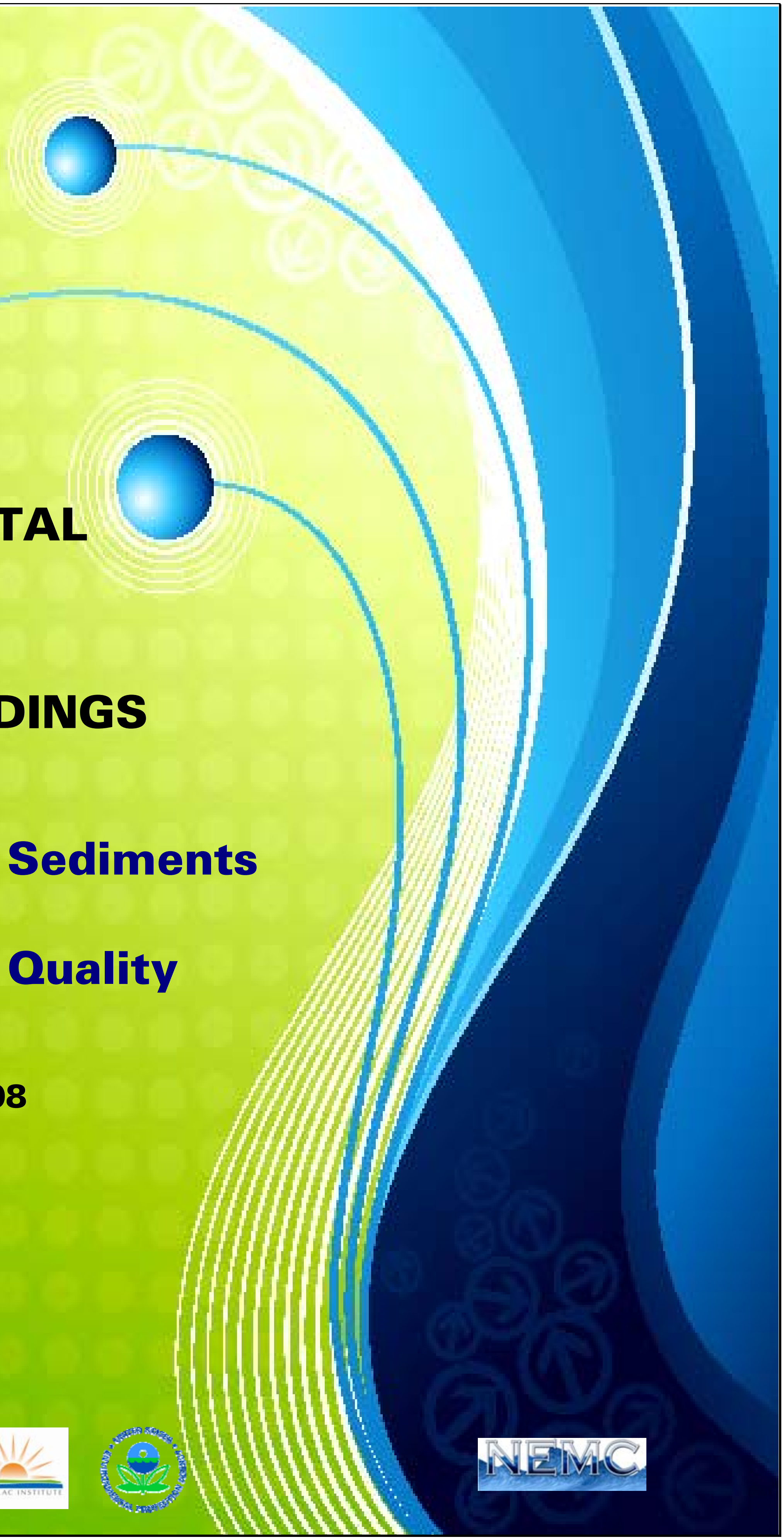


NATIONAL ENVIRONMENTAL MONITORING CONFERENCE

2008 PROCEEDINGS

Section 5:
Contaminated Sediments
Data Usability
Ensuring Data Quality

Washington DC
August 10 – 16, 2008

ILI
INDEPENDENT LABORATORIES INSTITUTE

ELAB

THE NELAC INSTITUTE

NEMC

NEMC 2008
SYMPOSIUM SPONSORS

ABSOLUTE
GET THE ABSOLUTEGRADE
STANDARDS

ENVIRONMENTAL
RESOURCE ASSOCIATES®
The Industry Standard™

FMS
Fluid Management Systems

NEMC 2008
PROGRAM COMMITTEE

CONFERENCE CHAIR

Lara Autry, USEPA Office of the Science Advisor

PROGRAM CHAIR

Earl Hansen, PhD., Independent Laboratories Institute

CONFERENCE ORGANIZER

Jerry Parr, The NELAC Institute

BOARD OF TRUSTEES

Robert Benz, NSI Solutions
H. M. (Skip) Kingston, PhD., Duquesne University
Matthew Sica, Maine Center for Disease Control and Prevention
David Speis, Accutest Laboratories
Jan Young, USEPA Office of Solid Waste

SESSION CHAIRS

Lara Autry, USEPA Office of Science Advisor
Robert Benz, NSI Solutions
Richard Burrows, PhD., TestAmerica
Charles Carter, PhD., TestAmerica
Nancie Copeland, Environmental Express
David Friedman, Friedman Consulting
Diane Gregg, USEPA Region 6
Zoe Grosser, PhD., PerkinElmer
Earl Hansen, PhD., Independent Laboratories Institute
H. M. (Skip) Kingston, PhD., Duquesne University
Douglas Later, PhD., Torion Technology
Gonzalo Manchego, Duquesne University
Particia McIsaac, TestAmerica
Marlene Moore, Advanced Systems
Stuart Nagourney, NJ Department of Environmental Protection
Nick Nigro, ECCS Nationwide Mobile Laboratories
Jerry Parr, Catalyst Information Resources
Joe Romano, Waters Corporation
Charles Sellers, USEPA Office of Solid Waste
David Speis, Accutest Laboratories
Shannon Sturgeon, USEPA Office of Solid Waste
Gary Ward, PhD., Columbia Analytical Services
Wayne Whipple, USEPA Region 5
Robert Wyeth, Columbia Analytical Services
Shen-yi Yang, USEPA Office of Solid Waste

NEMC 2008
CONFERENCE HIGHLIGHTS

The Environmental Measurement Symposium, a combined meeting of the National Environmental Monitoring Conference (NEMC) and The NELAC Institute (TNI) was held August 10 – 16, 2008 in Washington DC, just blocks from the nation's capitol. The conference was co-sponsored by the US Environmental Protection Agency, the Independent Laboratories Institute, and The NELAC Institute.

A total of 469 people attended the 2008 Forum, which was a 9% increase in attendance over 2007. The meeting included:

- 19 technical breakout sessions with 100 presentations;
- a 2-day poster program with 23 posters;
- 4 keynote presentations;
- 3 EPA general sessions with 13 presentations;
- 13 TNI committee meetings;
- an assessment forum;
- a laboratory mentoring session;
- an accreditation body forum;
- a meeting of the Environmental Laboratory Advisory Board;
- 5 training workshops; and
- a 3-day exhibit program with 43 exhibitors and sponsors.

Highlights of the week included the following keynote speakers:

- Dr. Jorg Feldman from the University of Aberdeen who spoke on elemental speciation in environmental monitoring;
- Dr. Heidelore Fielder from the UN Environmental Program who spoke on global monitoring of persistent organic pollutants;
- Dr. J. Clarence Davies from Resources for the Future who spoke on EPA and nanotechnology; and
- TNI's own Bob Wyeth who spoke on moving forward on national accreditation.

NATIONAL ENVIRONMENTAL MONITORING CONFERENCE PROCEEDINGS 2008

SECTION 5 TABLE OF CONTENTS

CONTAMINATED SEDIMENTS

DATA USABILITY

SECTION 5 TABLE OF CONTENTS cont.

ENSURING DATA QUALITY

AUTHOR INDEX

2008 NEMC Proceedings

CONTAMINATED SEDIMENTS

Characterizing Sediment Contamination Using A Passive Sampler

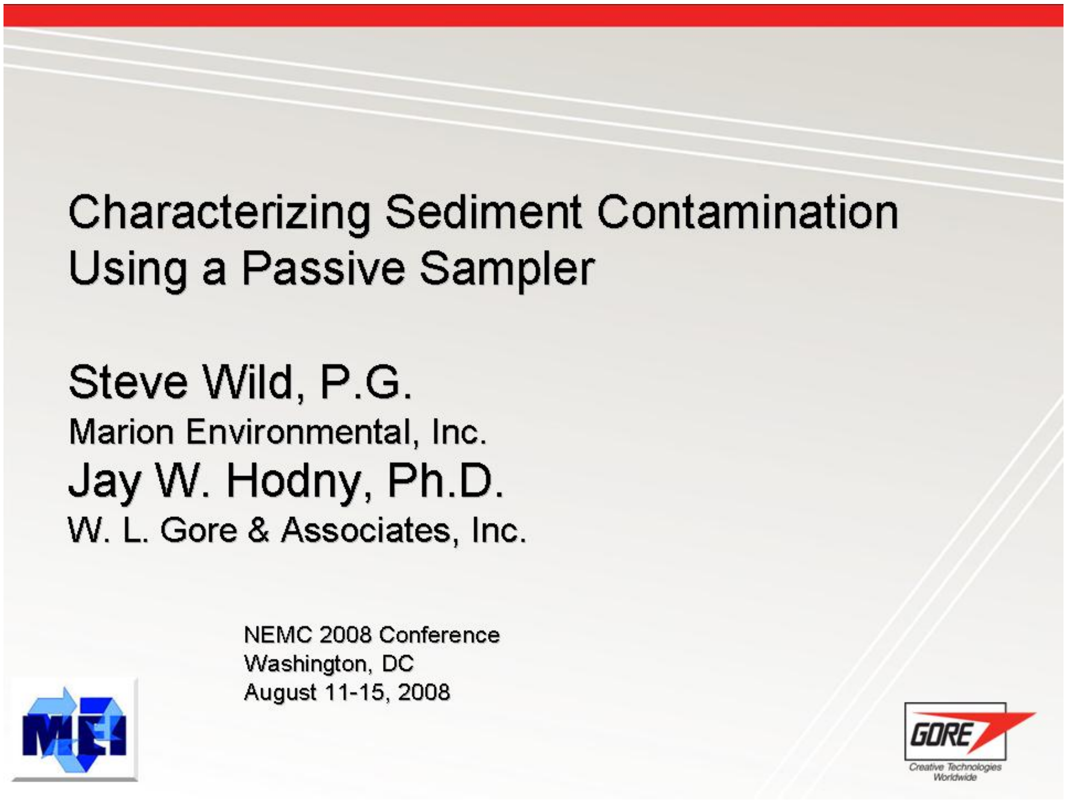
Jay Hodny
W.L. Gore & Associates, Inc.
100 Chesapeake Blvd.
Elkton, MD 21921
410-392-7600
jhodny@wlgore.com

ABSTRACT

Characterizing sediment contamination in freshwater and marine environments is challenging even under ideal sampling conditions. The challenges may lead to poor data quality, a weak conceptual site model, a remediation program that is not optimized, unnecessary damage to ecologically sensitive areas, and overall unneeded project waste and expense. Screening techniques, such as membrane-based passive samplers, provide a unique, efficient and cost-effective method to identify areas of sediment contamination. The approach minimizes the intrusive footprint in the sediment ecosystem while providing high-resolution data on the extent of contaminant impact. Subsequent sampling by more complex and invasive techniques is now focused, more effective, and economical. The investigations discussed here utilized a passive sampler constructed of a GORE-TEX® membrane tube, which surrounds hydrophobic engineered adsorbents. The adsorbents have an affinity for a broad range of organic compounds, while minimizing water vapor uptake. Compounds dissolved in the sediment porewater, partition to vapor in contact with the sampler membrane, and diffuse to the adsorbent virtually unimpeded. The samplers proved to be an accurate, sensitive, easy-to-use sediment porewater sampling tool.

The application of the membrane-based passive sampler at two sites is presented. In the first case, the Washington State Department of Ecology and the US EPA have been overseeing sediment characterization and cleanup efforts along the Lower Duwamish Waterway, now listed on the Superfund National Priorities List. The passive sampler was used to screen an embayment in the waterway to determine whether groundwater, contaminated by chlorinated compounds from upgradient sources, was entering the river by generalized upwelling throughout the embayment sediments, or through shallow localized groundwater seeps. Conventional sediment grab sampling, piezometer and peeper sampling confirmed the passive results through additional investigation stages, and showed good correlation with the original passive results. In the second case, a passive soil gas survey using the same membrane-based passive sampler was conducted at a manufacturing site along the Tennessee River to delineate on-shore subsurface impact to soil and groundwater. To determine if the on-shore impact was entering the river, the passive samplers were then deployed in the river sediment. Chlorinated compounds were observed in discreet locations from the river sediment sampling, which correlated spatially with the on-shore soil gas results. The presentation will include the discussion of the passive sampler and two case studies.

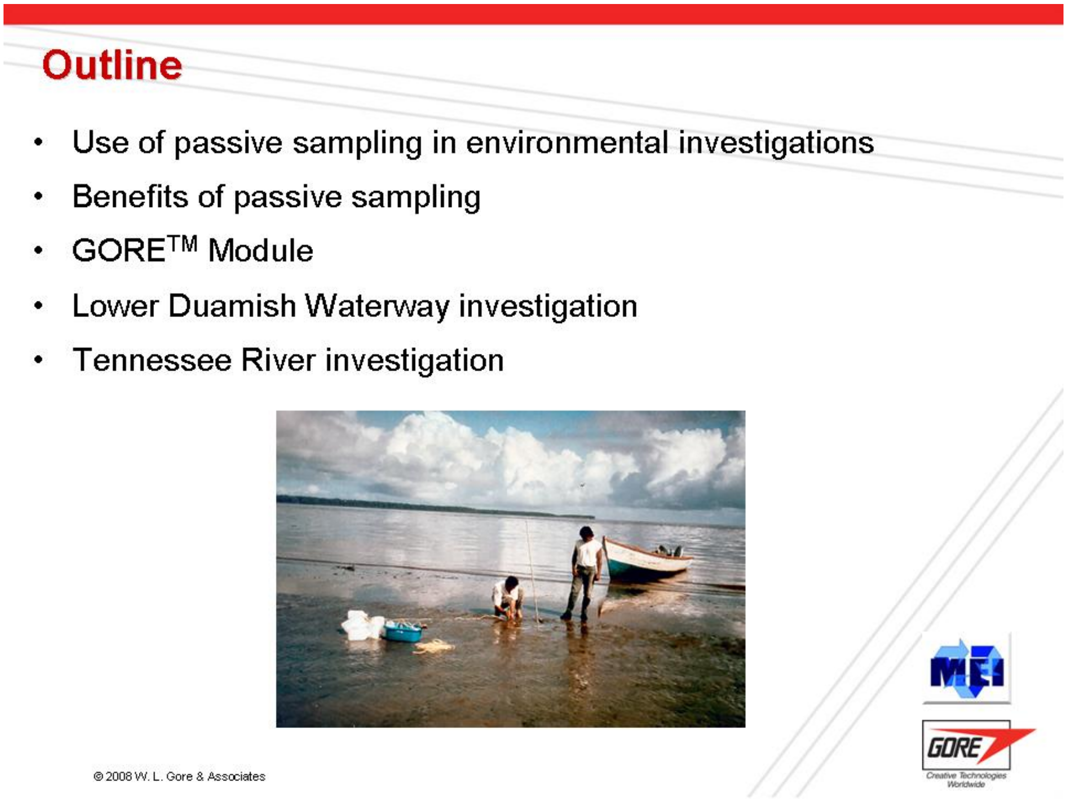
NEMC 2008



Characterizing Sediment Contamination Using a Passive Sampler

Steve Wild, P.G.
Marion Environmental, Inc.
Jay W. Hodny, Ph.D.
W. L. Gore & Associates, Inc.

NEMC 2008 Conference
Washington, DC
August 11-15, 2008



Outline

- Use of passive sampling in environmental investigations
- Benefits of passive sampling
- GORE™ Module
- Lower Duamish Waterway investigation
- Tennessee River investigation

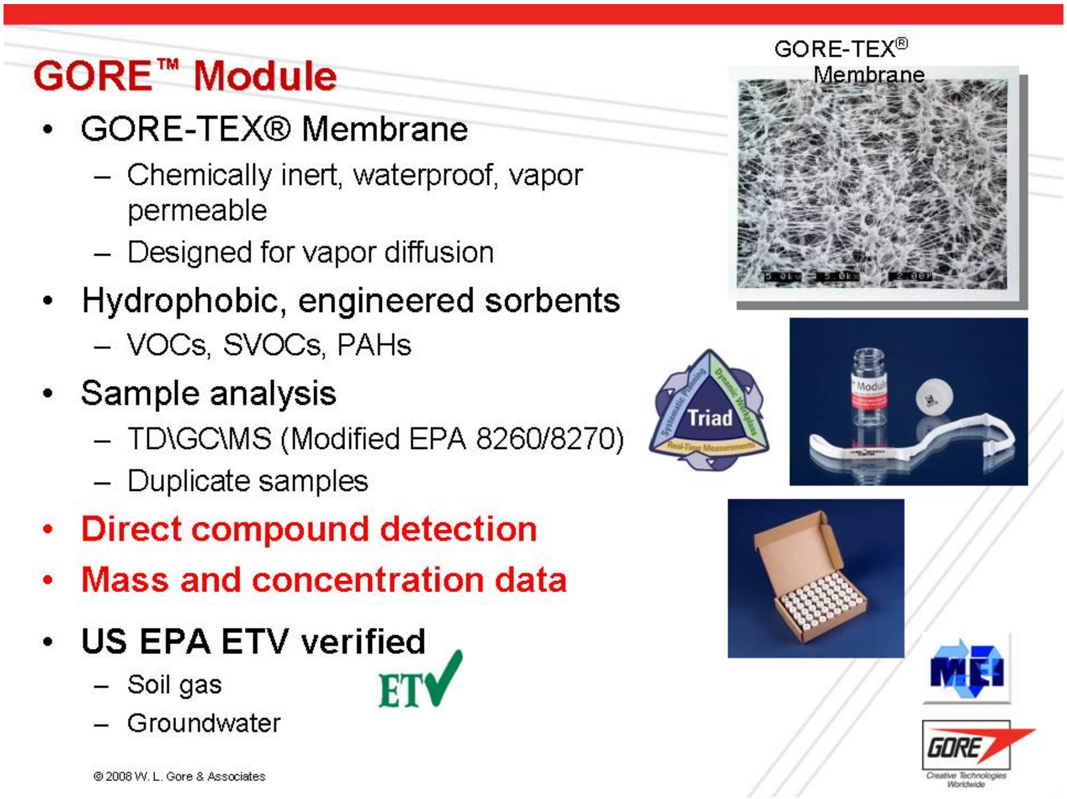
Common Applications for Passive Sampling

- Site assessment (Conceptual Site Models)
  - Rapid, high-resolution sampling
  - Shifts sampling from exploration to confirmation
  - Focuses more intrusive and expensive sampling
- Brownfields – property transfers
- Vapor intrusion
- Monitoring
  - Groundwater long-term
  - Site remediation
- Water sampling
  - **Sediment porewater;** ground- & surface water

*** - partial list**

Benefits of Passive Sampling

- Rapid, inexpensive, unobtrusive installation & retrieval
  - Minimal operator & field sampling error
  - Virtually no access restrictions
- Time-integrated sampling
  - Effective in low/high permeability - dry/moist soils
  - Sensitivity to low concentrations (ppb)
  - Sensitivity to VOCs, SVOCs, PAHs
  - Minimizes sampling variability
- No forced extraction
- No mechanical parts or connections
- No energy required
- Soil gas, sub-slab SG, air, water, sediment porewater



GORE™ Module

- GORE-TEX® Membrane
  - Chemically inert, waterproof, vapor permeable
  - Designed for vapor diffusion
- Hydrophobic, engineered sorbents
  - VOCs, SVOCs, PAHs
- Sample analysis
  - TD\GC\MS (Modified EPA 8260/8270)
  - Duplicate samples
- **Direct compound detection**
- **Mass and concentration data**
- **US EPA ETV verified**
  - Soil gas
  - Groundwater

GORE-TEX® Membrane

Installation in Soil Gas, Subslab Soil Gas & Air

Soil Gas

Slam bar

Hammer drill

Module insertion

Sample surface to any depth

Subslab Soil Gas

Sample to any depth

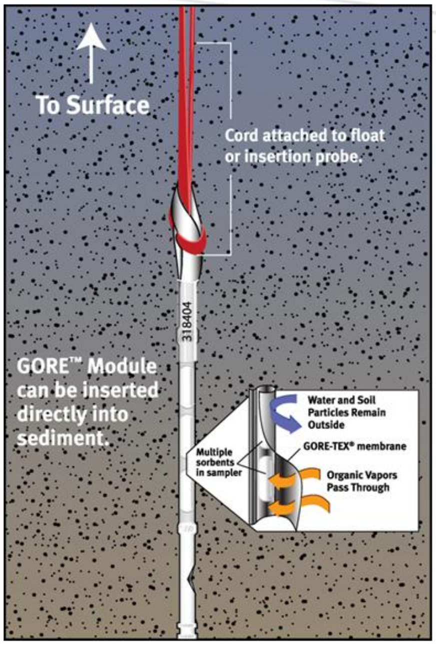
Angle beneath slab

Air

Crawlspace air

Indoor air

Installation in Sediment - Groundwater



Courtesy of Peregrine Ventures

Courtesy Marion Environmental

Site Characterization - Sediment Porewater Sampling

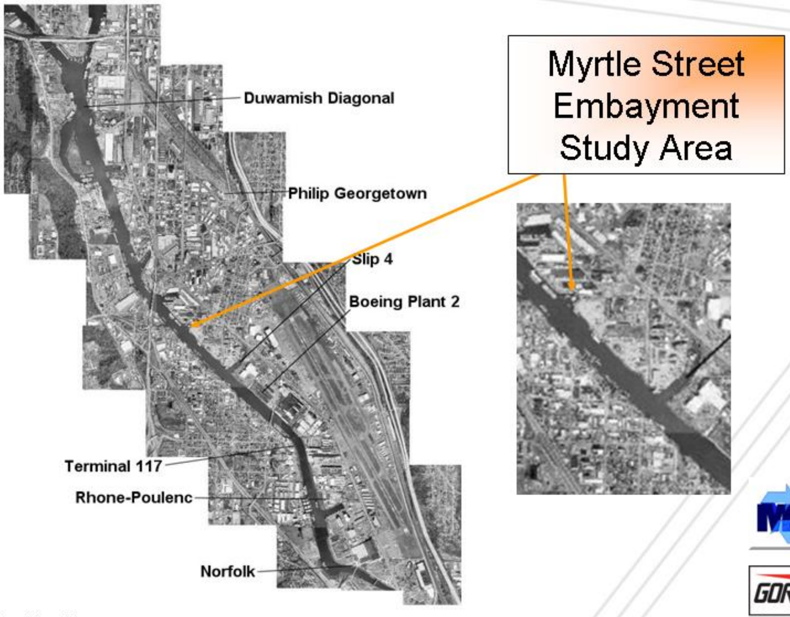
Lower Duwamish Waterway

Background

- Tidally influenced waterway
- Two overlapping discharging solvent plumes
- Shallow aerobic plume - mostly PCE and TCE
- Deeper anaerobic plume - mostly DCE and VC
- Groundwater concentrations >1000 times cleanup levels
- Identified seep concentrations >100 times cleanup levels
- Agencies' concern - "worst" groundwater may be discharging deep in waterway and polluting sediments

Site Characterization - Sediment Porewater Sampling

Lower Duwamish Waterway



Myrtle Street Embayment Study Area

Site Characterization - Sediment Porewater Sampling

Lower Duwamish Waterway, WA

The Problems

- Tides reverse groundwater gradient near discharge areas
  - Pronounced change in rivers and estuaries
- Saltwater wedges in formation
  - Focus less dense groundwater discharge upward above wedge
- “Seeps” of preferential discharge
  - Increasing gradients, differential permeabilities
  - Discharge below surface water, difficult to detect
- Difficult to delineate
  - Poor Conceptual Site Model (CSM)

Site Characterization - Sediment Porewater Sampling

Lower Duwamish Waterway

The Solution

- GORE^{TM} Modules
  - Easy-to-install by divers
  - Sample large areas, potential discharge areas and seeps
- Sample over multiple tide cycles
  - Time-integrated sampling
  - Tidal effect minimized due to sample design

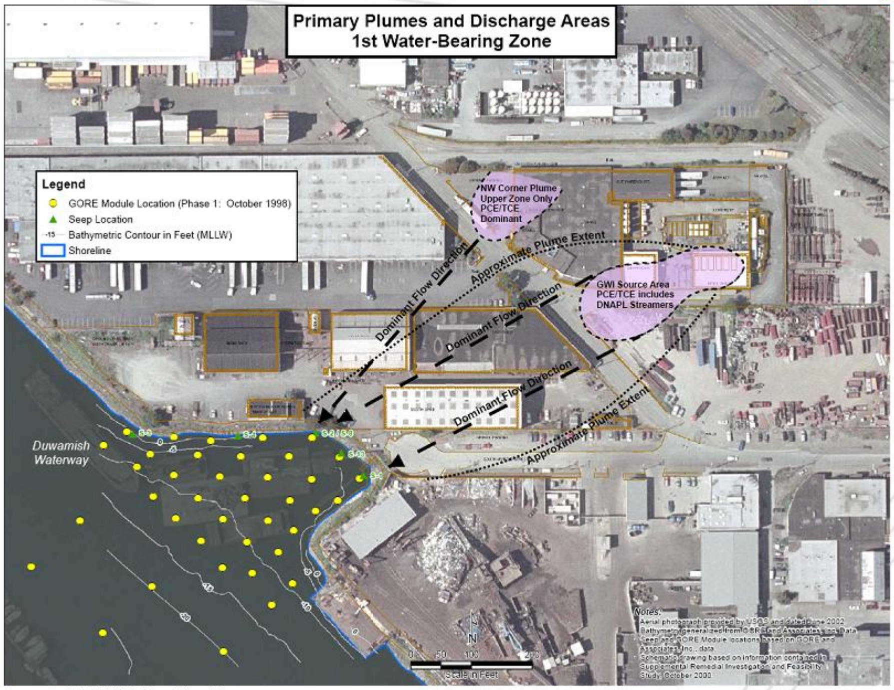
Site Characterization - Sediment Porewater Sampling

Lower Duwamish Waterway

Goals

- Map discharge areas easily and quickly
- Identify all seeps containing VOCs
- Demonstrate no VOC diffusion through embayment sediments
- Verify Conceptual Site Model
- Focus on subsequent sampling

Site Characterization - Sediment Porewater Sampling

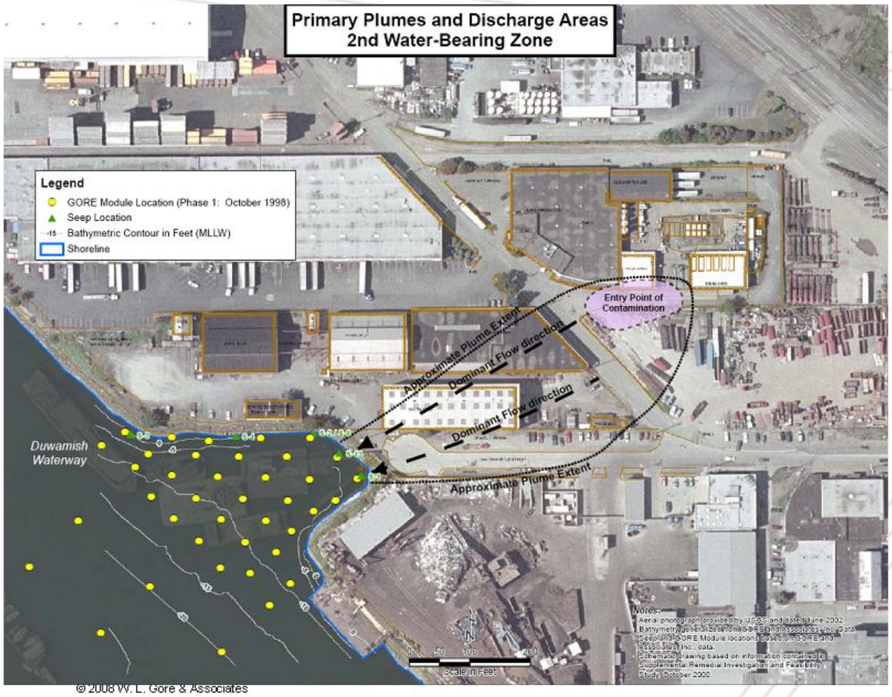


Notes:
- Aerial photograph provided by USGS and dated June 2002
- Bathymetry generalized from GSR and Associates, Inc. Data
- Seep and GORE Module locations based on GORE and Associates, Inc., data.
- Schematic drawing based on information contained in Supplemental Remedial Investigation and Feasibility Study, October 2000

© 2008 W. L. Gore & Associates

Creative Technologies Worldwide

Site Characterization - Sediment Porewater Sampling



Notes:
- Aerial photograph provided by USGS and dated June 2002
- Bathymetry generalized from GSR and Associates, Inc. Data
- Seep and GORE Module locations based on GORE and Associates, Inc., data.
- Schematic drawing based on information contained in Supplemental Remedial Investigation and Feasibility Study, October 2000.

© 2008 W. L. Gore & Associates

Creative Technologies Worldwide

Site Characterization - Sediment Porewater Sampling

Lower Duwamish Waterway

GORE^{TM} Survey

Phase 1: Embayment-wide

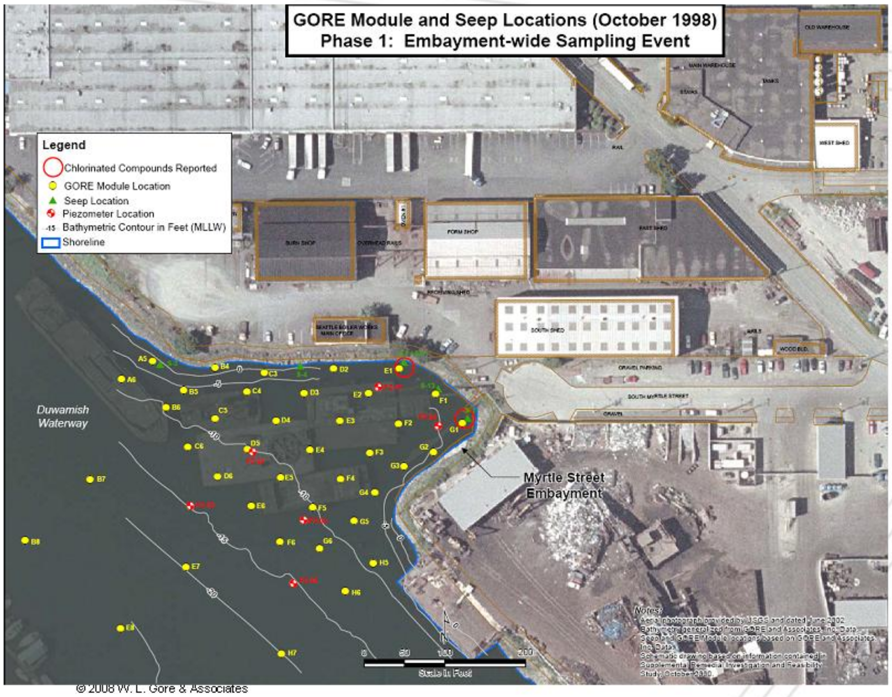
- 50 ft grid across embayment; chains; divers
- 12 to 18-inch insertion; rebar
- 48-hour deployment

Outcome:

- Identified new and expanded seep face near top of saltwater wedge
- Demonstrated lack of embayment discharge
- Confirmed discharge conceptual site model
  - Wedge effect

Creative Technologies Worldwide

Site Characterization - Sediment Porewater Sampling



Creative Technologies Worldwide

Site Characterization - Sediment Porewater Sampling

Lower Duwamish Waterway

GORE™ Survey

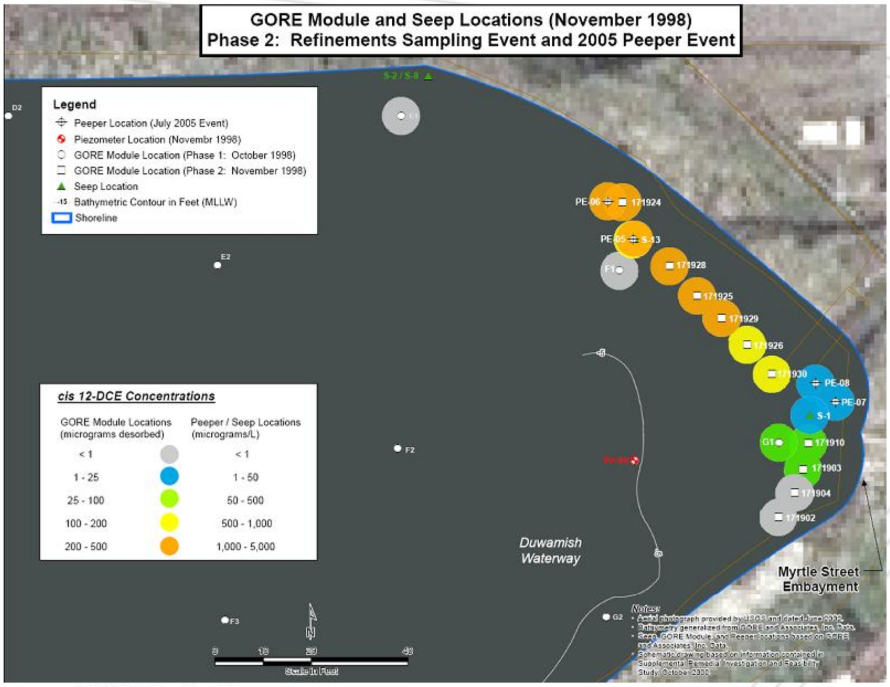
Phase 2: Refinements - Seeps

- 10 ft spacing along seep face
- Concurrent collection of sediment and grab samples

Outcome:

- Identified extent of seep face
- Identified location of seeps with maximum concentrations
- Discharge highly localized
  - Narrow vertical extent

Site Characterization - Sediment Porewater Sampling


GORE Module and Seep Locations (November 1998)
Phase 2: Refinements Sampling Event and 2005 Peeper Event

Notes:
- Aerial photograph provided by USGS and dated June 2002.
- Bathymetry generalized from GORE and Associates, Inc. Data.
- Seep, GORE Module, and Peeper locations based on GORE and Associates, Inc. Data.
- Schematic drawing based on information contained in Supplemental Remedial Investigation and Feasibility Study, October 2000.

Site Characterization - Sediment Porewater Sampling

Lower Duwamish Waterway

CONCLUSIONS

- GORE™ Survey - Objective and Goals met
  - Objective and goals met accurately
    - Rapid, critical, accurate sediment assessment
    - Saltwater wedge present
    - CSM redefined
  - Discharge via seeps, not generalized upwelling
    - Highly localized
    - Limited vertical extent, long horizontal extent

Site Characterization - Sediment Porewater Sampling

Tennessee Manufacturing Site

Background

- 10 acres, Adjacent to Tennessee River
- Operated 1961 – 1990
- Chemicals Stored
  - Tetrachloroethene (PCE) - Trichloroethene (TCE)
  - 1,1,1-Trichloroethane (111-TCA) - Dichloromethane (DCM)
  - Toluene - Styrene
- Geology = Prograded Floodplain Deposits
  - Land Surface → Bedrock =
  - Clay → Silt → Sand → Gravel → Bedrock

Site Characterization - Sediment Porewater Sampling

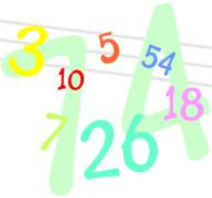
Tennessee Manufacturing Site

Goals

- Satisfy regulatory site assessment objectives in river
- Verify Conceptual Site Model
  - Generalized upwelling of VOCs into river?
- Map underwater discharge areas easily and quickly
- Focus on subsequent sampling, if necessary

Site Characterization - Sediment Porewater Sampling

Tennessee Manufacturing Site

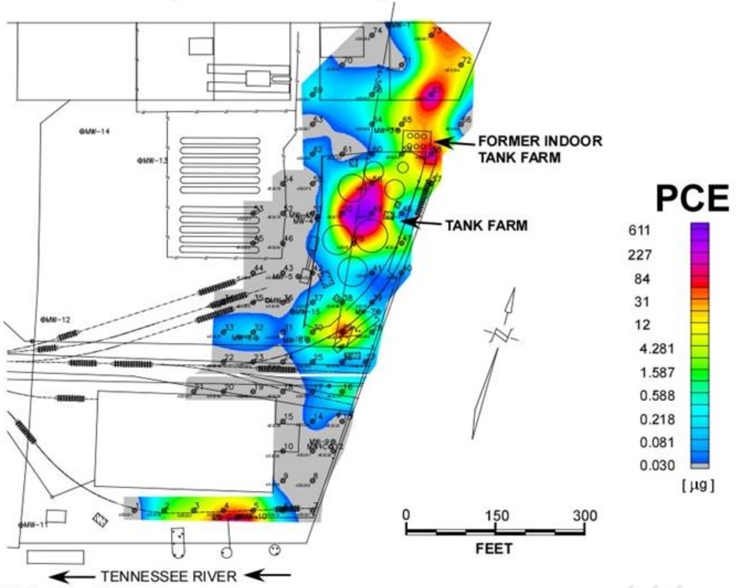


- GORE™ Survey – onshore – August 2004
  - Objective: Characterize subsurface contamination
  - 74 GORE™ Modules
  - ~20 day exposure
  - Chlorinateds, fuels observed
    - Correlated with onshore groundwater data
- GORE™ Survey – offshore – August 2007
  - 19 GORE™ Modules
  - 2-4 hour exposure
  - Upstream control modules
  - Chlorinateds observed in sediment porewater
    - Correlated with onshore GW data from MW-10

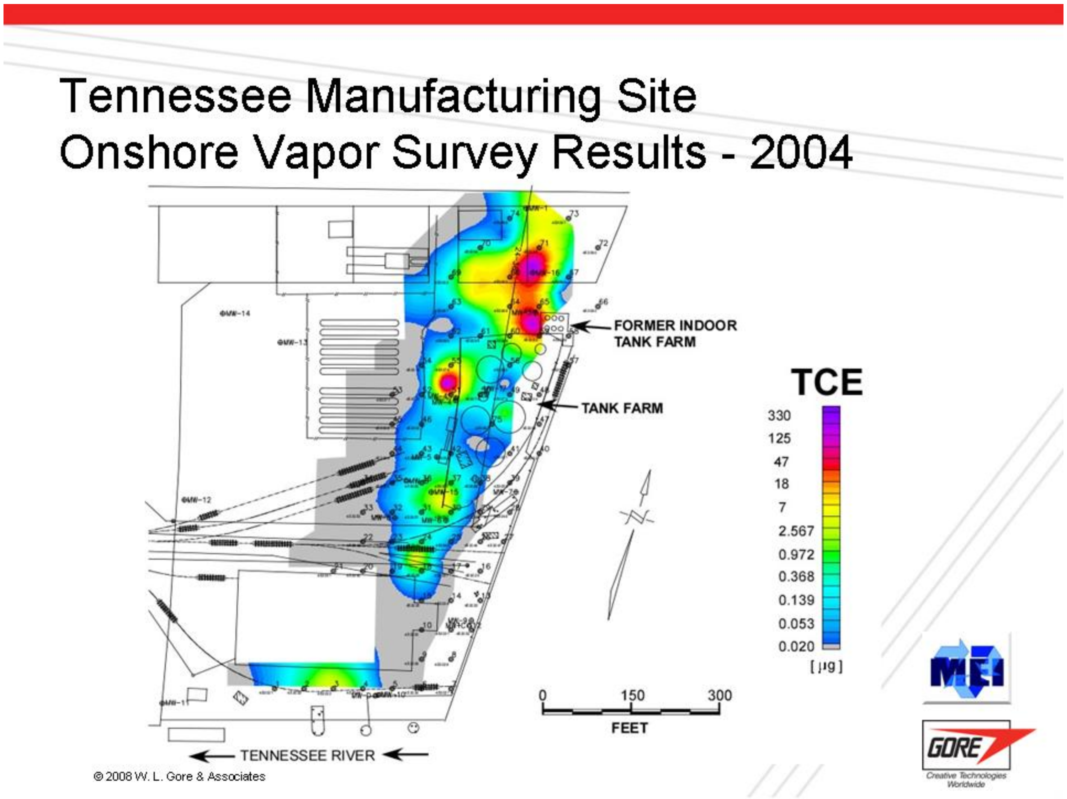
Tennessee Manufacturing Site

Creative Technologies Worldwide

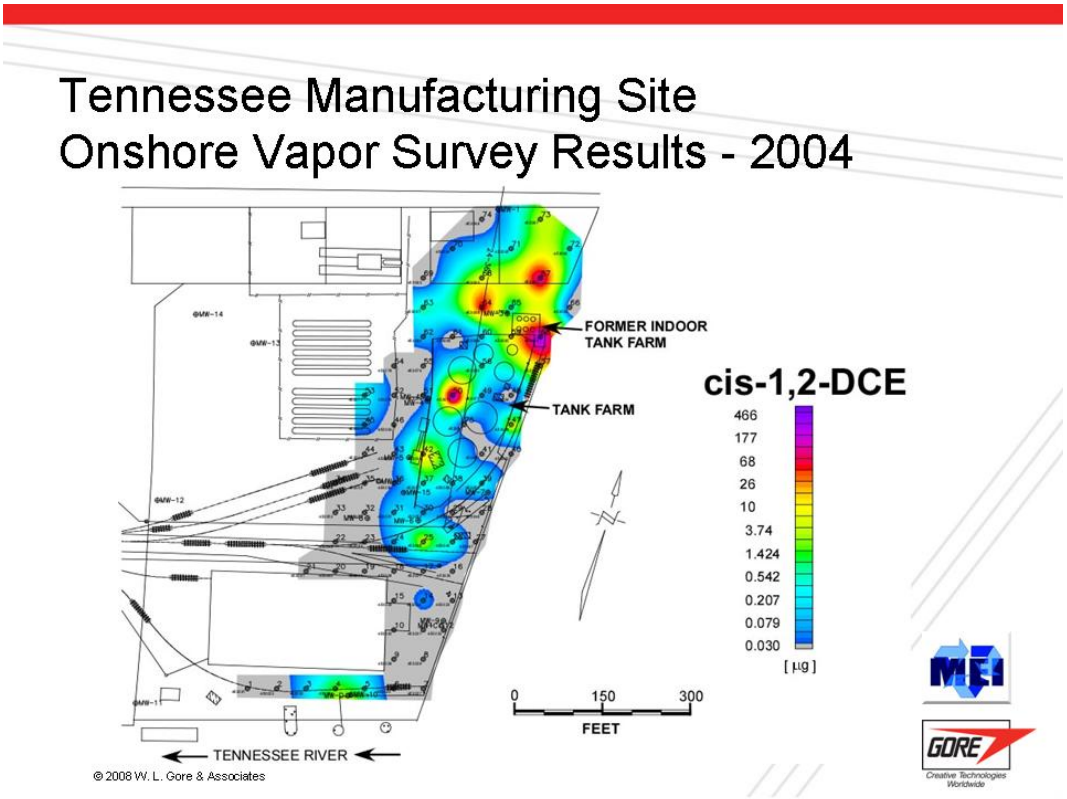
Tennessee Manufacturing Site
Onshore Vapor Survey Results - 2004



Creative Technologies Worldwide



Tennessee Manufacturing Site
Onshore Vapor Survey Results - 2004



Tennessee Manufacturing Site
Onshore Vapor Survey Results - 2004

Tennessee Manufacturing Site
Onshore Vapor Survey Results - 2004

Site Characterization - Sediment Porewater Sampling

Tennessee Manufacturing Site

- GORE™ Survey – Offshore – Installation/Retrieval
  - Diver installation
  - Underwater grid layout with string; Measured with cloth tape
  - Pilot insertion hole created with stainless lance
  - Module inserted into pilot hole with lance
  - Marked with string and float for retrieval

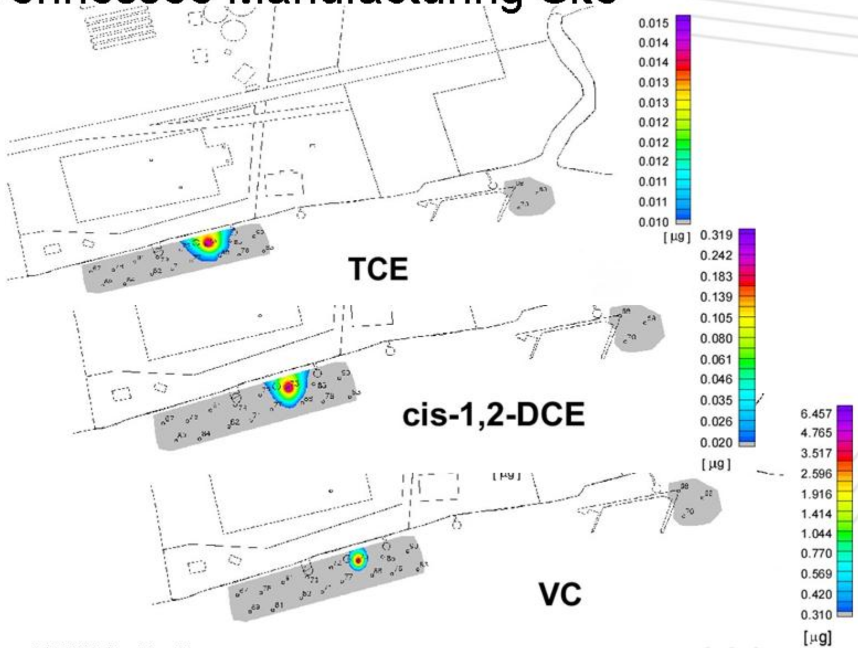
Site Characterization - Sediment Porewater Sampling

Tennessee Manufacturing Site

- GORE™ Survey – Offshore
  - Underwater locations GPS-verified at water surface
    - Diver-held survey rod
    - GPS from shore and boat

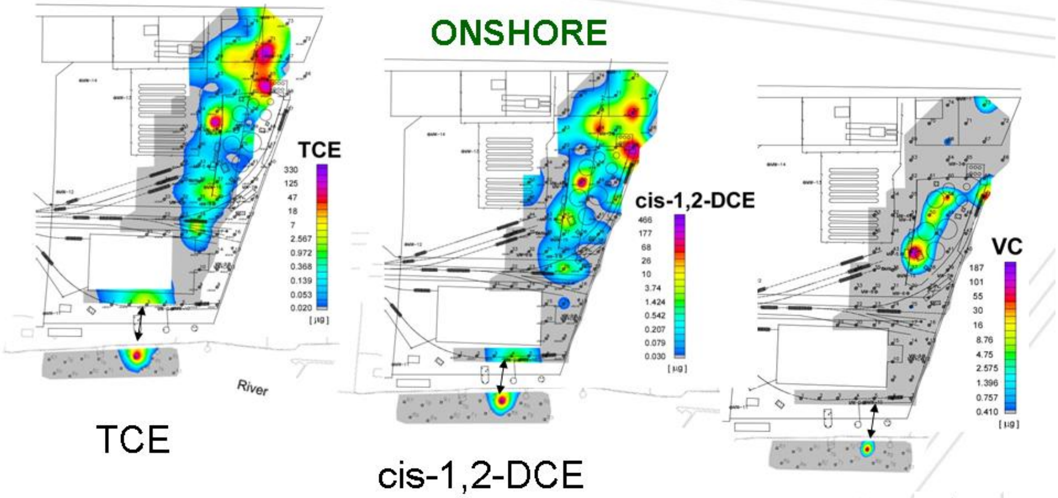
Site Characterization - Sediment Porewater Sampling

Tennessee Manufacturing Site



Site Characterization - Sediment Porewater Sampling

CORRELATION



ONSHORE

TCE

cis-1,2-DCE

VC

RIVER

Site Characterization - Sediment Porewater Sampling

Tennessee Manufacturing Site

CONCLUSIONS

- GORE™ Survey - Objective and Goals met
  - Objective and goals met accurately
    - Rapid, critical, accurate onshore and offshore sediment assessment
  - Regulatory assessment objectives met
  - Conceptual Site Model Revised
    - Localized seep of VOCs identified
    - No widespread upwelling into river
  - Client objective met

Conclusions

Passive sampling is…

- Simple
  - No mechanical parts
  - Easy to install on- & off-shore
  - Reduced field costs
- Effective
  - Low detection limits
  - Accurate
  - Focus further investigations
- Versatile
  - Soil gas
  - Subslab soil gas
  - Air
  - Water
- Sediment Porewater
  - Lower Duamish Waterway
  - Tennessee River

QUESTIONS?

Contact us:

- Jay Hodny

jhodny@wlgore.com

- Steve Wild

swild@marionenv.com

WE THANK
Teri A. Floyd
Floyd-Snider
Seattle, WA

Forensically Identifying Unique Sources of PCBs for a Large Sediment Characterization Project

Rock J. Vitale, CEAC, CPC – Environmental Standards, Inc.
Bryce E. Stearns – TestAmerica, Inc.
Kirk F. Young, PE – TestAmerica, Inc.

ABSTRACT

The characterization of polychlorinated biphenyls (PCBs) is generally performed based either on Aroclor patterns or on individual congeners. For a large river sediment project adjacent to an industrial site that was used for the manufacture of electrical cable during World War II, it was determined that residuals from manufacturing processes were not well characterized by an assessment of either Aroclors or PCB congeners. A method of analysis that provided homologue characterization of polychlorinated naphthalenes (PCNs) and polychlorinated terphenyls (PCTs) was developed and validated because of the need to definitively identify the sources of the PCBs. The characterization of PCBs by homologue group is not a new concept; of particular interest in this sediment characterization project, however, was the inclusion of PCTs and PCNs for source characterization.

INTRODUCTION

The characterization of PCBs has been historically performed based on matching the retention times of Aroclor patterns; it is becoming routine to characterize PCBs as their individual 209 congeners. Many environmental professionals tend to think of PCB Aroclors (*e.g.*, Aroclor-1248, Aroclor-1254) as formulations that were manufactured under very rigorous specifications. A number of manufacturing processes, however, produced and/or used PCB mixtures that do not conform well to an assessment based on Aroclor patterns. Furthermore, certain manufactured products cannot be properly characterized (in environmental samples) even with an assessment of PCB congeners. Manufactured mixtures contain a variety of other compounds, including polychlorinated naphthalenes (PCNs) and polychlorinated terphenyls (PCTs), that are not typically examined as part of current analyte lists.

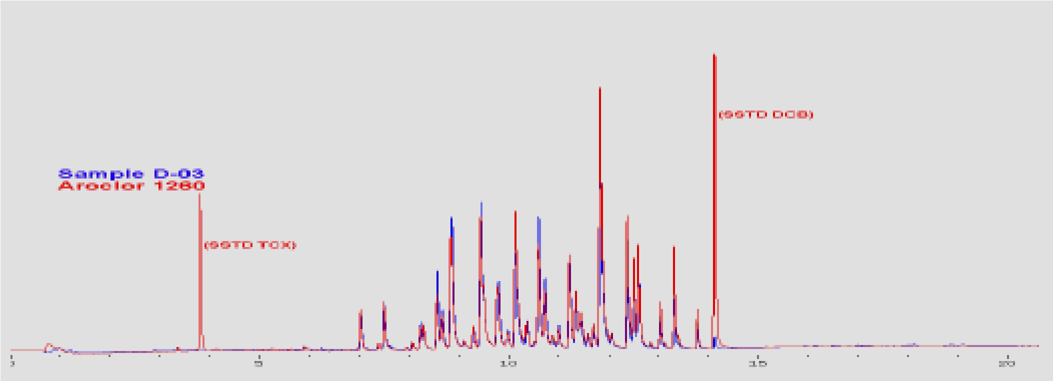
The former Anaconda Wire and Cable Company site in Hastings-on-Hudson, New York, provides an interesting case study. Between 1919 and 1977, the site was owned and operated by the Anaconda Wire and Cable Company (AWCC) for the manufacture of copper wire, lead shielded cable, high-voltage cable, and insulated wire. Beginning in the late 1930s, various PCB mixtures were used to saturate paper and asbestos-wrapped cable before the outer sheathing was applied. With the advent of World War II, the resources of key industries were applied to the war effort, resulting in two operators of the site. The objectives of the war-time operator were very specific relative to the production of cable for ship building at the Brooklyn Shipyard. The materials specifications for fireproof coatings changed, and the war-time operations at the site interactively worked with Monsanto in Anniston, Alabama, to design new insulation materials. These materials were specially synthesized mixtures of PCBs that were admixed with PCTs (in the form of Aroclor-5460) and PCNs (based on data that were generated), although the latter may have been an artifact of production.

TALE OF TWO SAMPLES

This section presents a “tale” of two samples that were collected at the site - each provided information as to its origin and the associated manufacturing process. The samples were originally analyzed in order to characterize the PCB constituents, and the analytical work was performed as many routine environmental investigations for which the investigators requested PCBs (as Aroclors) by GC/ECD analysis.

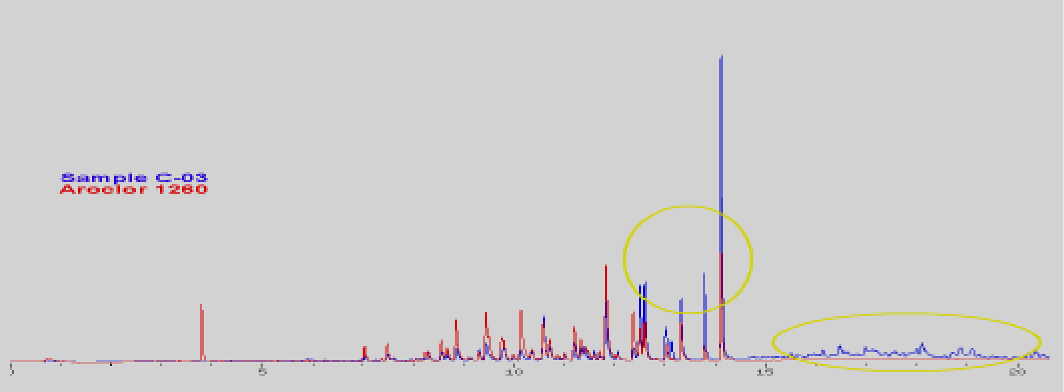
The two chromatographic views provided reflect what might typically be presented by a laboratory operation that is mindful of acquisition times and of maximizing the number of acquisitions in performing a routine Aroclor PCB analysis. These views reflect an acquisition of data that ends shortly after the elution of decachlorobiphenyl, which is the last eluting PCB congener (and also the PCB surrogate specified in Method 8082). The chromatogram of the first sample, identified as sample D-03, reflects PCB constituents that are well represented as a reasonably identified Aroclor-1260 pattern.

Figure 1. GC chromatogram of sample D-03 (reasonably identified Aroclor-1260 pattern)



The chromatogram of the second sample, identified as sample C-03, reflects PCB constituents that do not match an Aroclor-1260 pattern. Specifically, there is a high-end distortion of the Aroclor-1260 pattern and a number of later eluting constituents.

Figure 2. GC chromatogram of sample C-03 (high-end distortion of Aroclor-1260 with later eluting constituents)



In the Record of Decision for the site, the New York Department of Environmental Conservation (NYS DEC) made specific note of the fact that “the PCB mixture used at the site had a different chemical ‘fingerprint’ from routinely observed PCB Aroclors. As a result, sediment impacts attributable to the site can be distinguished from impacts originating upstream.” NYS DEC used the distinctly different chromatographic pattern of the PCBs, as characteristically represented in Figure 2, as the primary discriminator in its assessment relative to the origin of contamination in the local river system.

It is interesting to note that although it was known that the PCB mixtures used were unique in their formulation and that the NYS DEC used this fact as the discriminator, all references in the Record of Decision are to Aroclor-1260. These references indicate that the analytical work associated with the assessment had been performed in the context of routine analytical services, without the inclusion of either Aroclor-1262 or Aroclor-1268 in instrument calibration or in the analytical design.

Samples C-03 and D-03 were select samples from a site-wide sampling effort that primarily targeted sediments from drains within the system of buildings and wipes from walls and floors within the on-site buildings themselves. Sample C-03 represented a sample type that had considerable interest for the investigators, given what was known about the production aspect of the war-time operator. Of particular interest was the identification and characterization of halogenated constituents that were eluting well after decachlorobiphenyl.

With this knowledge and a review of the formulation records of the war-time operator, the investigators suspected the presence of PCTs as the later-eluting halogenated constituents in sample C-03 and believed that the responses in the later region of the chromatogram were evidence of that fact. The project laboratory secured a PCT analytical standard (Aroclor-5460) and evaluated the chromatogram produced from the analysis of that standard against the chromatograms from the analysis of sample C-03 and from the analysis of other samples in the sampling initiative.

Additionally, the project laboratory secured other analytical PCT standards (*viz.*, Aroclor-5432 and Aroclor-5442) and chromatographed those standards in order to more fully understand the characteristics of each of the common PCT Aroclors.

The GC/ECD analysis was sufficient to provide for the initial assessment; however, there was a need for a definitive analysis that that would generate defensible differentiating data in accordance with the project team's objectives.

With these objectives in mind, the project laboratory moved the analytical design to a GC/MS form of analysis in order to take advantage of the dimensionality of the mass detector and more importantly to definitely differentiate PCT mass ions from PCB mass ions. The developed PCT method provided for a low-resolution GC/MS (SIM) analysis that included a quantitative characterization of total PCBs by chlorination level and a quantitative characterization of total PCTs by Aroclor.

Later in the investigative process, the question was raised as to whether polychlorinated naphthalenes (PCNs) were present as constituents of samples that were collected from the site. The project laboratory revisited the full-scan GC/MS acquisitions from the method development work in order to provide a preliminary assessment relative to the qualitative presence of PCNs.

CONCLUSIONS

Although there was agreement with the conclusion of the NYS DEC Decision of Record that the site was the origin of contamination in the local river system, the investigative evaluation performed was critical to definitively link the contamination to the war-time operation. Specifically, the presence of Aroclor-1260 indicated a possible relationship to the operation of the facility in the pre-war operation of the facility; the presence of PCTs and PCNs in association with a highly chlorinated mixture of PCBs indicated a possible relationship to the war-time operation of the facility that continued into the post-war period.

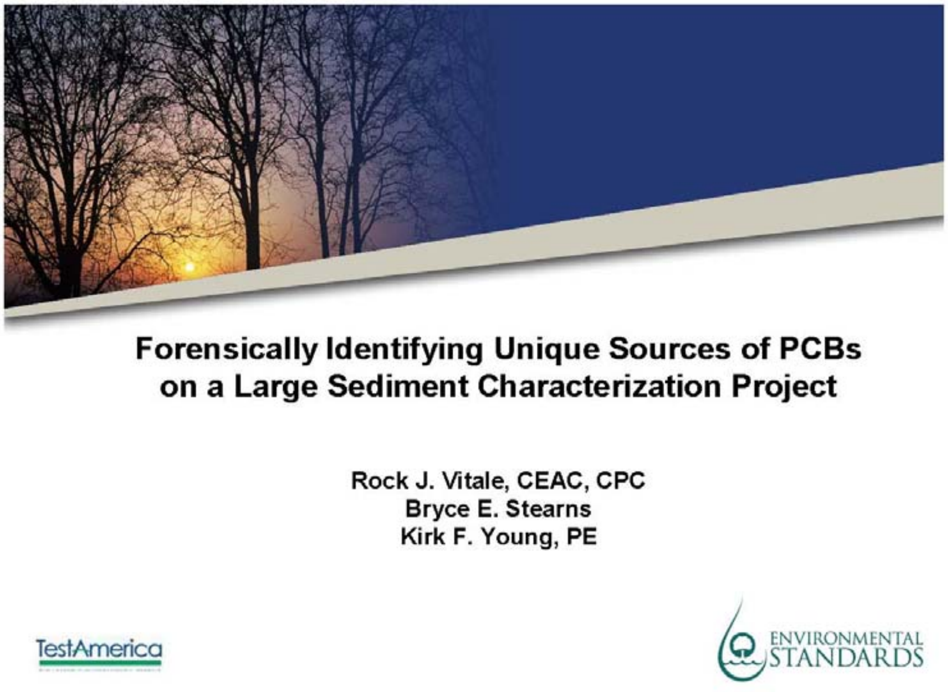
This forensic evaluation could have significant relevance to other industrial sites or other situations when "weathered" PCBs are observed and there are multiple potentially responsible parties. The logic could be applied to define the timelines of industrial use at a particular site involving different operators, different operations, and different manufactured products in the characterization of land-based contaminants or sediment contamination in local river systems.

With regard to aspects of site remediation work, the more that is known about a facility's original operations, the products used, and the products manufactured, the better the assessment of the source of the pollutants from a liability perspective that can be made. Although PCB characterization alone may currently provide adequate information for decisions relative to disposal, the associated presence of PCTs and PCNs in high concentrations may represent an unknown, but very real, future liability.

The conclusions of the project team's case study are presented below.

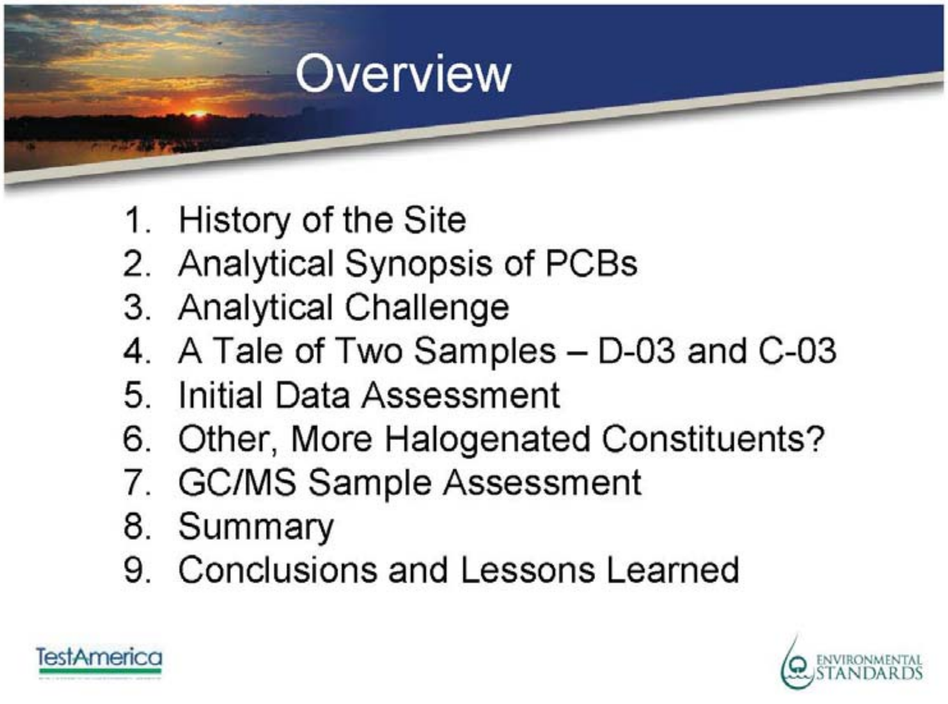
- Do not approach PCB contamination issues without considering the possibility of additional chlorinated contaminants.
- Thoroughly research site history and be prepared to explore options to differentiate historic use because different industrial processes use PCBs, PCTs, and PCNs in varied ways and, potentially, in varied combinations.
- Research the constituents at issue and think more broadly than PCBs in the context of Aroclors or in the context of congeners.

- Be mindful of the analytical design and the need for definitive and defensible data.
- When approaching an investigation for which PCBs are likely to drive remediation, investigators should be cognizant of the following:
- Routine analytical services for GC/ECD PCB characterization may not provide a characterization of the more highly chlorinated PCB Aroclors (Aroclor-1262 and Aroclor-1268).
- Routine analytical services for GC/ECD PCB characterization may not provide sufficiently for a consideration of the possible presence of PCTs given the need for a longer data acquisition time.
- Routine analytical services for GC/ECD PCB characterization will not provide for earlier eluting PCTs, even though the elution of these PCTS would be consistent with the elution of the PCB constituents; the same is true for PCNs.
- Specialized analytical services based on GC/ECD technology may not serve well as a definitive approach in evaluating complex mixtures. Low-resolution GC/MS technology allows for definitive qualitative assessments and provides a sound basis for a quantitative analysis and sensitivity that approximates that of GC/ECD (in selective ion monitoring mode).
- Instrument responses to Aroclor PCTs can be misleading insofar as Aroclor PCTs have a generally lower response than Aroclor PCBs at the same concentration. A lower response is particularly true for Aroclor-5460, which is less differentiated in its chromatographic aspect.



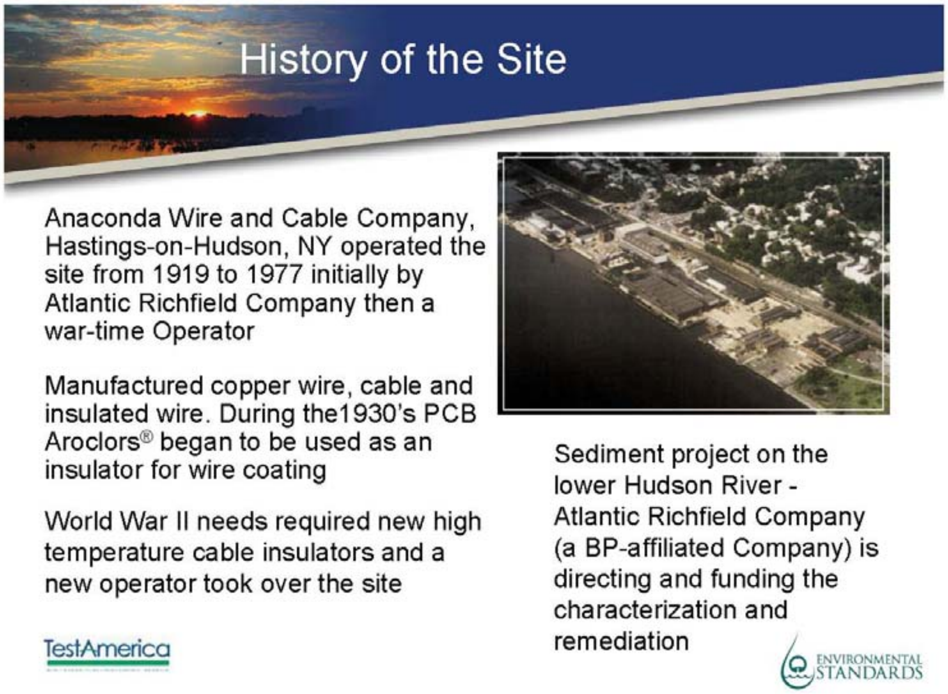
Forensically Identifying Unique Sources of PCBs on a Large Sediment Characterization Project

Rock J. Vitale, CEAC, CPC
Bryce E. Stearns
Kirk F. Young, PE



Overview

1. History of the Site
2. Analytical Synopsis of PCBs
3. Analytical Challenge
4. A Tale of Two Samples – D-03 and C-03
5. Initial Data Assessment
6. Other, More Halogenated Constituents?
7. GC/MS Sample Assessment
8. Summary
9. Conclusions and Lessons Learned



History of the Site

Anaconda Wire and Cable Company, Hastings-on-Hudson, NY operated the site from 1919 to 1977 initially by Atlantic Richfield Company then a war-time Operator

Manufactured copper wire, cable and insulated wire. During the1930's PCB Aroclors® began to be used as an insulator for wire coating

World War II needs required new high temperature cable insulators and a new operator took over the site

Sediment project on the lower Hudson River - Atlantic Richfield Company (a BP-affiliated Company) is directing and funding the characterization and remediation

TestAmerica

ENVIRONMENTAL STANDARDS

History of the Site (Cont.)

- During the World War II operations came the introduction of new and variable Aroclor® formulations that defined that era of operation and created a timeline by which the source of Aroclor® "fingerprinting" could be established
- Specific Aroclor® formulations were provided to the Site by Monsanto Company of Anniston, Alabama
  - Even today, many environmental professionals think that Aroclors® were manufactured under very rigorous specifications by chlorinating biphenyl
- Aroclor® formulations used at the Site contained more than just PCB congeners
  - Many of those additional chlorinated compounds do not appear on any of today's routine analyte lists

TestAmerica

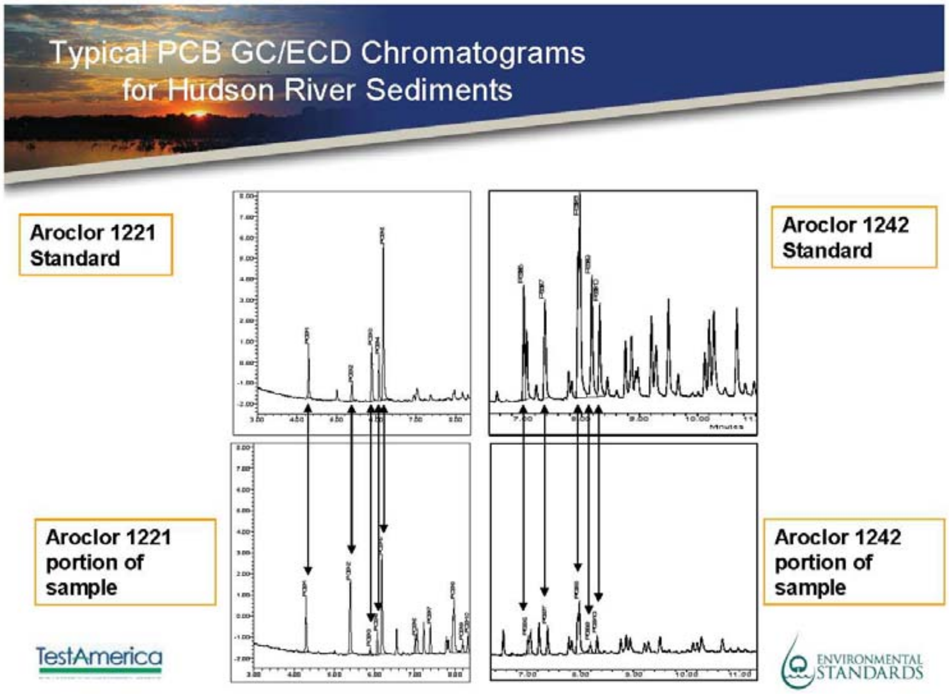
ENVIRONMENTAL STANDARDS

Analytical Synopsis of PCBs

- Site characterization is typically based on PCB Aroclor® evaluation which is most commonly performed (as Aroclors®) by GC/ECD
- Aroclor® are complex commercial formulations of many individual PCB congeners (*e.g.,* Aroclor 1248 has on average 48% of the biphenyl ring chlorinated)
- Aroclor® identifications are assigned by "pattern" matching between samples and Aroclor® standards on a GC/ECD

TestAmerica

ENVIRONMENTAL STANDARDS



Typical PCB GC/ECD Chromatograms for Hudson River Sediments

Aroclor 1221 Standard

Aroclor 1242 Standard

Aroclor 1221 portion of sample

Aroclor 1242 portion of sample

TestAmerica

ENVIRONMENTAL STANDARDS

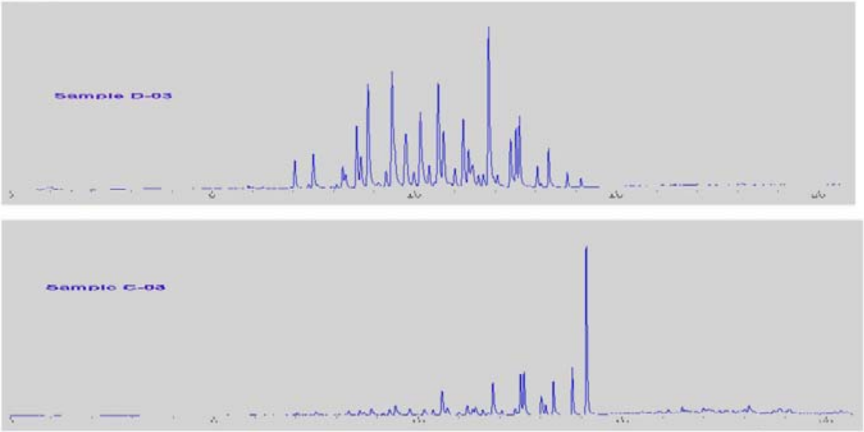
The Tale of Two Samples

- Two sample types were identified that were found to be generally representative of the site
- Each sample was profoundly unique in its chromatographic composition
- All samples were initially characterized using routine PCB methodology (Method 8082)
- Many Site samples were reported to contain PCB Aroclors
- So about those two Site samples…

TestAmerica

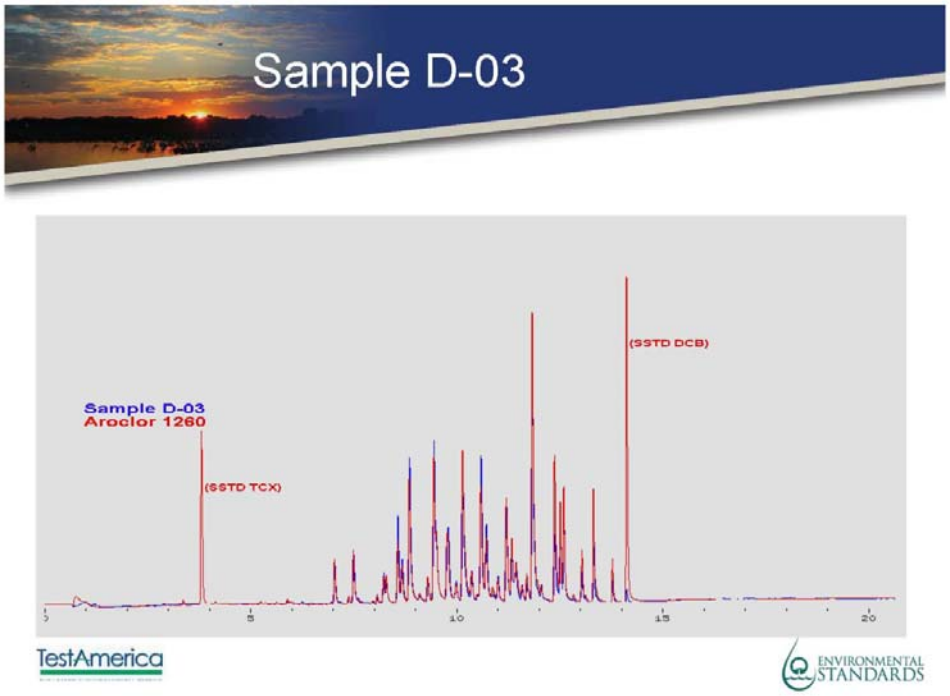
ENVIRONMENTAL STANDARDS

Samples D-03 and C-03

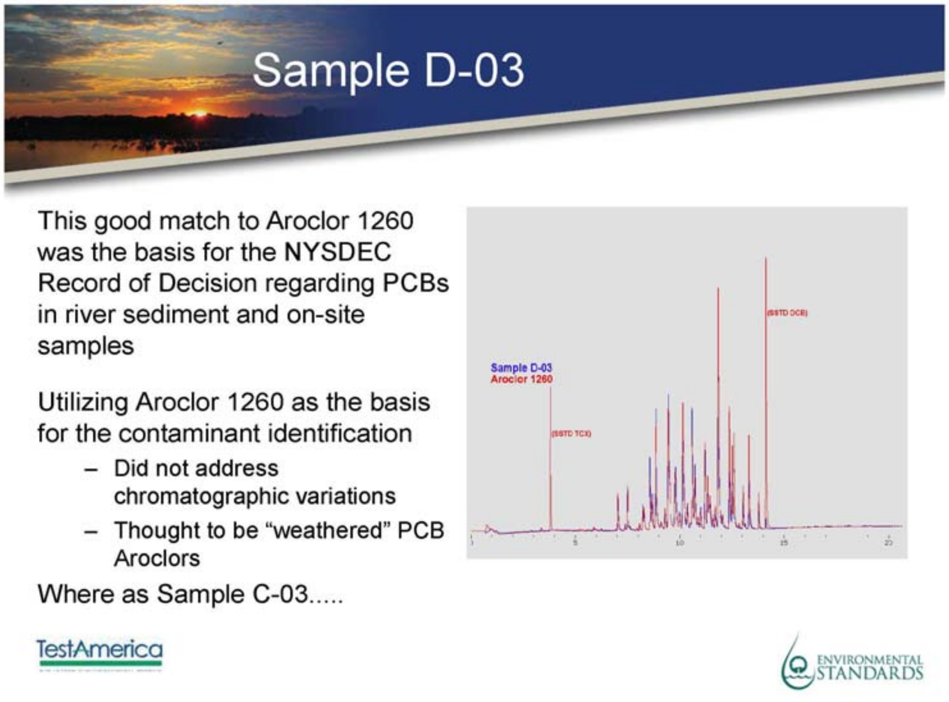


TestAmerica

ENVIRONMENTAL STANDARDS



Sample D-03



Sample D-03

This good match to Aroclor 1260 was the basis for the NYSDEC Record of Decision regarding PCBs in river sediment and on-site samples

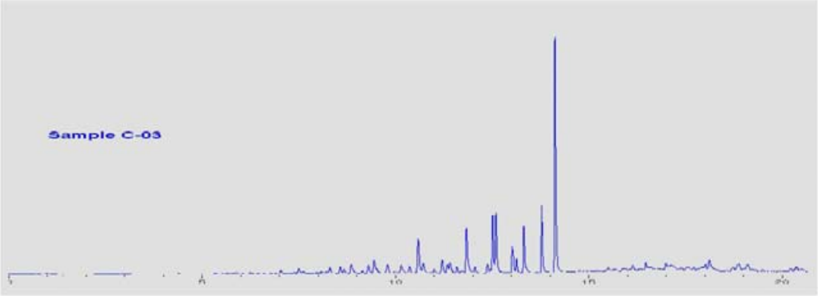
Utilizing Aroclor 1260 as the basis for the contaminant identification

- Did not address chromatographic variations
- Thought to be “weathered” PCB Aroclors

Where as Sample C-03.....

Sample C-03

Exhibited a more complex chromatogram



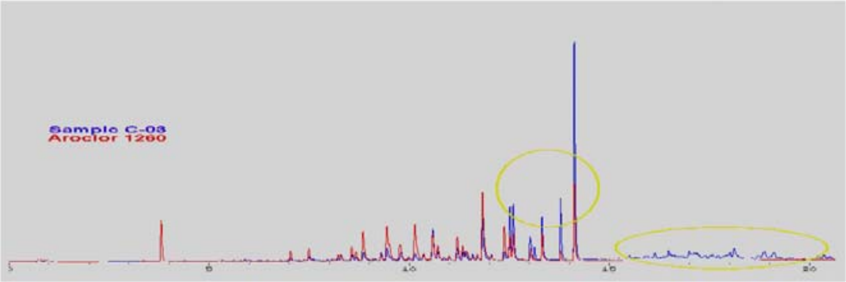
TestAmerica

ENVIRONMENTAL STANDARDS

Sample C-03

This sample appeared to contain higher halogenated, multi-component constituents versus Aroclor 1260

- Was it weathered PCBs or additional non-PCB components?



TestAmerica

ENVIRONMENTAL STANDARDS

Initial Data Assessment

- Routine SW-846 8082 PCB analyses did not fully represent all sample component information, particularly later eluting constituents
- The investigation team suspected components eluting after decachlorobiphenyl (current Method 8082 surrogate) were more highly halogenated species
- The extended analytical runtimes provided a broader scope of the actual sample characterization

TestAmerica

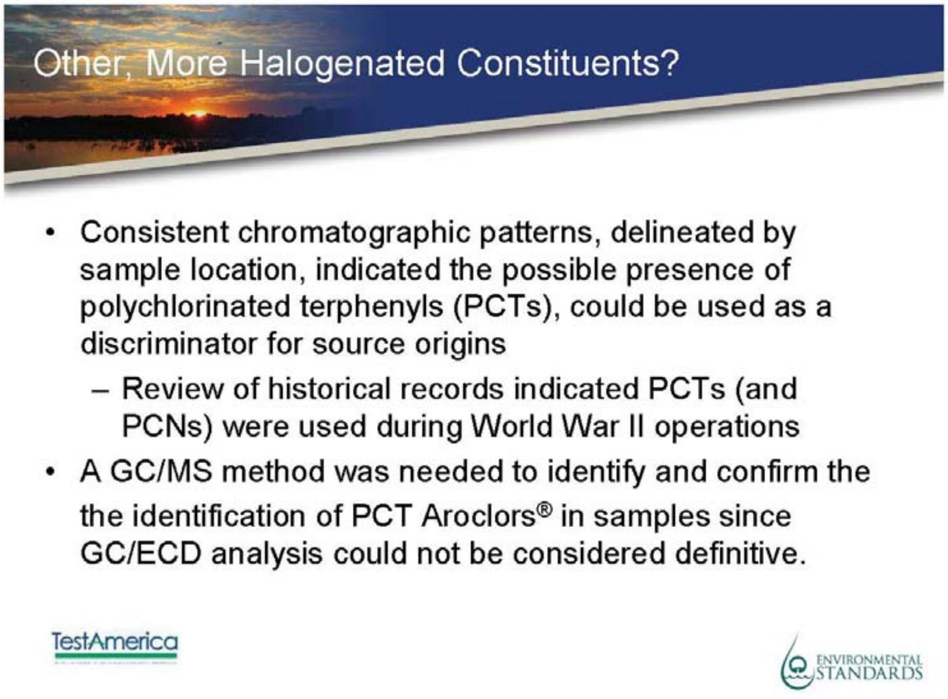
ENVIRONMENTAL STANDARDS

Analytical Challenge

- A better understanding of Aroclor® formulations used for manufacturing products used for different purposes seemed to be in order
- GC/ECD analysis for Aroclor® *may* not be appropriate
  - Environmental alteration (ex., volatilization or microbial dechlorination) – lack of clear pattern match leads to "inaccurate" reporting of PCB Aroclors
    - Inaccurate quantitation and qualitative identification
- There was a clear need for enhanced techniques for assessing complex samples with improved mechanisms for defining timelines of Aroclor® use

TestAmerica

ENVIRONMENTAL STANDARDS

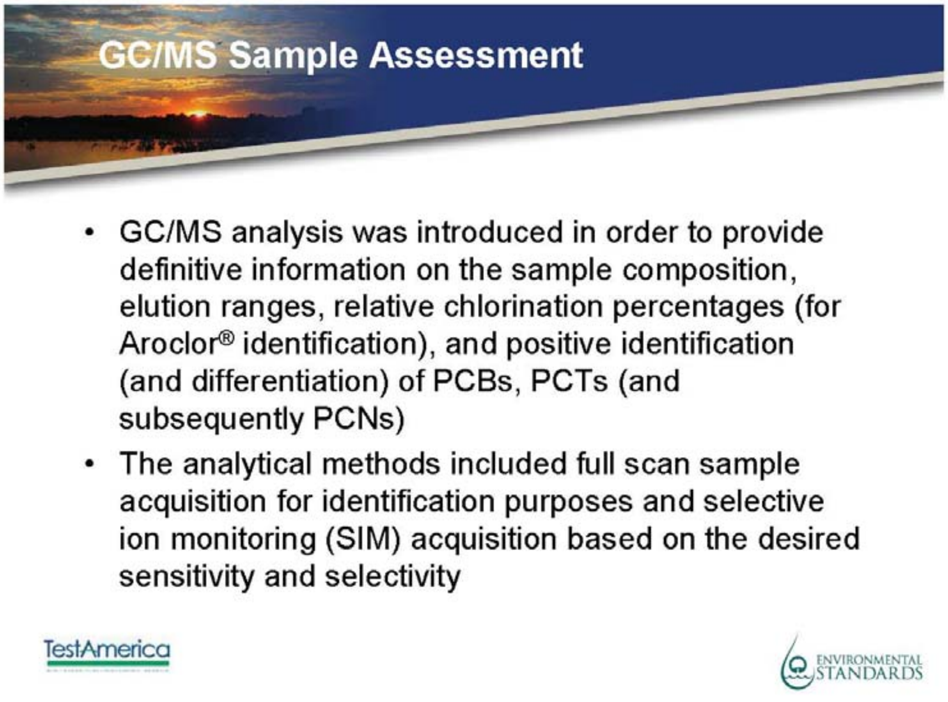


Other, More Halogenated Constituents?

- Consistent chromatographic patterns, delineated by sample location, indicated the possible presence of polychlorinated terphenyls (PCTs), could be used as a discriminator for source origins
  - Review of historical records indicated PCTs (and PCNs) were used during World War II operations
- A GC/MS method was needed to identify and confirm the the identification of PCT Aroclors® in samples since GC/ECD analysis could not be considered definitive.

TestAmerica

ENVIRONMENTAL STANDARDS

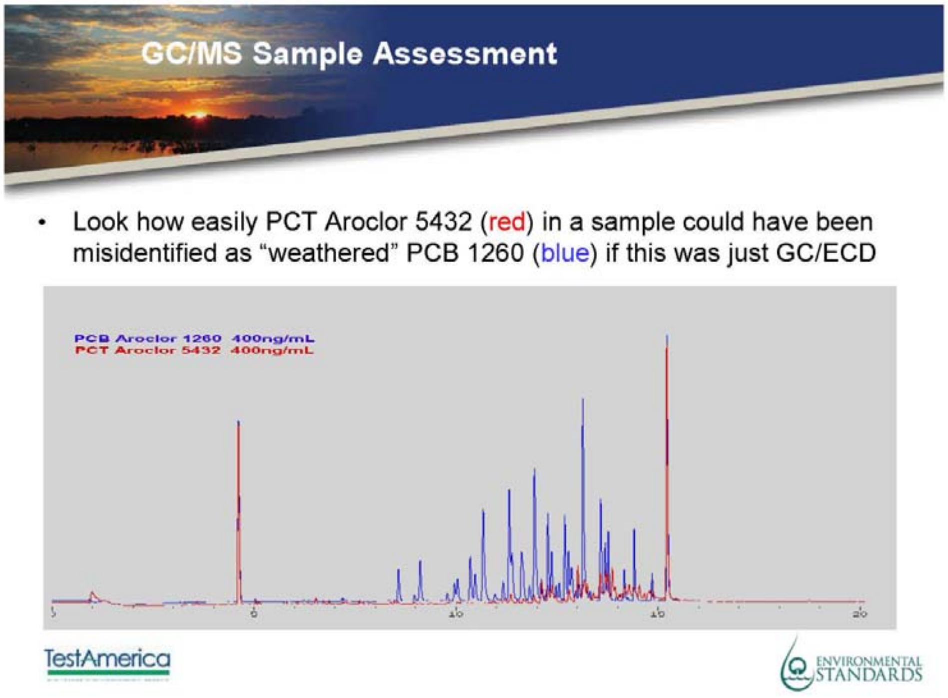


GC/MS Sample Assessment

- GC/MS analysis was introduced in order to provide definitive information on the sample composition, elution ranges, relative chlorination percentages (for Aroclor® identification), and positive identification (and differentiation) of PCBs, PCTs (and subsequently PCNs)
- The analytical methods included full scan sample acquisition for identification purposes and selective ion monitoring (SIM) acquisition based on the desired sensitivity and selectivity

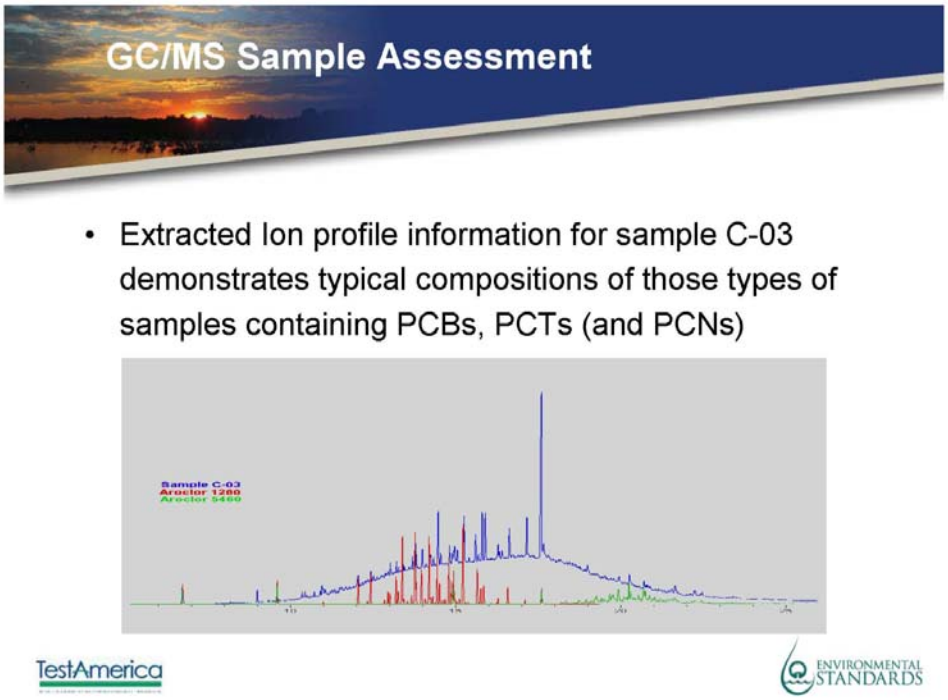
TestAmerica

ENVIRONMENTAL STANDARDS



GC/MS Sample Assessment

- Look how easily PCT Aroclor 5432 (red) in a sample could have been misidentified as "weathered" PCB 1260 (blue) if this was just GC/ECD

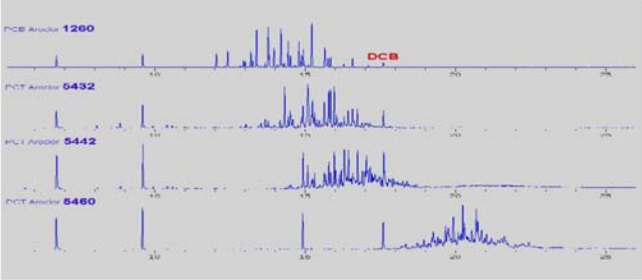


GC/MS Sample Assessment

- Extracted Ion profile information for sample C-03 demonstrates typical compositions of those types of samples containing PCBs, PCTs (and PCNs)

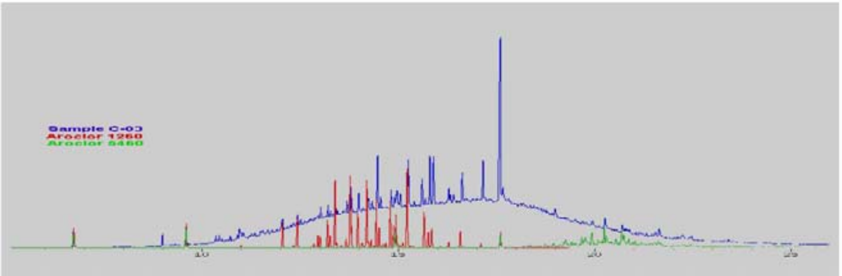
GC/MS Sample Assessment

- Lower level PCTs were evaluated to determine their potential for co-elution with PCB patterns, particularly those of PCB Aroclor 1262 and 1268



GC/MS Sample Assessment

- Mass spectral profiles help define elution ranges for the PCBs and PCT patterns encountered in Site samples.
- These evaluations confirmed PCT Aroclor 5460 as the primary PCT constituent in samples collected from certain Site locations

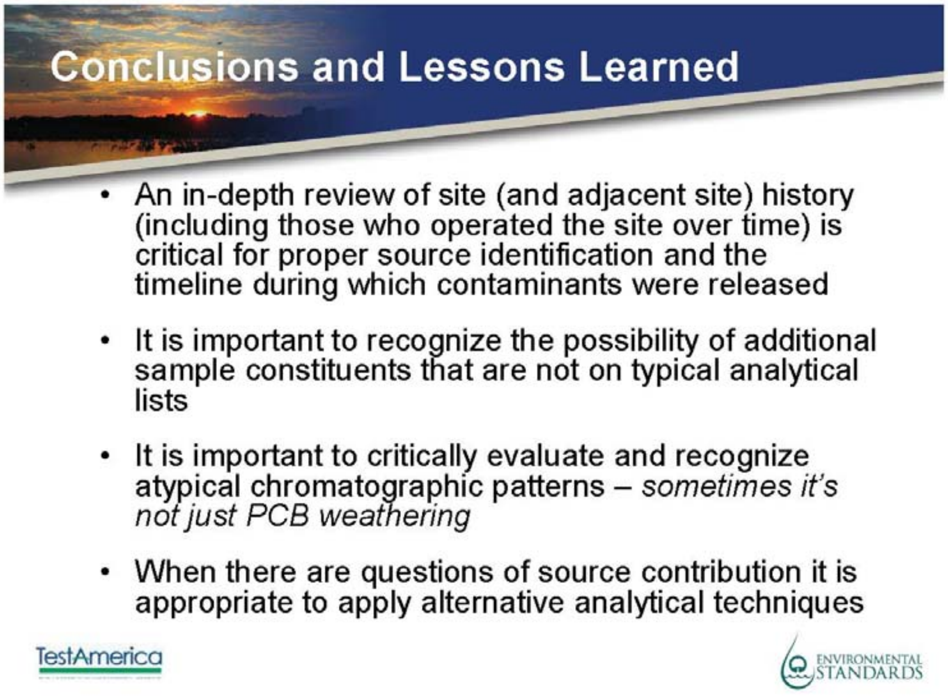


GC/MS Sample Assessment

- GC/MS full scan analysis was also used for evaluation of site samples for the presence of PCNs which seemed to mirror those samples that contained PCTs.
- Extracted ion current profiles (EICPs) and comparison to mass spectral libraries provided sufficient mass spectral confirmation for PCNs in those site samples that contained PCTs

Summary

- Characterization of Aroclor 5460 as the primary PCT constituent in select Site samples, in addition to the closely matching PCB patterns of Aroclor 1262 and 1268, helped fingerprint those areas of the Site that contained material specific to operations during World War II.
- GC/MS evaluation of samples allowed the investigative team to confirm both, the component species, and concentrations, with a higher degree of confidence than that could be derived from GC/ECD analysis alone.



Conclusions and Lessons Learned

- An in-depth review of site (and adjacent site) history (including those who operated the site over time) is critical for proper source identification and the timeline during which contaminants were released
- It is important to recognize the possibility of additional sample constituents that are not on typical analytical lists
- It is important to critically evaluate and recognize atypical chromatographic patterns – *sometimes it's not just PCB weathering*
- When there are questions of source contribution it is appropriate to apply alternative analytical techniques

TestAmerica

ENVIRONMENTAL STANDARDS

Thank You

Rock J. Vitale, CEAC, CPC
Valley Forge, PA
www.EnvStd.com
RVitale@EnvStd.com
610-935-5577

Bryce E. Stearn
Burlington, VT
www.testamericainc.com
Bryce.Stearn@testamericainc.com
802–660-1990

Kirk F. Young, PE
Burlington, VT
www.testamericainc.com
Kirk.Young@testamericainc.com
802–660-1990

TestAmerica

ENVIRONMENTAL STANDARDS

Interlaboratory Comparison Study of Measurement of Polychlorinated Biphenyl (PCB) Congeners from Sediment Samples with High Resolution (HRMS) and Low Resolution Mass Spectrometry (LRMS)

Jaana M.H. Pietari; Exponent Inc., 15375 SE 30th Place, Bellevue, WA 98007
Wayne J. Whipple; U.S. Environmental Protection Agency, Region 5 Chicago Regional Laboratory, 536 S. Clark St., Chicago, IL 60605; 312-353-9063; whipple.wayne@epa.gov

ABSTRACT

We designed an inter-laboratory comparison study to investigate the applicability of performance-based measurements for PCB congener analysis from sediments. We developed a method for PCB congener analysis employing low resolution mass spectrometry (LRMS) using two different ionization techniques. Electron impact (EI) ionization appeared to be more suitable for the measurement of Total PCBs as homologue groups, while negative chemical ionization (NCI) with methane as reagent gas would be suitable to measure dioxin-like PCB congeners from sediment samples. For the inter-laboratory study, we extracted sediment samples containing low, medium and high levels of PCBs, and shipped homogenized extracts for the analysis of select PCB congeners and/or Total PCBs to 10 participating government, academic and commercial laboratories. The laboratories analyzed the samples using either high resolution mass spectrometry (HRMS) or LRMS according to their own standard operating procedures (SOPs).

