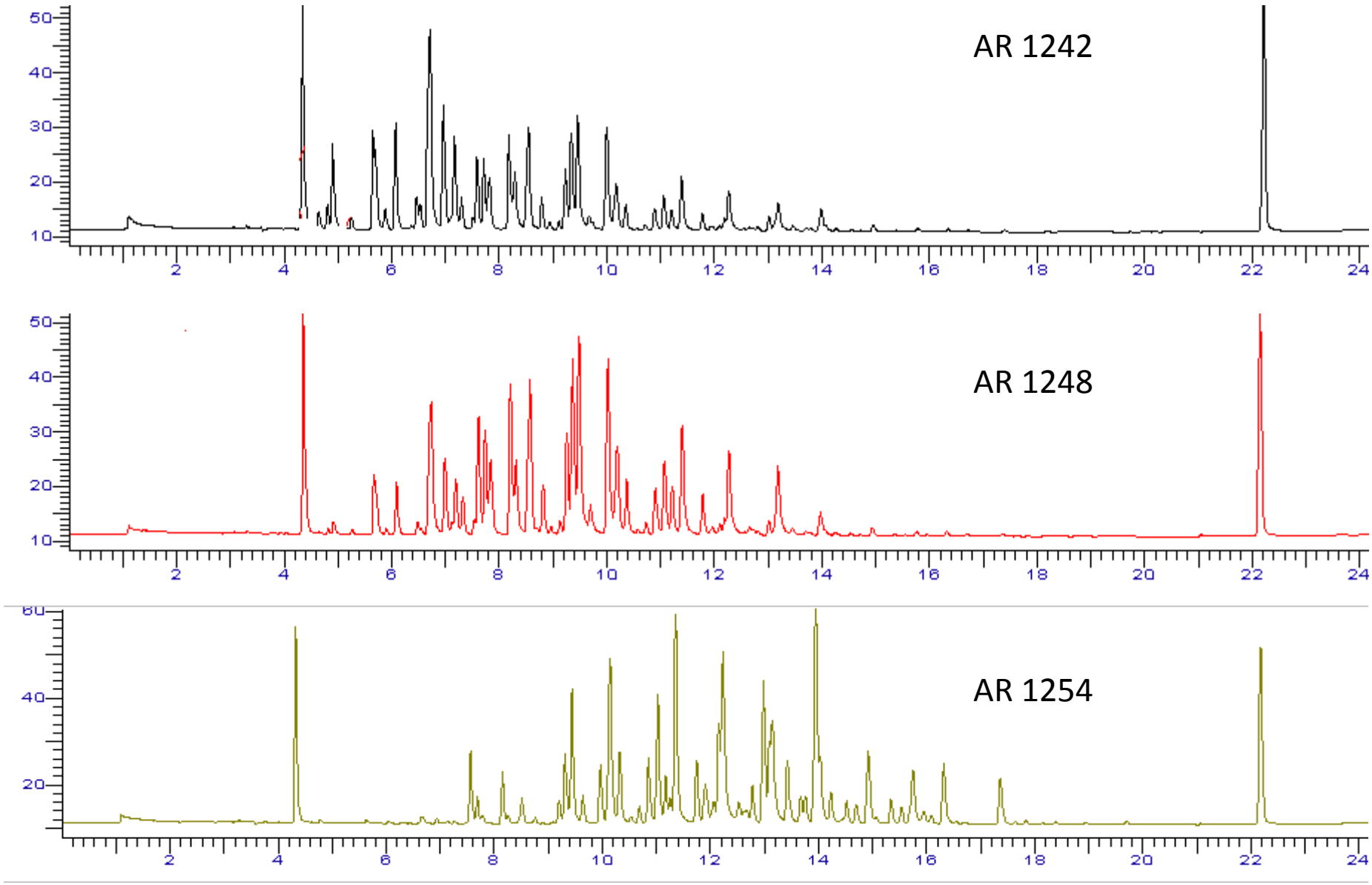
Aroclor Analysis

- Identification is subjective and dependent on analyst judgment
  - Unknowns must match pattern of Aroclor standard
  - When degraded / weathered Aroclors are present there is variability from lab to lab, and even analyst to analyst
- Lack of defined analytical guidance in method can lead to significant differences in results between labs
  - Variability from lab to lab on peaks used for quantitation can affect end result
- ECD is not selective
  - Potential high or low bias in reported results
- Power of chromatography software
  - “Chrom” has the ability to facilitate pattern matching