INTRODUCTION

The measurement of polychlorinated biphenyls (PCBs) is still a challenge for the analytical chemist. Despite being banned in the mid-1970s, PCBs are still part of many sediment cleanup projects. The successes of these projects largely depend on the chemical characterization of the contaminated sediments. Currently, the most widely used analytical tool for measuring PCBs is the Aroclor analysis (EPA Method 8082; 1), where the PCB congener profile of the sample is compared to that of a commercial Aroclor standard. The Aroclor measurement does not account for the potential changes in the PCB congener distribution profile resulting from environmental processes such as microbial degradation, transport and uptake into aquatic organisms. Moreover, Aroclor analysis does not allow the measurement of dioxin-like PCB congeners, which would aid risk assessment. A current state-of-art method, PCB congener analysis with high resolution gas chromatography (HRGC) combined with HRMS (EPA Method 1668; 2), provides more accurate and realistic analysis of the amount of PCBs in environmental samples in addition to the measurement of dioxin-like PCB congeners. The drawback of this method is that it is costly requiring expensive instrumentation, standards and maintenance. Further, the HRMS instruments are not necessarily widely available in EPA laboratories.

PCB congener methods employing cheaper and more widely available LRMS with different ionization techniques may allow for comparable data under certain conditions. LRMS has been used to quantify PCB congeners as homologue groups (3); however, it is not often used to quantify individual PCB congeners. Moreover, there is little information available on the comparability and interchangeability of PCB congener methods between LRMS and HRMS.

The use of performance-based measurements allows a greater flexibility for the analytical laboratory and the project planner to select the most appropriate analytical method in terms of cost and efficiency, and to utilize the most current technology to meet project specific data quality objectives. Therefore, the objective of our study was to develop a method for PCB congener analysis with LRMS employing different ionization methods, namely electron impact ionization (EI) and negative chemical ionization (NCI) using methane reagent gas. In addition, we conducted an inter-laboratory comparison study in partnership with 10 academic, commercial and government laboratories to demonstrate the applicability of performance-based measurements for PCB congener analysis. This presentation will discuss a study that was planned to investigate the applicability of performance-based measurements for the analysis of PCBs from sediment samples. Specifically, we will discuss the method development for PCB congener analysis utilizing LRMS, and the inter-laboratory study design and implementation, which compares PCB congener analyses with LRMS methods and HRMS.

MATERIALS AND METHODS

Chemicals

A PCB standard mixture containing 28 individual PCB congeners ranging from di- to decachlorinated PCB congeners was obtained from Accustandard (New Haven, CT). This standard included 12 dioxin-like congeners and several congeners considered to be more prevalent in the environment. A custom PCB mixture containing four congeners used as surrogates was also obtained from Accustandard. Internal standards consisting of ^{13}C labeled PCB congeners were obtained from Wellington Laboratories (Guelph, ON). Standard Reference Material (SRM) 1941b was obtained as a gift from NIST.

GC/MS Method

We developed a method for PCB congener analysis utilizing Agilent GC 6890 with a MS 5973 mass spectrometer (Santa Clara, CA) with capability of EI and NCI ionization. The GC/MS was equipped with a Combi Pal (CTC Analytics, Zwingen, Switzerland) autosampler and an OPTIC 3 Large volume injector (LVI; Atas GL International, Veldhoven, Netherlands). PCB congeners were separated in a DB-XLB (Agilent) 30m x 0.18 mm column with a 0.18 µm film thickness.

A volume of 50 µL of sample or standard dissolved in iso-octane was injected into the LVI, whose initial temperature was 60 °C. The excess solvent was evaporated during approximately 3 min time period, after which the injector was heated to 300 °C and the target analytes were desorbed and injected into the GC column. The carrier gas was helium with a flow rate of 1 mL/min. The initial GC oven temperature was 50 °C and was held for 2 min after injection. The temperature was increased with a rate of 30 °C/min to 120 °C after which the temperature was increased with a rate of 1.2 °C/min up to 253 °C. To bake off the column, the temperature was further increased with a rate of 30 °C/min to 340 °C where it was held for 3 min. The length of the program was 121 min, and the program was optimized to resolve most of the 28 target PCB congeners.

Sediment Sample Extraction for Inter-Laboratory Study

Samples for the inter-laboratory comparison study contained 10 samples: method blank (MB), low level laboratory control sample (LLCS), laboratory control sample (LCS), LCS duplicate, matrix spike (MS), MS duplicate, standard reference material (SRM), low PCB sample, medium PCB sample and high PCB sample. An aliquot of 20 g of homogenized sediment sample was mixed with hydromatrix and extracted with pressurized fluid extraction with ASE 300 (Dionex, Sunnyvale, CA) using 1:1 hexane:acetone. All samples were spiked with PCB surrogates and 1668 ^{13}C extractable internal standards prior to extraction. MS/MSD, LLCS, LCS/LCSD were also spiked with target PCB congeners. After extraction, water was removed by pipetting and by addition of baked Na_2SO_4, and the extracts were pre-concentrated to 10 mL with Turbo-Vap LV (Zymark Corp., Hopkinton, MA). A total of six sets of 10 samples were extracted. Extracts for same sample were combined, homogenized and concentrated to a final total volume of 48 mL. Aliquots of 4 mL of the homogenized extracts were sent to participating laboratories for analysis according to their own SOPs. The instrumentation included four HRMS instruments and eight LRMS instruments employing different ionization techniques.

RESULTS

PCB Congener Method Development

EI resulted in a fairly uniform overall response for all of the 28 target congeners. An even response within a homologue group is essential for the measurement of total PCBs with the homologue method, as the calibration is often based on a response from a single representative peak within a homologue group. The calibration range of the method was from 2 ng/mL to 500 ng/mL (100 pg to 25 ng on column) with a linear calibration model. A reporting limit (RL) of 10 ng/mL was set for the sediment samples. The spectra of the sample peaks showed significant fragmentation showing a loss of one or more chlorine atoms from the parent molecule. An analysis of a spiked sediment sample indicated that other organic compounds typically present in the sediments interfered with the analysis.

NCI resulted in an uneven response among the different PCB congeners, with the highest chlorinated congeners exhibiting highest response. The spectra of the lowest chlorinated congeners, typically the di- and tri-PCBs, did not show the presence of the parent ion. Instead, the Cl-ion signature was the dominant ion in the spectra with significantly reduced sensitivity. As ^{13}C internal standards were included in the samples, the di- and trichlorinated-PCBs were not reliably quantified. All the dioxin-like PCB congeners were quantified with their molecular ions. The calibration range of the NCI was similar to that of the EI ranging from 2 ng/mL to 500 ng/mL. The calibration model that fit the calibration data the best was quadratic. With optimizing the emission current from the instrument default value of 49 µA to 125 µA, the sensitivity of the instrument increased significantly. At low emission current, fragmentation of the target analytes was minimal; however, fragmentation increased with the increased emission current. Analysis of the spiked sediment extracts indicated that the interferences from the sample matrix were greatly reduced compared to PCB congener analysis with EI.

Inter-Laboratory Study

In order to investigate the interchangeability and comparability of PCB analysis between HRMS and LRMS, we conducted an inter-laboratory comparison study in partnership with 10 academic, commercial and government laboratories. In this study, laboratories using either HRMS or LRMS with different ionization techniques analyzed the same sediment extracts along with quality control samples for 28 PCB congeners that included the dioxin-like congeners and/or total PCBs using their own SOPs. Three sediment samples from Ashtabula River that were previously analyzed and expected to contain approximately 0.02, 1 or 10 µg/g of total PCBs along with quality control samples were extracted at Region 5 Chicago Regional Laboratory using pressurized fluid extraction. The extracts were homogenized, pre-concentrated and divided into 4 ml aliquots and were sent to the participating laboratories for the analysis of the 28 target PCB congeners and/or Total PCBs.

CONCLUSIONS

Both ionization methods, NCI and EI, resulted in a reproducible detection of target PCB congeners from both clean matrices and sediment samples. RL for both methods was set to 10 µg/Kg. EI resulted in an even response within a homologue group, thus making this ionization method suitable for total PCB analysis as homologue groups. NCI resulted in an uneven ionization; however, all the dioxin-like PCB congeners were reliably quantified using their parent ions. NCI also minimized the matrix interferences in sediment samples. With less interferences making the data analysis simpler and more confident, NCI could be potentially used to quantify the dioxin-like PCB congeners from sediment samples.

ACKNOWLEDGEMENTS

The authors thank all the participants to the inter-laboratory study.

This work was supported in part by appointment to the Research Participant Program at U.S. EPA, Region 5 administered by Oak Ridge Institute for Science and Education through an interagency agreement between the U.S. Department of Energy and the U.S. EPA.

REFERENCES

1. U.S. Environmental Protection Agency, 2007. *Method 8082A, Revision 1: Polychlorinated Biphenyls (PCBs) by Gas Chromatography*. In: SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical methods. Office of Solid Waste.

2. U.S. Environmental Protection Agency, 1999. *Method 1668, Revision A: Chlorinated Biphenyl congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS.* (EPA-821-R-00-002). Office of Water.

3. Gebhart, J.E., Hayes, T.L., Alford-Stevens, A.L. and Budde, W.L. 1985. *Mass spectrometric determination of polychlorinated biphenyls as isomer groups.* Anal. Chem., Vol. 57, pp. 2458-2463.

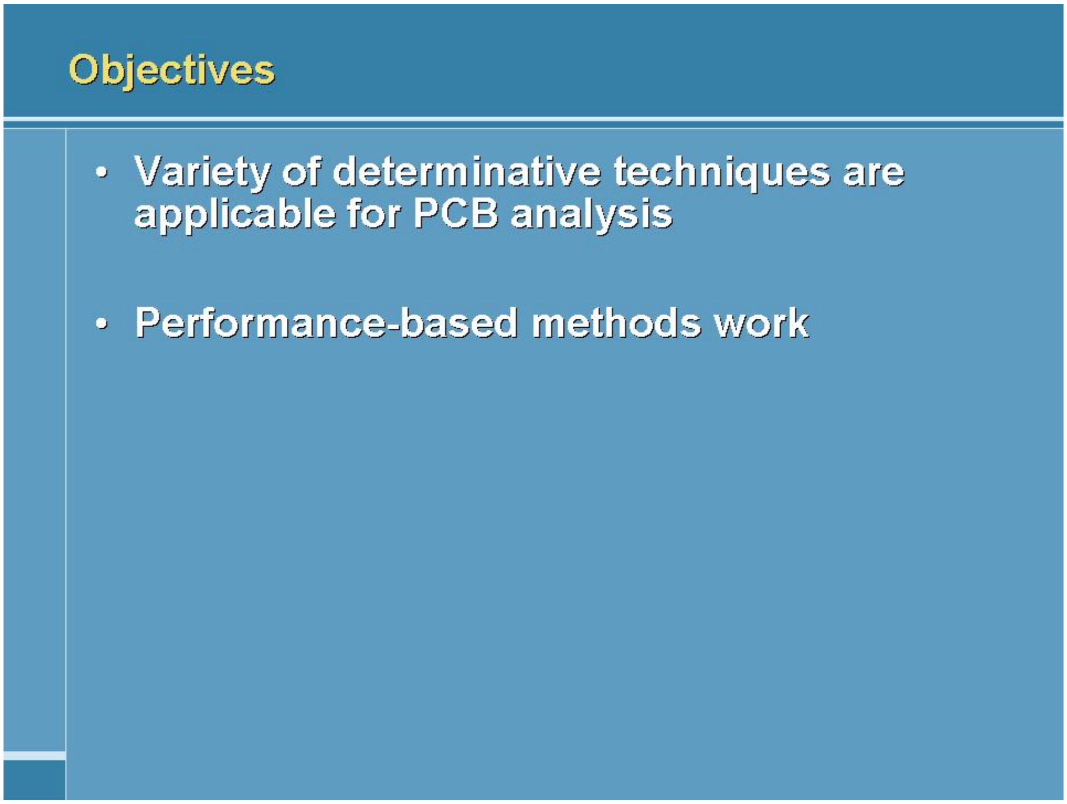
Inter-Laboratory Comparison Study of Measurement of Polychlorinated Biphenyl (PCB) Congeners from Sediment Samples with High Resolution (HRMS) and Low Resolution Mass Spectrometry (LRMS)

Jaana Pietari*, Amanda Wroble and
Wayne Whipple

Chicago Regional Laboratory
US EPA Region 5
Chicago, IL

August 15, 2008

*Current Address: Exponent, Bellevue, WA



Objectives

- Variety of determinative techniques are applicable for PCB analysis
- Performance-based methods work

PCB Congener Method Development with LRMS

Inter-Laboratory Comparison Project

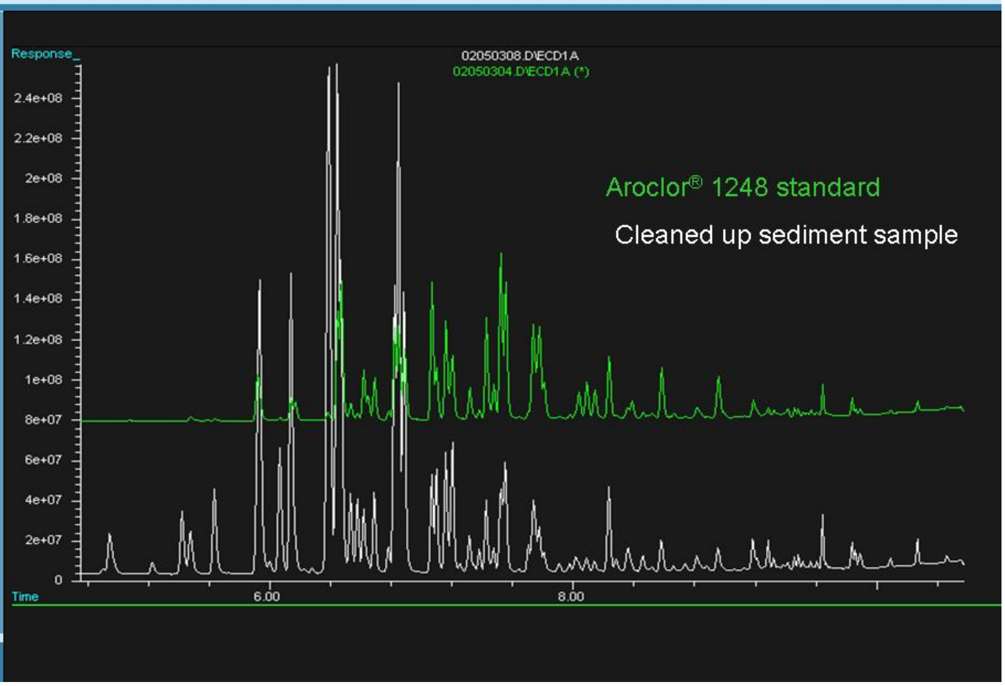
PCB Congener Method Development with LRMS

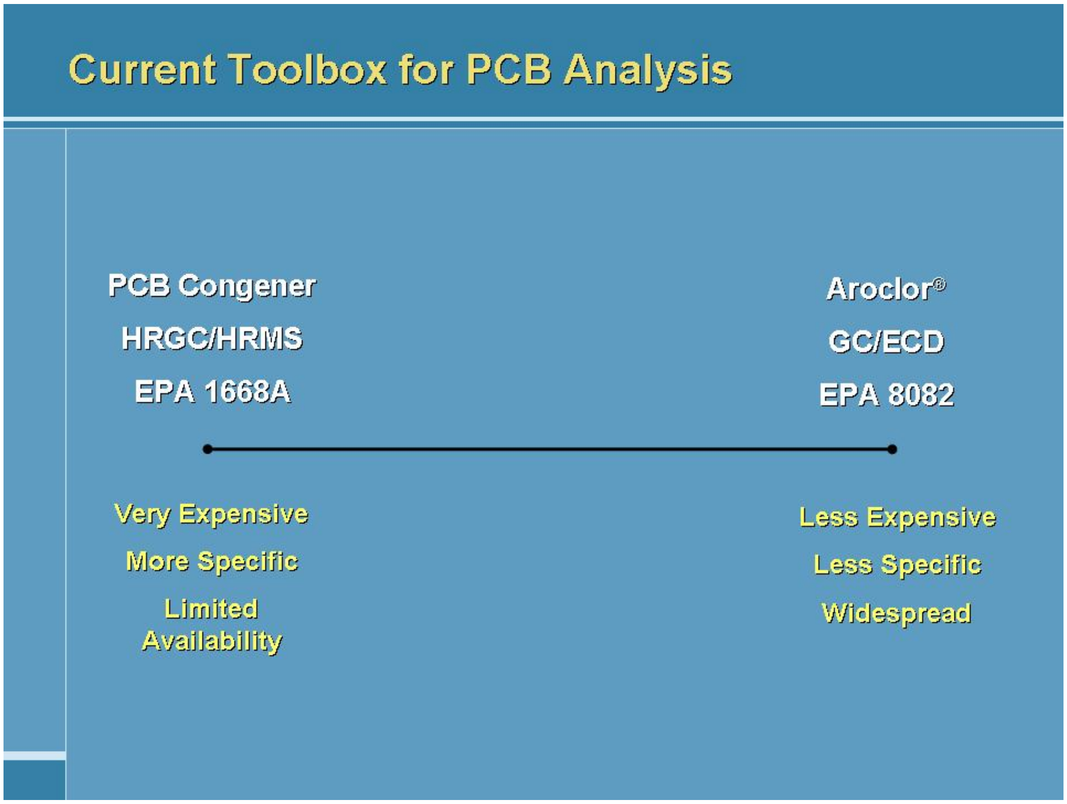
Inter-Laboratory Comparison Project

Current Toolbox for PCB Analysis

PCB Congener	Aroclor®
HRGC/HRMS	GC/ECD
EPA 1668A	EPA 8082
Very Expensive	Less Expensive
More Specific	Less Specific
Limited Availability	Widespread

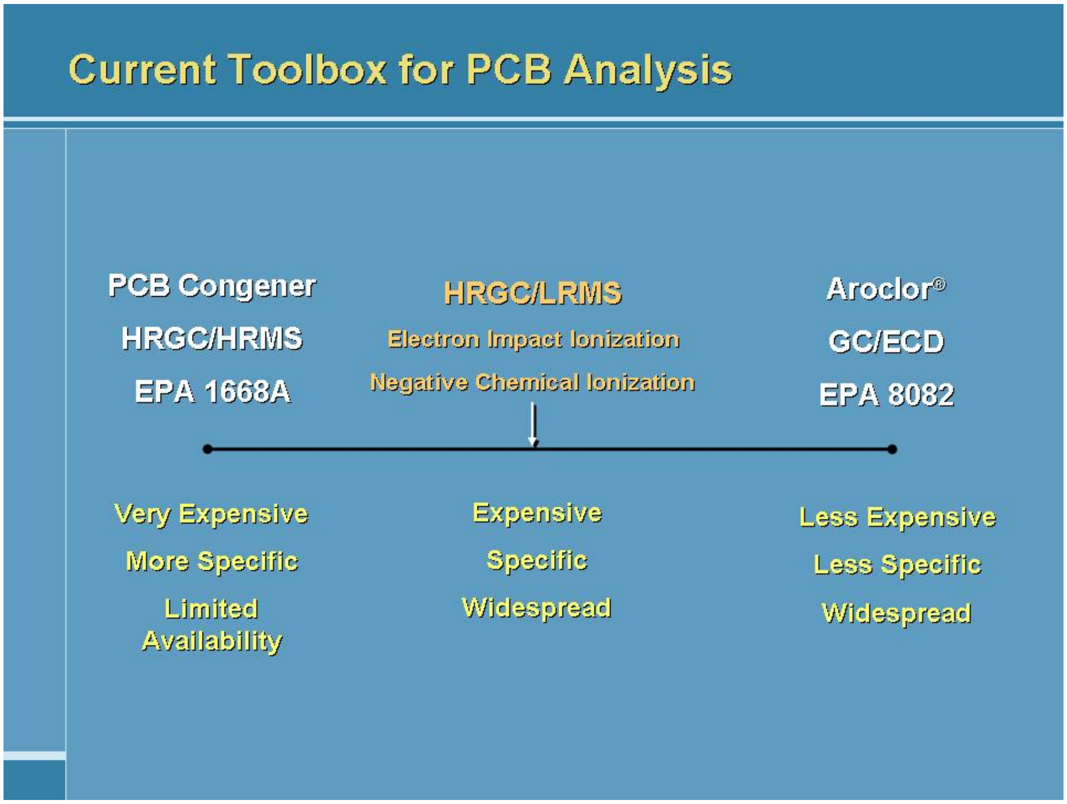
Aroclor® Analysis





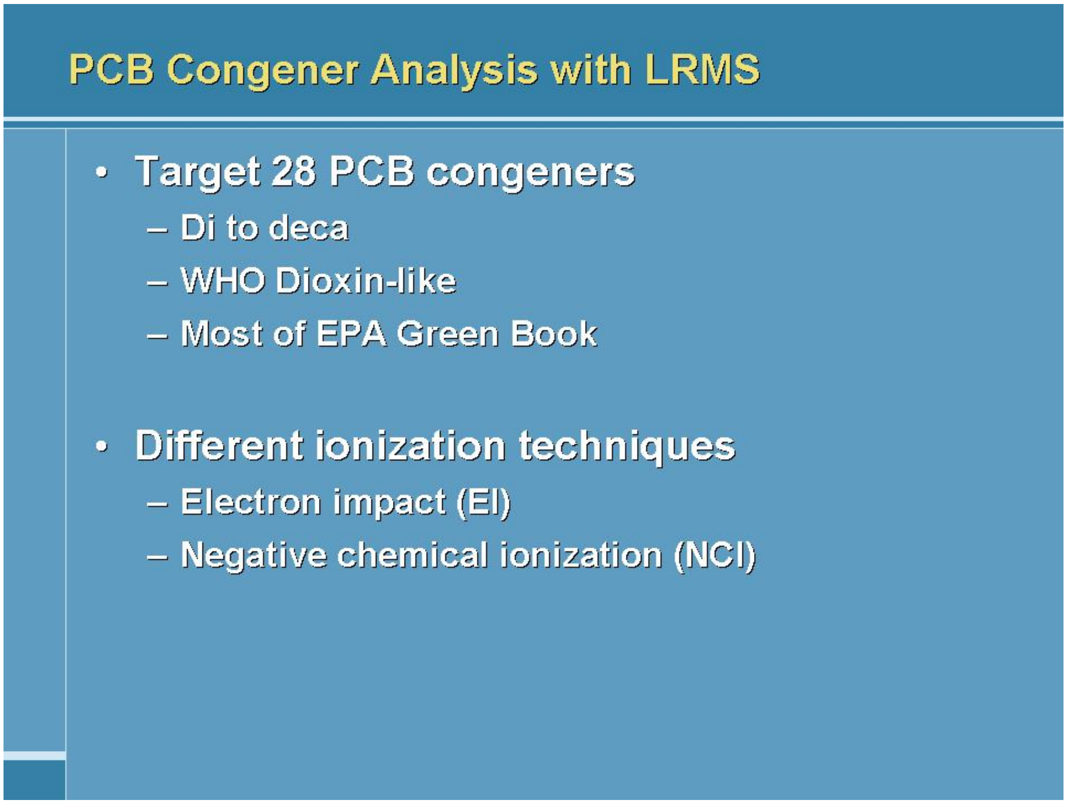
Current Toolbox for PCB Analysis

PCB Congener HRGC/HRMS EPA 1668A	Aroclor® GC/ECD EPA 8082
Very Expensive More Specific Limited Availability	Less Expensive Less Specific Widespread



Current Toolbox for PCB Analysis

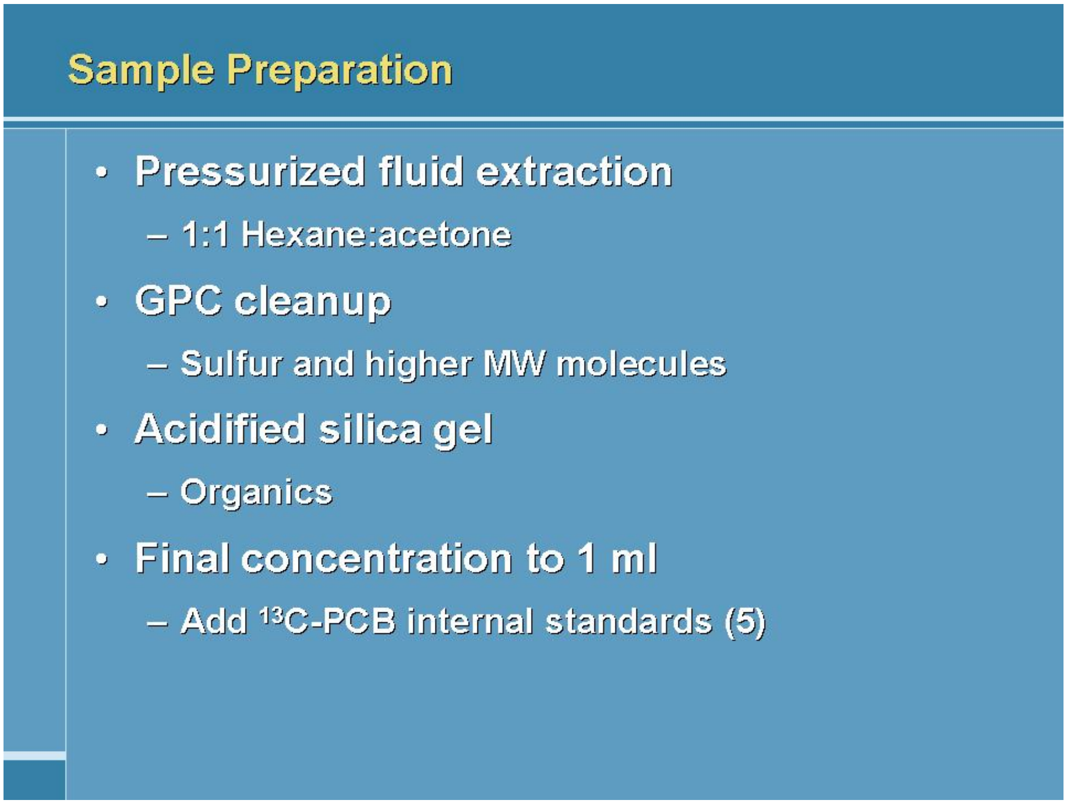
PCB Congener HRGC/HRMS EPA 1668A	HRGC/LRMS Electron Impact Ionization Negative Chemical Ionization	Aroclor® GC/ECD EPA 8082
Very Expensive More Specific Limited Availability	Expensive Specific Widespread	Less Expensive Less Specific Widespread



PCB Congener Analysis with LRMS

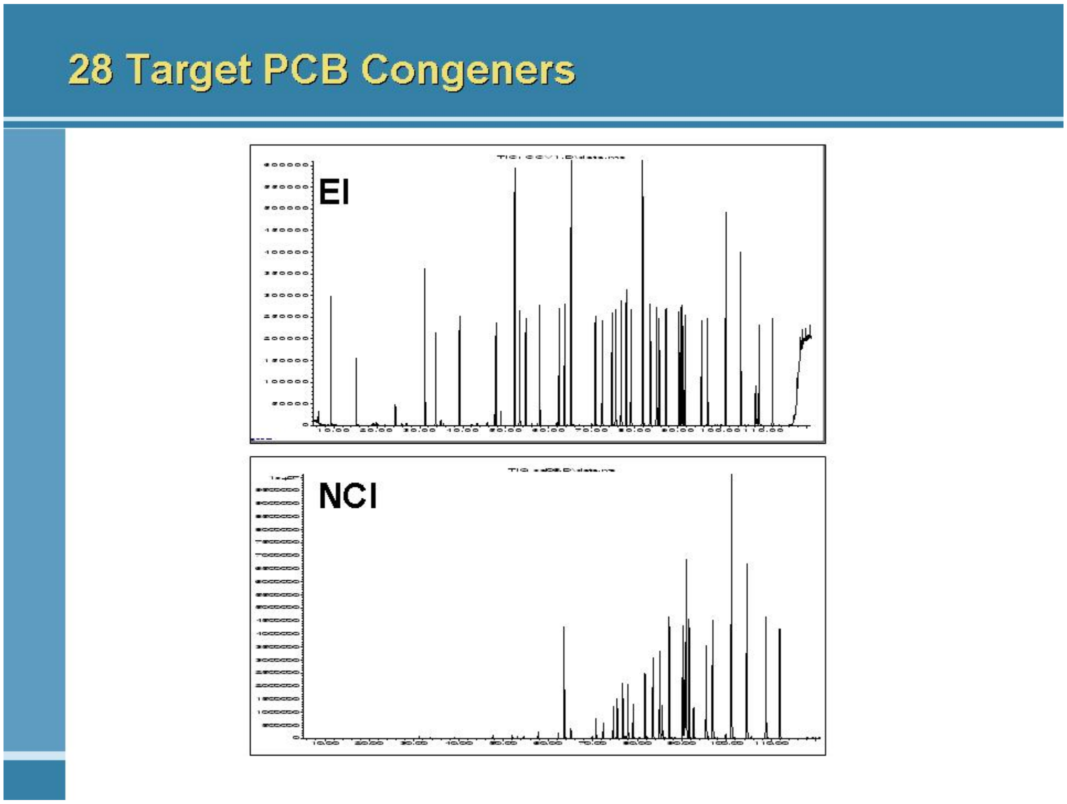
- Target 28 PCB congeners
  - Di to deca
  - WHO Dioxin-like
  - Most of EPA Green Book

- Different ionization techniques
  - Electron impact (EI)
  - Negative chemical ionization (NCI)

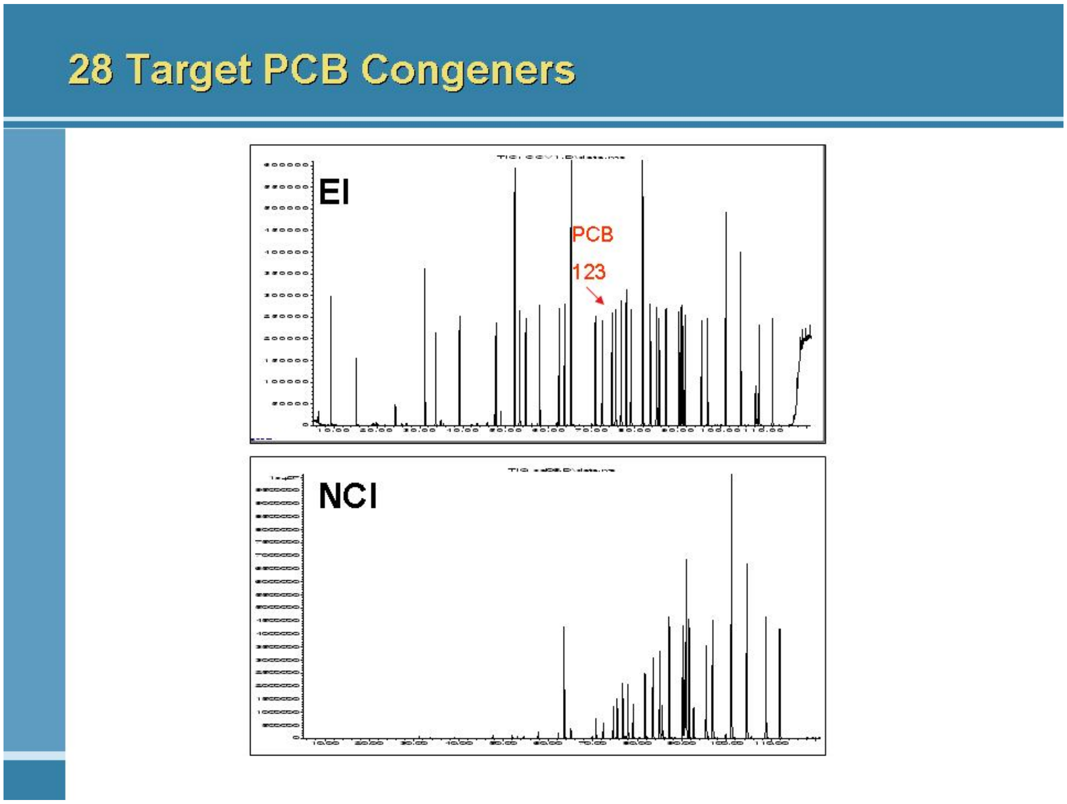


Sample Preparation

- Pressurized fluid extraction
  - 1:1 Hexane:acetone
- GPC cleanup
  - Sulfur and higher MW molecules
- Acidified silica gel
  - Organics
- Final concentration to 1 ml
  - Add ^{13}C-PCB internal standards (5)

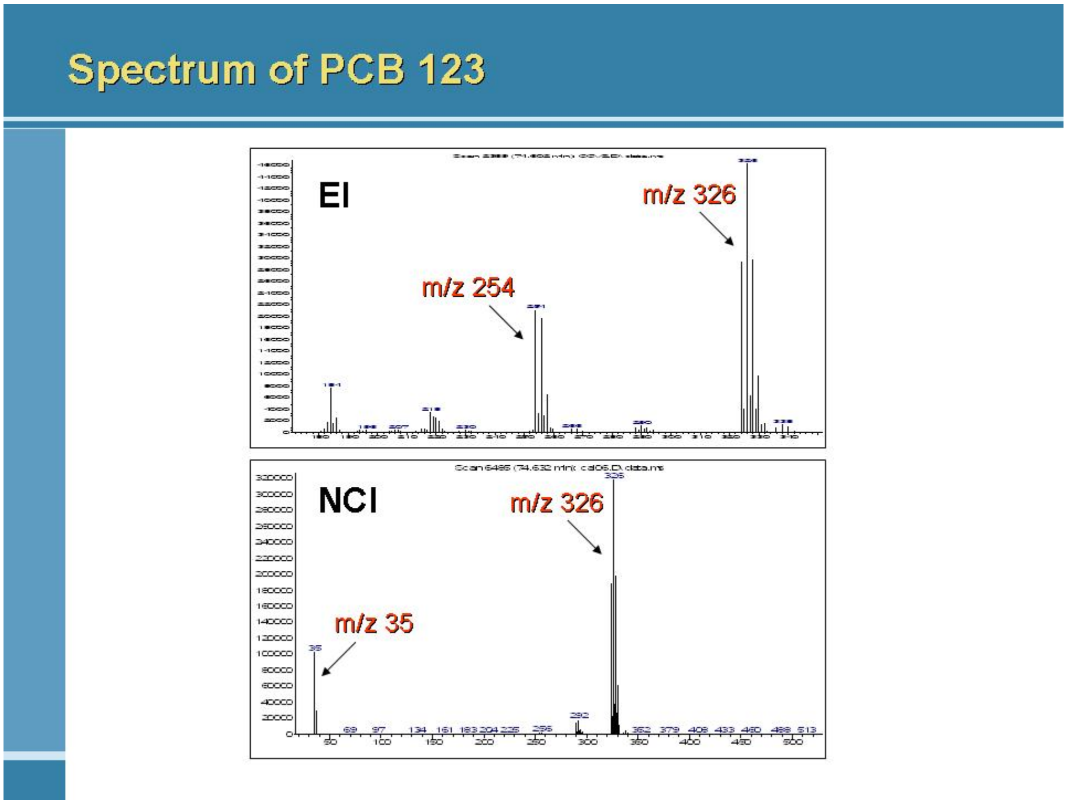


28 Target PCB Congeners

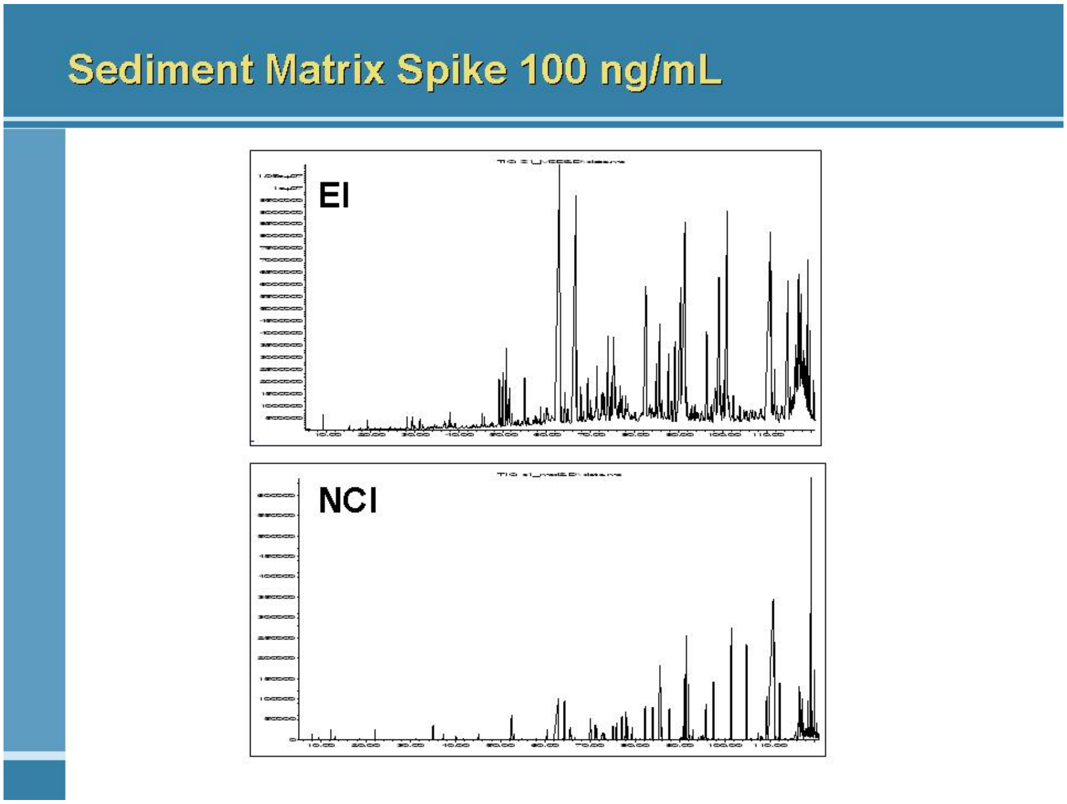


28 Target PCB Congeners

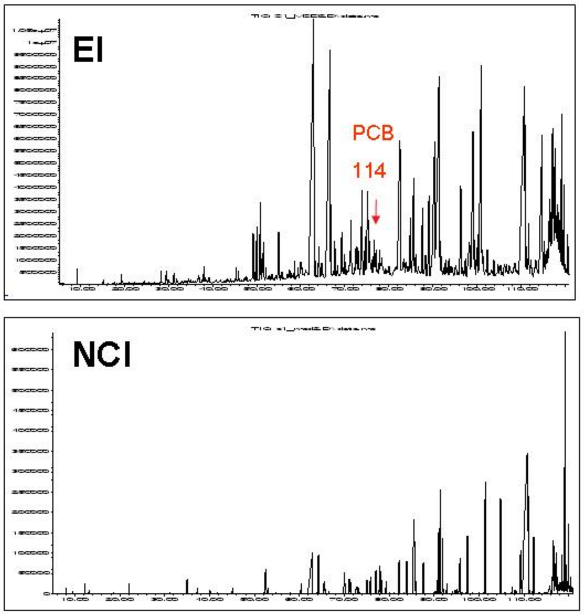
Spectrum of PCB 123



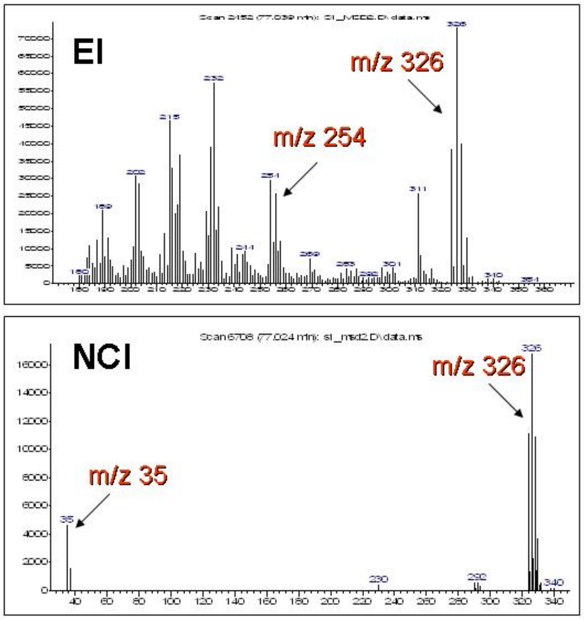
Sediment Matrix Spike 100 ng/mL



Sediment Matrix Spike 100 ng/mL



Spectrum of PCB 114



Method Development Summary

- PCB congeners with LRMS
  - Applicable to samples with high concentrations
    - RL 1.0 µg/kg
- Different ionization techniques – different applications
  - EI → Total PCBs with homologue
  - NCI → WHO congeners

PCB Congener Method Development with LRMS

Inter-Laboratory Comparison Project

Project Organization

- Project lead: R5 CRL
- In collaboration with:
  - Michele Schantz, NIST
  - Pamela Hamlett, Texas Parks and Wildlife
  - Gregory Santacroce, EPA R2
  - Stevie Wilding, EPA R3
  - Dennis Revell, EPA R4
  - David Spencer, EPA R6
  - Mark Murphy, EPA R8
  - James O'Keefe, Grand Valley State University
  - Thomas McDonald, B&B Laboratories
  - David Thal, TestAmerica

Project Organization

- Additional support
  - Marc Mills, EPA ORD
  - Brian Schumacher, EPA ORD
  - David Munch, EPA OW
  - Brian Englert, EPA OW
- Materials
  - Standards: R5 CRL
  - Sediment Samples: ORD and B&B Laboratories
  - Sediment Reference Material: NIST

Project Plan

Extract Samples at R5 CRL

↓

Homogenize Extracts of Same Sample

↓

Aliquot into 4 mL and Ship to Participants

↓

Cleanup and Analysis by Participants

Project Plan

- Three sediment samples
  - Low PCB < 0.1 ppm
  - Medium PCB ~ 1 ppm
  - High PCB >10 ppm
- Quality control samples
  - Method Blank (MB)
  - Low-Level Laboratory control sample (LLCS)
  - LCS/LCSD
  - MS/MSD
  - Standard Reference Material (SRM)

Extraction with ASE 300

Sediment Extracts: Adjusting Final Volume

Homogenized Extracts

Project Plan

Analyze Samples According to Laboratories' Own SOPs

↓

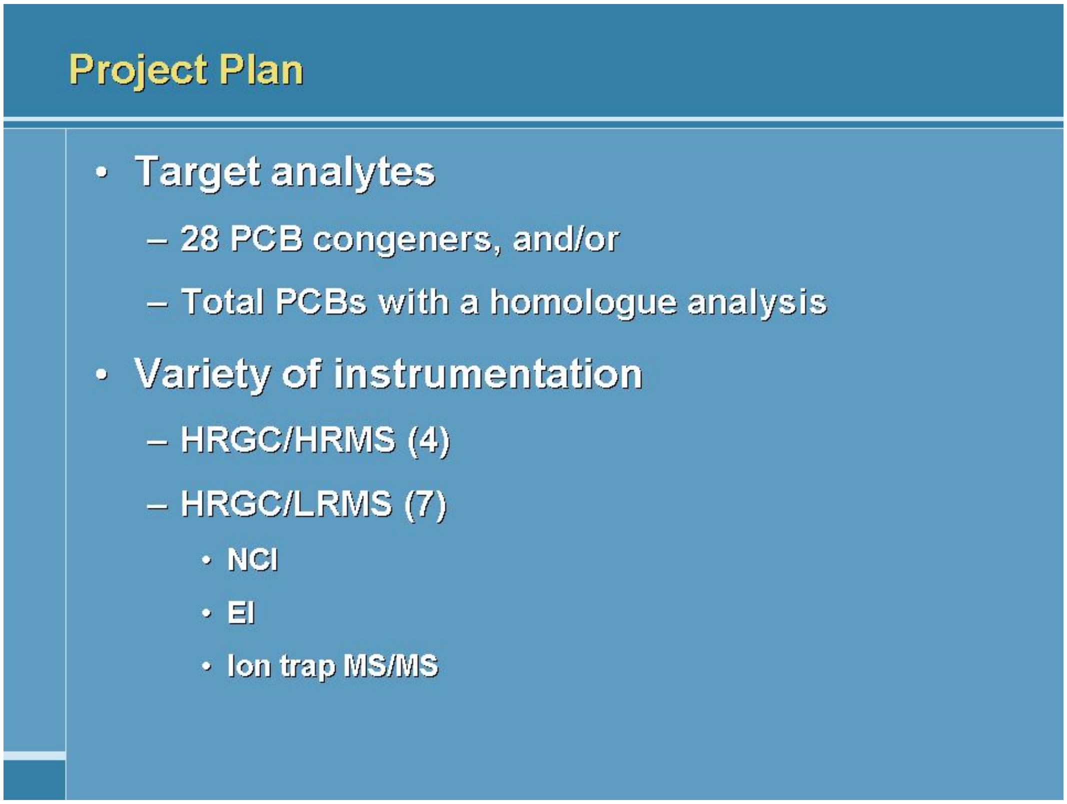
Report Data to R5 CRL

↓

Data Analysis by R5 CRL

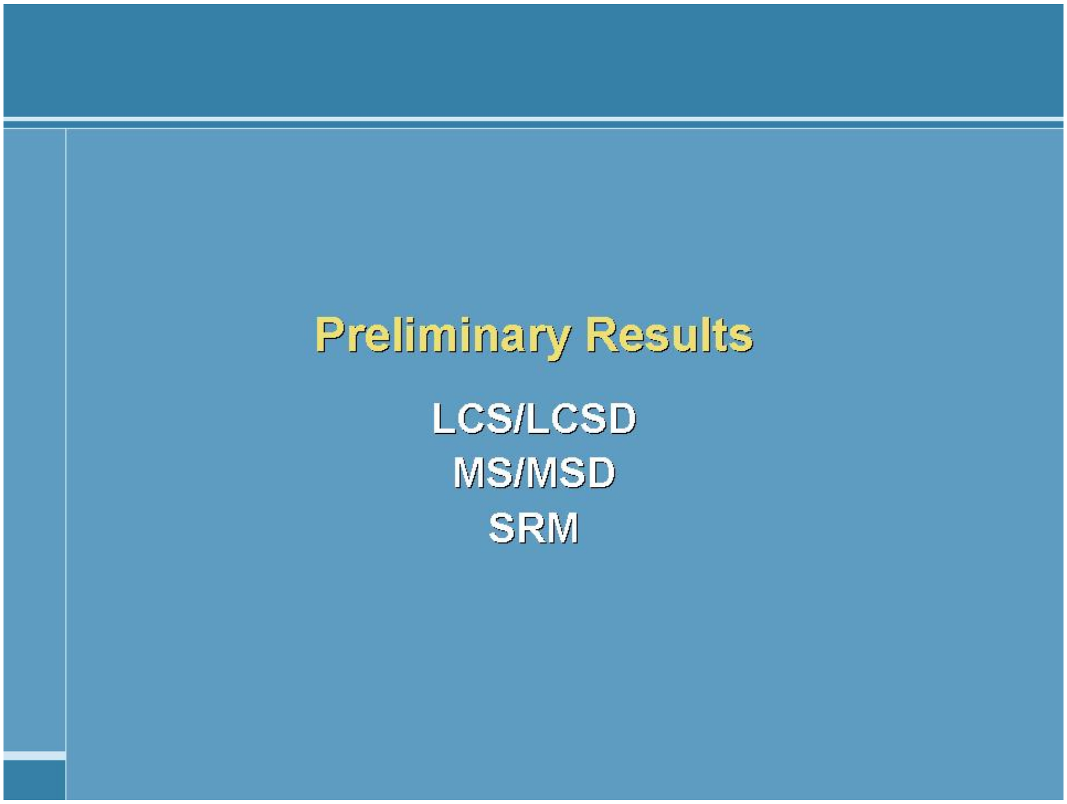
↓

Final Report and Journal Article



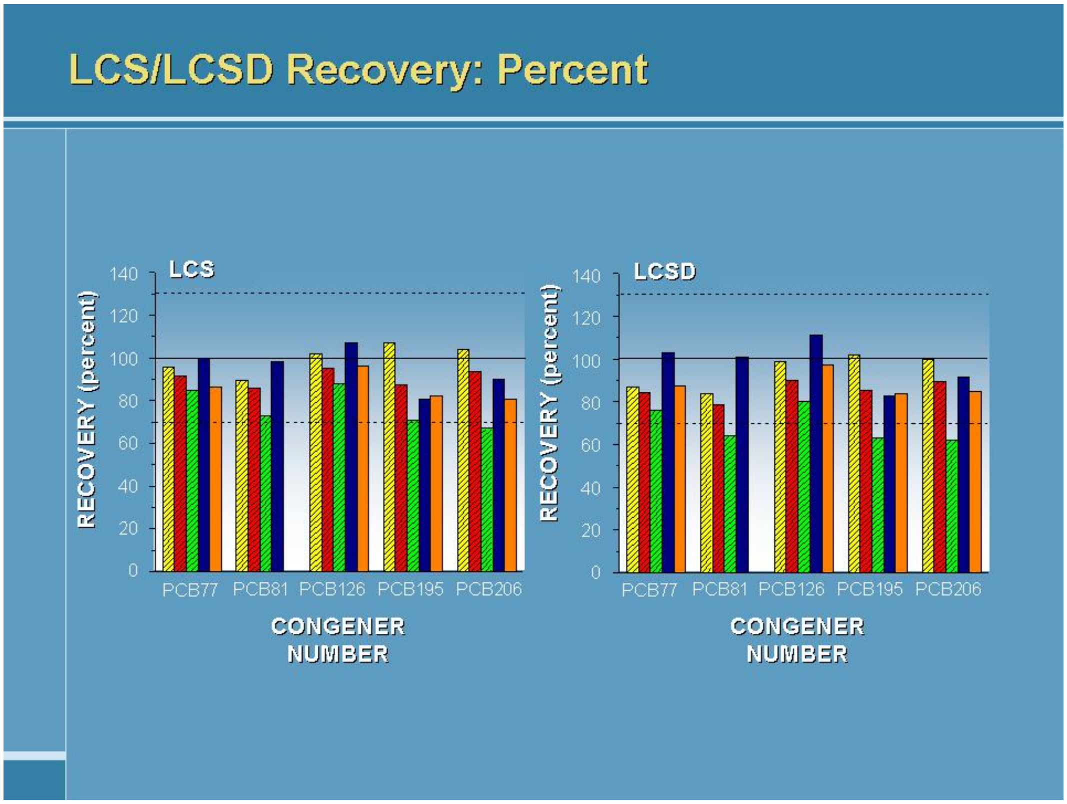
Project Plan

- Target analytes
  - – 28 PCB congeners, and/or
  - – Total PCBs with a homologue analysis
- Variety of instrumentation
  - – HRGC/HRMS (4)
  - – HRGC/LRMS (7)
    - NCI
    - EI
    - Ion trap MS/MS

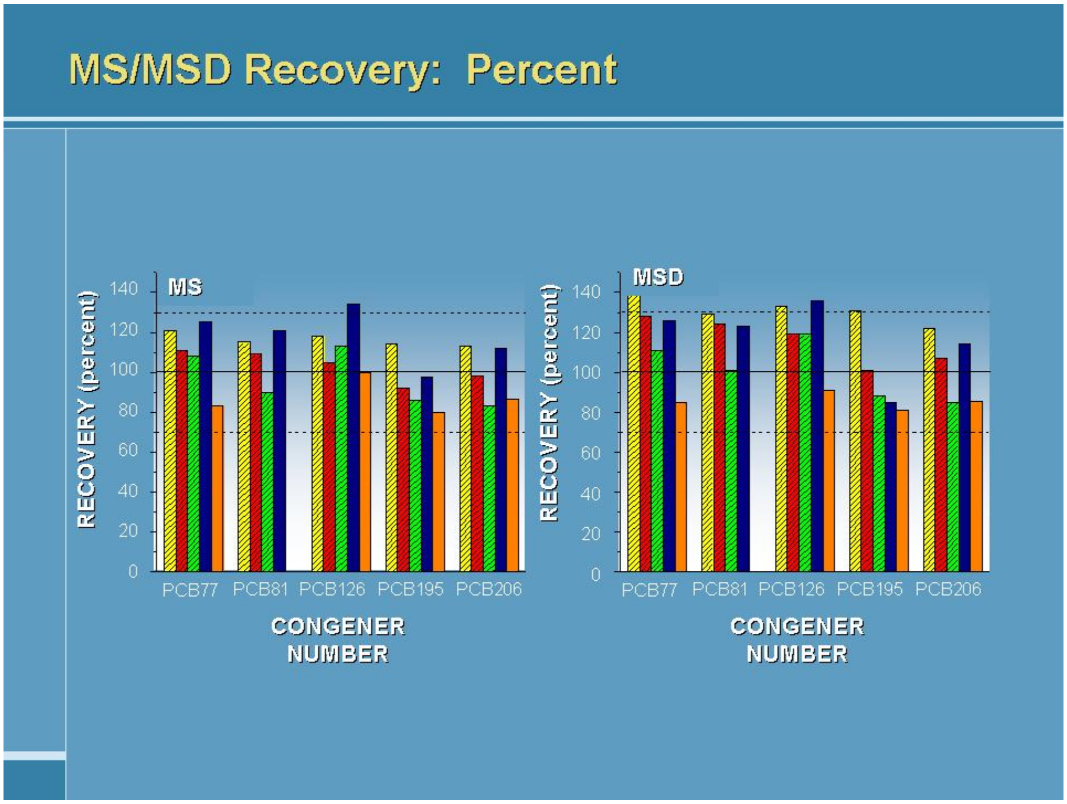


Preliminary Results

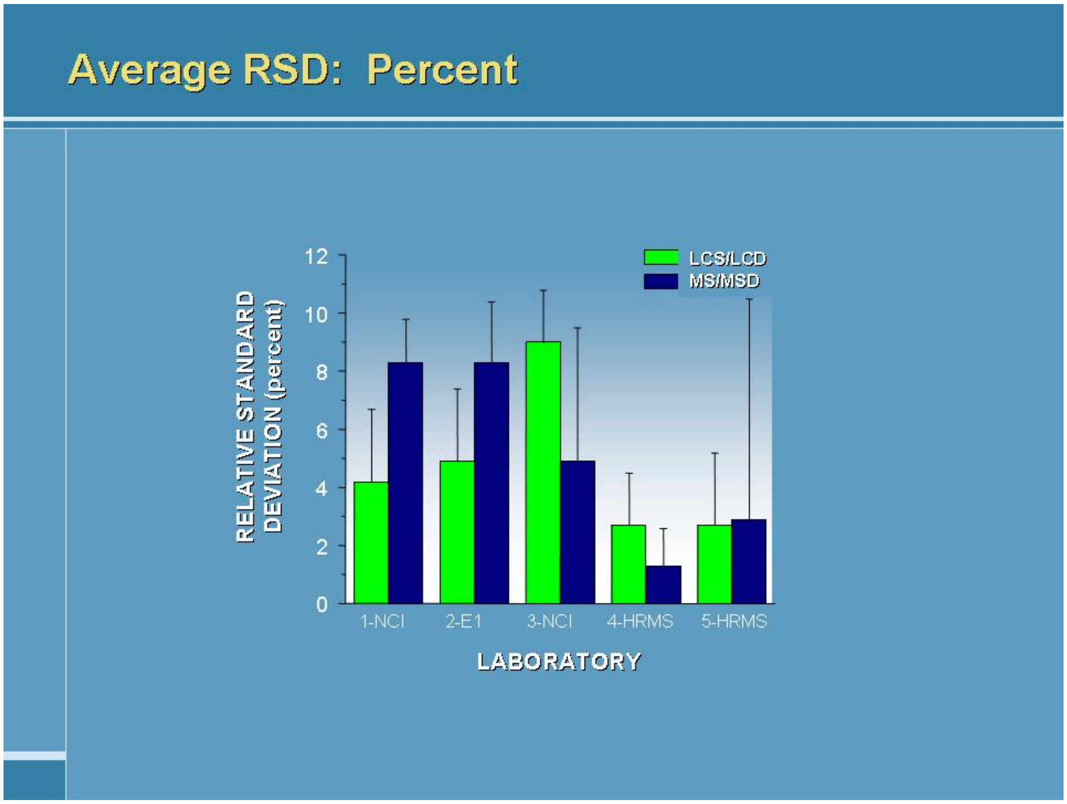
LCS/LCSD
MS/MSD
SRM



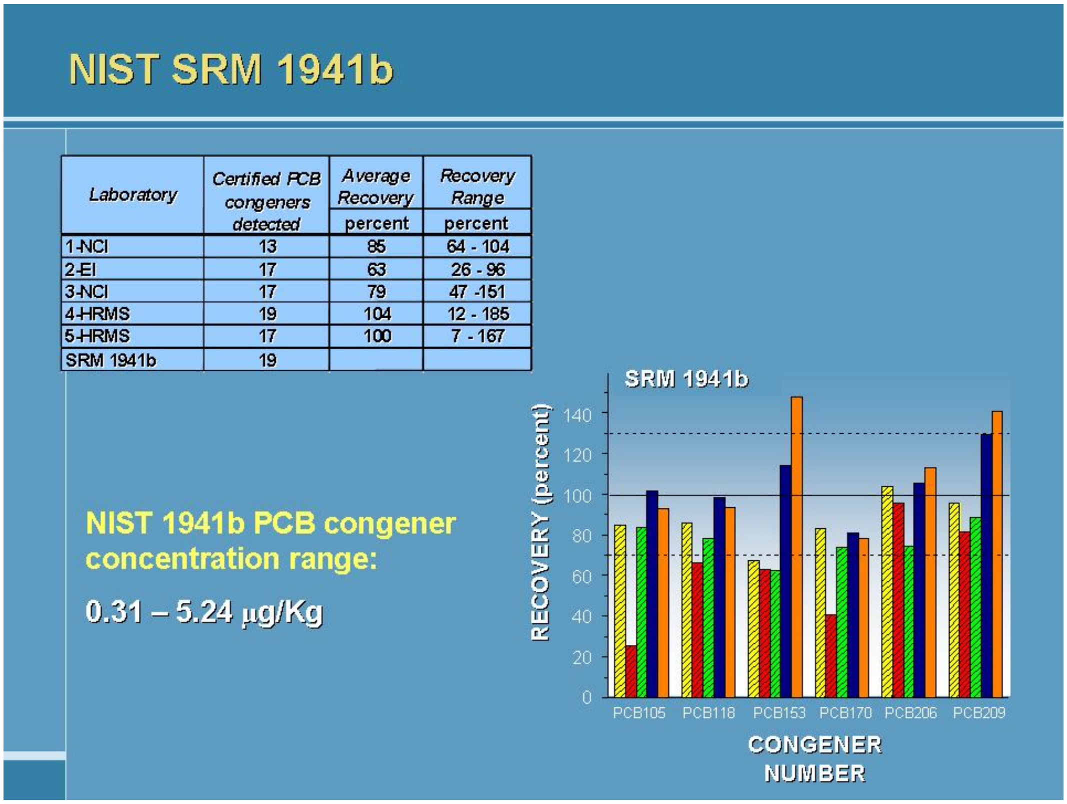
LCS/LCSD Recovery: Percent



MS/MSD Recovery: Percent



Average RSD: Percent

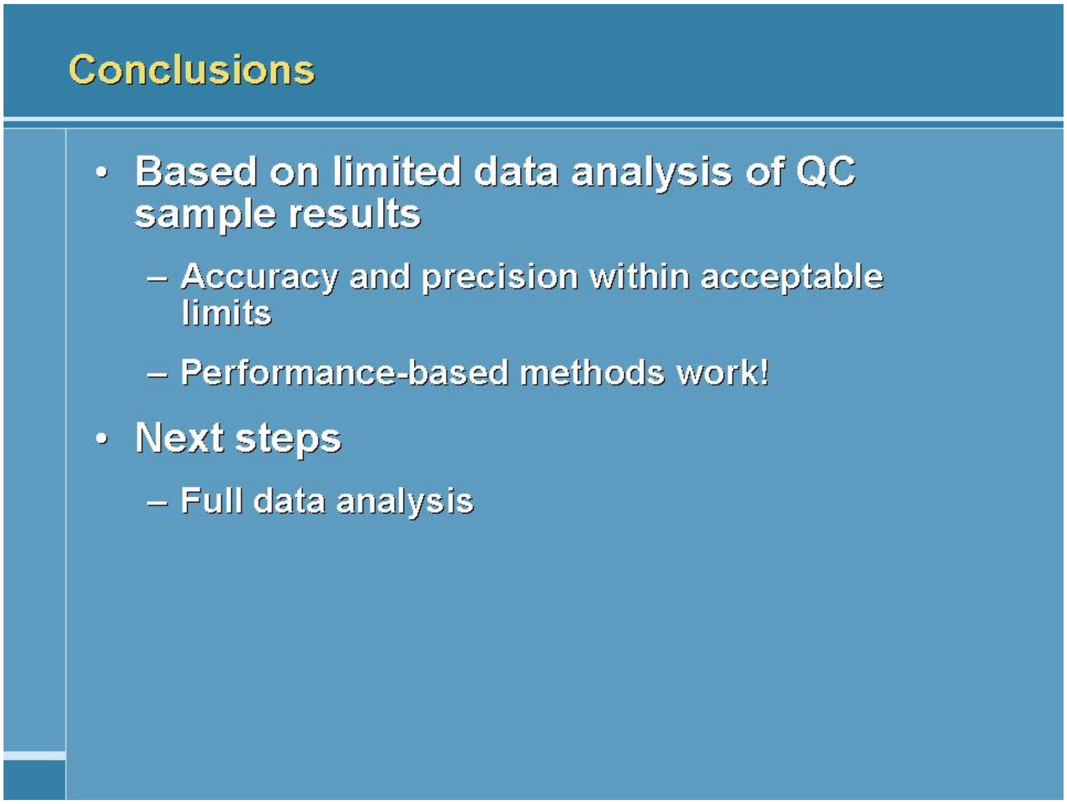


NIST SRM 1941b

Laboratory	*Certified PCB congeners detected*	*Average Recovery*	*Recovery Range*
		percent	percent
1-NCI	13	85	64 - 104
2-EI	17	63	26 - 96
3-NCI	17	79	47 -151
4-HRMS	19	104	12 - 185
5-HRMS	17	100	7 - 167
SRM 1941b	19		

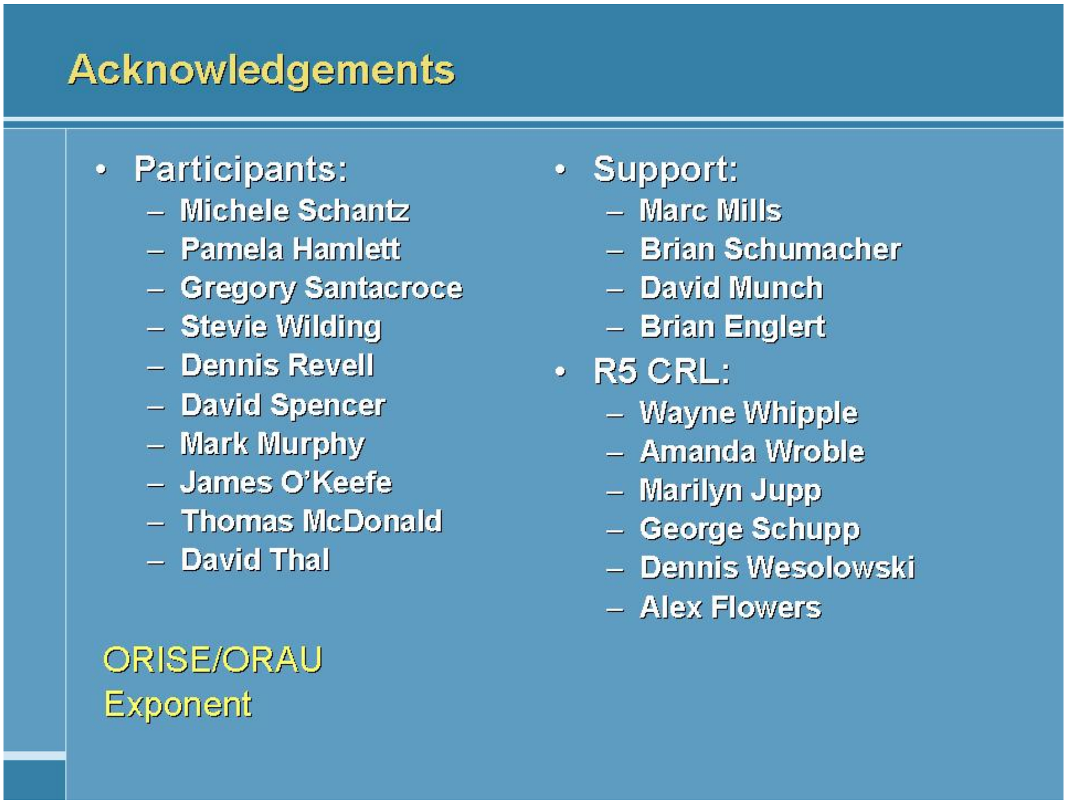
NIST 1941b PCB congener concentration range:

0.31 – 5.24 µg/Kg



Conclusions

- Based on limited data analysis of QC sample results
  - Accuracy and precision within acceptable limits
  - Performance-based methods work!
- Next steps
  - Full data analysis



Acknowledgements

- Participants:
  - Michele Schantz
  - Pamela Hamlett
  - Gregory Santacroce
  - Stevie Wilding
  - Dennis Revell
  - David Spencer
  - Mark Murphy
  - James O'Keefe
  - Thomas McDonald
  - David Thal

ORISE/ORAU
Exponent

- Support:
  - Marc Mills
  - Brian Schumacher
  - David Munch
  - Brian Englert
- R5 CRL:
  - Wayne Whipple
  - Amanda Wroble
  - Marilyn Jupp
  - George Schupp
  - Dennis Wesolowski
  - Alex Flowers

Thank You!

Analyzing Historical and Emerging Halogenated Flame Retardants in the Sediment of the Great Lakes

Hua Wei and An Li
School of Public Health, University of Illinois at Chicago

ABSTRACT

Laboratory procedures are developed for the quantitative analysis of 12 halogenated flame retardants (XFRs) in lake sediment samples. Method development is based on the modification and renovation of standard methods for other halogenated organic pollutants such as PCBs and PBDEs. The procedure includes Soxhlet extraction, multi-layer silica gel chromatographic cleanup, and instrumental analysis using programmable temperature vaporization (PTV) large volume injection on high resolution gas chromatography (HRGC) coupled with low resolution mass spectrometry (LRMS). Sediment cores were collected from 16 open-water locations of the Great Lakes. The cores were sectioned and each segment will be analyzed for the concentrations of selected XFRs, in order to investigate the spatial distribution and input chronology of these chemicals in the Great Lakes region.

INTRODUCTION

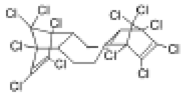
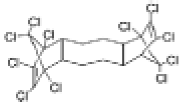
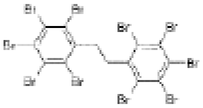
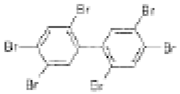
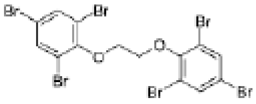
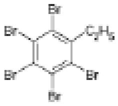
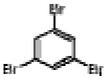
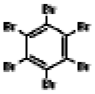
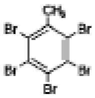
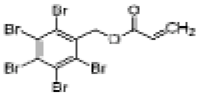
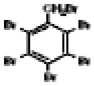
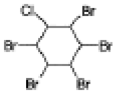
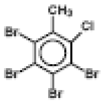
Vast majority of the approximately 30,000 chemical substances currently in wide commercial applications (>1 tonnes per year) have never been investigated for their presence and behavior in the environment [1]. Among these are various halogenated flame retardants (XFRs), which are added to the materials of consumer goods to prevent accidental fire from fast spreading. Due to their widespread uses, these compounds have rapidly accumulated in the environment.

In this work, 12 halogenated flame retardants (XFRs) were selected. They are dechlorane plus (DP), decabromodiphenylethane (DBDPE), pentabromoethylbenzene (PBEB), 1,3,5-tribromobenzene (TBB), 2-Bis(2,4,6-tribromophenoxy)ethane (TBE), hexabromobenzene (HBB), pentabromotoluene (PBT), pentabromobenzyl acrylate (PBBA), pentabromobenzyl bromide (PBBB), pentabromochlorocyclohexane (PBCCH), tetrabromo-o-chlorotoluene (TBCT), and 2,2',4,4',5,5'-hexabromobiphenyl (BB153). Their chemical structures are shown in Table 1. Some of these XFRs are on the EPA's High Production Volume (HPV) chemical list [2]; and some are regulated under the Toxic Substances Control Act. However, available information on their environmental level, distribution, and time trend is very limited.

More than often, the concentrations of these XFRs in environmental matrices are at trace levels, i.e., less than parts-per-billion (ppb) or even parts-per-trillion (ppt). Therefore, reliable laboratory procedures for sample treatment and a sensitive instrumental protocol are essential for the reliable detection and quantification of PBDEs. Challenges also arise from the lacks of standard methods and published reference papers, as well as the unavailability of the research purity chemical standards for some of the targeted analytes.

The objective of this work is to develop laboratory procedures and optimize instrumental conditions for the selected XFR analytes. The results of this work will be applied to the analyses of sediment samples collected from the Great Lakes, as well as other environmental samples.

Table 1. Halogenated Flame Retardants (XFRs) Analyzed in this Work

Abbr'n	Chemical Name	MW	Structure
syn-DP	Dechlorane plus (syn stereoisomer)	654	
anti-DP	Dechlorane plus (anti stereoisomer)	654	
DBDPE	Decabromodiphenylethane	972	
BB153	2,2',4,4',5,5'-hexabromobiphenyl	628	
TBE	1,2-Bis(2,4,6-tribromophenoxy)ethane	688	
PEB	Pentabromoethylbenzene	500	
TBB	1,3,5-Tribromobenzene	315	
HBB	hexabromobenzene	552	
PBT	pentabromotoluene	487	
PBBA	pentabromobenzyl acrylate	557	
PBBB	pentabromobenzyl bromide	523	
PBCCH	Pentabromochlorocyclohexane (several stereoisomers)	514	
TBCT	tetrabromo-o-chlorotoluene	443	

EXPERIMENTAL METHODS

Chemicals

The two individual DP isomers were purchased from Cambridge Isotope Laboratories. PEB was purchased from Wellington Laboratories. DBDPE, TBE, TBB, HBB, PBT, PBBA, PBBB, PBCCH and TBCT were purchased from AccuStandard. Silica gel (100 – 200 mesh, Davisil Grade 644) was purchased from Fisher Scientific. Hexane, dichloromethane and acetone were GC grade.

Sampling

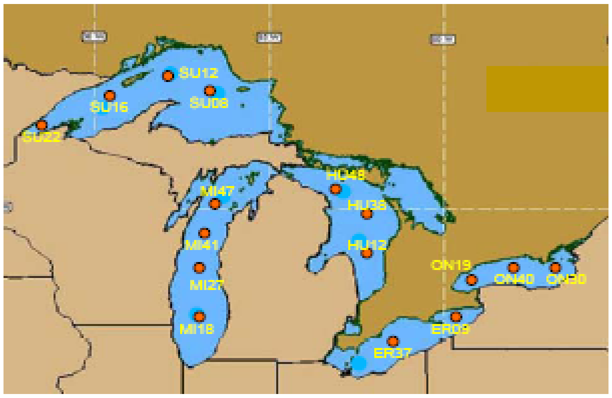


Figure 1. Great Lakes sampling locations, August 2007

Sediment sampling on all five Great Lakes was conducted from August 1 to 25, 2007 using a box corer deployed from the EPA *R/V Lake Guardian*. A total of 16 sites were chosen (Figure 1), including 14 used in our previous work [3-6], and two new sites (LM27 and ON19). All sites except SU22 are in depositional zones where chemical input is dominated by atmospheric deposition. The box corer was deployed from the deck and used to collect a bulk sediment sample, which was then sub-cored on deck with four polycarbonate tubes (7.0 cm I.D.). The sub-cored samples were then stored in the freezer room of the ship. They were transported to the laboratory in mid September 2007, and kept in a laboratory freezer.

All the cores were sectioned using a Torrey Model ST-295 PE electric saw. The saw blade was only 0.022" thick so that the material loss during the cutting was minimized. The frozen cores were extruded and sectioned at 0.5 or 1.0 cm intervals for the first 10 cm, then in 5 cm increments for the remainder of the core. The cutting was operated in a freezer room with the temperature kept at -20 °C to avoid the melting of the cores. The slices with corresponding depth from the same site were composited into a pre-cleaned amber glass jar with PTFE lined lid, and have been kept in a freezer. A total of 222 samples are obtained from the 16 cores.

The procedure described above eliminates the "smear" along the wall of the subcoring polycarbonate tube, which may occur if the fresh cores were extruded and sectioned onboard of the sampling ship immediately after sub-core collection. We expect that the current procedure will improve the accuracy in chronological trend determination.

Sample Pretreatment

The sample pretreatment procedure used in this work is similar to that used in our previous project on polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) [4-6].

Around 1 g aliquot of the same wet sample was weighed on tared, clean single-use aluminum trays and dried (60 °C, 48 h). Wet bulk density was determined as a ratio of the wet weight to the sample volume. After being dried, samples were reweighed, and the dry sediment mass, percent moisture, porosity, and percent solids were calculated. The organic content were measured by the loss on ignition (LOI) at 550 °C for about 5 hrs in a muffle furnace.

The samples were thawed and homogenized before treatment. About 20 g of wet sample was taken, air-dried and ground with sufficient anhydrous sodium sulfate, and then transferred to Whatman cellulose thimbles. The known amounts of surrogates of ^{13}C-labled BDE209 and PCB205L were spiked on the top of the sample. The spiked samples and method blank (silica gel plus anhydrous sodium sulfate as the matrix) were Soxhlet-extracted for 20 hours with 150 mL of 1:1(v) hexane-acetone solvent mixture. Elemental sulfur was removed by adding activated granular copper (Aldrich, Milwaukee, WI) to the Soxhlet flask during the extraction. The extracts were then concentrated on Kuderna-Danish (K-D) concentrators, solvent-exchanged to hexane, and subjected to a silica gel chromatographic cleanup procedure.

Silica gel was rinsed with dichloromethane, baked at 140 °C overnight in the oven, cooled in a desiccator, and stored in a precleaned glass bottle with screw-cap that prevents moisture from entering. Acid silica gel (30% w/w) was made by thoroughly mixing 40 g of concentrated sulfuric acid with 100 g of activated silica gel in a clean container. Basic silica gel was made by thoroughly mixing 30 g of 1N sodium hydroxide with 100 g of activated silica gel in a clean container.

The glass columns (30 cm × 1.1 cm ID) were pre-cleaned by acetone, dichloromethane and then filled with hexane. The multi-layer silica gel column was packed from bottom to top with glass wool, 2 g granular anhydrous sodium sulfate, 1 g neutral silica gel, 2 g basic silica gel, 1 g neutral silica gel, 4 g acidic silica gel, 1 g neutral silica gel, and 2 g granular anhydrous sodium sulfate. The acidic silica gel column was packed from bottom to top with 2 g granular anhydrous sodium sulfate, 4 g neutral silica gel, 4 g acidic silica gel, 1 g neutral silica gel, and 2 g granular sodium sulfate. After pre-eluting with 50 mL of hexane, 2 mL of an XFR solution was loaded using a transferring pipette. Then eluting solvent was added and the eluate collected. The flow rate was controlled at 1-2 drops per second using the column stopcock. The elutes were again concentrated on the K-D concentrators to about 8 mL, followed by gentle N_2 blowdown to less than 2 mL. The solutions were then transferred to 2 mL volumetric flasks to make exact 2 mL solution by rinsing the inside of the K-D tubes with hexane.

Instrumental Analyses

The Agilent Model 6890 gas chromatograph (GC) coupled with Model 5973 electron capture negative chemical ionization mass spectrometer (ECNI-MS) detector was used in this study. A DB-5MS (15 m × 0.25 mm i.d., 0.25 μm film thickness; J&W Scientific) capillary column was used for the separation with helium as the carrier gas. Each sample in hexane was introduced into a programmable temperature evaporation (PTV) inlet operated in the solvent vent mode with the pressure of 15 psi and initial inlet temperature of 0 °C (holding for 1.5 min). A total of 60 µL was injected with three injections of 20 µL each and 10 s intervals in between. Then the PTV inlet increased from 40 to 300 °C at 600°C/min. The column was kept at the constant flow of 1.5 mL/min from 1.4 min. The initial oven temperature was 90 °C, which lasted for 3 min, and then increased to 140 °C at 10° C/min and further to 300 °C at 5 °C /min. The final temperature was kept for 15 min until the run was completed. The GC/MS interface temperature is 280 °C. The mass flow controller of the reagent gas CH_4 was set to 40%. The temperatures of ion source and quadrapole were 150 and 106 °C, separately.

RESULTS AND DISCUSSION

Silica Gel Elution Fractionation

The elution pattern of the XFR mixture was investigated by sequentially collecting 10 mL of the eluate from each of the silica gel columns. Two different eluting solvents, hexane and mixture of hexane:dichloromethane (1:1 v:v), were used and resulted in different fractionation patterns.

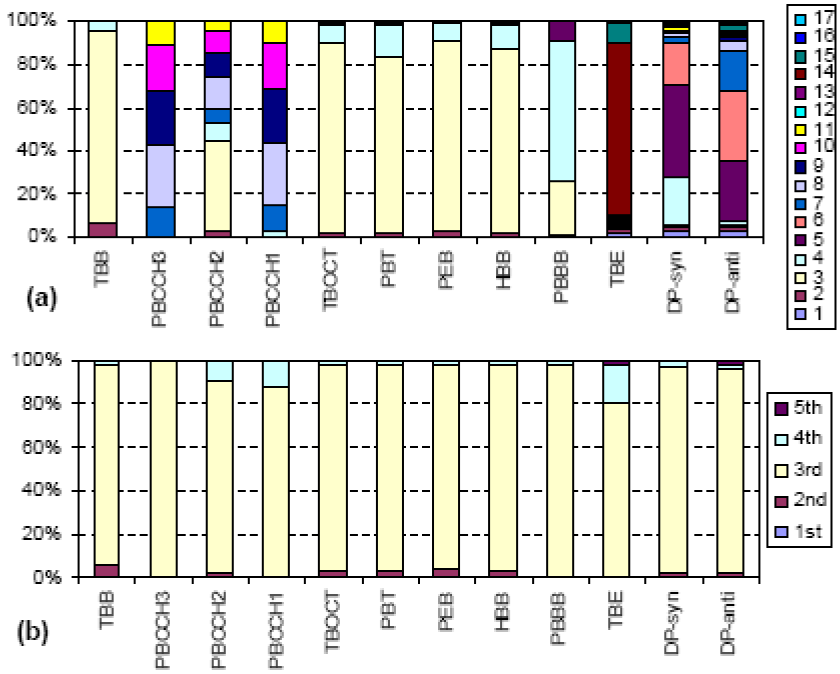


Figure 1. XFR fractions eluted from the multi-layer silica gel column using (a) hexane and (b) mixture of hexane and dichloromethane (1:1 v:v).

With hexane as the eluant, TBB, TBCT, PBT, PBBB, PEB and HBB were completely eluted in the first 50 mL (Figure 1-a), with majority eluted in the 3rd 10 mL. Syn- and anti- DP isomers were eluated mainly in the 4th 10 mL. Syn-DP was eluated earlier than anti-DP and the eluation order is the same as that from the GC column, reflecting the difference in polarity between the two isomers. The elution curves of the DP isomers are more spread than other compounds. For TBE, it was not eluted until the 14th 10 mL of hexane was collected. This may be the result of its stronger interaction with the silica gel, due to the two oxygen atoms between the biphenyl rings in the TBE molecule.

Using the mixture of hexane and dichloromethane, all targeted XFRs except PBBA were eluted with 40 mL of the eluant (Figure 1-b). With a high molecular polarity, PBBA did not elute until after the 9th 10 mL of the hexane:dichloromethane mixture. It may be completely eluted using a polar solvent; however, this may cause the co-elution of various unwanted polar substances in sediment extract.

GC Separation and MS Identification

The GC retention times as well as the m/z values of the major and minor ions of XFRs are summarized in Table 2. The total ion chromatogram (TIC) of selected XFRs is shown in Figure 2, against that of polybrominated biphenyl ethers (PBDEs). DBDPE has a longer retention time than BDE209; its peak is not shown in Figure 2.

Table 2. GC Retention Times and MS Ions of Selected XFRs

Abbr'n	RT	Major Ions	Minor ions
syn-DP	36.07	654, 652	652, 618, 584, 550, 512, 478, 440, 404, 368, 237
anti-DP	37.08	654, 652	652, 618, 584, 550, 512, 478, 440, 404, 368, 237
DBDPE	>47	79, 81	735, 652, 574, 493, 416, 161
BB153	28.93	79, 81	548, 468, 390
TBE	34.23	79, 81	252, 330
PEB	19.57	79, 81	501, 421, 392
TBB	6.72	79, 81	313
HBB	21.63	79, 81, 551	551, 471, 393, 314
PBT	18.7	79, 81	485, 407, 328
PBBA	25.25	71, 79, 81	485, 475, 431, 406, 398
PBBB	23.76	79, 81	485, 407, 325
PBCCH	14-18*	79, 81	160, 116, 35, 240, 194, 432, 478
TBCT	16.75	79, 81	441, 364, 282

* for the three major peaks

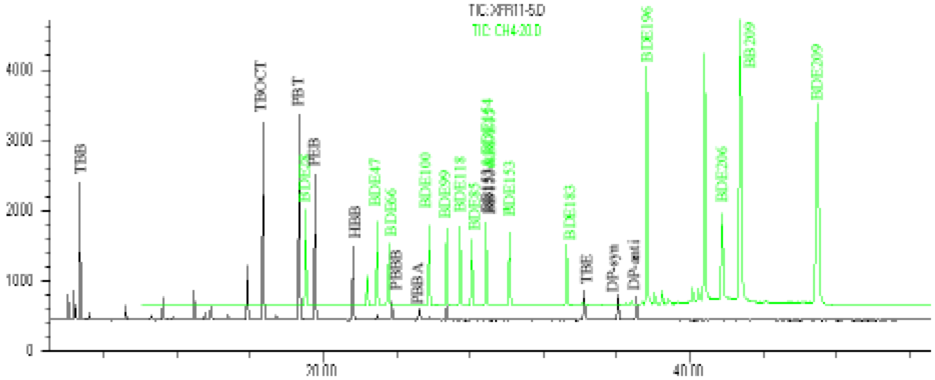


Figure 2: Total Ion Chromatogram (TIC) of Selected XFRs

Co-elution of BB153 and BDE154 was observed. With ECNI-MS, they are difficult to separately quantified because both rely on the sensitive bromine ions with m/z 79 and 81. Similar problem was reported by Eljarrat et al. [7], Focant et al. [8], and others. Because both BB153 and BDE154 have relatively high environmental levels, neither can be assumed negligible. Zhu and Hites [9] used a 60 m GC column to ensure their separation. Most other studies relied on the electronic impact MS (EI-MS) which quantifies BB153 using its molecular ion (m/z 628).

Multiple peaks appeared on the chromatogram of the chemical standard of PBCCH, as shown in Figure 3-a. The three major peaks had retention times ranging from 14 to 18 min. The mass spectra of these peaks are similar, suggesting that they are likely to be conformational isomers. This makes it difficult to obtain reliable quantitative results, because the isomers may have different relative MS response factor. Although PBCCH and other polybromo-polychloro-cyclohexanes have been analyzed by others [10-12], few investigate the effect of isomers on analytical reliability. A possible solution is to use the total peak area, assuming similar response factor among isomers.

Similarly, the chromatogram of chemical standard of 1,3,5-Tribromobenzene (TBB) showed one major and a few minor peaks, as shown in Figure 3-b. Structural isomer tribromobenzenes may be present as impurities.

XFRs in the Great Lakes Sediments

Preliminary analysis suggests the presence of relatively high levels of DP and TBE in the Great Lakes sediments. Example TICs are given in Figure 4.

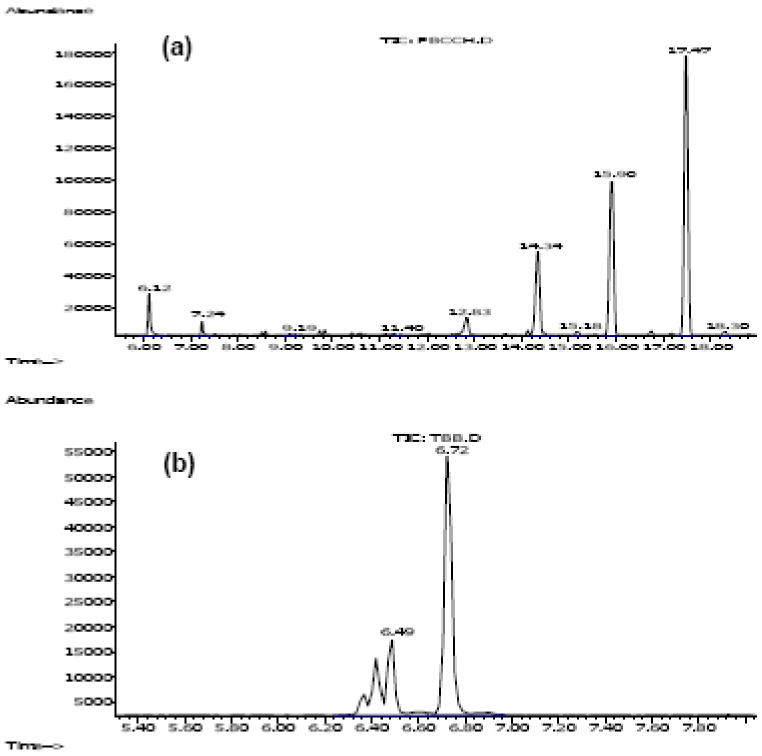


Figure 3. ECNI-MS TIC of (a) Technical PBCCH and (b) 1,3,5-Tribromobenzene

CONCLUSIONS

Due to their wide spread uses, halogenated flame retardants (XFRs) have rapidly accumulated in the environment in the past decades. Environmental monitoring on these XFRs is very limited, partially because of the challenges in developing reliable laboratory analyses. In this work, 12 XFRs were selected and laboratory procedures were developed in order to measure the concentrations in sediment samples collected from the Great Lakes. Method development is based on the modification and renovation of standard methods for other halogenated organic pollutants such as PCBs and PBDEs. The elution pattern of the targeted XFRs from a multiple phase silica gel chromatographic column was investigated. GC/MS analysis found interferences from co-eluting halogen-containing compounds, as well as the impurities and isomers of some XFR standards. The entire procedure is yet to be optimized and validated. Analysis of the sediment samples will use the procedures developed in this work. The concentration data will be used to demonstrate the spatial distribution and time trend of these chemicals in the Great Lakes region.

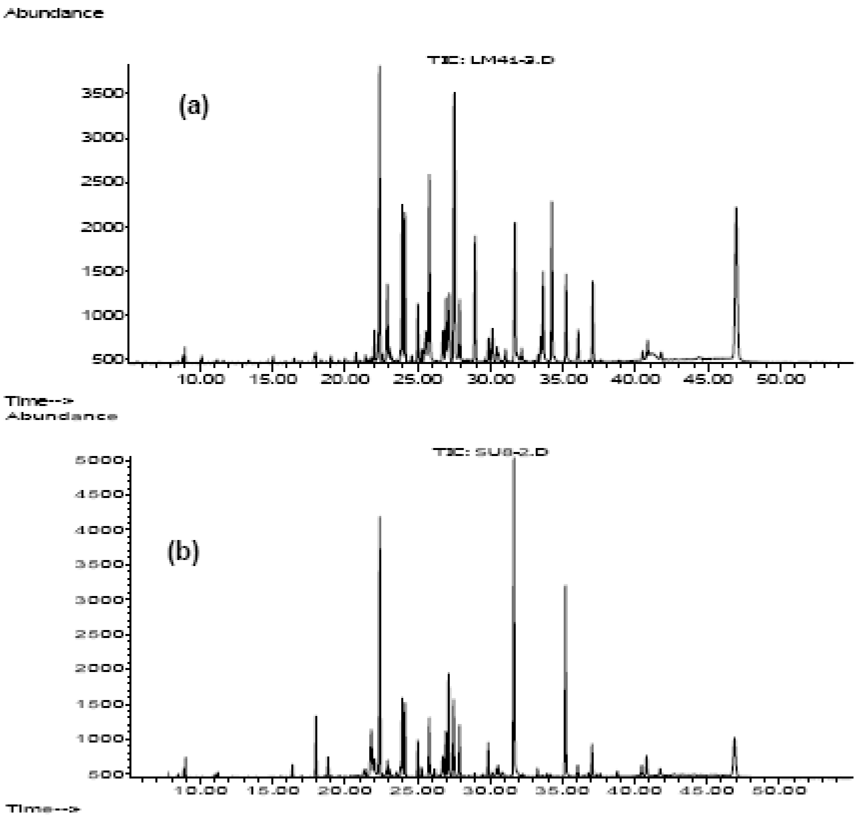


Figure 4. TICs of Sediment Samples: (a) LM41-3 from Lake Michigan, and (b) SU08-2 from Lake Superior. The selected ions included m/z 79, 81, 428, 430, 432, 484, 486, 652, 654.

ACKNOWLEDGEMENTS

This research was supported by funding from the Great Lakes National Program Office (GLNPO) of the U.S. Environmental Protection Agency (USEPA).

REFERENCES

1. Muir D. C. G.; Howard, P. H. 2006. Are There Other Persistent Organic Pollutants? A Challenge for Environmental Chemists. *Environ. Sci. Technol.* 40, 7157-7166.
2. USEPA, 2006. High Production Volume (HPV) Challenge: Robust Summaries & Test

Plans: Dechlorane Plus. Program. http://www.epa.gov/chemrtk/pubs/summaries/dechlorp/c15635tc.htm (Accessed 10/16/2006).

3. Li, A.; Rockne, K. J.; Sturchio, N. C.; Mills, W. J.; Song, W.; Ford, J. C.; Buckley, D. R. 2006a. Chronology of PBDE Air Deposition in the Great Lakes from Sedimentary Records. Final Report to USEPA. (http://tigger.uic.edu/~anli/Final2.pdf)
4. Song, W.; Ford, J. C.; Li, A.; Mills, W. J.; Buckley, D. R.; Rockne, K. J. 2004. Polybrominated diphenyl ethers in the sediment of the Great Lakes. 1. Lake Superior. Environ. Sci. Technol., 38, 3286-3293.
5. Song, W.; Ford, J. C.; Li, A.; Sturchio, N. C.; Rockne, K. J.; Buckley, D. R.; Mills, W. J. 2005b. Polybrominated diphenyl ethers in the sediment of the Great Lakes. 3 - Lakes Erie and Ontario. Environ. Sci. Technol., 39(15): 5600-5605.
6. Song, W.; Li, A.; Ford, J. C.; Sturchio, N. C.; Rockne, K. J.; Buckley, D. R.; Mills, W. J. 2005a. Polybrominated diphenyl ethers in the sediment of the Great Lakes. 2. Lakes Michigan and Huron. Environ. Sci. Technol., 39(10): 3474-3479.
7. Eljarrat, E.; de la Cal, A.; Barcelo, D. 2003. P otential chlorinated and brominated interferences on the polybrominated diphenyl ether determinations by gas chromatography–mass spectrometry. *J. Chromatogr. A,* 1008, 181–192.
8. Focant, J-F.; Sjödin, A.; Patterson Jr., D. G. 2003. Qualitative evaluation of thermal desorption-programmable temperature vaporization-comprehensive two-dimensional gas chromatography–time-of-flight mass spectrometryfor the analysis of selected halogenated contaminants. *J. Chromatogr. A,* 1019, 143–156.
9. Zhu, L-Y.; Hites, R. A. 2003. Determination of Polybrominated Diphenyl Ethers in Environmental Standard Reference Materials. *Anal. Chem.* 75, 6696-6700.
10. Kuosmanen K.; Hyotylainen T.; Hartonen K.; Riekkola M.-L. P. 2002. Hot water extraction coupled on-line with liquid chromatography-gas chromatography for the determination of brominated flame retardants in sediment samples. *J. Chromatogr. A*, 943(1), 113-22.
11. Hyoetylaeinen, T.; Hartonen, K.; S~yndjoki, S.; Riekkola, M-L. 2001. Pressurised Hot-Water Extraction of Brominated Flame Retardants in Sediment Samples. *Chromatographia*, 53, 301-305.
12. Hyoetylaeinen, T.; Hartonen, K. 2002. Determination of brominated flame retardants in environmental samples. *Trends Anal.Chem.* 21, 13-29.

Analyzing Historical and Emerging Halogenated Flame Retardants in the Sediment of the Great Lakes

An Li * and Hua Wei
School of Public Health
University of Illinois at Chicago

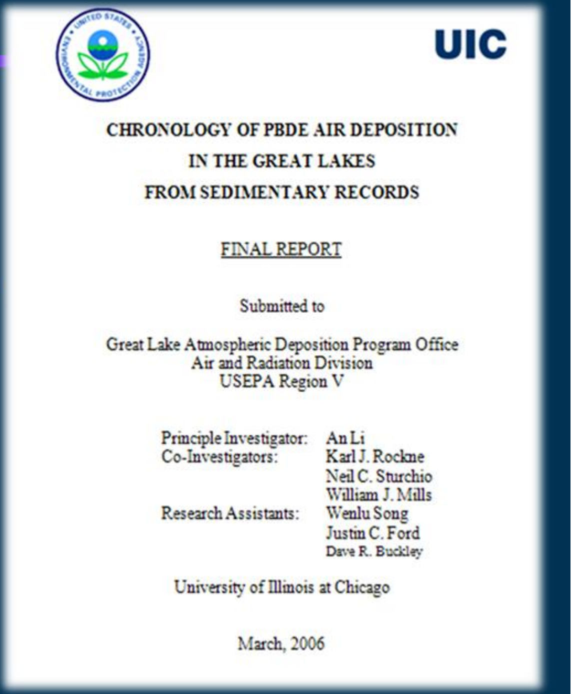
NEMC Conference, Washington DC
August 15, 2008

* anli@uic.edu

Related Projects

A relevant previously completed project –
http://www.uic.edu/~anli/Final2.pdf

A relevant current project –
Debromination of PBDEs in Aquatic Sediments
NSF funded, 2008-2011



UIC

CHRONOLOGY OF PBDE AIR DEPOSITION
IN THE GREAT LAKES
FROM SEDIMENTARY RECORDS

FINAL REPORT

Submitted to

Great Lake Atmospheric Deposition Program Office
Air and Radiation Division
USEPA Region V

Principle Investigator:	An Li
Co-Investigators:	Karl J. Rockne Neil C. Sturchio William J. Mills
Research Assistants:	Wenlu Song Justin C. Ford Dave R. Buckley

University of Illinois at Chicago

March, 2006

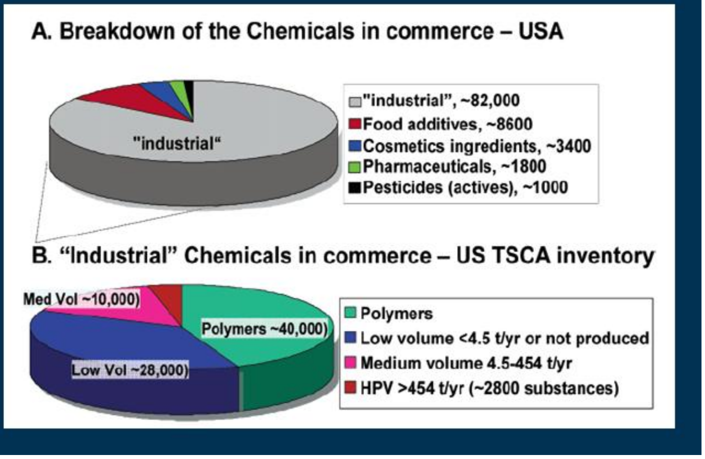
Publications on PBDEs (and PCBs)

- Li, A.; Rockne, K. J.; Mills, W.; Song, W.; Ford, J. C.; Buckley, D. **Polybrominated Diphenyl Ethers in the Sediment of the Great Lakes. 4 – Influencing Factors, Trends, and Implications**. *Environ. Sci. Technol.* 40(24), 7528 - 7534, 2006
- Song, W.; Ford, J. C.; Li, A.; Sturchio, N. C.; Rockne, K. J.; Buckley, D. R.; Mills, W. J. **Polybrominated Diphenyl Ethers in the Sediment of the Great Lakes. 3 - Lakes Erie and Ontario.** *Environ. Sci. Technol.* 39(15): 5600-5605, 2005
- Song, W.; Li, A.; Ford, J. C.; Sturchio, N. C.; Rockne, K. J.; Buckley, D. R.; Mills, W. J. **Polybrominated Diphenyl Ethers in the Sediment of the Great Lakes. 2 - Lakes Huron and Michigan.** *Environ. Sci. Technol.* 39(10), 3474-3479, 2005
- Song, W.; Ford, J. C.; Li, A.; Mills, W. J.; Buckley, D. R.; Rockne, K. J. **Polybrominated Diphenyl Ethers in the Sediment of the Great Lakes. 1 - Lake Superior.** *Environ. Sci. Technol.* 38(12), 3286-3293, 2004
- Buckley, D. R.; Rockne, K. J.; Li, A.; Mills, W. J. **Soot Deposition in the Great Lakes: Implications for Semi-Volatile Hydrophobic Organic Pollutant Deposition.** *Environ. Sci. Technol.* 38(6), 1732-1739, 2004
- Li, A.; Rockne, K. J.; Mills, W.; Song, W.; Ford, J. C.; Buckley, D. **PCBs in the Sediment of the Great Lakes: Distribution and Trend, Homolog and Congener Patterns, and In-situ Degradation.** *Environ. Pollution* (accepted)
- Buckley, D. R.; Rockne, K. J.; Li, A.; Ford, J. C.; Mills, W. J. **Organic Matter Degradation in Near-Surface Great Lakes Sediments** *Geochim Cosmochim Acta* (in review)
- Li, A.; Ford, J. C.; Song, W.; Buckley, D. R.; Rockne, K. J.; Sturchio, N. C.; Mills, W. J. **Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls in the Sediments of Seepage Lakes in the Great Lakes Region** (in preparation)

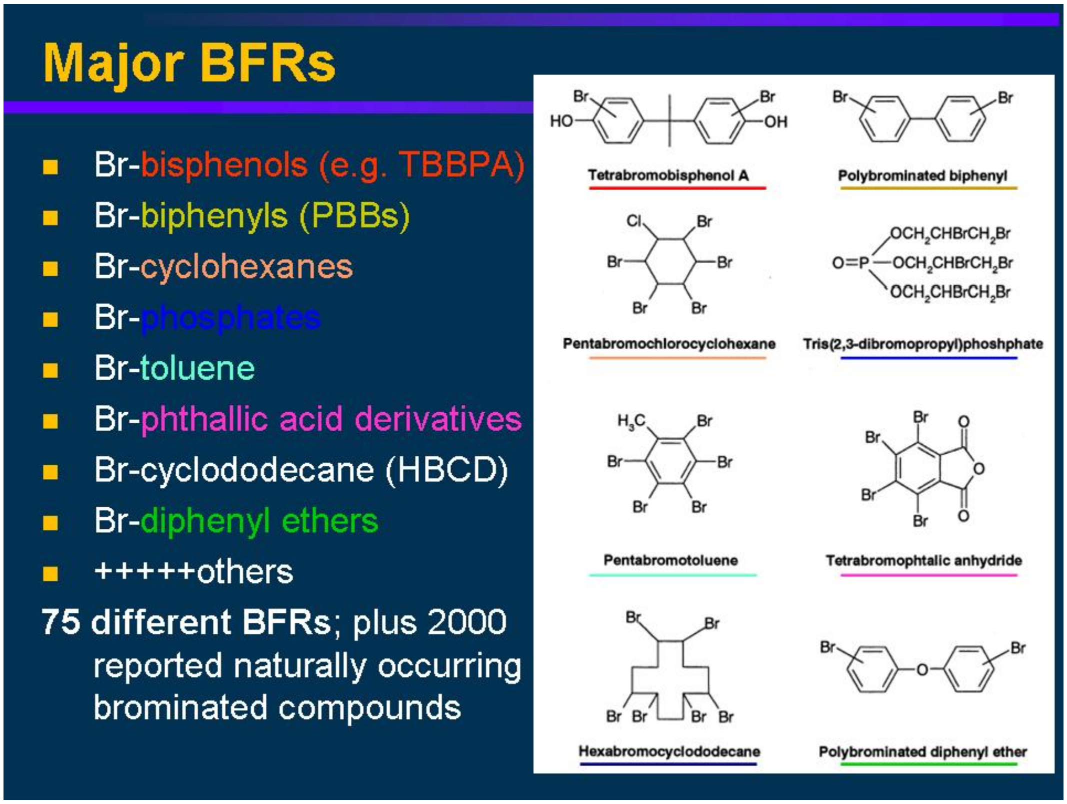
Chemical World

- About 8,400,000 substances are commercially available
- 240,000 are reported to be inventoried/regulated
- 82,000 are in EPA TSCA inventory
- 2,800 are in EPA HPV list

Only a tiny fraction of these have been environmentally monitored


A. Breakdown of the Chemicals in commerce – USA

B. "Industrial" Chemicals in commerce – US TSCA inventory



Major BFRs

- Br-bisphenols (e.g. TBBPA)
- Br-biphenyls (PBBs)
- Br-cyclohexanes
- Br-phosphates
- Br-toluene
- Br-phthallic acid derivatives
- Br-cyclododecane (HBCD)
- Br-diphenyl ethers
- +++++others

75 different BFRs; plus 2000 reported naturally occurring brominated compounds

Tetrabromobisphenol A

Polybrominated biphenyl

Pentabromochlorocyclohexane

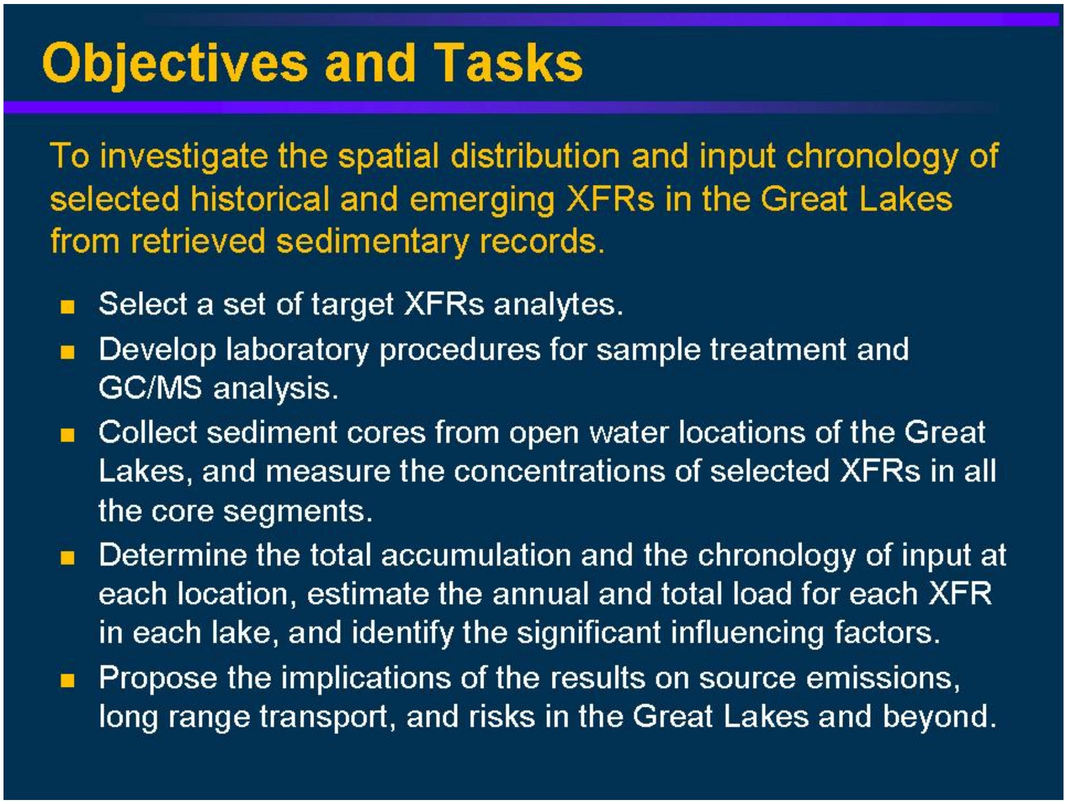
Tris(2,3-dibromopropyl)phoshphate

Pentabromotoluene

Tetrabromophtalic anhydride

Hexabromocyclododecane

Polybrominated diphenyl ether



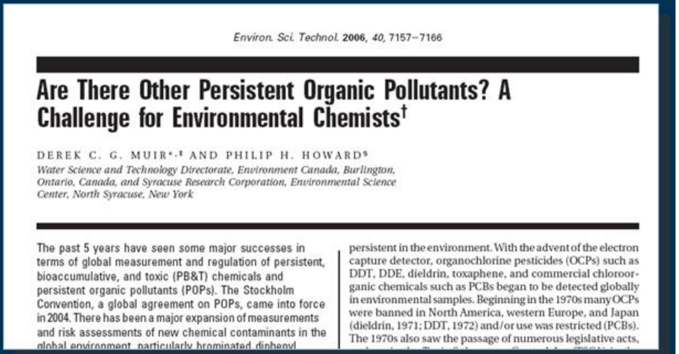
Objectives and Tasks

To investigate the spatial distribution and input chronology of selected historical and emerging XFRs in the Great Lakes from retrieved sedimentary records.

- Select a set of target XFRs analytes.
- Develop laboratory procedures for sample treatment and GC/MS analysis.
- Collect sediment cores from open water locations of the Great Lakes, and measure the concentrations of selected XFRs in all the core segments.
- Determine the total accumulation and the chronology of input at each location, estimate the annual and total load for each XFR in each lake, and identify the significant influencing factors.
- Propose the implications of the results on source emissions, long range transport, and risks in the Great Lakes and beyond.

Selection of target XFRs

- Production information
  - High production volume (HPV)
  - Application scales
- Regulations
  - TSCA
  - Priority chemical
- Analytical feasibility
  - Extractability
  - Cleanup
  - Instrument availability
- Expected environmental behavior:
  - Persistence
  - Bioaccumulation
  - Long range transport potential



Environ. Sci. Technol. 2006, 40, 7157–7166

Are There Other Persistent Organic Pollutants? A Challenge for Environmental Chemists†

DEREK C. G. MUIR*,‡ AND PHILIP H. HOWARD§

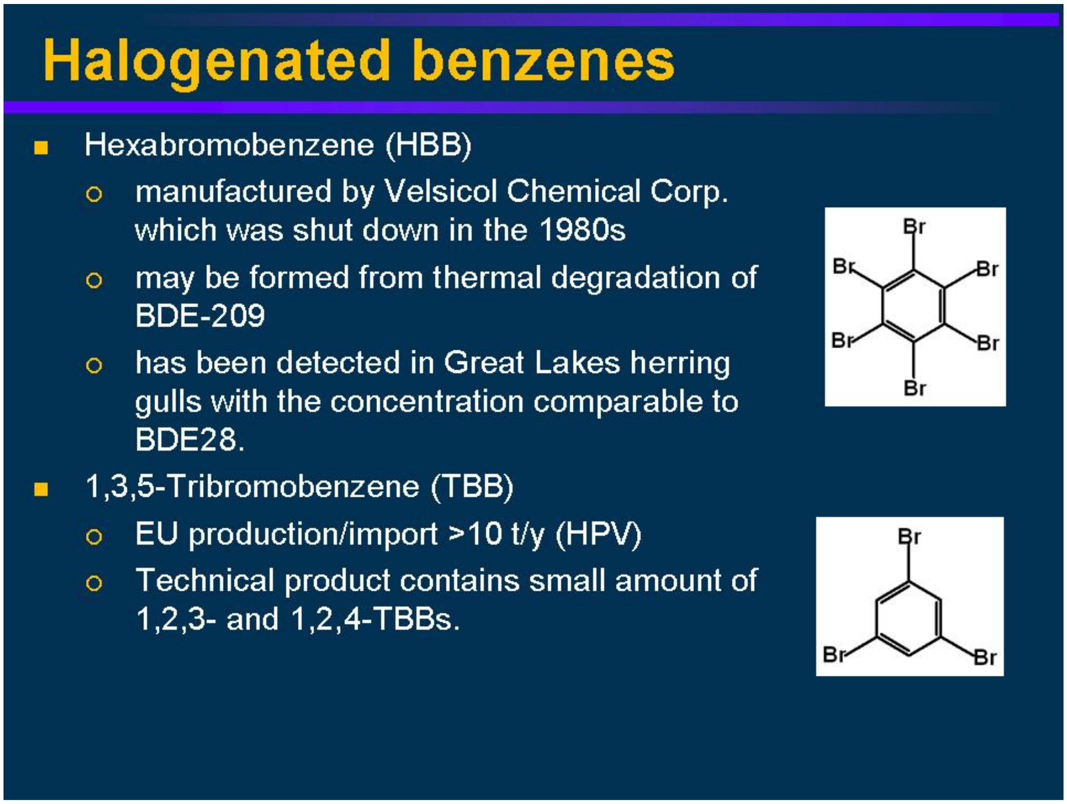
Water Science and Technology Directorate, Environment Canada, Burlington, Ontario, Canada, and Syracuse Research Corporation, Environmental Science Center, North Syracuse, New York

The past 5 years have seen some major successes in terms of global measurement and regulation of persistent, bioaccumulative, and toxic (PB&T) chemicals and persistent organic pollutants (POPs). The Stockholm Convention, a global agreement on POPs, came into force in 2004. There has been a major expansion of measurements and risk assessments of new chemical contaminants in the global environment, particularly brominated diphenyl

persistent in the environment. With the advent of the electron capture detector, organochlorine pesticides (OCPs) such as DDT, DDE, dieldrin, toxaphene, and commercial chloroorganic chemicals such as PCBs began to be detected globally in environmental samples. Beginning in the 1970s many OCPs were banned in North America, western Europe, and Japan (dieldrin, 1971; DDT, 1972) and/or use was restricted (PCBs). The 1970s also saw the passage of numerous legislative acts,

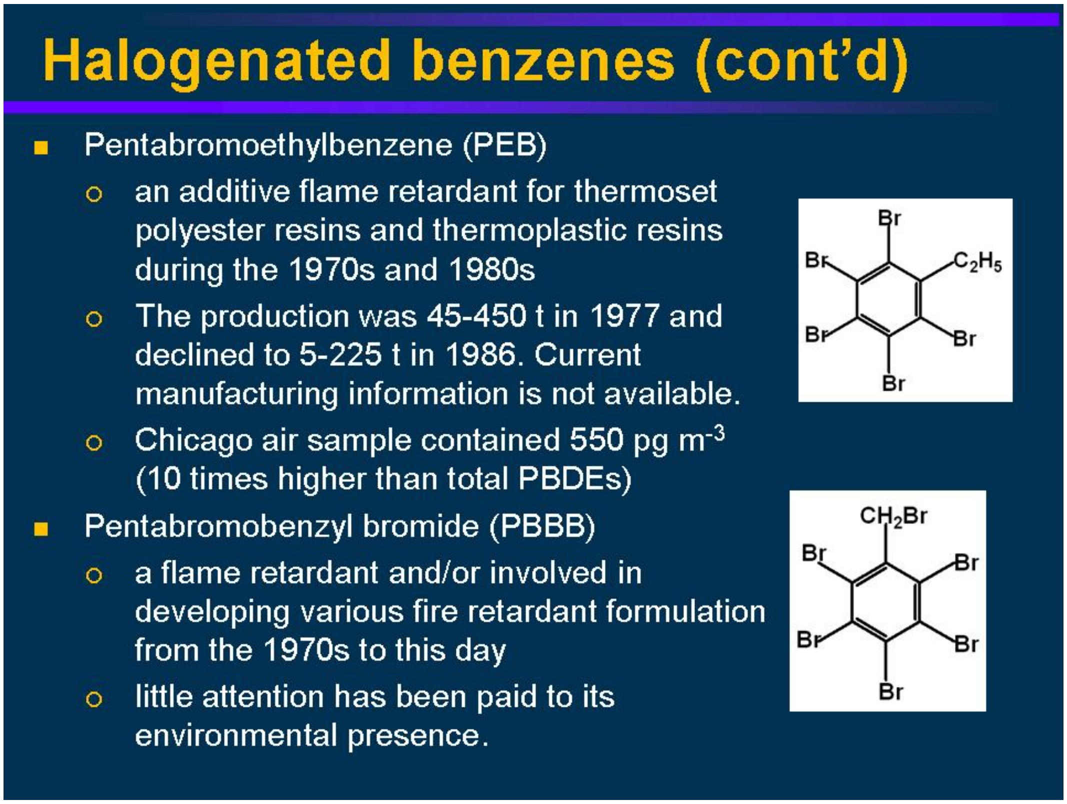
Targeted XFRs in this study

Abbr'n	Name	Formular	MW
HBB	Hexabromobenzene	C_6Br_6	551.5
TBB	1,3,5-Tribromobenzene	$C_6H_3Br_3$	314.8
PBT	Pentabromotoluene	$C_7H_3Br_5$	486.6
PEB *	Pentabromoethylbenzene	$C_8H_5Br_5$	500
TBCT	Tetrabromo-o-chlorotoluene	$C_7H_3ClBr_4$	442.5
PBBB	Pentabromobenzyl bromide	$C_7H_2ClBr_5$	522.5
TBTCH	Tribromotrichloro-cyclohexane	$C_6H_6Cl_3Br_3$	468
TBDCH	Tetrabromodichloro-cyclohexane	$C_6H_6Cl_2Br_4$	468
PBCCH	Pentabromochlorocyclo-hexane	$C_6H_6ClBr_5$	513.5
DBMCH	1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane	$C_8H_{12}Br_4$	428
HCCP	Hexachlorocyclopentadiene	C_5Cl_7	308.5
HCDBCO	Hexachlorocyclopentadienyl-dibromocyclooctane	$C_{13}H_{10}Cl_6Br_2$	536
DP	Dechlorane Plus	$C_{18}H_{12}Cl_{12}$	654
DBDPE	Decabromodiphenylethane	$C_{14}H_4Br_{10}$	972
BB153	2,2',4,4',5,5'-hexabromobiphenyl	$C_{12}H_4Br_6$	628
TBE	1,2-Bis(2,4,6-tribromophenoxy)ethane	$C_{14}H_8O_2Br_6$	688
TBPYR	1,3,6,8-Tetrabromopyrene	$C_{16}H_6Br_4$	518



Halogenated benzenes

- Hexabromobenzene (HBB)
  - manufactured by Velsicol Chemical Corp. which was shut down in the 1980s
  - may be formed from thermal degradation of BDE-209
  - has been detected in Great Lakes herring gulls with the concentration comparable to BDE28.
- 1,3,5-Tribromobenzene (TBB)
  - EU production/import >10 t/y (HPV)
  - Technical product contains small amount of 1,2,3- and 1,2,4-TBBs.

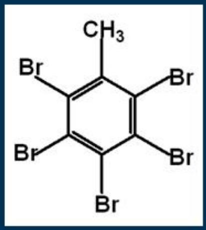


Halogenated benzenes (cont'd)

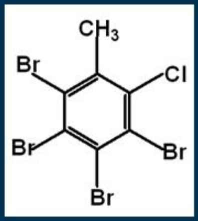
- Pentabromoethylbenzene (PEB)
  - an additive flame retardant for thermoset polyester resins and thermoplastic resins during the 1970s and 1980s
  - The production was 45-450 t in 1977 and declined to 5-225 t in 1986. Current manufacturing information is not available.
  - Chicago air sample contained 550 pg m^{-3} (10 times higher than total PBDEs)
- Pentabromobenzyl bromide (PBBB)
  - a flame retardant and/or involved in developing various fire retardant formulation from the 1970s to this day
  - little attention has been paid to its environmental presence.

Halogenated toluenes

- Pentabromotoluene (PBT)
  - a flame retardant in textiles, polyester resins, and paint emulsions, but the production volume is unknown.
  - trade name FR-105 by Ameribrom (Fort Lee, NJ).
  - has been detected in Baltic Sea sediment, at a Swedish wastewater treatment plant, in the egg pools from all six herring gull colonies.

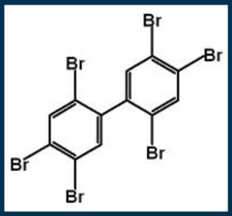


- Tetrabromo-o-chlorotoluene (TBCT)
  - Little research has been done for substituted toluenes containing both bromine and chlorine

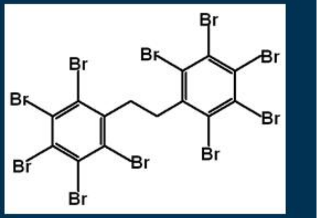


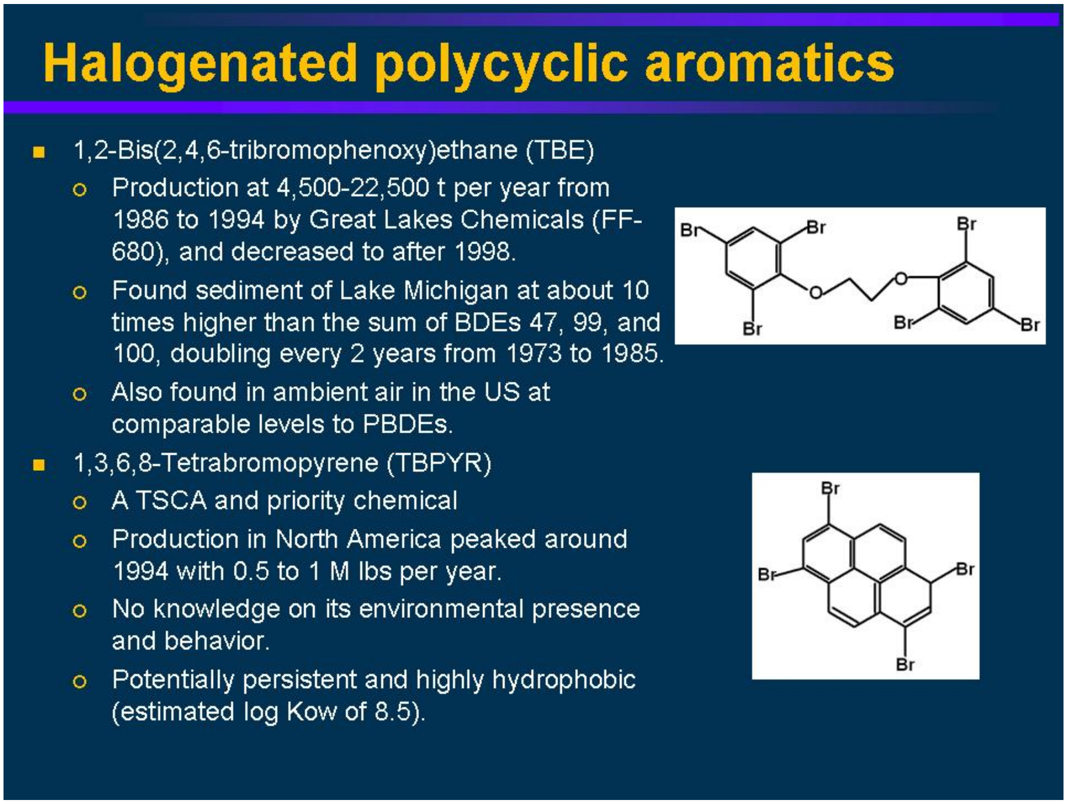
Halogenated polycyclic aromatics

- 2,2',4,4',5,5'-hexabromobiphenyl (BB153)
  - most commonly detected PBBs
  - About 11.8 million pounds PBBs manufactured 1970-1974 and almost exclusively applied to a particular thermoplastic in electronic equipment housings
  - Although a legacy pollutant, PBBs still exist in human blood, fish and sediment of the Great Lakes region.



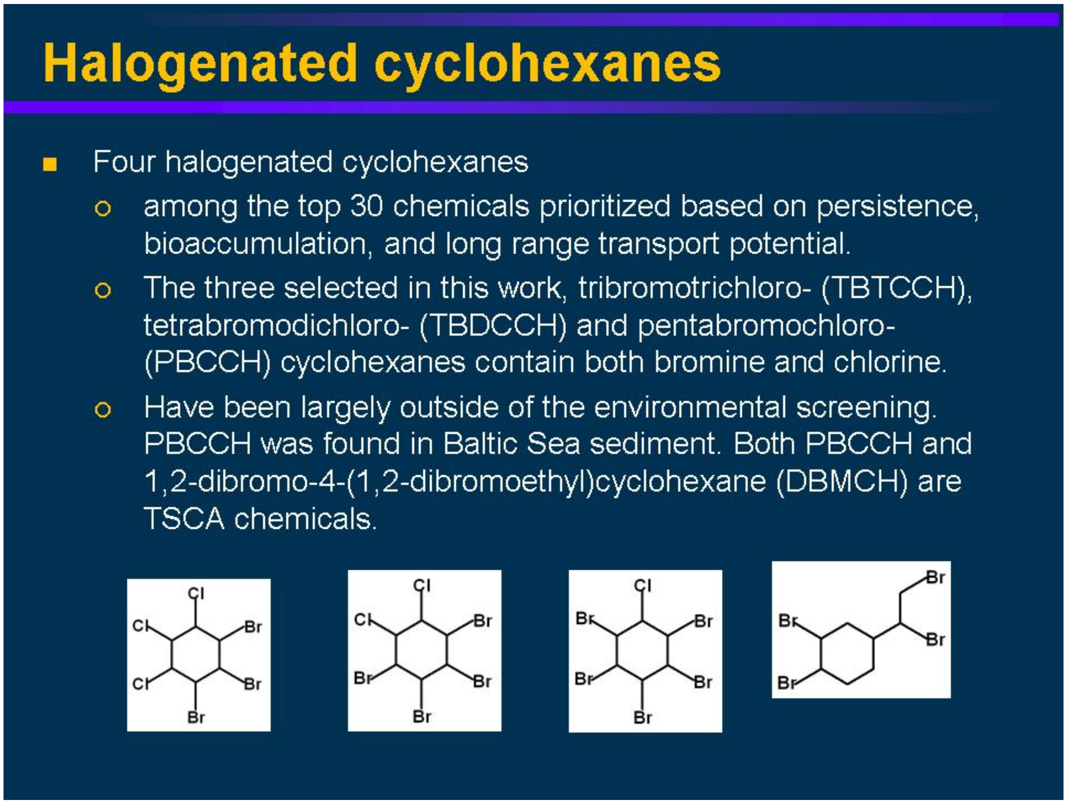
- Decabromodiphenylethane (DBDPE)
  - Additive flame retardant introduced in the early 1990s (SAYTEX 8010, Firemaster® 2100)
  - For the same applications as BDE209. However, due to lack of oxygen, it does not form PBDD/Fs during combustion.
  - Found in the air of the Great Lakes





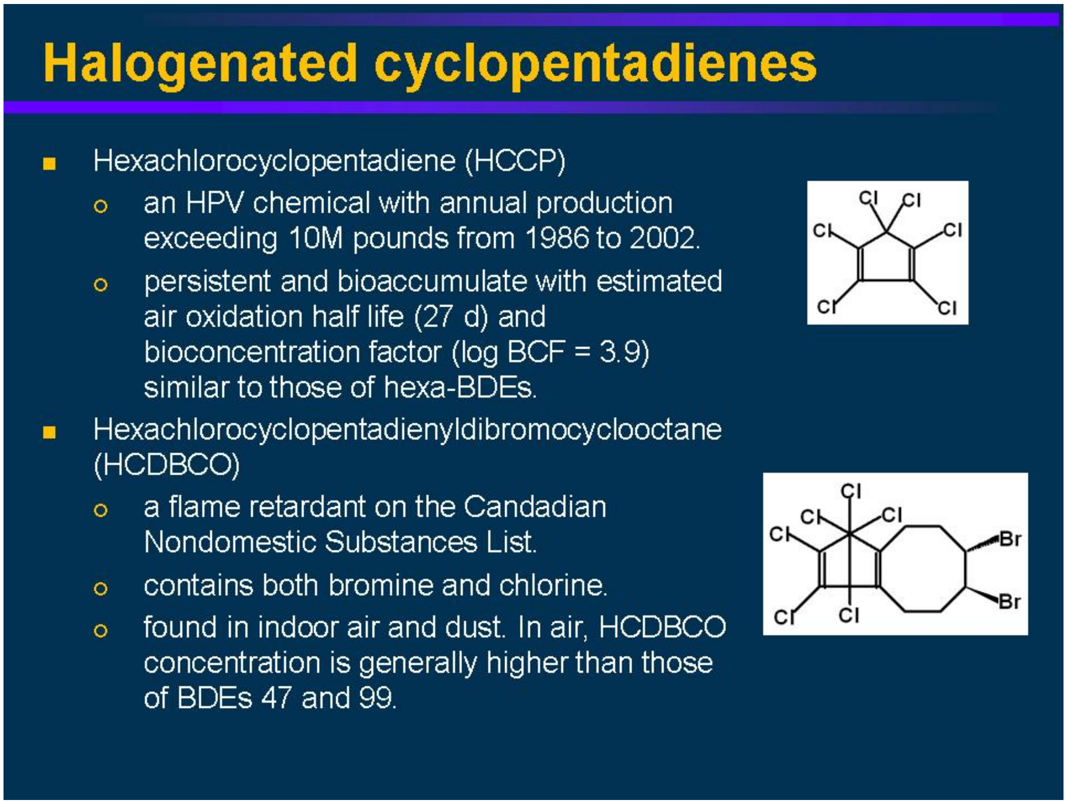
Halogenated polycyclic aromatics

- 1,2-Bis(2,4,6-tribromophenoxy)ethane (TBE)
  - Production at 4,500-22,500 t per year from 1986 to 1994 by Great Lakes Chemicals (FF-680), and decreased to after 1998.
  - Found sediment of Lake Michigan at about 10 times higher than the sum of BDEs 47, 99, and 100, doubling every 2 years from 1973 to 1985.
  - Also found in ambient air in the US at comparable levels to PBDEs.
- 1,3,6,8-Tetrabromopyrene (TBPYR)
  - A TSCA and priority chemical
  - Production in North America peaked around 1994 with 0.5 to 1 M lbs per year.
  - No knowledge on its environmental presence and behavior.
  - Potentially persistent and highly hydrophobic (estimated log Kow of 8.5).



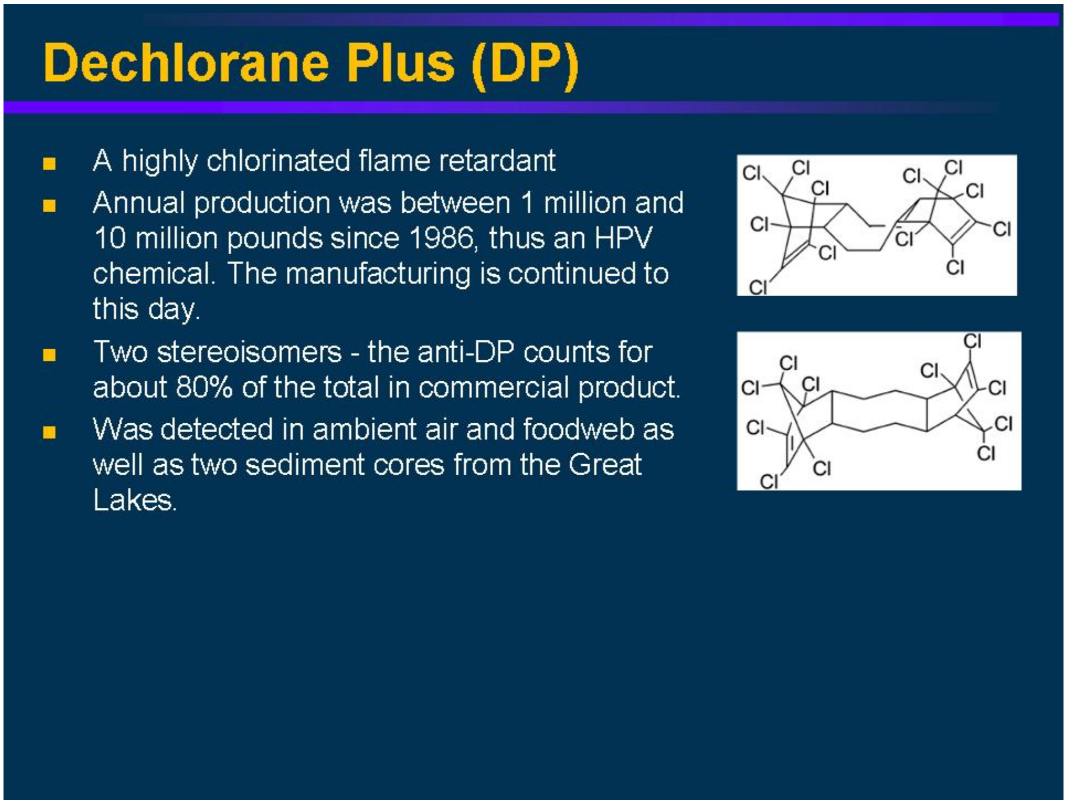
Halogenated cyclohexanes

- Four halogenated cyclohexanes
  - among the top 30 chemicals prioritized based on persistence, bioaccumulation, and long range transport potential.
  - The three selected in this work, tribromotrichloro- (TBTCCH), tetrabromodichloro- (TBDCCH) and pentabromochloro- (PBCCH) cyclohexanes contain both bromine and chlorine.
  - Have been largely outside of the environmental screening. PBCCH was found in Baltic Sea sediment. Both PBCCH and 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (DBMCH) are TSCA chemicals.



Halogenated cyclopentadienes

- Hexachlorocyclopentadiene (HCCP)
  - an HPV chemical with annual production exceeding 10M pounds from 1986 to 2002.
  - persistent and bioaccumulate with estimated air oxidation half life (27 d) and bioconcentration factor (log BCF = 3.9) similar to those of hexa-BDEs.
- Hexachlorocyclopentadienyldibromocyclooctane (HCDBCO)
  - a flame retardant on the Candadian Nondomestic Substances List.
  - contains both bromine and chlorine.
  - found in indoor air and dust. In air, HCDBCO concentration is generally higher than those of BDEs 47 and 99.

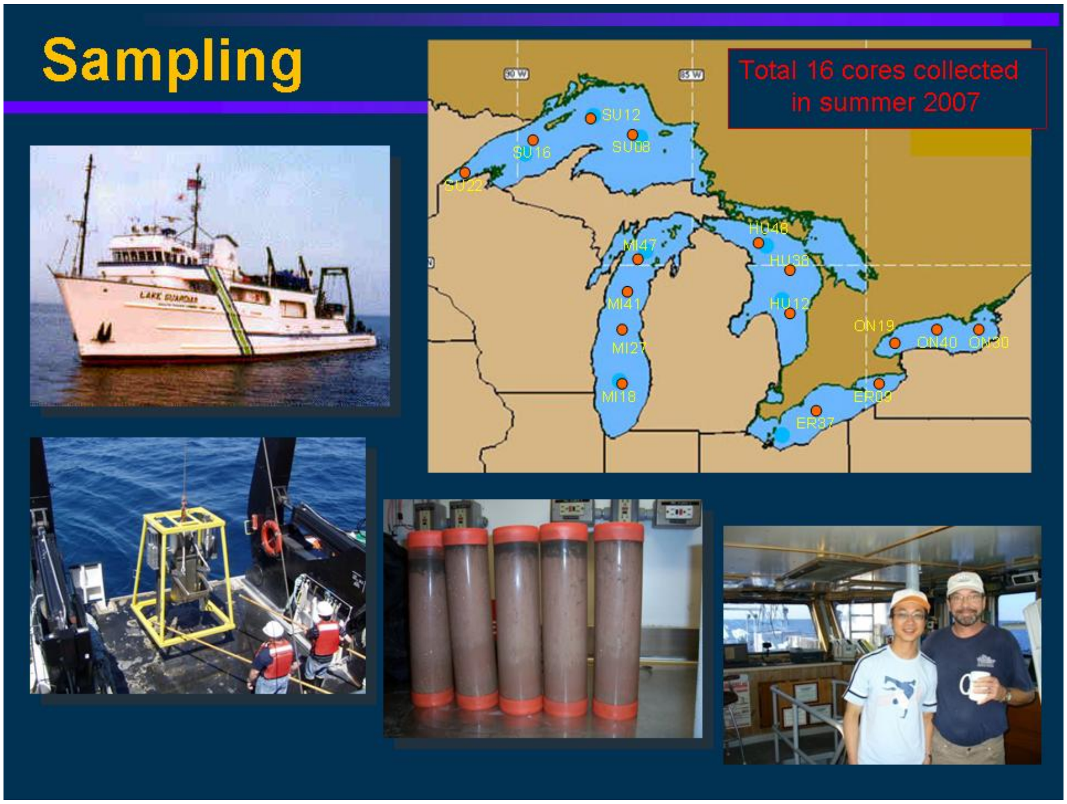


Dechlorane Plus (DP)

- A highly chlorinated flame retardant
- Annual production was between 1 million and 10 million pounds since 1986, thus an HPV chemical. The manufacturing is continued to this day.
- Two stereoisomers - the anti-DP counts for about 80% of the total in commercial product.
- Was detected in ambient air and foodweb as well as two sediment cores from the Great Lakes.

XFRs may not be included in this work

- Hexabromocyclo-dodecane (HBCD)
  - Best by LC/MS
- Tetrabromobisphenol A (TBBPA)
  - Best by LC/MS
- Pentabromobenzyl acrylate (PBBA)
  - a flame retardant substitute of PBDEs
  - does not elute from the multi-phase silica gel cleanup column with up to 140 mL of pure hexane or hexane:dichloromethane mixture.
- Tetrafluorobromobenzene and 1,2-dichloro-4-(trifluoromethyl)benzene
  - HPV chemicals
  - high volatility may cause high uncertainty in lab analysis.
- Chlorinated paraffins (CPs)
  - several homologs each having many isomers, often resulting in unresolved peaks on normal GC columns and requiring HRMS or tandem MS/MS



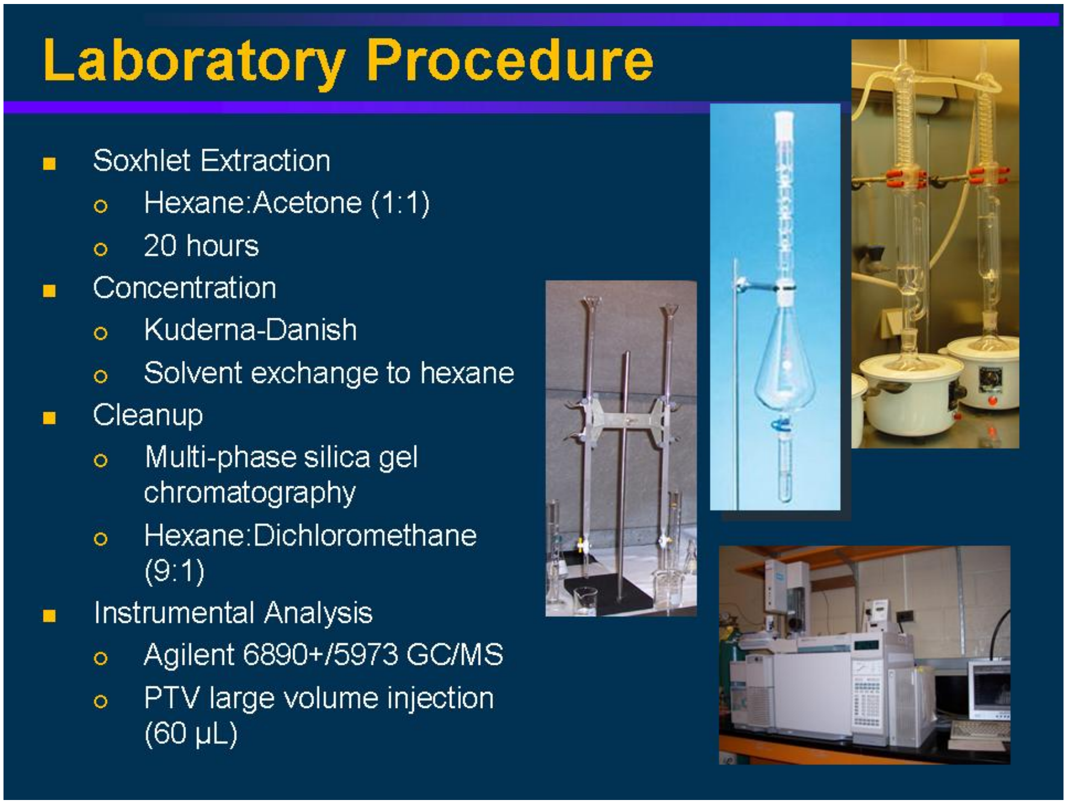
Sampling

Total 16 cores collected in summer 2007

Core cutting

The 16 cores were cut into 222 segment samples in a freezer room.

Torrey saw



Laboratory Procedure

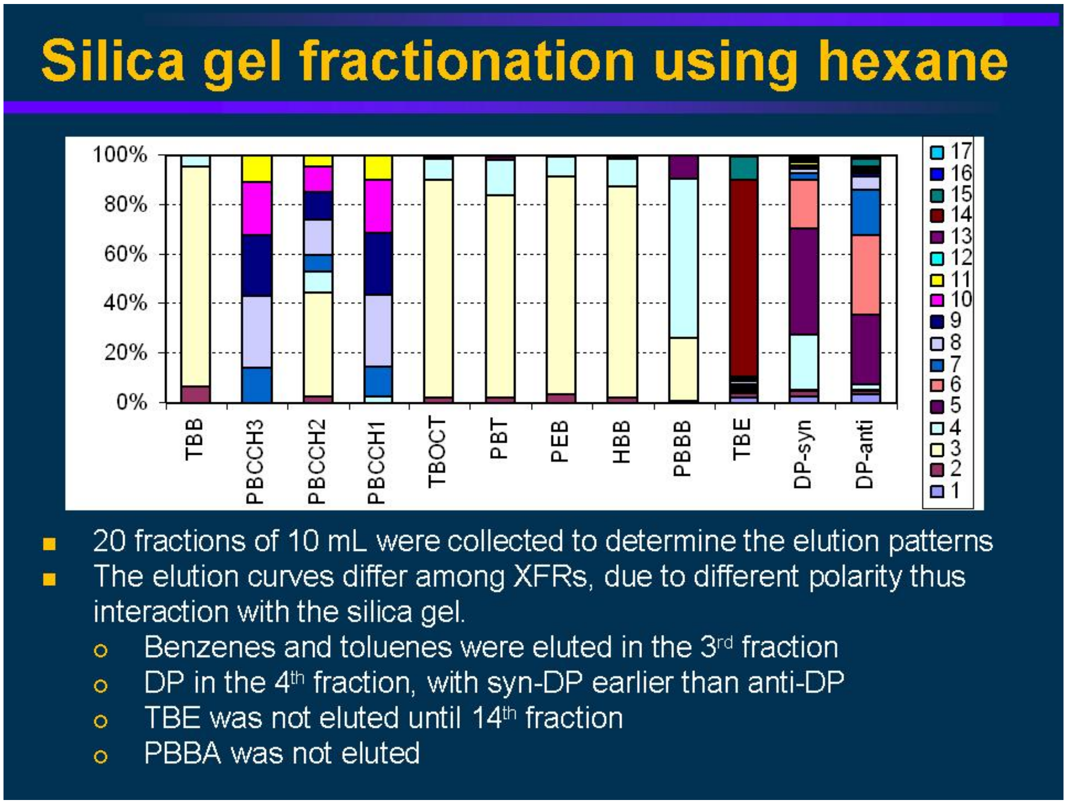
- Soxhlet Extraction
    - Hexane:Acetone (1:1)
    - 20 hours
- Concentration
    - Kuderna-Danish
    - Solvent exchange to hexane
- Cleanup
    - Multi-phase silica gel chromatography
    - Hexane:Dichloromethane (9:1)
- Instrumental Analysis
    - Agilent 6890+/5973 GC/MS
    - PTV large volume injection (60 μL)

Challenges

- Challenges raised from
  - Lacks of standard methods
  - Few published reference papers
  - Unavailability of the research purity chemical standards
  - Contacting the XFR manufacturers
- Laboratory key processes
  - Extraction efficiencies
  - Fractionation elution behavior
    - Type of silica gel
    - Amount of silica gel
    - Solvent used
  - GC/MS
    - PTV operating parameters
    - GC separation
    - MS operating parameters

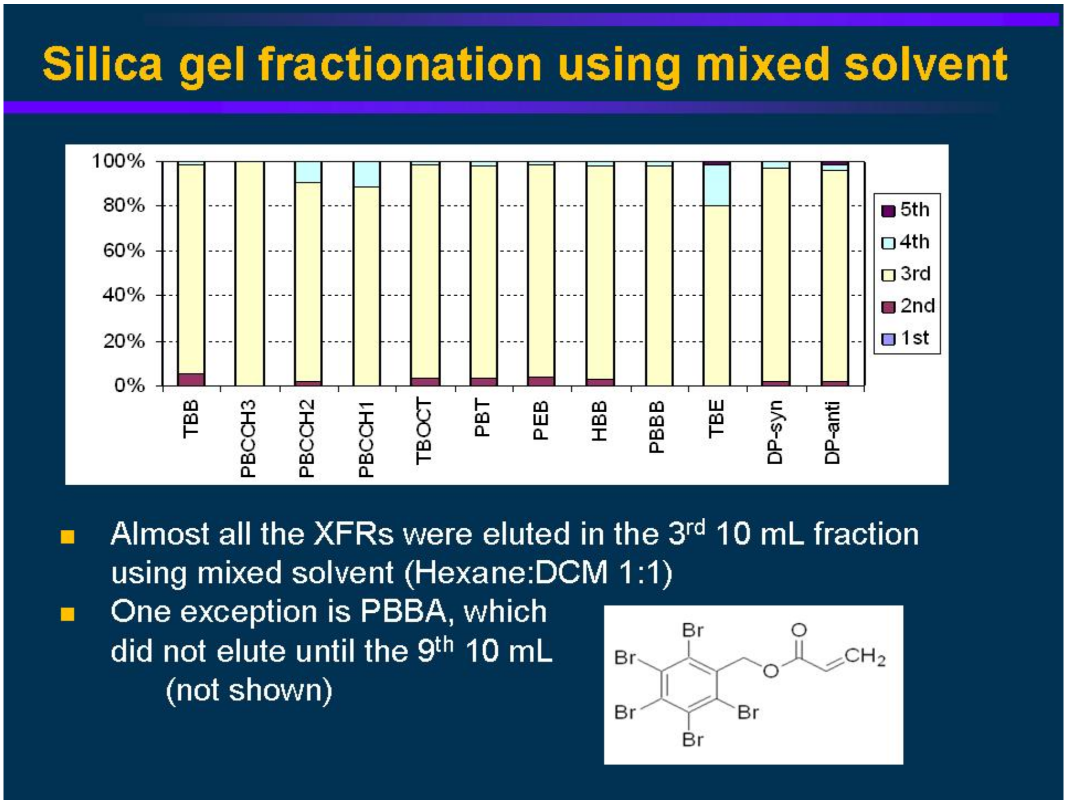
Silica gel column optimization

- Objective – to ensure the complete elution in sample cleanup and to lower the solvent consumption
- Micro silica gel column may be sufficient for relatively clean samples. For dirty samples, we use a total of 9 g silica gel
- Acidic/neutral silica column was found to have the same efficiency as the acidic/basic/ neutral column
- Two elution solvents compared
- Flow rate 1-2 drop per sec



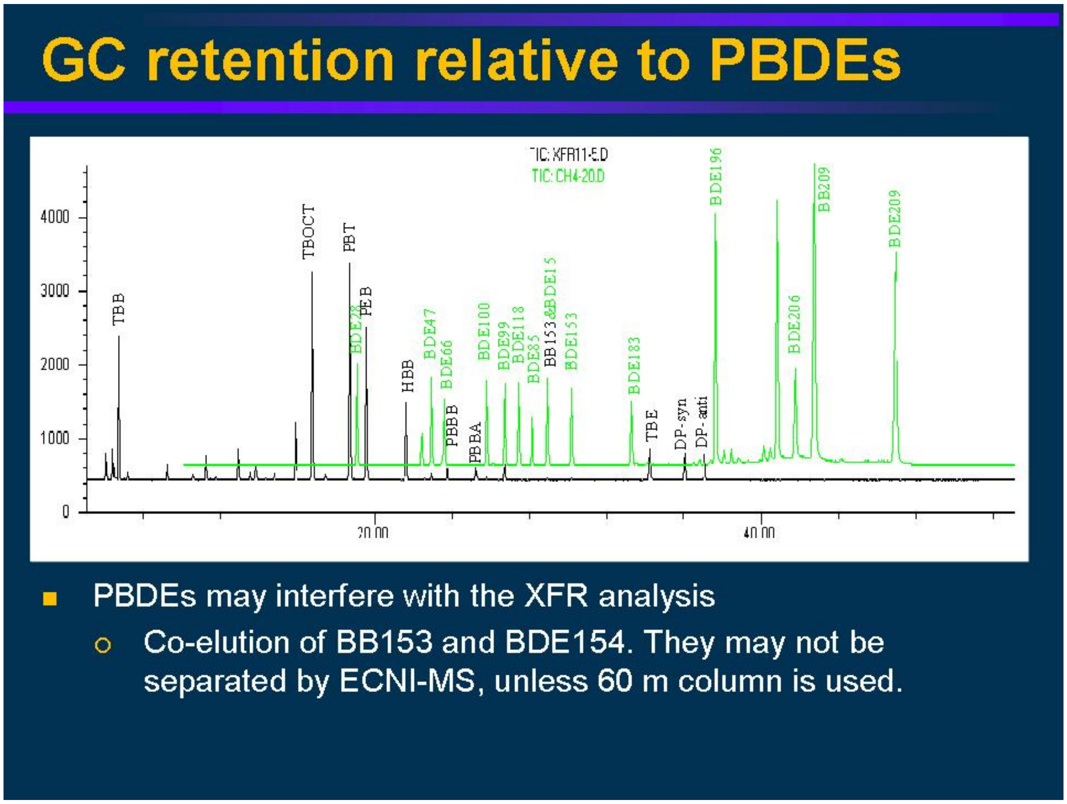
Silica gel fractionation using hexane

- 20 fractions of 10 mL were collected to determine the elution patterns
- The elution curves differ among XFRs, due to different polarity thus interaction with the silica gel.
  - Benzenes and toluenes were eluted in the 3rd fraction
  - DP in the 4th fraction, with syn-DP earlier than anti-DP
  - TBE was not eluted until 14th fraction
  - PBBA was not eluted



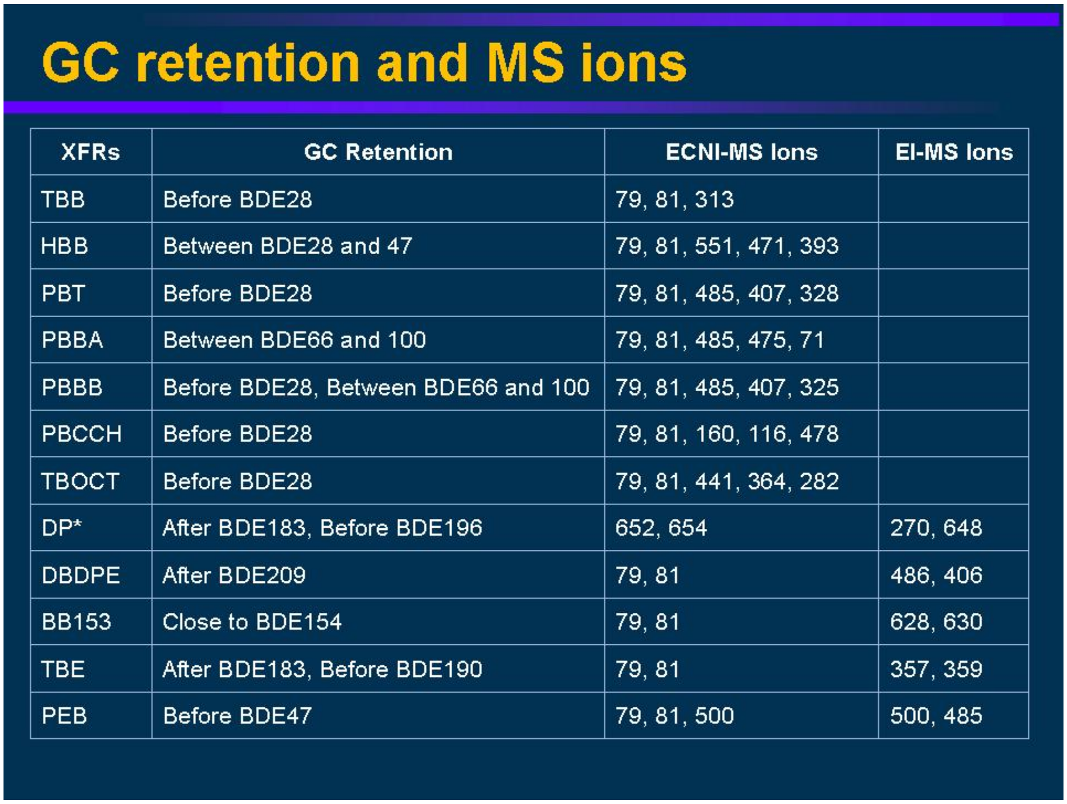
Silica gel fractionation using mixed solvent

- Almost all the XFRs were eluted in the 3rd 10 mL fraction using mixed solvent (Hexane:DCM 1:1)
- One exception is PBBA, which did not elute until the 9th 10 mL (not shown)



GC retention relative to PBDEs

- PBDEs may interfere with the XFR analysis
  - Co-elution of BB153 and BDE154. They may not be separated by ECNI-MS, unless 60 m column is used.

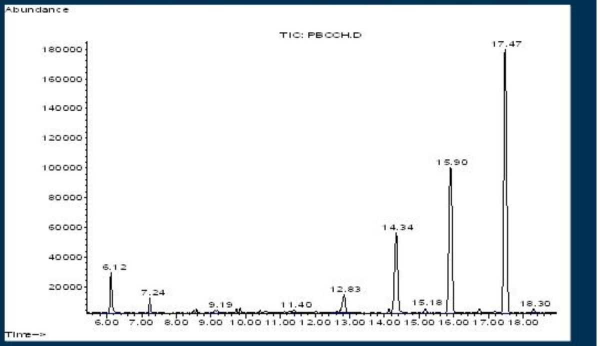


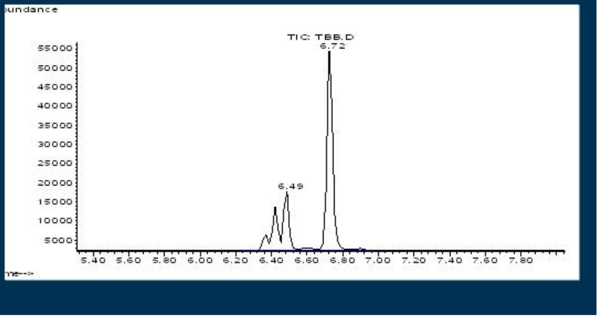
GC retention and MS ions

XFRs	GC Retention	ECNI-MS Ions	EI-MS Ions
TBB	Before BDE28	79, 81, 313	
HBB	Between BDE28 and 47	79, 81, 551, 471, 393	
PBT	Before BDE28	79, 81, 485, 407, 328	
PBBA	Between BDE66 and 100	79, 81, 485, 475, 71	
PBBB	Before BDE28, Between BDE66 and 100	79, 81, 485, 407, 325	
PBCCH	Before BDE28	79, 81, 160, 116, 478	
TBOCT	Before BDE28	79, 81, 441, 364, 282	
DP*	After BDE183, Before BDE196	652, 654	270, 648
DBDPE	After BDE209	79, 81	486, 406
BB153	Close to BDE154	79, 81	628, 630
TBE	After BDE183, Before BDE190	79, 81	357, 359
PEB	Before BDE47	79, 81, 500	500, 485

Other problems to be solved

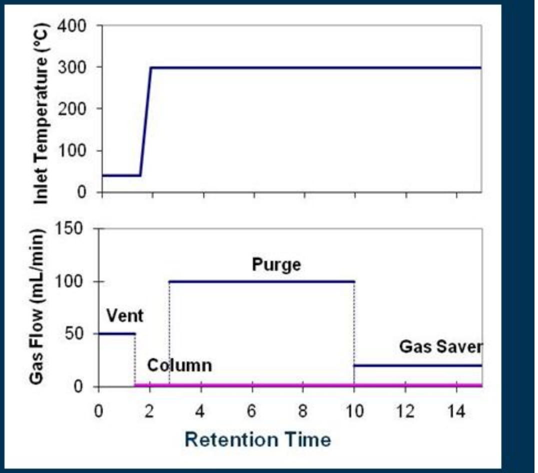
- Isomers
  - Cyclohexanes have isomers which may have different response factors
- Impurities
  - 1,3,5-TBB standard has impurities of other TBB isomers
- Quantitation is complicated in these cases



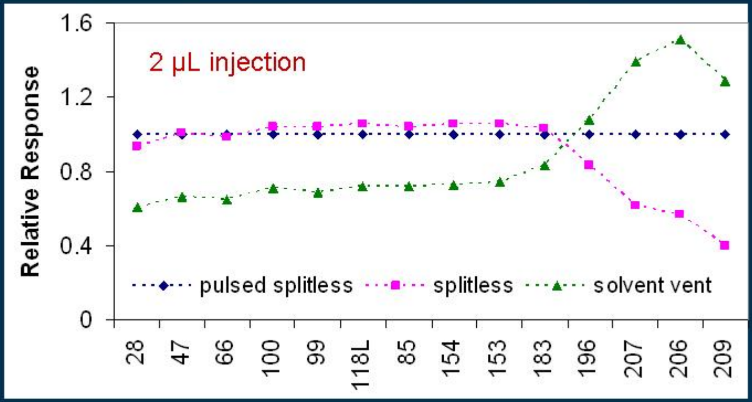


PTV parametric evaluation

- Programmable temperature vaporizing (PTV) injection:
  - one of the LVI methods
  - designed to handle semi-volatile analytes in complex or dirty samples
- Objective – enhance analytical sensitivity and compare with splitless
- Parameter evaluation
  - Linearity with volume
  - Initial and final PTV inlet temperature
  - Vent and purge flow rate



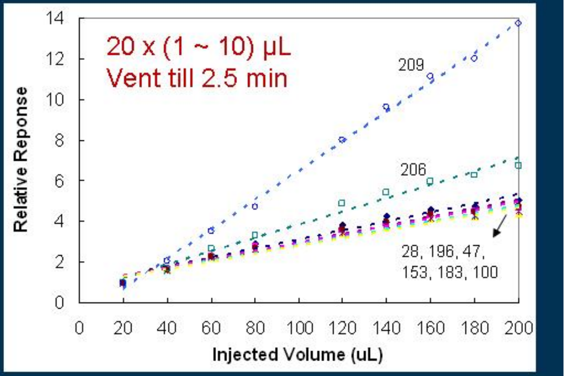
Comparison of injection methods



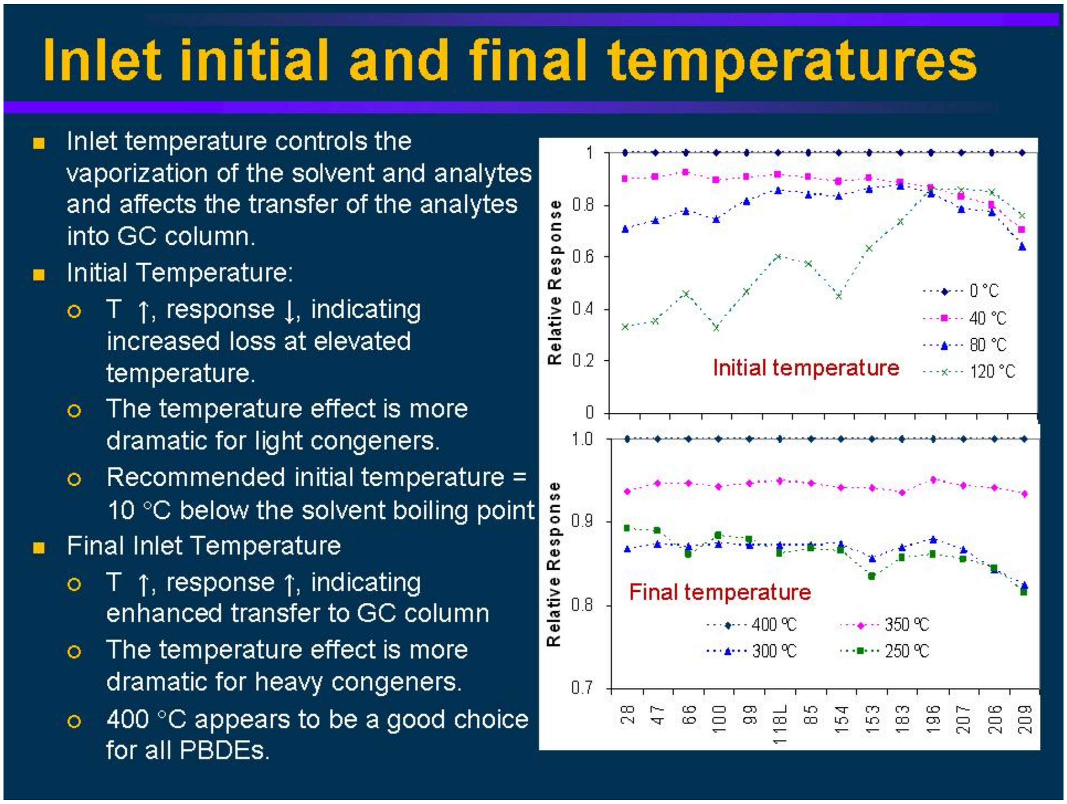
- For light congeners, pulsed splitless ≈ splitless > PTV.
  - Lower response by PTV suggests lost (17-39%) during solvent vent
- For heavy congeners, PTV > pulsed splitless > splitless
  - Lower response using splitless may indicate degradation in the glass-wool-packed liner at 300 °C.

Linear response with injection volume

- MS responses increased linearly with increasing total injected volumes in the range of 20-200 µL.
- The linearity for BDE209 (R^2 = 0.997) was better than for other congeners (R^2 = 0.970-0.985).
- Further increase in injection volume may overwhelm the inlet, causing invasion of solvent liquid into the column.
- Multiple injections may be better than a single injection of the same total volume

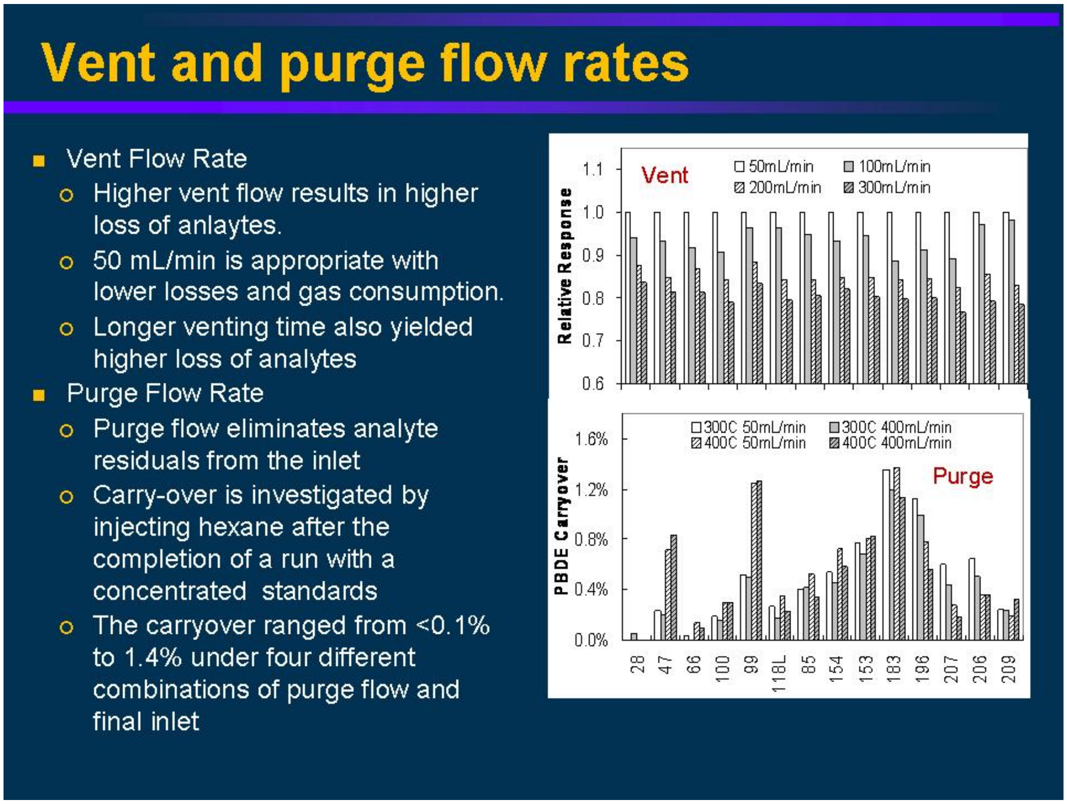


- Injected volume should balance with the vapor elimination rate, which depends on the initial inlet temperature and pressure, venting duration and vent flow rate.



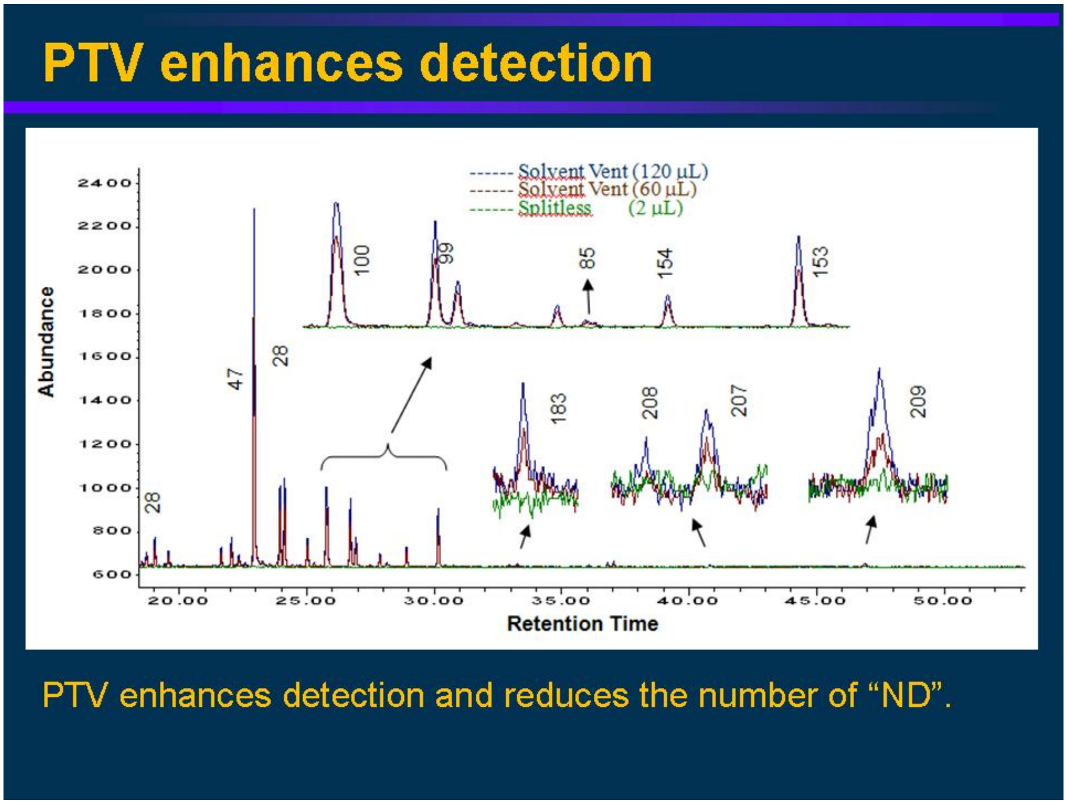
Inlet initial and final temperatures

- Inlet temperature controls the vaporization of the solvent and analytes and affects the transfer of the analytes into GC column.
- Initial Temperature:
  - T ↑, response ↓, indicating increased loss at elevated temperature.
  - The temperature effect is more dramatic for light congeners.
  - Recommended initial temperature = 10 °C below the solvent boiling point
- Final Inlet Temperature
  - T ↑, response ↑, indicating enhanced transfer to GC column
  - The temperature effect is more dramatic for heavy congeners.
  - 400 °C appears to be a good choice for all PBDEs.



Vent and purge flow rates

- Vent Flow Rate
  - Higher vent flow results in higher loss of anlaytes.
  - 50 mL/min is appropriate with lower losses and gas consumption.
  - Longer venting time also yielded higher loss of analytes
- Purge Flow Rate
  - Purge flow eliminates analyte residuals from the inlet
  - Carry-over is investigated by injecting hexane after the completion of a run with a concentrated standards
  - The carryover ranged from <0.1% to 1.4% under four different combinations of purge flow and final inlet



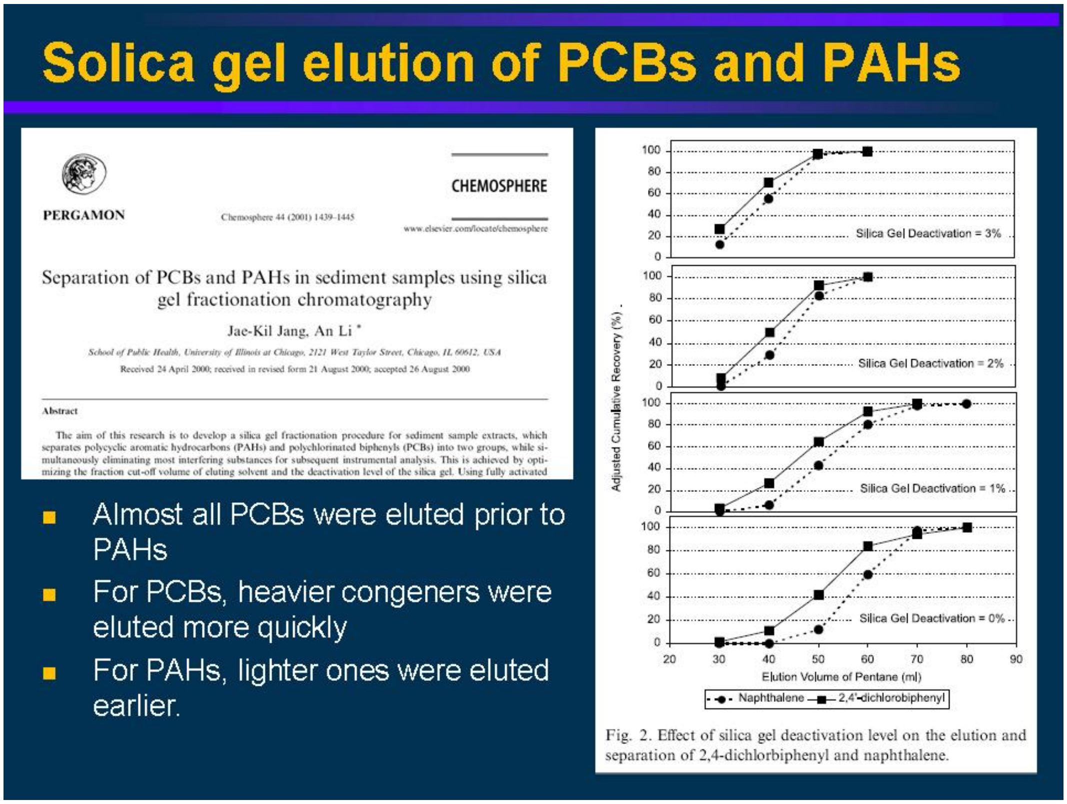
PTV enhances detection

PTV enhances detection and reduces the number of “ND”.

Acknowledgements

- Funding from USEPA - Great Lakes National Program Office (GLNPO).
- We thank the crew of EPA R/V Lake Guardian for assistance in sediment sampling

Thank YOU for listening!



Solica gel elution of PCBs and PAHs

PERGAMON

Chemosphere 44 (2001) 1439–1445

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Separation of PCBs and PAHs in sediment samples using silica gel fractionation chromatography

Jae-Kil Jang, An Li *

School of Public Health, University of Illinois at Chicago, 2121 West Taylor Street, Chicago, IL 60612, USA

Received 24 April 2000; received in revised form 21 August 2000; accepted 26 August 2000

Abstract

The aim of this research is to develop a silica gel fractionation procedure for sediment sample extracts, which separates polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) into two groups, while simultaneously eliminating most interfering substances for subsequent instrumental analysis. This is achieved by optimizing the fraction cut-off volume of eluting solvent and the deactivation level of the silica gel. Using fully activated

- Almost all PCBs were eluted prior to PAHs
- For PCBs, heavier congeners were eluted more quickly
- For PAHs, lighter ones were eluted earlier.

Fig. 2. Effect of silica gel deactivation level on the elution and separation of 2,4-dichlorbiphenyl and naphthalene.

In a Green World, Shouldn't All Analyses Be Micro?

David Mauro
Meta Environmental, Inc.
49 Clarendon Street
Watertown, MA 02472
dmauro@metaenv.com

ABSTRACT

Most methods for the analysis of organic compounds in water, soil or other solids rely on an extraction step where the sample is treated with solvents to collect and concentrate trace constituents. This step can be labor intensive and costly, as well as generate substantial volumes of potentially hazardous solvents as wastes. In addition, large quantities of soil and water, which may contain hazardous chemicals, are collected but never analyzed, and must also be handled as waste. For several years, microextraction methods have been promoted by a relatively small group of advocates for reducing the labor needed and minimizing the amount of waste generated in the laboratory over existing methods. One such approach was developed at META Environmental, Inc. in the early 1990s with support of EPRI and its member utilities. Two microscale solvent extraction (MSE) methods for the simultaneous extraction and analysis of volatile and semivolatile organic compounds in soil or water were developed. Validation reports were sent to EPA's Office of Solid Waste on September 27, 1996 and on April 11, 1997. The methods were reviewed by the SW-846 Organic Methods Workgroup and, after several rounds of review and comment, EPA published Methods 3511 and 3570 on their web site as part of the SW-846 Update IVB in November 2002. MSE methods require smaller sample volumes, use up to 90% less solvent and generate up to 90% less waste, and can result in faster and lower cost sample preparation overall. MSE methods have been used successfully by META under both field and fixed laboratory conditions for over 15 years and have been shown to produce data comparable to other EPA methods. This paper will review META's experience with EPA Methods 3511 and 3570 and highlight the advantages and disadvantages of the methods.

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Method Development Studies for the GC/MS Determination of Polyaromatic Hydrocarbons (PAHs) and Alkyl-PAH (APAH).

National Environmental Monitoring Conference – Washington D.C. 2008

David Thal
Operations Manager – Sediments and Tissues

Aug 15, 2008

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Addressing PAHs in Contaminated Sediments

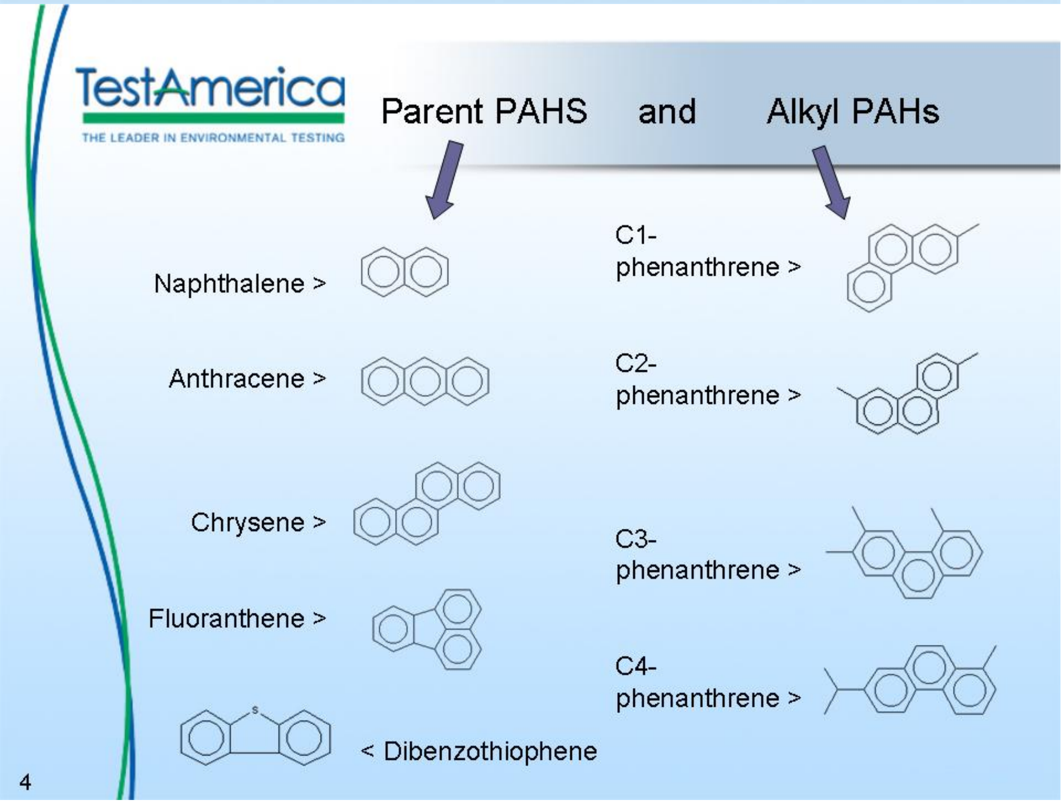
- Which PAHs/APAHs to study?
- At what concentrations do we need to demonstrate good performance? (i.e., sensitivity, specificity, accuracy & precision)
- What are the qualitative identification criteria for alkyl PAHs?
- How do we quantify alkyl PAHs?
- Do we need SIM for sediments work?
- How comparable are typical GC/MS methods?
- What cautions should labs and users observe?

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Part 1

Structure, Sources and Risk



TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Parent PAHS and Alkyl PAHs

Naphthalene >

Anthracene >

Chrysene >

Fluoranthene >

< Dibenzothiophene

C1-phenanthrene >

C2-phenanthrene >

C3-phenanthrene >

C4-phenanthrene >

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Sources of PAHs to Sediments

- Petrogenic – low temperature formation – petroleum distillates and residues
- Biogenic – low temperature formation – diagenesis in marine sediments
- Pyrolytic - high temperature formation -compounds generated in combustion processes
  - ~ Low temperature formation permits and preserves alkylation
  - ~ High temperature formation and treatment produces the unsubstituted parent or substrate.
- MGP Plants, Aluminum Smelters, thermal processes, crankcase oils, asphalt and concrete sealants.

TestAmerica

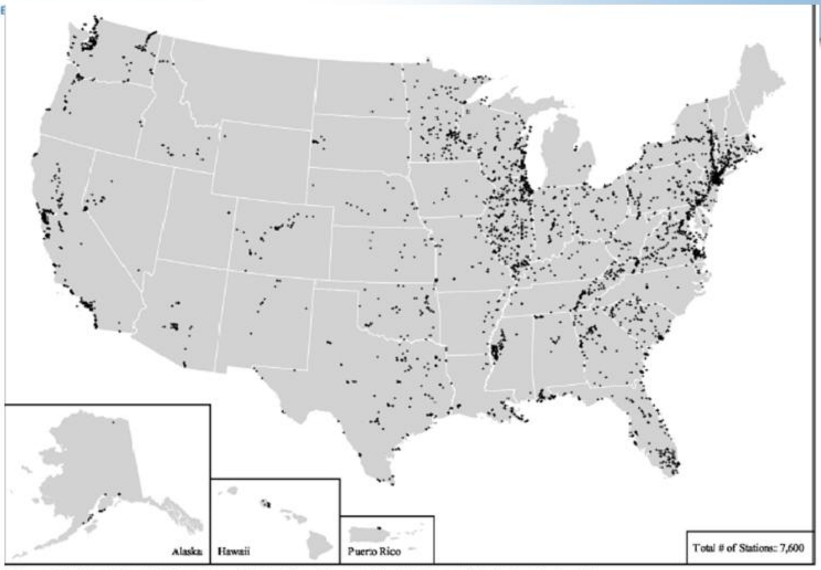
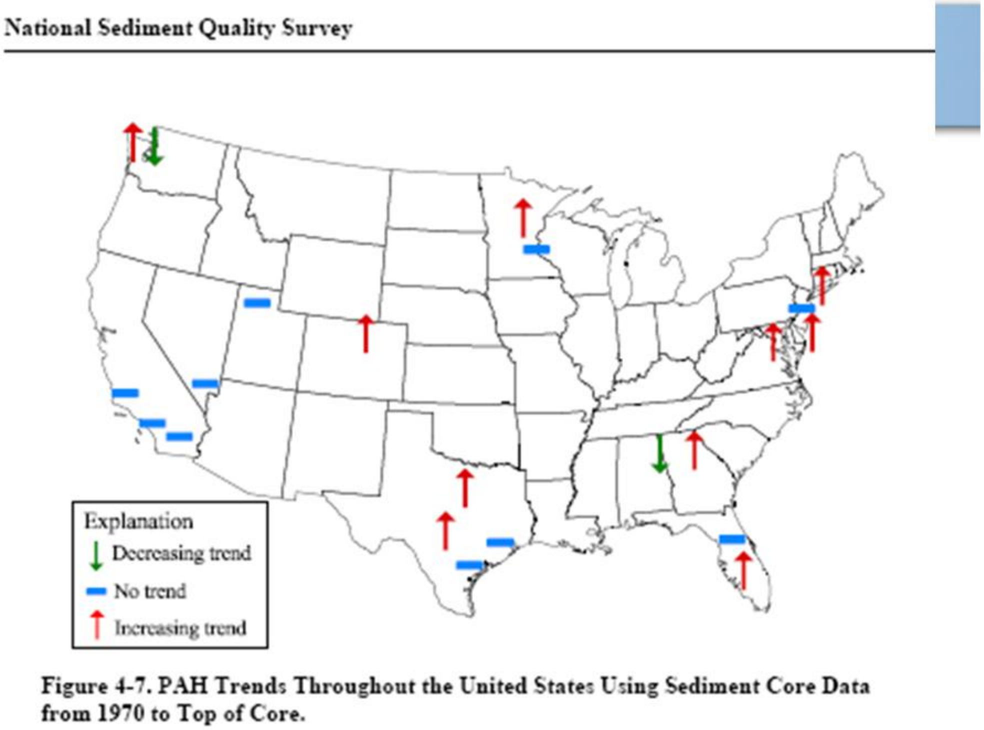


Figure 3-2. Sampling Stations Classified as Tier 1 (Associated Adverse Effects Are Probable).



National Sediment Quality Survey

Figure 4-7. PAH Trends Throughout the United States Using Sediment Core Data from 1970 to Top of Core.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Risk from PAH Exposures

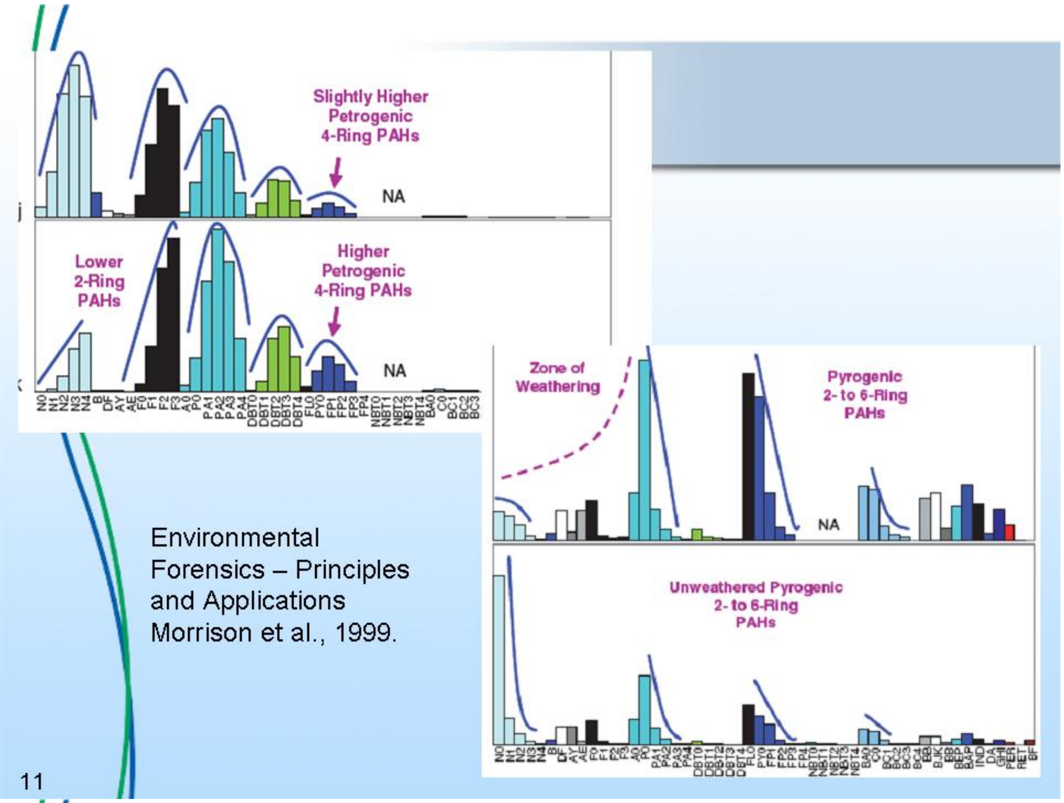
- BaP and 6 others recognized as probable human carcinogens in 2001 (IRIS).
- EPA is currently performing an assessment of PAH Mixtures for IRIS.
- Ecological risk to benthic receptors in sediments has been defined, benchmarks established using narcosis, EqP approach.
- Dioxin-Like Aryl Hydrocarbon Receptor induced genotoxic properties (e.g. BaP).
- Recent studies at University of Utrecht, Sweden identify specific alkyl PAHS has having higher ArH responses than parents.

Part 2

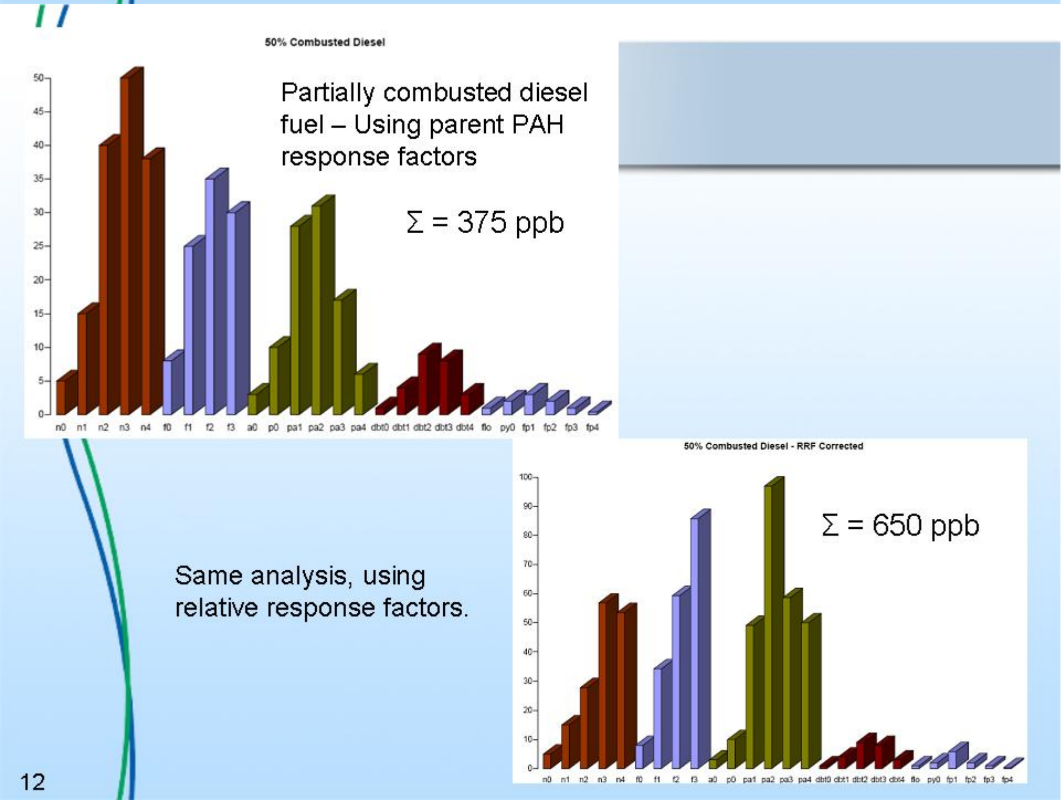
Approaches to PAH & Alkyl PAH Analysis

PAH Analysis Continuum

- Method 8270C (GC/MS) (1-10 ug)
- Method 8270C SIM (GC/MS) (0.1-1 ug)
- Method 8270C (Full Scan GC/MS, Inert Source, upgraded signal path – includes Alkyl Homologs) (0.1 ug)*
- Method 8310 (HPLC) (0.1 ug)
- NOAA Status and Trends – GC/MS SIM w/ Alkyl Homologs (0.02 ug)
- NYSDEC ASP (NJDEP CARP, CARB 429) Isotope Dilution Method (GCMS-SIM) (10 ng) (0.01 ug)
- NYSDEC ASP (NJDEP CARP, CARB 429) Isotope Dilution with Alkyl Homologs (GCMS-SIM)(0.01-0.02 ng)
- Method 8272 (ASTM D7363) – Isotope Dilution Solid Phase Microextraction (SPME), for dissolved Toxic Units.



Environmental Forensics – Principles and Applications Morrison et al., 1999.



Partially combusted diesel fuel – Using parent PAH response factors

$\Sigma = 375$ ppb

Same analysis, using relative response factors.

$\Sigma = 650$ ppb

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

United States
Environmental Protection
Agency

Office of Research and Development
Washington, DC 20460

EPA-600-R-02-013
www.epa.gov

EPA

Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

ESB Procedures for PAH Mixtures (Benthic Organism)

- Documents the procedures for establishing ESBs.
- Uses Equilibrium Partitioning (EqP) approach to account for differing bioavailability of each PAH.
- Uses a larger range of PAHS and Alkyl PAH homologs (APAH), to more fully capture the loadings. Defines the "EPA 34" list.
- Uses Narcosis Theory to demonstrate that the acute toxicity-K_{OW} slope is similar across species.
- Establishes the relationship between acute and chronic thresholds.
- Uses the final chronic value in water, and K_{OC} to calculate the sediment quality benchmark in ug/g_{OC}.

March 2007 - EPA Circulated Draft Revision ERA Guidelines

- Recognizes that pore water methods are logistically difficult and may be expensive
- Refines the traditional approach (sediment to pore water conversion).
- Recommends sediment testing for 18 parent and 16 alkyl homologs. (EPA 34 PAH List)
- Recognizes that no EPA method is available to address the homologs
- Identifies Lauenstein & Cantillo (1998) as a method. [aka NOAA Method]
- Clarifies conversion of sediment conc's to sum of toxic units (ΣTU).

Consider Adding These NOAA Analytes

Biphenyl
Dibenzothiophene
C1-C4 – Dibenzothiophenes
1-Methylphenanthrene
2,6-Dimethylnaphthalene
1,6,7-Trimethylnaphthalene

Equilibrium Sediment Benchmarks

- Relates dry-weight sediment conc. to pore water, sediment OC-sorbed organics & sulfide bound (metals) conc.
- For metals the risk is calculated in terms of molar excess of the metal over the moles/g acid volatile sulfides. (Corrections for salinity and pH).
- For nonionic organics the dissolved fraction is calculated using equilibrium with “organic carbon”:
- $C_{sed} = C_{dis}\ f_{OC}\ K_{OC}$
- $C_{sed\ OC} = C_{dis}\ K_{OC}$

What Levels of Quantitation are needed for PAHs and Alkyl PAHs in sediment?

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

How Much TOC to Expect?

Study	Location/Type	Range (%)
Y. Ouyanga,, J. E. Zhang and L.-T. Ou. J. Environ. Qual. 35:93-100 (2006)	Cedar and Ortega Rivers	**2.3-22.6**
Juracek, et al. USGS 1962-99	Tuttle Creek Lake, KS	**0.84-2.0**
Johnson, T.C., et al *Limnology and Oceanography 1982*	Lake Superior/ Surficial	**0.5-5**
South Carolina Estuarine and Coastal Assessment Program. 1999-2000	Tidal creeks in South Carolina/ 30 Stations	**<0.1 to 5.4%**
Florida Institute of Technology October 25, 2002	Gulf of Mexico sandy sediments/ surficial grabs.	**0.06-1.39**
Patton et al., DOE PNNL-13417 January 2001	Columbia and Snake Rivers	**0.29 - 4.3**
Valente et al., SAIC for Massachusetts Coastal Zone Management Agency	Buzzards Bay, MA/	**0.5-5.8**
Davis et al., Washington State Pesticide Monitoring Program, 1994	Lake Sacajawea, Okanogan River, Lake Chelan, Entiat River, Soleduck River	**0.6-2.0**
Chalmers et al., NAWQA, cited in Water-Resources Investigations Report 02-4179	46 streambeds nationwide	**0.6 to 5.6**

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

What levels of TOC do we need to account for?

- In sediments with > 0.2 % TOC, the predominant phase for sorption of nonionic organic chemicals to sediment particles appears to be organic carbon.

- In sediments with < 0.2 percent TOC, other factors, such as particle size and sorption to nonorganic mineral fractions, play a relatively important role.

    – National Sediment Quality Survey &
    – Karickhoff, 1984

Sediment Quality Benchmarks- OC Basis vs Sediment Basis

	WQB			SQB	%OC	SQB
	FCV	Koc	$\text{Log}_{10}K_{OC}$	FCV	0.1	FCV
Analyte	ug/mL			ug/goc	goc/g sed	ng/g sed
Naphthalene	0.19350	1991	3.30	385	0.001	385
1-Methylnaphthalene	0.07537	5916	3.77	446	0.001	446
2-Methylnaphthalene	0.07216	6194	3.79	447	0.001	447
Acenaphthylene	0.30690	1472	3.17	452	0.001	452
Acenaphthene	0.05585	8790	3.94	491	0.001	491
C2 - Naphthalenes	0.03024	16866	4.23	510	0.001	510

Sediment Extraction Methods

- Sonication
- Soxhlet (or SDS), Accelerated Soxhlet
- Microwave Assisted Extraction
- Pressurized Fluid Extraction
- Supercritical Fluid Extraction

- Solid phase microextraction of porewater.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Cleanup Methods

- Alumina Columns (Separate linear from planar)
- Silica Gel Bulk and Columns (Polarity trapping)
- Gel-Permeation Columns (Size exclusion*)
- Mercury, Copper, Tert-butyl ammonium sulfite (Sulfur removal)

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Instrument Analysis

- PAH Analysis
  - High Performance Liquid Chromatography (uV, photo diode array, mass spec detectors)
  - Gas Chromatography (flame ionization, nitrogen/phosporous, electron capture, mass spec, high resolution mass spec detectors)
  - For GC/MS – Major options include:
    - Full Scan
    - SIM
    - HRMS SIM
    - internal standard
    - isotope dilution

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Jonkers et al. ES&T 2002

- Extracted soots, coal, charcoal, and sooty sediments with 7 organic solvents.
- Saw individual recoveries as low as 16% as compared to the best extracting solvent.
- These differences were much larger for soot than for
- sediments.
- Dichloromethane, toluene and acetone hexane generally had lower recoveries than alcohol/aromatic combinations.
- Toluene:methanol (1:6) gave the best results!