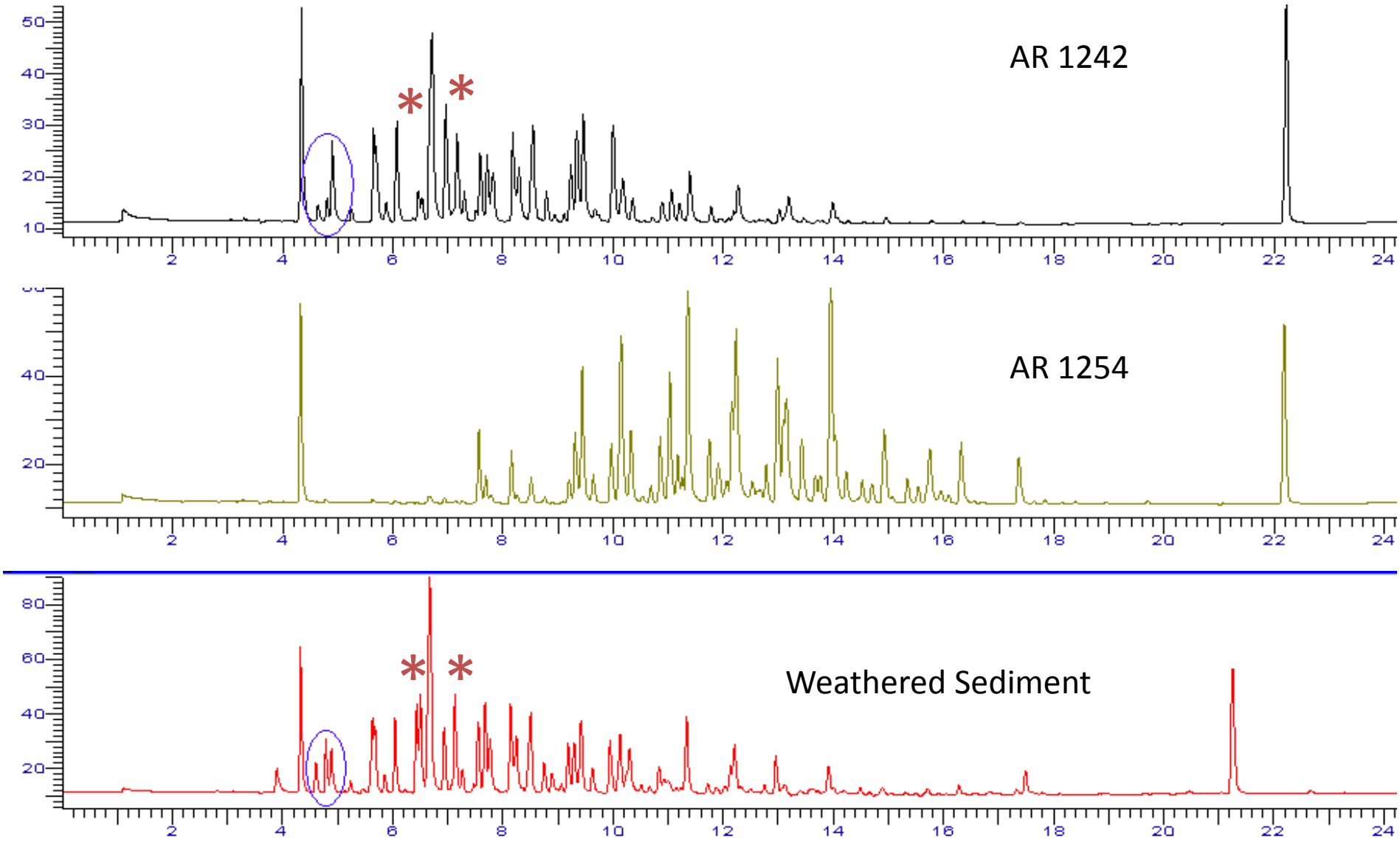
Aroclor Analysis

- Matrix effects
- Soxhlet extraction – 18 hours
- Aroclors determined by pattern recognition & peak ratios
    - “weathering” / biodegradation
    - Complex mixtures
- What if there is no match?
- “Double counting” of aroclors?