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

NIST 2007 Intercomparison

- SRM 1944 and NIST Sediment 14 – a stabilized, wet, homogenized sediment used for the 2007-8 Intercomparison. 25-2050 ng/g 3.96 % TOC
- Evaluated in 6 Sediment & Tissue Program Laboratories.
- Study design for PAHs – all done on GC/MS, using DB-5 DB-5 MS or RTx-5. 1 lab used 60 m capillary.
- Compared soxhlet, accelerated soxhlet, sonication, a quick screening method.
- Compared extraction solvents (acetone/DCM vs DCM).
- Compared cleanups – none, GPC, Silica Gel, GPC/SG.
- Dixon Test (tau statistic), 40% RPD as acceptance criteria.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

2007/8 NIST Intercomparison Exercise

PAHs on SRM 1944 - Recovery vs Certified & Reference Values

Summary Statistics With Outliers Included

		ACE-DCM	ACE-DCM	DCM-60m	DCM	ACE-DCM	DCM
		Acc. Sox	Acc. Sox w/ GPC	Sox, GPC + Sil Gel-ID	Sox + Sil Gel 8270	Son + GPC + Sil Gel ID	Shake + Sonic Bath
Analytes Attempted	n	**17**	**18**	**22**	**22**	**21**	**19**
Accepted Results		**16**	**17**	**20**	**20**	**19**	**18**
Mean Recovery		**69%**	**64%**	77%	72%	**95%**	**42%**
Mean Abs. Deviation		**41%**	**36%**	25%	28%	**31%**	**58%**
PAHs on Sediment IV (Wet) - Recovery vs Exercise Assigned							
Analytes Attempted	n	**17**	**18**	**24**	**17**	**21**	**18**
Accepted Results		**16**	**18**	**24**	**17**	**21**	**15**
Mean Recovery		**86%**	**82%**	**109%**	**90%**	**93%**	**12%**
Mean Abs. Deviation		**17%**	**19%**	**17%**	**15%**	**22%**	**88%**

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Observations

- Screening method (shake & sonic bath) was rejected.
- Overall, Soxhlet & Horn Sonication were a bit better. Accelerated Soxhlet is accepted.
- No clear advantage from acetone. Paradoxical effect was that DCM-only worked better on wet samples vs dry.
- Isotope dilution strategy correlated better with consensus values; was less prone to negative bias.
- Silica Gel and GPC / Silica Gel improved performance.
- No sweeping advantage from 60 m column.
- Benzo(j)anthracene coeluted with either b or k isomer on both 60 and 30 m column.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Specialized Technique

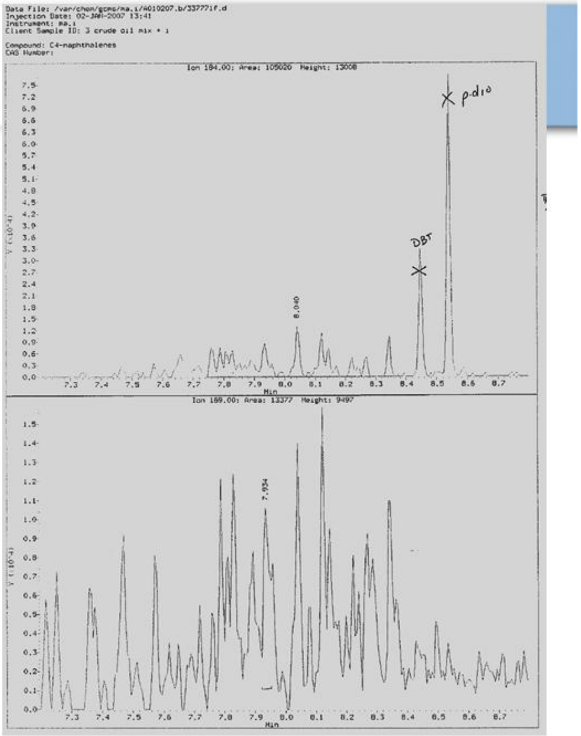
- Traditional practice of APAH analysis includes SIM acquisition of a primary and a confirmation ion.
- Clusters of the primary ion patterns are integrated and quantified using the parent ion.
- Secondary ion is used to help identify the pattern.
- Analyst experience and judgment is required.
- Laboratories setting up the analysis must carefully evaluate the patterns.
- SIM has traditionally been the only tool available.
- Today's more sensitive LRMS instruments can detect all necessary homologs under full scan conditions.
- May require a combination of crude oils and coal tar.

29

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Dibenzothiophene and phenanthrene d10 have strong m/z signals on the c4 naphthalene trace…

DBT also shows up on the confirmation ion trace.



Data File: /var/chem/gcms/ma.i/A010207.b/337771f.d
Injection Date: 02-JAN-2007 13:41
Instrument: ma.i
Client Sample ID: 3 crude oil mix + 1

Compound: C4-naphthalenes
CAS Number:

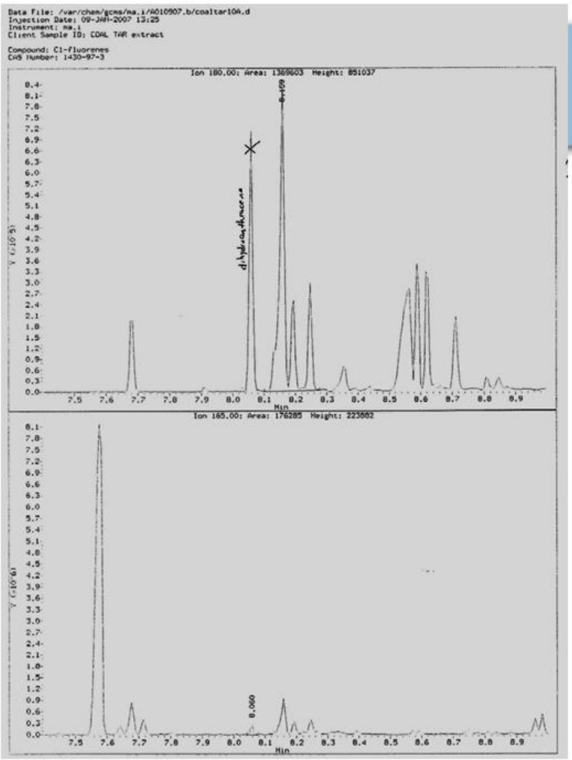
30

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Full MS scanning shows not all peaks in the selected ion chromatograms are the target alkyl PAH.

Dihydroanthracene interferes with c1 fluorenes…

PAH diones have also been tentatively identified.

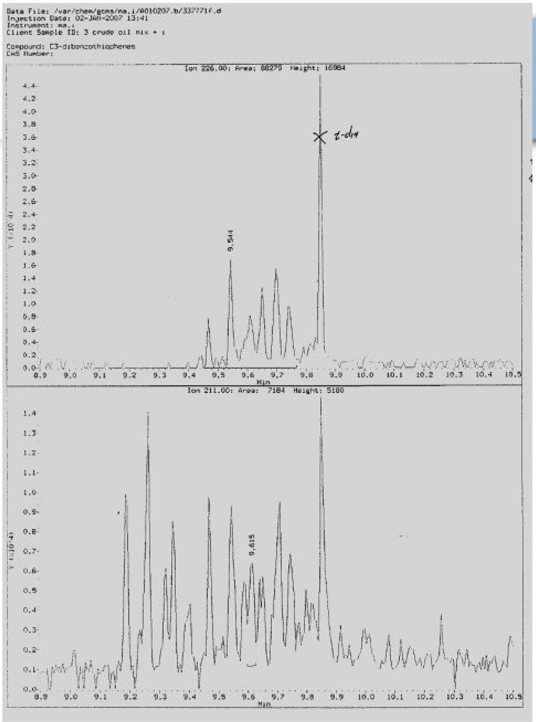


Data File: /var/chem/gcms/ma.i/A010907.b/coaltar10A.d
Injection Date: 09-JAN-2007 13:25
Instrument: ma.i
Client Sample ID: COAL TAR extract

Compound: C1-fluorenes
CAS Number: 1430-97-3

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Terphenyl d14 (surrogate) can interfere with the c3 dibenzothiophenes…



Data File: /var/chem/gcms/ma.i/A010207.b/337771F.d
Injection Date: 02-JAN-2007 13:41
Instrument: ma.i
Client Sample ID: 3 crude oil mix + i

Compound: C3-dibenzothiophenes
CAS Number:

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Summary

- The EPA 34 list appearing in the "Derivation of ESB" document, plus the NOAA 2005 statement of work list provide a reasonable extended list for sediment work in support of ecological risk and source classification work.
- Extraction by Soxhlet, Horn Sonication or Accelerated Soxhlet are demonstrated.
- DCM solvent is OK unless the sample is predominantly soot. Then consider methanol:toluene.
- Reporting limits of 100 ng/g will give data below ESBs down to 0.1% TOC and up to 70% moisture.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Summary Cont'd

- This RL (100 $ng/g_{DRY\ SED}$) is easily within reach of full scan methods, but will require silica gel or GPC/silica gel at a minimum for robustness.
- Laboratory must be absolutely clear on what basis the Alkyls are calculated. (RF_{Parent} or RRF)
- 30m or 60m 5% phenyl column will work equally well. Either way, the benzo(j)flouranthene coelutes with something.
- Until a method is published, work should be coupled with full scan confirmation of patterns.
- To flex the method down for low-level work, consider isotope dilution – particularly for low-level samples.

Future Work

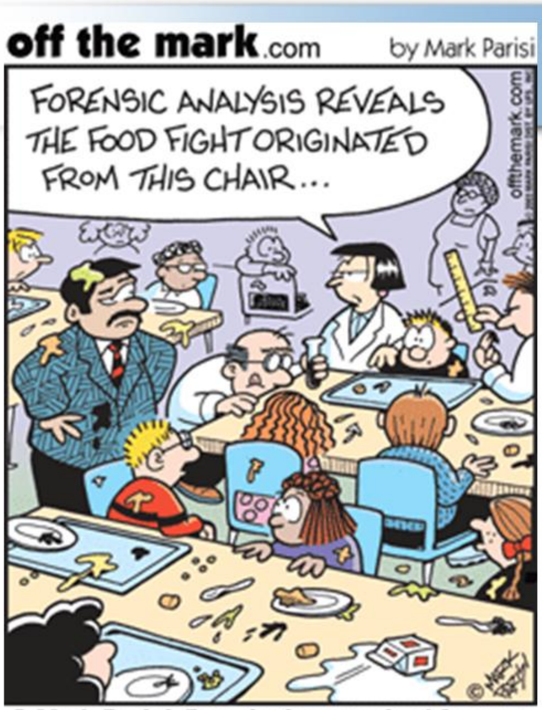
- Examine microwave assisted extraction.
- Work with vendors to increase the standard materials available.
- Evaluate negative chemical ionization.
- In situ and in vitro equilibrium studies using passive samplers (SPME fibers, polyoxymethylene sheets).

Acknowledging:

David Wiles

Bryce Stearns

Questions?



© Mark Parisi, Permission required for use.

2008 NEMC Proceedings

DATA USABILITY

Data and Information Quality Framework for Environmental Measures

Jeffrey Worthington
USEPA Office of Environmental Information
472 Penwood Drive
Edgewater, MD 20137
202-566-0995
worthington.jeffrey@epa.gov

ABSTRACT

Many disciplines establish a central “body of knowledge” (BOK) that serves as a reference point for concepts, theories, processes, facts, and other agreed to aspects of that discipline. An information and data quality BOK can be the basis for a more universal understanding and comparability of environmental measures. Such a BOK would rest within the existing BOK for the quality discipline.

The existing quality BOK includes elements such as quality planning, quality assessment, continuous improvement, quality control processes, reliability, maintainability, statistics, inspection processes, etc. At this time, there is no firm information and data quality BOK. In lieu of the needed BOK, professionals working with environmental measures for information and data quality can rely on a basic Information and Data Quality Framework. The purpose of the framework is to provide a roadmap to considering how to plan, implement, and assess processes that develop information and data products and services, including environmental measures. This presentation considers key elements of an information and data quality framework including:

- Identification of information and data products and services
- Identification of information and data features, definition, and measures
- Organizing information and data features into logical management groups
- Recognizing information states and mapping those information states to features and supporting information processes, and
- Relating governance processes (i.e., quality and information policies) to the organization’s information and data quality.

OFFICE OF ENVIRONMENTAL INFORMATION

"Information and Data Quality" MATRIX

Environmental Measurements

Jeffrey C. Worthington, CQA, CQMgr.
OEI Director of Quality
Office of Environmental Information
U.S. Environmental Protection Agency

National Environmental
Management Conference
Washington, D. C.
August 14, 2008

American Society for Quality
ENERGY AND ENVIRONMENTAL DIVISION
ASQ

iaidq

Jeffrey Worthington- BIO

- **Director of Quality - USEPA Office of Environmental Information**.
  - Director of Quality - USEPA ORD National Risk Management Research Laboratory (NRMRL)
  - Director of Quality Assurance for TechLaw, Inc.
  - American Society for Quality (ASQ) Certified Quality Manager and Certified Quality Auditor.
  - ASQ Fellow
  - Founding member - ASQ Government Division
  - Past-Chair -ASQ Energy & Environment Division
  - ASQ Division Affairs Council member
  - Founding member and past Director of the International Association for Information and Data Quality (IAIDQ).
  - Editorial Board member for:
    - Quality Assurance, Science, and the Law,
    - Journal of Environmental Forensics,
    - Environmental Laboratory magazine, and
    - Environmental Testing and Analysis magazine.
- Federal Government since 1994. Jeff co-led a team authoring the combined quality and management system for EPA's Environmental Technology Verification (ETV) program. He co-led the EPA team developing EPA's Information Quality Guidelines.
- Jeff co-authored peer review journal papers receiving:
  - the USEPA Science and Technological Achievement Award (STAA), Level III for equating EPA policies and procedures to U.S. Supreme Court Sound Science Criteria (2002) and
  - an STAA Honorable Mention for developing electronic recordkeeping QA parameters (2006).
- 2008 - National Security Telecommunications and Information Systems Security (NSTISSI) 4011 Certificate for information systems security (INFOSEC) professionals at the National Defense University (NDU) Information Resources Management College (IRMC)
- Currently studying Chief Information Officer curriculum at IRMC.

DISCLAIMER

The opinions expressed in this technical presentation are those of the author and do not necessarily reflect the views of the US EPA.

ABSTRACT

- Many disciplines establish a central "body of knowledge" (BOK) that serves as a reference point for concepts, theories, processes, facts, and other agreed to aspects of that discipline. An information and data quality BOK can be the basis for a more universal understanding and comparability of environmental measures. Such a BOK would rest within the existing BOK for the quality discipline.

- The existing quality BOK includes elements such as quality planning, quality assessment, continuous improvement, quality control processes, reliability, maintainability, statistics, inspection processes, etc. At this time, there is no firm information and data quality BOK. In lieu of the needed BOK, professionals working with environmental measures for information and data quality can rely on a basic Information and Data Quality Framework. The purpose of the framework is to provide a roadmap to considering how to plan, implement, and assess processes that develop information and data products and services, including environmental measures. This presentation considers key elements of an information and data quality framework including:
  - Identification of information and data products and services
  - Identification of information and data features, definition, and measures
  - Organizing information and data features into logical management groups
  - Recognizing information states and mapping those information states to features and supporting information processes, and
  - Relating governance processes (i.e., quality and information policies) to the organization's information and data quality.

OVERVIEW

- Background
- Existing Body of Knowledge (BOK) for quality discipline (data quality)
- Alternative Quality Models for *information and data quality*
- For **what**…. do we need to address quality? SCOPE
- What are the important quality considerations?
  - Information and data quality features
  - Information and data states
  - Quality components
  - Quality supporting activities
  - (information and data) Quality governance processes
- Conclusion

A question to consider today

What makes data “usable”?

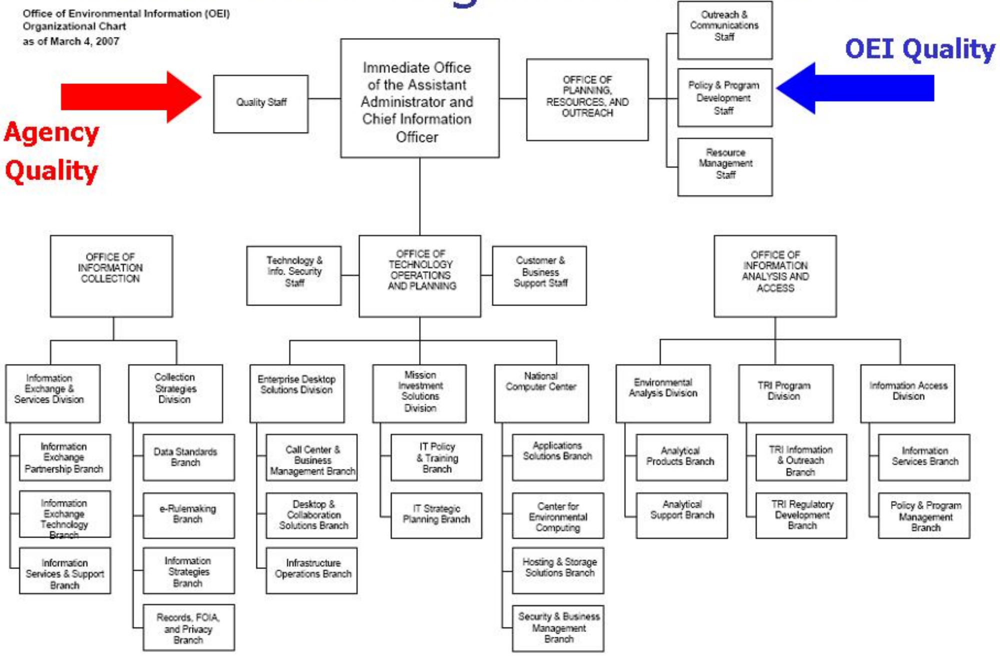
OEI Background

The Office of Environmental Information (OEI), headed by the Chief Information Officer, manages the life cycle of information to support our goal of protecting human health and the environment by:

- Collecting Information: OEI collects, manages, provides and safeguards your environmental information.
- Ensuring Quality Information: OEI ensures that the information we use are accurate, representative, and reliable
- Analyzing and Accessing Information: OEI offers tools for you to access and analyze environmental information
- Information Technology: OEI provides technology services and manages our Agency's IT investments

7

USEPA OEI Organization Chart



Office of Environmental Information (OEI)
Organizational Chart
as of March 4, 2007

Agency Quality

OEI Quality

Quality Staff

Immediate Office of the Assistant Administrator and Chief Information Officer

OFFICE OF PLANNING, RESOURCES, AND OUTREACH
- Outreach & Communications Staff
- Policy & Program Development Staff
- Resource Management Staff

OFFICE OF INFORMATION COLLECTION
- Information Exchange & Services Division
  - Information Exchange Partnership Branch
  - Information Exchange Technology Branch
  - Information Services & Support Branch
- Collection Strategies Division
  - Data Standards Branch
  - e-Rulemaking Branch
  - Information Strategies Branch
  - Records, FOIA, and Privacy Branch

Technology & Info. Security Staff

OFFICE OF TECHNOLOGY OPERATIONS AND PLANNING

Customer & Business Support Staff
- Enterprise Desktop Solutions Division
  - Call Center & Business Management Branch
  - Desktop & Collaboration Solutions Branch
  - Infrastructure Operations Branch
- Mission Investment Solutions Division
  - IT Policy & Training Branch
  - IT Strategic Planning Branch
- National Computer Center
  - Applications Solutions Branch
  - Center for Environmental Computing
  - Hosting & Storage Solutions Branch
  - Security & Business Management Branch

OFFICE OF INFORMATION ANALYSIS AND ACCESS
- Environmental Analysis Division
  - Analytical Products Branch
  - Analytical Support Branch
- TRI Program Division
  - TRI Information & Outreach Branch
  - TRI Regulatory Development Branch
- Information Access Division
  - Information Services Branch
  - Policy & Program Management Branch

Background
OEI Current Activity

- OEI's National Dialogue on Access to Environmental Information
- National Meeting – Phoenix, December 2008
- www.epa.gov/oei

Background - EPA Quality

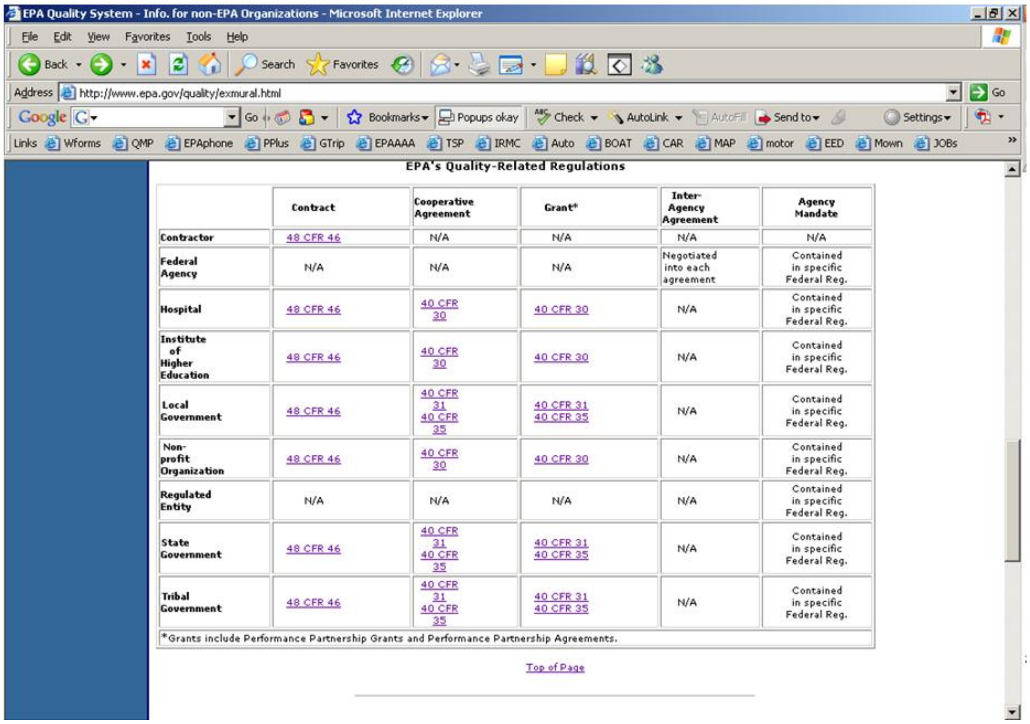
- CIO Policy 2105.0 (AKA EPA Order 5360.1 A2)
- CIO 2105-P-01-0 (AKA EPA Manual 5360 A1)
- "**R**" documents – quality requirements
- "**G**" documents – quality guidance

- Annual Conference
- Annual Training Meeting and Training Modules

www.epa.gov/quality

- FAQs
- Quality Management Tools
- Information for EPA Organizations
- Information for non-EPA Organizations

For non-EPA organizations



EPA's Quality-Related Regulations

	Contract	Cooperative Agreement	Grant*	Inter-Agency Agreement	Agency Mandate
Contractor	48 CFR 46	N/A	N/A	N/A	N/A
Federal Agency	N/A	N/A	N/A	Negotiated into each agreement	Contained in specific Federal Reg.
Hospital	48 CFR 46	40 CFR 30	40 CFR 30	N/A	Contained in specific Federal Reg.
Institute of Higher Education	48 CFR 46	40 CFR 30	40 CFR 30	N/A	Contained in specific Federal Reg.
Local Government	48 CFR 46	40 CFR 31 40 CFR 35	40 CFR 31 40 CFR 35	N/A	Contained in specific Federal Reg.
Non-profit Organization	48 CFR 46	40 CFR 30	40 CFR 30	N/A	Contained in specific Federal Reg.
Regulated Entity	N/A	N/A	N/A	N/A	Contained in specific Federal Reg.
State Government	48 CFR 46	40 CFR 31 40 CFR 35	40 CFR 31 40 CFR 35	N/A	Contained in specific Federal Reg.
Tribal Government	48 CFR 46	40 CFR 31 40 CFR 35	40 CFR 31 40 CFR 35	N/A	Contained in specific Federal Reg.

*Grants include Performance Partnership Grants and Performance Partnership Agreements.

Top of Page

Existing Body of Knowledge (BOK) for quality discipline (data quality)

- Plan – do – check – act (PDCA cycle)
- EPA: graded approach
- Data (PARCCS)
  - Precision
  - Accuracy
  - Representativeness
  - Completeness
  - Comparability
  - Sensitivity

What does the

quality system

apply to?

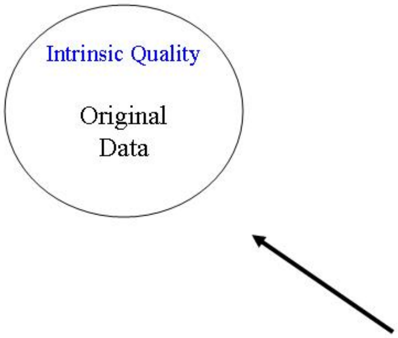
Quality Staff Product & Service Categories FY07/08 QAARWP instructions

- Reports
  - Progress, performance, characterization reports
  - Fact sheets
- Data and Information Systems
  - Environmental
  - Administrative
- Guidance
  - Programmatic
  - State/local
- Assessments
  - Risk assessments
  - Scientific assessments
  - Remedial investigations & feasibility studies
- Research
  - Scientific
  - Economic
- Environmental technology
  - Planning
  - Development
- Information management and technology
  - Planning
  - Development
- Grants
  - State/local/tribes
  - othe

Information and Data - Product & Services

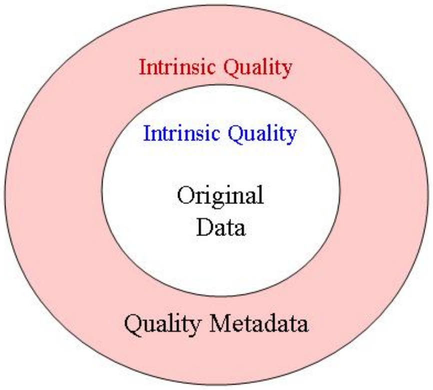
- Environmental measurements
  - Chemical
  - Biological
  - Physical
  - Geospatial
  - Time
- Technical reports
- Databases
- Access services (e.g., web)
- Interactive information products

What is data quality for environmental measurements?

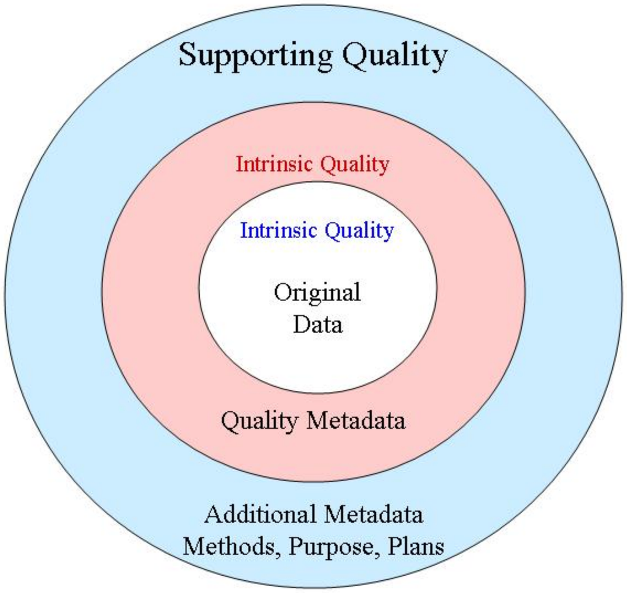


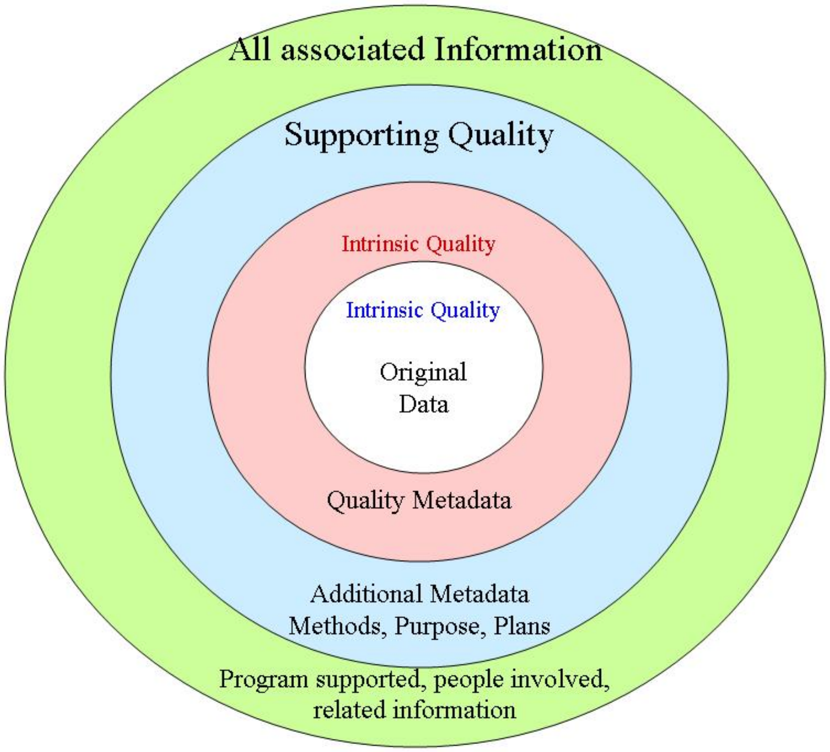
One small
“data package”
This only contains the original
data

Some data, which specifically describes quality features of the data may accompany the original data to form a larger data package.



These data and the "quality metadata" represent quality that is "intrinsic" to the data that is central to the work.





All associated Information

Supporting Quality

Intrinsic Quality

Intrinsic Quality

Original
Data

Quality Metadata

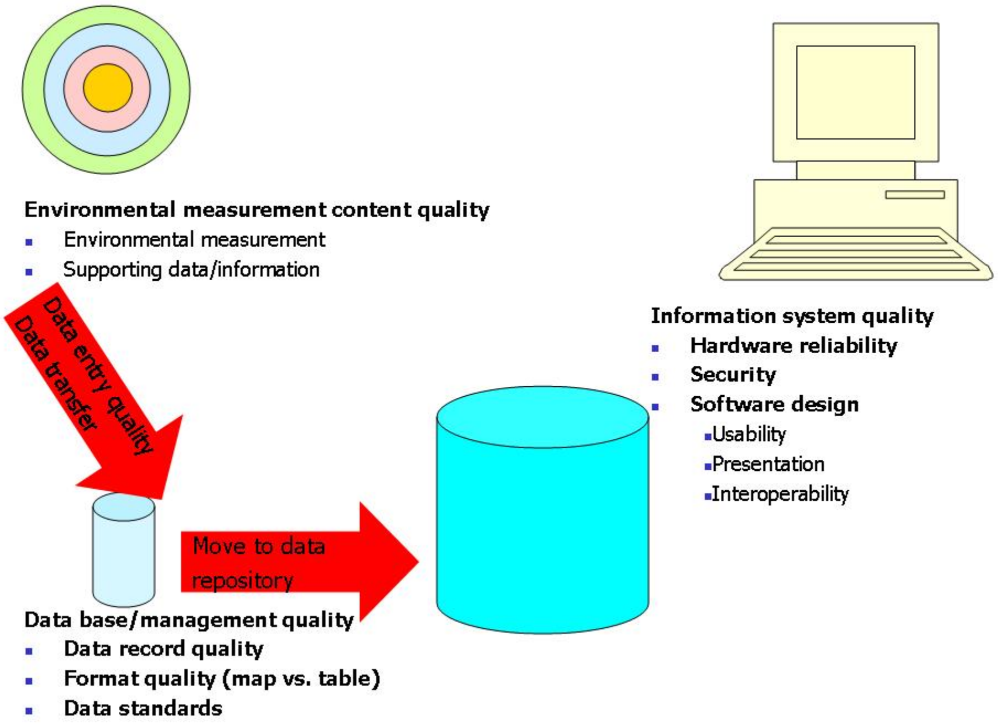
Additional Metadata
Methods, Purpose, Plans

Program supported, people involved,
related information

META DATA = data about data

- Computer metadata vs.
- supporting data for environmental measurements

- Transparency = when the correct metadata is shared (correct = meta data for "it's intended purpose)
  - Data pedigree
  - Data provenance



Environmental measurement content quality

- Environmental measurement
- Supporting data/information

Data entry quality

Data transfer

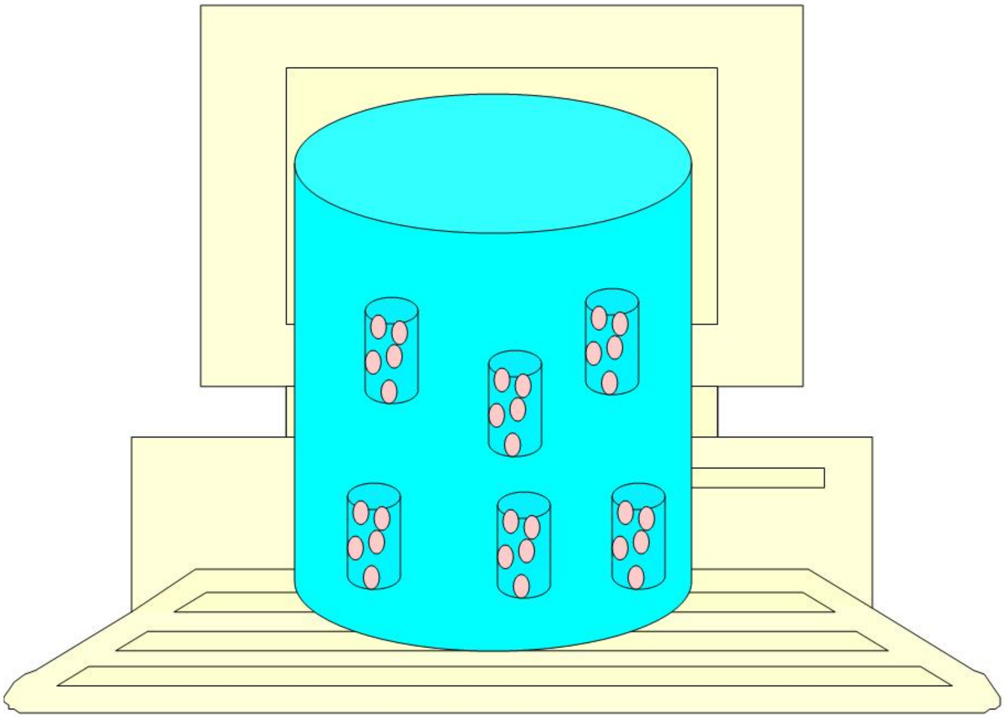
Information system quality

- **Hardware reliability**
- **Security**
- **Software design**
  - Usability
  - Presentation
  - Interoperability

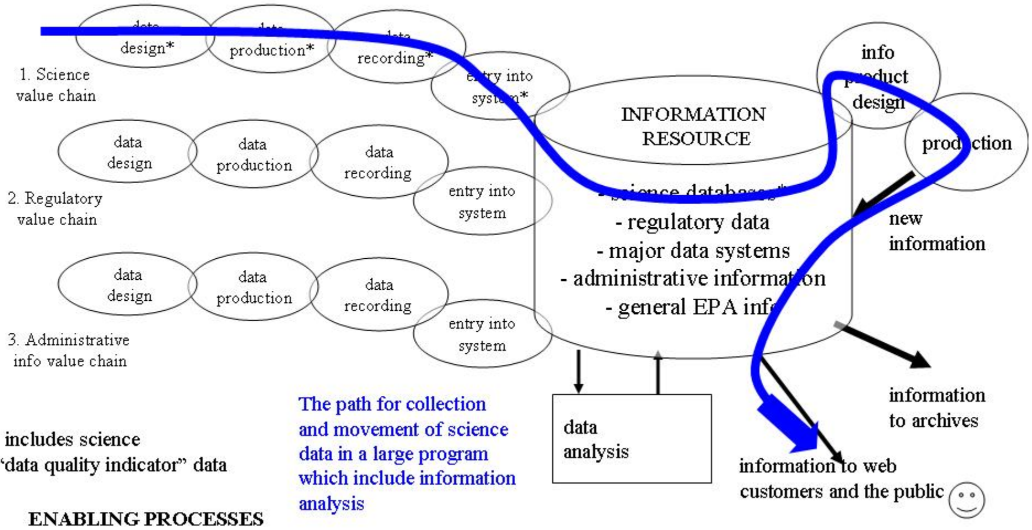
Move to data repository

Data base/management quality

- **Data record quality**
- **Format quality (map vs. table)**
- **Data standards**



3 MAJOR DATA TYPES **DATA QUALITY AND INFORMATION QUALITY RELATIONSHIPS**



The path for collection and movement of science data in a large program which include information analysis

* includes science "data quality indicator" data

ENABLING PROCESSES

Information processes data standards development, information policies, information measures, architectures

IT processes software design/development, hardware operations

Planning processes - programs, projects, quality, resource, integration

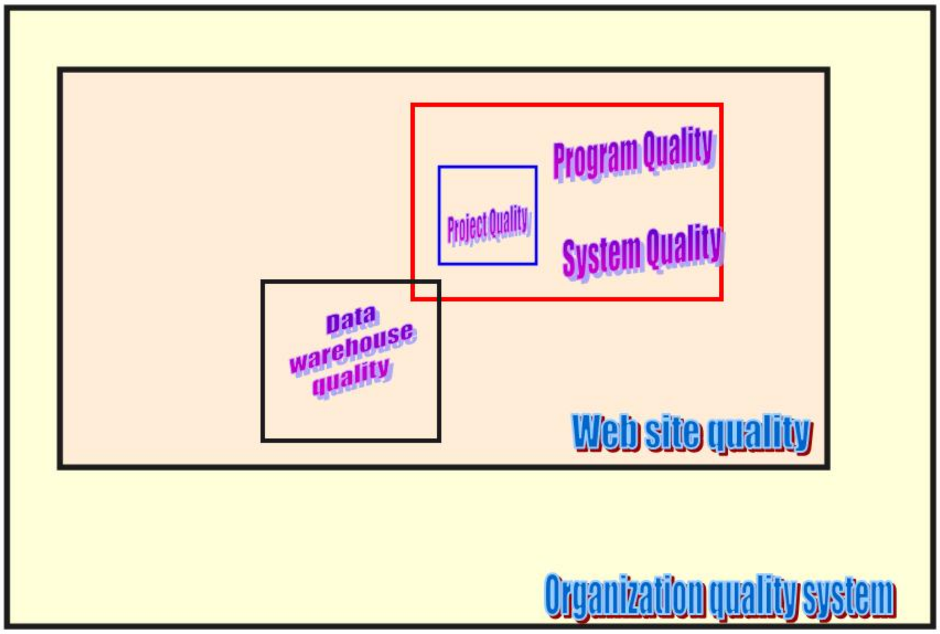
Alternative Quality Models for:

delivery of government services

- Quality in Depth*
- Criticality assessment* (similar to "graded approach")
- Information Quality Cube (Modified McCumber Cube)*

*discussed at NEMC 2007

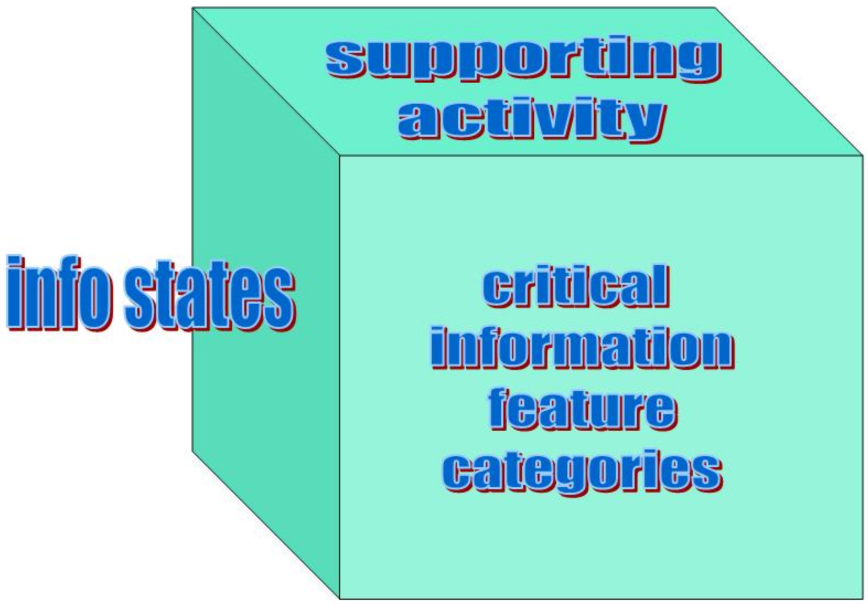
Quality in Depth



Criticality assessment

		impact attributes (from McCumber Cube)		
		confidentiality	integrity	availability
Information product types	environmental measurement	L	H	M
	regulatory study	L	H	H
	information policy	L	M	H

Information/data Quality Cube

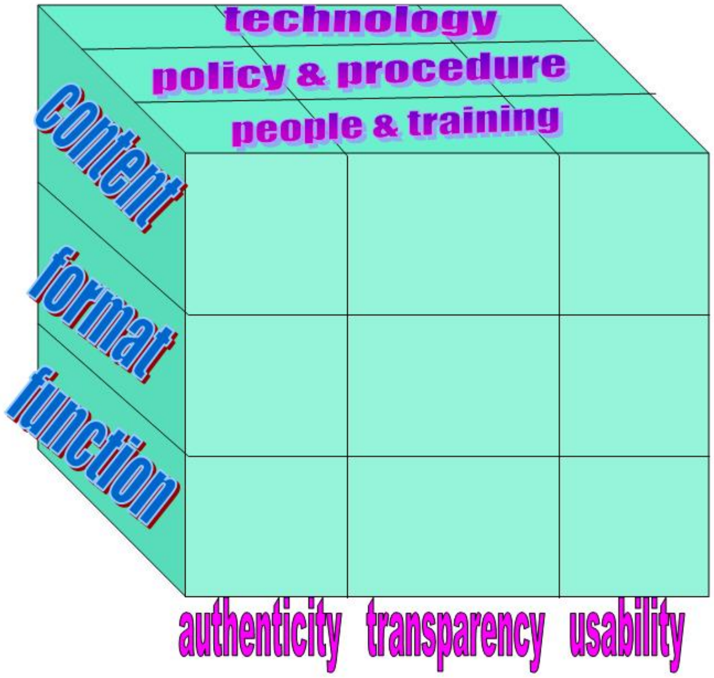


supporting activity

info states

critical information feature categories

Information/data Quality Cube



technology

policy & procedure

people & training

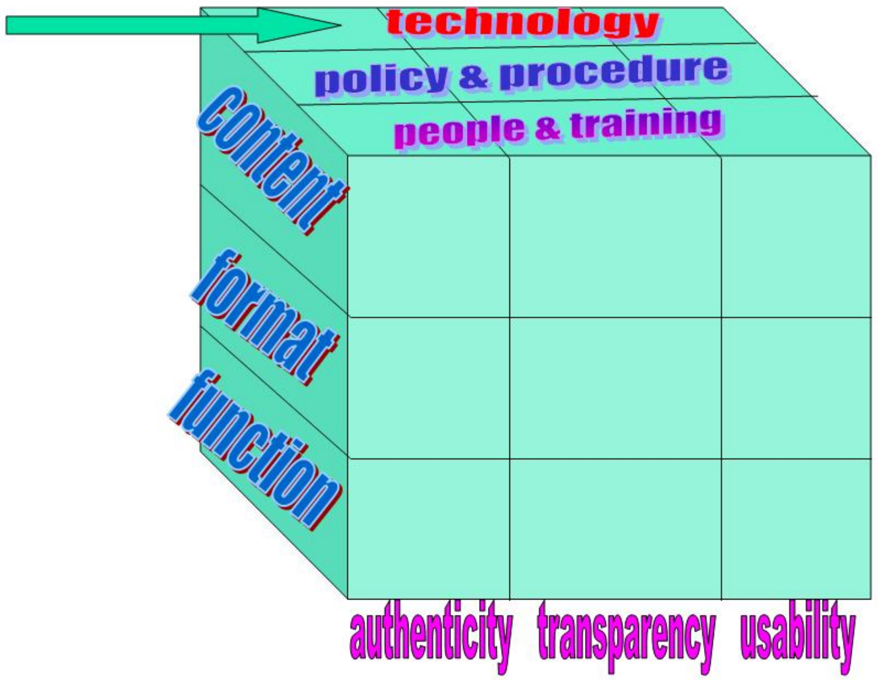
content

format

function

authenticity transparency usability

Information/data Quality Cube



Original analysis: mapping features and terms: TECHNOLOGY

		Critical Information Features Categories (and features)		
		authenticity	**transparency**	**usability**
Information States	**Content**	Accurate Representative Correct Comparable	Recorded methods Recorded work	Complete Current Timely Correct Integrity
	Format	Representative of content	Reproducible/repeatable understandable	Informative Correct Clear Concise Presentable Accessible understandable
	Function	Well-designed Reliable Integrity IT security	Ease of use Recorded methods Recorded work Documented IT security	Serviceable Accessible Informative Maintainable Available Reliable Confidential integrity

Quality Components

- **Features** – does the product have the features or characteristics that I desire?
- **Defects/errors or controls** – do the features work all the time, are there are problems or mistakes?
- **Customer service** – are the people easy to deal with? Am I comfortable when contacting them?
- **Efficiency and effectiveness** – can I afford to make the product or buy the product? Do I know there is value for the purchase or manufacture?

Information and Data Quality Features
MAJOR CATEGORIES

1. **Authenticity** – it is what it purports to be
2. **Transparency** – there is enough information about the information to know it can meet the intended use
3. **Usability** (e.g., utility) – the information is of the correct content, format, and functionality for use

Authenticity Features - "It is what it purports to be."

Technical

- Technical protocols selected were robust
- Technical protocols were followed
- Records were adequately kept, and adequately maintained
- Matrix sampled securely maintained
- All movement and custody records maintained
- Analysis performed in accordance with protocols

Quality control and management

- Plans developed and followed

Transparency Features - "There is enough information about the information to know it can meet the intended use."

- Non-biased presentation
- Availability of science methods used
- Comparability of data to know data sets
- Sufficient information to reproduce data sets
- Information regarding source of data is known
- Location where additional information is identified

Usability Features - "The information is of the correct content, format, and functionality for use.

- Completeness of data
- Interoperability of data with the format desired
- All values needed are available
- Data is provided in time to be useful

Quality Components

- **Features** – does the product have the features or characteristics that I desire?
- **Defects/errors or controls** – do the features work all the time, are there are problems or mistakes?
- **Customer service** – are the people easy to deal with? Am I comfortable when contacting them?
- **Efficiency and effectiveness** – can I afford to make the product or buy the product? Do I know there is value for the purchase or manufacture?

Defects/errors or controls

If the information or data has the features needed:

- What controls ensure that the procedures were followed?
- Are all the data entered correctly into databases?
- Are the instruments reliable?
- What controls are in place to ensure mistakes are detected and corrected?
- Do users understand that there may be an acceptable level of error?

- Defects
  - Data entry defects
  - Software failures
  - Downtime

Quality Components

- Features – does the product have the features or characteristics that I desire?
- Defects/errors or controls – do the features work all the time, are there are problems or mistakes?
- Customer service – are the people easy to deal with? Am I comfortable when contacting them?
- Efficiency and effectiveness – can I afford to make the product or buy the product? Do I know there is value for the purchase or manufacture?

Example one – DIMENSIONS OF SERVICE QUALITY Parasuraman 09.13.02

- Access
- Communications
- Competence
- Credibility
- Reliability
- Responsiveness
- Security
- Tangibles
- Understanding/knowing the customers

Example two – E-service Quality – Service via the internet Parasuraman??

- Access
- Ease of navigation
- Efficiency
- Customization/personalization
- Security/privacy
- Responsiveness
- Assurance/trust
- Knowledge
- Site aesthetics
- Reliability
- Flexibility

Quality Components

- **Features** – does the product have the features or characteristics that I desire?
- **Defects/errors or controls** – do the features work all the time, are there are problems or mistakes?
- **Customer service** – are the people easy to deal with? Am I comfortable when contacting them?
- **Efficiency and effectiveness** – can I afford to make the product or buy the product? Do I know there is value for the purchase or manufacture?

Efficiency and effectiveness – can I afford to make the product or buy the product? Do I know there is value for the purchase or manufacture?

- Total resources needs
- Cost relative to projected costs
- Cumulative cost
- Cost per unit
- Work time needed
- Software design efficiency

Information and Data States

- Content – Does the information/data include the content I need? Quality of "content" comes from the processes that produce the content.
- Format – Is the data in a format I can use? Map vs. table.
- Function – Does the process to provide or interact with the information and data work well?

Possible categories for products

- Science processes
    - Environmental Measurement
    - Environmental Technology
- Hardware
    - Purchase
    - Installation
    - Configuration
    - Reliability
    - Maintainability
- Software
    - Purchase
    - Plan, Design, Test, Maintain, Operate
    - Reliability
    - Maintainability

Governance considerations

Products and services and the processes to produce products and services may need to comply with:

- Administrative requirements
  - FMFIA
  - GPRA
  - Peer review
  - Products review
- Information (CIO) "administrative" policy requirements
  - Records management
  - Privacy policy
  - 508 accessibility
- Information (CIO) "technical" policy requirements
  - Data standards
  - Configuaration requirements
- Information (CIO) system policy requirements
  - System Development Lifecycle

INFORMATION AND DATA QUALITY MATRIX

PRODUCTS	**Basic quality areas**				
	Features	**Controls defects**	**Customer service**	**Efficiency effectiveness**	**Policy conformity**
Environmental Measurements	Format Function Content	Format Function Content	Format Function Content	Format Function Content	Format Function Content
Hardware	Content Format Function	Format Function Content	Format Function Content	Format Function Content	Format Function Content
Software	Content Format Function	Format Function Content	Format Function Content	Format Function Content	Format Function Content
Info systems	Format Function Content	Format Function Content	Format Function Content	Format Function Content	Format Function Content
Databases	Format Function Content	Format Function Content	Format Function Content	Format Function Content	Format Function Content
Web site	Format Function Content	Format Function Content	Format Function Content	Format Function Content	Format Function Content
Reports	Format Function Content	Format Function Content	Format Function Content	Format Function Content	Format Function Content

A question to consider today

What makes data “usable”?

What makes data usable?

- Right content
- Right format
- Right functionality
- Authentic
- Accessible
- Transparent

Conclusion

Environmental measurement quality can be viewed in terms of:

- STATES – content, format, function
- COMPONENTS – features, defects, efficiency
- FEATURE CATEGORIES – authenticity, transparency, and usability
- SUPPORTING ELEMENTS – technology, governance, and people/training

---

OFFICE OF
ENVIRONMENTAL
INFORMATION

Contact Information

Jeffrey Worthington – EPA
Office of Environmental Information
202-566-0997

worthington.jeffrey@epa.gov

What Do You Do With Field Duplicates? Case Studies on Usability Assessment and Application to Site Investigations

Stephen T. Zeiner, CEAC
Environmental Standards, Inc.
1140 Valley Forge Road, PO Box 810
Valley Forge, PA 19482
Telephone: 610-935-5577
Fax: 610-935-5583
Email: szeiner@envstd.com

ABSTRACT

Field duplicate samples are frequently required quality control samples collected and analyzed as part of field investigations. The data generated from the analyses of field duplicates provide a means to evaluate sample collection procedures, sample homogeneity, and analytical precision. The process of collecting a field duplicate pair typically entails taking an aliquot of sample, homogenizing the aliquot, and splitting the aliquot into two distinct samples prior to shipment to the laboratory. True field duplicates cannot be collected for volatile analyses because volatile samples should not be homogenized. Some field teams, however, do not perform a thorough homogenization of field duplicate samples (especially solid samples) before submittal to the laboratory; these samples are actually field replicates or even collocated samples. Field replicates are samples collected from the same site at the same time and are not homogenized in the field. Interestingly, field replicates, co-located samples, and field duplicates are typically evaluated for data usability by the same criteria.

Several regulatory agencies (*e.g.,* US EPA Regions I and II) have established data validation criteria for the usability evaluation of field duplicate results. The usability criteria across these guidelines lack consistency and suggest the use of professional judgment for evaluating the results when criteria are not provided. Furthermore, most data validation guidelines do not take into account the concentrations of the target analytes found in the field duplicate pair relative to the sample reporting limit. Environmental Standards has developed criteria for the evaluation of field duplicate results based on scrutiny of field duplicate results from thousands of projects that involved a variety of matrices and methods while performing third-party data validation.

Environmental Standards has been involved in projects for which there was clear evidence that field duplicate samples had been homogenized in the field before submittal to the laboratory and in projects for which there was no evidence that field duplicate samples had been homogenized in the field before submittal to the laboratory. Project teams must determine how to utilize field duplicate data when generating site models, when developing risk assessments, and for other data applications.

Details regarding the field duplicate data usability assessment criteria developed by Environmental Standards will be presented. In addition, two case studies will be presented – case studies that were significantly different relative to knowledge about field duplicate collection and how this knowledge impacted the way that field duplicate data were utilized.

INTRODUCTION

Two case studies involve sites in the Northeast where off-shore river sediments were contaminated with PCBs, metals, and other constituents. The PCB data generated by samples from both sites were loaded into enterprise-level relational databases used to guide remediation planning and efforts.

The collection of field duplicate samples is a common quality control measure as part of sample collection schemes. For sample locations where field duplicate samples were collected, the author searched the guidance documents for how to most appropriately utilize the field duplicate data. Regulatory guidance document mandates on the collection of field duplicates were identified, but the same documents provided very little guidance on the assessment and utilization of the field duplicate data. Furthermore, very few of the data validation guidance documents provide criteria for the evaluation of the field duplicate results.

How to appropriately assess and utilize the field duplicate sample results is one of the challenges that face the end data user. Variables need to be considered - how was the field duplicate collected, how do the results compare, and will the use of the results bias the data set?

As with many site characterization efforts, field duplicate samples were collected and analyzed over the history of both sites. Understanding the limitation and reliability of data is easily accomplished through the assignment of a data quality objective for the field duplicates.

CASE STUDY BACKGROUNDS

For Case Study A, a river sediment characterization project in the Northeast, a private sector company sponsored the collection and analysis of several thousand samples. These samples were analyzed for PCBs, total organic carbon, dioxin/furans, and several metals. The sample collection and processing were performed utilizing a standard operating procedure included in the project quality assurance documents. The samples were analyzed by five different laboratories under a single standard operating procedure for the preparation and analysis of the samples included in the project quality assurance documents.

For Case Study B, a river sediment characterization for another project in the Northeast, multiple private sector and regulatory entities sponsored the collection of several thousand samples that were analyzed for PCBs and a variety of metals. The samples were analyzed by multiple laboratories, but the majority of the samples were analyzed by a single laboratory. The site for Case Study B has several quality assurance documents; however, the sample collection, field processing, analytical sample preparation, and analysis procedures were not included in the quality assurance documents.

FIELD DUPLICATE SAMPLE COLLECTION

Understanding the process by which the samples and specifically the field duplicate samples are collected provides information for proper assessment and utilization. In Case Study A, the field samples were collected via VibraCore® and the samples underwent a rigorous homogenization. In Case Study B, the field documentation did not include sufficient detail to adequately understand the collection process; as a result, the project team was not able to determine how the field duplicate samples were collected or if the samples had been homogenized.

In Case Study A, the field duplicate samples were collected and processed using the following procedure:

- Utensils used were properly decontaminated.
- The sediment was mixed thoroughly while avoiding excess aeration.
- Samples were mixed to an even texture and color.
- Sample aliquots were split evenly, containerized, preserved, and submitted for analysis.

EVALUATION OF FIELD DUPLICATE RESULTS

While some data validation guidance documents provide approaches to the evaluation of field duplicate results, wide acceptance criteria are used (*i.e.*, 100% relative percent difference [RPD]) and sample concentration is not considered an important variable. Environmental Standards thinks that when evaluating field duplicate results, it is important to carefully consider the concentrations of the field duplicate samples relative to the quantitation limits. Concentrations that are closer to the quantitation limits are likely to be impacted by instrument variations and "large differences" (*i.e.*, larger calculated RPDs) between the samples may not represent a truly significant difference (see Tables 1 and 2 for examples).

Environmental Standards applied the following criteria for the evaluation of field duplicate samples:

- If the concentration of an analyte in both samples is greater than or equal to 5-times its quantitation limit, the RPD between the results is used for evaluation. The RPD criterion is 40% for solid samples and 20% for aqueous samples. If the RPD between the results is greater than the quantitation limit, results in the field duplicate samples are qualified as estimated.
- If the concentration of an analyte in at least one of the samples is less than 5-times its quantitation limit, the difference between the results is used for evaluation. The difference criterion is twice the quantitation limit for solid samples and the quantitation limit for aqueous samples. If one of the results is a "not-detected" result, the quantitation limit is used for comparison. The quantitation limit used for evaluation is the higher of the two samples.

Table 1 presents some examples from the data collected as part of Case Study A. The evaluation criterion for the samples on Table 1 was that the RPD between the results should be less than or equal to 40%. Samples 1 and 3 results demonstrate that sediment is a difficult matrix to homogenize. Sample 2 results demonstrate that even samples that display seemingly large absolute differences can be relatively similar.

Table 1: Case Study A: Examples of Field Duplicate Comparisons

	Sample 1		Duplicate 1			
Analyte	Result	QL	Result	QL	RPD	Difference
AR-1221	4500	200	3500	150	25.0%	1000
AR-1242	2600	200	1100	150	81.1%	1500
AR-1254	1100	200	1200	150	8.7%	100
	Sample 2		Duplicate 2			
Analyte	Result	QL	Result	QL	RPD	Difference
AR-1221	27000	1400	39000	2000	36.4%	12000
AR-1242	24000	1400	33000	2000	31.6%	9000
	Sample 3		Duplicate 3			
Analyte	Result	QL	Result	QL	RPD	Difference
AR-1221	8400	420	4400	230	62.5%	4000
AR-1242	9000	420	4800	230	60.9%	4200

Notes:
Concentrations in µg/kg
AR - Aroclor
QL - quantitation limit

Table 2 presents some examples from the data collected as part of Case Study B. The criterion used for the evaluation of the field duplicates on Table 2 was that the difference between the results should be less than twice the quantitation limit. These samples demonstrate that large RPDs (> 40%) can be obtained while the difference between the results is less than twice the quantitation limit.

Table 2: Case Study B: Examples of Field Duplicate Comparisons

	Sample 1		Duplicate 1			
Analyte	Result	QL	Result	QL	RPD	Difference
AR-1242	2100	620	4000	1500	62.3%	1900
AR-1254	4100	620	5300	1500	25.5%	1200
AR-1262	2400	620	2100	1500	13.3%	300
	Sample 2		Duplicate 2			
Analyte	Result	QL	Result	QL	RPD	Difference
AR-1262	3200	860	1900	580	51.0%	1300
AR-1268	1300	860	730	580	56.2%	570

Notes:
Concentrations in µg/kg
AR - Aroclor
QL - quantitation limit

UTILIZATION OF FIELD DUPLICATE RESULTS

The modeling programs used for the case studies allowed only a single value per collection point and depth. Approaches to field duplicate data use are listed below:

- Use the average of the field duplicate results
- Use the higher of the results
- Use the lower of the results
- Use the investigative sample result only

The average of the field duplicate results may provide a fairly representative value for the site location. For most projects, this approach works well. If the process for the collection of the field duplicates is poor and results in a significant variability, the use of the average may not be appropriate. For Case Study A, the field duplicate samples were well homogenized and the average of the concentrations was used for the sample collection points with field duplicate samples.

Table 3 provides the initial investigative sample and field duplicate results along with the average and the value that was utilized. The author notes that in spite of the thorough homogenization of the sediment samples, there was some variability in the field duplicate results. For the majority of field duplicate pairs in Case Study A, the average appears to be representative of the samples. Samples 4 and 5 demonstrate that even with a consistent and thorough process, sometimes the matrix is highly variable.

Table 3: Case Study A: Example of Field Duplicate Results Disparity

Analyte	Sample 1 Result	Duplicate 1 Result	Average	Utilized
AR-1221	4500	3500	4000	4000
AR-1242	2600	1100	1850	1850
AR-1254	1100	1200	1150	1150
AR-1260	670	1200	935	935
Analyte	Sample 2 Result	Duplicate 2 Result	Average	Utilized
AR-1221	27000	39000	33000	33000
AR-1242	24000	33000	28500	28500
Analyte	Sample 3 Result	Duplicate 3 Result	Average	Utilized
AR-1221	2100	2100	2100	2100
AR-1242	1500	1700	1600	1600
AR-1254	270	330	300	300
Analyte	Sample 4 Result	Duplicate 4 Result	Average	Utilized
AR-1221	83000	11000	47000	47000
AR-1242	73000	9600	41300	41300
Analyte	Sample 5 Result	Duplicate 5 Result	Average	Utilized
AR-1221	8400	4400	6400	6400
AR-1242	9000	4800	6900	6900

Notes:
Concentrations in µg/kg
AR - Aroclor

The selective use of the higher or lower result for the site locations would present a bias and the data set selected may not necessarily be reflective of the conditions at the site. This approach may be appropriate for projects for which the model is conservative or favors the use of "worst case" scenarios.

The use of the initial investigative sample results for sample data is a viable approach; however, a concern for this approach is possible bias on the data. To test this theory, Environmental Standards evaluated the frequency at which the concentrations of the initial investigative sample were greater than the concentrations of the associated field duplicate for Case Study B. The evaluation indicated that the number of investigative samples with a higher concentration than the associated field duplicate sample was not significantly greater than the number of field duplicate samples that had a higher concentration than the associated investigative sample. At least for Case Study B, the use of the initial investigative sample would not unduly bias the data set. Table 4 provides examples of field duplicates for Case Study B.

Table 4 provides the initial investigative sample and field duplicate results along with the average and the value that was utilized. The average was provided for comparison. In general, the field duplicate samples for Case Study B displayed poor comparability. The consistent use of the initial investigative sample for this Case Study did not appear to present a bias. Historical projects typically involve assessing the available data and making decisions based on that data because there is no opportunity to redo the work. Environmental Standards would like to point out that the data for Samples 4 and 5 were not utilized for the Case Study B because of the extreme difference between the results.

Table 4: Case Study B: Examples of Field Duplicate Results Disparity

Analyte	Sample 1 Result	Duplicate 1 Result	Average	Utilized
AR-1242	1300	1000	1150	1300
AR-1254	720	520	620	720
Analyte	Sample 2 Result	Duplicate 2 Result	Average	Utilized
AR-1242	2100	4000	3050	2100
AR-1254	4100	5300	4700	4100
AR-1262	2400	2100	2250	2400
Analyte	Sample 3 Result	Duplicate 3 Result	Average	Utilized
AR-1262	3200	1900	2550	3200
AR-1268	1300	730	1015	1300
Analyte	Sample 4 Result	Duplicate 4 Result	Average	Utilized*
AR-1260	940	36000	18470	940
Analyte	Sample 5 Result	Duplicate 5 Result	Average	Utilized*
AR-1260	22000	840	11420	22000

Notes:
Concentrations in µg/kg
AR - Aroclor
* - Results not utilized for project.

CONCLUSIONS

Data validation guidance for the evaluation of field duplicates provides wide acceptance criteria and does not consider the important variable of sample concentration relative to the quantitation limit. Proper field duplicate assessment must carefully consider the concentration relative to the quantitation limit. Proper field duplicate assessment must include considerations of the use of the difference between the results for low-concentration field duplicate samples and the calculated RPD between the duplicate pair for higher concentration samples. Using judgment to evaluate field duplicate data seems reasonable, but how can a basis for that judgment be acquired when guidance is so varied? Environmental Standards thinks that future data validation guidance documents should include an assessment of the concentration of the samples relative to the quantitation limit and should specify different criteria for assessment based on the concentration.

Appropriate use of field duplicate data is not detailed in the guidance documents. Using the average of the field duplicate results may not be the best approach for a site. If questions about sample collection and homogenization procedures are raised, the average may not be representative of the site conditions. For historical sites, understanding the process for sample collection and homogenization is critical. As presented in the two case studies, determining how to utilize field duplicate data can be difficult. Environmental Standards thinks that future guidance documents should include information for the design, execution, and evaluation of field data for environment projects.

Based on Environmental Standards' experience, field duplicate data use is not always straightforward, and a site-specific approach is recommended. The case studies presented demonstrate that interpreting field duplicate data is challenging. Project teams should be aware that establishing standard operating procedures and maintaining adequate documentation can greatly increase confidence in and the utility of the field duplicate data on a project basis, and establishing procedures for sample collection with the end use of the data in mind can enhance the reliability of the data.

What Do You Do With Field Duplicates? Case Studies on Usability Assessment and Application to Site Investigations

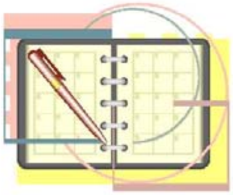
National Environmental
Monitoring Conference

Stephen T. Zeiner, CEAC
August 13, 2008

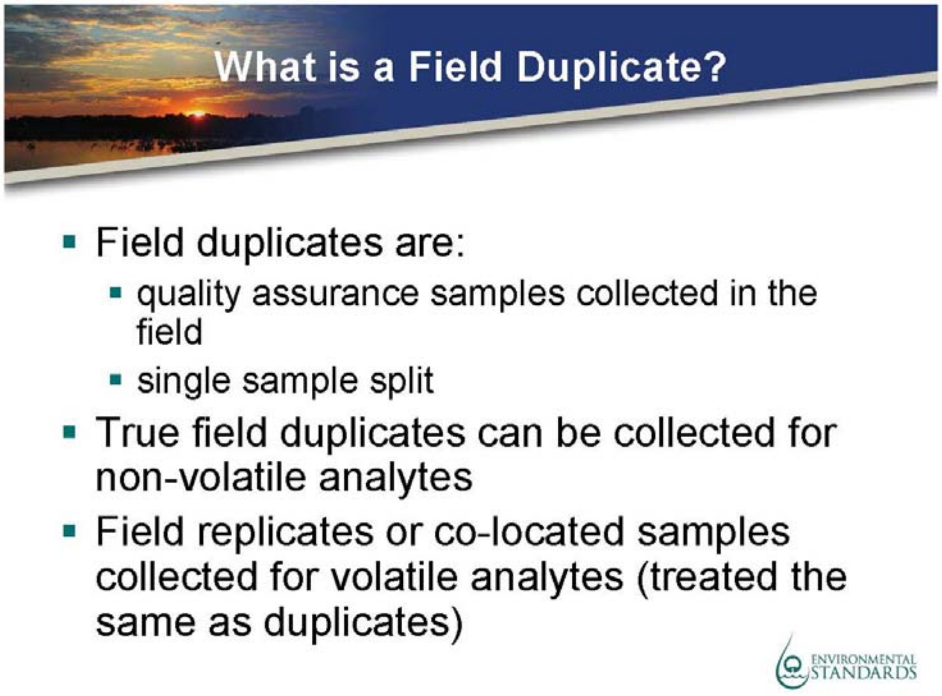
ENVIRONMENTAL STANDARDS

Coming Up...

- What are field duplicates
- How field duplicates should be collected
- Usability evaluation
- Four approaches to data use
- Case study examples
- Conclusions

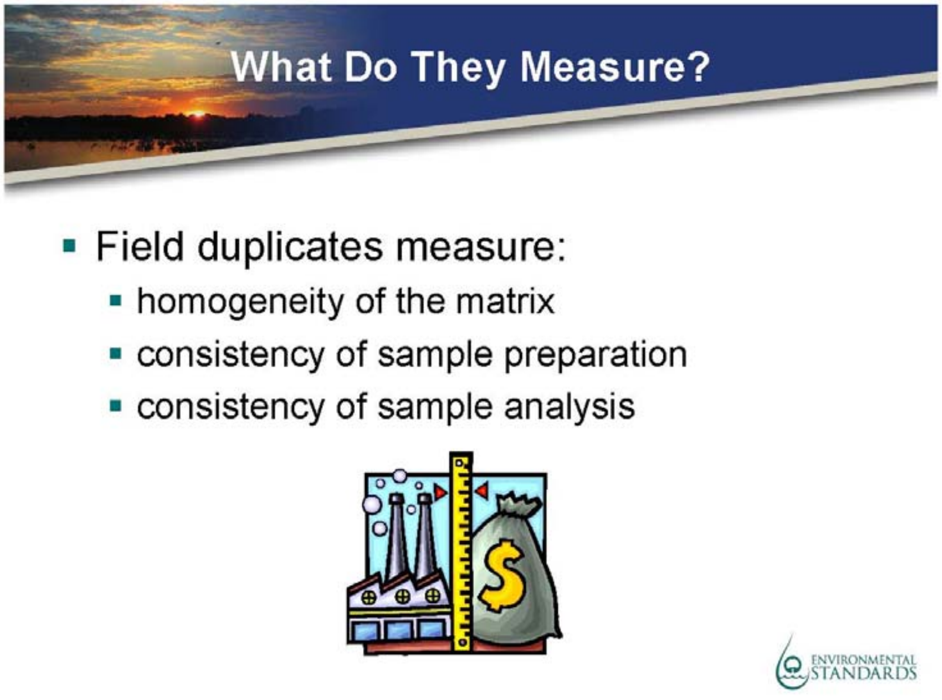


ENVIRONMENTAL STANDARDS



What is a Field Duplicate?

- Field duplicates are:
  - quality assurance samples collected in the field
  - single sample split
- True field duplicates can be collected for non-volatile analytes
- Field replicates or co-located samples collected for volatile analytes (treated the same as duplicates)

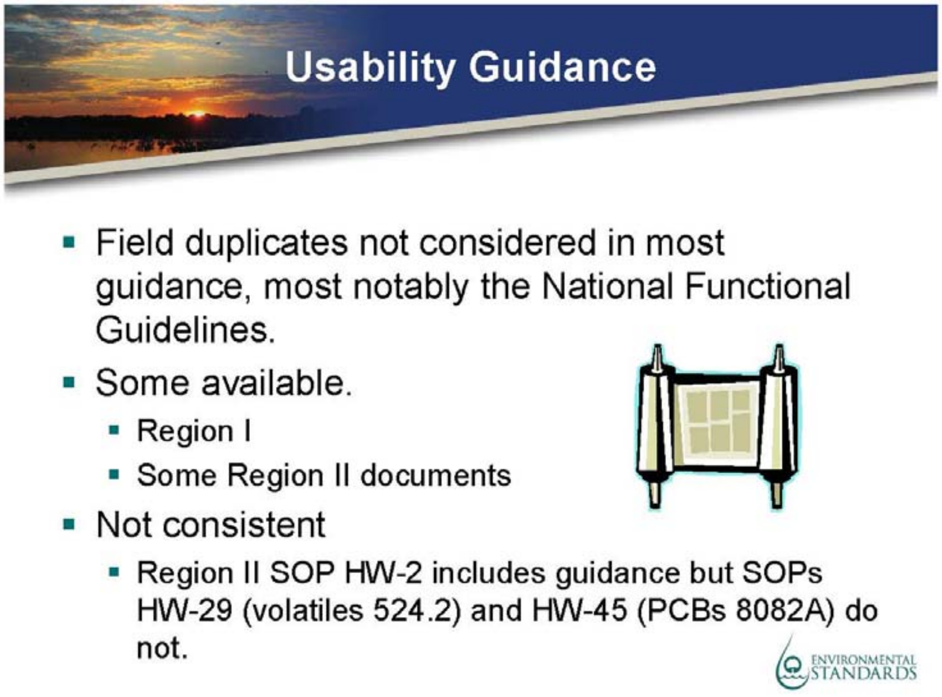


What Do They Measure?

- Field duplicates measure:
  - homogeneity of the matrix
  - consistency of sample preparation
  - consistency of sample analysis

How Should They Be Collected?

- Collection of samples is a very important step in a project
- Simple process for field duplicate samples
  - clean utensils
  - mix thoroughly, avoid excess aeration
  - mix to even texture and color
  - split evenly



Usability Guidance

- Field duplicates not considered in most guidance, most notably the National Functional Guidelines.
- Some available.
  - Region I
  - Some Region II documents
- Not consistent
  - Region II SOP HW-2 includes guidance but SOPs HW-29 (volatiles 524.2) and HW-45 (PCBs 8082A) do not.

Usability Guidance (cont.)

- Different criteria based on a concentration are not typical
- Results near quantitation limits may vary more
- Use absolute difference near quantitation limit
- Use RPD when sufficiently above quantitation limit

ENVIRONMENTAL STANDARDS

Environmental Standards Criteria

- Both results ≥ 5× quantitation limit:
  - RPD ≤ 40% for solids
  - RPD ≤ 20% for aqueous
- At least one result < 5× quantitation limit:
  - Difference ≤ twice quantitation limit for solids
  - Difference ≤ quantitation limit for aqueous

ENVIRONMENTAL STANDARDS

Utilization of Data

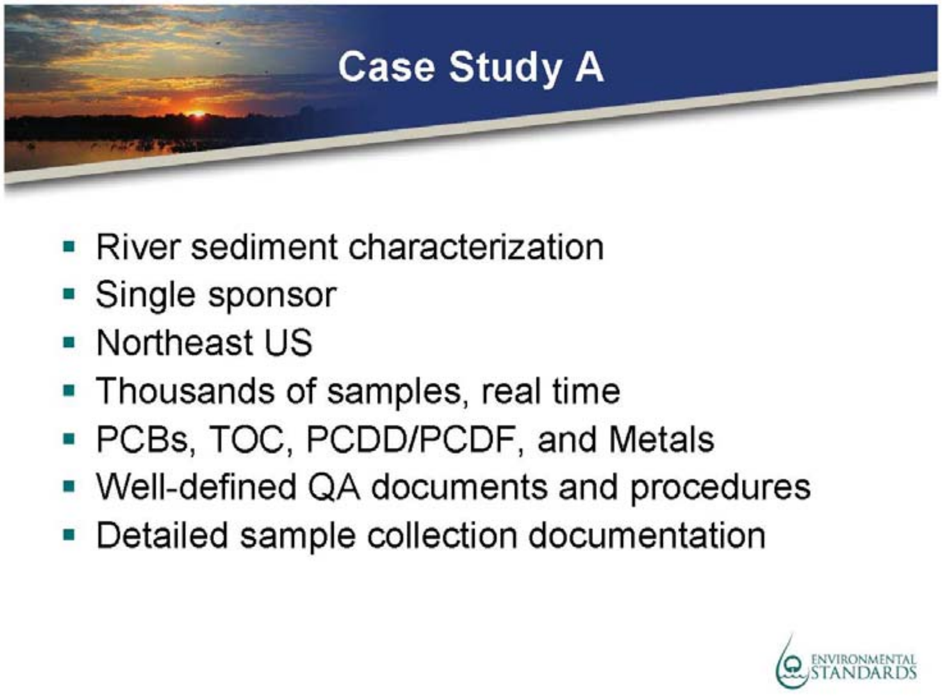
- Only one concentration per point
- Four approaches for use:
  - average of results
  - highest result
  - lowest result
  - investigative sample result only

ENVIRONMENTAL
STANDARDS

Utilization of Data

- Average – may be most representative
- Higher – will give a “worst case” view
- Lower – will give a conservative view
- Investigative only – needs to have the data set reviewed to assess for bias

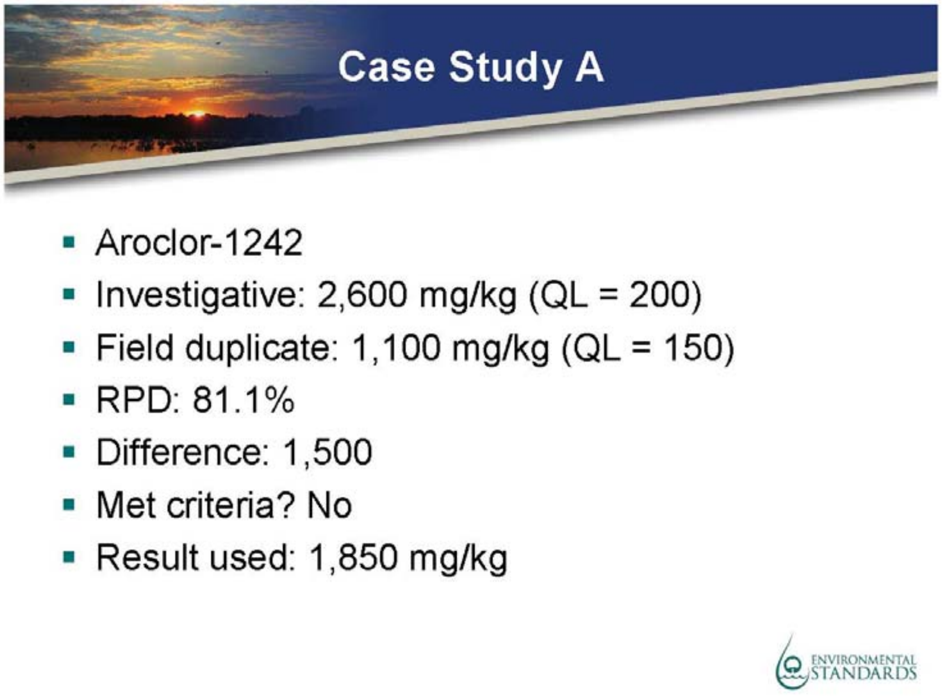
ENVIRONMENTAL
STANDARDS



Case Study A

- River sediment characterization
- Single sponsor
- Northeast US
- Thousands of samples, real time
- PCBs, TOC, PCDD/PCDF, and Metals
- Well-defined QA documents and procedures
- Detailed sample collection documentation

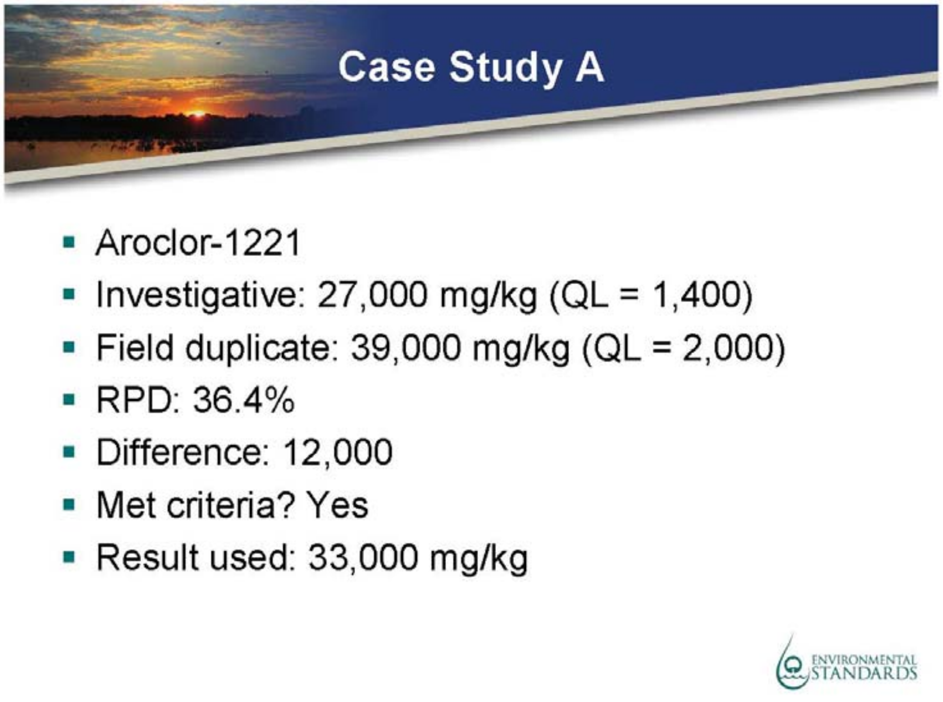
ENVIRONMENTAL STANDARDS



Case Study A

- Aroclor-1242
- Investigative: 2,600 mg/kg (QL = 200)
- Field duplicate: 1,100 mg/kg (QL = 150)
- RPD: 81.1%
- Difference: 1,500
- Met criteria? No
- Result used: 1,850 mg/kg

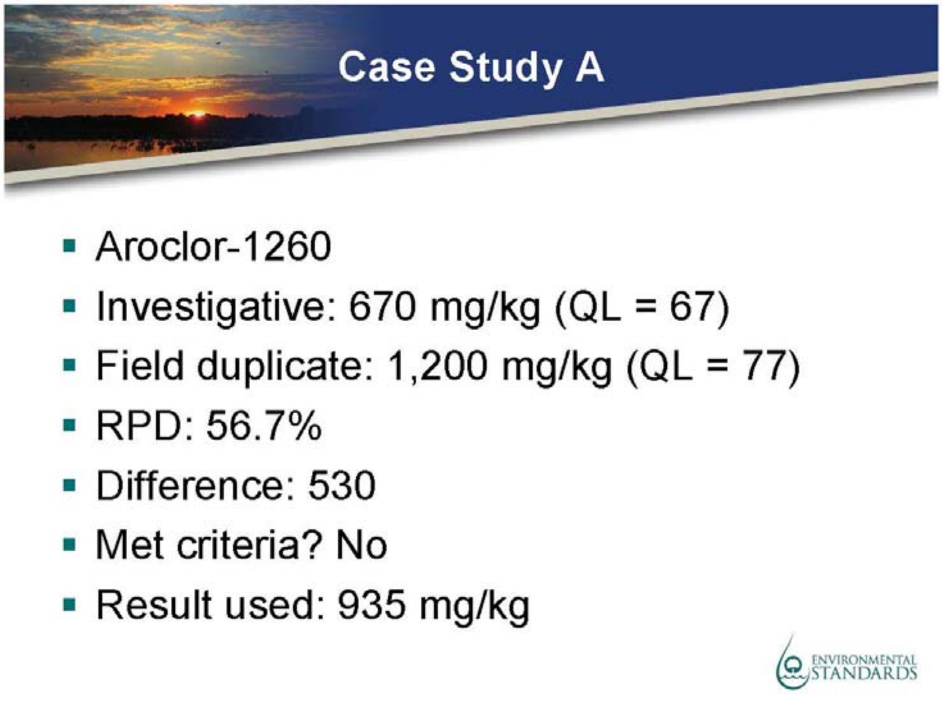
ENVIRONMENTAL STANDARDS



Case Study A

- Aroclor-1221
- Investigative: 27,000 mg/kg (QL = 1,400)
- Field duplicate: 39,000 mg/kg (QL = 2,000)
- RPD: 36.4%
- Difference: 12,000
- Met criteria? Yes
- Result used: 33,000 mg/kg

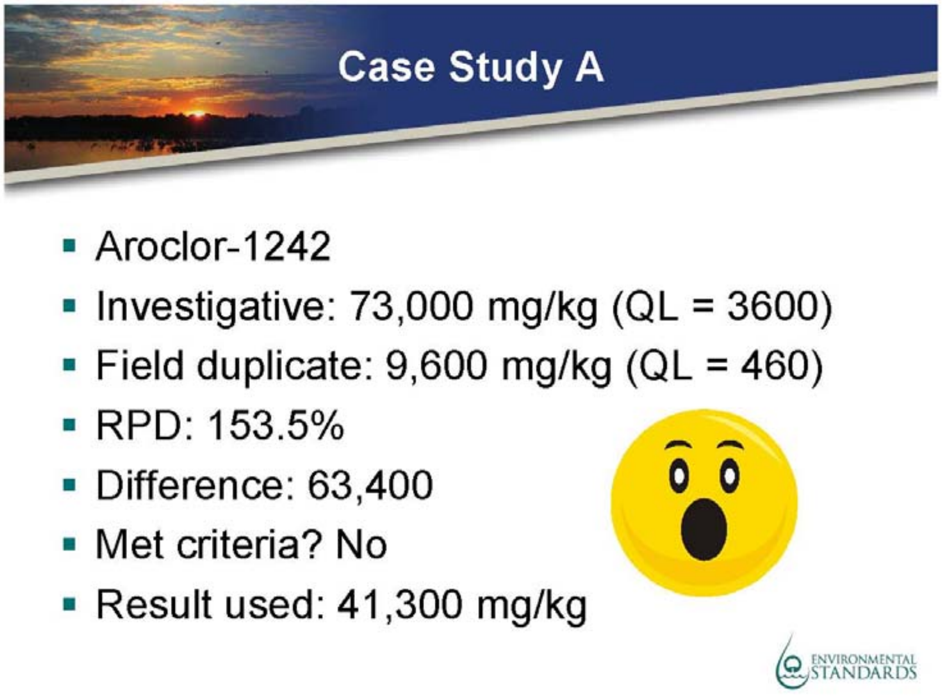
ENVIRONMENTAL STANDARDS



Case Study A

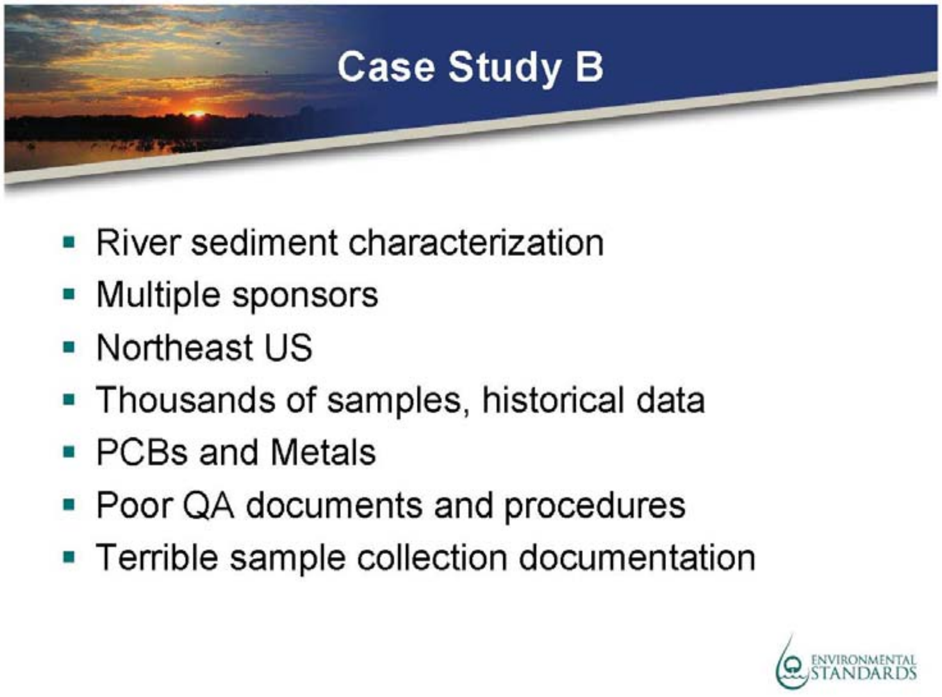
- Aroclor-1260
- Investigative: 670 mg/kg (QL = 67)
- Field duplicate: 1,200 mg/kg (QL = 77)
- RPD: 56.7%
- Difference: 530
- Met criteria? No
- Result used: 935 mg/kg

ENVIRONMENTAL STANDARDS



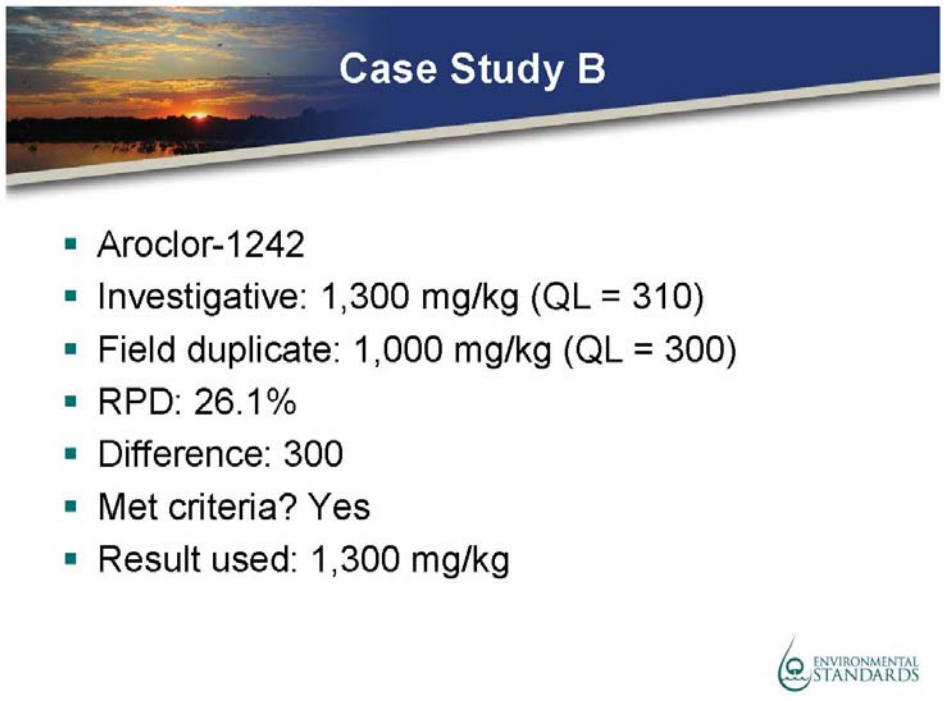
Case Study A

- Aroclor-1242
- Investigative: 73,000 mg/kg (QL = 3600)
- Field duplicate: 9,600 mg/kg (QL = 460)
- RPD: 153.5%
- Difference: 63,400
- Met criteria? No
- Result used: 41,300 mg/kg



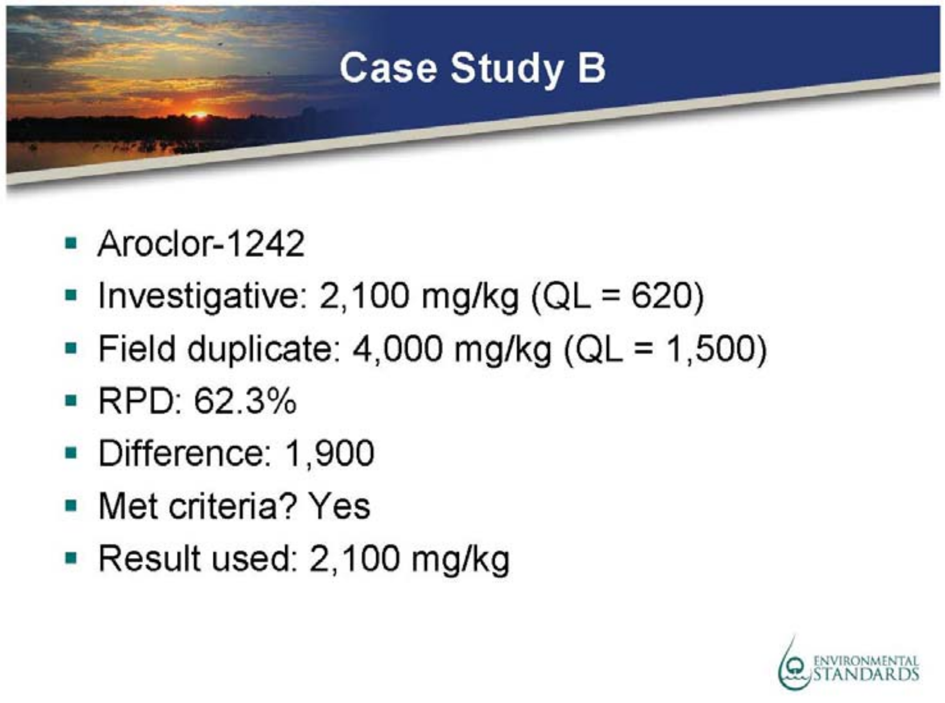
Case Study B

- River sediment characterization
- Multiple sponsors
- Northeast US
- Thousands of samples, historical data
- PCBs and Metals
- Poor QA documents and procedures
- Terrible sample collection documentation



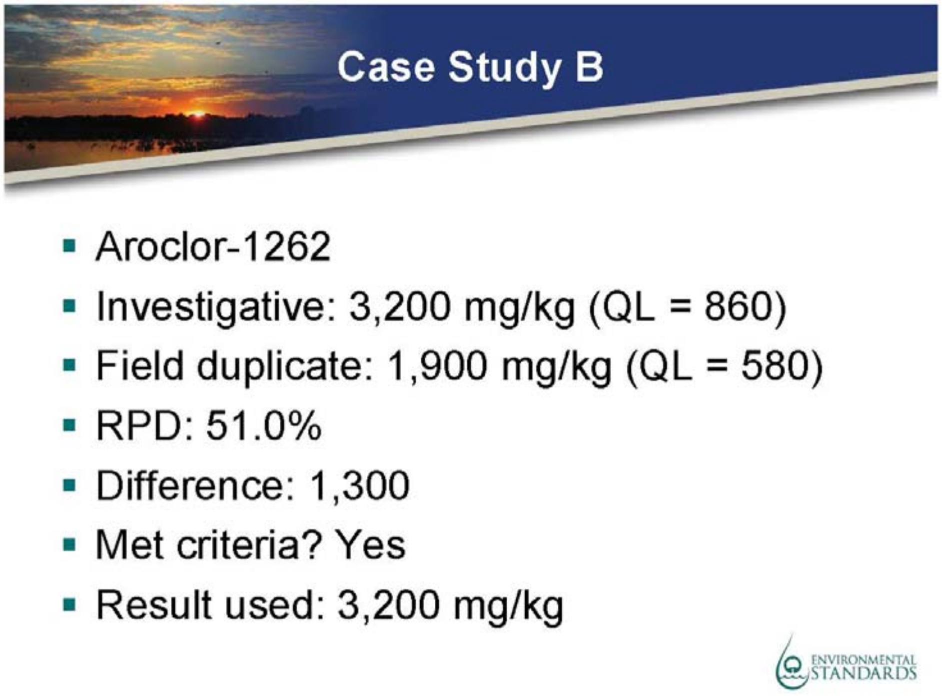
Case Study B

- Aroclor-1242
- Investigative: 1,300 mg/kg (QL = 310)
- Field duplicate: 1,000 mg/kg (QL = 300)
- RPD: 26.1%
- Difference: 300
- Met criteria? Yes
- Result used: 1,300 mg/kg



Case Study B

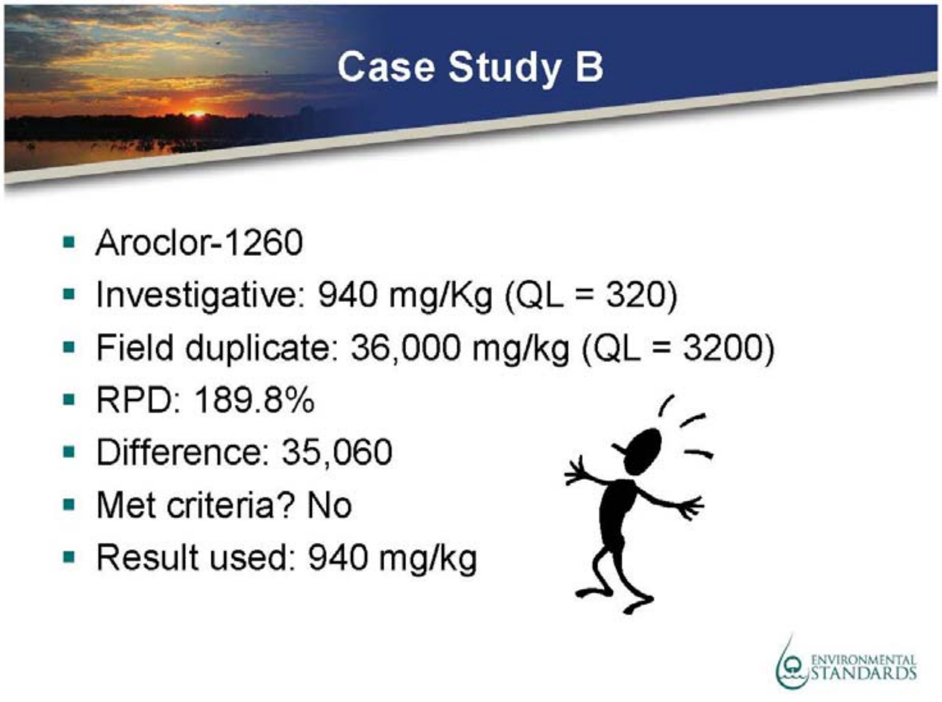
- Aroclor-1242
- Investigative: 2,100 mg/kg (QL = 620)
- Field duplicate: 4,000 mg/kg (QL = 1,500)
- RPD: 62.3%
- Difference: 1,900
- Met criteria? Yes
- Result used: 2,100 mg/kg



Case Study B

- Aroclor-1262
- Investigative: 3,200 mg/kg (QL = 860)
- Field duplicate: 1,900 mg/kg (QL = 580)
- RPD: 51.0%
- Difference: 1,300
- Met criteria? Yes
- Result used: 3,200 mg/kg

ENVIRONMENTAL STANDARDS



Case Study B

- Aroclor-1260
- Investigative: 940 mg/Kg (QL = 320)
- Field duplicate: 36,000 mg/kg (QL = 3200)
- RPD: 189.8%
- Difference: 35,060
- Met criteria? No
- Result used: 940 mg/kg

ENVIRONMENTAL STANDARDS

Case Study B

- Aroclor-1260
- Investigative: 22,000 mg/kg (QL = 3300)
- Field duplicate: 840 mg/kg (QL = 310)
- RPD: 185.3%
- Difference: 21,160
- Met criteria? No
- Result used: 22,000 mg/kg

ENVIRONMENTAL STANDARDS

Conclusion

- Field duplicate assessment and use are not always straightforward.
- Better guidance is needed.
- Planning and procedures benefit data.
- Documentation allows for confidence with historic data.
- Establishing acceptance criteria and utilization of field duplicates during project planning is preferable.

ENVIRONMENTAL STANDARDS

Thank You

“Setting the Standards for Innovative Environmental Solutions”

Environmental Standards, Inc.
1140 Valley Forge Road
P.O. Box 810
Valley Forge, PA 19482
610.935.5577
solutions@envstd.com
www.envstd.com

Data Usability: A Small Town Case Study

June Flowers
Flowers Chemical Laboratories, Inc.
P.O. Box 150-597
Altamonte Springs, FL 32715-0597
407-339-5984 ext. 212
june@flowerslabs.com

ABSTRACT

A small Florida town does a property transfer with a developer and approves a shopping center to be constructed. The arrangement includes the city performing an environmental assessment of the property that was the city maintenance yard housing a utility shed that stored pesticides. The developer proceeds with construction, while the low levels of organo-chlorine pesticide dieldrin that were detected in temporary monitoring wells is being investigated.

INTRODUCTION

This is a typical small town case study. Years ago on city-owned property there stood a shed used by the utilities department. This property is located in the center of downtown, and is a perfect site for a shopping center and a parking lot. Developer "A" offers to redevelop and purchase this property from the city, so soil testing was performed to test for suspected contaminants. Dieldrin was detected in excess of the Direct Exposure Soil Cleanup Target Levels, (SCTLs) so the contaminated soil was excavated and removed. The suspected contamination source was the location where the utility shed stood. This particular area is now beneath the new grocery store interior meat cooler. The city authorized 35 temporary monitoring wells be installed surrounding this <1 square acre property.

BACKGROUND

Developer B wishes to build 300 condominiums including 40,000 square feet of retail shops and restaurants, but since dieldrin was detected in the adjacent property, interested parties were concerned, so soil borings and temporary monitoring wells continue to be tested to try and define the source of the contamination and delineate the plume. Temporary monitoring wells were placed around this site, and low detection levels of dieldrin was found on this property.

It is presumed that pesticides were applied to each of these properties in the past to eliminate termites and other insects. The developer may not want to purchase the property from the city if it is contaminated. The State of Florida Department of Environmental Protection (FDEP) has concerns and requests for the environmental consultant to delineate the plume and determine the extent of the contamination.

City staff and council representatives allocated public funding of $600,000-800,000. Four (4) environmental consultant firms and eight (8) years later, the project continues with FDEP staff holding the cards on how to continue moving forward.

Dieldrin Facts:

1. Produced in 1948 to replace DDT
2. Banned in the 70's due to toxicity studies
3. Neurotoxin
4. Linked to Parkinson's disease
5. Priority Pollutant for effluent monitoring (Clean Water Act)
6. Currently an "Unregulated" drinking water pesticide compound

Dieldrin Site Data:

In the 22 original wells that were monitored around the site, there was detection in 5 wells that were confirmed on several sampling dates. Additional wells were constructed on the adjacent property. A detection of 0.017 ug/L was the highest concentration detected on the city "shed" site. On Developer "B's" property, 0.05 ug/L was detected, but this is a site where a strip mall used to be, and likely had been treated for pests.

Table 1: Dieldrin Published Detection Limits (DL)

REFERENCE	DL (ug/L)
EPA Method 505	0.012
EPA Method 508.1	0.010
EPA Method 525.2	0.120
EPA Method 608	0.002
FDEP GCTL	0.002
FDEP Guidance PQL	0.020

While there are several acceptable EPA published methodologies for detecting Dieldrin at ppt levels, the SW846 methods were used for the liquid-liquid extraction and GC/ECD analysis (Methods 3520 and 8081). In order to detect down to the required 0.002 ug/L cleanup limit, the methylene chloride extracts had to be concentrated. The only approved EPA method that demonstrated a 0.002 ug/L detection limit is EPA 608, a packed column method written in the early 1980's for the Clean Water Act. The more recent versions of this analytical technique generated studies of detection ranging from 0.010 to 0.120 ug/L. Yet there are regulatory limits requesting detection below the approved method capabilities. The levels detected in monitoring wells at this site by concentrating the extracts are no higher than 0.050 ug/L, and as low as 0.017 ug/L. So, this typical small town is posed with the decision of spending more taxpayer dollars to cleanup the site, or evaluate other institutional control options that will be accepted by the regulators and the new land owners. Since the concentration is higher on the neighboring property, the city doesn't want to continue paying for remediation. The plume is not migrating, nor is the high concentration well downgradient from the city site. The strip mall most likely had its own pesticide treatment in the 1950's and 60's, and it is not the city's concern.

A new factor is introduced into the equation: a City Council member with environmental testing experience, and a Ph.D. in chemistry. A complete review of the recent data generated revealed that only the pesticide Dieldrin was being quantitated in the monitoring wells, since this is the only pesticide that was confirmed in the contaminated soil that had been removed from the site. Several questions and concerns were raised the first was why is there a regulatory limit below current EPA approved method detection limits? Toxicology studies and equations by statisticians are responsible for several unrealistic detection goals for the monitoring of organic compounds. The regulatory ruling on this project was that since the initial laboratory results reported to the Groundwater Cleanup Target Level (GCTL) of 0.002 ug/L, and there was detection above this limit, 2 ppt must be achieved for all subsequent sampling events. This being the case, it was later learned that FDEP QA had published practical quantitation guidance limits for projects that could not achieve the published SCTLs and GCTLs, and the Dieldrin guidance PQL is 0.020 ug/L. This PQL is 10 times higher than the GCTL, so the very 1st ground water detection would have been less than this limit. Unfortunately, the FDEP QA PQL had never entered in to the equation for this project.

The next discussion thought was to consider that the dieldrin peaks were actually chlordane breakdown since there were other peaks on the sample chromatograms that appear in the chromatograms for the calibration curve for chlordane. Since chlordane was not detected in the initial monitoring of this project, no one ever considered evaluating it in new areas around the site. EPA method criteria were met by the GC/ECD analysis to call it Dieldrin, and it had been proven that the extraction and analytical scheme could detect these low levels. The new argument raised is that there is no scientific certainty that it is dieldrin because the concentrations are too low for GC/MS confirmation.

This project is coming to fruition and with new knowledge of a 0.020 ug/L guidance PQL and the reasonable doubt that the peaks detected could have actually been remnants of chlordane, the city may have spent its last dollar on this site. The decision being presented is to use the deed restriction approach to save time and city taxpayer dollars.

Institutional Controls include:

- Deed restriction never to place a potable or non-potable well on-site;
- If there was a well, although it may meet drinking water standards, it will not be permitted to use the water for irrigation.

City staff are not educated to question the suggestions and recommendations of the many consultants, especially regarding detection levels. Could the dieldrin peaks at this low concentration actually be chlordane? Must state clean-up standards be the sole source of direction for projects? Sometimes cleanup is not the right option. That is why other avenues are available. At this level of detection, laws allow you to drink this water, but not discharge it back on the ground.

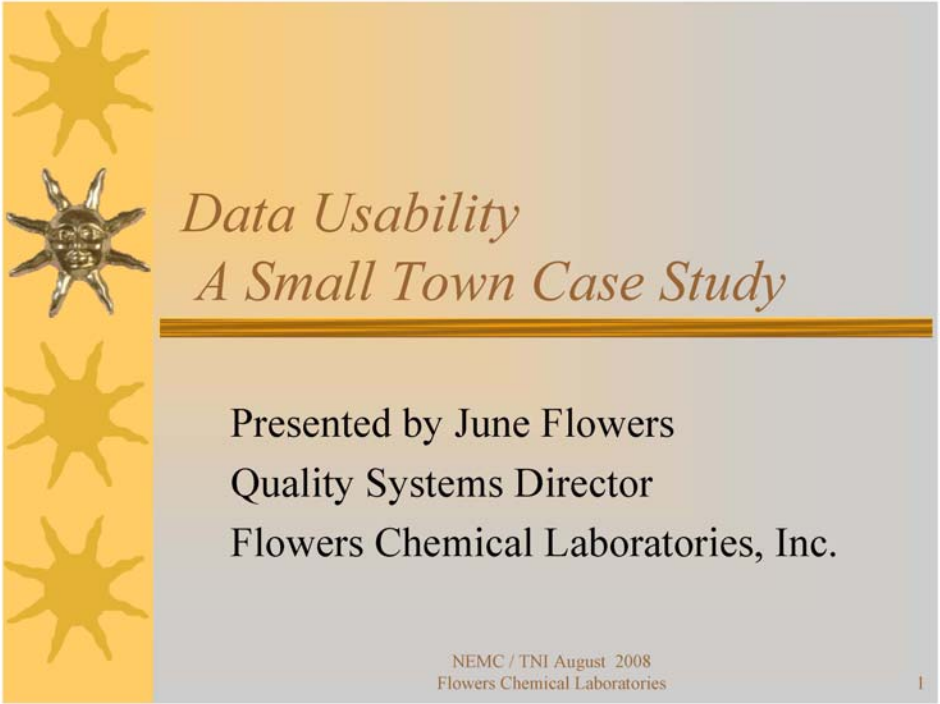
CONCLUSIONS

Municipalities across the country are making decisions to redevelop properties that are public and privately owned. Due to State budget cuts, many cities in Florida are struggling to maintain the high level of services their citizens expect and deserve. The typical City Manager and staff are not always well versed in environmental regulations and often depend on consultation from environmental specialists. It is difficult to find consultation that is versed in every possible detail that could arise on a specific project. Thousands of dollars can easily be spent due to a simple error or omission of knowledge. It is imperative to research all possible scenarios before making a decision to clean up a suspected contaminated site.

REFERENCES

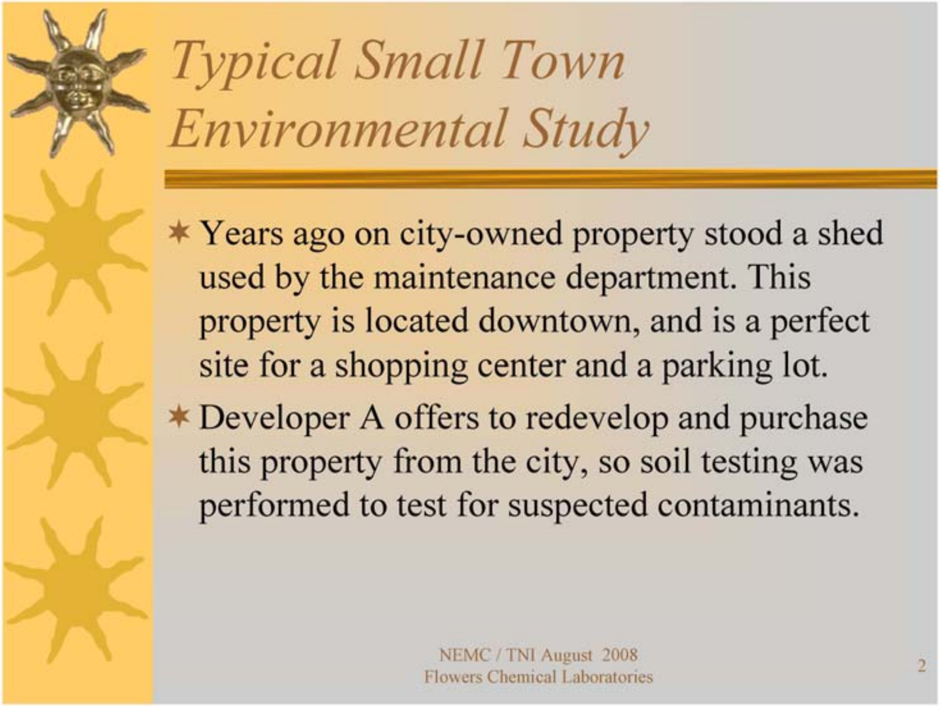
1. Florida Administrative Code (FAC) Part 62-777, Groundwater and Surface Water Cleanup Target Levels, Table I, Updated April 2005

2. Guidance for the Selection of Analytical Methods and for the Evaluation of Practical Quantitation Limits, FDEP, Division of Resource Assessment and Management for the Division of Waste Management Cleanup Programs, October 12, 2004. Table C Groundwater.



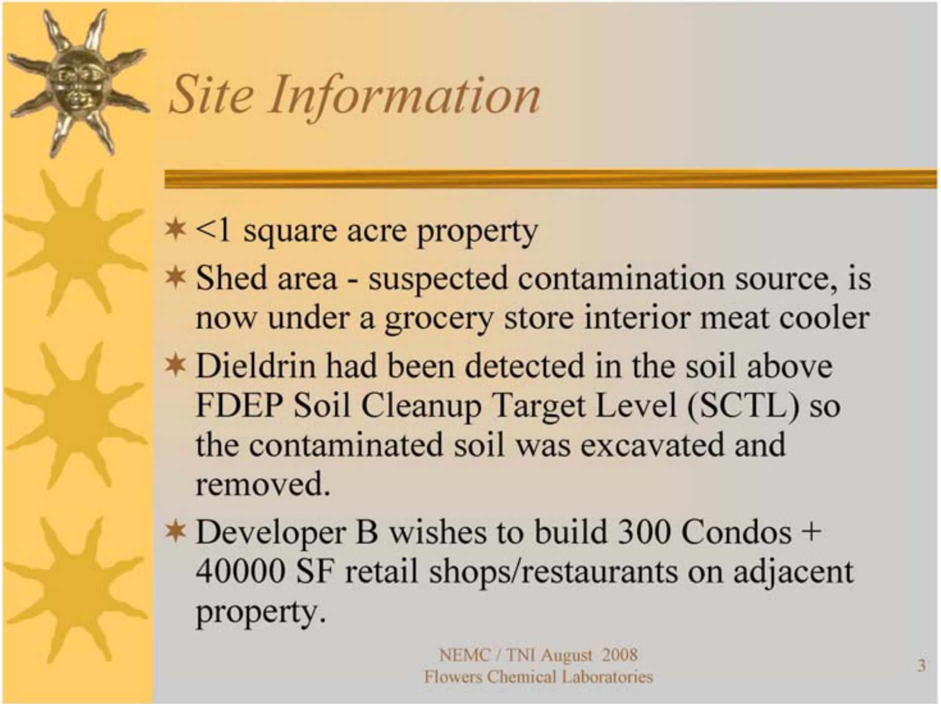
Data Usability
A Small Town Case Study

Presented by June Flowers
Quality Systems Director
Flowers Chemical Laboratories, Inc.



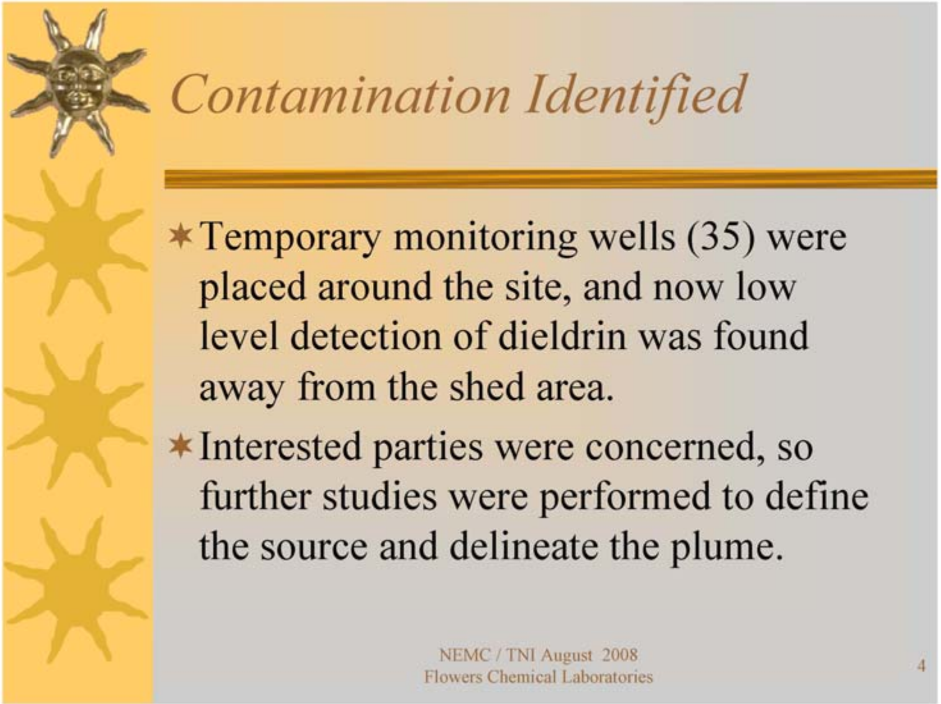
Typical Small Town Environmental Study

- Years ago on city-owned property stood a shed used by the maintenance department. This property is located downtown, and is a perfect site for a shopping center and a parking lot.
- Developer A offers to redevelop and purchase this property from the city, so soil testing was performed to test for suspected contaminants.



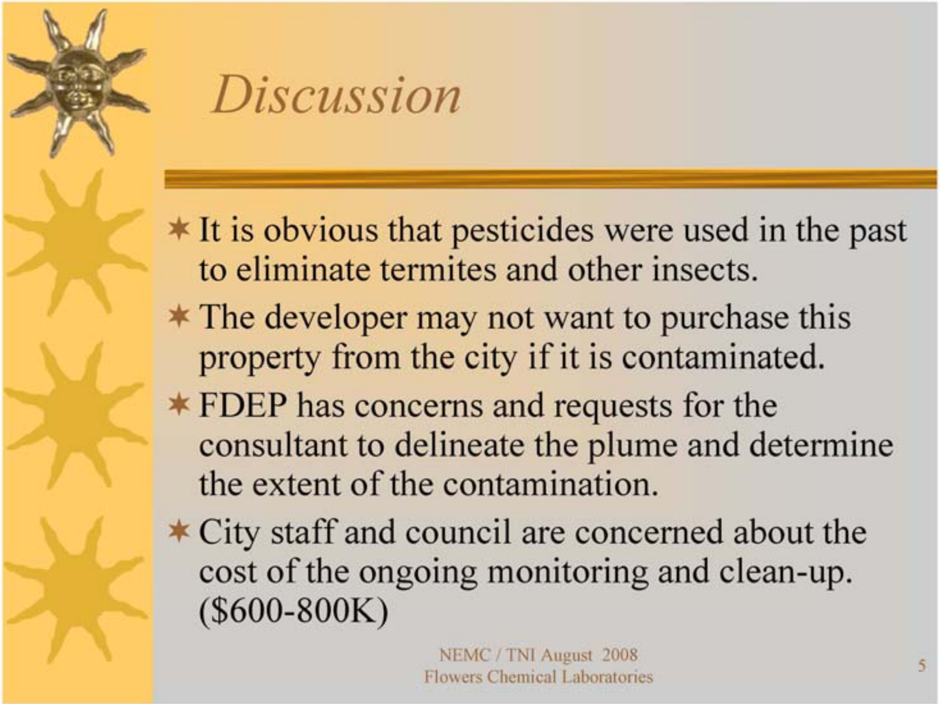
Site Information

- <1 square acre property
- Shed area - suspected contamination source, is now under a grocery store interior meat cooler
- Dieldrin had been detected in the soil above FDEP Soil Cleanup Target Level (SCTL) so the contaminated soil was excavated and removed.
- Developer B wishes to build 300 Condos + 40000 SF retail shops/restaurants on adjacent property.



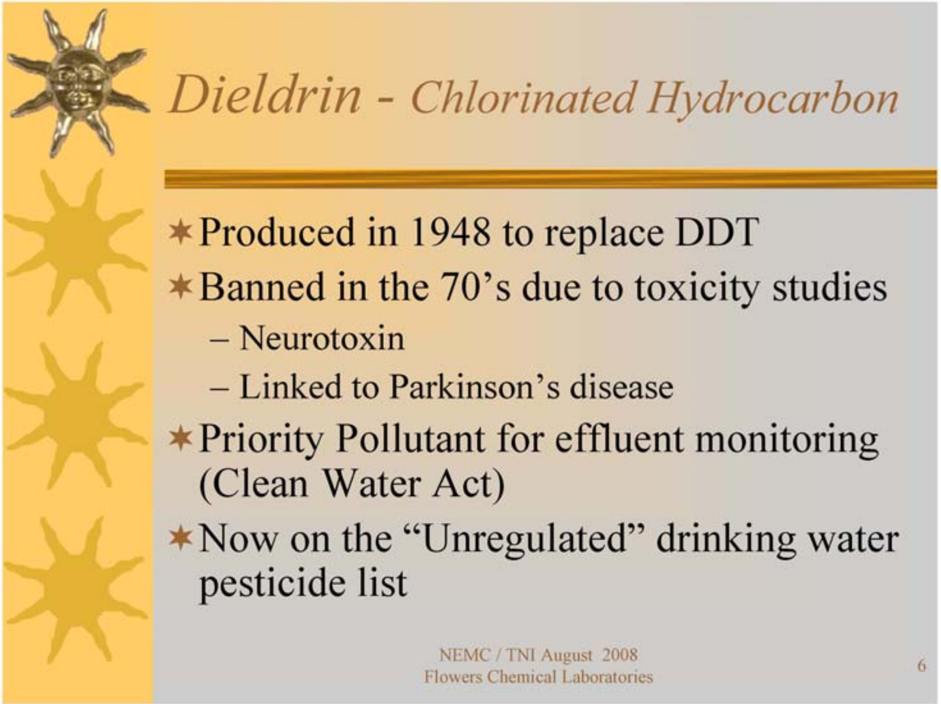
Contamination Identified

- Temporary monitoring wells (35) were placed around the site, and now low level detection of dieldrin was found away from the shed area.
- Interested parties were concerned, so further studies were performed to define the source and delineate the plume.



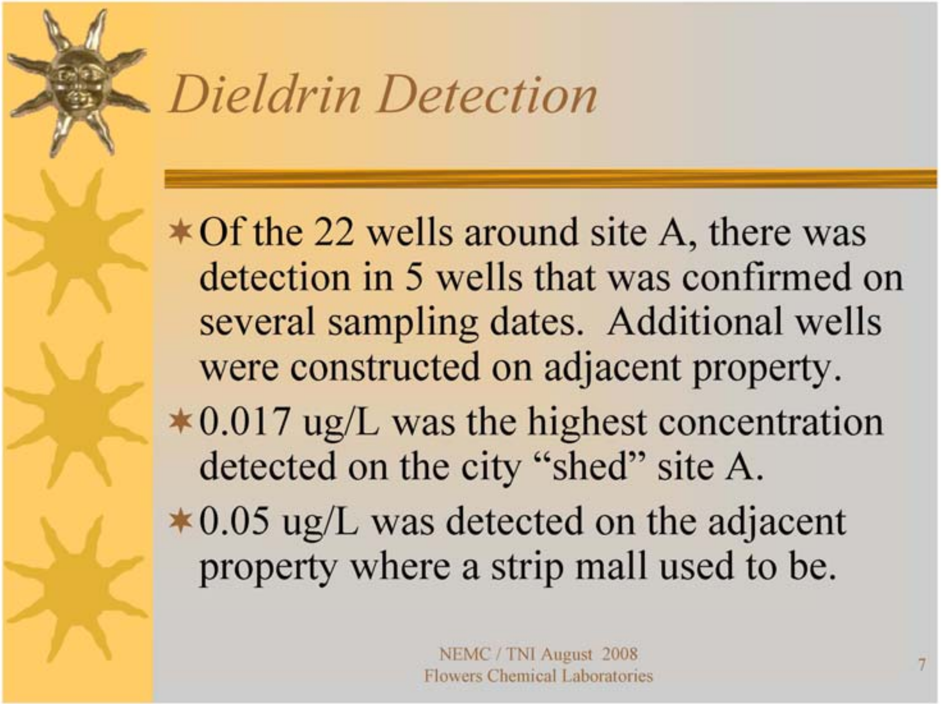
Discussion

- It is obvious that pesticides were used in the past to eliminate termites and other insects.
- The developer may not want to purchase this property from the city if it is contaminated.
- FDEP has concerns and requests for the consultant to delineate the plume and determine the extent of the contamination.
- City staff and council are concerned about the cost of the ongoing monitoring and clean-up. ($600-800K)



Dieldrin - Chlorinated Hydrocarbon

- Produced in 1948 to replace DDT
- Banned in the 70’s due to toxicity studies
  - Neurotoxin
  - Linked to Parkinson’s disease
- Priority Pollutant for effluent monitoring (Clean Water Act)
- Now on the “Unregulated” drinking water pesticide list

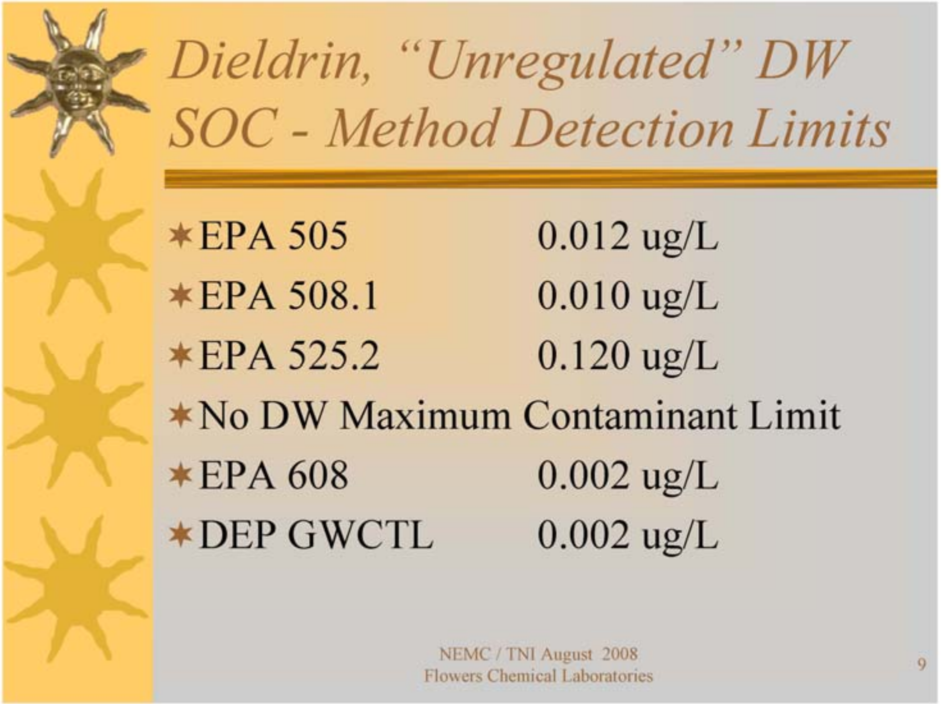


Dieldrin Detection

- Of the 22 wells around site A, there was detection in 5 wells that was confirmed on several sampling dates. Additional wells were constructed on adjacent property.
- 0.017 ug/L was the highest concentration detected on the city "shed" site A.
- 0.05 ug/L was detected on the adjacent property where a strip mall used to be.

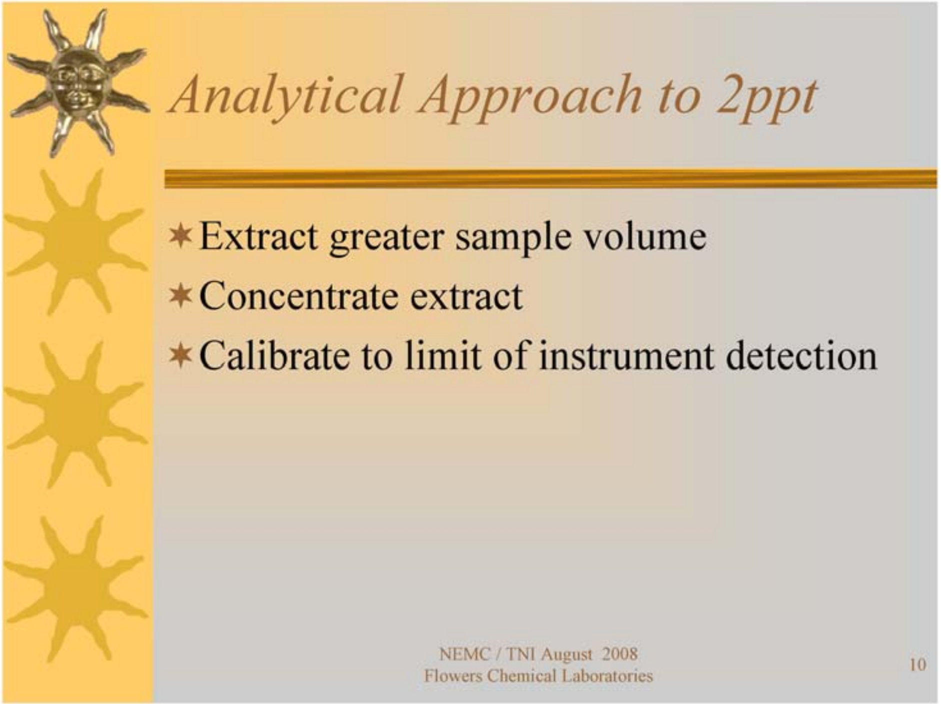
New Data User Arrives

- New City Councilman with environmental laboratory experience gets involved
- Requests data package - only gets most recent (project began 3 years and 4 consultants prior)
- Concern about detection level is raised and reviewed



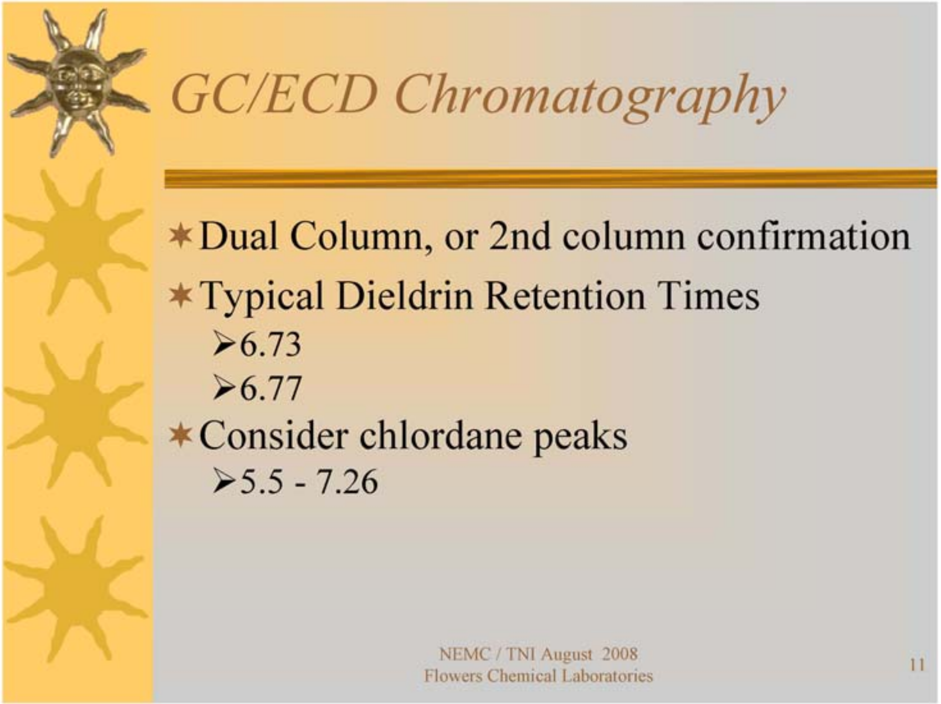
Dieldrin, "Unregulated" DW SOC - Method Detection Limits

- EPA 505 0.012 ug/L
- EPA 508.1 0.010 ug/L
- EPA 525.2 0.120 ug/L
- No DW Maximum Contaminant Limit
- EPA 608 0.002 ug/L
- DEP GWCTL 0.002 ug/L



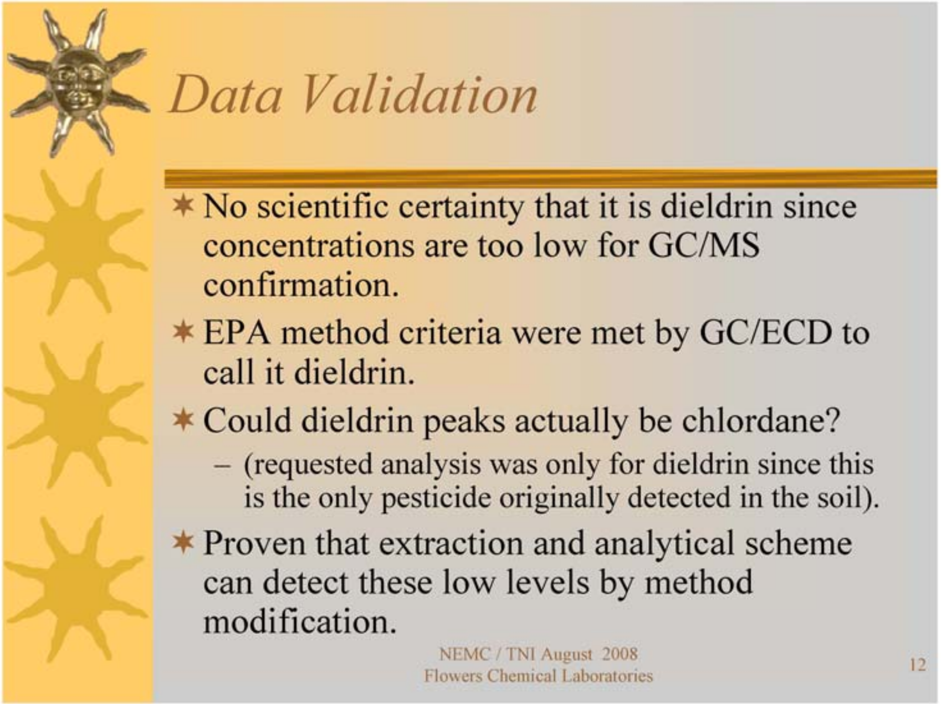
Analytical Approach to 2ppt

- Extract greater sample volume
- Concentrate extract
- Calibrate to limit of instrument detection



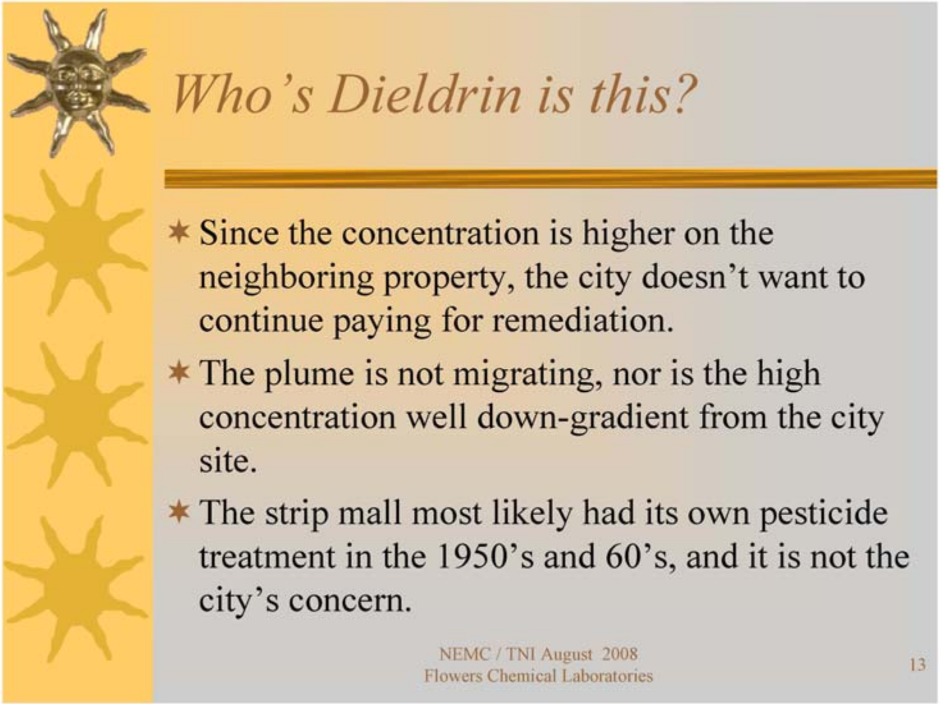
GC/ECD Chromatography

- Dual Column, or 2nd column confirmation
- Typical Dieldrin Retention Times
  - 6.73
  - 6.77
- Consider chlordane peaks
  - 5.5 - 7.26



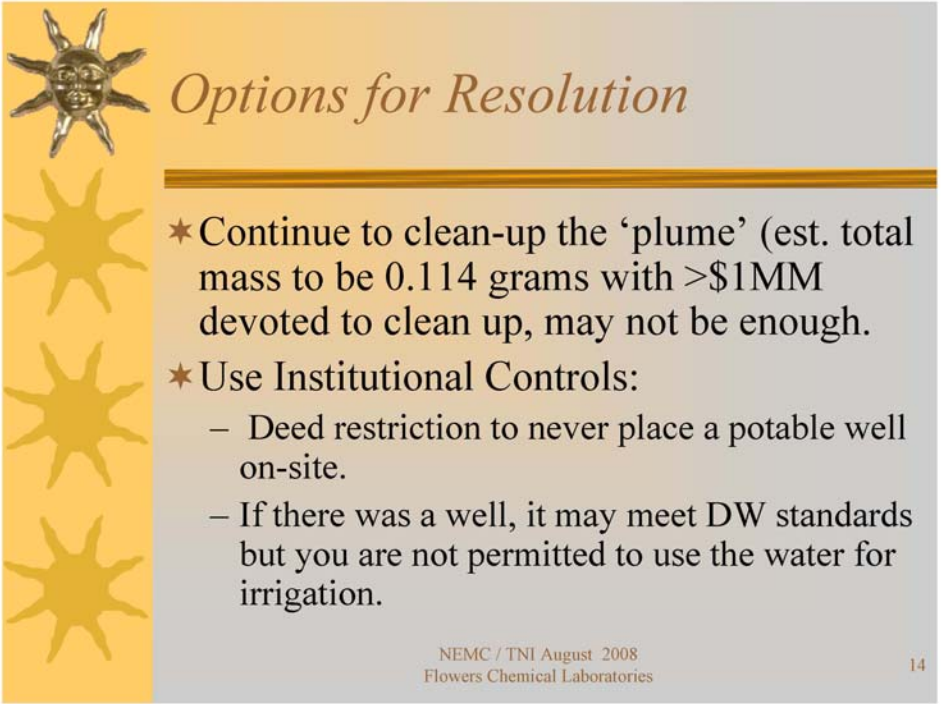
Data Validation

- No scientific certainty that it is dieldrin since concentrations are too low for GC/MS confirmation.
- EPA method criteria were met by GC/ECD to call it dieldrin.
- Could dieldrin peaks actually be chlordane?
  - (requested analysis was only for dieldrin since this is the only pesticide originally detected in the soil).
- Proven that extraction and analytical scheme can detect these low levels by method modification.



Who's Dieldrin is this?

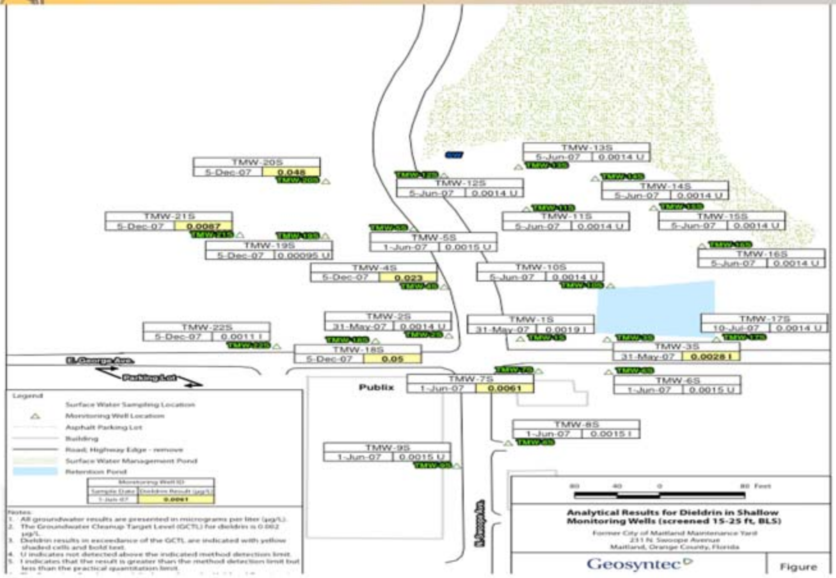
- Since the concentration is higher on the neighboring property, the city doesn't want to continue paying for remediation.
- The plume is not migrating, nor is the high concentration well down-gradient from the city site.
- The strip mall most likely had its own pesticide treatment in the 1950's and 60's, and it is not the city's concern.

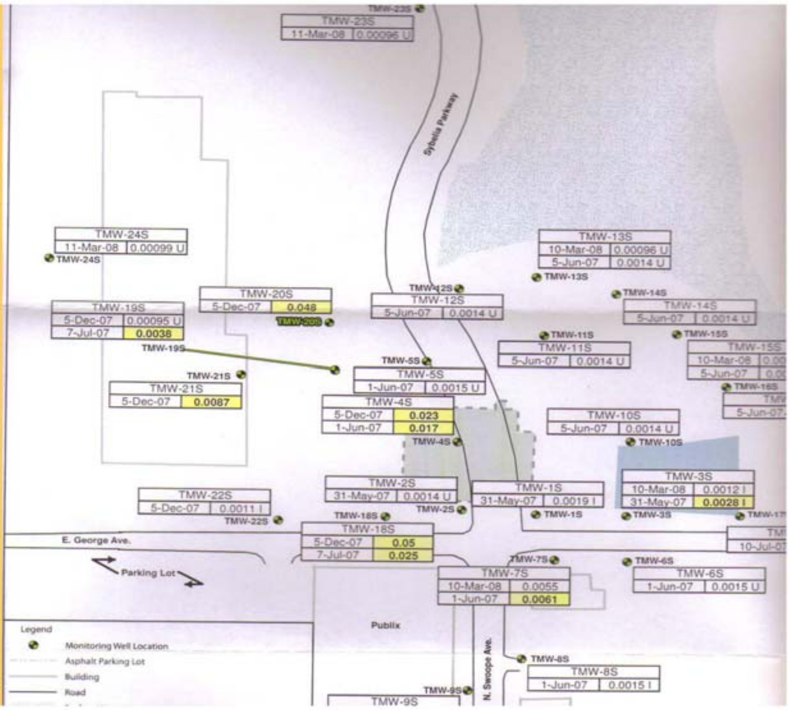


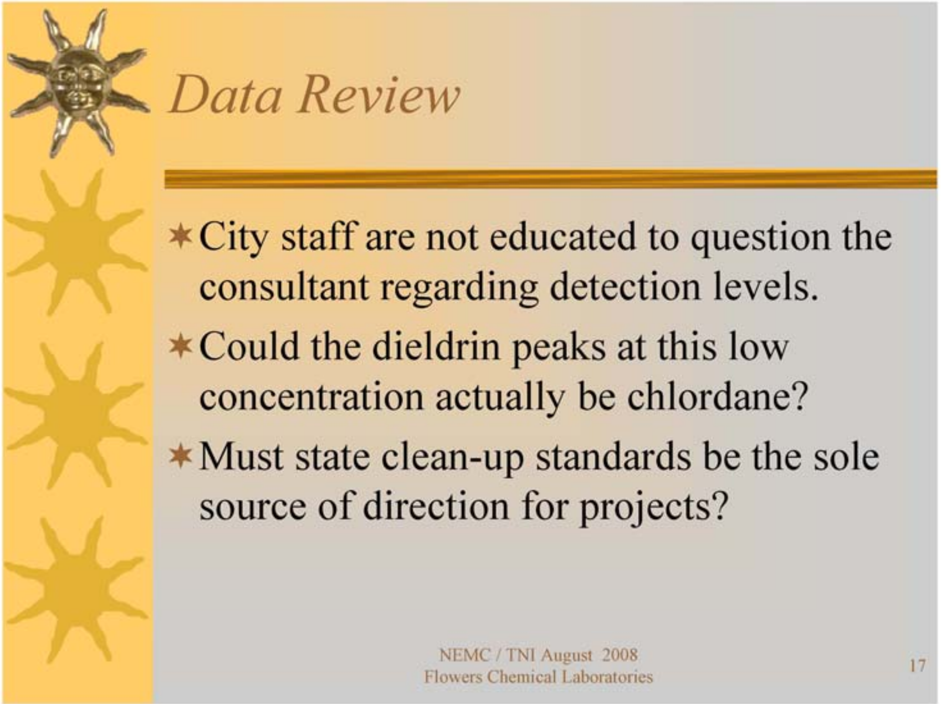
Options for Resolution

- Continue to clean-up the 'plume' (est. total mass to be 0.114 grams with >$1MM devoted to clean up, may not be enough.
- Use Institutional Controls:
  - Deed restriction to never place a potable well on-site.
  - If there was a well, it may meet DW standards but you are not permitted to use the water for irrigation.

Site Schematic

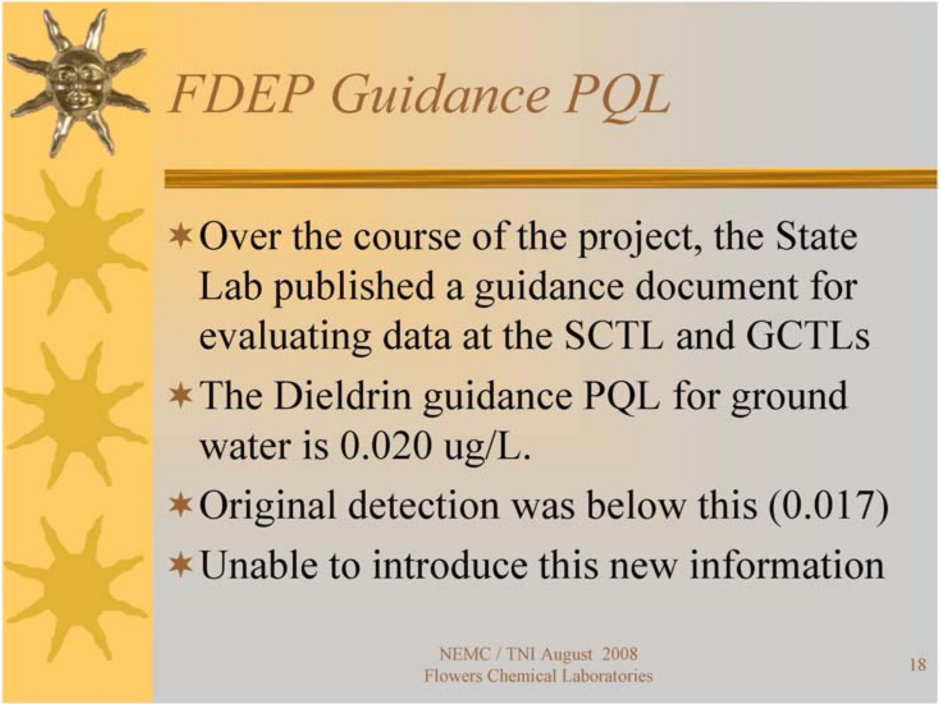






Data Review

- City staff are not educated to question the consultant regarding detection levels.
- Could the dieldrin peaks at this low concentration actually be chlordane?
- Must state clean-up standards be the sole source of direction for projects?

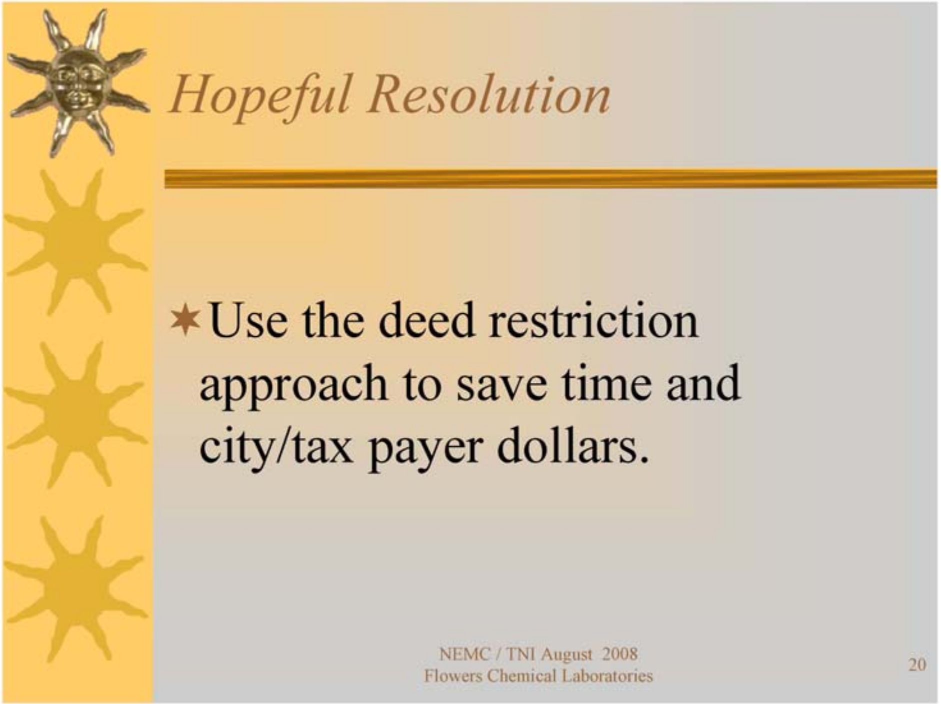


FDEP Guidance PQL

- Over the course of the project, the State Lab published a guidance document for evaluating data at the SCTL and GCTLs
- The Dieldrin guidance PQL for ground water is 0.020 ug/L.
- Original detection was below this (0.017)
- Unable to introduce this new information

Someone has to decide

- Sometimes Cleanup is not the right option. That is why other avenues are available.
- At this level of detection, laws allow you to drink this water, but not discharge it back on the ground.



Hopeful Resolution

- Use the deed restriction approach to save time and city/tax payer dollars.

UCMR2 – Lessons Learned in Year 1

Andrew Eaton and Linda Geddes
MWH Laboratories
750 Royal Oaks Drive #100
Monrovia, CA 91016
626-386-1125
andrew.d.eaton@us.mwhglobal.com

ABSTRACT

2008 marked the beginning of monitoring for the USEPA mandated drinking water Unregulated Contaminant Monitoring Program (UCMR2) that requires analysis of Point of Entry samples for up to 20 contaminants using 5 different methods and distribution system analysis for nitrosamines. With the experience gained through analysis of up to 50 samples per week for each of the UCMR2 methods, it is possible to use experience from year 1 to help labs and utilities in years 2 and 3 of this program. Most of the methods have proved to be relatively robust, but the program is complex and not without "issues", that range from educating lab staff on the program details to ensuring that utilities are clear on the field requirements.

INTRODUCTION

UCMR1 was conducted from 2001 to 2005 to provide national data on contaminant occurrence that might be used to determine what analytes to regulate in drinking water. EPA used the information on study design and implementation from UCMR1 to make improvements for the UCMR2 program, for which monitoring commenced in January 2008 and will continue for a 3 year period. MWH was heavily involved in UCMR1 monitoring and is also one of the larger lab participants in UCMR2, analyzing as many as 50 or more samples per week under this program. There are a number of changes in UCMR2 compared to UCMR1 that impact both laboratories and utilities and were designed to ensure a more rigorous set of quality standards for data. This paper discusses those changes and experience with implementation. We can also compare UCMR1 and UCMR2 with respect to improvements in the design of the program from a "user" perspective. Lessons include a) database issues for SDWARS/CDX information and uploads; b) sample collection issues relating to COCs, adequate sample volume for required matrix QC and appropriate preservation and finally c) issues with each of the UCMR2 methods in terms of blanks, spike recovery concentrations and variability, and general sample processing issues.

LABORATORY APPROVAL

In UCMR1, the only method that required specific EPA certification was perchlorate. In UCMR2, there was a rigorous application process for all 5 methods (521, 525, 527, 529, and 535). This process required a) submittal of IDOC, MDL, and LCMRL determination for each method to an EPA contractor; b) completion of SOPs; c) development of a UCMR2 specific QAPP; d) review of selected raw data by the contractor; and e) passing a PT sample for each analyte. This rigorous screening process led to a very limited number of labs being approved for several of the methods. The trend in lab approval timeline reflected the relative complexity of the different UCMR2 methods. Initially a large number of labs were approved for method 525.2, with a somewhat smaller number approved for 527 and 529 (traditional GCMS methods). It required 5 rounds of PT samples before a reasonable number of labs were approved for methods 535 and 521, the most complex methods. The difficulty of going through the approval process was illustrated by the fact that only about 5 labs nationwide were approved for all methods through the first 2 rounds of PT samples.

SDWARS/CDX SYSTEM AND SAMPLE POINT SELECTION

Although the SDWARS/CDX system was used by utilities in UCMR1, there were relatively extensive changes implemented for UCMR2. One key element of UCMR2 was the ability for utilities to reduce the number of sampling points through representative groundwater monitoring plans. Although simple in concept, utilities varied in their ability to take advantage of this opportunity. Setting up sample points in the data system was relatively simple once the system was understood. Unfortunately EPA initially populated the system with all potential sample points from various state databases so some utilities (e.g. ones with very large numbers of POEs) had to spend a lot of time marking particular sites as not applicable, or alternatively for states that have sample collection before disinfection (not an option in UCMR2), utilities had to create new sample points in the system. Because there was not a consistent sample identification scheme, labs working with multiple utilities have had to sometimes "interpret" a utility's sample location identification to ensure that the proper tests are performed (e.g. the distribution system sample point ONLY gets method 521, but some utilities did not consistently identify the distribution system point – leading to potential extra analyses).

Seeing the myriad of variations applied by utilities in the SDWARS database leads to both recommendations for more consistency in the next round and also for ways utilities can help themselves and labs in the next few years of monitoring under UCMR2.

STARTUP ISSUES

For SDWARS/CDX, the biggest issues relate to misidentification of sample point ID and missing sample event information for large systems which creates problems with the upload. The upload file itself is much simpler to create than the UCMR1 file, and this has already minimized errors at the back-end. Direct notification of utilities when uploads are completed is also positive. For sample collection, clear instructions, getting all required information and ensuring collection of extra volume for MS/MSD and rechecks is critical. There have been cases where utilities have apparently rinsed out the preservative, requiring recollection. If this happens to be a 535, simultaneous recollection of 525 is needed, creating both laboratory and field issues. Confirming preservation is critical for many of the methods and early on we switched to test strips when false positives using DPD powder occurred.

In the lab we expected the most problematic methods to be 527 (dimethoate recovery on high level spikes is problematic but can be overcome by use of multiple disks) and 521 due to trace blank levels for several nitrosamines. However in reality the biggest method problem appears to be EPA 535, the LC-MS-MS method. Careful transfer of extracts is critical and we switched from adding internal standard in the extraction department to adding it just prior to injection. We have found that calibration every day that samples are analyzed is necessary or reruns may be needed. Since the MRL Check must be within acceptance criteria calibration type is also a factor. The HPLC columns have a limited life span and must be changed every 100-200 injections, depending on the matrices.

LESSONS LEARNED

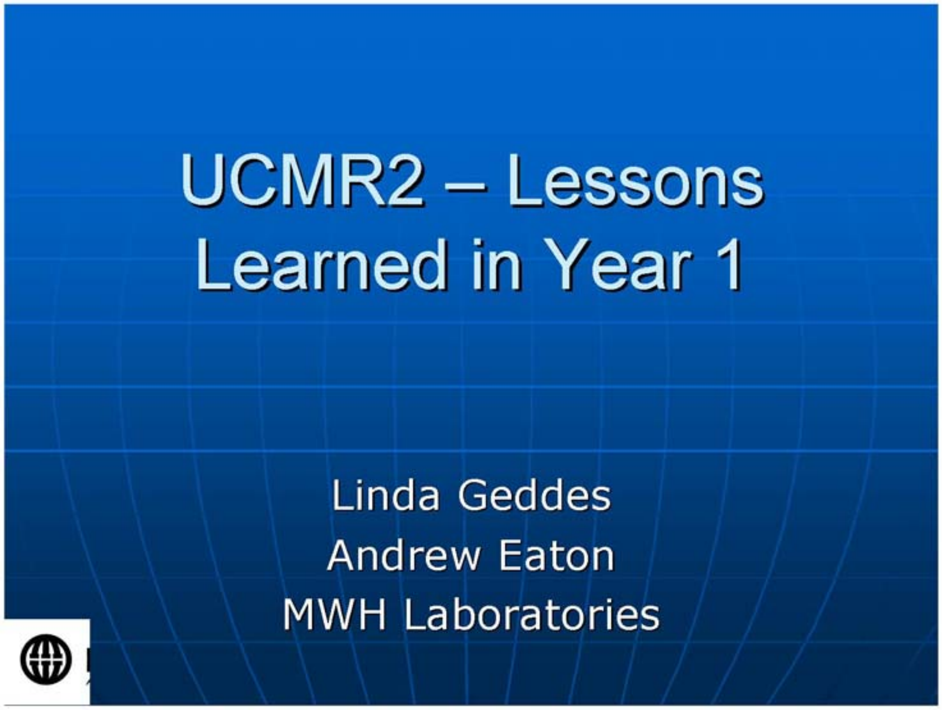
In order to upload data correctly the utility must be registered and the PWSID, Facility ID, Sample Point ID, and Sample Event must be accurate. While data can be corrected after entry to the CDX it is not an easy process. The utility can send the data back to the lab for correction, but once it gets beyond the utility there is no mechanism in place for the lab to correct the problem.

The UCMR2 Quality Assurance Manual requirements are tighter than the method requirements, imposing stricter QA/QC than we had originally planned for. MRL Checks, which were not part of the methods, are required and must pass for data to be reported. Also, if samples were Not Detected, the methods would allow the closing calibration check to be out high. This is not the case for UCMR2; all calibration and method reporting level checks must be within acceptance criteria. All of this information had to be transferred to the laboratory staff to ensure that program requirements were met through meetings with each department.

While we tried to prepare by analyzing test samples in 2007, the amount and frequency were not sufficient to truly hone the methods in our laboratory for daily use. Practice does make perfect!

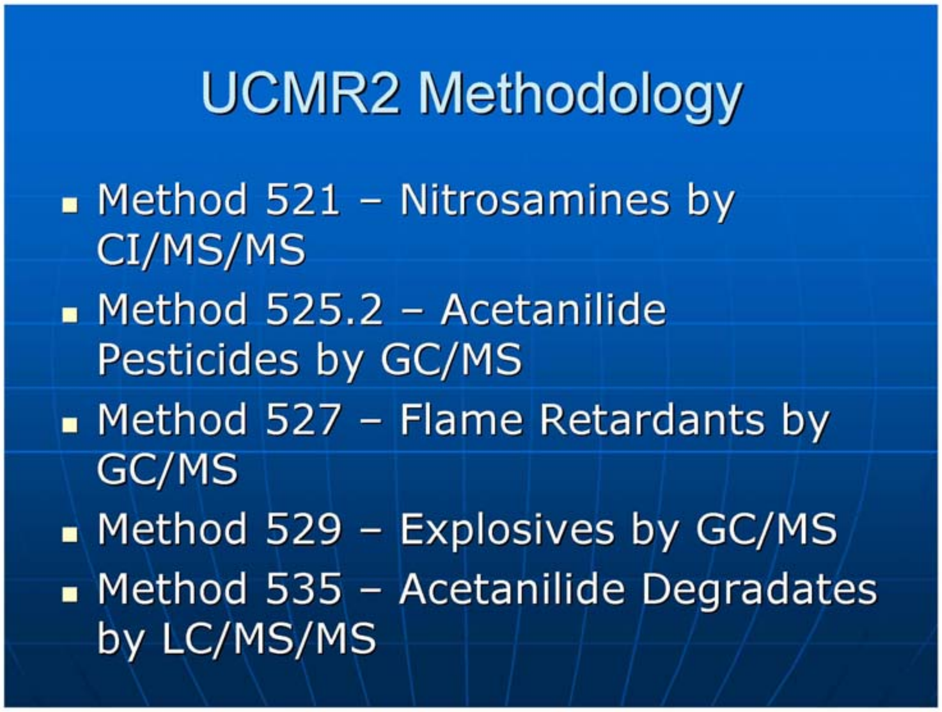
CONCLUSIONS

UCMR2 requires the use of 4 analytical methods that had not previously been widely tested (521, 527, 529, and 535), along with one tried and true method (525). Each of the new methods was developed by EPA specifically for the UCMR2 program. Two of them, 521 for nitrosamines and 535 for pesticide degradates, involved relatively new (for the environmental testing world) technologies – GCMS with chemical ionization and LC-MS-MS. UCMR2 also introduced the concept of LCMRL to the laboratory world. In spite of the challenges of using relatively untried methods, UCMR2 in year one has been marked more by successes than by failures. The method that most laboratories anticipated to be problematic (521) has been relatively trouble-free, even though it is measuring part per trillion levels of nitrosamines. Method 527, while anecdotally a problem in some labs, has proven to be relatively robust. Method 529 has been challenging for some labs, but not a major issue. The biggest problem area appears to be with method 535, the LC-MS-MS method, with some inconsistent recoveries.



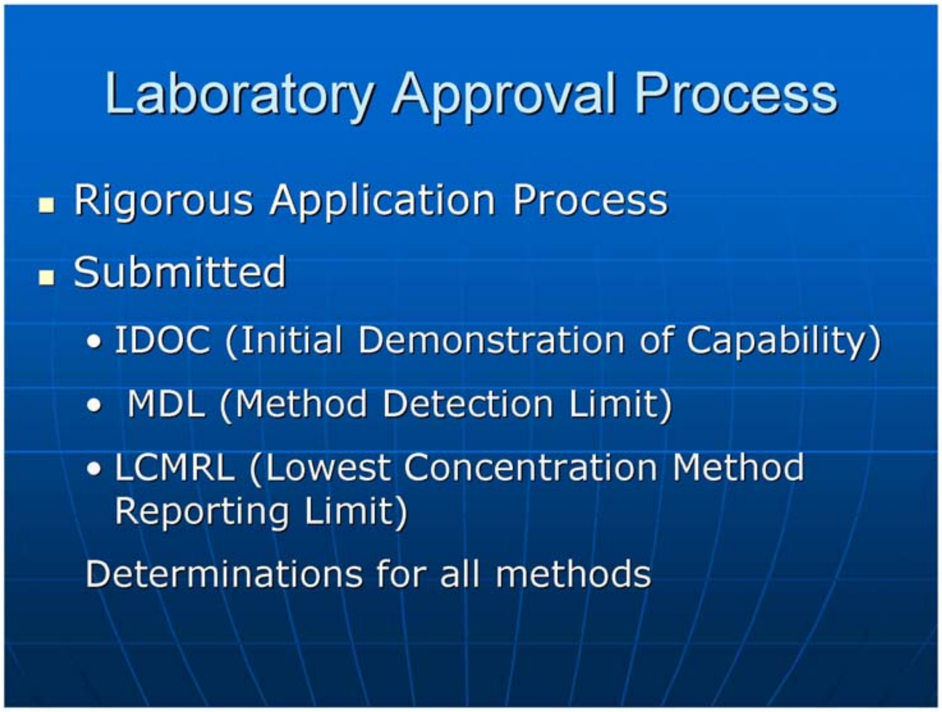
UCMR2 – Lessons Learned in Year 1

Linda Geddes
Andrew Eaton
MWH Laboratories



UCMR2 Methodology

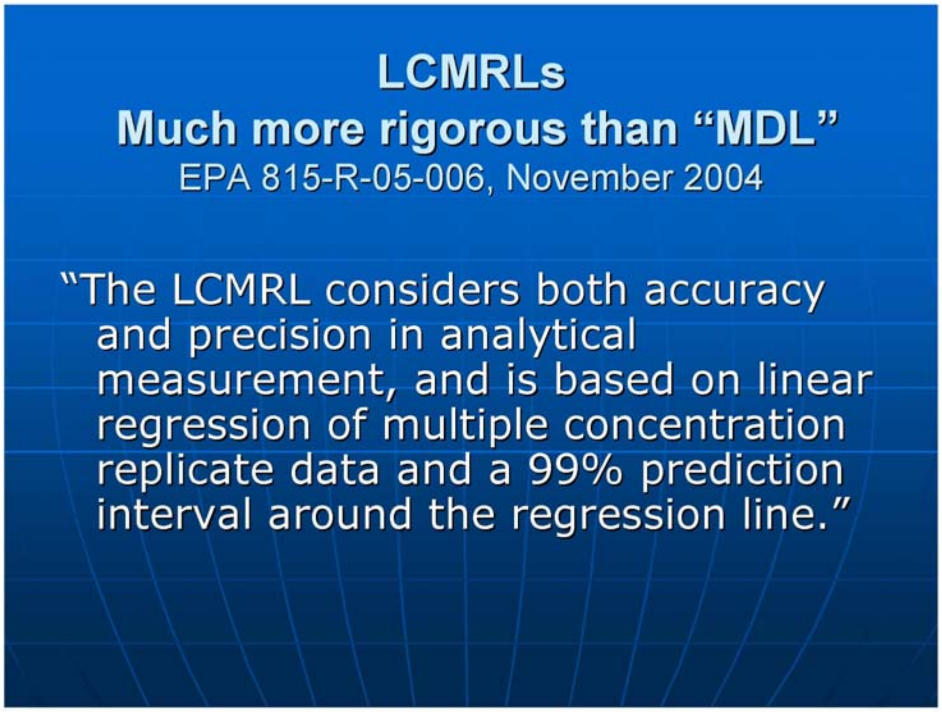
- Method 521 – Nitrosamines by CI/MS/MS
- Method 525.2 – Acetanilide Pesticides by GC/MS
- Method 527 – Flame Retardants by GC/MS
- Method 529 – Explosives by GC/MS
- Method 535 – Acetanilide Degradates by LC/MS/MS



Laboratory Approval Process

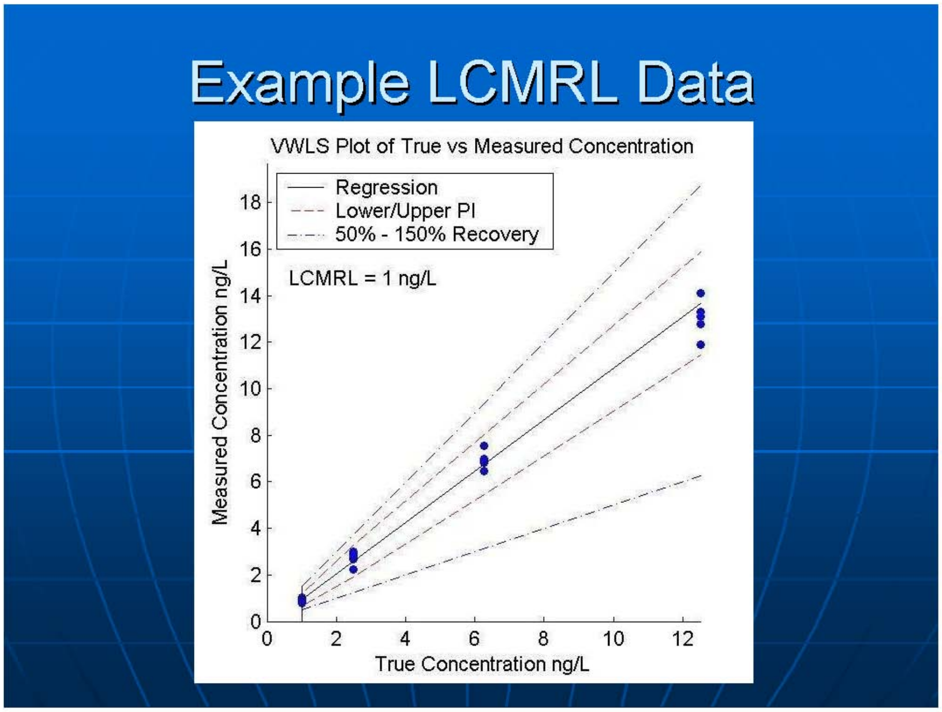
- Rigorous Application Process
- Submitted
  - IDOC (Initial Demonstration of Capability)
  - MDL (Method Detection Limit)
  - LCMRL (Lowest Concentration Method Reporting Limit)

Determinations for all methods



LCMRLs
Much more rigorous than "MDL"
EPA 815-R-05-006, November 2004

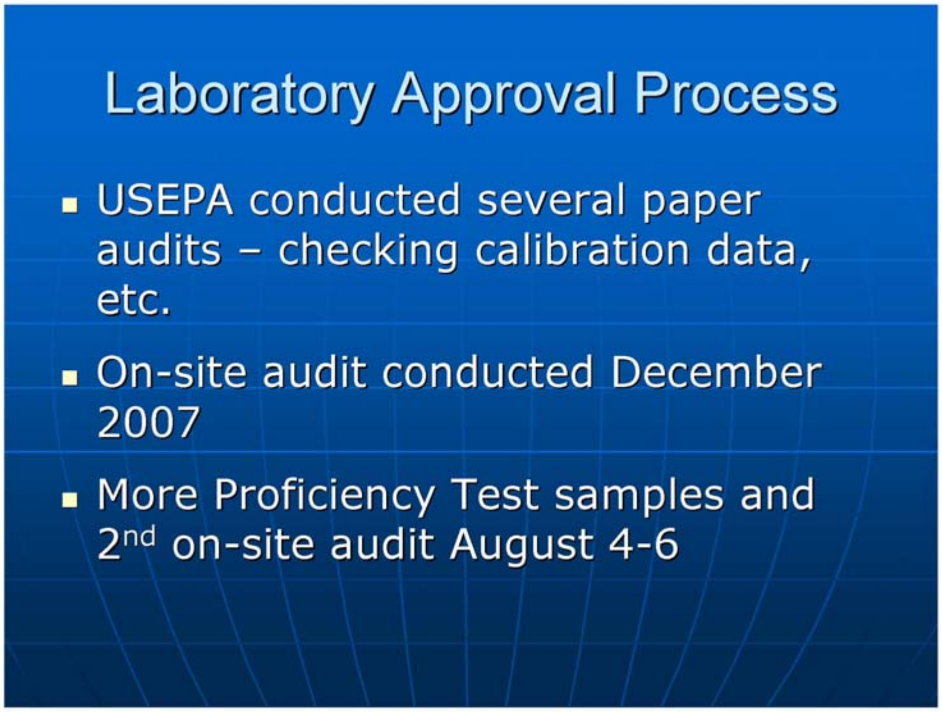
"The LCMRL considers both accuracy and precision in analytical measurement, and is based on linear regression of multiple concentration replicate data and a 99% prediction interval around the regression line."



Example LCMRL Data

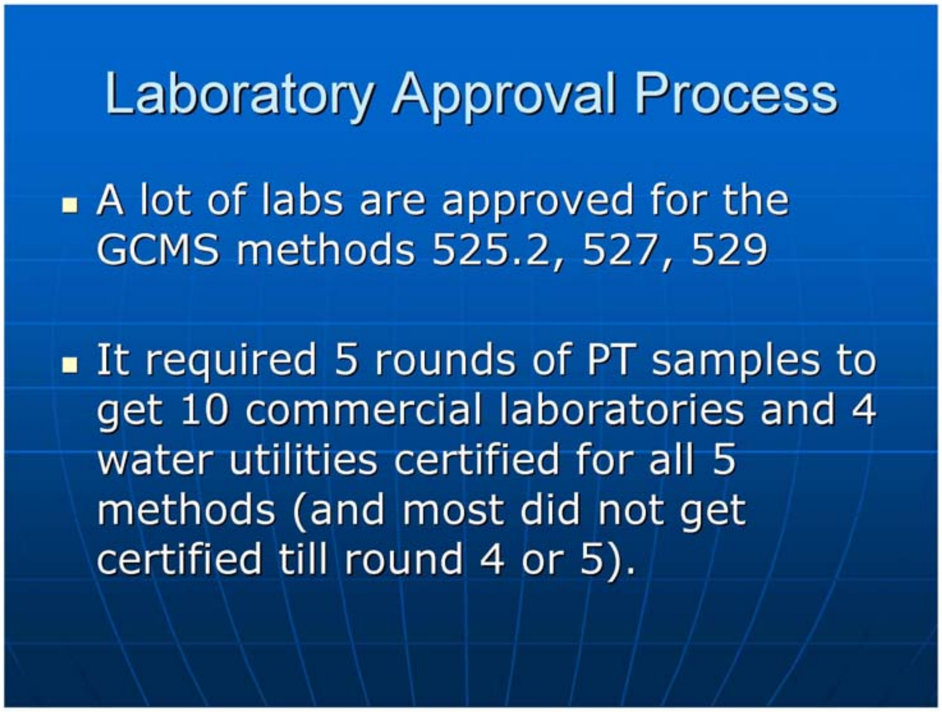
Laboratory Approval Process

- USEPA sent out Proficiency Test samples
- MWH Wrote Standard Operating Procedures (SOPs)
- Developed UCMR2 specific QA Project Plan March 2007, revised July 2008



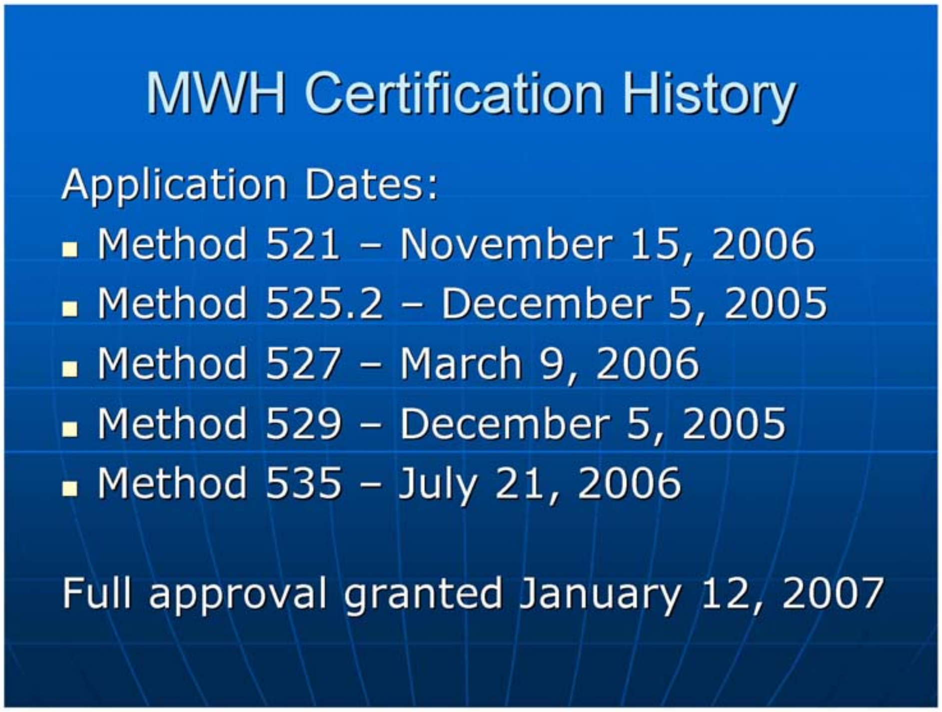
Laboratory Approval Process

- USEPA conducted several paper audits – checking calibration data, etc.
- On-site audit conducted December 2007
- More Proficiency Test samples and 2nd on-site audit August 4-6



Laboratory Approval Process

- A lot of labs are approved for the GCMS methods 525.2, 527, 529
- It required 5 rounds of PT samples to get 10 commercial laboratories and 4 water utilities certified for all 5 methods (and most did not get certified till round 4 or 5).

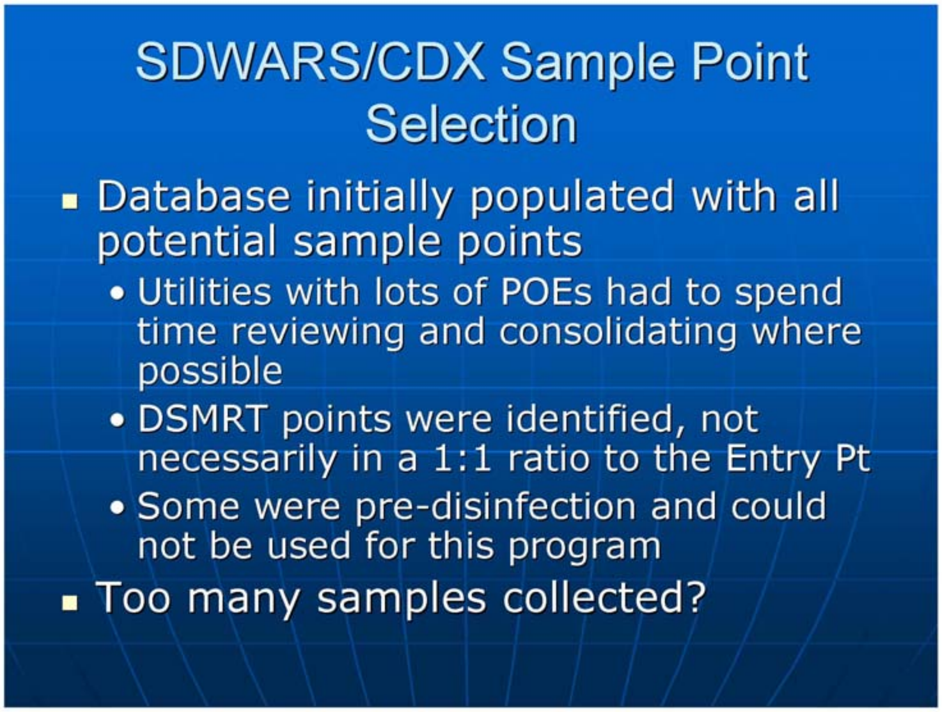


MWH Certification History

Application Dates:

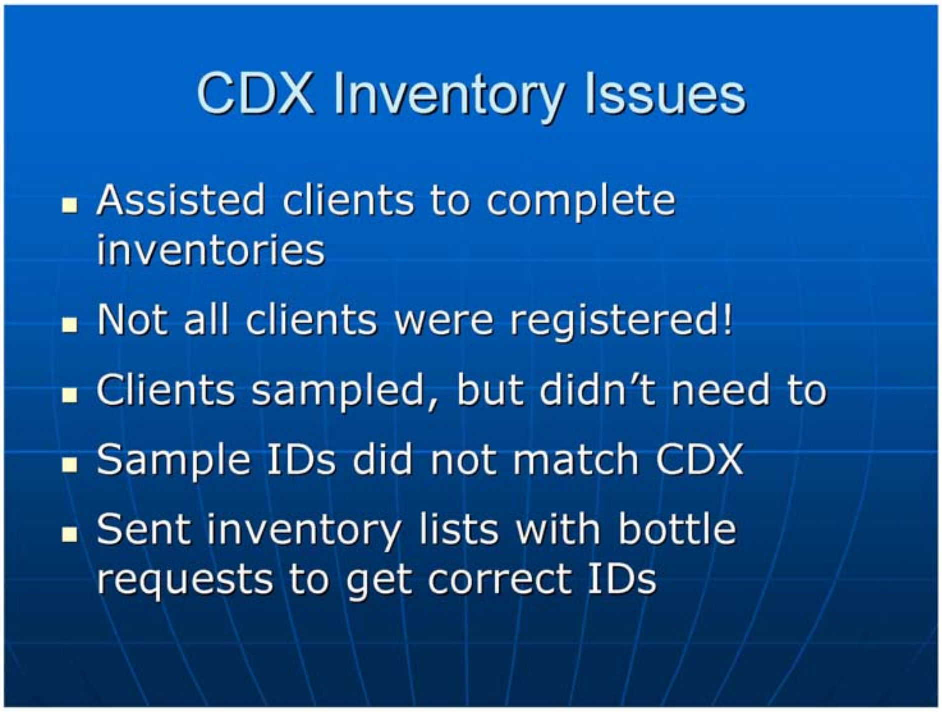
- Method 521 – November 15, 2006
- Method 525.2 – December 5, 2005
- Method 527 – March 9, 2006
- Method 529 – December 5, 2005
- Method 535 – July 21, 2006

Full approval granted January 12, 2007



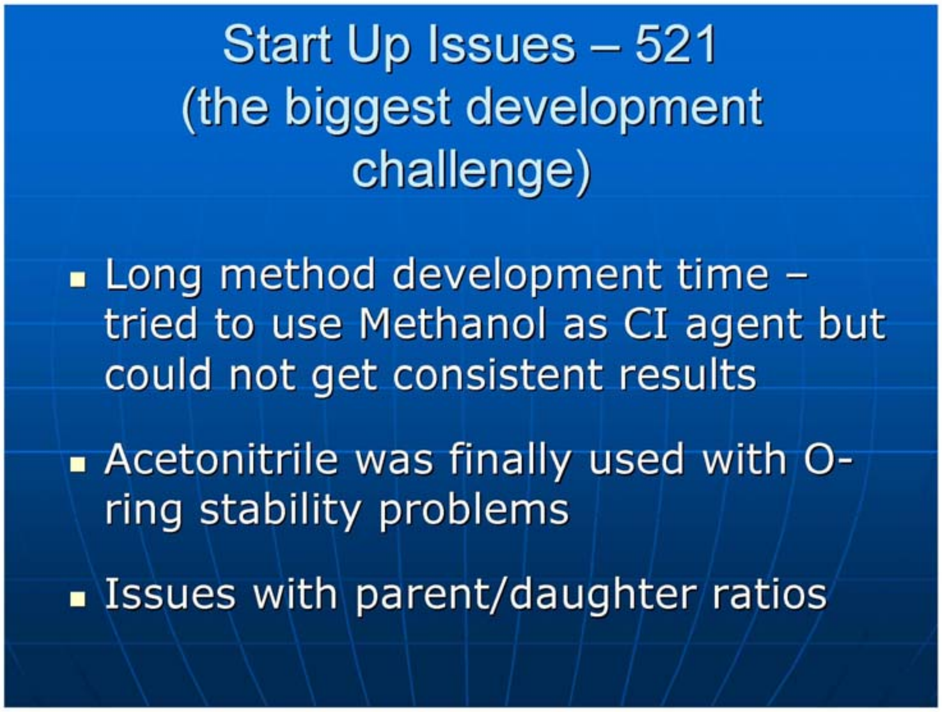
SDWARS/CDX Sample Point Selection

- Database initially populated with all potential sample points
  - Utilities with lots of POEs had to spend time reviewing and consolidating where possible
  - DSMRT points were identified, not necessarily in a 1:1 ratio to the Entry Pt
  - Some were pre-disinfection and could not be used for this program
- Too many samples collected?



CDX Inventory Issues

- Assisted clients to complete inventories
- Not all clients were registered!
- Clients sampled, but didn't need to
- Sample IDs did not match CDX
- Sent inventory lists with bottle requests to get correct IDs



Start Up Issues – 521 (the biggest development challenge)

- Long method development time – tried to use Methanol as CI agent but could not get consistent results
- Acetonitrile was finally used with O-ring stability problems
- Issues with parent/daughter ratios

Start Up Issues

- 525.2 - was already in full production for all analytes
- 527 – had to use 2 disks during extraction process due to breakthrough
- 529 – modified GC temperature program for better peak shapes

Start Up Issues

- EPA Method 535 turned out to be a bigger challenge than was originally thought
- Purchased new instrument due to need for gradient HPLC system
- Trained backup personnel essential
- Adding Internal Standard at the Instrument rather than immediate post extraction

Start Up Issues (535)

- Daily calibration required
- Watch the calibration type so that the MRL Check passes
  - We saw as much as 10% difference depending on the curve type
- Instrument *was* used for other methodology and had to be changed out

Preparation for UCMR2

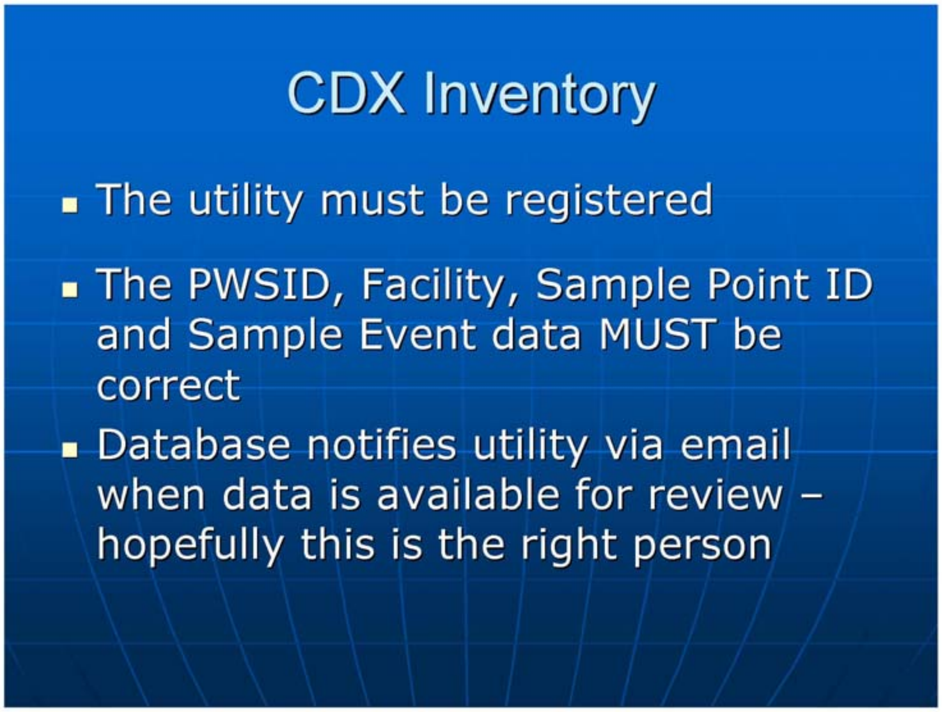
- Developed capacity plan in extractions and instrumentation with primary and backups assigned (people and equipment)
- Identified and scheduled key clients to keep the workload at manageable levels (or at least to try….)
- Prepared detailed sampling instructions

Preparation for UCMR2

- Strategized bottle count and preservatives
- Purchased pre-preserved containers to improve efficiency
- Created UCMR specific COC documents

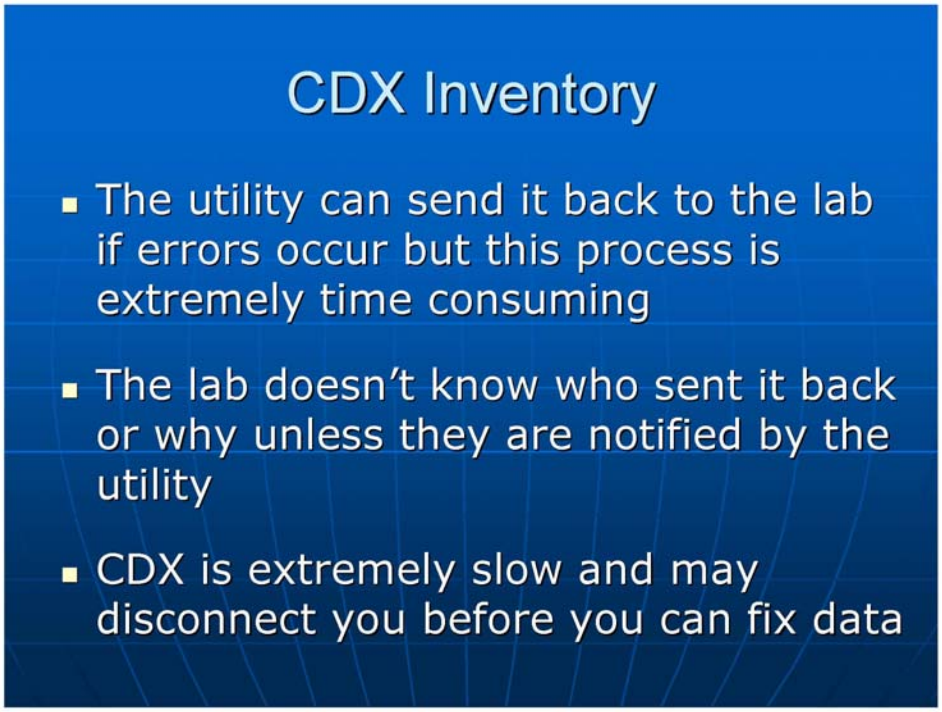
Lessons Learned

- CDX Inventory
- Verifying Preservation
- Reporting
- Data Quality
- Electronic Data Upload Glitches



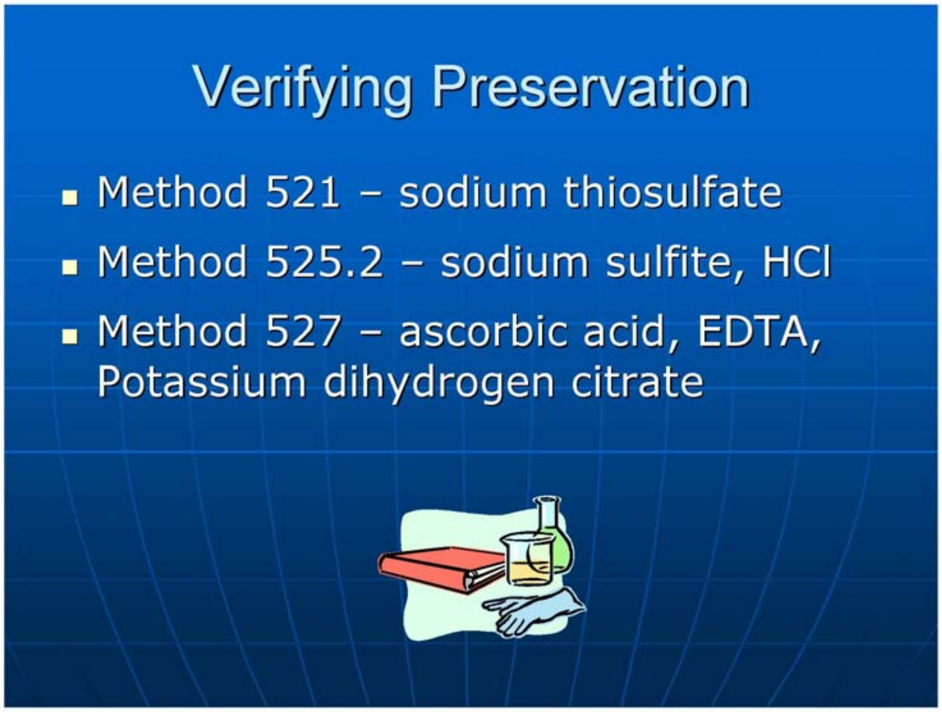
CDX Inventory

- The utility must be registered
- The PWSID, Facility, Sample Point ID and Sample Event data MUST be correct
- Database notifies utility via email when data is available for review – hopefully this is the right person



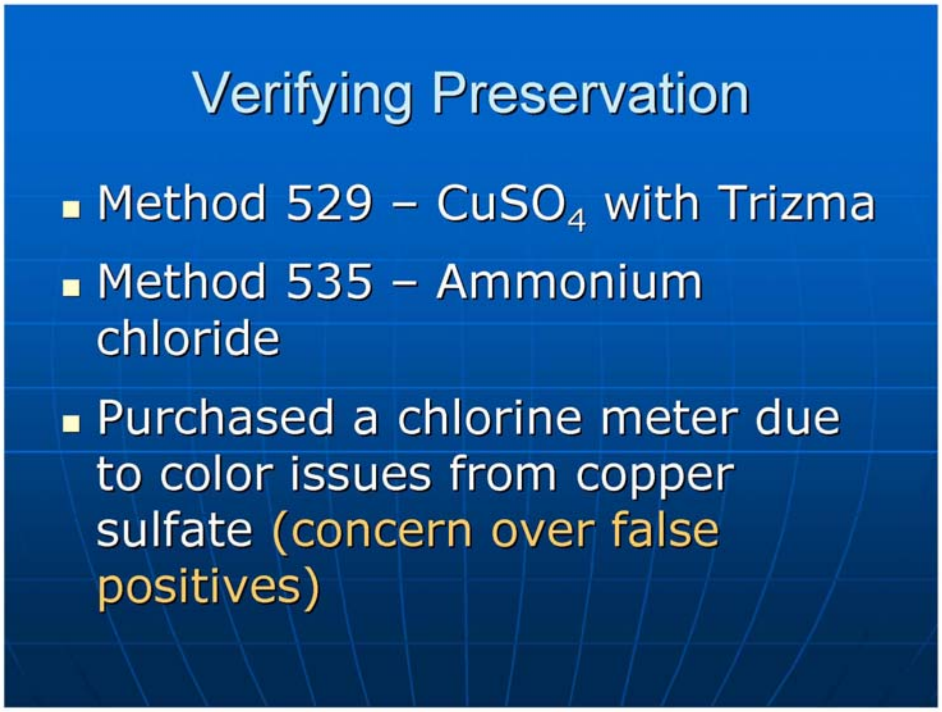
CDX Inventory

- The utility can send it back to the lab if errors occur but this process is extremely time consuming
- The lab doesn’t know who sent it back or why unless they are notified by the utility
- CDX is extremely slow and may disconnect you before you can fix data



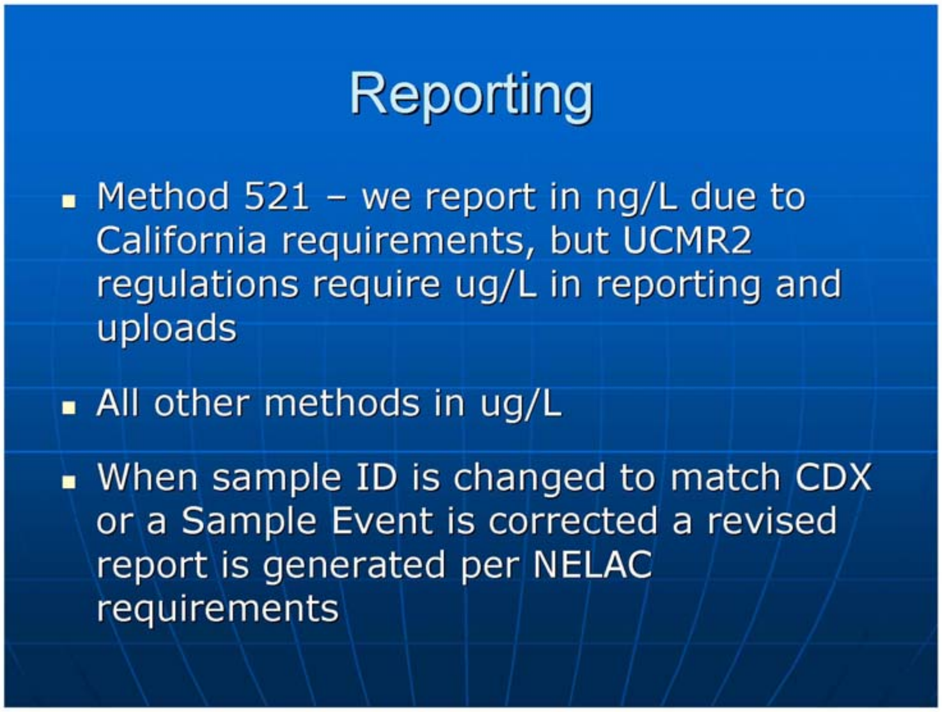
Verifying Preservation

- Method 521 – sodium thiosulfate
- Method 525.2 – sodium sulfite, HCl
- Method 527 – ascorbic acid, EDTA, Potassium dihydrogen citrate



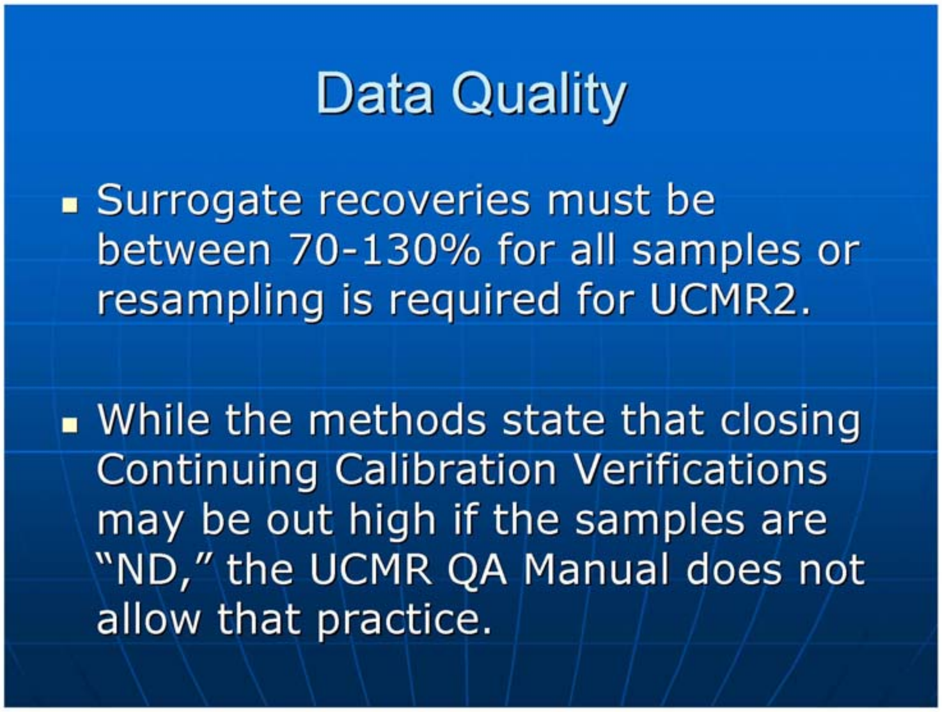
Verifying Preservation

- Method 529 – $CuSO_4$ with Trizma
- Method 535 – Ammonium chloride
- Purchased a chlorine meter due to color issues from copper sulfate (concern over false positives)



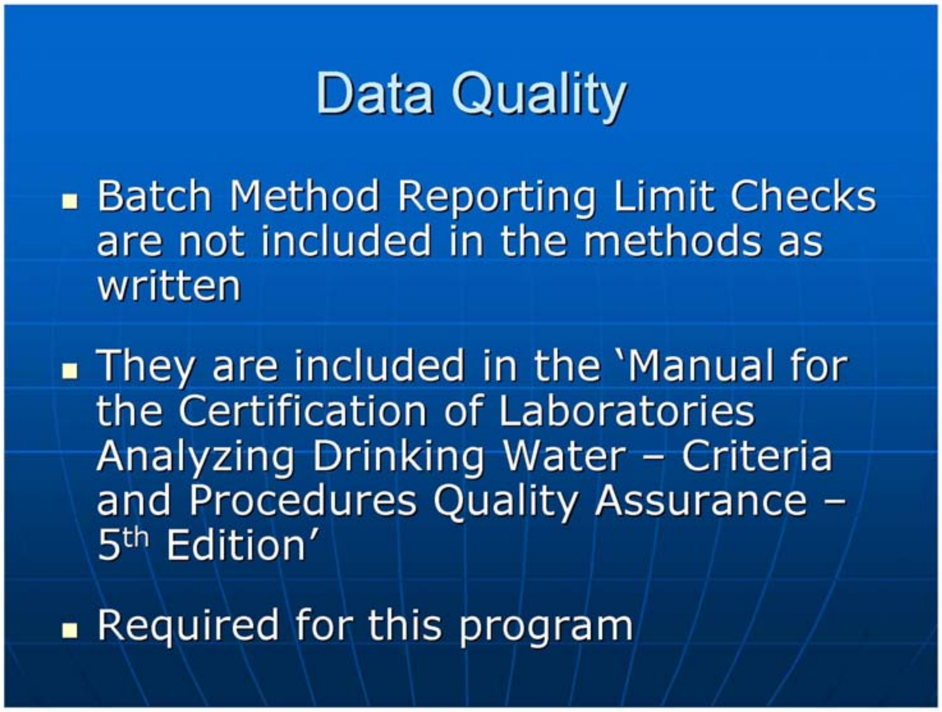
Reporting

- Method 521 – we report in ng/L due to California requirements, but UCMR2 regulations require ug/L in reporting and uploads
- All other methods in ug/L
- When sample ID is changed to match CDX or a Sample Event is corrected a revised report is generated per NELAC requirements



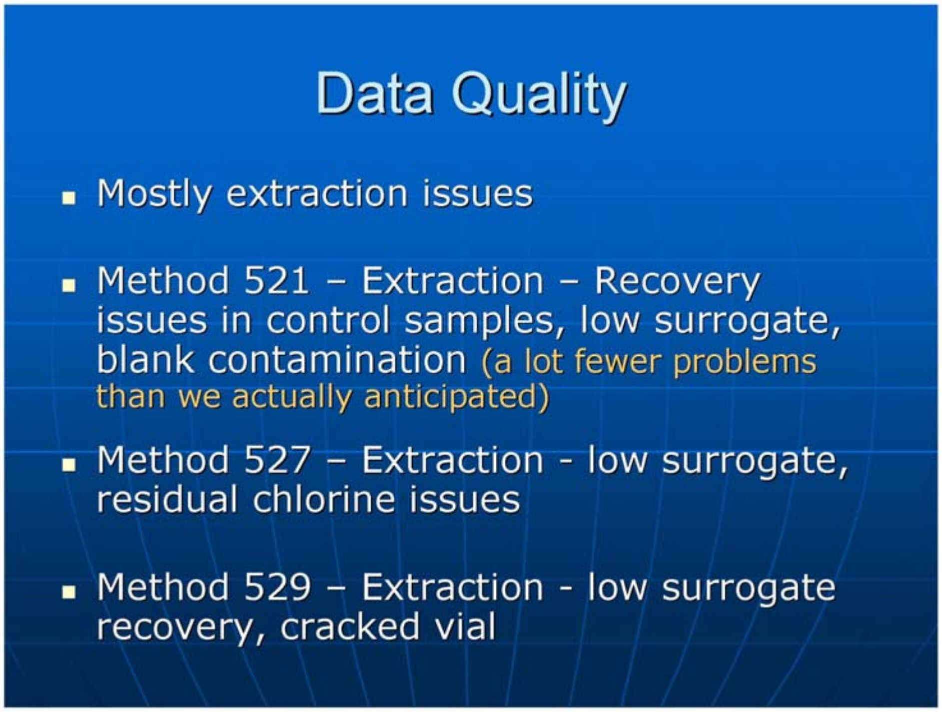
Data Quality

- Surrogate recoveries must be between 70-130% for all samples or resampling is required for UCMR2.
- While the methods state that closing Continuing Calibration Verifications may be out high if the samples are "ND," the UCMR QA Manual does not allow that practice.