Aroclors by Method 8082



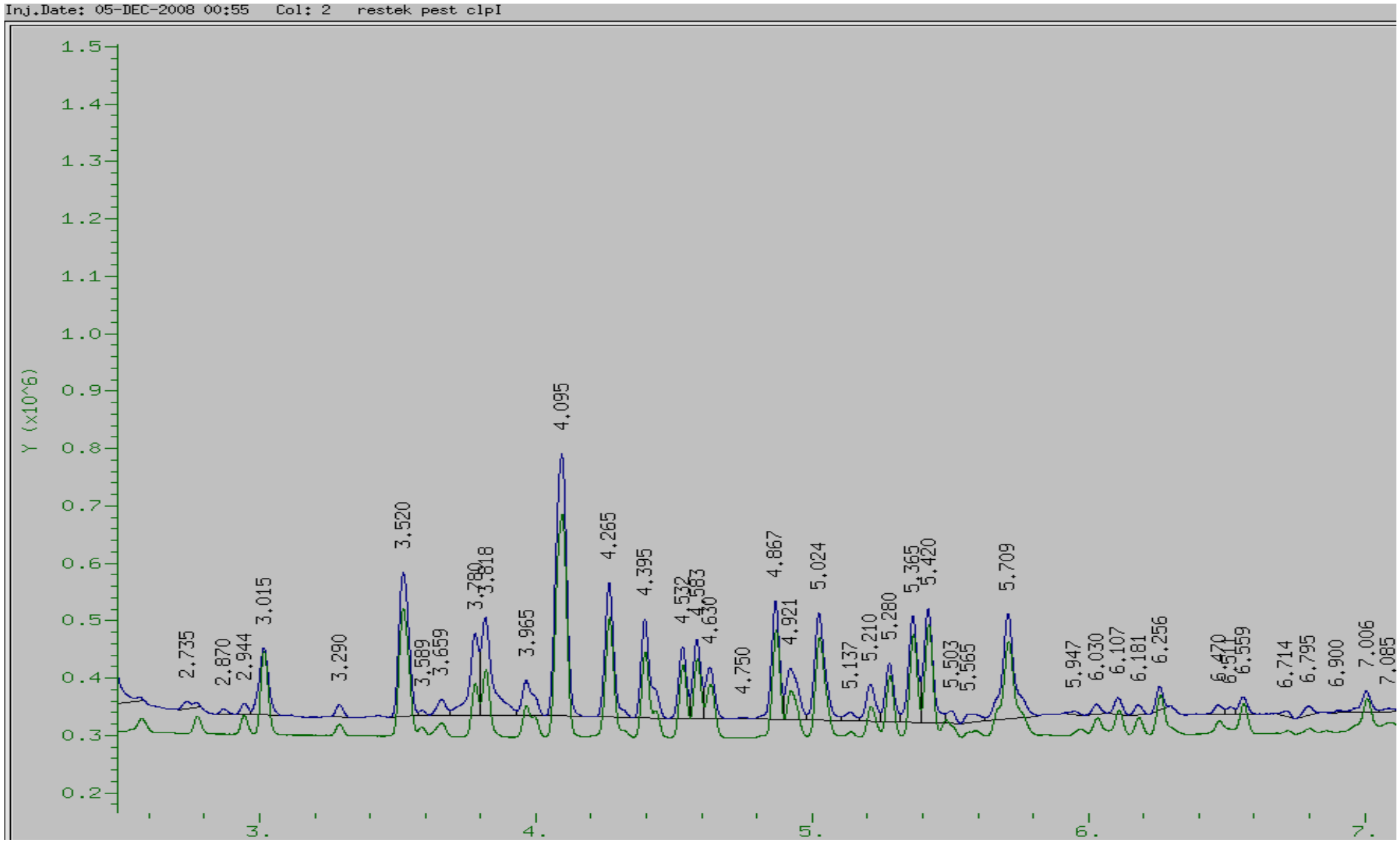
Qualitative ID



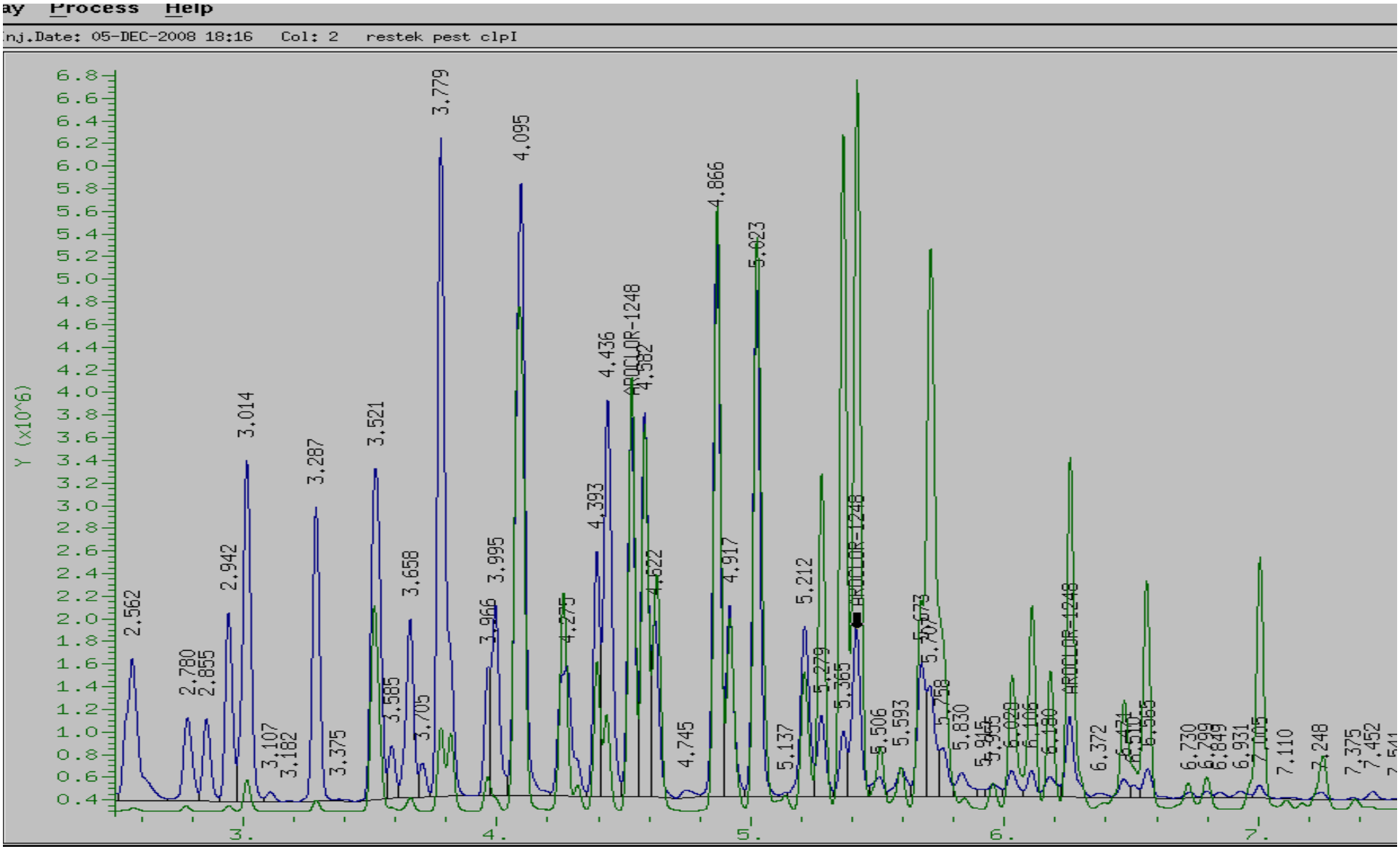
Impact of Moisture Content

- Wet weight targeted concentration: **RL 10 mg/Kg**
- Dry weight concentration
  - @ 80% solids **10** mg/Kg / .80 = **12.5**
  - @ 65% solids **10** mg/Kg / .65 = **15.4**
  - @ 40% solids **10** mg/Kg / .40 = **25.0**
  - ***EPA Region 1 recommendation 30% total solids limit***
- > moisture content, the > reporting limit
- > moisture, the < extraction efficiency
- % moisture can determine extraction procedure