Data Quality

- Batch Method Reporting Limit Checks are not included in the methods as written
- They are included in the 'Manual for the Certification of Laboratories Analyzing Drinking Water – Criteria and Procedures Quality Assurance – 5th Edition'
- Required for this program



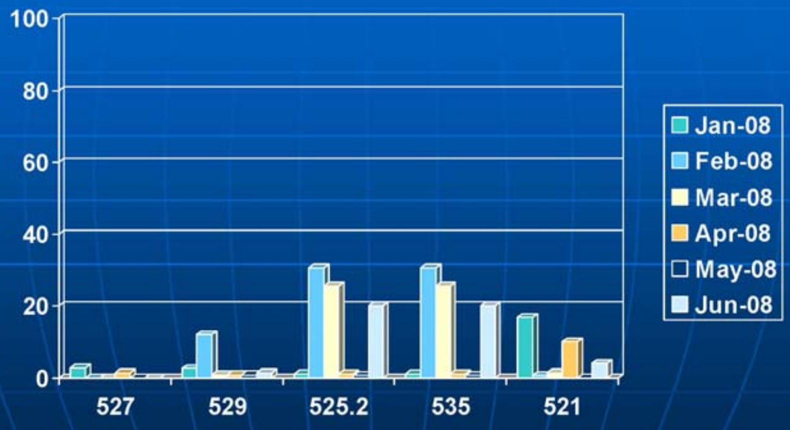
Data Quality

- Mostly extraction issues
- Method 521 – Extraction – Recovery issues in control samples, low surrogate, blank contamination (a lot fewer problems than we actually anticipated)
- Method 527 – Extraction - low surrogate, residual chlorine issues
- Method 529 – Extraction - low surrogate recovery, cracked vial

Data Quality

- Method 525.2 – Only 1 surrogate failure so far, but because 535/525.2 are dependent methods, both have to be recollected when either fails
- Method 535 – Extraction - low surrogate, training issues

% Resamples- The Impact of Training and Experience

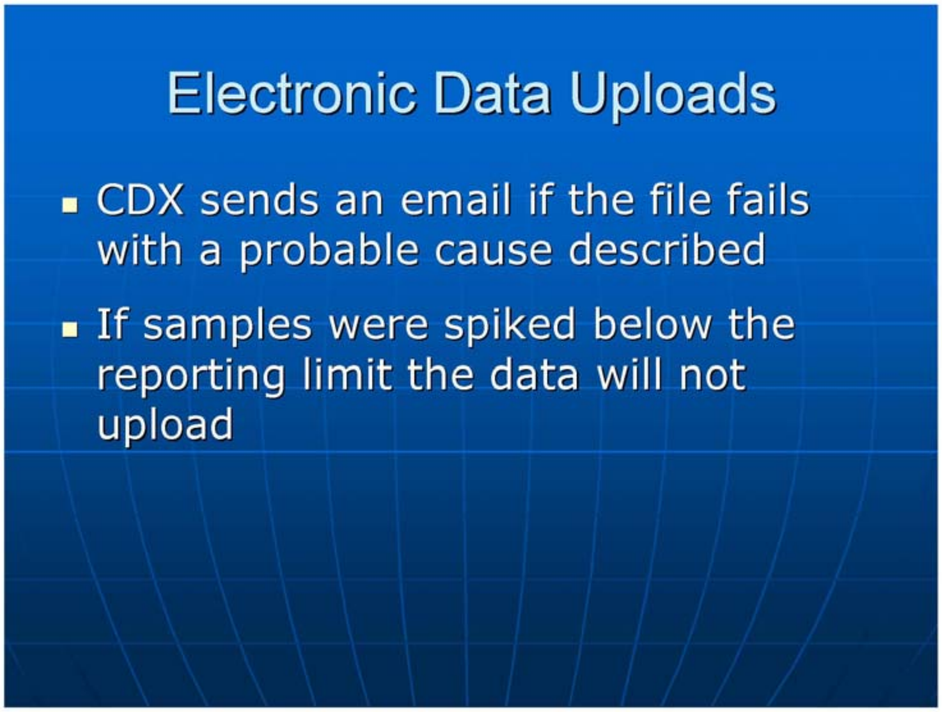


Electronic Data Uploads

- No delays – Database ready to go
- Format requirements were not clear
- Errors might have been identified through a practice upload
- MWH currently using a 2 week delay to allow PWS to review data for errors prior to upload to CDX

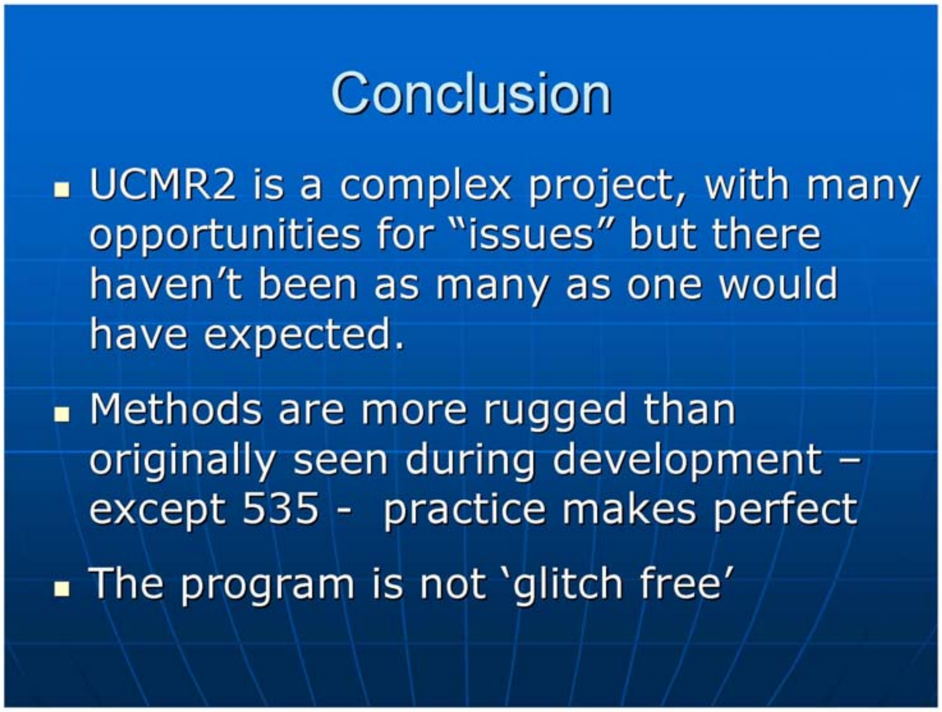
Electronic Data Uploads

- Utility must be registered to the lab
- Facility and Sample IDs must be correct
- Time consuming to update just the Sampling Event if an error is made
- Not easy to find out what data is being returned by the PWS to the laboratory



Electronic Data Uploads

- CDX sends an email if the file fails with a probable cause described
- If samples were spiked below the reporting limit the data will not upload



Conclusion

- UCMR2 is a complex project, with many opportunities for “issues” but there haven’t been as many as one would have expected.
- Methods are more rugged than originally seen during development – except 535 - practice makes perfect
- The program is not ‘glitch free’

Contact Information

- Linda Geddes
  linda.geddes@mwhglobal.com

- Andrew D. Eaton
  andrew.d.eaton@mwhglobal.com

Uncertainty - A Laboratory Viewpoint

Robert Di Rienzo
DataChem Laboratories, Inc.
960 West LeVoy Drive
Salt Lake City, UT 84123
801-266-7700
dirienzo@datachem.com

ABSTRACT

Uncertainty is associated with results obtained in the laboratory testing activities. It is meaningful to estimate the extent of the uncertainty associated with each result generated by the laboratory. It is also useful to recognize that this measurement uncertainty is likely to be much less than that associated with sample collection activities.

In practice, the uncertainty of a result may arise from many possible sources. The relative contribution of major sources of error and the approach adopted by the laboratory to estimate uncertainty results in the conclusion that many sources of error are insignificant compared to the processes of sample preparation, calibration, and instrumental measurement. The uncertainty associated with these processes can be estimated from quality control data.

Other sources of error are associated with the sample matrix. Laboratory sub-sampling error is not captured by the use of quality control data and can be significant. How a lab approaches sub-sampling may significantly impact decision making.

INTRODUCTION

Measurement uncertainty narrows down the difference between the actually measured value and the true value. The result of a measurement comprises two parts: an estimate of the true value and the uncertainty of this estimate. Every measurement has a degree of uncertainty associated with it. The uncertainty derives from the measuring device and from the skill of the person doing the measuring.

DEFINITIONS

Random errors are statistical fluctuations (in either direction) in the measured data due to the precision limitations of the measurement device. (Type 1)

Systematic errors, by contrast, are reproducible inaccuracies that are consistently in the same direction. (Type 2)

PROCEDURES FOR ESTIMATION OF UNCERTAINTY

Analytical Uncertainty

Sources of Error in the Analytical Procedure

Mass:	Both analytical balances and the weights used for verification of performance.
Purity:	The purity of material can be a factor if used to prepare QC samples
Volume:	Volumetric measurements using volumetric flasks, pipettes, and burets.
Temperature:	Devices used for the measurement of temperature.
Atomic Weights:	The uncertainty of published atomic weights can contribute to total, combined uncertainty in processes in which atomic weights are used for calculations contributing to the generation of results.
Calibration Standards:	Calibration standards frequently have published (provided) uncertainties; these are generally 0.5 – 1% for solution standards and much less for solid standards.
Pressure:	Pressure is rarely a factor in analytical chemistry measurements
Standardization Process:	The standardization process for most instrumental analyses introduces uncertainty because of the inexact nature of the process.
Instrumentation Sensors:	Sensors have uncertainty because of lack of stability.

The 9-Step Process for Estimation of Uncertainty in an Analytical Procedure

Step 1: Identification of major sources of uncertainty for applicable types of laboratory measurements.

Step 2: Determination of the type of the error associated with each major source of uncertainty.

Step 3: Estimation of the extent of the error of each major source.

Step 4: Conversion of the estimate of error for each major source to a standard uncertainty using the estimated distribution for each source.

Step 5: Calculate square of each standard error.

Step 6: Estimation of the combined, total uncertainty by combining the square of the standard error for all sources of error.

Source	Estimate of Error	Type of Error	Standard Error	Square of the Standard Error
Mass	0.03	1	0.03	0.0009
Volume	0.05	1	0.05	0.0025
Temperature	0.012	1	0.012	0.0001
Calibration Standards	1	2	0.5	0.25
Atomic Weights	0.02	2	0.01	0.0001
Standardization Process	3	1	3	9.0
Purity	0.1	2	0.05	0.0025
Combined Uncertainty:				9.26

Step 7: Identification of sources of uncertainty of significant importance and of insignificant importance. The Standardization process, which includes instrument calibration and measurement of samples, is the most significant factor contributing to error.

Step 8: Estimation of error solely from significant sources (The insignificant sources of error are not included in this estimation.) Estimation of error from the standardization process can be assessed using the Quality Control Samples (Historical Control Limits).

Step 9: Calculation of expanded uncertainty based only on significant sources of error

$$\text{Result } (1 \pm 2Sr)$$

Note: Sr is the relative standard deviation (expressed as a fraction) calculated from the pertinent quality control results. Using 2Sr expresses the 95% confidence interval.

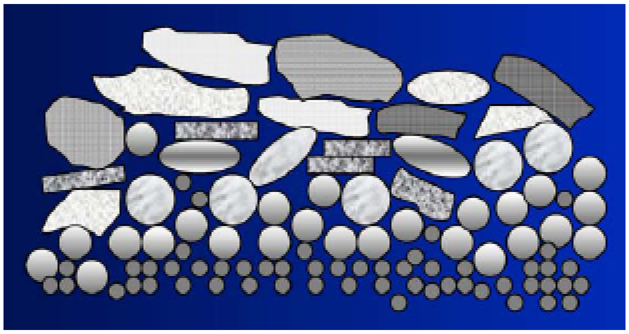
Sample Preparation Uncertainty

Sources of Error in the Sample Preparation Procedure (SOILS)

Compositional Heterogeneity: Size, shape, physical/chemical properties of particles

Distributional Heterogeneity: Spatial grouping clumping of particles–Stratified segregation of particles

Compositional and Distributional Heterogeneity



The Process for Estimation of Uncertainty for Sample Preparation Procedures

The laboratory sub-sampling strategy must be determined from the systematic project planning. It must be consistent with the project data quality objectives and addressed in the Sampling and Analytical Plan.

ASTM D 6323 Table 1 – Limitations and Advantages of Sample Preparation Options

Instruction	Limitations	Advantages
Remove artifacts, such as rocks and twigs, from the sample prior to sub-sampling,	1) May bias analytical results by altering contaminant concentration. 2) May bias sample if results are not properly weight averaged.	1) May be easier to subsample. 2) May be easier to analyze. 3) Appropriate if the target population is material minus artifacts.
Dry sample	May alter chemistry or change stability of some compounds.	1) Allows for consistency of sub-sampling for liquid/solid mixtures. 2) Analytes reported unbiased by moisture content.
Reduce particle size	1) Increasing surface area may affect data in some procedure with particle digestion or extraction. 2) May be difficult, depending on matrix.	Allows for consistency of sub-sampling.

CONCLUSIONS

A laboratory must have a procedure on estimating uncertainty in analytical procedures. The procedure will help to understand the contributions of each step in the analytical process. On the other hand the sample preparation instructions must be given to the laboratory for each project that is consistent with systematic project planning and data quality objectives.

Sources of Error for Total Uncertainty

Field Sampling and Sample Design	Up to 1000%[1]
Sample Preparation	*50%* of Sampling Error? Proportional
Analysis	2% to 20%[1]

1 - Industrial Waste Dumps, Sampling and Analysis, Encyclopedia of Analytical Chemistry, 2000

Up to now, the estimation of uncertainty efforts has been a laboratory issue and has helped to improve laboratory performance by understanding the components of uncertainty. The fact of the matter is that analytical uncertainty is really insignificant when compared to the total measurement uncertainty.

REFERENCES

1. *ANSI/NCSL Z540-2-1997, Guide to the Estimation of Uncertainty in Measurement. (GUM)*

2. *EURACHEM/CITAC Guide CG-4 – "Quantifying Uncertainty in Analytical Measurement," Second Edition, 2000*

3. *UKAS M3003, The Expression of Uncertainty and Confidence in Measurement, 1997.*

4. *G103-A2LA, Guide for Estimation of Uncertainty of Dimensional Calibration & Testing Results, 2002*

5. *http://www.eurachem.org/*

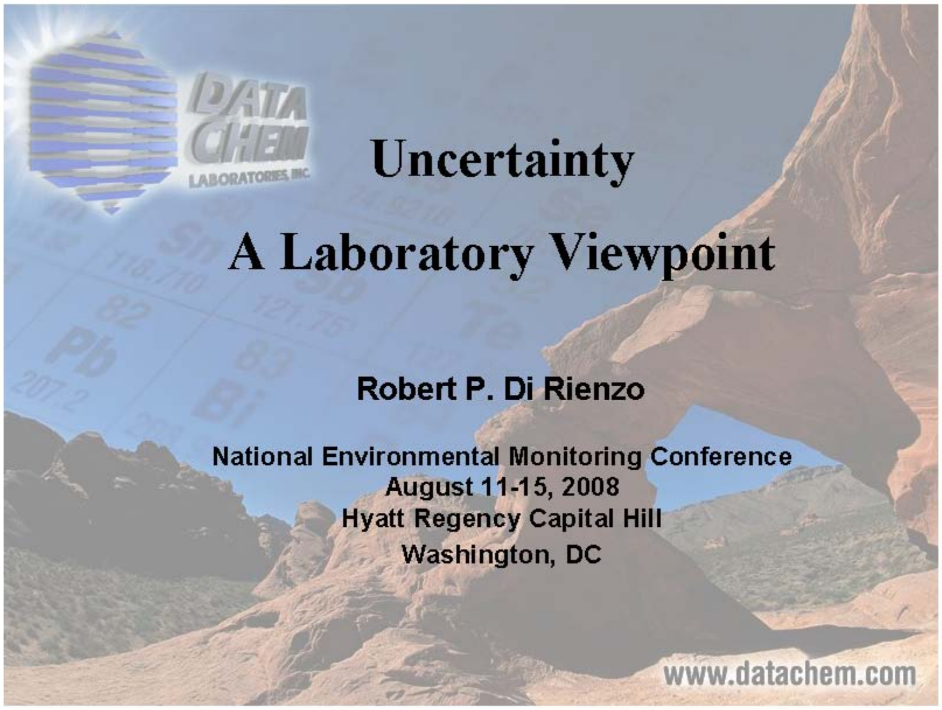
6. *http://www.measurementuncertainty.org/*

7. *http://physics.nist.gov/cuu/Uncertainty/index.html*

8. ASTM D 6323 – 98 (Reapproved 2003), Standard Guide for Laboratory Subsampling of Media Related to Waste Management Activities

9. EPA/600/R-03/027, Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples, November 2003

10. Method 8330B, Nitroaromatics, Nitramines, and Nitrate Esters by High Performance Liquid Chromatography (HPLC), Revision 2, October 2006, Appendix A



Uncertainty

A Laboratory Viewpoint

Robert P. Di Rienzo

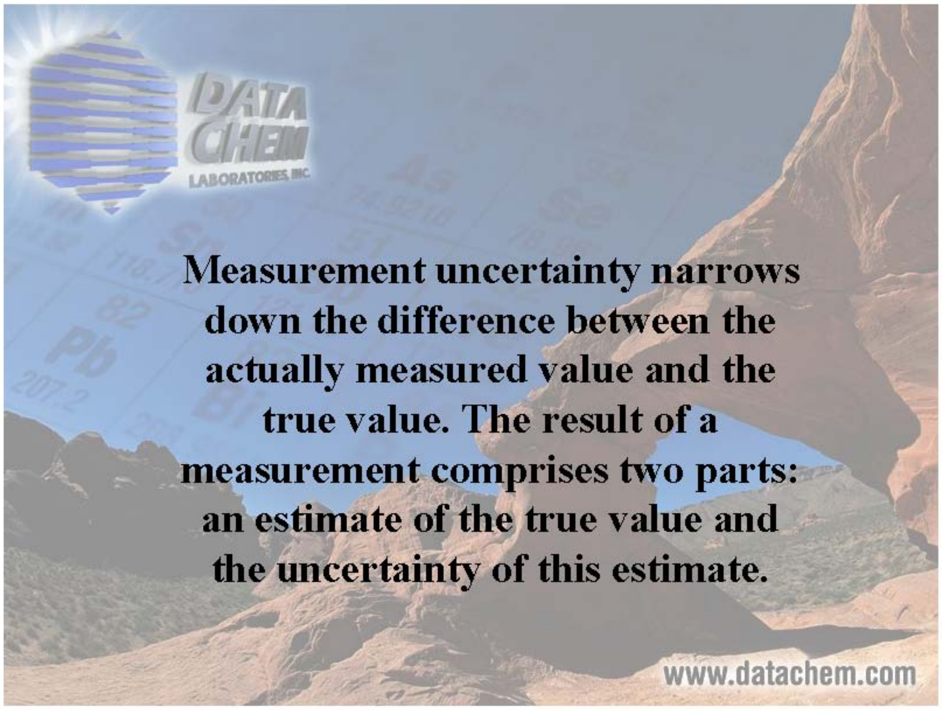
National Environmental Monitoring Conference
August 11-15, 2008
Hyatt Regency Capital Hill
Washington, DC

www.datachem.com

Overview

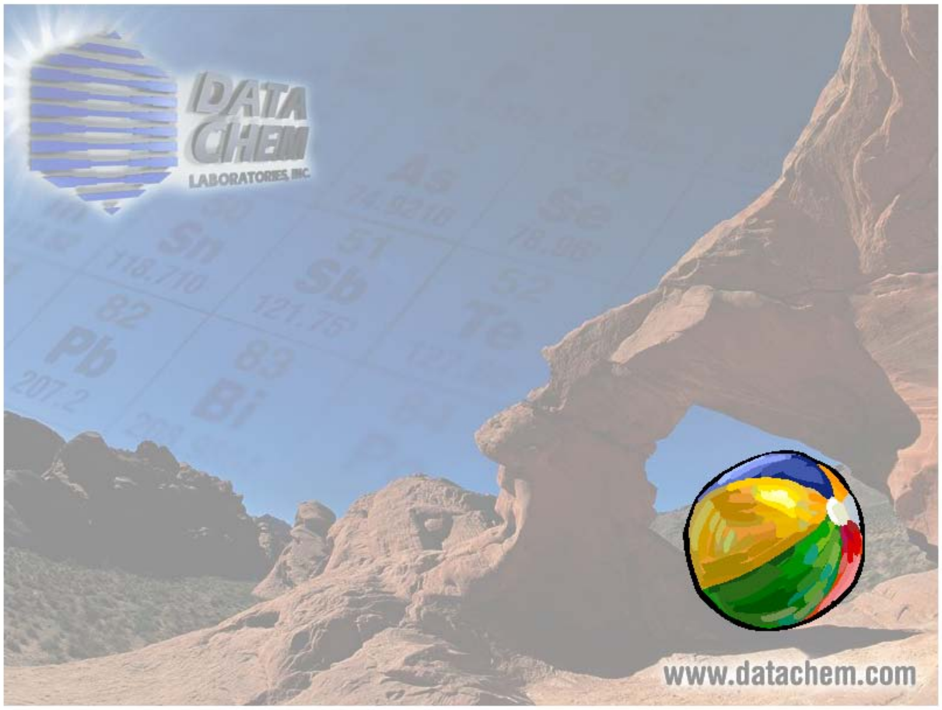
- Definitions
- Components of Uncertainty
- Analytical Testing Uncertainty
  - ❖ References
  - ❖ Sources of Error
  - ❖ Estimation of Uncertainty
- Sample Preparation Uncertainty
  - ❖ References
  - ❖ Sources of Error
  - ❖ Estimation of Uncertainty
- Conclusions

www.datachem.com



Measurement uncertainty narrows down the difference between the actually measured value and the true value. The result of a measurement comprises two parts: an estimate of the true value and the uncertainty of this estimate.

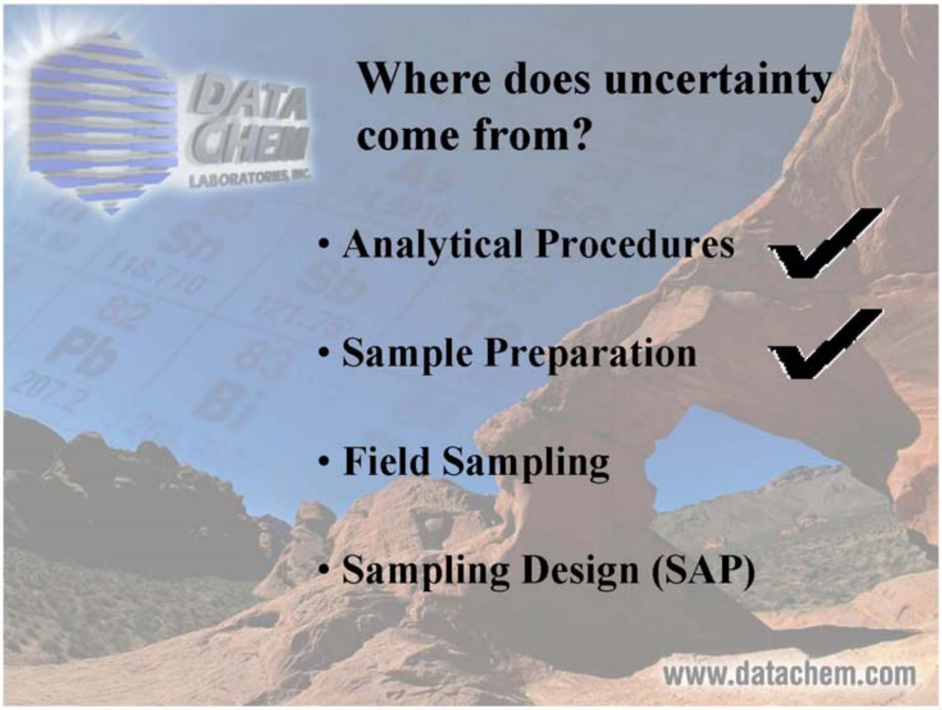
www.datachem.com



www.datachem.com

Every measurement has a degree of uncertainty associated with it. The uncertainty derives from the measuring device and from the skill of the person doing the measuring.

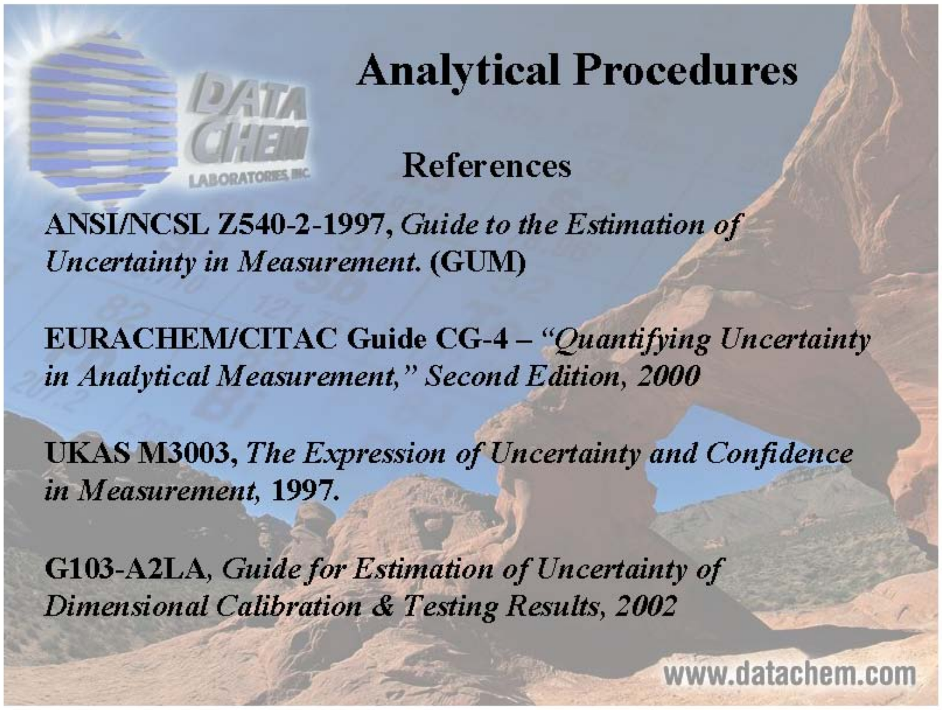
www.datachem.com



Where does uncertainty come from?

- Analytical Procedures ✓
- Sample Preparation ✓
- Field Sampling
- Sampling Design (SAP)

www.datachem.com



Analytical Procedures

References

ANSI/NCSL Z540-2-1997, *Guide to the Estimation of Uncertainty in Measurement.* **(GUM)**

EURACHEM/CITAC Guide CG-4 – *"Quantifying Uncertainty in Analytical Measurement," Second Edition, 2000*

UKAS M3003, *The Expression of Uncertainty and Confidence in Measurement,* **1997.**

G103-A2LA, *Guide for Estimation of Uncertainty of Dimensional Calibration & Testing Results, 2002*

www.datachem.com

Analytical Procedures

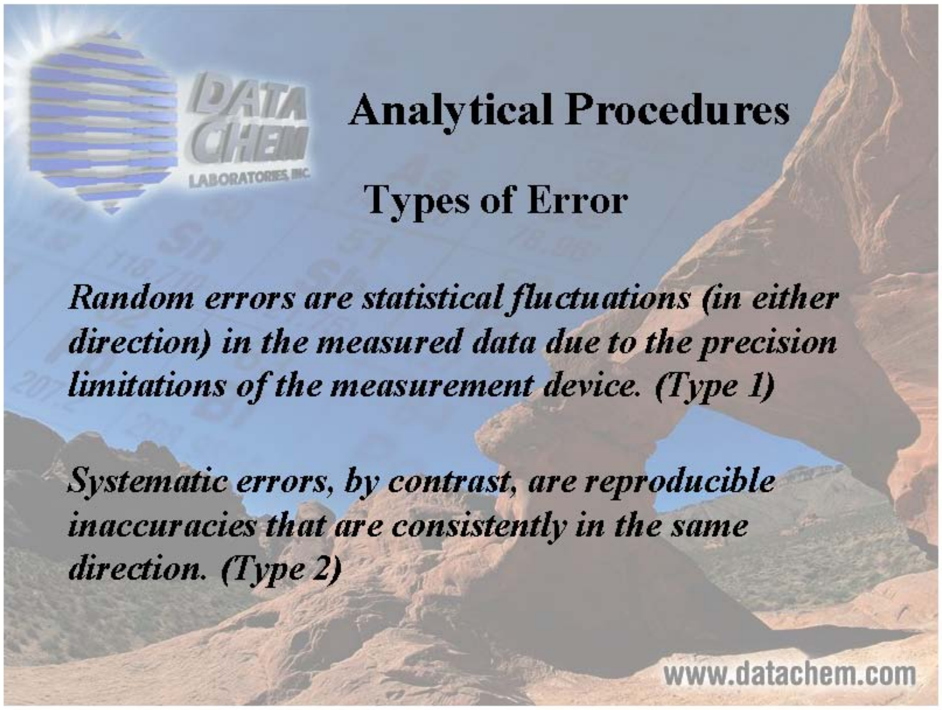
Websites

http://www.eurachem.org/

http://www.measurementuncertainty.org/

http://physics.nist.gov/cuu/Uncertainty/index.html

www.datachem.com



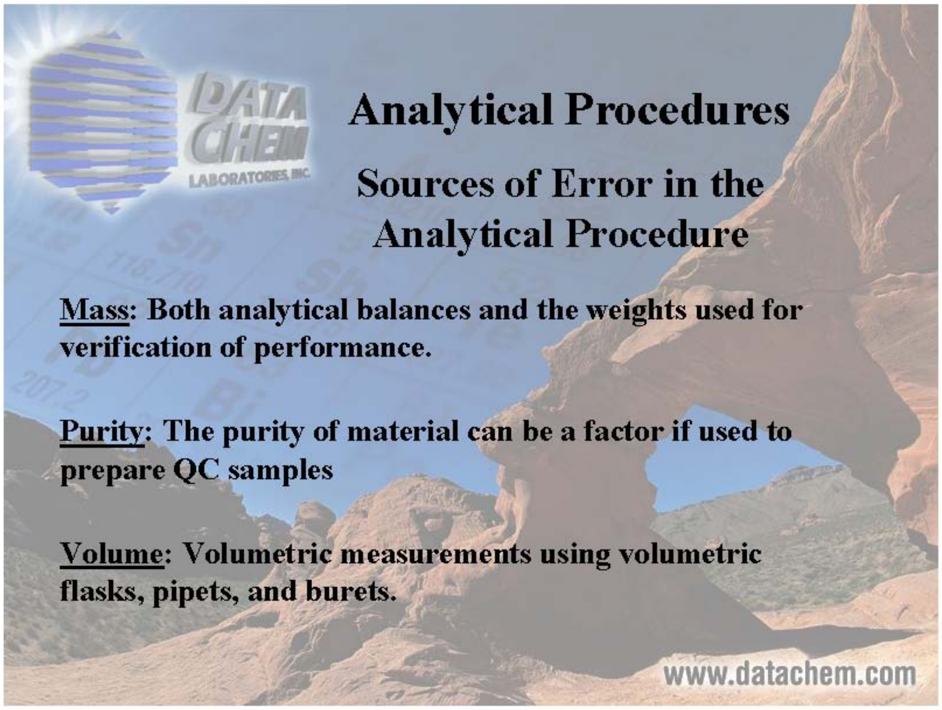
Analytical Procedures

Types of Error

Random errors are statistical fluctuations (in either direction) in the measured data due to the precision limitations of the measurement device. (Type 1)

Systematic errors, by contrast, are reproducible inaccuracies that are consistently in the same direction. (Type 2)

www.datachem.com



Analytical Procedures

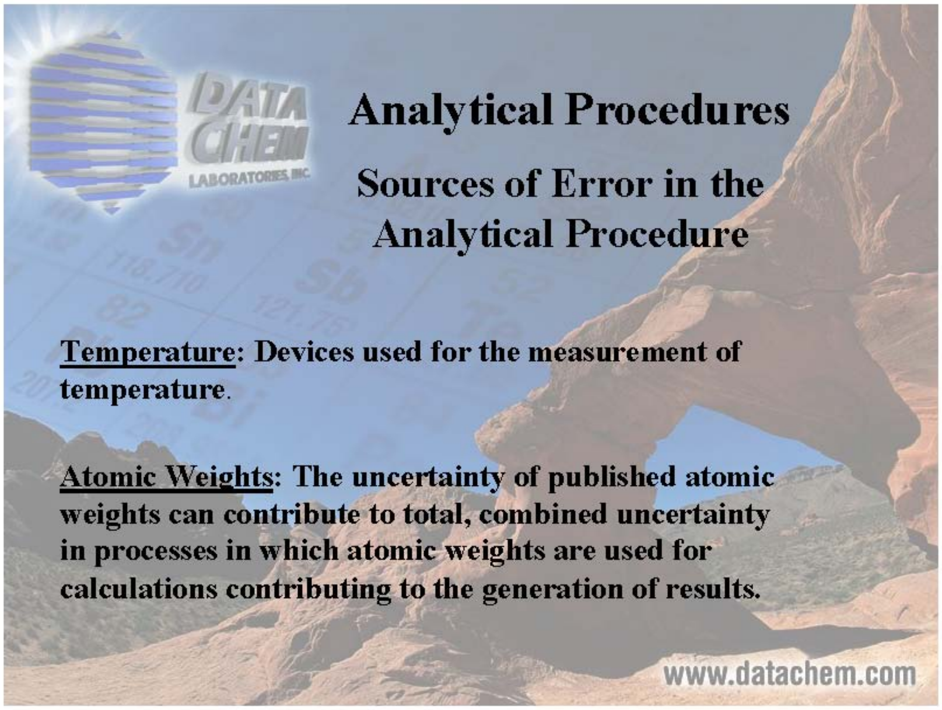
Sources of Error in the Analytical Procedure

Mass: Both analytical balances and the weights used for verification of performance.

Purity: The purity of material can be a factor if used to prepare QC samples

Volume: Volumetric measurements using volumetric flasks, pipets, and burets.

www.datachem.com



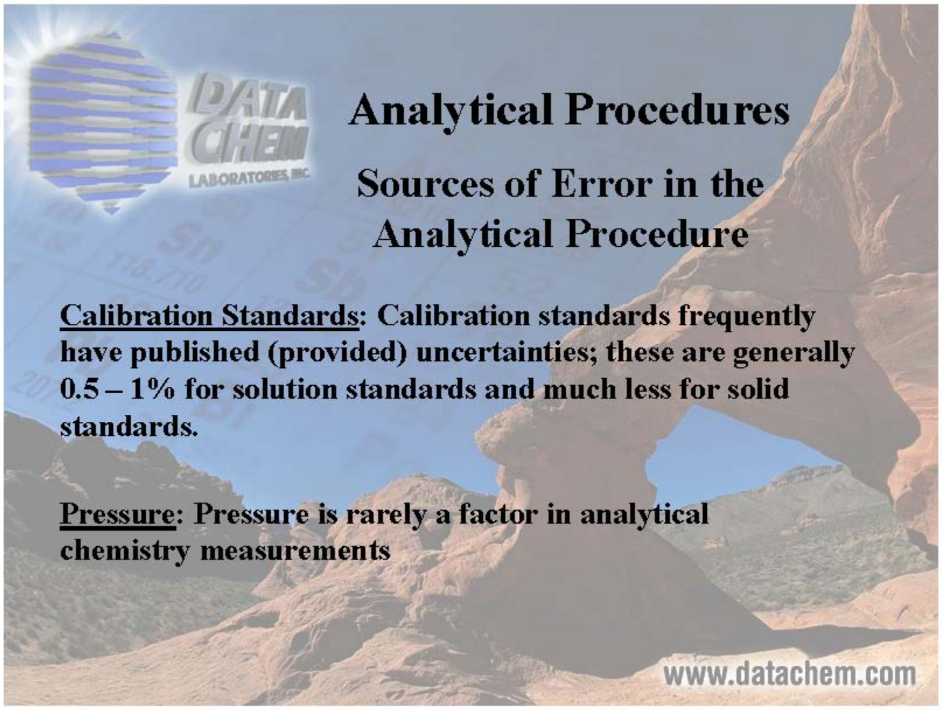
Analytical Procedures

Sources of Error in the Analytical Procedure

Temperature: Devices used for the measurement of temperature.

Atomic Weights: The uncertainty of published atomic weights can contribute to total, combined uncertainty in processes in which atomic weights are used for calculations contributing to the generation of results.

www.datachem.com



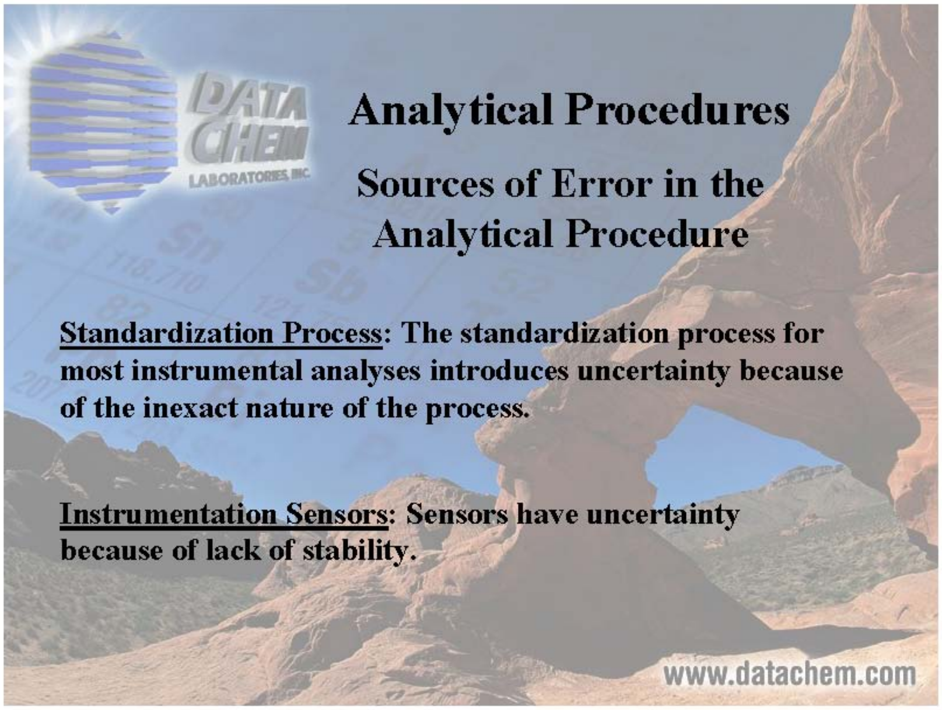
Analytical Procedures

Sources of Error in the Analytical Procedure

Calibration Standards: Calibration standards frequently have published (provided) uncertainties; these are generally 0.5 – 1% for solution standards and much less for solid standards.

Pressure: Pressure is rarely a factor in analytical chemistry measurements

www.datachem.com



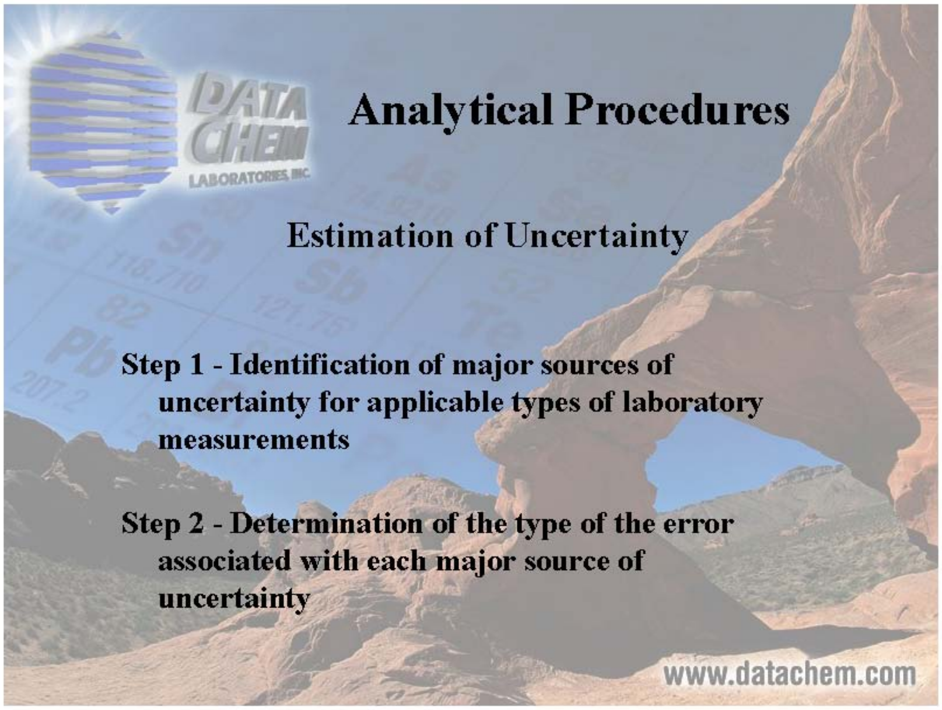
Analytical Procedures

Sources of Error in the Analytical Procedure

Standardization Process: The standardization process for most instrumental analyses introduces uncertainty because of the inexact nature of the process.

Instrumentation Sensors: Sensors have uncertainty because of lack of stability.

www.datachem.com



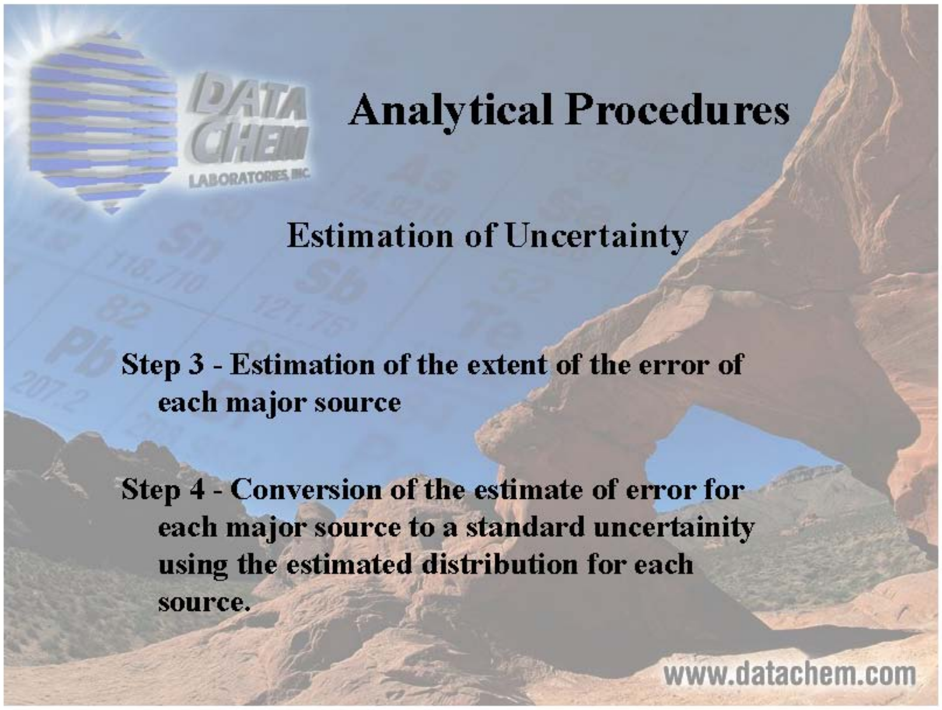
Analytical Procedures

Estimation of Uncertainty

Step 1 - Identification of major sources of uncertainty for applicable types of laboratory measurements

Step 2 - Determination of the type of the error associated with each major source of uncertainty

www.datachem.com



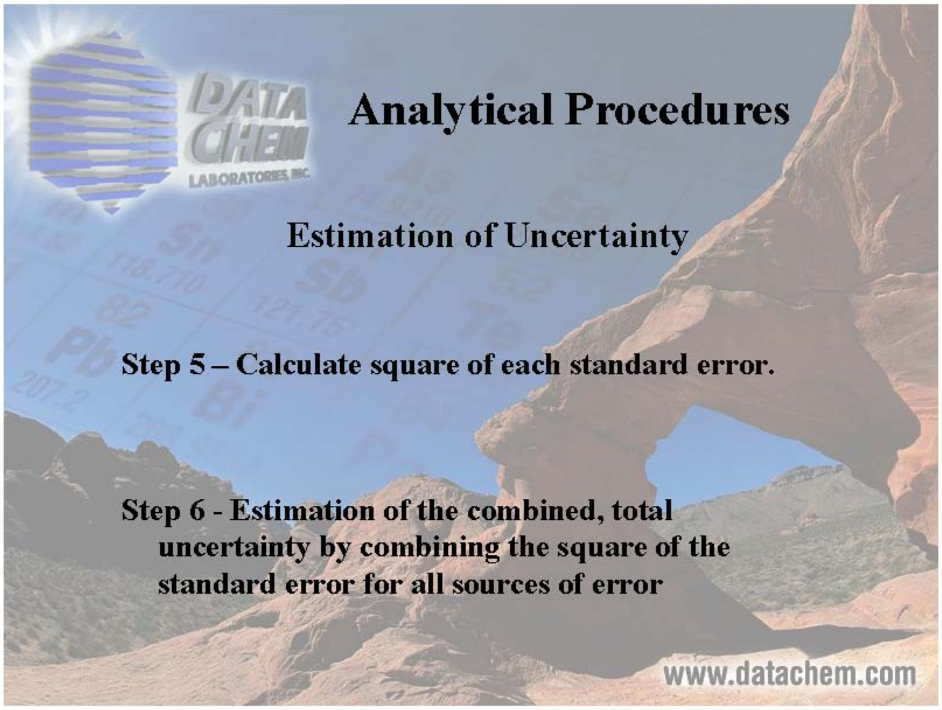
Analytical Procedures

Estimation of Uncertainty

Step 3 - Estimation of the extent of the error of each major source

Step 4 - Conversion of the estimate of error for each major source to a standard uncertainity using the estimated distribution for each source.

www.datachem.com



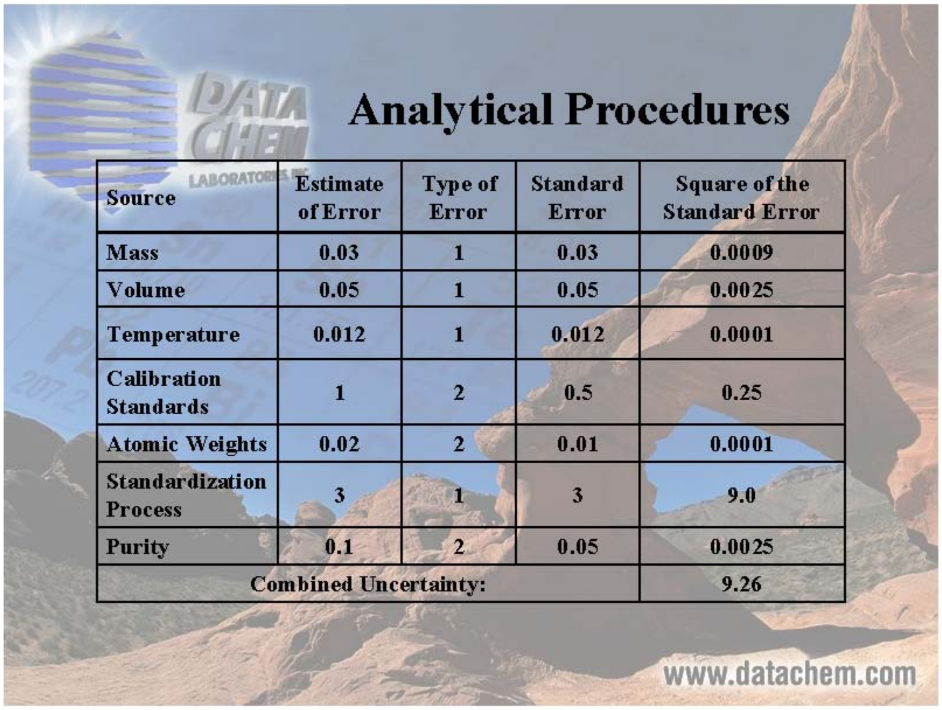
Analytical Procedures

Estimation of Uncertainty

Step 5 – Calculate square of each standard error.

Step 6 - Estimation of the combined, total uncertainty by combining the square of the standard error for all sources of error

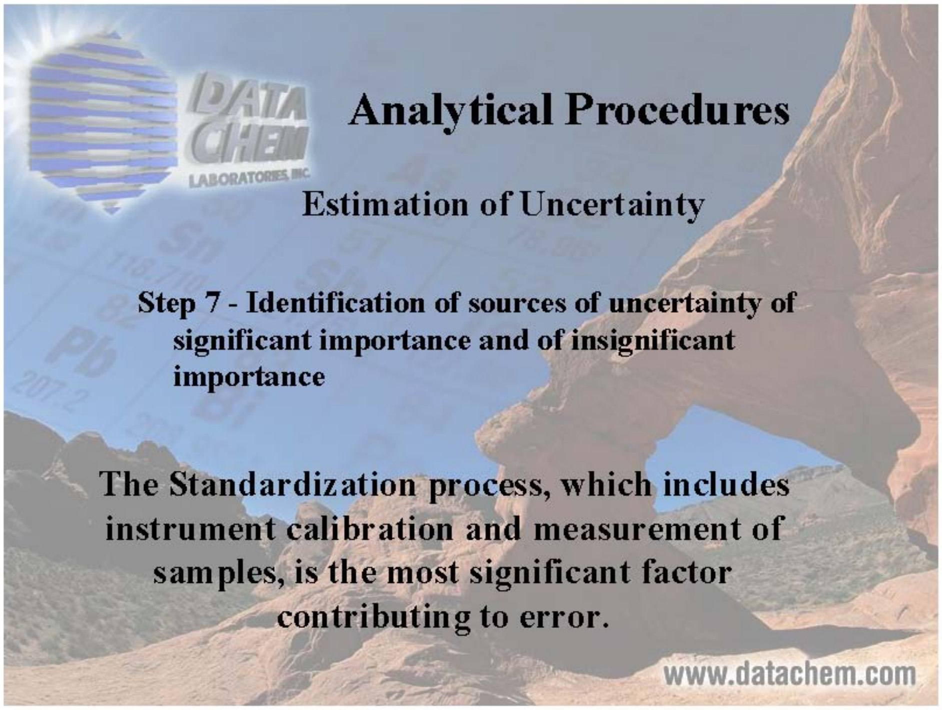
www.datachem.com



Analytical Procedures

Source	Estimate of Error	Type of Error	Standard Error	Square of the Standard Error
Mass	0.03	1	0.03	0.0009
Volume	0.05	1	0.05	0.0025
Temperature	0.012	1	0.012	0.0001
Calibration Standards	1	2	0.5	0.25
Atomic Weights	0.02	2	0.01	0.0001
Standardization Process	3	1	3	9.0
Purity	0.1	2	0.05	0.0025
Combined Uncertainty:				9.26

www.datachem.com



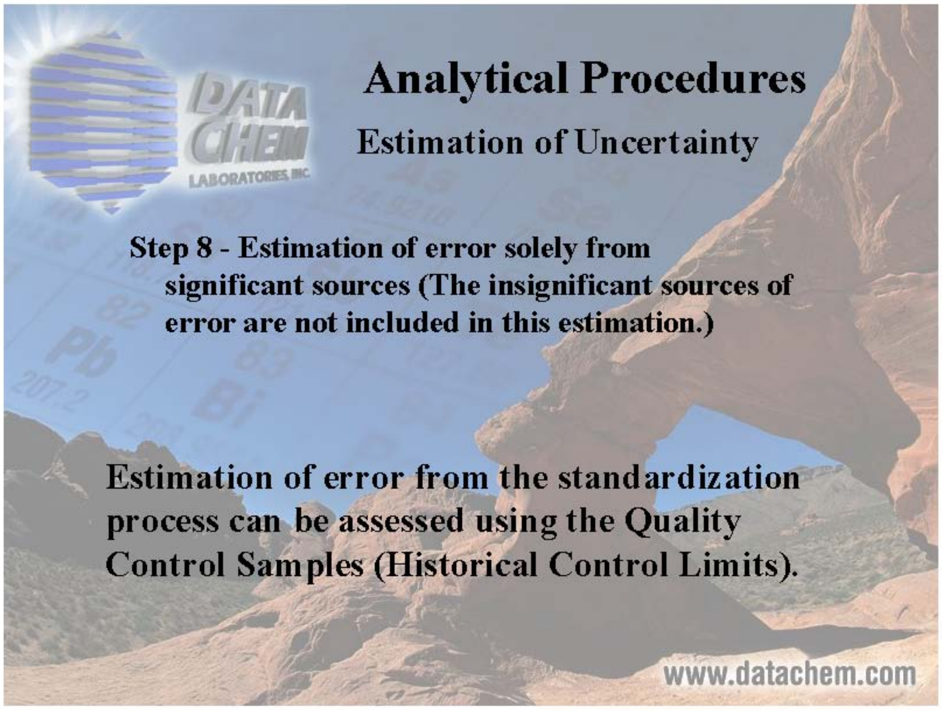
Analytical Procedures

Estimation of Uncertainty

Step 7 - Identification of sources of uncertainty of significant importance and of insignificant importance

The Standardization process, which includes instrument calibration and measurement of samples, is the most significant factor contributing to error.

www.datachem.com



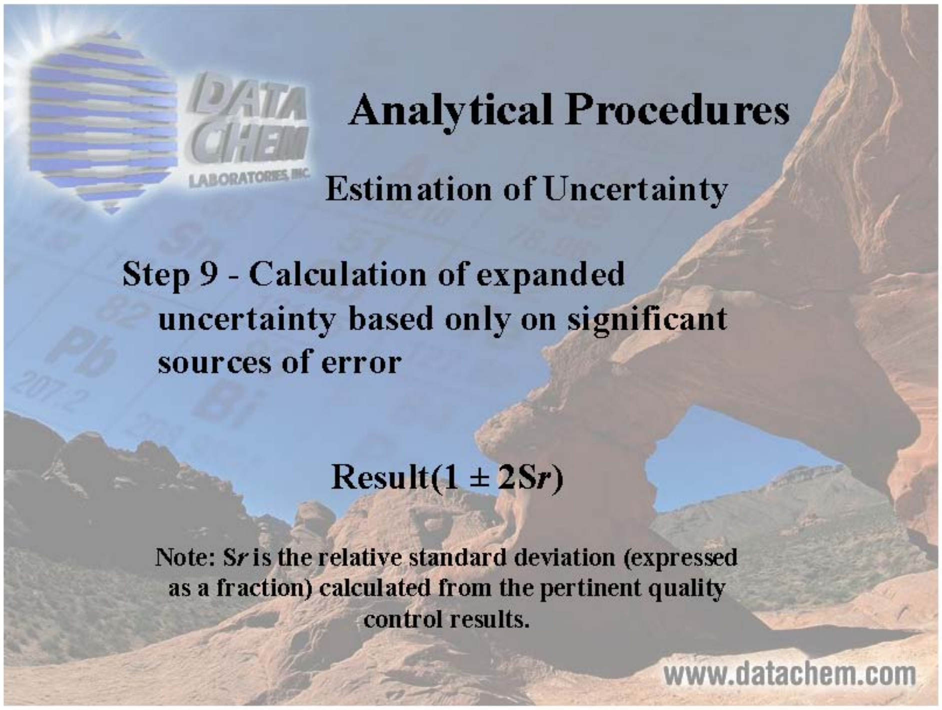
Analytical Procedures

Estimation of Uncertainty

Step 8 - Estimation of error solely from significant sources (The insignificant sources of error are not included in this estimation.)

Estimation of error from the standardization process can be assessed using the Quality Control Samples (Historical Control Limits).

www.datachem.com



Analytical Procedures

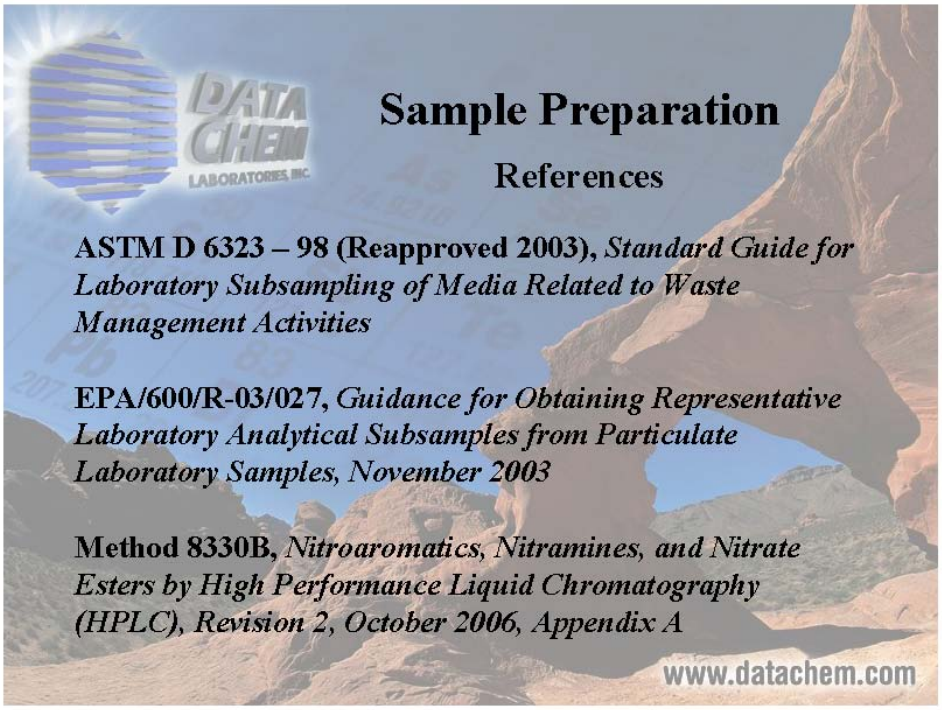
Estimation of Uncertainty

Step 9 - Calculation of expanded uncertainty based only on significant sources of error

$$\text{Result}(1 \pm 2S_r)$$

Note: *Sr* is the relative standard deviation (expressed as a fraction) calculated from the pertinent quality control results.

www.datachem.com



Sample Preparation

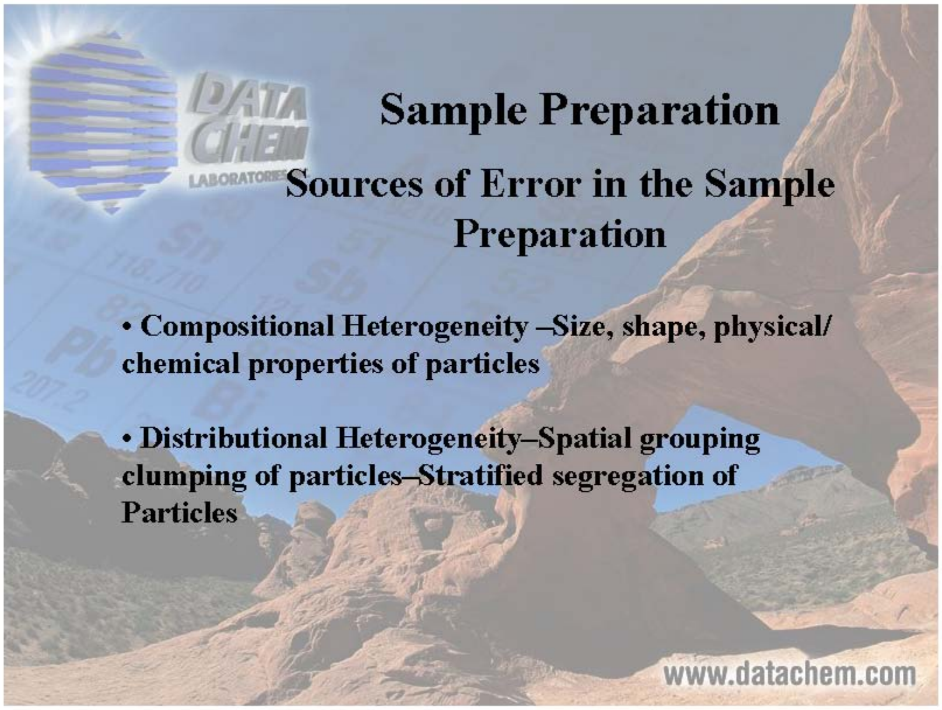
References

ASTM D 6323 – 98 (Reapproved 2003), *Standard Guide for Laboratory Subsampling of Media Related to Waste Management Activities*

EPA/600/R-03/027, *Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples, November 2003*

Method 8330B, *Nitroaromatics, Nitramines, and Nitrate Esters by High Performance Liquid Chromatography (HPLC), Revision 2, October 2006, Appendix A*

www.datachem.com

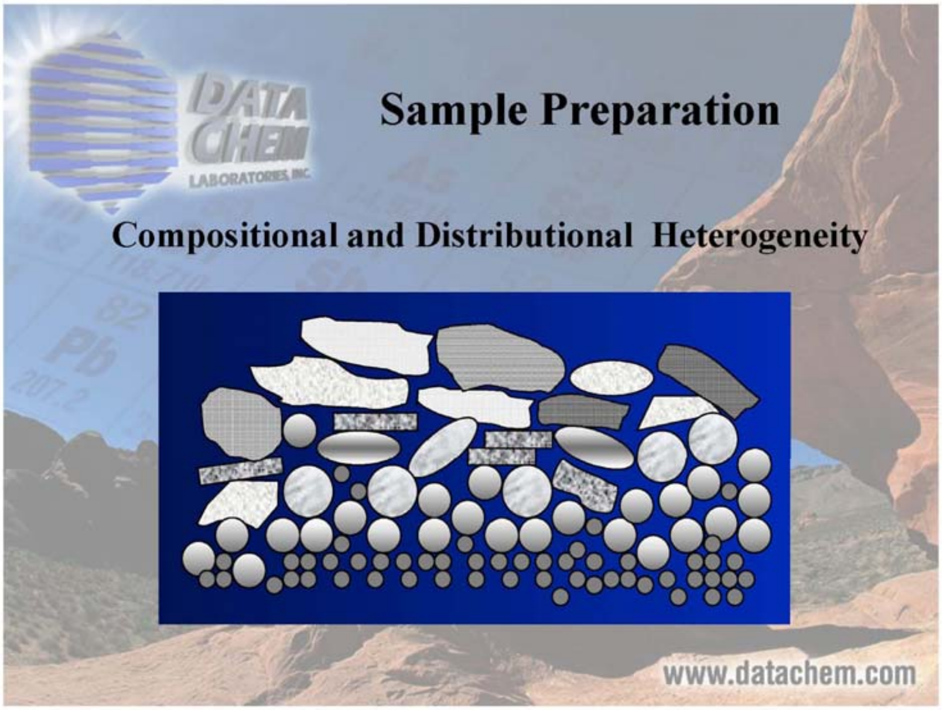


Sample Preparation

Sources of Error in the Sample Preparation

- **Compositional Heterogeneity –Size, shape, physical/ chemical properties of particles**
- **Distributional Heterogeneity–Spatial grouping clumping of particles–Stratified segregation of Particles**

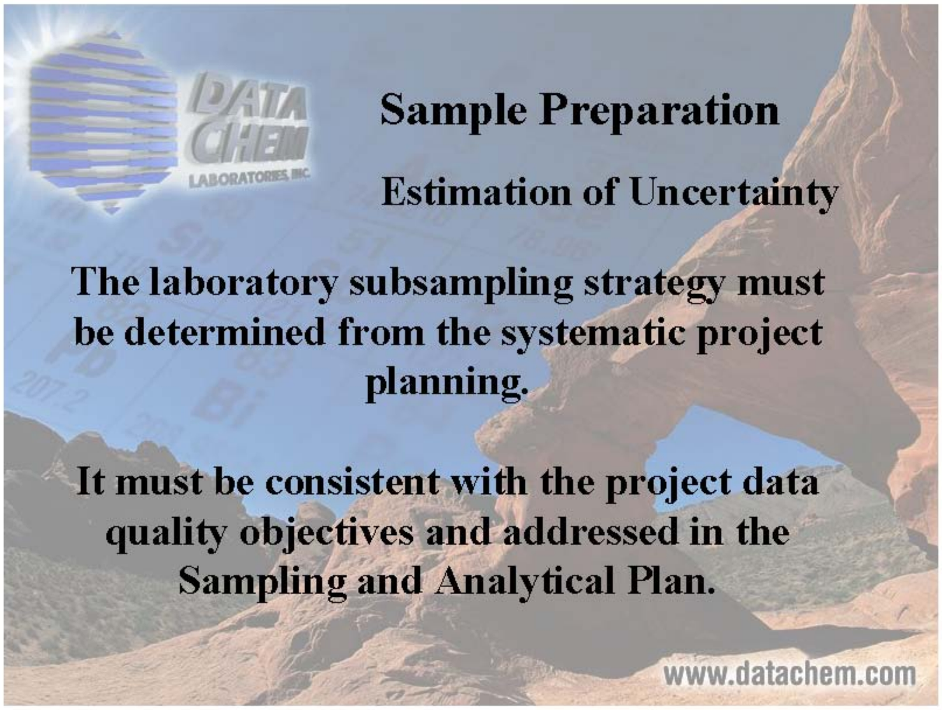
www.datachem.com



Sample Preparation

Compositional and Distributional Heterogeneity

www.datachem.com



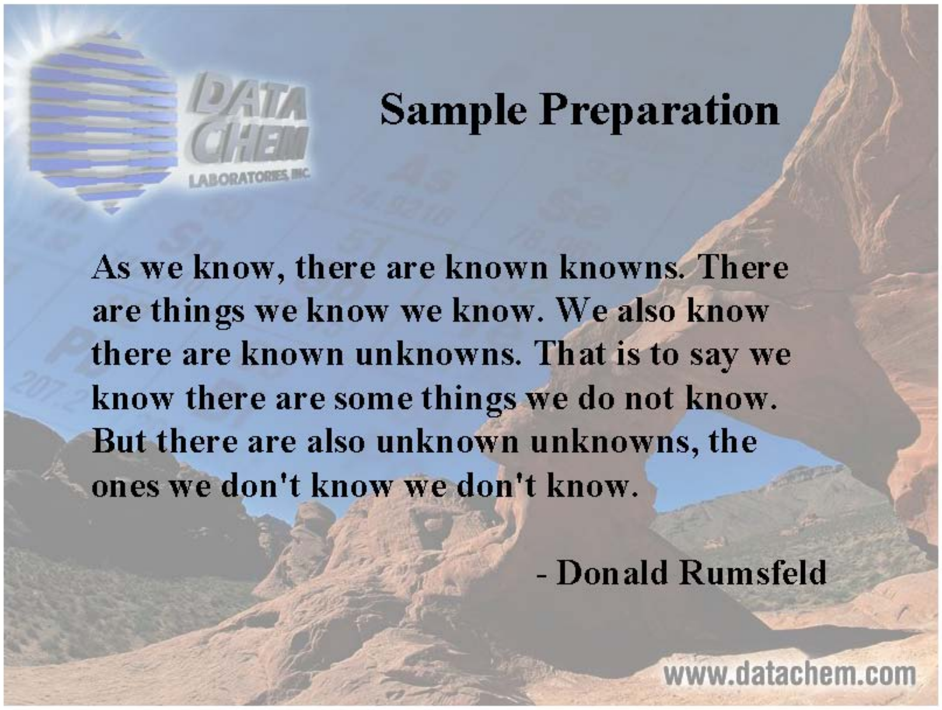
Sample Preparation

Estimation of Uncertainty

The laboratory subsampling strategy must be determined from the systematic project planning.

It must be consistent with the project data quality objectives and addressed in the Sampling and Analytical Plan.

www.datachem.com

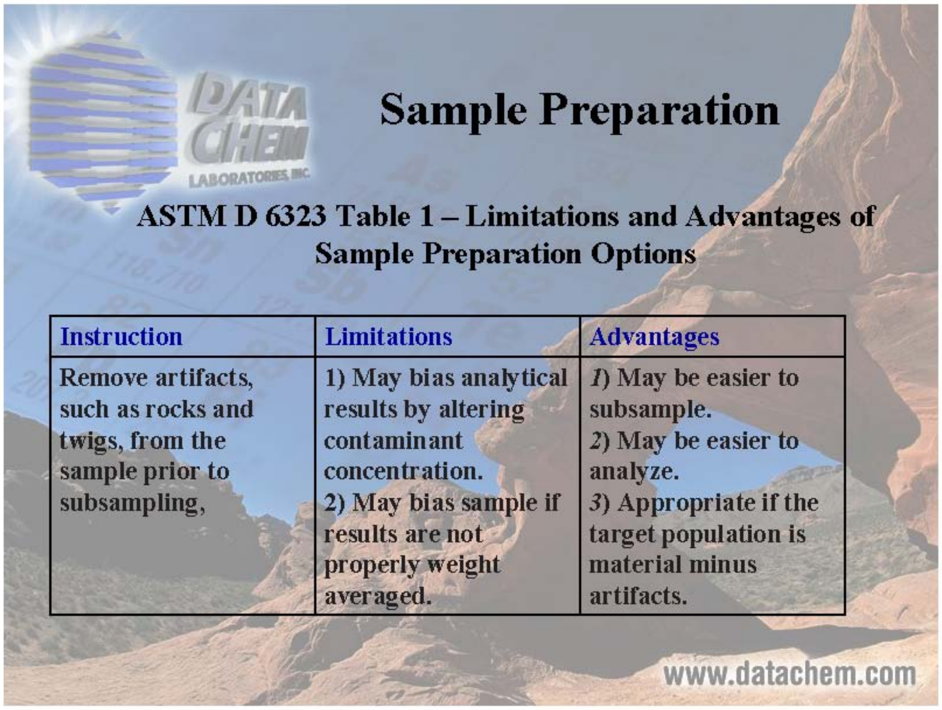


Sample Preparation

As we know, there are known knowns. There are things we know we know. We also know there are known unknowns. That is to say we know there are some things we do not know. But there are also unknown unknowns, the ones we don't know we don't know.

- Donald Rumsfeld

www.datachem.com

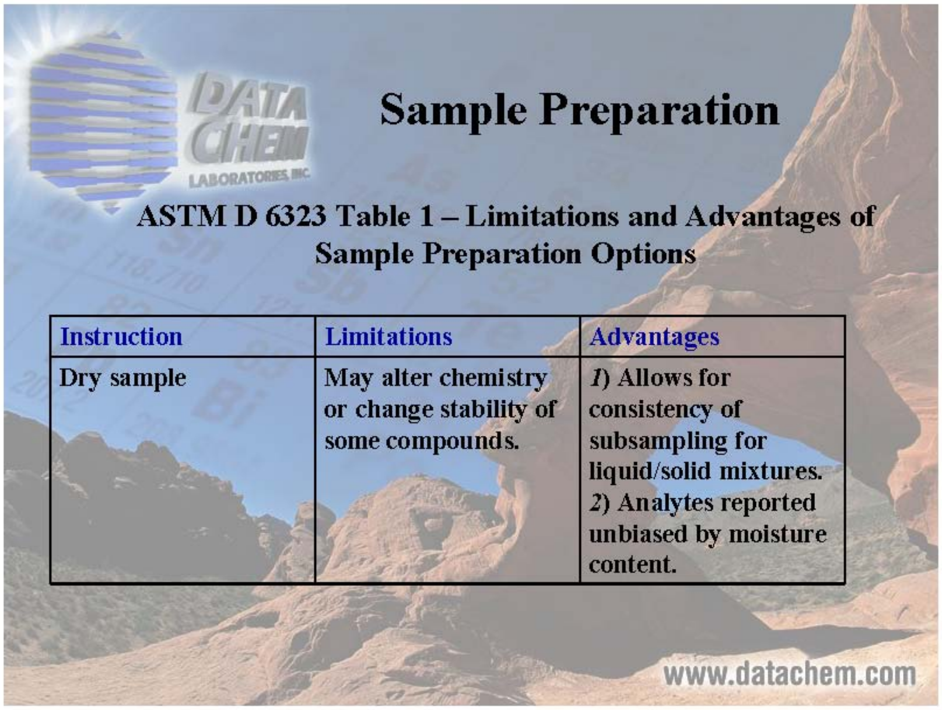


Sample Preparation

ASTM D 6323 Table 1 – Limitations and Advantages of Sample Preparation Options

Instruction	Limitations	Advantages
Remove artifacts, such as rocks and twigs, from the sample prior to subsampling,	1) May bias analytical results by altering contaminant concentration. 2) May bias sample if results are not properly weight averaged.	*1)* May be easier to subsample. *2)* May be easier to analyze. *3)* Appropriate if the target population is material minus artifacts.

www.datachem.com

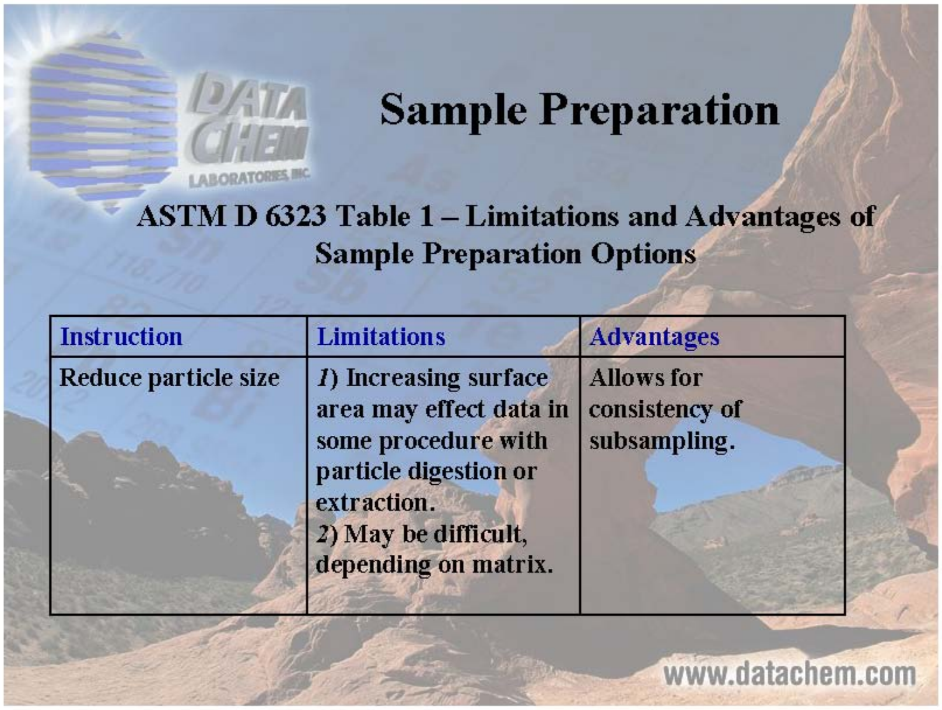


Sample Preparation

ASTM D 6323 Table 1 – Limitations and Advantages of Sample Preparation Options

Instruction	Limitations	Advantages
Dry sample	May alter chemistry or change stability of some compounds.	*1)* Allows for consistency of subsampling for liquid/solid mixtures. *2)* Analytes reported unbiased by moisture content.

www.datachem.com

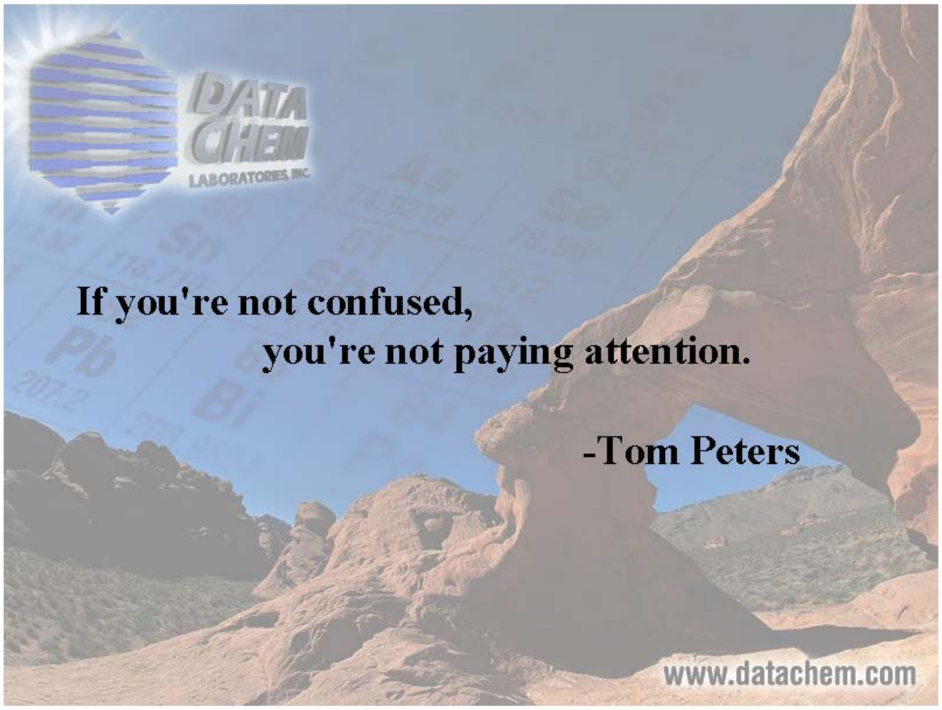


Sample Preparation

ASTM D 6323 Table 1 – Limitations and Advantages of Sample Preparation Options

Instruction	Limitations	Advantages
Reduce particle size	*1)* Increasing surface area may effect data in some procedure with particle digestion or extraction. *2)* May be difficult, depending on matrix.	Allows for consistency of subsampling.

www.datachem.com

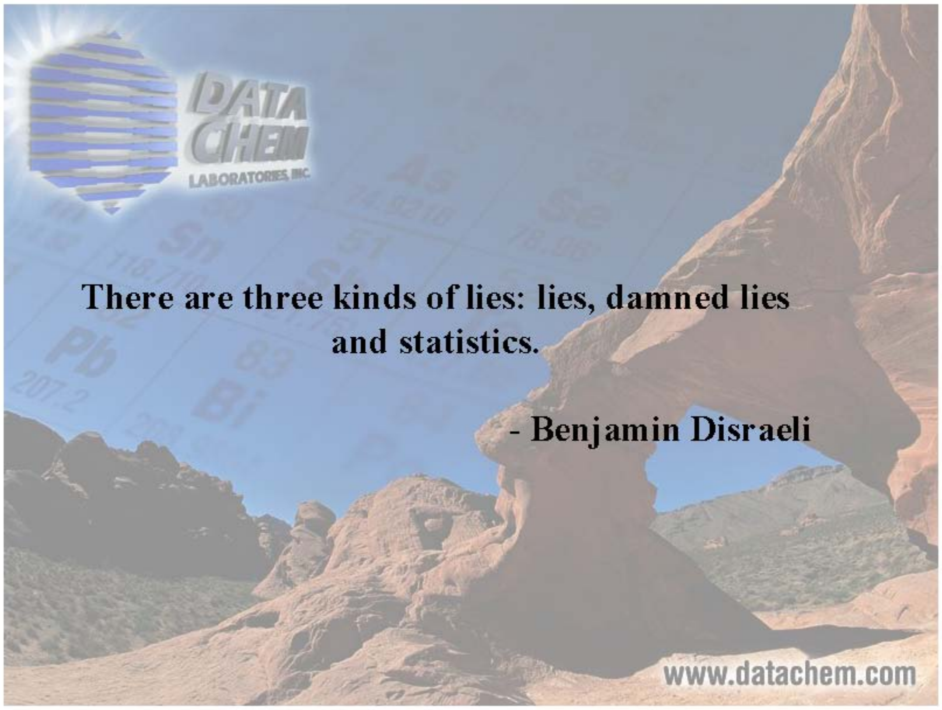


DATA CHEM LABORATORIES, INC.

If you're not confused,
you're not paying attention.

-Tom Peters

www.datachem.com

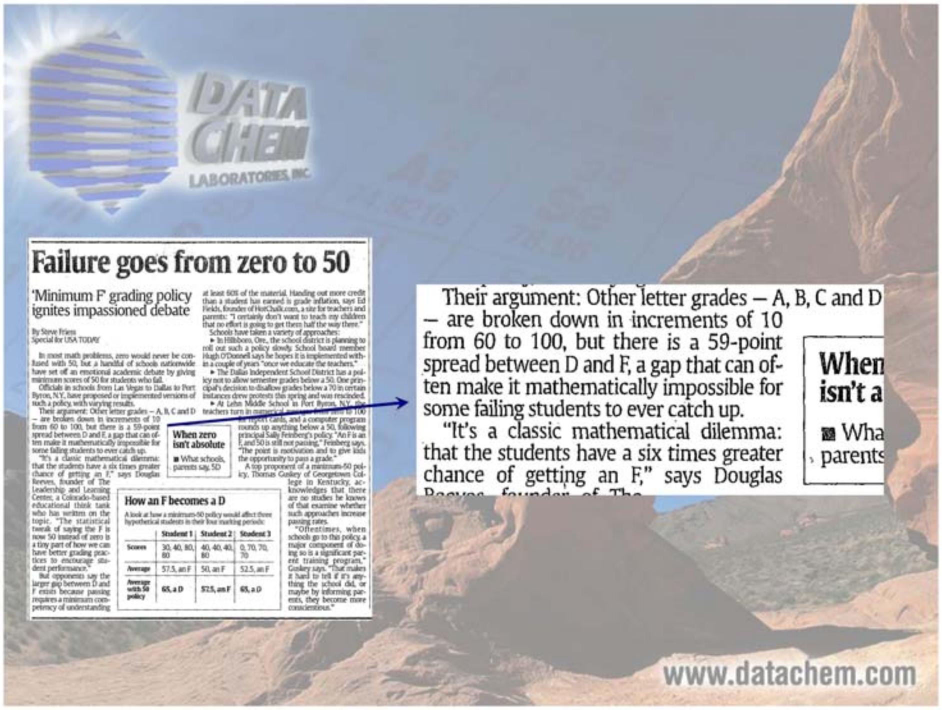


DATA CHEM LABORATORIES, INC.

There are three kinds of lies: lies, damned lies
and statistics.

- Benjamin Disraeli

www.datachem.com



DATA CHEM LABORATORIES, INC.

Failure goes from zero to 50

'Minimum F' grading policy ignites impassioned debate

By Steve Friess
Special for USA TODAY

In most math problems, zero would never be confused with 50, but a handful of schools nationwide have set off an emotional academic debate by giving minimum scores of 50 for students who fail.

Officials in schools from Las Vegas to Dallas to Port Byron, N.Y., have proposed or implemented versions of such a policy, with varying results.

Their argument: Other letter grades — A, B, C and D — are broken down in increments of 10 from 60 to 100, but there is a 59-point spread between D and F, a gap that can often make it mathematically impossible for some failing students to ever catch up.

"It's a classic mathematical dilemma: that the students have a six times greater chance of getting an F," says Douglas Reeves, founder of The Leadership and Learning Center, a Colorado-based educational think tank who has written on the topic. "The statistical tweak of saying the F is now 50 instead of zero is a tiny part of how we can have better grading practices to encourage student performance."

But opponents say the larger gap between D and F exists because passing requires a minimum competency of understanding at least 60% of the material. Handing out more credit than a student has earned is grade inflation, says Ed Fields, founder of HotChalk.com, a site for teachers and parents: "I certainly don't want to teach my children that no effort is going to get them half the way there."

Schools have taken a variety of approaches:

► In Hillsboro, Ore., the school district is planning to roll out such a policy slowly. School board member Hugh O'Donnell says he hopes it is implemented within a couple of years "once we educate the teachers."

► The Dallas Independent School District has a policy not to allow semester grades below a 50. One principal's decision to disallow grades below a 70 in certain instances drew protests this spring and was rescinded.

► At Lehn Middle School in Port Byron, N.Y., the teachers turn in numerical [illegible] to 100 for report cards, and a computer program rounds up anything below a 50, following principal Sally Feinberg's policy. "An F is an F, and 50 is still not passing," Feinberg says. "The point is motivation and to give kids the opportunity to pass a grade."

A top proponent of a minimum-50 policy, Thomas Guskey of Georgetown College in Kentucky, acknowledges that there are no studies he knows of that examine whether such approaches increase passing rates.

"Oftentimes, when schools go to this policy, a major component of doing so is a significant parent training program," Guskey says. "That makes it hard to tell if it's anything the school did, or maybe by informing parents, they become more conscientious."

When zero isn't absolute

■ What schools, parents say, 5D

How an F becomes a D

A look at how a minimum-50 policy would affect three hypothetical students in their four marking periods:

	Student 1	Student 2	Student 3
Scores	30, 40, 80, 80	40, 40, 40, 80	0, 70, 70, 70
Average	57.5, an F	50, an F	52.5, an F
Average with 50 policy	65, a D	57.5, an F	65, a D

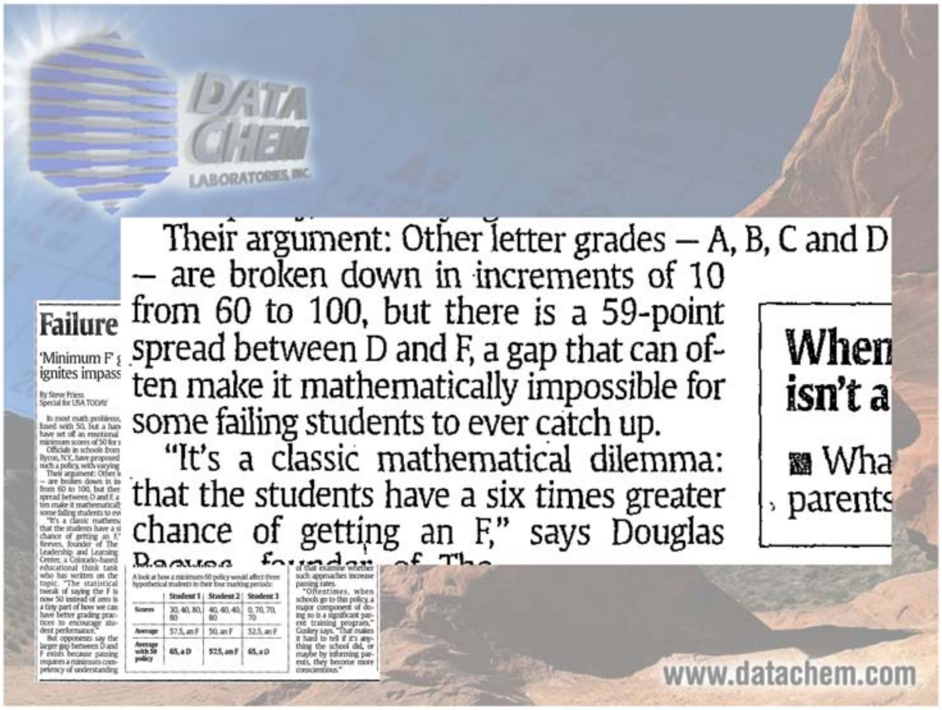
Their argument: Other letter grades — A, B, C and D — are broken down in increments of 10 from 60 to 100, but there is a 59-point spread between D and F, a gap that can often make it mathematically impossible for some failing students to ever catch up.

"It's a classic mathematical dilemma: that the students have a six times greater chance of getting an F," says Douglas

When
isn't a

■ Wha
parents

www.datachem.com



DATA CHEM LABORATORIES, INC.

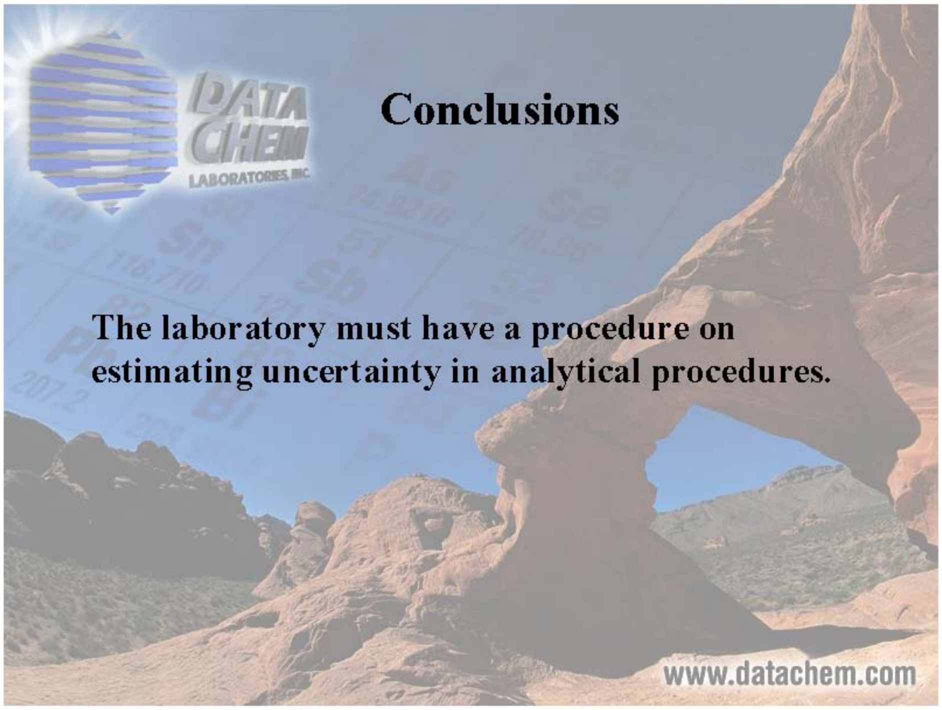
Their argument: Other letter grades — A, B, C and D — are broken down in increments of 10 from 60 to 100, but there is a 59-point spread between D and F, a gap that can often make it mathematically impossible for some failing students to ever catch up.