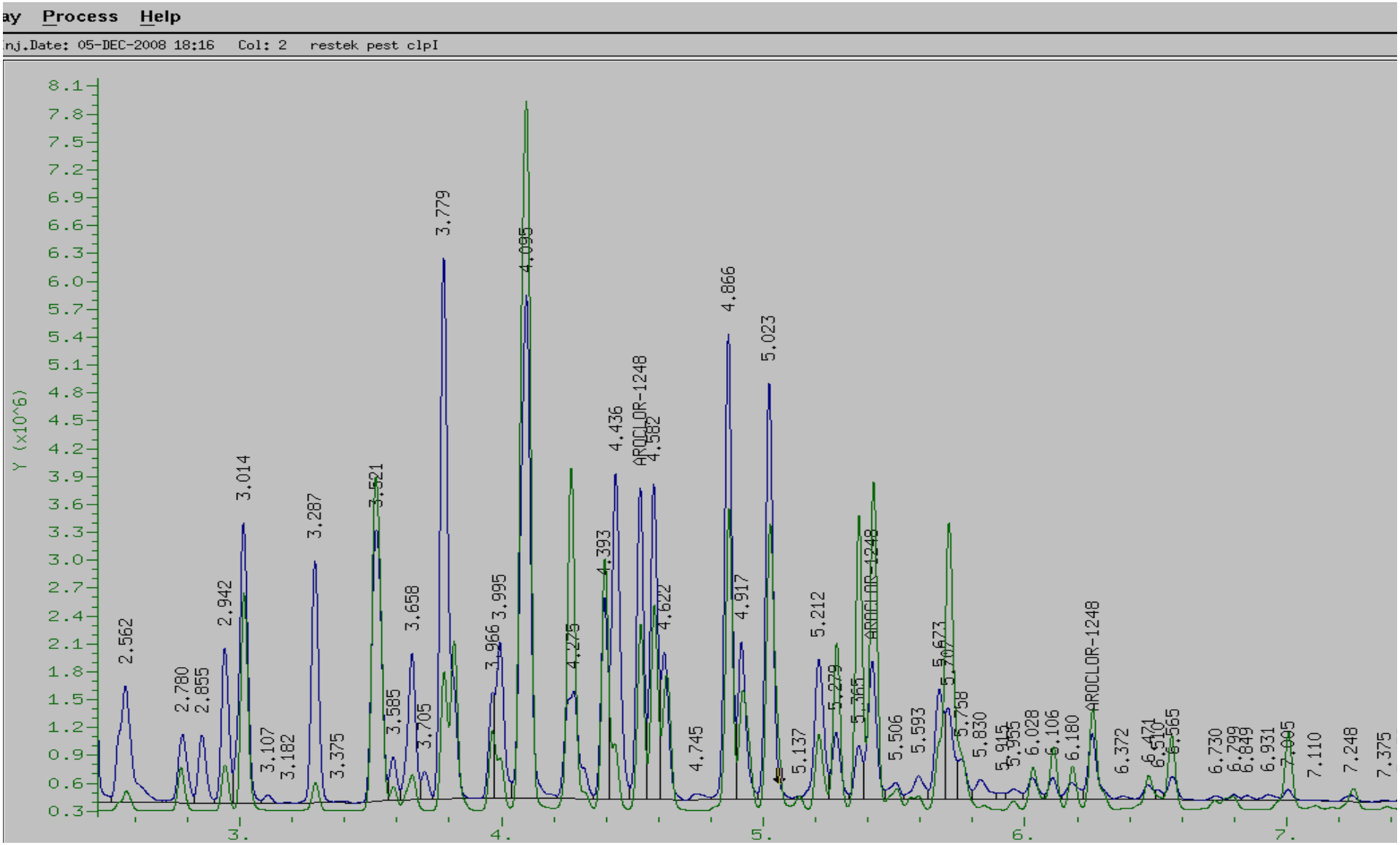
Unknown + Aroclor 1242



Unknown w/ Aroclor 1248 overlay



Unknown w/ Aroclor 1242 overlay



Method 8082- Aroclors by ECD

- Target Analytes- Aroclors
- Sample Prep- Matrix-specific extraction with limited extract clean-up and concentration
- Analysis/Detection- capillary GC with Electron Capture Detector
- Identification- Aroclors based on pattern matching
- Quantitation- 3-5 selected peaks vs external standard
- Reporting Limit-
  - 33 ppb (ng/g) for solid matrices
  - 1 ppb (ug/L) for aqueous matrices
  - Method detection limits (MDLs) can be 2-5X lower
  - Background contributions are not a factor
- Cost range- $50-150/sample, depending on matrix, RLs, volume etc.

Analytical Methodology
PCB Congeners by GC ECD

PCB Congeners by GC/ECD

- SW846 Method 8082 has Congeners as an option
  - The congeners listed in the method do not represent the congeners of greatest toxicological significance
- PCB have been historically analyzed to meet project specific requirements
  - Inland Testing Manual – 22 PCB Congeners
  - Project specific lists
  - Limited list of Congeners
- PCB concentration are quantified by a comparison to Congener standards

Method 8082- Congeners by ECD

- Target Analytes- Congeners [limited list]

- Sample Prep- Sample Prep: Methods 3510 for waters and 3541 for solids
- Analysis/Detection- capillary GC with Electron Capture Detector

- Identification- Congeners based on dual column analysis

- Quantitation- Quantitation- 5-point calibration curve

- Reporting limit: 1 ppb (ng/g) for solid matrices
  1 ppt (ng/L) for aqueous matrices

- Cost range- $200-350/sample depending on congener list, matrix, RLs, volume etc.

Analytical Methodology- PCB Homologs by Method 680/8270

Method 8270- Homologs by GC/MS SIM

- Target Analytes- Homologs
- Sample Prep- Sample Prep: Methods 3510C for waters and 3550B for solids
- Analysis/Detection- capillary GC with Mass Spectrometer Detector
- Identification- based on exact mass spectra and relative retention time
- Quantitation- Quantitation- 5-point calibration curve
- Reporting limit: 0.6 - 6.0 (ug/g) for solid matrices
  20-170 (ng/L) for aqueous matrices
- Cost range- $ 400/sample depending on matrix, RLs, volume etc.
- Tiered Testing option
- Method 680 is an older PCB Homolog method [1985]

Analytical Methodology- PCB Congeners and Homologs by Method 1668, 1668A, 1668B or 1668C

Method 1668, 1668A, 1668B or 1668C
Analytes of Interest - Congeners and Homologs

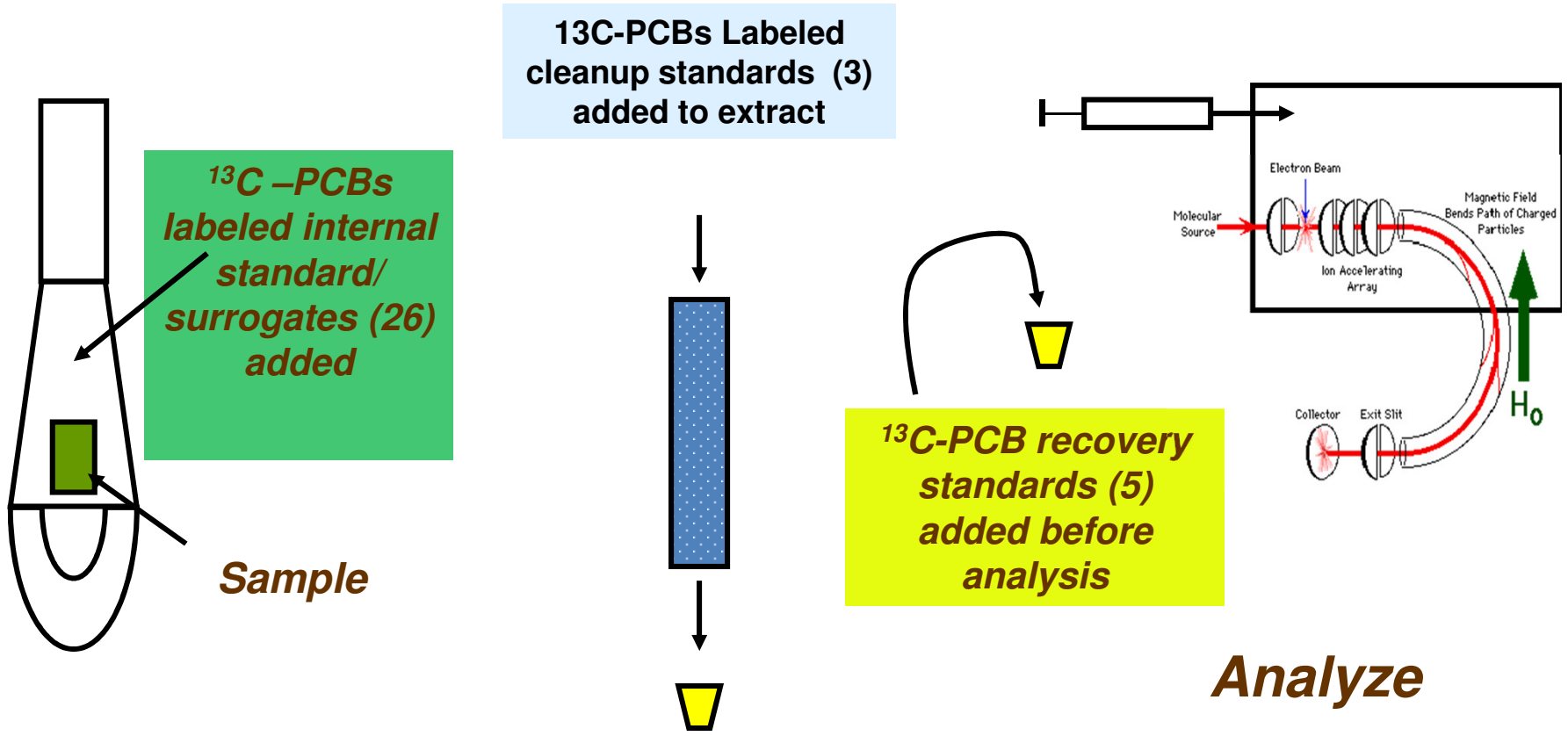
- Analysis for PCB congeners
  - **WHO congeners- 12 Congeners with TEF (1994/1997/2005) with**
    - **coplanar PCBs**
    - **dioxin-like PCBs**
  - A variety of project-specific congener lists
  - 209 congeners
  - Total PCBs

- Analysis for PCB Homologs
  - 10 homologs
  - Total PCBs

Soxhlet by Method 3540

- Advantages
  - Exhaustive extraction technique (16-24 hours)
  - Demonstrated consistency and accuracy
  - Useful for difficult matrices (paint chips, caulk, concrete, waste, biota, sediments)
- Disadvantages
  - Long
  - Lots of solvent, hood space/ventilation
  - Trained analyst to set and monitor

Schematic of Isotope Dilution Method



High Resolution Mass Spectrometer

Advantages of High Resolution Analysis

- **A target analyte's exact mass is highly characteristic of its identity**
- **Mass resolution measures the ability of the instrument to isolate and detect a particular exact mass**
- **Triple sector instruments operate at mass resolution of ~10,000 (high) vs ~100 (low) for quadrupole instruments.**
- **High Res analyses are nominally 100 times better at filtering interferences than conventional Low Res analyses**
- **High Res analyses offer improved sensitivity, selectivity, and ruggedness for PCB congener analyses**

Method 1668A- Congeners and Homologs by HRMS

- Target Analytes- PCB congeners and homolog totals.
- Sample Prep- matrix-specific extraction with extensive extract clean-up and concentration. Usually Soxhlet for soils
- Analysis/Detection- capillary GC with High-Resolution Mass Spectrometer.
- Identification- congeners based on characteristic exact mass, ion ratio, and relative retention time
- Quantitation- C13 labeled analogs of target analytes as internal standard/surrogates (isotope dilution technique)
- Reporting Limit-
  - 2 ppt (pg/g) for solid matrices
  - 20 ppq (pg/L) for aqueous matrices
  - Estimated detection limits (EDLs) can be 2-10X lower
  - Background contributions are a factor
- Cost- $400-900/sample, depending on congener list, matrix, RLs, etc

Method 1668 vs 8082

Advantages of 1668

- More reproducible extraction procedure.
- Most specific cleanup processes.
- Identification based on ion ratio (exact mass) and retention time.
- Quantitation using isotope dilution technique.
- Least impacted by matrix interference.
- Lowest detection limits.
- Large instrument dynamic range.
- Highest overall data quality

Disadvantages of 1668

- Highest analytical cost.
- Longer turnaround time.
- Limited industry-wide capacity.
- Applicable for low level sample concentrations. Limited dilution capability.
- Limited information on Aroclor concentration

Method 1668vs 8270 vs 8082
Which one to use for PCBs?

Use 1668 when…

- Ultra-trace detection limits are required
- Matrices are complex
- Highest possible level of data quality is required
- Risk assessment includes a TEQ component
- Congener-specific information is required
- PCBs are highly weathered or transformed
- PCB source is non-conventional
- Fingerprinting or source apportionment is desirable

Use 8082 when…

- A single Aroclor is the only source of PCBs
- Risk assessment and/or cleanup is based exclusively on Aroclor concentrations
- High sample loads are expected
- Some estimation of total PCB content is acceptable
- High PCB concentrations are present
- Cost/TAT constraints prohibit use of 1668
- Matrices are simple soil/water

Use 8270 when…

- Samples contain complex mixtures of Aroclors
  - Samples have degraded Aroclor patters
- PCB Homolog or Total PCB Data supports project needs
  - Cost/TAT constraints prohibit the use of 1668

Options for Analytical Support

‘Screening’

Mobile/Onsite Lab

Fixed Based Laboratory

Field Screening

- Immunoassay based test kits (ELISA)
  - SW-846 Method 4020
  - (M i l l i p o re Enviro G a rd™, Ensys PCB RISc™)
- Total organic chlorine / chloride ion test kits
  - Chemical based testing device
    - Dexsil L2000 PCB Analyzer™
- Most studies based on soils & transformer oils
  - Project specific method development suggested
  - Sample matrix, aroclors present, results may vary
  - Correlation with lab testing

United States Environmental Protection Agency | Office of Research and Development Washington, D.C. 20460 | August 2000

Environmental Technology Verification Program

Verification Test Plan

Evaluation of Field Polychlorinated Biphenyl (PCB) Detection Technologies

U.S. EPA Contaminated Site Cleanup Information (CLU-IN)

Polychlorinated Biphenyls (PCBs)

Detection and Site Characterization

PCB analysis can be performed in the field or at a fixed laboratory using a variety of techniques. PCB immunoassay kits utilize analyte-specific antibodies to bind and remove PCBs from complex sample matrices. The process is colorimetric in nature with the change in color indicting approximate concentrations. The color change can be measured using an instrument (e.g., spectrophotometer) or visual color card. Soil samples require an extraction step that can be difficult with very fine-grained materials. The kits are generally calibrated against a specific Aroclor standard (e.g., 1254) but are not able to differentiate between Aroclors. Also, some Aroclors respond better than others. The test can be used as a screening tool during cleanups where a specific cleanup goal such as 1 ppm or 10 ppm has been set and analysis is done to determine whether the contaminant level is above or below the goal. Analysis time varies but can take over 30 minutes per sample.