"It's a classic mathematical dilemma: that the students have a six times greater chance of getting an F," says Douglas

When
isn't a

■ Wha
parents

www.datachem.com



Conclusions

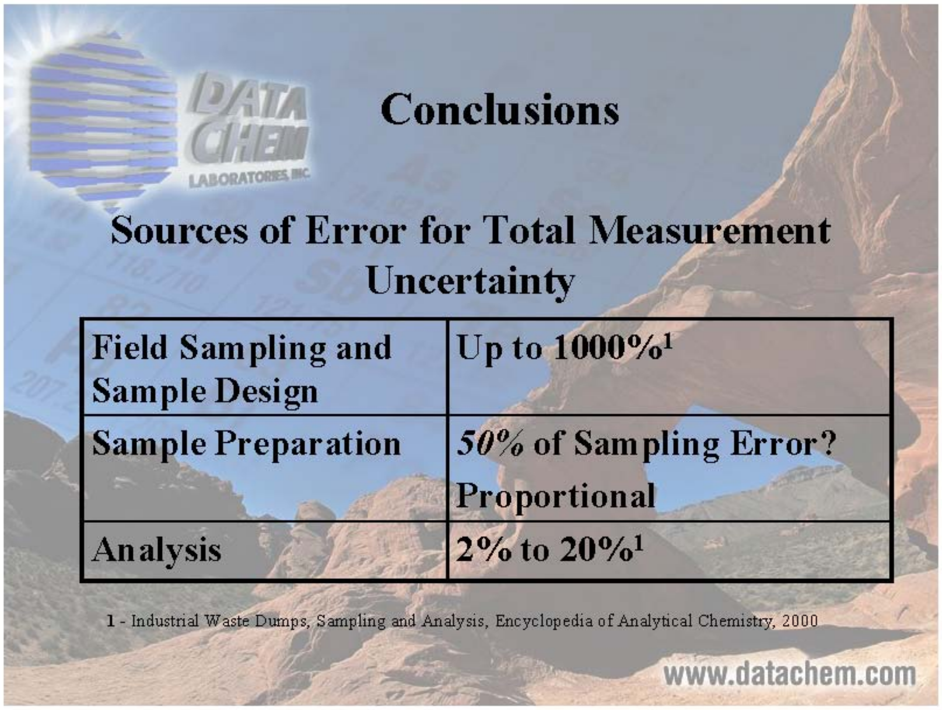
The laboratory must have a procedure on estimating uncertainty in analytical procedures.

www.datachem.com

Conclusions

Subsampling instruction must be given to the laboratory consistent with systematic project planning and data quality objectives.

www.datachem.com



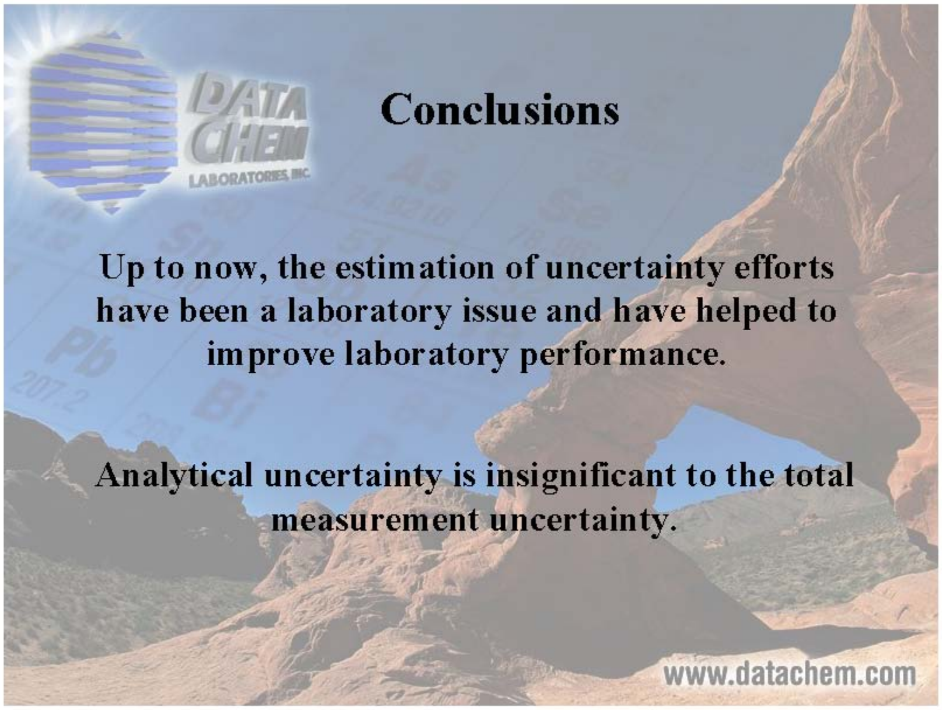
Conclusions

Sources of Error for Total Measurement Uncertainty

Field Sampling and Sample Design	Up to 1000%[1]
Sample Preparation	*50%* of Sampling Error? Proportional
Analysis	2% to 20%[1]

1 - Industrial Waste Dumps, Sampling and Analysis, Encyclopedia of Analytical Chemistry, 2000

www.datachem.com



Conclusions

Up to now, the estimation of uncertainty efforts have been a laboratory issue and have helped to improve laboratory performance.

Analytical uncertainty is insignificant to the total measurement uncertainty.

www.datachem.com

DATA CHEM LABORATORIES INC.

Questions?

www.datachem.com

Utilizing Laboratory Information Management Systems (LIMS) to Optimize Laboratory Performance and Enhance Data Usability with a Web Portal to the LIMS

Chuck Hindbaugh
Accelerated Technology Laboratories, Inc.
496 Holly Grove School Rd
West End, NC 27376
910-673-8165

ABSTRACT

In today's fast paced laboratory environment it is not only essential that data be available quickly to the customer the data integrity and usability are equally important. LIMS (Laboratory Information Management Systems) databases are designed to aid the laboratory in all aspects of sample analyses by helping with QA/QC, regulatory compliance, as well as accreditation requirements. Tasks associated with samples, from scheduling to disposal, benefit through the entire process when using a well implemented LIMS.

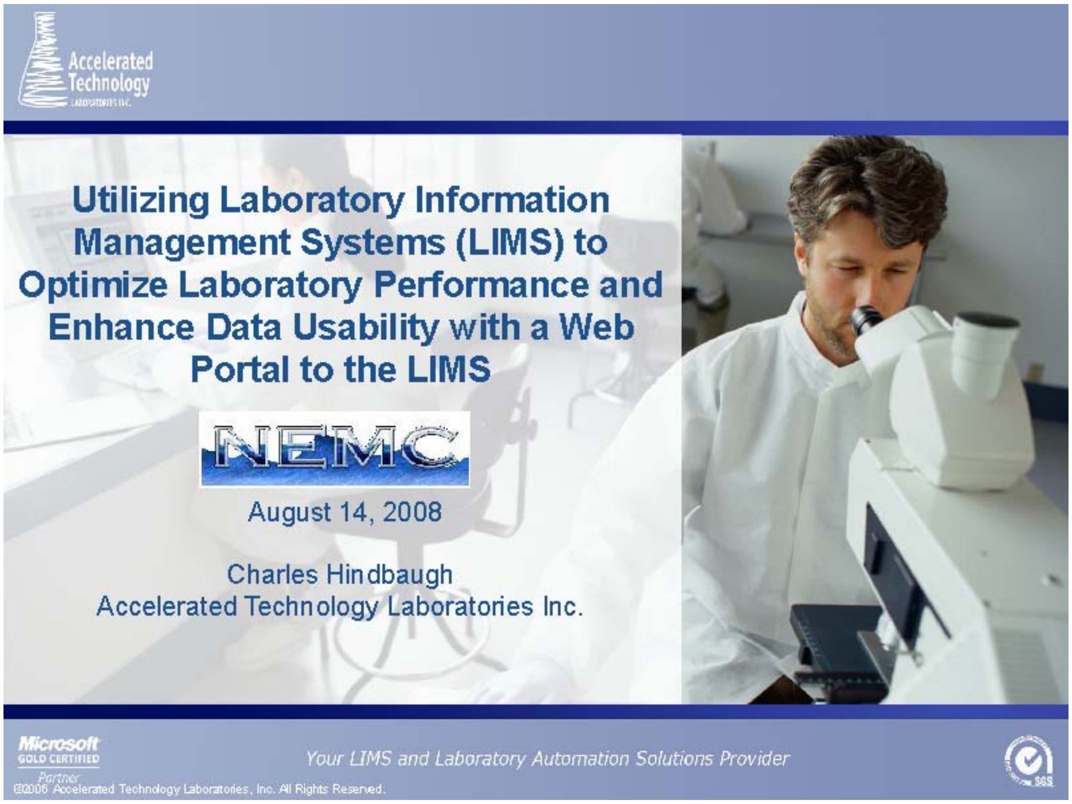
A LIMS utilizing Electronic Data Transfer (EDT) from the instrumentation eliminates the re-typing of data and reduces the chances of data entry errors. When that same LIMS is linked to a web based portal the advantage of customers having access to their data and the status of the samples in a real-time interface, access to linked files, pdf reports and chain of custody forms.

This presentation will review how a properly integrated LIMS system with a Web Portal can automate routine tasks as well as streamline some of the more cumbersome tasks. Benefits from such a system include:

- Automation of sample login with the use of automated scheduling.
- Efficient sample tracking in the laboratory.
- Increased data accuracy using data transfer into the LIMS.
- Timely and accurate reports automatically generated from the database.
- With the use of a web portal customers can check the status of their samples and even view preliminary results at anytime and print reports.
- Customers have access to all their data when they need it.
- Ease in creating EDD (Electronic Data Deliverables) packages for customers.

Attendees will walk away with a basic understanding on how a properly integrated LIMS can increase the overall efficiency of a laboratory, optimizing resources and maximizing profitability.

NEMC 2008



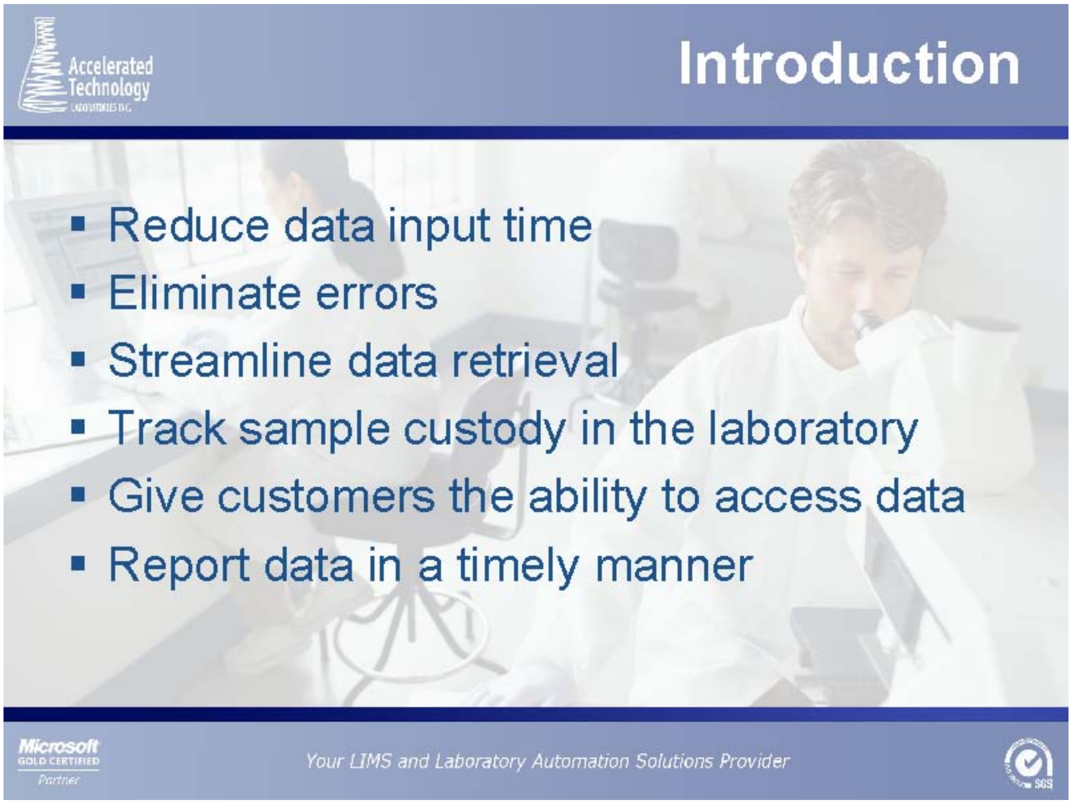
Utilizing Laboratory Information Management Systems (LIMS) to Optimize Laboratory Performance and Enhance Data Usability with a Web Portal to the LIMS

NEMC

August 14, 2008

Charles Hindbaugh
Accelerated Technology Laboratories Inc.

Your LIMS and Laboratory Automation Solutions Provider



Introduction

- Reduce data input time
- Eliminate errors
- Streamline data retrieval
- Track sample custody in the laboratory
- Give customers the ability to access data
- Report data in a timely manner

Your LIMS and Laboratory Automation Solutions Provider

Accelerated Technology Laboratories Inc.

Key Elements of a LIMS

- Sample Tracking
- Data Entry
- Sample Scheduling
- QA/QC
- Electronic Data Entry
- Chemical/Reagent Inventory
- Personnel and Equipment Management
- Time Tracking
- Customer Relationship Management
- Maintenance

SAMPLE MASTER

Microsoft Gold Certified Partner

Your LIMS and Laboratory Automation Solutions Provider

SGS

Accelerated Technology Laboratories Inc.

Automating Sample Login

- Accurate sample login is essential.
- The ability to automatically login reoccurring samples cuts down on login time.

Microsoft Gold Certified Partner

Your LIMS and Laboratory Automation Solutions Provider

SGS

Accelerated Technology Laboratories Inc.

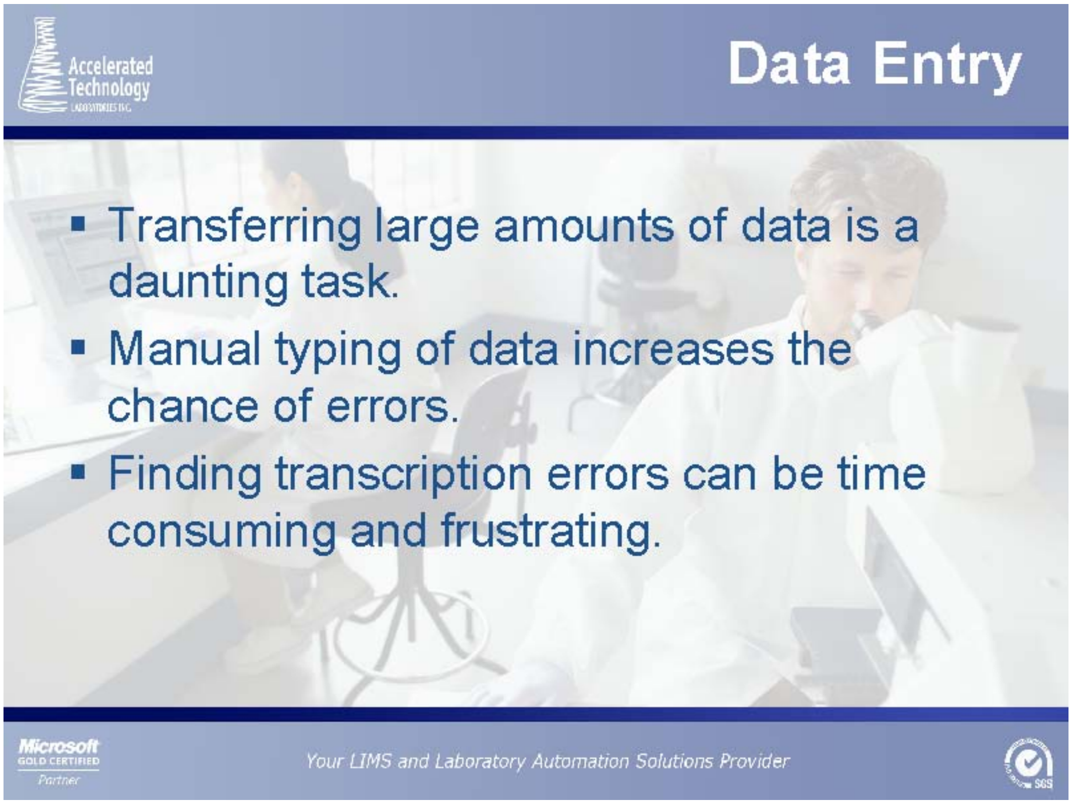
Sample Tracking

- Keep sample custody chain intact
- Know where samples are

Microsoft Gold Certified Partner

Your LIMS and Laboratory Automation Solutions Provider

SGS



Accelerated Technology Laboratories Inc.

Data Entry

- Transferring large amounts of data is a daunting task.
- Manual typing of data increases the chance of errors.
- Finding transcription errors can be time consuming and frustrating.

Microsoft Gold Certified Partner

Your LIMS and Laboratory Automation Solutions Provider

SGS

Accelerated Technology Laboratories Inc.

Electronic Data Transfer

- Reduce transcription errors.
- Increase throughput.
- Avoid duplication.
- Increase accuracy.
- Hundreds of instrument files have been integrated with Sample Master® Pro LIMS, for a partial listing visit our web site.
- ROI typically within 1 year.
- Enhance productivity.

Microsoft Gold Certified Partner

Your LIMS and Laboratory Automation Solutions Provider

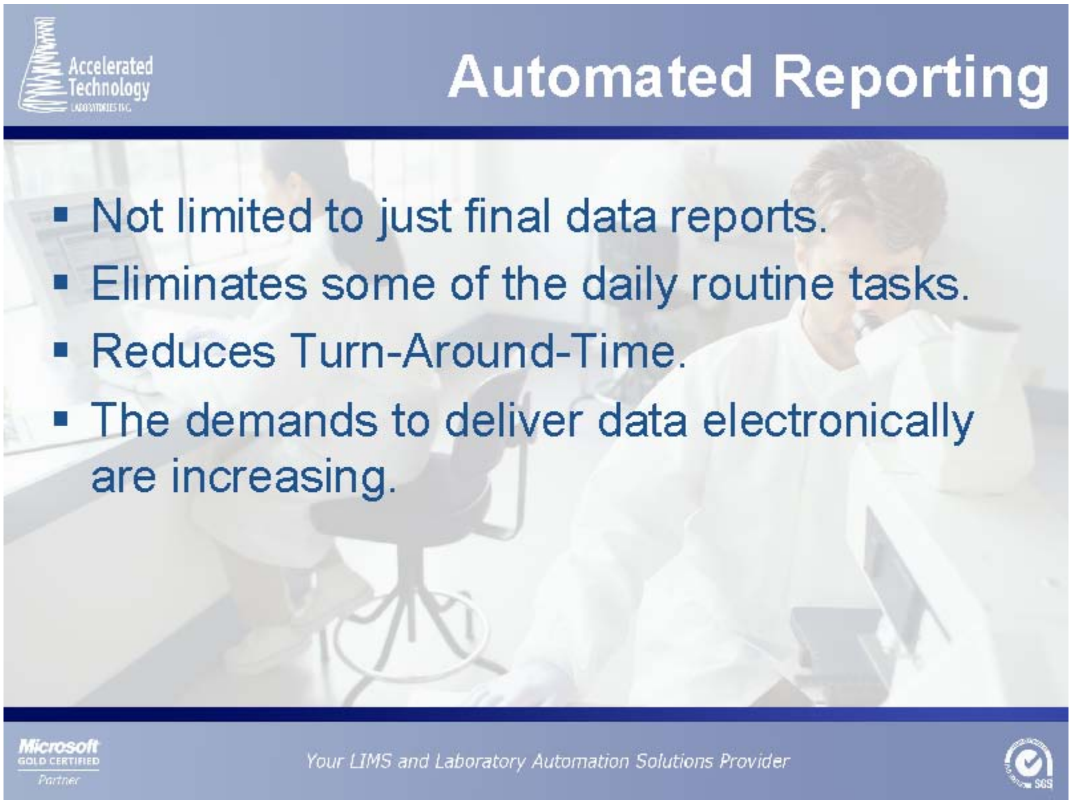
Accelerated Technology Laboratories Inc.

Reporting

- Is the report reader friendly?
- Does it contain all the necessary information?
- Proper data handling = Useable report

Microsoft Gold Certified Partner

Your LIMS and Laboratory Automation Solutions Provider



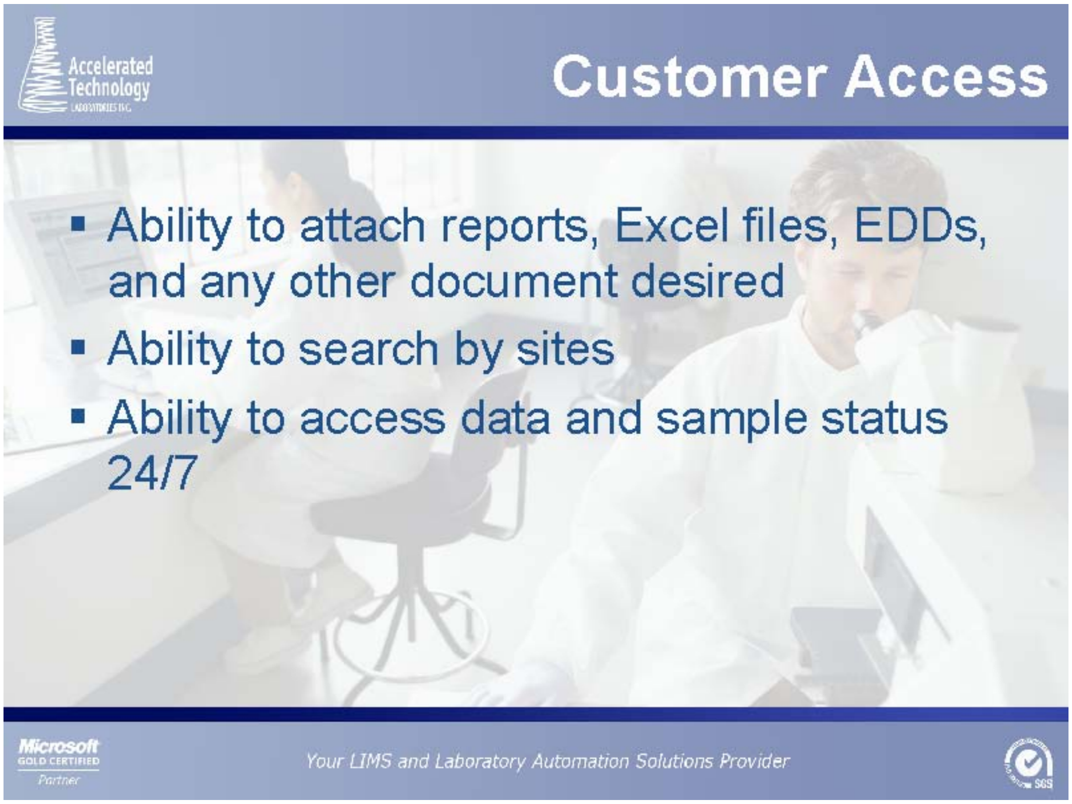
Accelerated Technology

Automated Reporting

- Not limited to just final data reports.
- Eliminates some of the daily routine tasks.
- Reduces Turn-Around-Time.
- The demands to deliver data electronically are increasing.

Microsoft GOLD CERTIFIED Partner

Your LIMS and Laboratory Automation Solutions Provider



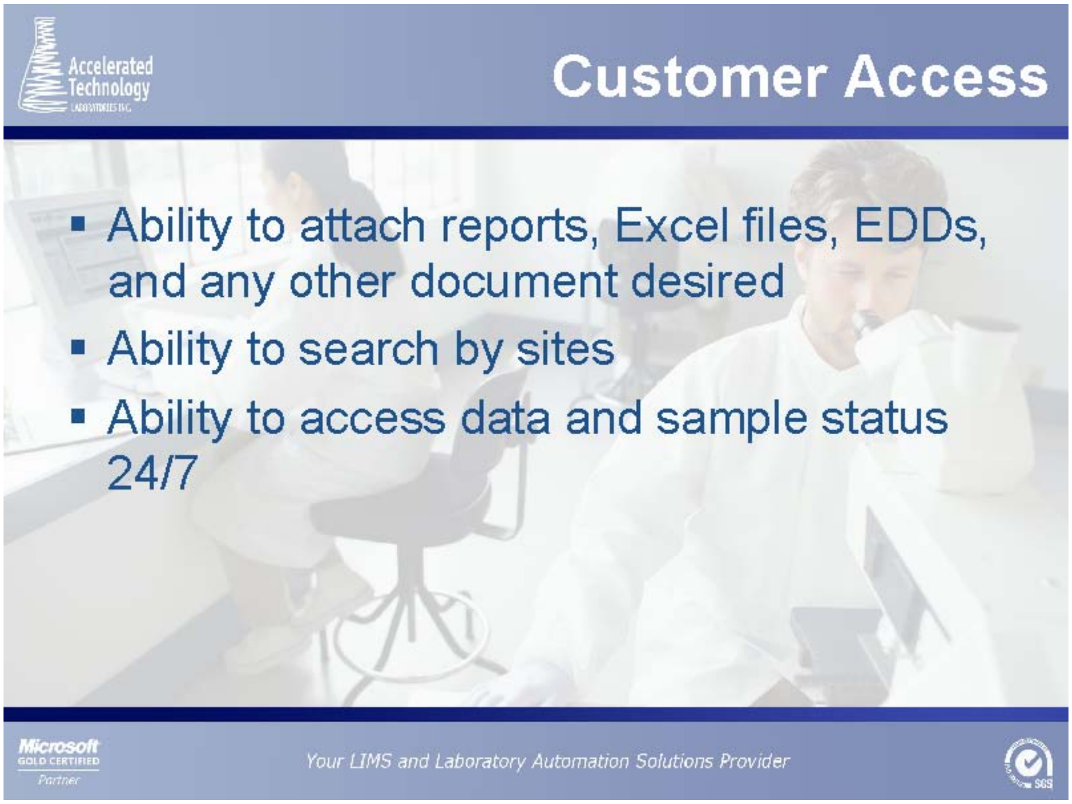
Accelerated Technology

Customer Access

- Ability to attach reports, Excel files, EDDs, and any other document desired
- Ability to search by sites
- Ability to access data and sample status 24/7

Microsoft GOLD CERTIFIED Partner

Your LIMS and Laboratory Automation Solutions Provider



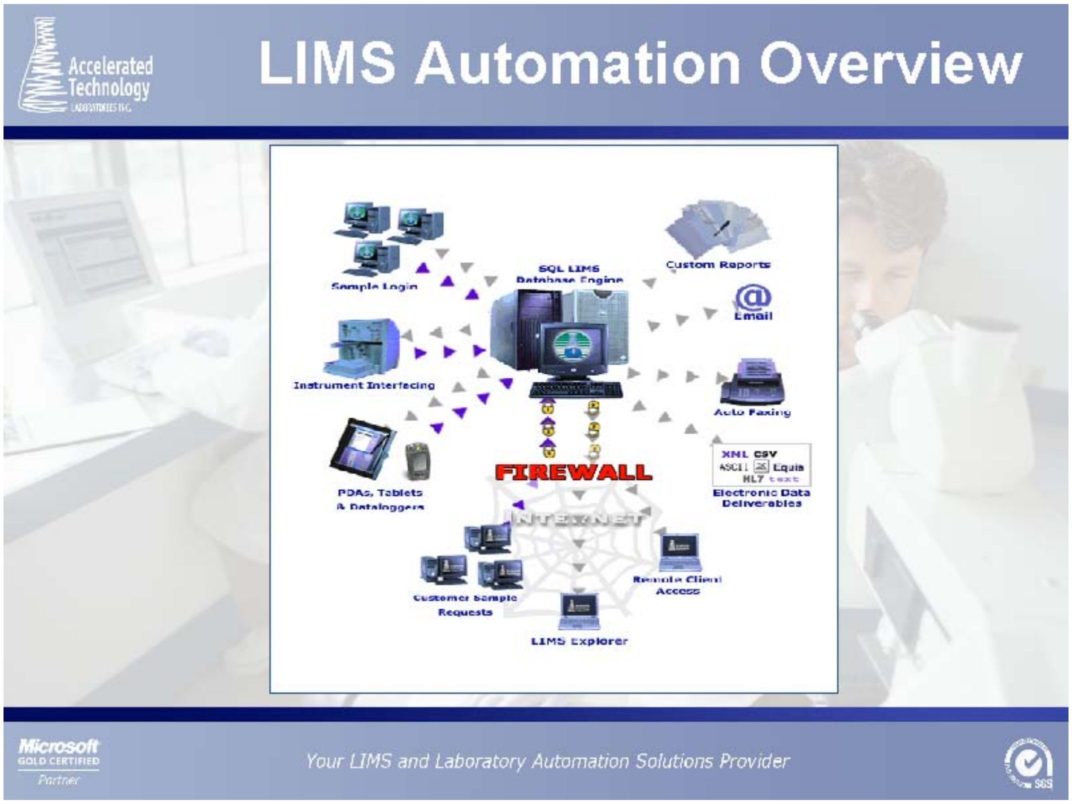
Accelerated Technology Laboratories Inc.

Customer Access

- Ability to attach reports, Excel files, EDDs, and any other document desired
- Ability to search by sites
- Ability to access data and sample status 24/7

Microsoft Gold Certified Partner

Your LIMS and Laboratory Automation Solutions Provider

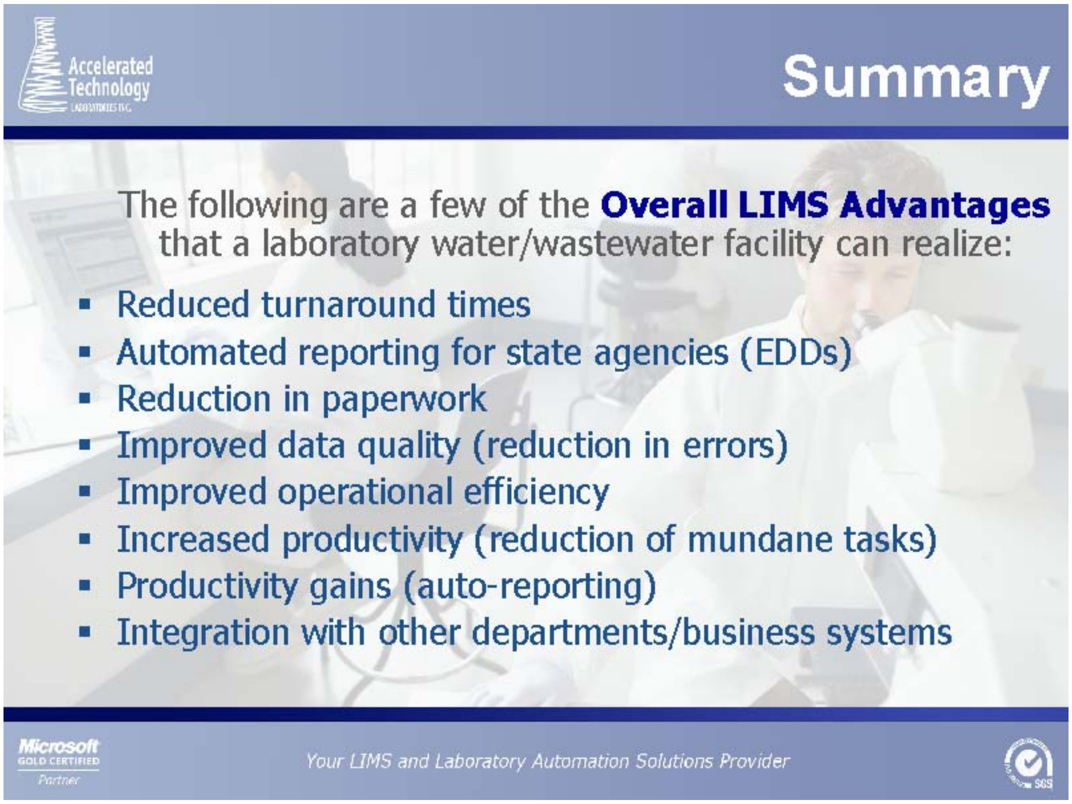


Accelerated Technology Laboratories Inc.

LIMS Automation Overview

Microsoft Gold Certified Partner

Your LIMS and Laboratory Automation Solutions Provider



Summary

The following are a few of the **Overall LIMS Advantages** that a laboratory water/wastewater facility can realize:

- Reduced turnaround times
- Automated reporting for state agencies (EDDs)
- Reduction in paperwork
- Improved data quality (reduction in errors)
- Improved operational efficiency
- Increased productivity (reduction of mundane tasks)
- Productivity gains (auto-reporting)
- Integration with other departments/business systems

Your LIMS and Laboratory Automation Solutions Provider

Contact Information

Chuck Hindbaugh
Accelerated Technology Laboratories, Inc.
496 Holly Grove School Rd
West End, NC 28387

Phone: 800-565-LIMS (5467)
Email: chindbaugh@atlab.com

Your LIMS and Laboratory Automation Solutions Provider

2008 NEMC Proceedings

ENSURING DATA QUALITY

Purpose (or Reason) for Using Sound Science and Following QA/QC Processes and Procedures

James J. McAteer, Jr.
Managing Member
QA/QC Solutions, LLC
7532 Champion Hill Rd. SE
Salem, OR 97306
503-763-6948
jjmcateer@msn.com

ABSTRACT

The purpose (or reason) for using sound science and following quality assurance and quality control (QA/QC) processes and procedures with regards to using analytical data is really quite simple: if the overall quality usability, and limitations of the data is not known or clearly defined, then the data collected may not be usable for its intended purpose(s) and the decision(s) made may be incorrect. It is important to remember to so everything possible to make sure the data collected in the field and in the laboratory are scientifically meaningful, valid, usable and legally defensible.

Presented below is a very brief overview of some of the QA/QC processes and procedures that should be completed to be able to define the overall quality of analytical data. Next, a very brief summary regarding data verification, data validation, data quality assessment (DQA), and data usability evaluation is presented. To more clearly illustrate the purpose (or reason) for using sound science and following QA/QC processes and procedures with regards to using analytical data, two examples are presented. One example is to show how incorrect interpretations and decisions are be made when the most appropriate analytical method(s) was not used. The other example is to show how incorrect interpretations and conclusions are made when "sound science" is not used and the available data reported by the laboratory are not properly evaluated.

It should be noted that all elements regarding QA/QC processes and procedures, data verification, data validation, DQA, and data usability evaluation cannot be presented herein. The main purpose of the information presented here in to show how when one, or more of the required elements are not completed or are completed incorrectly will result in making an incorrect decision.

INTRODUCTION

When completing environmental investigations, chemical data may be used for many purposes — delineating the nature and extent of contamination, verifying that a contaminated site has been adequately cleaned up, identifying and quantifying potential risks to the environment and/or human health, and many other reasons. For data to be usable for its intended purpose(s) it must be of sufficient quality and quantity to know that the decisions that are made have an acceptable and known degree of confidence. Further, the data collected must be of such quality and quantity to withstand third-party scrutiny and be legally defensible.

Assessment of the overall quality and usability of analytical data requires meticulous attention to the "details" as well as an understanding of the "big picture." Establishing well-defined management policies and procedures, QA/QC processes and procedures, and quality assessment checkpoints are necessary to meet the data quality objectives (DQOs)[1-3] of any project. It is very likely that by not instituting and following a systematic planning process may result in not collecting the right type of data, making incorrect decisions, incurring unnecessary costs, and/or resulting in actions by applicable regulatory agencies.

Appropriate decisions (or end uses of the data) are made with an acceptable degree of confidence by knowing, in part, the following: 1) the purpose of the project was clearly stated[1,3]; 2) appropriate DQOs[1-3] were established; 3) proper types and numbers of samples were collected, that sampling locations were appropriate, and that correct sample collection techniques were used[2-5]; 4) that appropriate analytical methods were used and the analyses were completed properly[2-5]; 5) data verification and data validation[3,6-8] were properly completed and that the overall quality of the data and its limitations were clearly documented); 6) the data sets were subjected to a proper DQA[3,6-8] and data usability evaluation and the findings documented in a report; and, 7) that a "reality check" was completed to confirm the findings and that any decision(s) made were correct.

OVERVIEW OF QA/QC PROCESSES AND PROCEDURES

Proper planning is essential at the start of any project. The overall project objectives should be clearly stated and understood by all team members (e.g., project mangers and staff, field sampling team members, applicable laboratory staff, and QA/QC personnel). Existing data that may be available should be thoroughly reviewed to assess its quality and usefulness, and to help identify data gaps that may need to be filled to meet project objectives — in other words you must do your research. Logical and attainable DQOs (including project quality objectives [PQOs] and measurement quality objectives [MQOs]) should be established. Pertinent documents (e.g., the work plan, field sampling plan, and quality assurance project plan) should be prepared. Appropriate field sampling design (e.g., location, number, and type of samples) and sampling techniques should be determined. The most appropriate analytical methods should be selected to try to meet the established DQOs, PQOs, MQOs, reporting limit requirements, and data quality indicators (DQIs)[3] (e.g., end-point measurements for precision, accuracy, representativeness, comparability, completeness, and sensitivity). A qualified analytical laboratory (or laboratories) should be selected and a technical system audit[8] (TSA) may also be required.

It is important to remember to use sound science and follow appropriate and well-defined QA/QC processes and procedures. This is a process to be able to be confident with a known degree of certainty of the overall quality (or usefulness) and potential limitations of the data that is collected. Using data of poor quality and insufficient quantity will always result in making incorrect decisions and incurring unnecessary expenses.

DATA VERIFICATION, DATA VALIDATION, AND DATA QUALITY ASSESSMENT, AND DATA USABILITY EVALUATION

Data verification, data validation, DQA, and data usability evaluation are tasks that should be completed to understand the overall quality of the data, to be able to identify if there are potential limitations with the data, and to be able to know with a known degree of confidence that the data are usable for its intended purpose(s). All too often, however, these fundamental tasks are not considered as really necessary by many data users because of the misconception that "approved agency methods" were used, the analyses were conducted by a certified/approved laboratory, it's money not worth spending, and a plethora of other excuses.

It is important understand why data verification and data validation are necessary. Some reasons for completing data verification[3,6-8] are, in part, to ensure that all procedures specified in the project planning documents were followed; that correct protocols were used in the field to collect samples; that the samples were correctly prepared and analyzed at the laboratory; to verify the completeness of the data set and supporting documentation; and, to verify the accuracy of the database. Some reasons for completing data validation[3,6-8] are, in part, to evaluate the technical quality of the verified data with respect to the project DQOs, MQOs, and PQOs, assess and document performance of field and analytical process, and determine compliance with specified requirements (e.g., contractual, method-specific, QAPP requirements, etc.). There are many other reasons why completing data verification and data validation are important, but are not discussed herein.

After the field and analytical data have been verified and validated, a DQA and data usability evaluation (i.e., a thorough scientific and statistical analysis of the data) should be conducted. This step is a means to determine if the overall quality of the data is sufficient to support its intended purpose(s) and to identify (and possibly minimize) the areas of uncertainty in the decision(s) that are made. The general purpose of completing this "part" of the overall QA/QC process is to evaluate the quality of the data collected during sampling and analysis. This will assist with answering such questions as can a decision be made with the desired degree of confidence with respect to the quality of the data, how well has the sampling design and supporting data meet the DQOs established during the systematic planning process, and does the data support or refute the assumptions that were made at the beginning of the project.

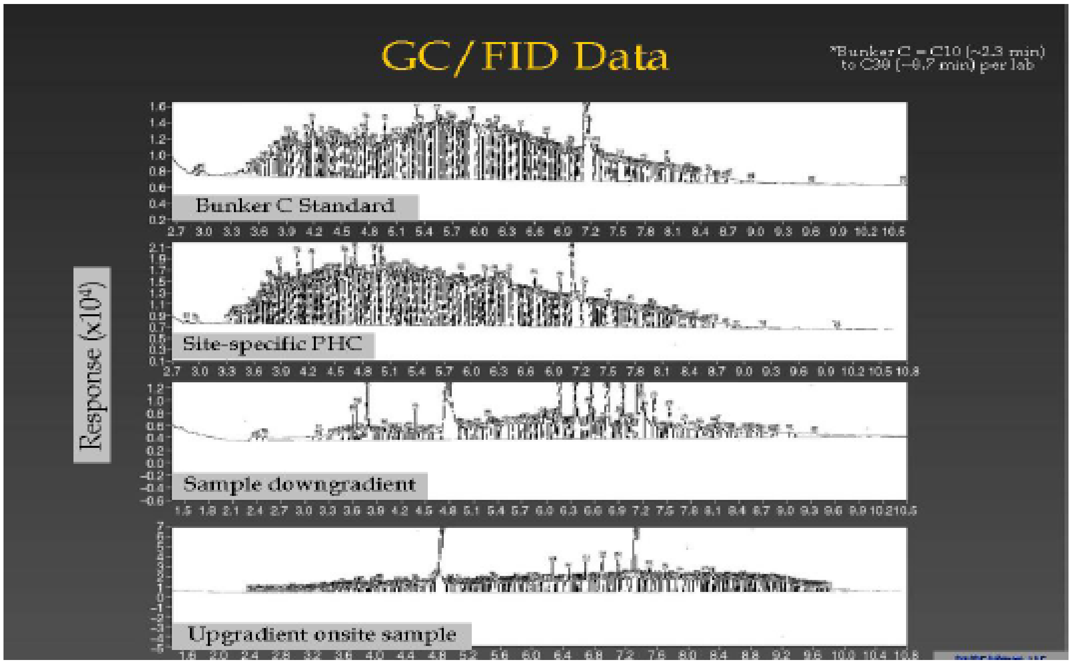
When appropriate project planning, data verification, data validation, DQA, and data usability evaluation are not completed, or are completed without the appropriate level of detail, then the overall reliability of the data may exhibit a much higher degree of uncertainty. In other words, if there are significant errors associated with the field data, the laboratory data, and/or the interpretation of the data, then the subsequent decisions that are made will most likely be incorrect.

EXAMPLE 1: APPROPRIATE ANALYTICAL METHOD NOT USED

When an inappropriate analytical method is used, the data obtained may not be of the necessary quality (or type) needed to meet its intended purpose. This is an example where it was necessary to determine the reliability of historical and recent data sets to evaluate if site-specific petroleum hydrocarbons (PHCs) were migrating offsite. The concern was to find out if site-specific PHCs are possibly impacting surrounding groundwater and migrating toward a nearby river due to a potential failure of a barrier wall installed at the site. The available data included analyses for diesel- and residual-range petroleum hydrocarbons analyzed using gas chromatography/flame ionization detection (GC/FID) on groundwater samples collected in and around the site over several years.

After reviewing the existing PHC data (Figure 1), it was determined it was not of sufficient quality to state with definitive confidence that the site-specific PHC was present, or not present, in selected samples. This determination was made, in part, because the sample extracts were not subjected to silica gel column cleanup to remove potential biogenic interferences and late-eluting chromatographic peaks attributed to paraffin compounds indicative of plant waxes of terriginous origin were often, but not always, included in quantification. In addition, the laboratory did not consistently flag (or qualify) the results reported. For example, data were flagged to indicate that an exact match to the Bunker C fuel oil standard that was used for compound identification was not apparent in the samples, or the that the PHC in the samples appears to be weathered, or the results were not flagged implying that unweathered Bunker C fuel oil was present. The problem was that the data were not consistently flagged.

Figure 1: GC/FID Diesel- and Residual-Range PHC Data



To more confidently answer the questions of concern, detailed chemical analyses (e.g., chemical fingerprinting) were required to determine the chemical composition(s) of the site-specific PHC (i.e., a Bunker C fuel oil). Also, the new detailed chemical analyses would help with evaluating if any PHC that may be present in the surrounding offsite groundwater can be attributed to the PCH from the site and to provide sufficient data to evaluate if there is a similarity in any PHCs in samples from the site and the surrounding groundwater.

The detailed chemical fingerprinting analyses that were determined to be appropriate at this time included analyses for saturated hydrocarbons (i.e., *n*-Alkanes) using GC/FID, polycyclic aromatic hydrocarbons (PAHs) and alkylated PAHs using gas chromatography/mass spectrometry (GC/MS) operated in the selected ion monitoring (SIM) mode, and chemical biomarkers (e.g., steranes and triterpanes) using GC/MS SIM.

To facilitate the data analysis, a sample indicative of the site-specific PCH was collected from an extraction well to be used as the reference sample to compare to all other samples. Other groundwater samples were collected from locations upgradient (onsite) and downgradient (offsite). The new data were verified, validated, and evaluated. The evaluation involved directly comparing the distributions and concentrations of the *n*-Alkanes (Figure 2a), the PAHs and alkylated PAHs (Figure 2b), and the biomarker compounds (Figure 2c). The evaluation of the PHC "fingerprints" was completed by reviewing the sample chromatograms, mass spectra, and histograms of the data obtained. In each of the figures the order sample locations is the site-specific PHC, a sample immediately downgradient of the barrier wall, a sample further downgradient, and a sample upgradient and onsite.

Figure 2a: *n*-Alkane Data

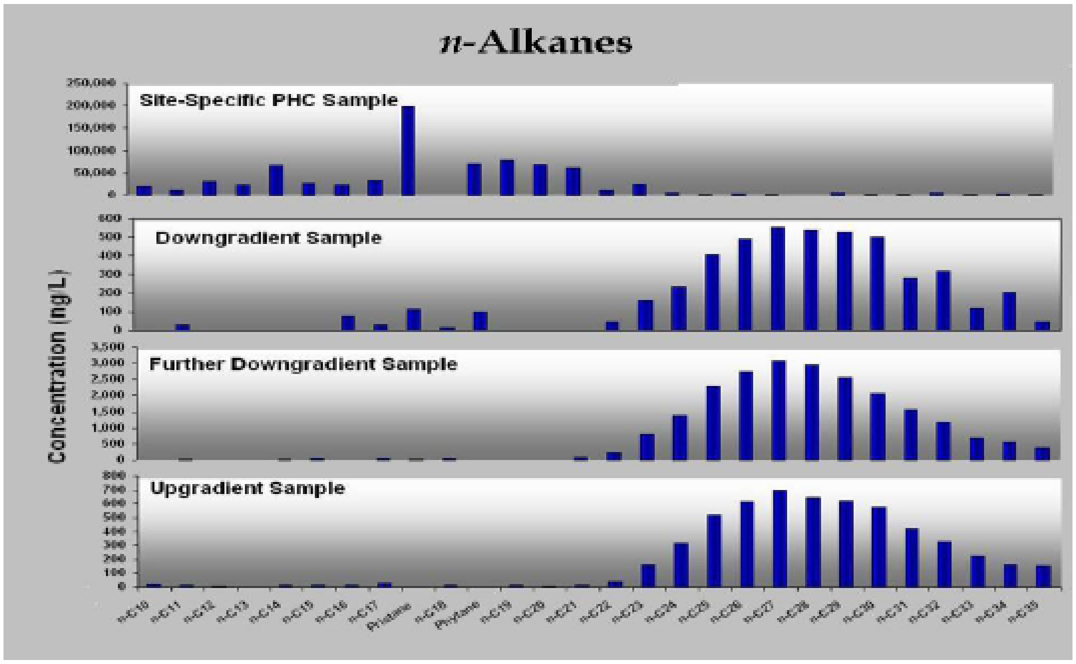


Figure 2b: PAH and Alkylated PAH Data

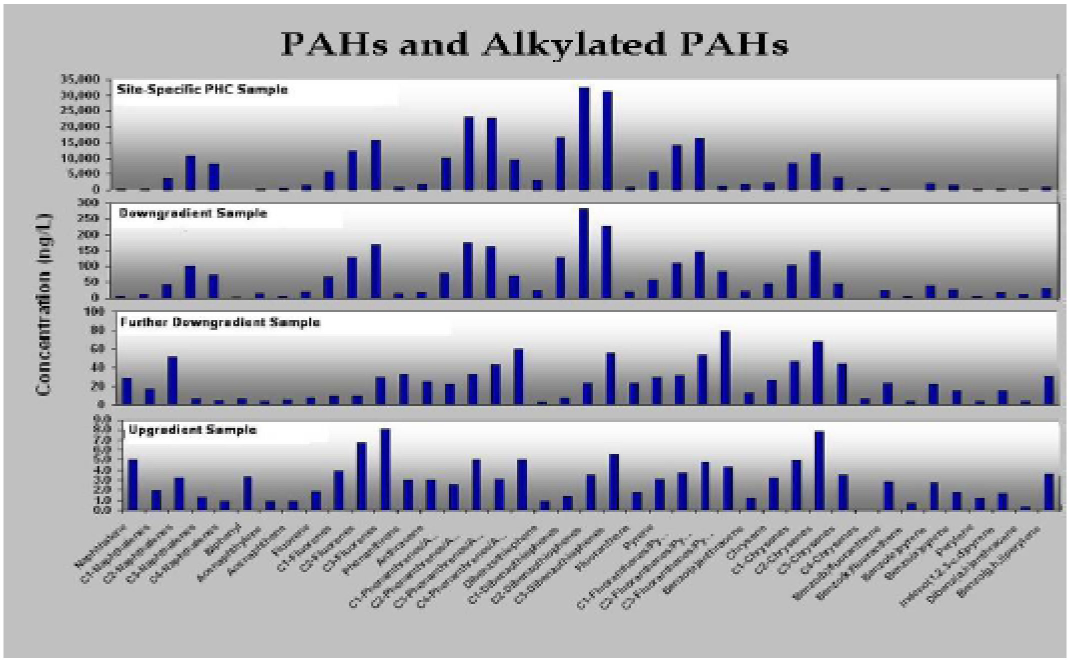
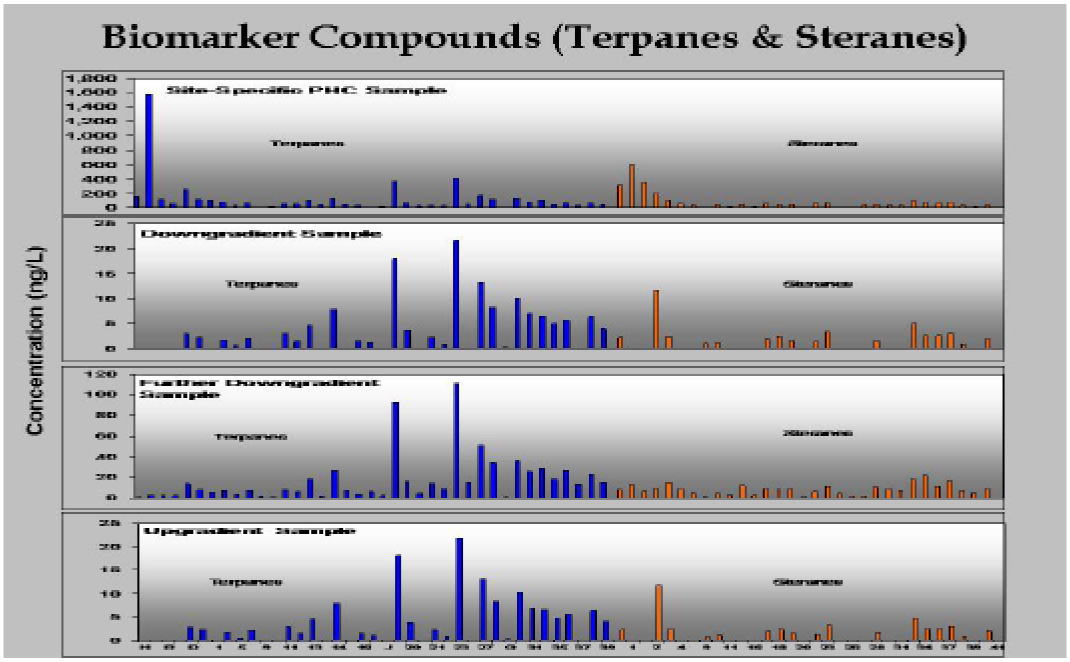


Figure 2c: Biomarker Compound Data



The new data gathered indicates that a slightly weathered heavy fuel oil (i.e., No. 6 or Bunker C fuel oil) is present onsite, which agrees with historical site usage records. The distributions of the saturated hydrocarbons (i.e., *n*-Alkanes), PAHs and alkylated PAHs, and the chemical biomarkers (i.e., steranes [blue histograms in Figure 2c] and terpanes [orange histograms in Figure 2c]) are not likely related to the site-specific PHC.

It is readily apparent upon review of the new data that a similar PAH/Alkylated PAH fingerprint can bee seen between the site-specific PHC and the downgradient sample (Figure 2b, first and second histogram plots). It is important to note that the *n*-Alkane and biomarker compound signatures (Figures 2a and 2c, respectively) are markedly different between these two samples and indicates there is another source other than the site PHC that also results in a similar PAH profile. Upon further research of historical records, the similarity of the PAHs in the one downgradient sample and the site sample can be attributed to a similar type of fuel oil that was likely present in a relic tank that was excavated in the past at a location near to where the affected sample was collected.

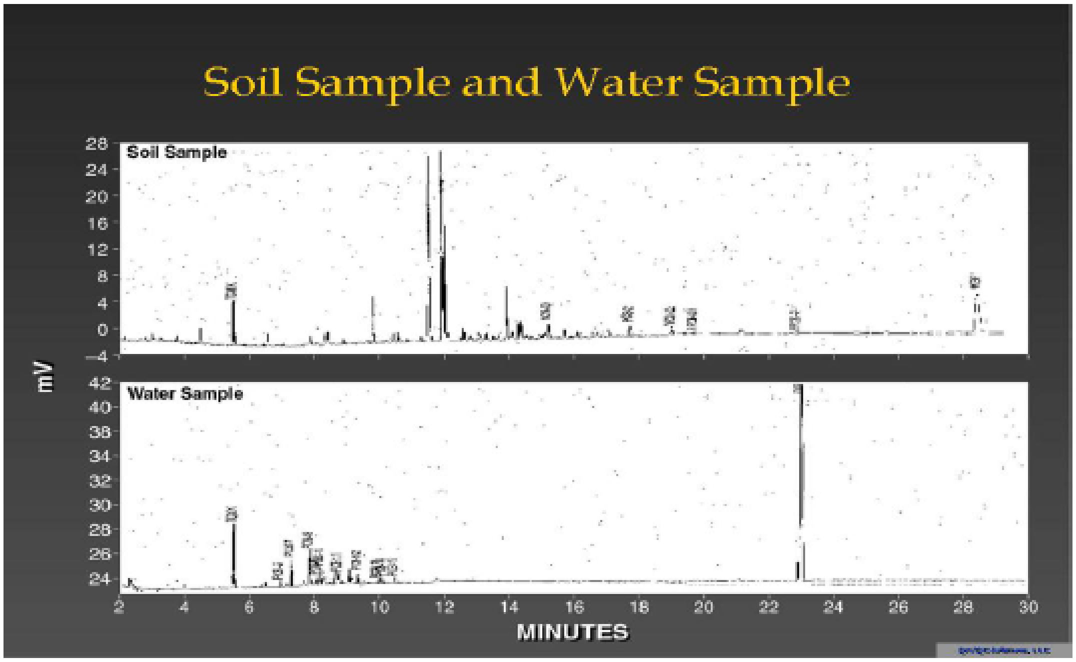
The results of the new data indicate that the site-specific PHCs do not appear to be migrating offsite at this time and is not the source of the trace (or low levels) of a PHCs that were found in the other groundwater samples. Based on the *n*-Alkane data, the predominate constituent present in most of the other samples are paraffins that can be attributed to plant waxes of terriginous origin. The conclusion is that by analyzing the samples with more appropriate chemical methods the data obtained more confidently support the interpretation that the site-specific PHC is not impacting surrounding groundwater, there is no threat to the river, and that there is no indication that the barrier wall has failed at this time.

EXAMPLE 2: YOU CAN'T MAKE THE DATA SAY WHAT YOU WANT

It is not possible to make good quality data say what you want by making unsubstantiated interpretations of the data and making factually incorrect statements. This is an example where it was necessary to determine the reliability of the identification and quantification of polychlorinated biphenyls (PCBs) reported for analyses completed on surface soil and groundwater samples and evaluate if the PCBs may be from the same source. Available information included site investigation reports, expert reports, and analytical data. Aroclor® 1260 was reported as detected in soil samples (Figures 3a and 3b) and Aroclor® 1242 was reported as detected in groundwater (Figures 3a and 3c).

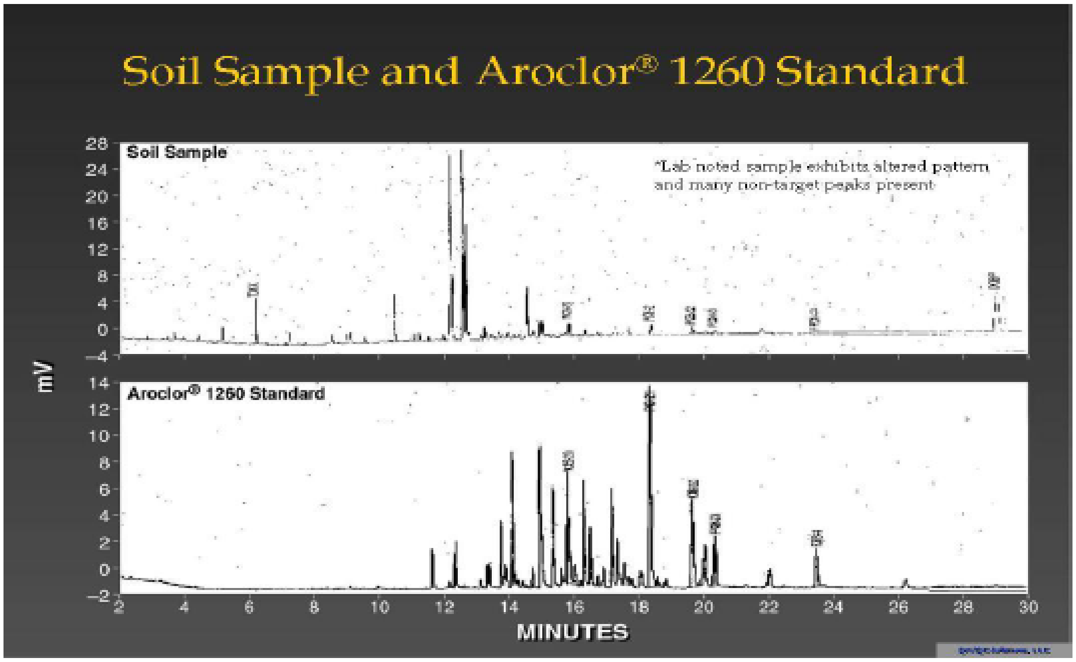
The "expert" in this project stated that Aroclor® 1260 is present in the surface soil (this is plausible) and the Aroclor® 1242 in the groundwater (this is also plausible) likely resulted from contaminated soil that was introduced during well installation/construction or perhaps is due to degradation of Aroclor® 1260 during migration from the soil into the groundwater (both of these suggestions are not plausible).

Figure 3a: Soil Sample and Water Sample Chromatograms



Soil Sample and Water Sample

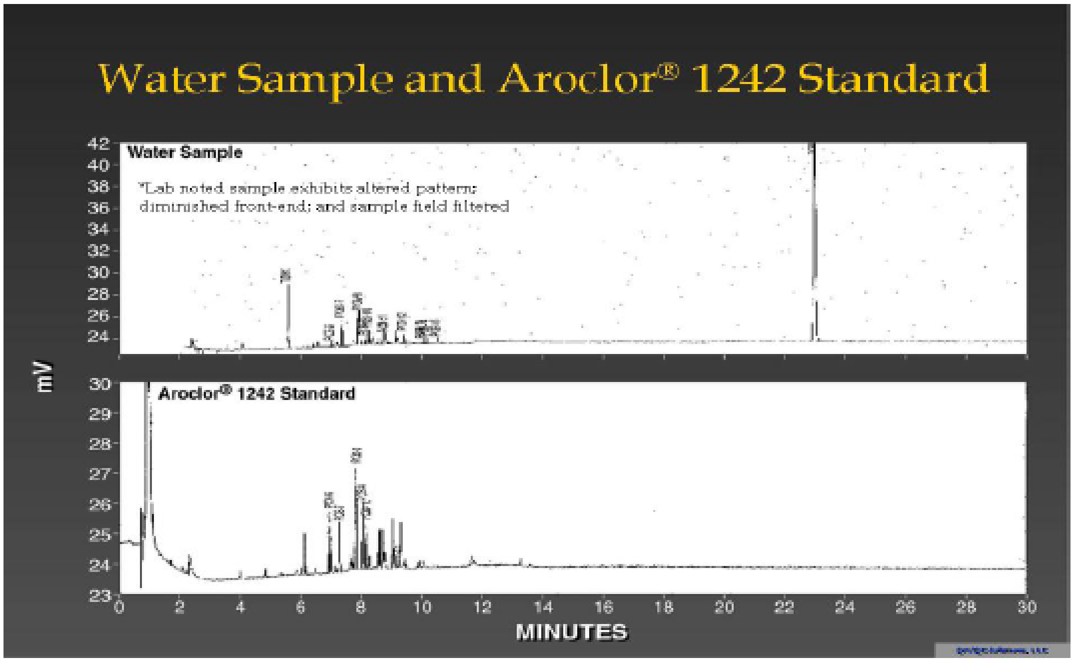
Figure 3b: Soil Sample and Aroclor® 1260 Standard Chromatograms



Soil Sample and Aroclor® 1260 Standard

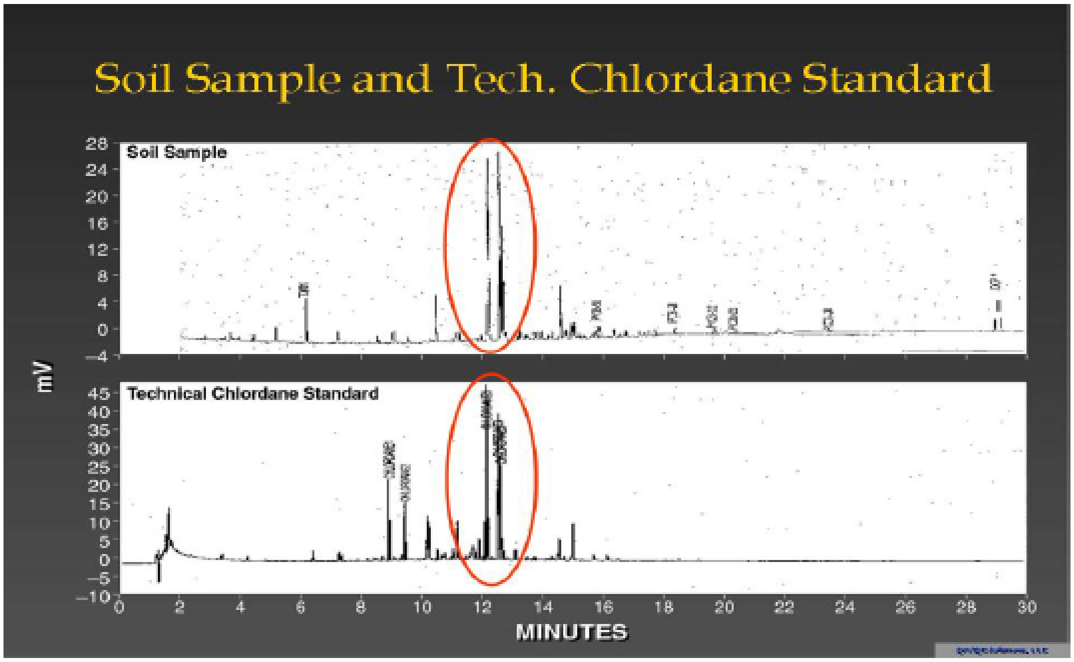
*Lab noted sample exhibits altered pattern and many non-target peaks present

Figure 3c: Water Sample and Aroclor® 1242 Standard Chromatograms



Water Sample and Aroclor® 1242 Standard

Figure 3d: Soil Sample Comparison to Chlordane Standard Chromatograms



Soil Sample and Tech. Chlordane Standard

To facilitate data review, the original PCB data were obtained (e.g., chromatograms and instrument printouts). The review of the data indicated it is plausible that a weathered Aroclor® 1260 is present in the surface soil (Figure 3b). More importantly, however, the presence of multiple non-PCB peaks (as was correctly noted by the laboratory) is most likely attributed to the technical grade chlordane (an organochlorine pesticide). To confirm the presence of technical grade chlordane, the laboratory was contacted and agreed this organochlorine pesticide was likely present (see Figure 3d) in the soil sample. It should be noted that the laboratory provided a chromatogram of a standard of technical grade chlordane that was analyzed on the same instrument around the same time that the sample PCBs analyses were completed. Further, review of the chromatograms also indicated it is plausible that a relatively unweathered Aroclor® 1242 (or possibly Aroclor® 1016) was present (Figure 3c) in the groundwater sample.

While the laboratory data was of overall good quality, the problem is that the arguments by the "expert" could not be supported. Specifically, the explanation that the presence of Aroclor® 1242 in the groundwater was due to contaminated surface soil introduced during well installation/construction, or is due to the weathering of Aroclor® 1260 in the surface soil as it migrated from the surface soil to the groundwater, or is due to Aroclor® 1242 that was once present in the surface soil are all preposterous rationales and cannot be supported. It is not possible to "create" a relatively unweathered Aroclor® 1242 (or possibly Aroclor® 1016) by the dechlorination (or degradation) of a very weathered Aroclor® 1260 that also has technical grade chlordane present via known biological, chemical, or physical processes. Furthermore, if Aroclor® 1242 (or possibly Aroclor® 1016) was present in the soil, a chromatographic "fingerprint" would most likely have been evident in the soil sample chromatograms, but was not.

By conducting an objective review and validation of the data reported, working openly with the analytical laboratory, and using sound science, it was shown that technical grade chlordane is very likely present in the soil and that this mixture is likely to be more of a concern than the weathered Aroclor® 1260. The detection of Aroclor® 1242 (or possibly Aroclor® 1016) in the groundwater was confirmed, but its presence cannot be attributed to the Aroclor® 1260 and technical grade chlordane found in the surface soil. The interpretations made by the "expert" regarding PCB identification, sources, and transport and fate assumptions were factually inaccurate based on the data reported. The PCBs detected in the surface soil and groundwater are from two different sources. Overall, the conclusions drawn from the existing data were unfounded and there was not sufficient evidence presented to substantiate the claims made and the findings given were not legally defensible.

CONCLUSIONS

The examples shown above are just a few of many to illustrate what can happen when incorrect analytical methods are used, when data of insufficient quality is used but cannot support its intended use(s), when incorrect interpretations are made but cannot be supported by the available data, or how incorrect (or unfounded) decisions will be made. These types of issues will result in increased project costs, may result in regulatory actions, or wind up in litigation — how much of a chance are you willing to take? If the overall quality, usability, and limitations of the data collected are not known or clearly defined, then the data collected may not be usable for its intended purpose(s) and the decision(s) made may be incorrect. Some key points to keep in mind are:

- Develop and follow appropriate and well-defined applicable QA/QC processes and procedures from start to finish in every project
- Get the sampling, QA, and laboratory staff involved during initial project planning
- Require that the analytical data are verified and validated is completed by an experienced professional and that the results are documented in a clear and concise report
- Complete a DQA and usability evaluation using an experienced professional and that the findings are documented in a clear and concise report
- Make sure the data, interpretations and conclusions drawn from the data, and the decisions that are sound of the sufficient quality to minimize uncertainty
- Critically evaluate and re-evaluate the data, do a "reality check" to make sure the data make sense, and always use the scientific method.

In closing it is important to remember that using sound science and following appropriate QA/QC processes and procedures are critical to make sure the data that are collected and used are scientifically meaningful, valid, usable, and legally defensible! It's all about using the scientific method!

REFERENCES

1. U.S. EPA. 2006. *Guidance on Systematic Planning using the Data Quality Objective Process*. EPA QA/G-4. EPA/240/B-06/001. U.S. Environmental Protection Agency, Office of Environmental Information, Washington, DC.

2. Crumbling, D.; Groenjes, C.; Lesnik, B.; Lynch, K.; Shockley, J.; Van, E. E. J.; Howe, R.; Keith, L.; McKenna, J. *Managing Uncertainty in Environmental Decisions. Environ. Sci. Technol.* **2001**, *35* (19), 404-409.

3. U.S. EPA. 2005. Intergovernmental Data Quality Task Force. *Uniform Federal Policy for Quality Assurance Project Plans.* http://www.epa.gov/swerffrr/documents/qualityassurance.htm. Accessed March 2, 2008. U.S. Environmental Protection Agency.

4. U.S. EPA. 2001. *Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual*. EPA-823-B-01-002. U.S. Environmental Protection Agency, Office of Water, Washington, D.C.

5. U.S. EPA. 1995. QA/*QC Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations–Chemical Evaluations*. EPA 823-B-95-001. U .S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Standards and Applied Science Division, Washington, DC.

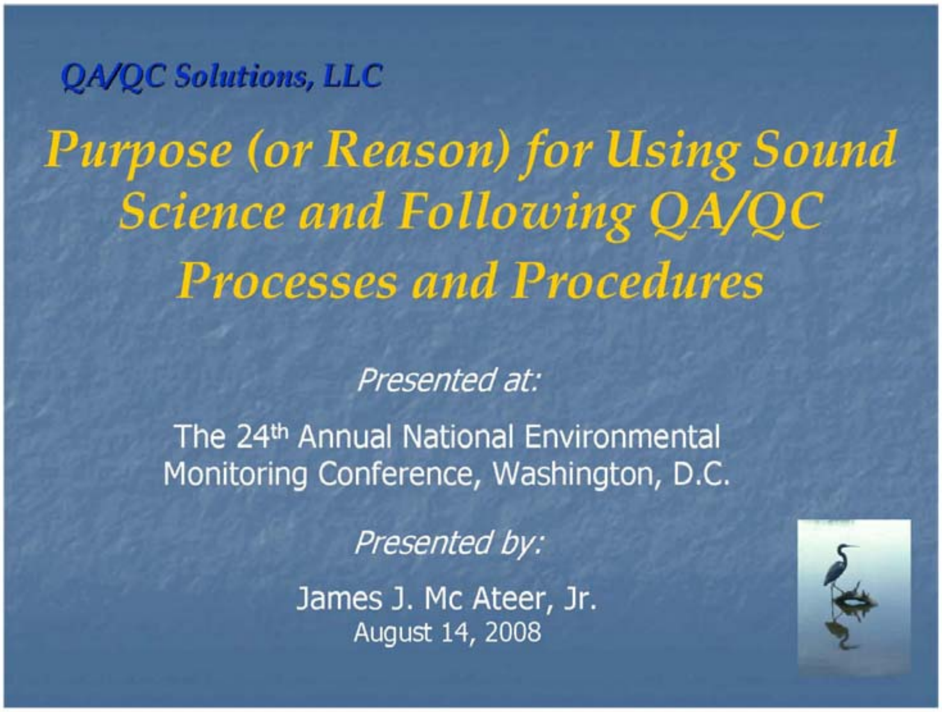
6. U.S. EPA. 2002. *Guidance on Environmental Data Verification and Data Validation*. EPA QA/G-8. EPA/240/R-02/004. November 2002. U.S. Environmental Protection Agency, Office of Environmental Information, Washington DC.

7. U.S. EPA. 2006. *Data Quality Assessment: A Reviewer's Guide*. EPA QA/G-9R. EPA/240/B-06/002. February 2006. U.S. Environmental Protection Agency, Office of Environmental Information, Washington DC.

8. U.S. EPA. *Guidance for Data Usability in Risk Assessment (Parts A and B) Final*. Publications 9285.7-09A and 9285.7-09B. EPA-540/G-90-008. . U.S. Environmental Protection Agency, Office of Emergency Response and Remedial Response, Washington DC. 1992

9. U.S. EPA. 2000. *Guidance on Technical Audits and Related Assessments for Environmental Data Operations*. Final. EPA QA/G-7. EPA/600/R-99/080. U.S. Environmental Protection Agency, Office of Environmental Information, Washington DC.

Note: The sources of the data, site locations, and laboratories discussed herein are not mentioned to maintain confidentiality and are not necessary to illustrate the opinion of the author. All elements regarding all aspects of QA/QC processes and procedures, data verification, data validation, DQA, and data usability evaluation cannot be presented this type of paper.



QA/QC Solutions, LLC

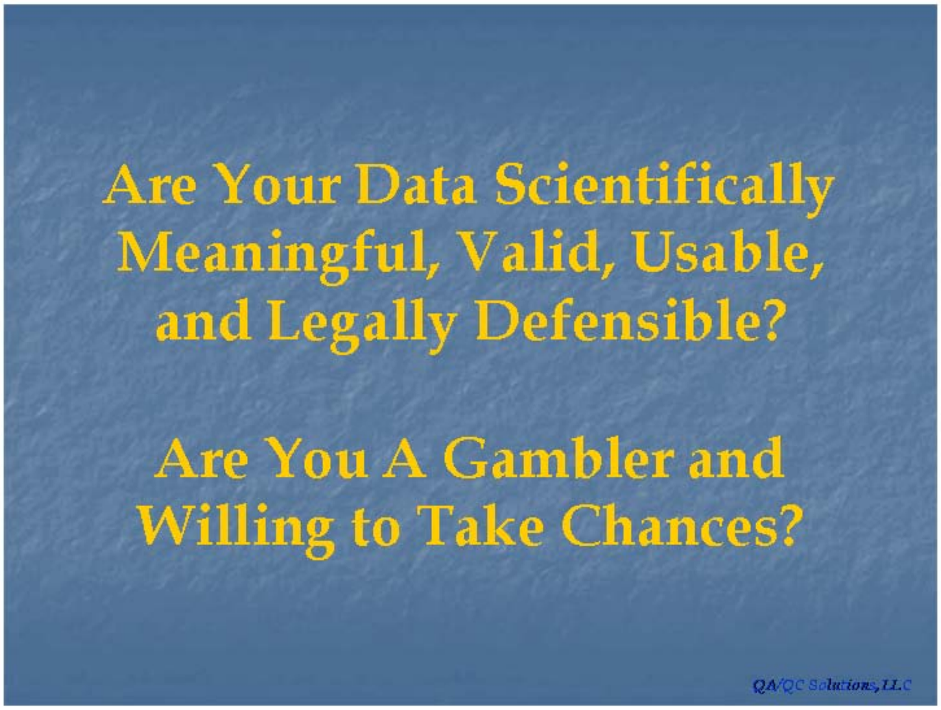
Purpose (or Reason) for Using Sound Science and Following QA/QC Processes and Procedures

Presented at:

The 24th Annual National Environmental
Monitoring Conference, Washington, D.C.

Presented by:

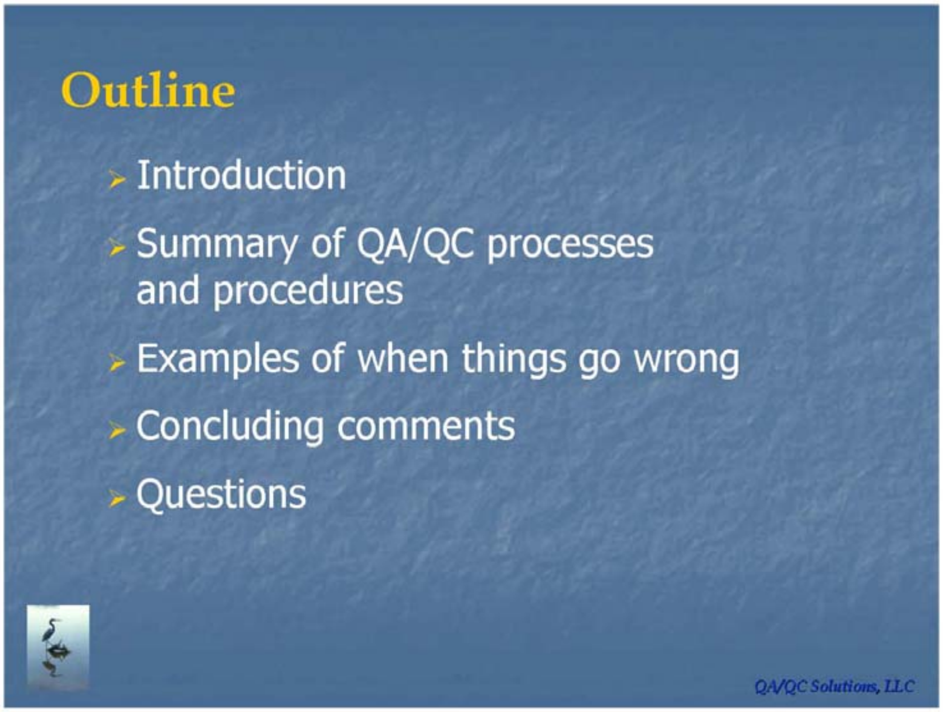
James J. Mc Ateer, Jr.
August 14, 2008



Are Your Data Scientifically Meaningful, Valid, Usable, and Legally Defensible?

Are You A Gambler and Willing to Take Chances?

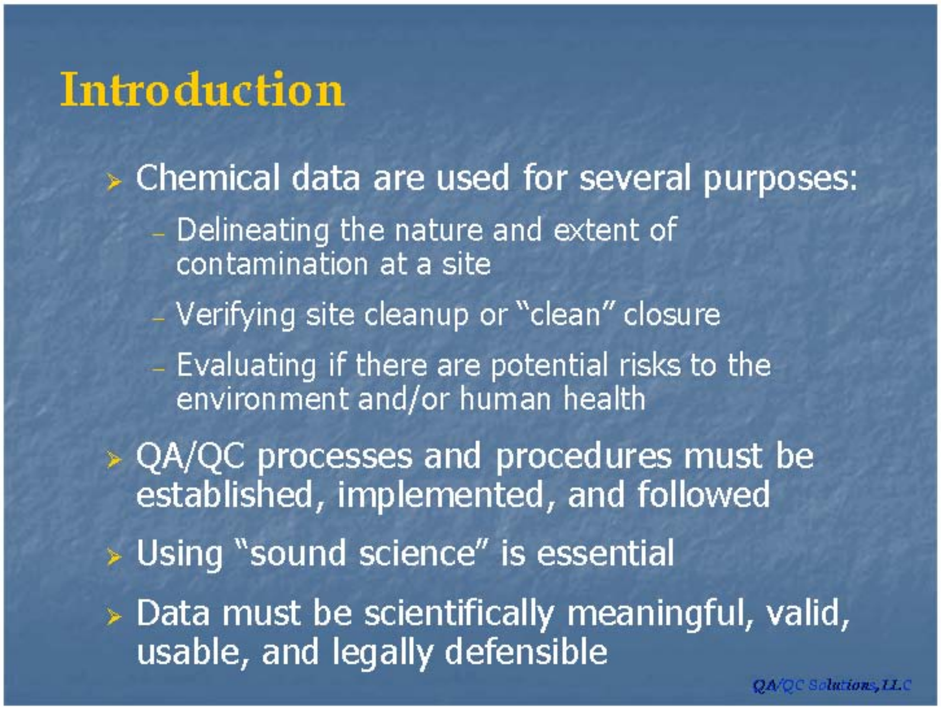
QA/QC Solutions, LLC



Outline

- Introduction
- Summary of QA/QC processes and procedures
- Examples of when things go wrong
- Concluding comments
- Questions

QA/QC Solutions, LLC



Introduction

- Chemical data are used for several purposes:
  - Delineating the nature and extent of contamination at a site
  - Verifying site cleanup or "clean" closure
  - Evaluating if there are potential risks to the environment and/or human health
- QA/QC processes and procedures must be established, implemented, and followed
- Using "sound science" is essential
- Data must be scientifically meaningful, valid, usable, and legally defensible

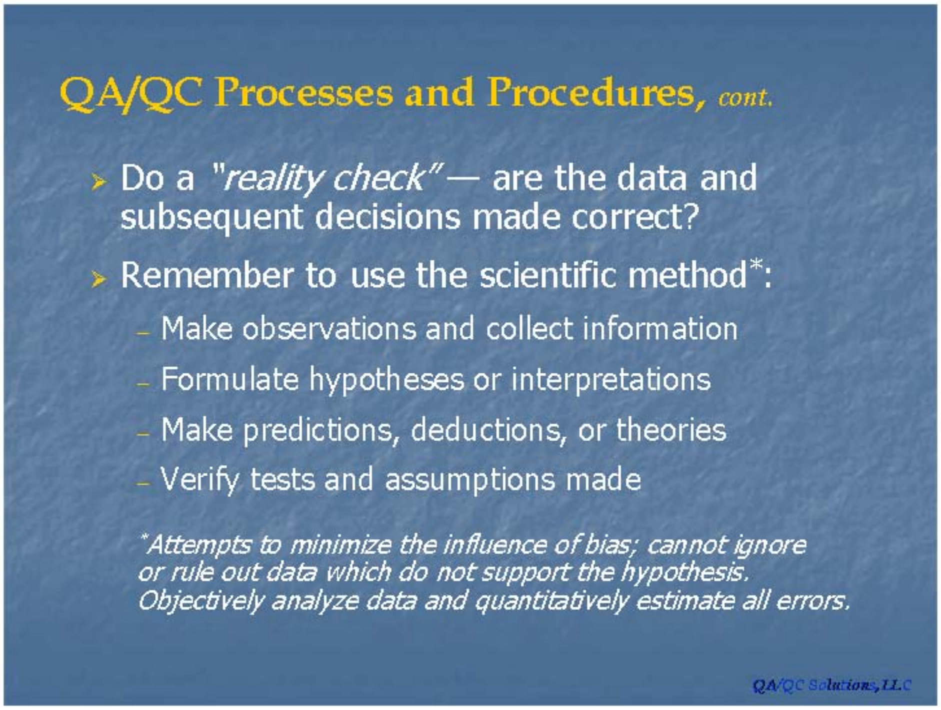
QA/QC Solutions, LLC

QA/QC Processes and Procedures

- Rigorous QA/QC requires meticulous attention to details
- Understand the "big picture" — know the purpose(s) and do the research
- Establish logical (and attainable) DQOs, PQOs, MQOs, DQIs, etc.
- Prepare appropriate and complete work plans, FSPs, QAPPs, etc.
- Get sampling, QA, and laboratory staff involved during initial planning

QA/QC Processes and Procedures, *cont.*

- Identify appropriate sampling rationale (e.g., type, number, and location of samples)
- Use correct sample collection technique(s)
- Use most appropriate analytical method(s)
- Define type of data deliverables needed
- Complete data verification and data validation
- Conduct a DQA and usability evaluation
- Prepare a data quality/usability report

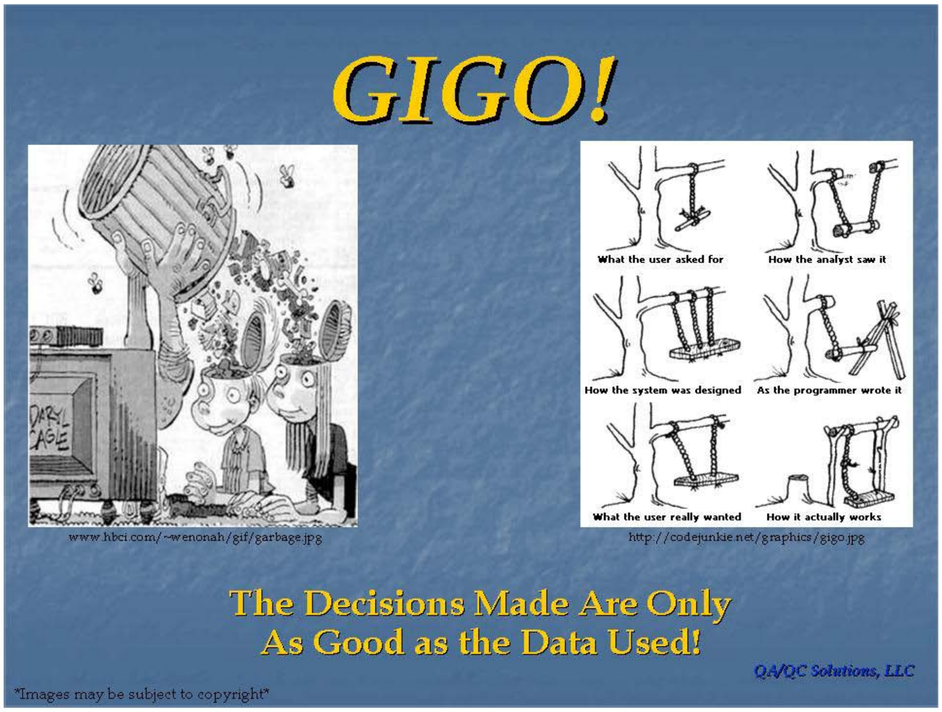


QA/QC Processes and Procedures, *cont.*

- Do a *"reality check"* — are the data and subsequent decisions made correct?
- Remember to use the scientific method*:
  - Make observations and collect information
  - Formulate hypotheses or interpretations
  - Make predictions, deductions, or theories
  - Verify tests and assumptions made

**Attempts to minimize the influence of bias; cannot ignore or rule out data which do not support the hypothesis. Objectively analyze data and quantitatively estimate all errors.*

QA/QC Solutions, LLC



GIGO!

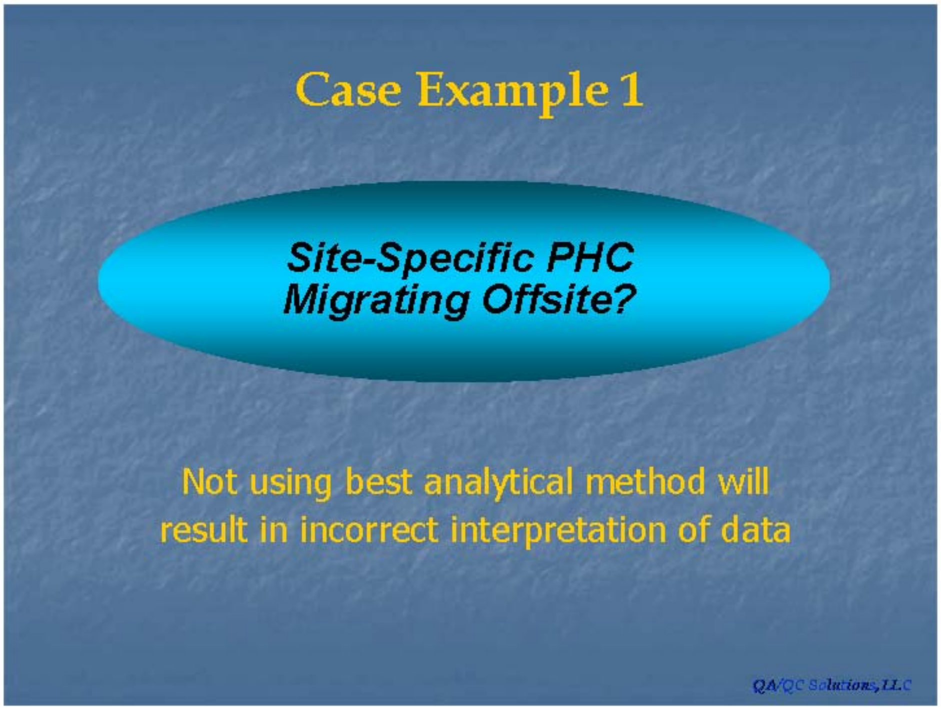
www.hbci.com/~wenonah/gif/garbage.jpg

http://codejunkie.net/graphics/gigo.jpg

The Decisions Made Are Only As Good as the Data Used!

QA/QC Solutions, LLC

"Images may be subject to copyright"

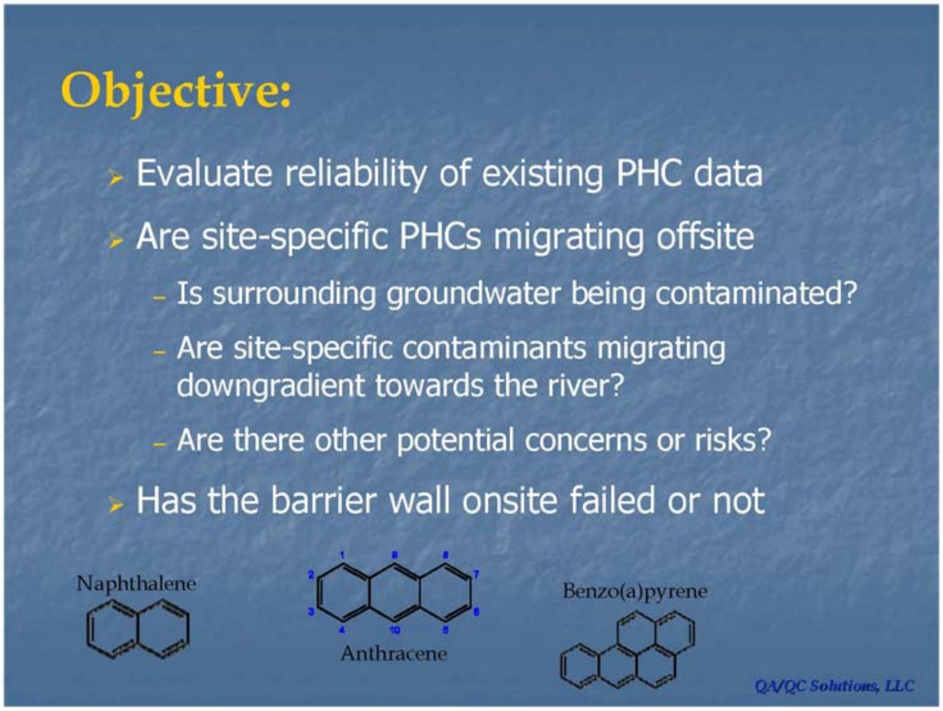


Case Example 1

Site-Specific PHC Migrating Offsite?

Not using best analytical method will result in incorrect interpretation of data

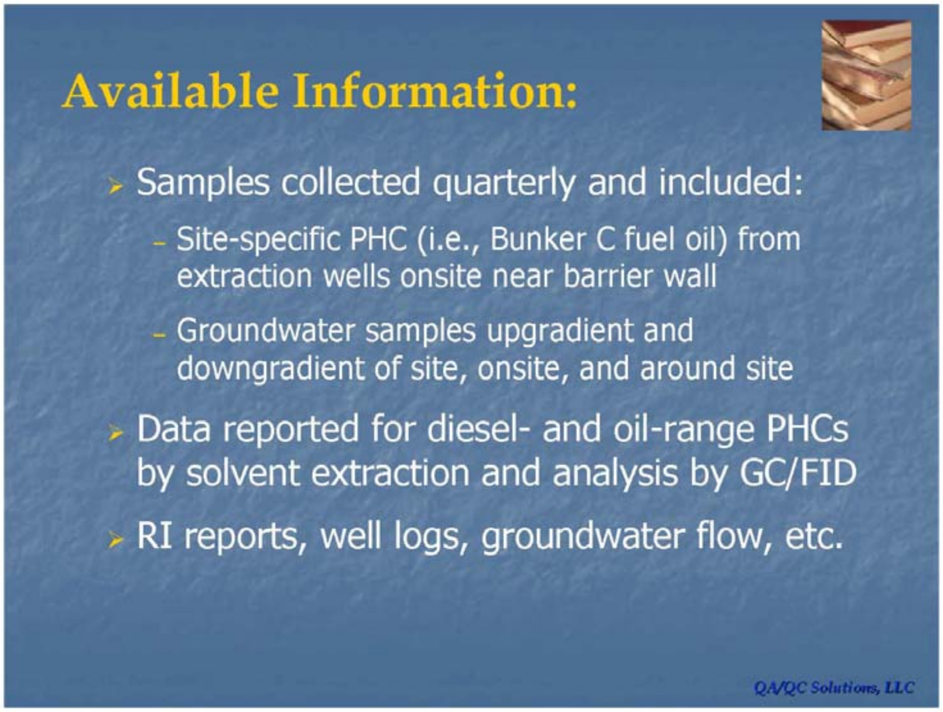
QA/QC Solutions, LLC



Objective:

- Evaluate reliability of existing PHC data
- Are site-specific PHCs migrating offsite
  - Is surrounding groundwater being contaminated?
  - Are site-specific contaminants migrating downgradient towards the river?
  - Are there other potential concerns or risks?
- Has the barrier wall onsite failed or not

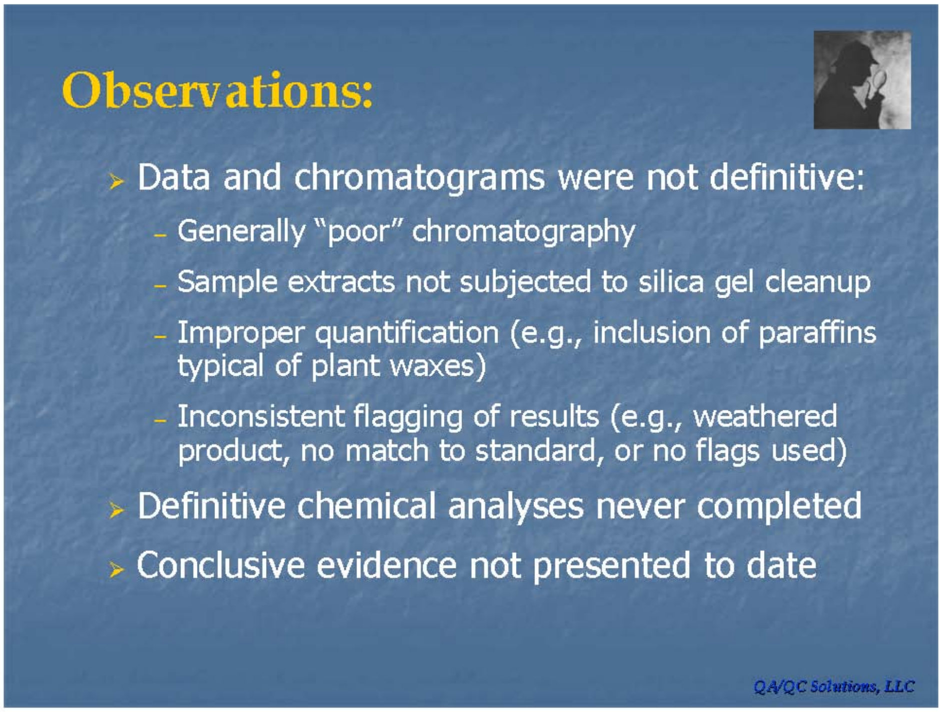
QA/QC Solutions, LLC



Available Information:

- Samples collected quarterly and included:
  - Site-specific PHC (i.e., Bunker C fuel oil) from extraction wells onsite near barrier wall
  - Groundwater samples upgradient and downgradient of site, onsite, and around site
- Data reported for diesel- and oil-range PHCs by solvent extraction and analysis by GC/FID
- RI reports, well logs, groundwater flow, etc.