Ion-specific analysis uses a chloride-specific electrode to measure the amount of chlorine in a sample extract that

www.clu-in.org/contaminantfocus/default.focus/sec/Polychlorinated_Biphenyls_PCBs/cat/Detection_and_Site_Characterization/

Mobile/Onsite Lab

Mobile / Onsite Labs are configured to meet client specifications

- **Screening for PCB Aroclors based on Method 8082 can be defined as:**
    - Modified extraction
    - Smaller sample size, surrogate spike, acid clean up
- **Definitive PCB Aroclors based on Method 8082**
    - Based on laboratories fixed based SOP
    - Samples analyzed at onsite lab
    - Preliminary data provided from mobile lab
    - All final data review and reporting from fixed based lab to be able to provide final data report, EDD and online data view

Fixed Based Laboratory

- Fixed Based Laboratories can provide:
  - Screening Options
  - Definitive Analysis
- Advantages
  - Infrastructure in place
  - Capacity and wide variety of turnaround options
  - Certifications
  - Flexible resources [equipment, supplies, staff]
  - Cost for analysis on unit rate basis [mobile/onsite lab on daily rate with mob and demob rates]
  - All data deliverables which are required

Media and Methods

Water

Soil

Sediment

Biota

Air

Building Material

Water

- Method Selection based on data required, matrix and reporting limits required
  - Drinking Water
  - Groundwater
  - NPDES – permit requirements
  - Surface Waters
    - TMDL programs → Many programs require 1668A or project specific 1668A for 209 congeners and RL
    - Water Quality Monitoring during sediment removal
    - Long Term Monitoring to determine effectiveness of remedial selection

Know the intended use of the data which will be generated!

Soil

- Method selection based on data required and reporting limits required
  - Source Investigation
  - Site Characterization
    - Determining the presence or absence of PCBs
    - Recent release
    - Complex mixtures of Aroclors
    - Weather Aroclors with degraded patterns

Know the intended use of the data which will be generated!

Sediment

- Method selection based on data required and reporting limits
  - Baseline monitoring
  - Site Characterization
  - Ecological Risk Assessment
  - Human Health Risk Assessment
  - Monitored Natural Attenuation
  - Dredged Material Evaluation

Know the intended use of the data which will be generated!

Biota

- Method selection based on data required and reporting limits
- A limited number PCB Congeners bioaccumulate and bioamplify up the food chain
- Toxicity data does exist for Aroclors, but the toxicity of PCBs generally require the use of TEF, which are congener specific
  - WHO congeners- 12 Congeners with TEF (1994/1997/2005) for fish, birds or mammals
-

Know the intended use of the data which will be generated!

Air

- Indoor air
  - Potential indicator of a problem
- Fence line monitoring
- Can analyze Aroclors, homologs or congeners
  - Are Aroclors representative in air?

- Method TO-10 low- volume sampling
- Method TO-4 high-volume sampling

Air Sampling Equipment

- **PAH Analysis via PUF cartridges**
  - **Low volume** Method TO-10
    - flow range = 1-5 L/min
  - **High volume** Method TO-4
    - flow range = 200-280 L/min

Low Volume **High Volume**

Air Sampling Equipment- PCB Sampling

- Hi vol / Low vol Cartridges
- Personal Sampling Pumps
- Hi-vol samplers

Analysis of Building-Related Materials

- Concrete & bricks
    - Sealers
- Surfaces
  - Wipe testing, 100 CM^2
- Indoor air
  - Initial indication of a problem?
  - Methods TO-10 low- vol, TO-4 high-vol
    - PUF cartridges
    - Homologs or congeners recommended
- All of the above – soxhlet extraction

Caulking and Paints

- Soxhlet extraction
  - Can be difficult matrix
- Potential for high concentrations!
  - “One bad sample can ruin your whole day(s)”
- Laboratory screening
  - Minimize potential for cross-contamination

PCB Analysis at TSCA Sites

- TSCA Subpart B 761.292
  - Extraction method 3540C Soxhlet
  - Extraction method 3550B Sonication
    - EPA Reg 1, CAM & RCP do not allow sonication
- TSCA Subpart Q 761.320
  - Alternative extraction procedures/Comparability Study
  - Matrix-matched, i.e. sand, clay, loam, etc.
  - Not much options with building materials
  - Study must be approved prior to sampling

PCB Analysis in Accordance with MCP CAM Guidance

- Sample preparation
  - Soils, solid samples
    - Method 3550 (ultrasonic extraction) not allowed
    - Acid clean up should be performed on all samples
    - Sulfur clean up should be performed on sediment samples
- Dual column analysis, higher result reported
- Holding time – one year to extraction

Sulfur Interference

```
File       :O:\Organics\DATA\ECD1-5890\2009\DEC\DEC07\F1120796.D
Operator   : ECD1:JR
Acquired   :  9 Dec 2009   3:02 pm using AcqMethod A1081760.M
Instrument :   ECD1-5890
Sample Name: L0916458-66,42,2
Misc Info  : WG392179,WG390050
Vial Number: 96
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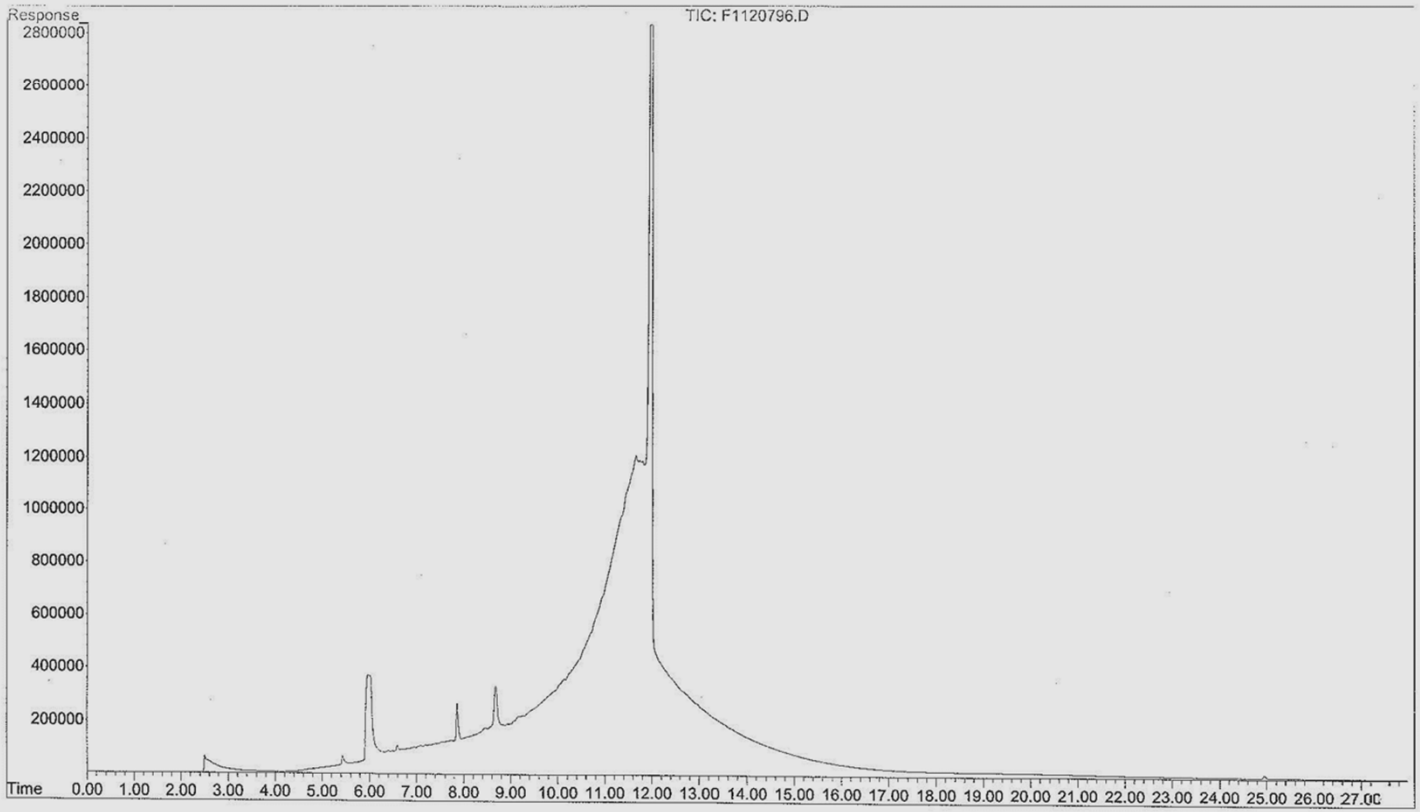
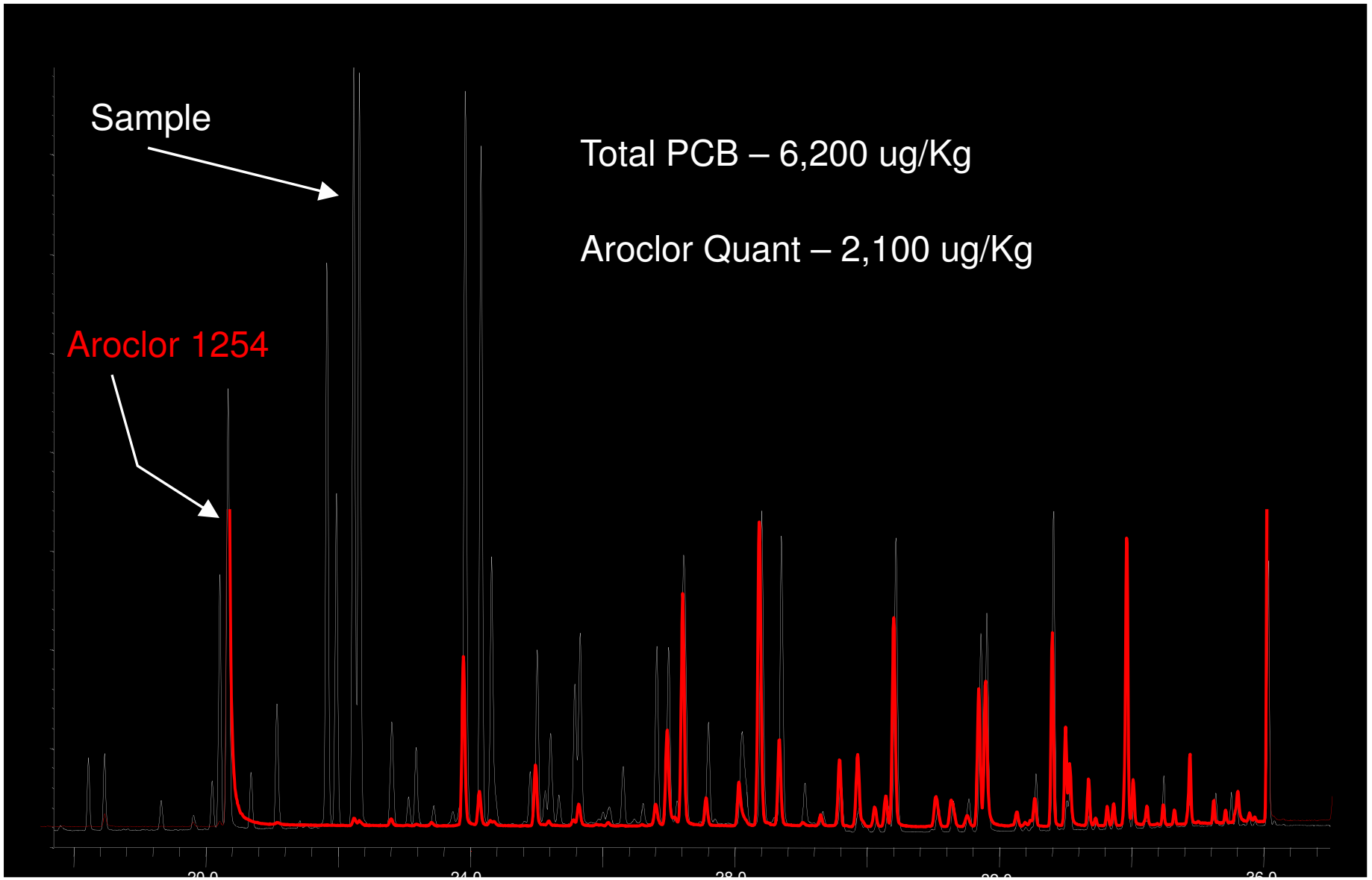


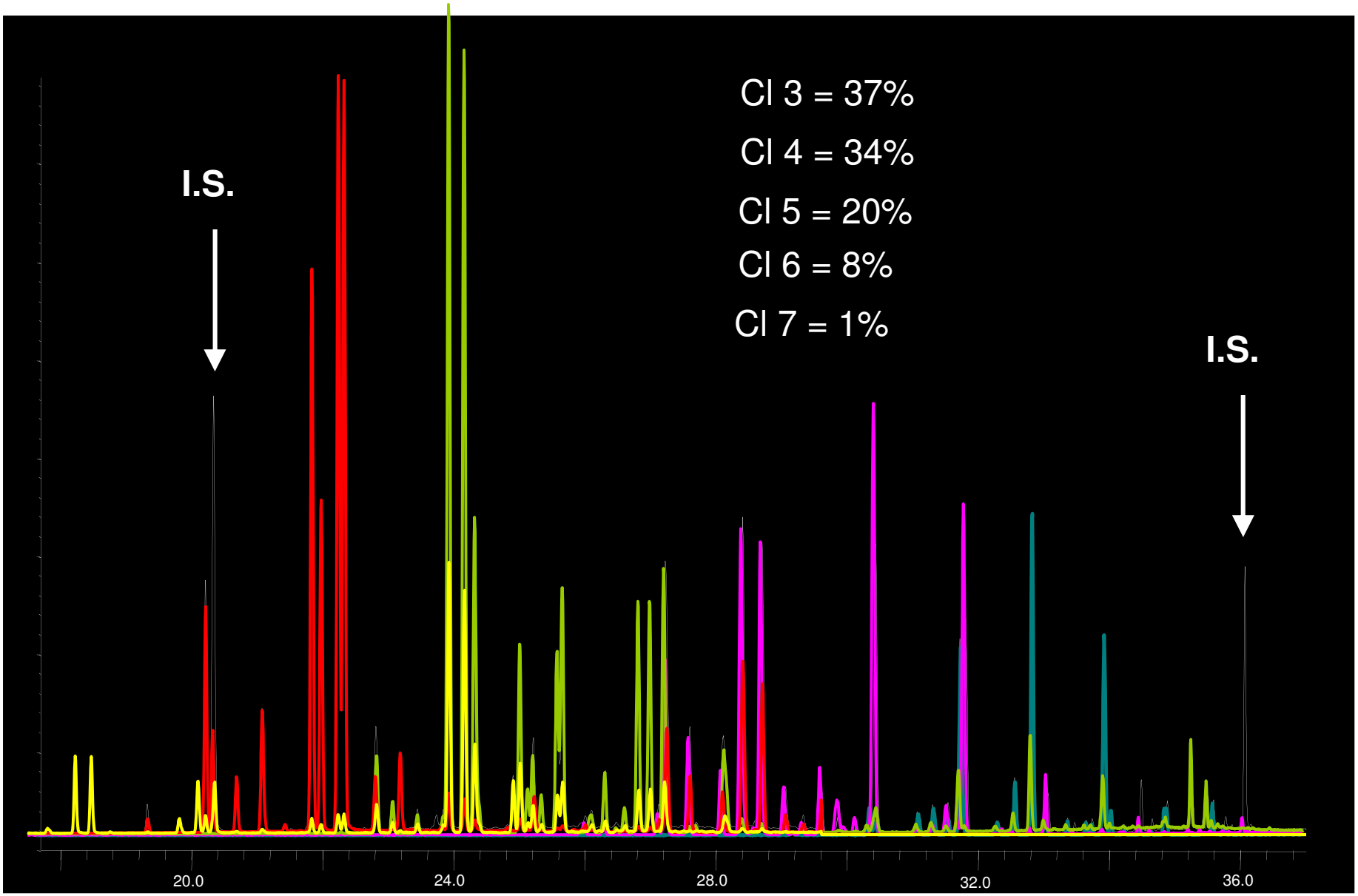
PCB Analysis in Accordance with MCP CAM Guidance

- Aroclors not detected, do you have no PCBs?
- Aroclors identified by pattern recognition & peak ratios
  - Highly “weathered” samples, complex mixtures
- Could result in no Aroclors reported, but presence of PCB congeners strongly suspected
  - Laboratory to narrate, suggest that the sample be analyzed by GC/MS
  - Attach chromatogram

Quahog Quantitation



Quahog PCB Composition



PCB Analysis in Accordance with CT RCP Guidance

- From a laboratory perspective, same protocols in place as Massachusetts CAM
- Ultrasonic extraction – Method 3550C
  - "Contaminated solids"

  "Sonication may only be used for the extraction of highly contaminated (free product) non-soil/sediments (debris). Any other use of ultrasonic extraction is not allowed"

PCB Analysis in Accordance with CT RCP Guidance

- Aroclors 1262 & 1268 not specifically listed
  - Laboratory to include if requested or if present in sample
- Requirements for Aroclor versus “stray congeners” not as specifically defined

PCB Analysis in Accordance with NY Guidance

- Not specified in comparison with CAM & RCP
- Aroclor target compound list
  - Specifically request Aroclors 1262 & 1268

Conclusion

- Environmental PCBs occur as mixture of congeners and their composition will be different than the Aroclor technical standard
- Many choices for PCB Analysis
- No ‘ Silver Bullet’ single method which will provide Aroclor, Congener & Homolog analysis for all purposes
- Understand the strengths & weaknesses associated with GC/ECD, GC/LRMS & HRGC/HRMS
- Take sample media, project application & regulatory oversight into consideration for proper method selection

Know the intended use of the data which will be generated!