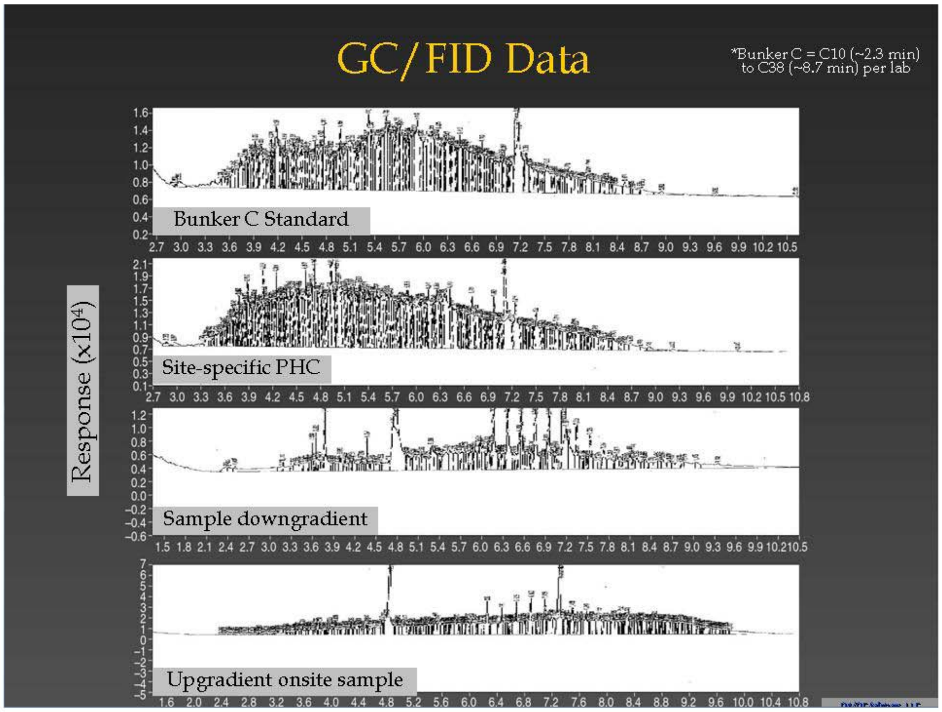
QA/QC Solutions, LLC



Observations:

- Data and chromatograms were not definitive:
  - Generally "poor" chromatography
  - Sample extracts not subjected to silica gel cleanup
  - Improper quantification (e.g., inclusion of paraffins typical of plant waxes)
  - Inconsistent flagging of results (e.g., weathered product, no match to standard, or no flags used)
- Definitive chemical analyses never completed
- Conclusive evidence not presented to date

QA/QC Solutions, LLC



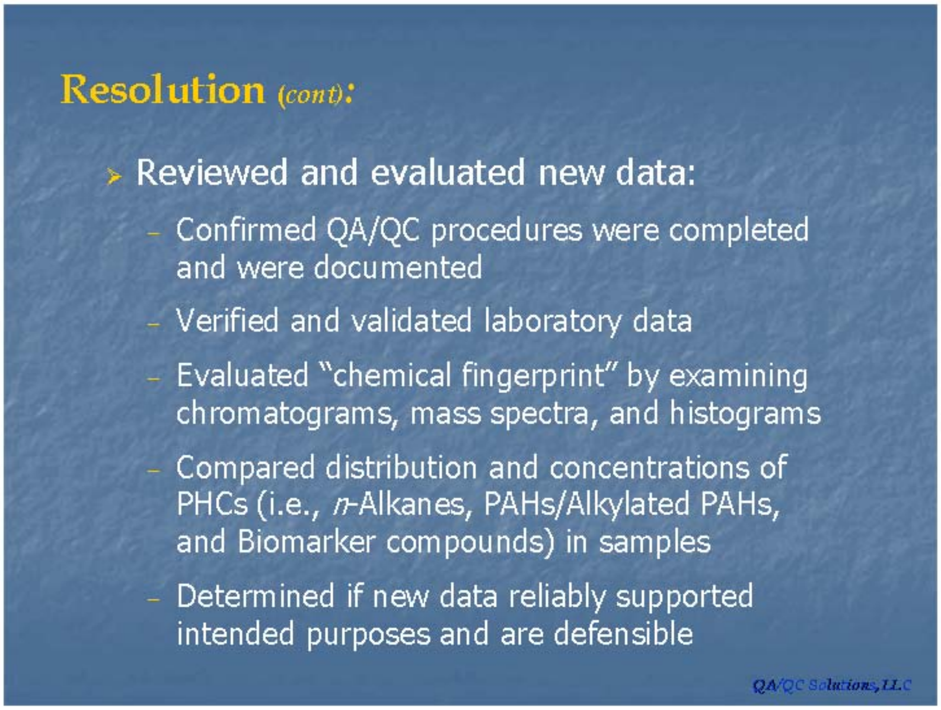
GC/FID Data

*Bunker C = C10 (~2.3 min)
to C38 (~8.7 min) per lab

Resolution:

- Collect new samples and analyze for:
  - Saturated hydrocarbons (i.e., *n*-Alkanes) by GC/FID
  - PAHs/Alkylated PAHs by GC/MS SIM
  - Chemical biomarkers (e.g., terpanes and steranes) by GC/MS SIM
- Evaluate "chemical fingerprinting" data:
  - What is composition of the site-specific PHC?
  - What is composition of PHC(s) (if present) in surrounding groundwater?
  - Are PHC(s) onsite and offsite similar?

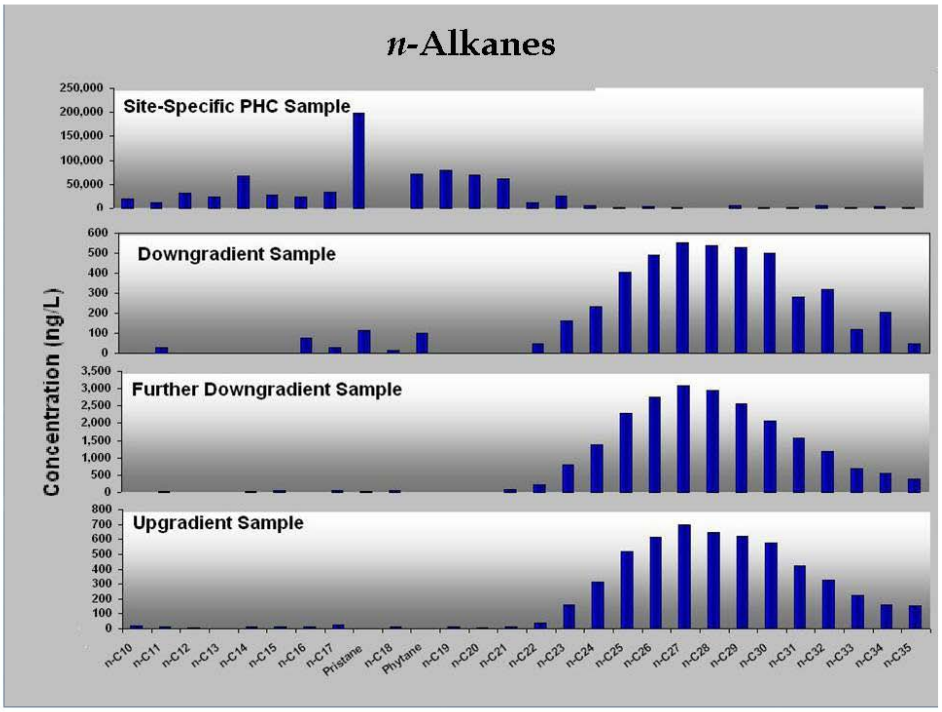
QA/QC Solutions, LLC



Resolution *(cont)*:

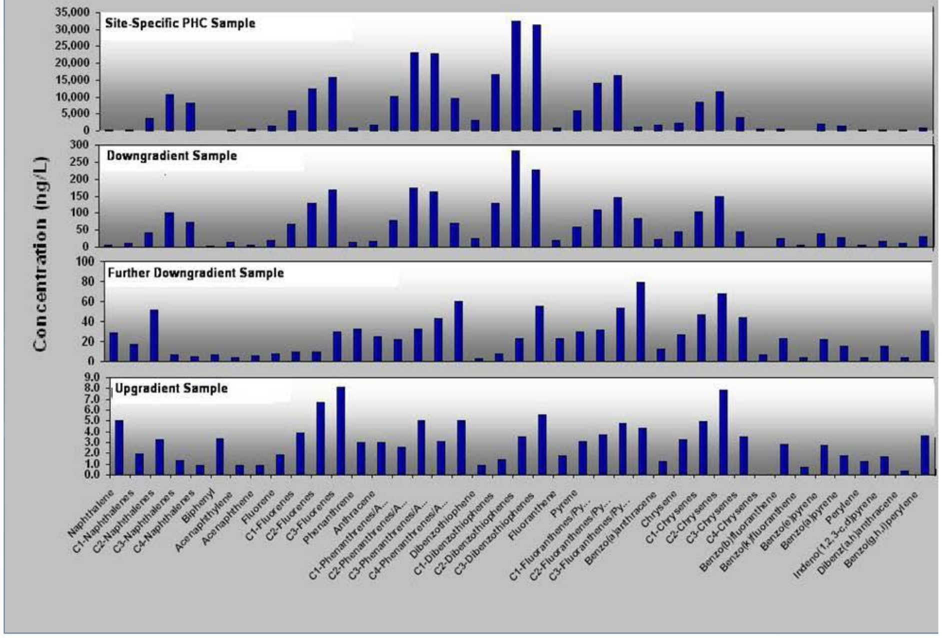
- Reviewed and evaluated new data:
  - Confirmed QA/QC procedures were completed and were documented
  - Verified and validated laboratory data
  - Evaluated "chemical fingerprint" by examining chromatograms, mass spectra, and histograms
  - Compared distribution and concentrations of PHCs (i.e., *n*-Alkanes, PAHs/Alkylated PAHs, and Biomarker compounds) in samples
  - Determined if new data reliably supported intended purposes and are defensible

QA/QC Solutions, LLC

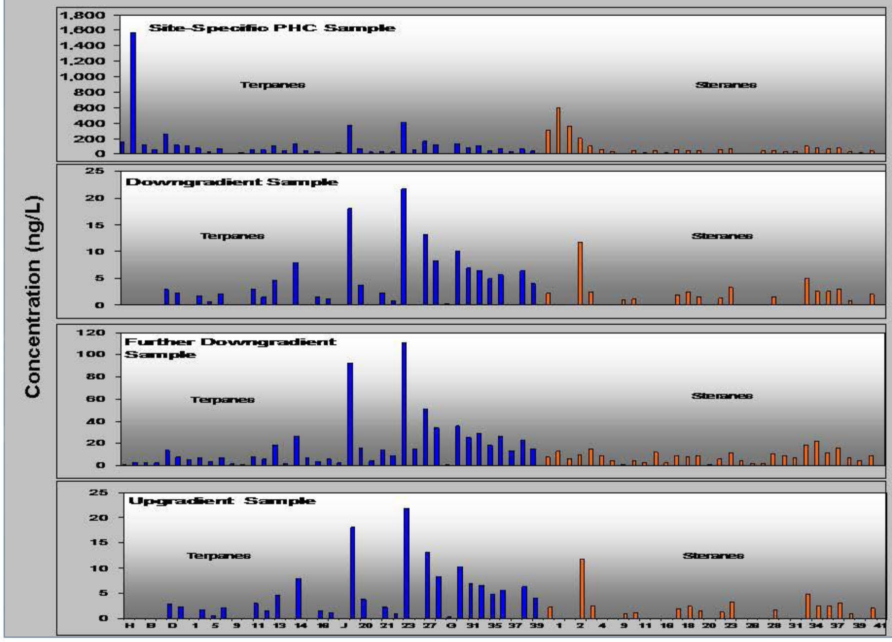


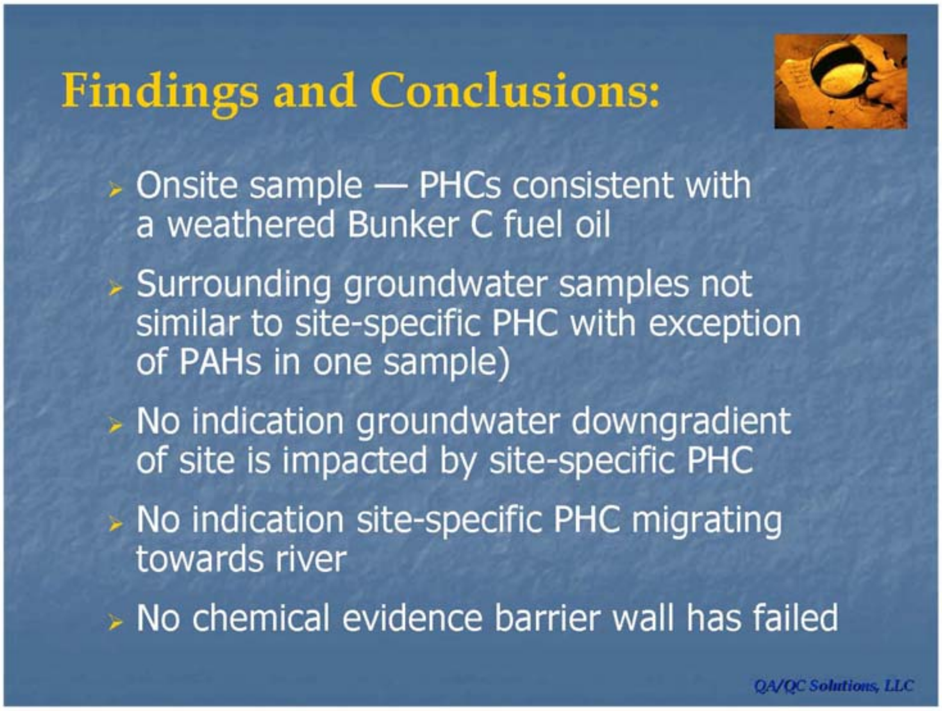
n-Alkanes

PAHs and Alkylated PAHs



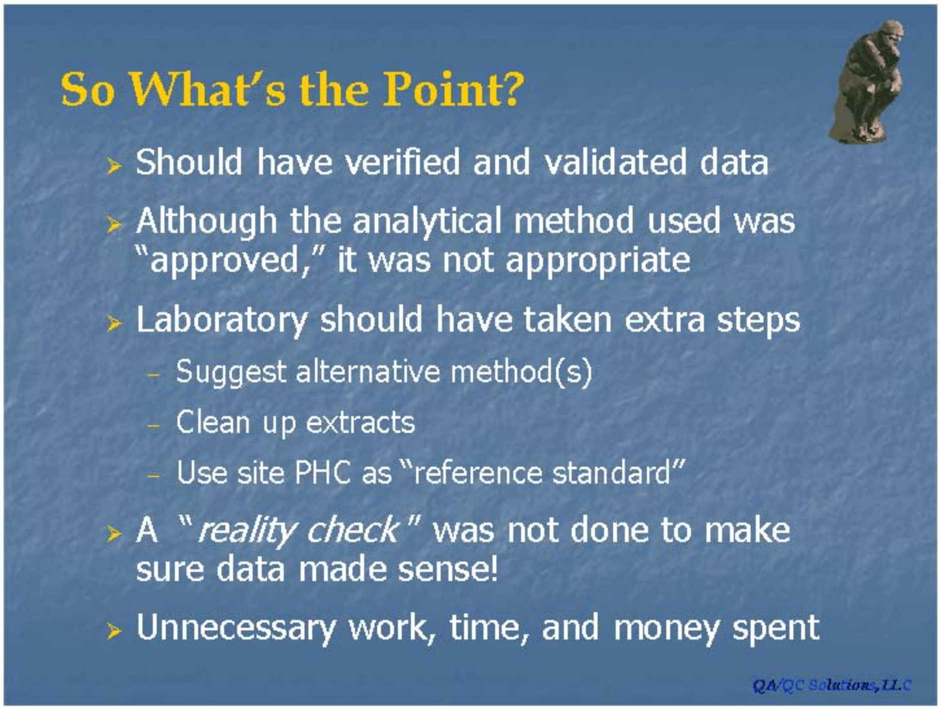
Biomarker Compounds (Terpanes & Steranes)





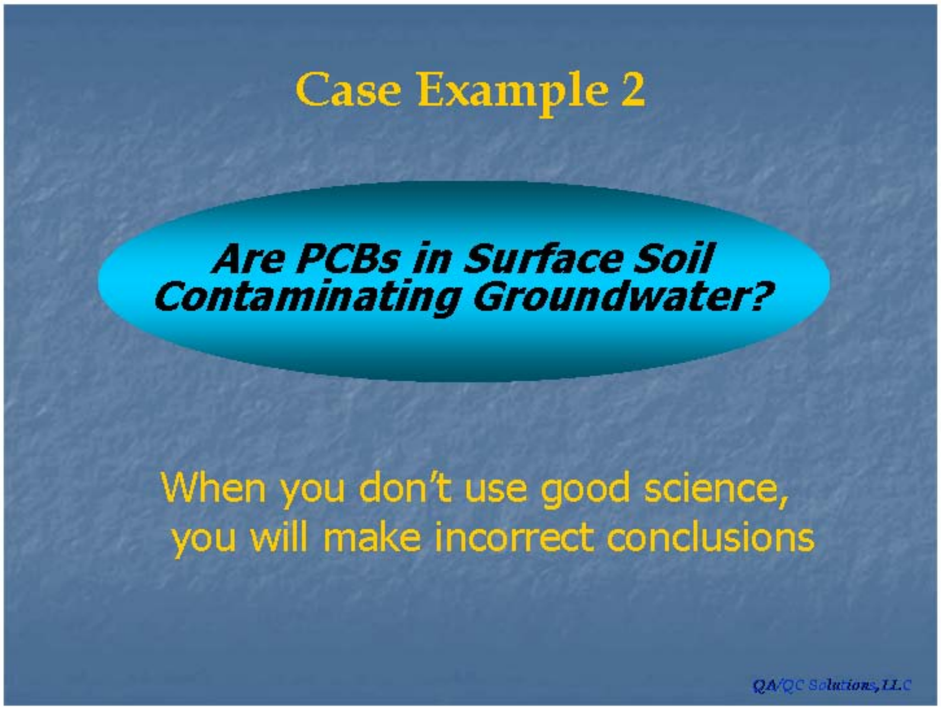
Findings and Conclusions:

- Onsite sample — PHCs consistent with a weathered Bunker C fuel oil
- Surrounding groundwater samples not similar to site-specific PHC with exception of PAHs in one sample)
- No indication groundwater downgradient of site is impacted by site-specific PHC
- No indication site-specific PHC migrating towards river
- No chemical evidence barrier wall has failed



So What's the Point?

- Should have verified and validated data
- Although the analytical method used was "approved," it was not appropriate
- Laboratory should have taken extra steps
  - Suggest alternative method(s)
  - Clean up extracts
  - Use site PHC as "reference standard"
- A "*reality check*" was not done to make sure data made sense!
- Unnecessary work, time, and money spent

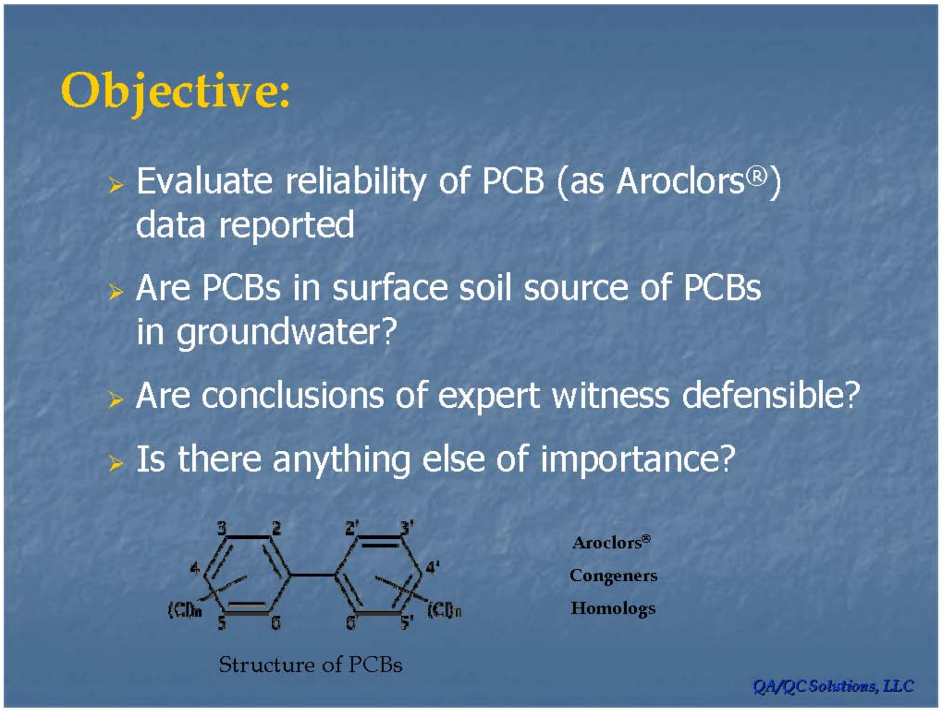


Case Example 2

Are PCBs in Surface Soil Contaminating Groundwater?

When you don't use good science,
you will make incorrect conclusions

QA/QC Solutions, LLC



Objective:

- Evaluate reliability of PCB (as Aroclors®) data reported
- Are PCBs in surface soil source of PCBs in groundwater?
- Are conclusions of expert witness defensible?
- Is there anything else of importance?

Structure of PCBs

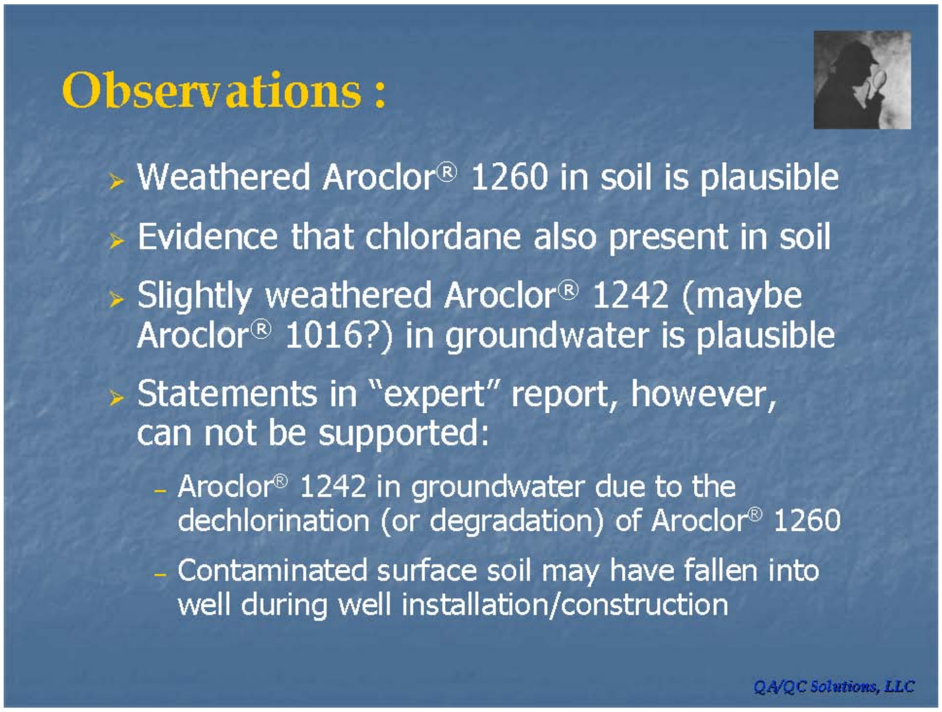
Aroclors®
Congeners
Homologs

QA/QC Solutions, LLC

Available Information:

- Remedial investigation reports
- "Expert" reports
- Data from other site investigations
- Original laboratory data
- Field sampling records

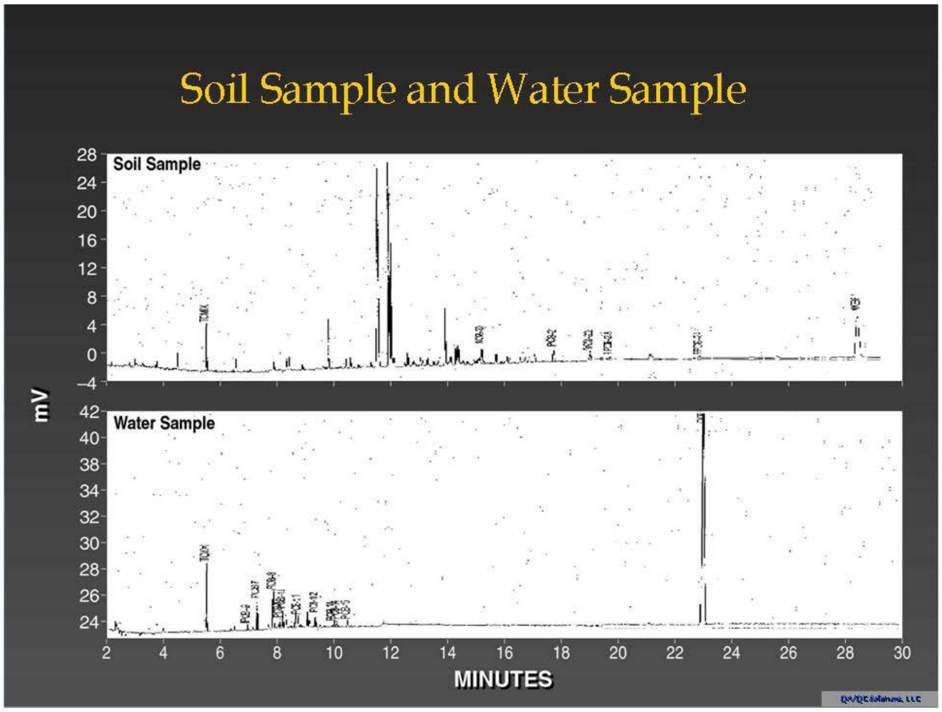
QA/QC Solutions, LLC



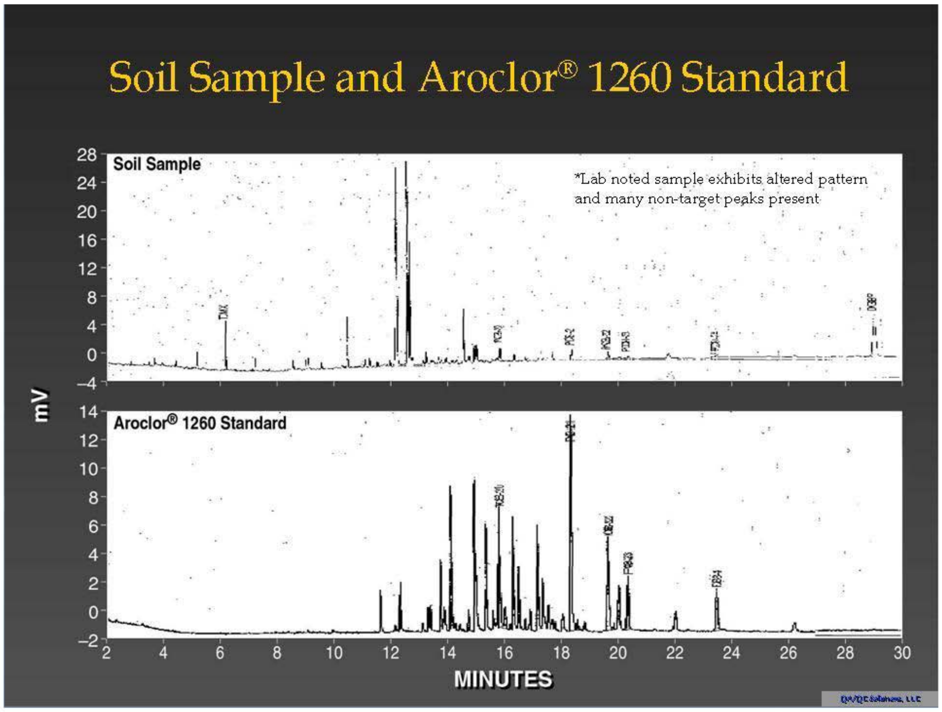
Observations :

- Weathered Aroclor® 1260 in soil is plausible
- Evidence that chlordane also present in soil
- Slightly weathered Aroclor® 1242 (maybe Aroclor® 1016?) in groundwater is plausible
- Statements in "expert" report, however, can not be supported:
  - Aroclor® 1242 in groundwater due to the dechlorination (or degradation) of Aroclor® 1260
  - Contaminated surface soil may have fallen into well during well installation/construction

QA/QC Solutions, LLC

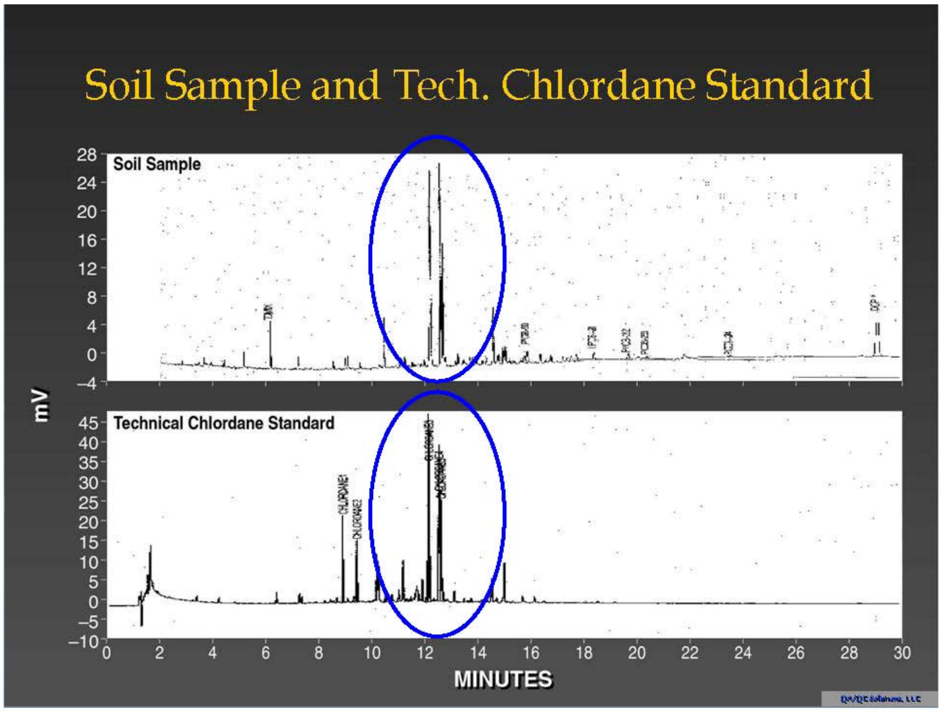


Soil Sample and Water Sample

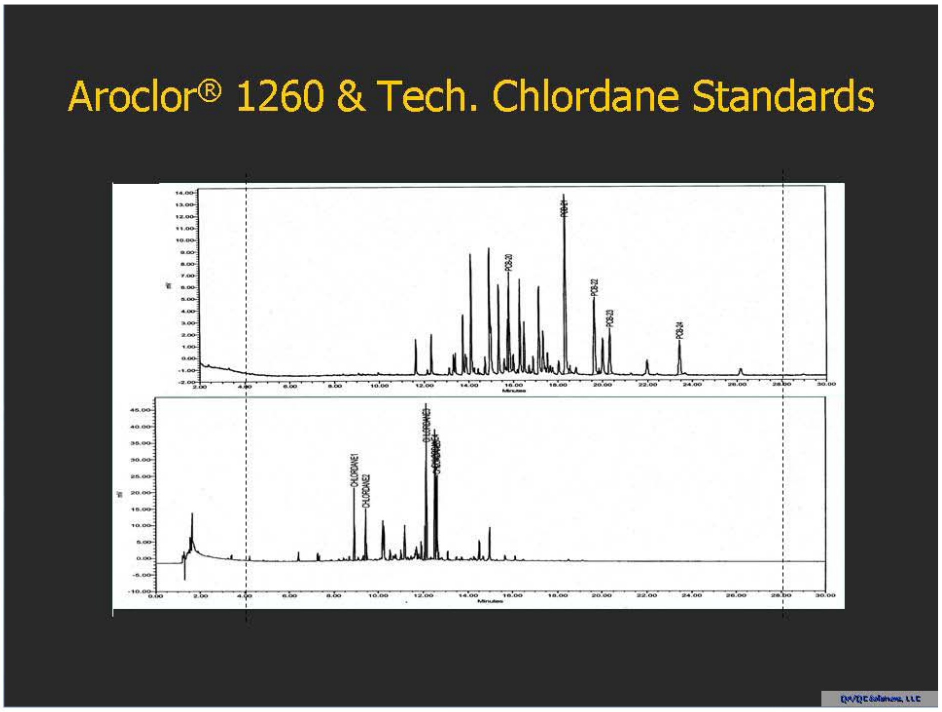


Soil Sample and Aroclor® 1260 Standard

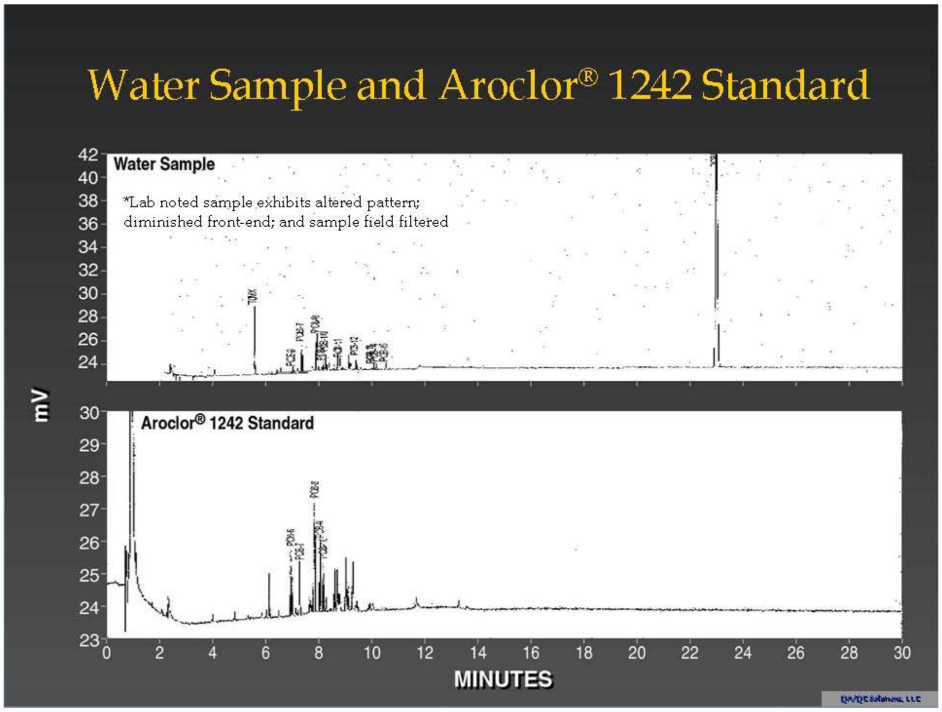
*Lab noted sample exhibits altered pattern and many non-target peaks present



Soil Sample and Tech. Chlordane Standard

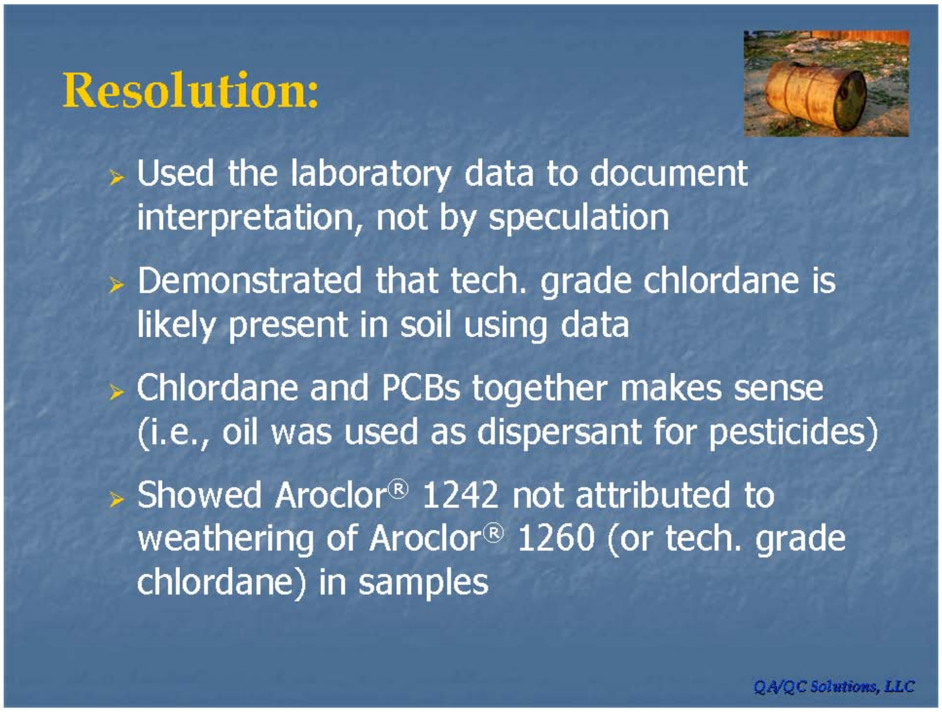


Aroclor® 1260 & Tech. Chlordane Standards



Water Sample and Aroclor® 1242 Standard

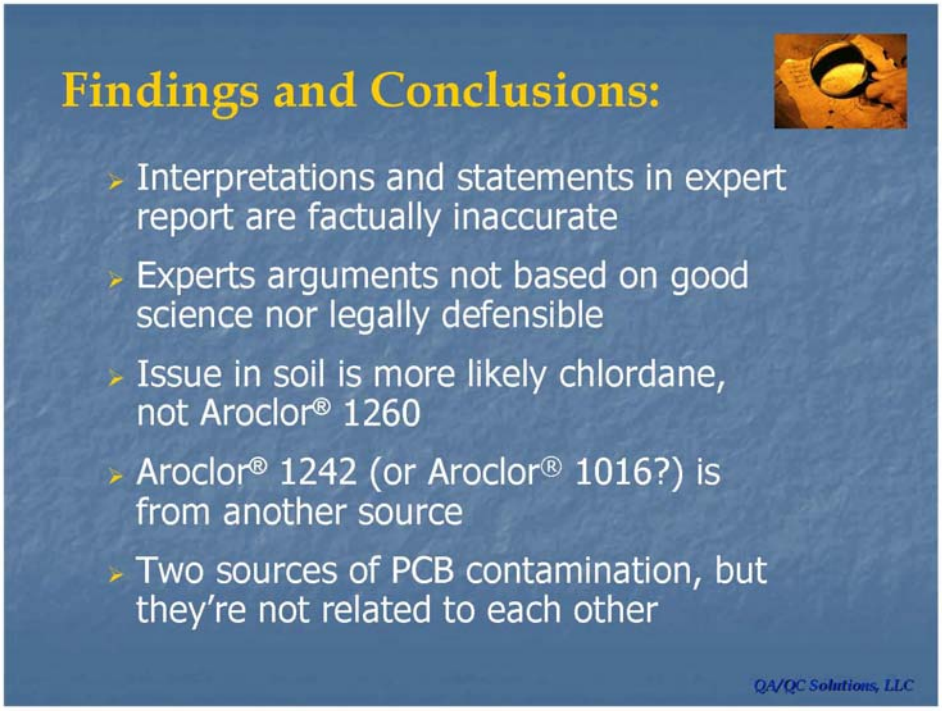
*Lab noted sample exhibits altered pattern; diminished front-end; and sample field filtered



Resolution:

- Used the laboratory data to document interpretation, not by speculation
- Demonstrated that tech. grade chlordane is likely present in soil using data
- Chlordane and PCBs together makes sense (i.e., oil was used as dispersant for pesticides)
- Showed Aroclor® 1242 not attributed to weathering of Aroclor® 1260 (or tech. grade chlordane) in samples

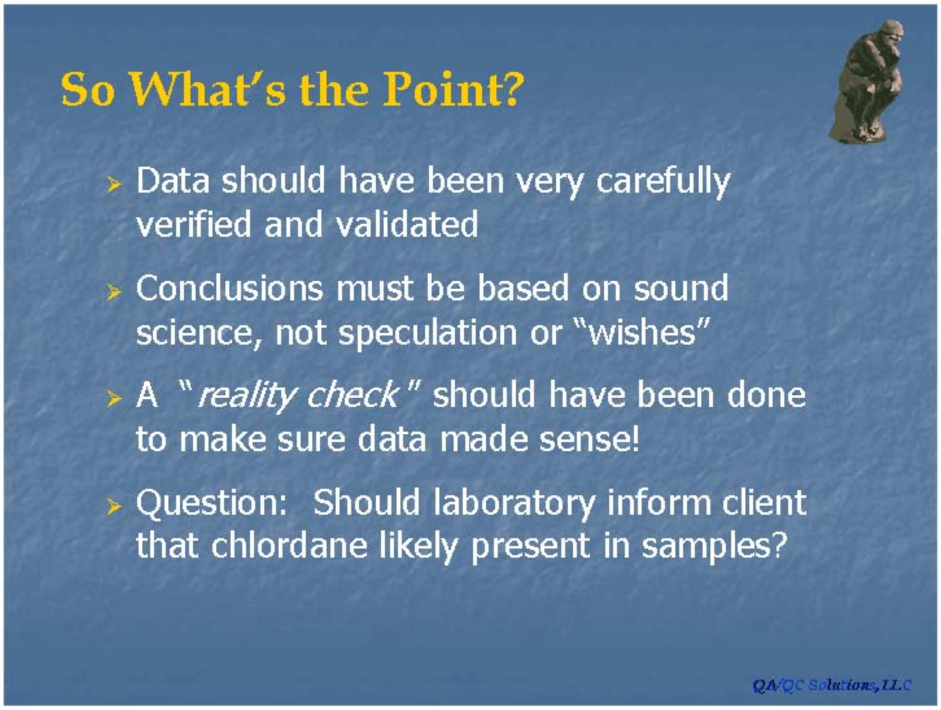
QA/QC Solutions, LLC



Findings and Conclusions:

- Interpretations and statements in expert report are factually inaccurate
- Experts arguments not based on good science nor legally defensible
- Issue in soil is more likely chlordane, not Aroclor® 1260
- Aroclor® 1242 (or Aroclor® 1016?) is from another source
- Two sources of PCB contamination, but they're not related to each other

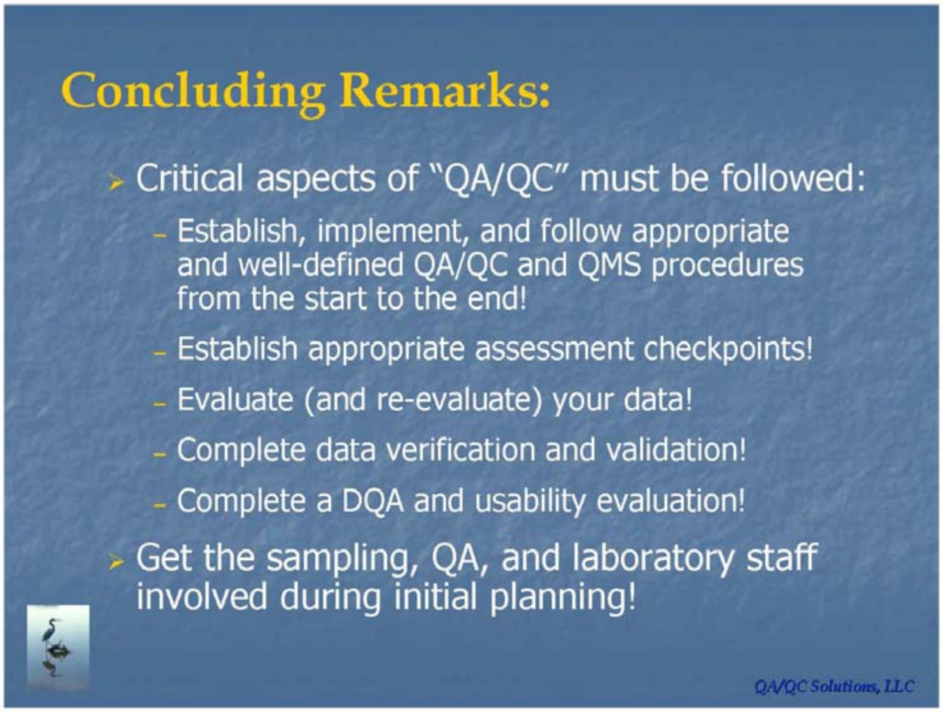
QA/QC Solutions, LLC



So What's the Point?

- Data should have been very carefully verified and validated
- Conclusions must be based on sound science, not speculation or "wishes"
- A "*reality check*" should have been done to make sure data made sense!
- Question: Should laboratory inform client that chlordane likely present in samples?

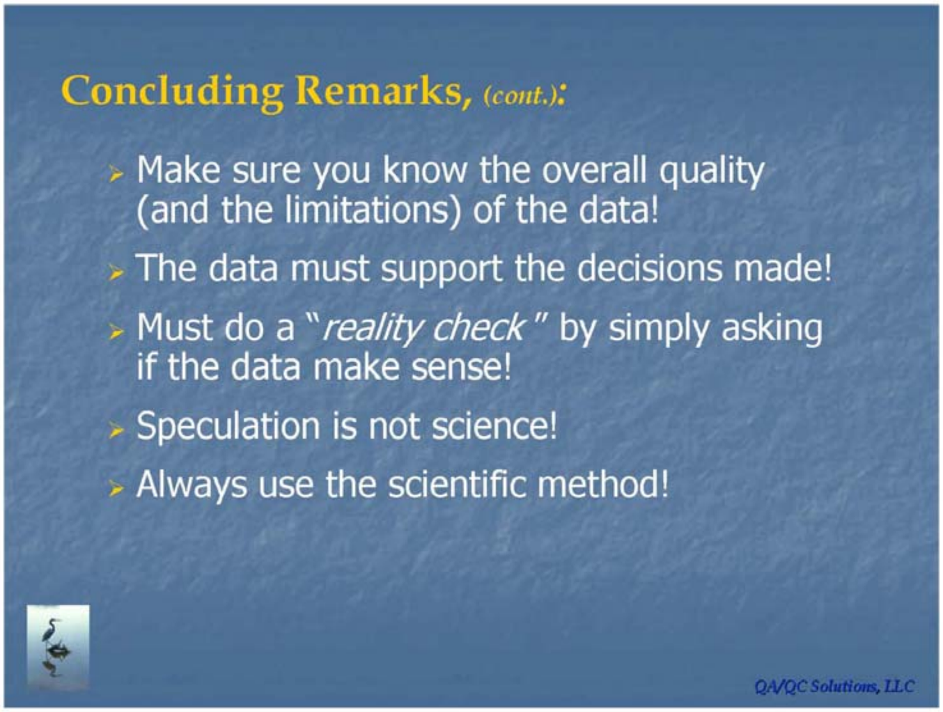
QA/QC Solutions, LLC



Concluding Remarks:

- Critical aspects of "QA/QC" must be followed:
  - Establish, implement, and follow appropriate and well-defined QA/QC and QMS procedures from the start to the end!
  - Establish appropriate assessment checkpoints!
  - Evaluate (and re-evaluate) your data!
  - Complete data verification and validation!
  - Complete a DQA and usability evaluation!
- Get the sampling, QA, and laboratory staff involved during initial planning!

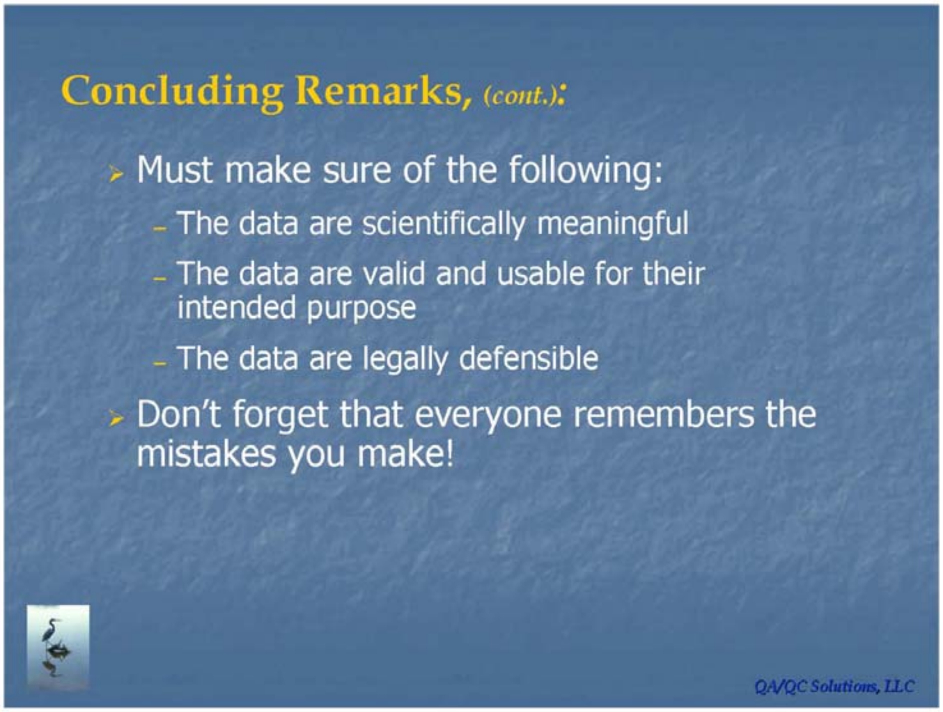
QA/QC Solutions, LLC



Concluding Remarks, *(cont.)*:

- Make sure you know the overall quality (and the limitations) of the data!
- The data must support the decisions made!
- Must do a "*reality check*" by simply asking if the data make sense!
- Speculation is not science!
- Always use the scientific method!

QA/QC Solutions, LLC



Concluding Remarks, *(cont.)*:

- Must make sure of the following:
  - The data are scientifically meaningful
  - The data are valid and usable for their intended purpose
  - The data are legally defensible
- Don't forget that everyone remembers the mistakes you make!

QA/QC Solutions, LLC

A Thought To Remember

"Quality Assurance is the Thread that Weaves Together the Fabric of Diverse Disciplines"

A quote (with permission) by George M. Brilis, QA Manager, Environmental Sciences Division,
National Exposure Research Laboratory,
U.S. Environmental Protection Agency,
Las Vegas, Nevada

QA/QC Solutions, LLC

Questions?

QA/QC Solutions, LLC

Acronyms

- DQA – Data Quality Assessment
- DQI – Data Quality Indicator
- DQO – Data Quality Objective
- FSP – Field Sampling Plan
- GC/FID – Gas Chromatography/Flame Ionization Detection
- GC/MS - Gas Chromatography/Mass Spectrometry
- MQO – Measurement Quality Objective
- PAH – Polycyclic Aromatic Hydrocarbon
- PCB – Polychlorinated Biphenyl
- PHC – Petroleum Hydrocarbon
- PQO – Project Quality Objective
- QA/QC – Quality Assurance/Quality Control
- QAPP – Quality Assurance Project Plan
- QMS – Quality Management System
- RI – Remedial Investigation
- SIM – Selected Ion Monitoring

QA/QC Solutions, LLC

Development of a Consensus Standard for Quality Systems in Environmental Testing Laboratories

Robert DiRienzo
DataChem Laboratories, Inc.
960 West LeVoy Drive
Salt Lake City, UT 84044
801-266-7700
dirienzo@datachem.com

ABSTRACT

The NELAC Institute (TNI) has developed and approved a consensus quality systems standard for use by environmental testing laboratories. The standard is based on ISO 17025:2005, NELAC 2003 Chapter 5 and DoD QSM.

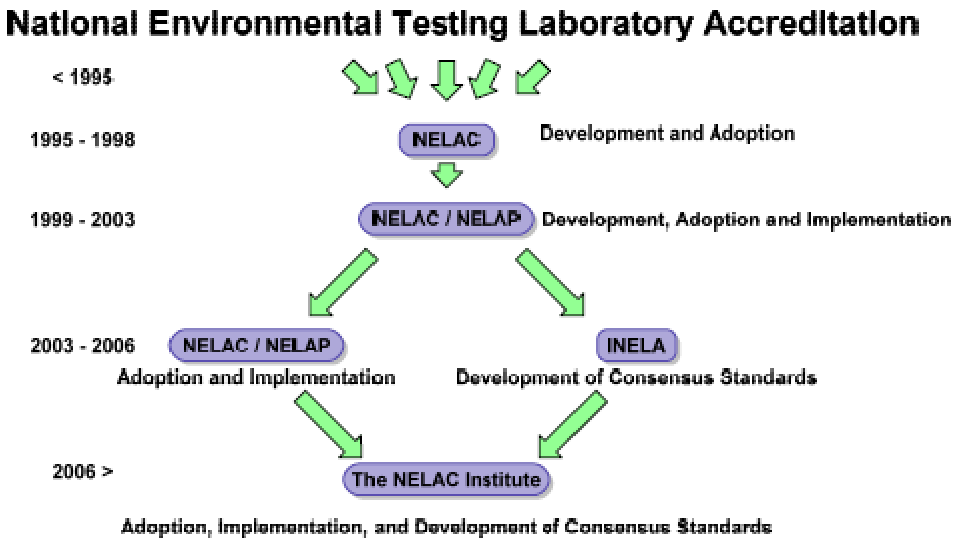
TNI has a policy on standards development that has been reviewed by ANSI. The TNI policy not only addresses development of standards used by TNI but also the consensus process which includes open meetings, participation by stakeholders and addressing stakeholder comments. This standard is structured following ISO 17025:2005 and has additional elements from NELAC 2003 Chapter 5. This new standard begins with a general requirements module which outlines management system requirements for all environmental testing laboratories. This standard also includes modules for technical areas, Asbestos, Chemistry, Microbiology, Radiochemistry and Toxicity, and can be expanded to include new technologies, new programs (Drinking Water or Homeland Security) and possibly contract compliance (DoD, Superfund or DOE).

INTRODUCTION

The call for one certification program for environmental testing laboratories was initiated as far back as 1999. The process of developing, adopting and implementing NELAP was finally realized in 1999 with its first set of laboratories and eleven accrediting bodies (States).

The process of developing the first TNI standards for Environmental Testing Laboratory has also been a long journey that started after the NELAC 2003 approval. This journey included splitting NELAC between adoption/implementation and the development of standards. NELAC continued to implement the NELAC 2003 Standards and was limited to government employees, while the standards development process under INELA became a consensus standard development organization which included all stakeholder groups.

In 2007 the two organizations were combined again as TNI with separate boards directing the various activities of adoption, implementation, technical assistance, proficiency testing, administrative and consensus standards development. Recently new standards for environmental testing laboratories were approved through the consensus process.



DEFINITIONS

Consensus is a decision-making process that not only seeks the agreement of most participants, but also to resolve or mitigate the objections of the minority to achieve the most agreeable decision.

A *standard* is an established norm or requirement. It is usually a formal document that establishes uniform engineering or technical criteria, methods, processes and practices.

REQUIREMENTS FOR CONSENSUS STANDARD DEVELOPMENT

The Federal Office of Management and Budget (OMB) Circular A-119 defines a voluntary consensus standards body as one having the following attributes: (i) openness; (ii) balance of interest; (iii) due process; (iv) an appeals process; and (v) consensus, which is general agreement, but not necessarily unanimity, and includes a process for attempting to resolve objections by interested parties, as long as all comments have been fairly considered, each objector is advised of the disposition of his or her objection(s) and the reason(s) why, and the consensus body members are given an opportunity to change their votes after reviewing the comments.

The American National Standards Institute (ANSI) facilitates the development of consensus standards by accrediting the procedures used by standards developing organizations. These groups work cooperatively to develop voluntary national consensus standards. Accreditation by ANSI signifies that the procedures used by the standards body in connection with the development of American National Standards meet the Institute's essential requirements for openness, balance, consensus and due process:

- Openness - Committee membership is open to all, all meetings open to all members, minutes of all meetings are posted, and the public may provide input
- Balance of Interest - No single interest category can constitute a majority of committee members on any committee.
- Consensus - General agreement, but not necessarily universal agreement
- Due Process - Any person with a direct and material interest has a right to participate by expressing a position with its basis. That position will be considered.
- Appeals Process - Any person with a direct and material interest has the right to appeal a decision.

TNI Policy

The TNI "POLICY GOVERNING STANDARDS DEVELOPMENT" contains rules concerning the establishment and operations of Expert Committees are provided as well as criteria for ensuring a balance of interests. The Policies also stipulate voting procedures and provide detailed requirements for considering all negative votes. The Policies cover the following topics:

- **Openness, Lack of Dominance, and Balance**

Openness - Participation is open to all TNI members and to all members of the public who are directly and materially affected by TNI's standards development activities. Voting membership is not conditional upon membership in any other organization, nor unreasonably restricted on the basis of technical qualifications or other such requirements. Any member of the public may provide written input on any TNI standard, or may provide comment by following the ANSI public comment process.

Lack of Dominance - The standards development process will not be dominated by any single interest category, individual, or organization. Dominance means a position of, or exercise of dominant authority, leadership, or influence by reason of superior leverage, strength, or representation which would be fair and equitable consideration of other viewpoints. Unless claimed in writing, to the Chair of the TNI Board of Directors, by any directly or materially affected party, that a single interest category, individual, or organization dominated the standards development process, no test for dominance is required.

Balance - The standards development process should have a balance of interests. Participants from diverse interest categories are sought with the objective of achieving balance. The criteria for balance are that no single interest category constitutes a majority of committee members on any Expert Committee. The interest categories are:

- accreditation bodies and other governmental agencies that operate environmental accreditation programs (federal or state)
- accredited laboratories (commercial, municipal, state and federal)
- all others (consultants, proficiency test providers, non-accredited laboratories, state and federal agencies that do not run accreditation programs, etc.)

- **Conducting Business**

Meetings - Generally there are two (2) meetings per year (a summer and winter) where the Expert Committees meet to present any proposed standard or amendments to standards and to receive input for further development of any standards. Any member of the public may register for and attend these meetings. Working meetings of Expert Committees held face-to-face or via conference calls are open to any TNI member or Affiliate who has joined the Expert Committee as a committee member, to any TNI member who chooses to participate in the role of Associate Committee Member, or to any member of the public who requests to be included. Minutes from these meetings are published on the TNI website. All official votes of Expert Committees require a minimum of two thirds of committee members voting. It is permissible to hold closed meetings only when discussing personnel or other sensitive issues. Issues relating to standards development may not be discussed in closed meetings.

Notification - Notification of proposed standards activity are announced on the TNI website to offer the opportunity for participation by all directly and materially affected persons. This notification will include: (a) an explanation of the need for the standard; and (b) the identification of stakeholders (e.g., laboratories, engineering firms, PT providers, etc.) likely to be directly impacted by the standard.

- **Standards Development**

Expert Committees members develop standards by telephone conference and/or face-to-face meetings, as appropriate serving in a leadership role in standards development. All Committee Members, Affiliates and Associate Committee Members will be given the opportunity to provide comments at appropriate times during meetings in a managed process. Any TNI member or member of the public may provide written input to a committee. Committees will consider all written comments and suggestions and will notify the correspondents of the disposition of their comments. At the initiation of a project to develop or revise a standard, notification of such activity will be posted on the TNI website, to allow for participation by all directly and materially affected persons. A simple diagram of this process is shown in Figure 2:

Figure 2

- **Voting Procedures, Due Process and Appeals**

Working Draft Standard

During the approximately six-month period preceding a TNI semi-annual meeting, the Expert Committees develop modules of a working draft standard. The Committee Chair may delegate the standard-writing process to the Committee Members or to any task group formed from the Committee Members, Affiliates and Associate Committee Members. All Committee Members, Affiliates and Associate Committee Members are afforded the opportunity to contribute to the standard-development process.

An official vote of the Committee Members, with at least two-thirds of the members in concurrence, is required for release of the working draft standard for publication. The working draft standard is published at least thirty (30) days prior to the TNI semi-annual meeting at which it is discussed publicly. at the TNI semi-annual meeting. At this time, any TNI member or member of the public may propose changes from the floor for consideration by an Expert Committee. In addition, any TNI member or member of the public may submit to the committee written comments within fifteen (15) days following the semi-annual meeting.

Voting Draft Standard

Ninety (90) days following the above comment period ends the TNI semi-annual meeting. An Expert Committee may then modify the working draft standard considering the comments received during the public debate and those received within the fifteen (15) day timeframe following the TNI semi-annual meeting. The Committee Members vote to accept the modified working draft standard. A two-thirds favorable majority vote of the Committee Members is required for passage. The working draft standard then becomes the TNI Voting Draft Standard. All Committee Members, Affiliates and Associate Committee Members may vote on their committee's modules of the Voting Draft Standard. Each Committee Member, Affiliate and Associate Committee Member has one vote. All voting is conducted by electronic ballot.

At least fifteen (15) days prior to voting, the Voting Draft Standard is published, together with an electronic ballot form. TNI shall indicate conspicuously on the ballot that negative votes should be accompanied by written comments related to the proposal and that negative votes unaccompanied by such written comments will be recorded as "negative without comments". Such ballots, will not be counted as either negative or positive. TNI is not required to solicit any comments from the negative voter.

At least fifteen (15) days after publication of the Voting Draft Standard, the voting period for ballots begins and continues for thirty (30) days. Early voting will be permitted; i.e., all votes cast from the date of publication of the electronic ballot form up to forty-five (45) days after the date of its publication will be accepted. Each Committee Member, Affiliate and Associate Committee Member will vote on one of the following positions:

- Affirmative
- Affirmative with comment
- Negative with comment
- Abstain

A negative vote may be withdrawn at any time by written electronic submission to TNI. The voter shall instruct TNI if the withdrawn negative is to be changed to an affirmative vote or to an abstention.

In order for the Voting Draft Standard to pass, an affirmative vote of at least two-thirds of the Committee Members is required, and all written comments accompanying votes cast by Committee Members, Affiliates and Associate Committee Members will be considered and brought to resolution as described below. Ballot items returned as negative without comment are recorded as negative without comment. Ballot items returned unmarked shall be considered as unreturned ballots.

All written comments accompanying negative or affirmative votes cast by Committee Members, Affiliates and Associate Committee Members will be recorded and considered publicly during the next TNI semi-annual meeting. Each Expert Committee will meet in separate session to consider those comments received on its modules of the standard. These meetings will be open to the public. Following its discussion, each written comment shall be ruled persuasive or non-persuasive by a simple two-thirds vote of the Committee Members present. No written comment will be dismissed because it does not provide alternative language or a specific remedy to the negative vote. The committee may prioritize the comments and place any comments on hold until the next revision cycle of the standard, if the comments are too numerous to be dealt with in the time-frame available until the TNI Standard is published. Any comment placed on hold must be addressed during the next revision cycle of the standard and must be recorded and considered as a comment at that time.

An Expert Committee may prioritize the comments received and may place a comment on hold until the next revision cycle of the standard if all of the following conditions are met:

- The comment introduces a concept that had not been subject to public review by being included in a related proposal as published in the Voting Draft Standard.
- The comment changes the text proposed by the Expert Committee to the point that the Expert Committee would have to restudy the text of the Voting Draft Standard
- The comment proposes something that could not be handled properly within the time frame for processing the changes.

In making the determination whether to place a comment on hold, the Expert Committee may consider relevant factors, including but not limited to: the extent to which the comment proposes a change that is new and/or substantial; the complexity of the issues raised; and whether sufficient debate and public review have taken place. The negative commenter must be informed, in writing, of the reasons the comment has been placed on hold.

A persuasive negative vote or an objection received from a member of the public will require the Expert Committee to consider whether modification of the Voting Draft Standard is appropriate. The committee may modify the standard, if such modification will lead to removal of the cause for the negative vote. The modified standard must then be made available through posting on the TNI website, together with a Response to Comments document summarizing all persuasive and non-persuasive votes and their resolution, and any objections received from the public and their resolution, for all Committee Members, Affiliates, Associate Committee Members and the public to review. Within fifteen (15) days of this posting, any Committee Member may change his or her vote, through written electronic notice to TNI. The vote is then re-tallied and requires an affirmative vote of at least two-thirds of the combined affirmative and negative votes cast by Committee Members in order to pass. Within fifteen (15) days the tally from the vote on the Voting Draft Standard is published as: number of affirmative votes; number of persuasive negative votes; number of non-persuasive negative votes; number of negative votes without comment; and number of abstentions.

TNI Standard

If the Voting Draft Standard passes, it becomes the TNI Standard. If any module fails, it is returned to the Expert Committee for processing during the next revision cycle. All individuals who provided votes or who submitted public review comments that were ruled non-persuasive will be so notified and will be informed of their right to appeal.

The TNI Standard is made available to all interested parties, including standards-adoption organizations.

Appeals

Persons who have directly and materially affected interests, and who have been or may be adversely affected by a procedural action or inaction of TNI, shall have the right to appeal. Negative voters shall be notified of the disposition of their negative votes and their right to appeal. The burden of proof to show adverse effect shall be on the appellant.

In connection with an objection articulated during a public comment period, or submitted with a vote, an effort to resolve any expressed objections accompanied by comments related to the proposal under consideration will be made, and each objector is advised in writing (including electronic communications) of the disposition of the objection and the reasons thereof. If resolution is not achieved, each objector shall be informed in writing that an appeals process exists.

Any negative voter, whose negative comment has been found non-persuasive by a vote of the Expert Committee on the Voting Draft Standard, may appeal the decision in writing. Also, any member of the public who has submitted an objection on the Voting Draft Standard that has been found non-persuasive by a vote of the Expert Committee on the Voting Draft Standard may appeal the decision in writing. The appellant shall file a written complaint with the Executive Director of TNI within thirty (30) days after the date of publication of the result of the vote on the Voting Draft Standard. Written appeals associated with any other aspect of the standard development process may be filed with the Executive Director of TNI following notification of action or at any time with respect to inaction. The complaint shall state the nature of the objection(s) including any adverse effects, the clause(s) of these procedures or the standard that is at issue, actions or inactions that are at issue, and the specific remedial action(s) that would satisfy the appellant's concerns. Previous efforts to resolve the objection(s) and the outcome of each shall be noted. Within seven (7) days of receiving the complaint, the Executive Director will notify and provide a copy of the complaint to the Chair of the TNI Board of Directors and the Chair of the Expert Committee against which the complaint is made.

Within thirty (30) days after receipt of the complaint, the Executive Director will prepare a written response that meets the approval of the Board of Directors and the Chair of the affected Expert Committee and will submit the response to the appellant. The response will specifically address each allegation of fact in the complaint to the extent of the respondent's knowledge. The

Executive Director may solicit other individuals with specific knowledge of the matter in question to assist with the response.

If the appellant and TNI are unable to resolve the written complaint informally in a manner consistent with these procedures, the Executive Director shall schedule a telephone conference hearing with an appeals panel on a date agreeable to all participants, giving at least fifteen (15) working days notice.

The appeals panel consists of three (3) individuals who are knowledgeable of laboratory accreditation issues and familiar with the operation of consensus standards organizations, have not been directly involved in the matter in dispute, and who will not be materially or directly affected by any decision made in the dispute. The TNI Executive Director shall, with input from the appellant, develop a list of five (5) potential appointees for the appeal panel within fifteen (15) days, and the appellant will select three (3) of those names. This list of three (3) names will then be submitted to the TNI Executive Committee, which will appoint the members of the appeals panel. If the parties to the appeal cannot agree on an appeals panel within a reasonable amount of time, the matter shall be referred to the TNI Executive Committee, which shall appoint members of the appeals panel.

The appellant has the burden of demonstrating adverse effects, improper actions or inactions, and the efficacy of the requested remedial action. The respondent has the burden of demonstrating that TNI and the Executive Director took all actions in compliance with these procedures and that the requested remedial action would be ineffective or detrimental. Each party may adduce other pertinent arguments, and members of the appeals panel may address questions to individuals. Robert's Rules of Order shall apply to questions of parliamentary procedure for the hearing not covered herein. The appeals hearing proceedings shall be documented.
The appeals panel will provide a determination to the TNI Board of Directors in writing within thirty (30) days, stating findings of fact and conclusions, based on a preponderance of the evidence presented to the appeals panel. The decision of the appeals panel is final and shall be endorsed by the TNI Board of Directors.

If any appeal is upheld by the appeals panel, the affected module or section of the TNI Standard is withdrawn by the Expert Committee that developed that module or section for processing during the next revision cycle.

APPROVAL OF TNI

Having met all requirements, the TNI Consensus Standards Development Program was approved by ANSI, effective December 18, 2007.

TNI STANDARDS

The TNI Standards are based on the concept of sectors, volumes, and modules.

Environmental Laboratory Sector:
Volume 1 – Laboratory Requirements
Volume 2 – Accreditation Body Requirements
Volume 3 – Proficiency Testing Provider Requirements
Volume 4 – Proficiency Testing Oversight Requirements

Field Services and Measurement Organization Sector:
Volume 1 – FSMO Requirements
Volume 2 – FSMO Accreditation Body Requirements

Modules addressing requirements for management systems, process and technical requirements are included with each volume.

LABORATORY REQUIREMENTS – VOLUME 1

- Includes all standards for laboratories
- Uses ISO/IEC 17025:2005 for quality systems
- Flexible and consistent
- Technical modules can be added as needed

Modules

Module 1 – Proficiency Testing
Module 2 – Quality Systems: General Requirements
Module 3 – Asbestos Testing
Module 4 – Chemical Testing
Module 5 – Microbiological Testing
Module 6 – Radiochemical Testing
Module 7 – Toxicity Testing

Quality Systems

OUTLINE: (ISO/IEC 17025:2005 FORMAT)

INTRODUCTION, SCOPE AND APPLICABILITY

Introduction and Scope

NORMATIVE REFERENCES

TERMS AND DEFINITIONS

Additional Terms and Definitions, Definition Sources, and Exclusions and Exceptions

MANAGEMENT REQUIREMENTS

Organization, Management, Document Control, Review of Request, Tenders and Contracts, Subcontracting of Environmental Tests, Purchasing Services and Supplies, Service to the Client, Complaints, Control of Nonconforming Environmental Testing Work, Improvement, Corrective Action, Preventive Action, Control of Records, Internal Audits, Management Review, and Data Integrity Surveillance

TECHNICAL REQUIREMENTS

General, Personnel, Accommodation and Environmental Conditions, Environmental Test Methods and Method Validation, Calibration Requirements, Measurement Traceability, Collection of Samples, Handling Samples and Test Items, Quality Assurance for Environmental Testing, and Reporting the Results

EXAMPLE:

4.14 Internal Audits (ISO/IEC 17025:2005(E), Clause 4.14)

ISO text 4.14.1 to 4.14.4 here

4.14.5 Additional Items

a) The laboratory shall have a policy that specifies the time frame for notifying a client of events that cast doubt on the validity of the results.

b) The laboratory management shall ensure that these actions are discharged within the agreed time frame.

c) The Internal audit schedule shall be completed annually.

Technical Modules

Technical Modules for Asbestos, Chemistry, Microbiology, Radiochemistry, and Toxicity Testing are included and they have no ISO 17025 Language, Specific to testing activity, and consistent in format and structure.

FORMAT:
Introduction
Scope
Terms and Definitions
Method Selection
Method Validation
    Validation of Methods, Limit of Detection and Limit of Quantitation, Evaluation of Precisions and Bias, and Evaluation of Selectivity
Demonstration of Capability (DOC)
    General, Initial DOC, and Ongoing DOC
Technical Requirements
    Initial Calibration, Continuing Calibration, Quality Control for Chemistry, Data Reduction, Reagent Quality, Water Quality and Checks, Data Acceptance/Rejection Criteria, and Sample Handling

EXAMPLE:

1.6 Demonstration of Capability (DOC)

1.6.1 General

Prior to acceptance and institution of any method for which data will be reported, a satisfactory initial DOC is required (see Section 1.6.2). Thereafter, ongoing DOC (Section 1.6.3), as per the quality control requirements in Section 1.7.3 (such as laboratory control samples) is required. In cases where a laboratory analyzes samples using a method that has been in use by the laboratory for at least one year prior to applying for accreditation, and there have been no significant changes in instrument type, personnel or method, the ongoing DOC shall be acceptable. The laboratory shall have records on file to demonstrate that a DOC is not required. For the initial DOC, appropriate records as discussed in Section 1.6.2 shall be completed. An initial DOC shall be completed each time there is a change in instrument type, personnel, or method.
All demonstrations shall be documented. All data applicable to the demonstration shall be retained and readily available at the laboratory.

CONCLUSIONS

The TNI consensus standards for environmental testing laboratory accreditation have general agreement between all stakeholders. The TNI standards for Laboratories are consistent with the ISO 17025:2005 format, have removed redundant language from NELAC 2003, provides a consistent technical module format addressing all aspects of a specific testing activity, and a volume/module structure which allows for growth and flexibility.

Additional modules addressing new technologies and or programs may be added without wholesale revisions to existing modules.

TNI has adopted a well defined consensus standard development process which meets the requirements of Office of Management and Budget (OMB) Circular A-119 "Federal Participation in the Development and Use of Voluntary Consensus Standards and in Conformity Assessment Activities" and is ANSI approved as a consensus standards development organization.

REFERENCES

1. TNI SOP 2-100, Procedures Governing Standards Development
2. TNI SOP 2-101, Procedures for Expert Committee Operations
3. 2003 NELAC Standard, Chapter 5
4. www.ansi.org
5. www.nelac-institute.org

Development of a Consensus Standard for Quality Systems in Environmental Testing Laboratories.

Robert P. Di Rienzo

National Environmental Monitoring Conference
August 11-15, 2008
Hyatt Regency Capital Hill
Washington, DC

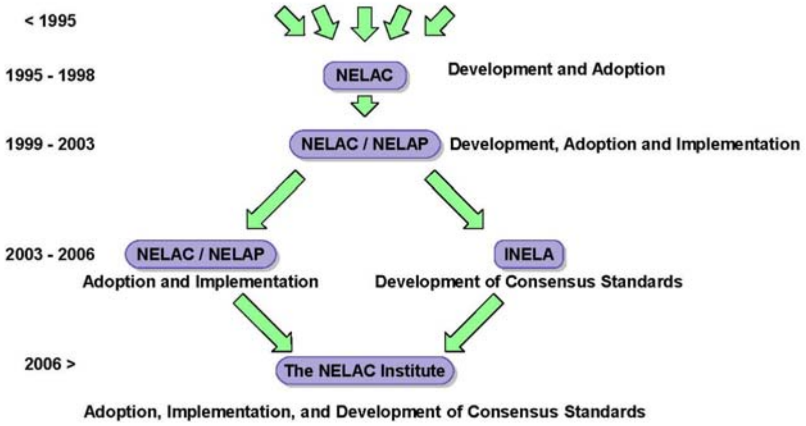
What is NELAC?

What is NELAP?

What is INELA?

What is TNI?

National Environmental Testing Laboratory Accreditation



< 1995

1995 - 1998 **NELAC** Development and Adoption

1999 - 2003 **NELAC / NELAP** Development, Adoption and Implementation

2003 - 2006 **NELAC / NELAP** Adoption and Implementation — **INELA** Development of Consensus Standards

2006 > **The NELAC Institute**

Adoption, Implementation, and Development of Consensus Standards

---

What is Consensus?

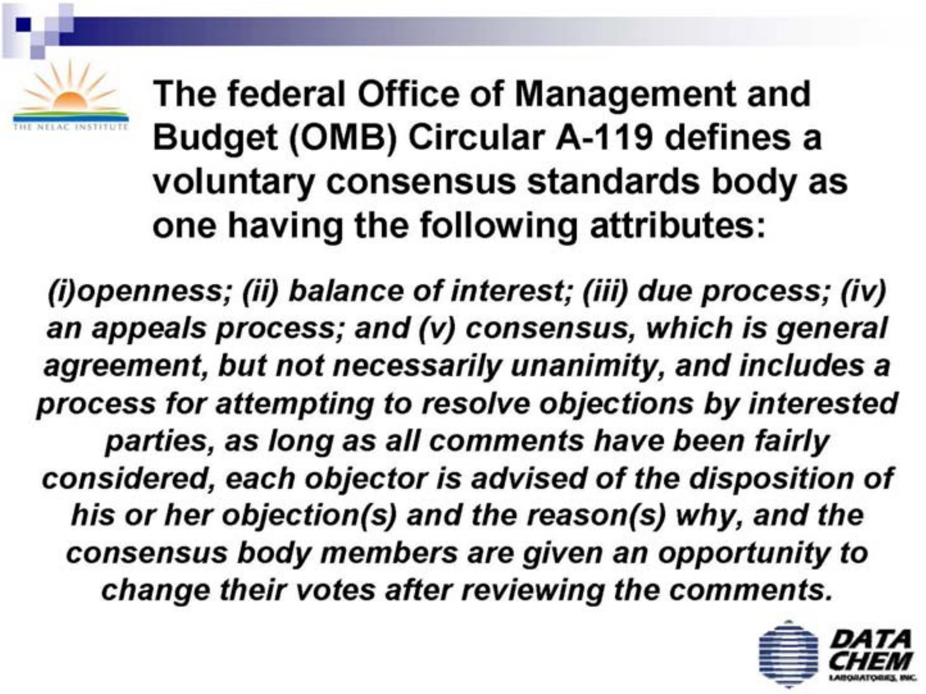
Consensus is a decision-making process that not only seeks the agreement of most participants, but also to resolve or mitigate the objections of the minority to achieve the most agreeable decision.

What is a Standard?

A **standard** is an established norm or requirement. It is usually a formal document that establishes uniform engineering or technical criteria, methods, processes and practices.

ANSI Requirements of a Consensus Standards Development Body

- Openness
- Balance of interest
- Consensus
- Due Process
- Appeals Process



The federal Office of Management and Budget (OMB) Circular A-119 defines a voluntary consensus standards body as one having the following attributes:

(i)openness; (ii) balance of interest; (iii) due process; (iv) an appeals process; and (v) consensus, which is general agreement, but not necessarily unanimity, and includes a process for attempting to resolve objections by interested parties, as long as all comments have been fairly considered, each objector is advised of the disposition of his or her objection(s) and the reason(s) why, and the consensus body members are given an opportunity to change their votes after reviewing the comments.

Having met all requirements, the TNI Consensus Standards Development Program was approved by ANSI, effective December 18, 2007.

The TNI consensus standard development process meets the requirement of Office of Management and Budget (OMB) Circular A-119 "Federal Participation in the Development and Use of Voluntary Consensus Standards and in Conformity Assessment Activities".

The NELAC Institute (TNI) Standards Development Process

Monthly Meetings — Expert Committee submits Working Draft Standard for public comment

Public Meeting

Monthly Meetings — Working Draft Standard is modified from public comment

Monthly Meetings — Modified WDS is voted to Draft Interim Standard

Public Meeting

All Stakeholders vote and comment on Draft Interim Standard

Monthly Meetings — Draft Interim Standard is modified by persuasive comments and all comments are addressed.

Monthly Meetings — Commitee votes Draft Interim Standard to Final Standard

Public Meeting

How did we get here?

Working Draft Standards

Dallas, Jan 2004

Charleston, Aug 2004

Philadelphia, Jan 2005

Austin, April 2005

Raleigh, Aug 2005

Chicago, Jan 2006

Kansas, Aug 2006

Tallahasse, Oct 2006

Denver, Jan 2007

THE NELAC INSTITUTE

How did we get here?

Draft Interim Standards	Cambridge, Aug 2007 ***Lancaster, Oct, 2007***
Final Standards	Newport Beach, Jan 2008

DATA CHEM LABORATORIES, INC.

THE NELAC INSTITUTE

Where are we today?

Final Standards have been reviewed for consistency.

Final Standards will be published to Website. June 2008

Appeals Process will begin when published. June/July

Appeals process through TNI Board of Directors.

Final Standards will be submitted to TNI NELAP Board. Aug 2008

DATA CHEM LABORATORIES, INC.

TNI Quality Systems Expert Committee

Accreditation Bodies

Aaren Alger, State of Pennsylvania
Laurie Carhart, State of New York
Michelle Potter, State of New Jersey

Accredited Laboratories

Robin Cook, City of Daytona Beach
Robert Di Rienzo, DataChem Laboratories
Wilson Hershey, Lancaster Laboratories
Paul Junio, Test America

Other

Silky Labie, State of Florida
Fred McLean, DoD
Randy Querry, A2LA

DATA CHEM LABORATORIES, INC.

The TNI Standards are based on the concept of sectors, volumes, and modules.

Environmental Laboratory Sector

Volume 1 – Laboratory Requirements
Volume 2 – Accreditation Body Requirements
Volume 3 – Proficiency Testing Provider Requirements
Volume 4 – Proficiency Testing Oversight Requirements

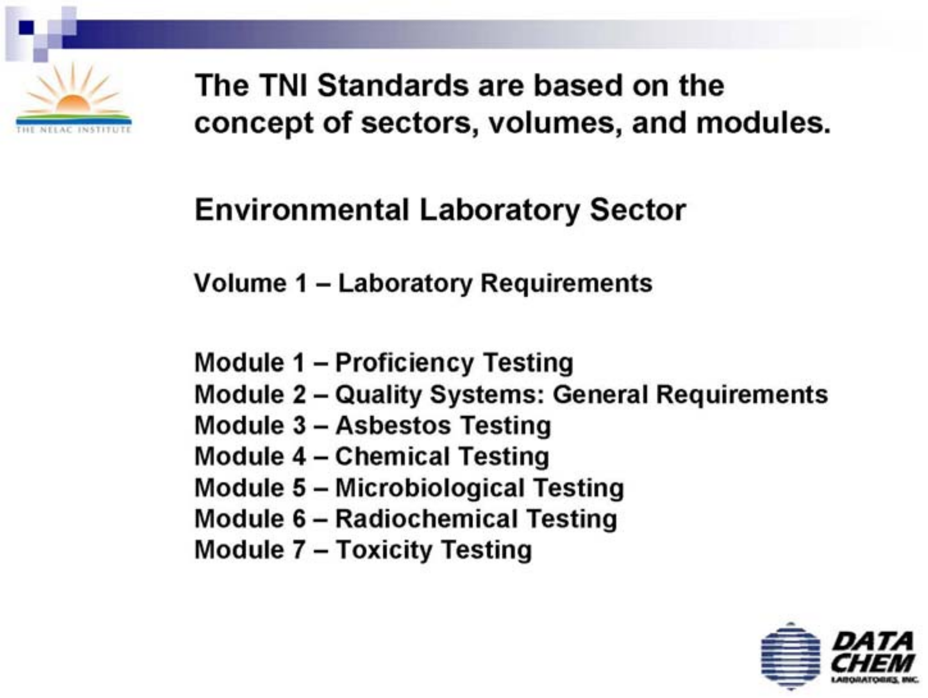
DATA CHEM LABORATORIES, INC.

The TNI Standards are based on the concept of sectors, volumes, and modules.

Field Services and Measurement Organization Sector

Volume 1 – FSMO Requirements
Volume 2 – FSMO Accreditation Body Requirements

How does a laboratory know what to do?

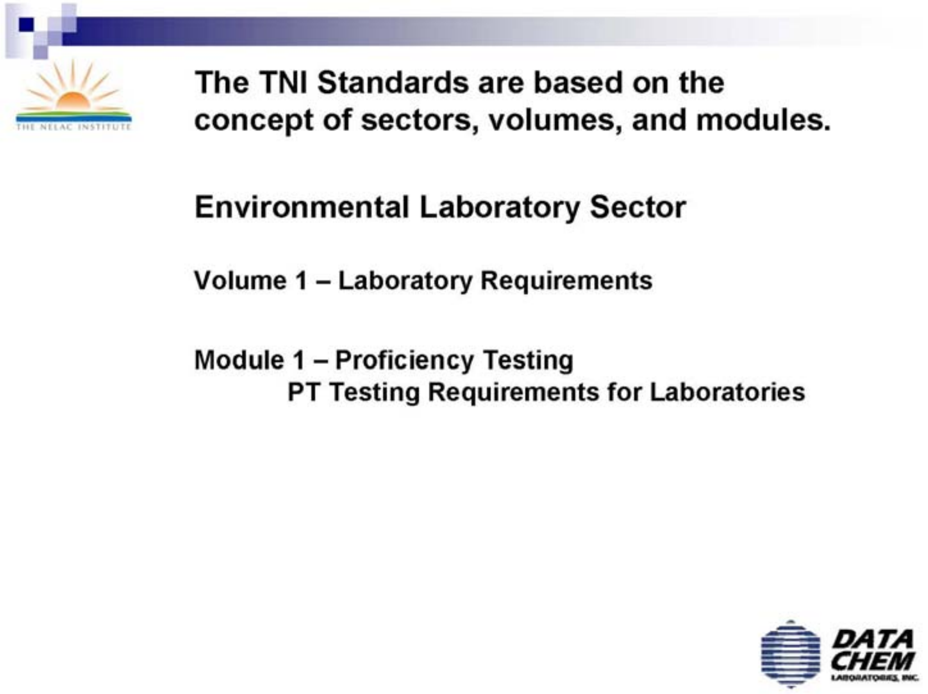


The TNI Standards are based on the concept of sectors, volumes, and modules.

Environmental Laboratory Sector

Volume 1 – Laboratory Requirements

Module 1 – Proficiency Testing
Module 2 – Quality Systems: General Requirements
Module 3 – Asbestos Testing
Module 4 – Chemical Testing
Module 5 – Microbiological Testing
Module 6 – Radiochemical Testing
Module 7 – Toxicity Testing



The TNI Standards are based on the concept of sectors, volumes, and modules.

Environmental Laboratory Sector

Volume 1 – Laboratory Requirements

Module 1 – Proficiency Testing
PT Testing Requirements for Laboratories

The TNI Standards are based on the concept of sectors, volumes, and modules.

Environmental Laboratory Sector

Volume 1 – Laboratory Requirements

Module 2 – Quality Systems: General Requirements
A Quality System for all laboratories

The TNI Standards are based on the concept of sectors, volumes, and modules.

Environmental Laboratory Sector

Volume 1 – Laboratory Requirements

Module 3 – Asbestos Testing
Module 4 – Chemical Testing
Module 5 – Microbiological Testing
Module 6 – Radiochemical Testing
Module 7 – Toxicity Testing

Technical Modules

Volume 1
Environmental Laboratory Sector Laboratories Requirements

- Includes all standards for laboratories
- Uses ISO/IEC 17025:2005 for Quality Systems
- Flexible and Consistent
- Technical Modules can be added as needed
- Available for purchase with ISO Language
  www.nelac-institute.org

Volume 1
Environmental Laboratory Sector Laboratories Requirements

Module 2 - Quality Systems: General Requirements

- Format consistent with ISO 17025:2005
- Additional NELAC requirements follow applicable ISO sections
- Redundant language has been removed
- Specific technical requirements in Modules 3 to 7

Module 2 - Quality Systems: General Requirements

1.0 **INTRODUCTION, SCOPE AND APPLICABILITY**
Introduction and Scope
2.0 **NORMATIVE REFERENCES**
3.0 **TERMS AND DEFINITIONS**
Additional Terms and Definitions, Definition Sources, and Exclusions and Exceptions
4.0 **MANAGEMENT REQUIREMENTS**
Organization, Management, Document Control, Review of Request, Tenders and Contracts, Subcontracting of Environmental Tests, Purchasing Services and Supplies, Service to the Client, Complaints, Control of Nonconforming Environmental Testing Work, Improvement, Corrective Action, Preventive Action, Control of Records, Internal Audits, Management Review, and Data Integrity Surveillance

---

Module 2 - Quality Systems: General Requirements

5.0 **TECHNICAL REQUIREMENTS**
General, Personnel, Accommodation and Environmental Conditions, Environmental Test Methods and Method Validation, Calibration Requirements, Measurement Traceability, Collection of Samples, Handling Samples and Test Items, Quality Assurance for Environmental Testing, and Reporting the Results

Module 2 - Quality Systems: General Requirements

Example Section from Module 2 – Non ISO version

4.14 Internal Audits *(ISO/IEC 17025:2005(E), Clause 4.14)*
ISO text 4.14.1 to 4.14.4 here

4.14.5 Additional Items

a) The laboratory shall have a policy that specifies the time frame for notifying a client of events that cast doubt on the validity of the results.

b) The laboratory management shall ensure that these actions are discharged within the agreed time frame.

c) The Internal audit schedule shall be completed annually.

Volume 1

Environmental Laboratory Sector Laboratories Requirements

Modules 3 to 7 - Technical Modules for Asbestos, Chemistry, Microbiology, Radiochemistry, and Toxicity Testing

- **No ISO language**
- **Specific to Testing Activity**
- **Consistent Format and Structure in all Technical Modules**

Modules 3 to 7 - Technical Modules for Testing

______________TESTING

1.1 Introduction
1.2 Scope
1.3 Terms and Definitions
1.4 Method Selection
1.5 Method Validation
    Validation of Methods, Limit of Detection and Limit of Quantitation, Evaluation of Precisions and Bias, and Evaluation of Selectivity

---

Modules 3 to 7 - Technical Modules for Testing

______________TESTING

1.6 Demonstration of Capability (DOC)
    General, Initial DOC, and Ongoing DOC
1.7 Technical Requirements
    Initial Calibration, Continuing Calibration, Quality Control for Chemistry, Data Reduction, Reagent Quality, Water Quality and Checks, Data Acceptance/Rejection Criteria, and Sample Handling

Modules 3 to 7 - Technical Modules for Testing Example Section

1.6 Demonstration of Capability (DOC)

1.6.1 General

Prior to acceptance and institution of any method for which data will be reported, a satisfactory initial DOC is required (see Section 1.6.2).

Thereafter, ongoing DOC (Section 1.6.3), as per the quality control requirements in Section 1.7.3 (such as laboratory control samples) is required.

In cases where a laboratory analyzes samples using a method that has been in use by the laboratory for at least one year prior to applying for accreditation, and there have been no significant changes in instrument type, personnel or method, the ongoing DOC shall be acceptable.

Modules 3 to 7 - Technical Modules for Testing Example Section

1.6 Demonstration of Capability (DOC)

1.6.1 General (Continued)

The laboratory shall have records on file to demonstrate that a DOC is not required.

For the initial DOC, appropriate records as discussed in Section 1.6.2 shall be completed.

An initial DOC shall be completed each time there is a change in instrument type, personnel, or method.

All demonstrations shall be documented.

All data applicable to the demonstration shall be retained and readily available at the laboratory.

Questions?

False Positives in Environmental Measurements – An Analysis of Method Blank Data

Charles Carter
TestAmerica, Inc.
3275 S. Tioga Way
Las Vegas, NV 89117
702-592-6792
charlie.carter@testamericainc.com

ABSTRACT

Environmental measurements have become increasingly sensitive, and as a result we are detecting analytes at lower and lower concentrations. Despite this, in many situations laboratories are asked to report results below their routine reporting limits all the way to the method detection limit. It is widely accepted that the results reported below the reporting limit are less reliable than those above the reporting limit, but there have been few studies that would quantify the extent of the decreased reliability.

One aspect of the decreased reliability is the risk of an increased number of false positives when results are reported below the reporting limit. While we can not actually determine whether the results in each sample are false positives, we can analyze the frequency of positive results in our method blanks. It is reasonable to conclude that the rate of false positives in environmental samples will be similar to the rate of positive detections in method blanks.

This presentation will summarize the results of thousands of method blank results over a large population of laboratories. This will include the frequency of detections, the average concentrations detected, an analysis of the reasons for the positive results, and the differences between laboratories.

For most analytes, there is virtually no risk of false positives, but there are many environmentally relevant analytes with a substantial frequency of detections in method blanks. For these analytes, environmental decisions can be seriously compromised when using data that is reported to the MDL.

Determining Detection and Quantitation Limits - Designing a Straightforward Procedure that Actually Works

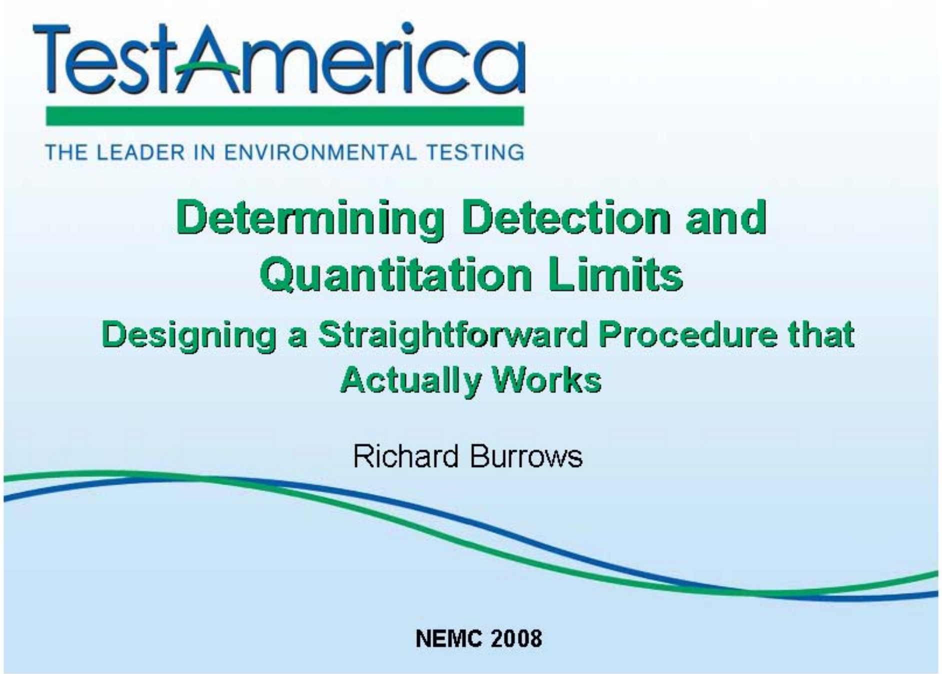
Richard Burrows
TestAmerica, Inc.
4955 Yarrow St.
Arvada, CO 80002
Richard.burrows@testamericainc.com

ABSTRACT

This presentation will discuss the development of a new procedure for determination of detection and quantitation limits by an EPA sponsored Federal Advisory Committee. The new procedure is intended to replace the current MDL procedure found in 40CFR Part 136, Appendix B.

The general concepts incorporated into the new procedure will be explored and the reasons for several difficult decisions that went into the development of the procedure will be discussed. These decisions include:

- Use of definitions for Detection and Quantitation that are different from those in ISO and IUPAC standards
- Use of a two level detection / quantitation scheme rather than the three level scheme first proposed by Currie
- Use of method blanks (rather than the spiked samples used in the current MDL) to determine detection limits wherever possible
- Use of ongoing verification rather than starting a new study every year as it the case with the current MDL
- Items incorporated into the verification process
- How much data should be required for detection and quantitation limit determinations
- Use of new concepts such as the "Lowest Expected Result" (LER)



TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Determining Detection and Quantitation Limits

Designing a Straightforward Procedure that Actually Works

Richard Burrows

NEMC 2008

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

FACDQ

- Federal Advisory Committee for Detection and Quantitation
- Established May 2005
- Recommend Detection and Quantitation procedures for compliance monitoring under 40CFR Part 136
- Provide advice and recommendations on policy issues related to detection and quantitation

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

FACDQ

- Participants drawn from
  - ~ States
  - ~ Regulated industry
  - ~ Publicly owned treatment works
  - ~ Testing laboratories
  - ~ Environmental Community

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

What do we need a Procedure to do?

- MQOs
  - ~ Produce an estimate of bias
  - ~ Produce an estimate of precision
  - ~ False Positives
  - ~ False negatives

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

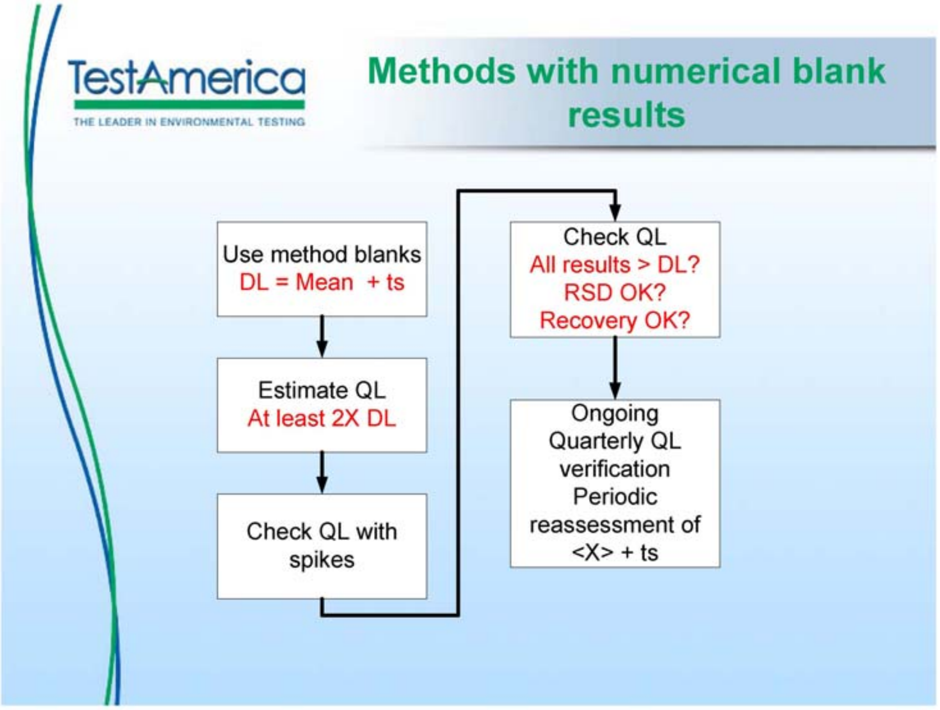
What do we need a procedure to do?

- Incorporate temporal variability
- Reflect routine performance
- Address matrices
- Evaluate the entire test method
- Address blank bias
- Address intermittent blank contamination

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Other considerations for procedures

- How complex is the data to process?
- How complex is the procedure to implement in the laboratory?
- Is the procedure clearly written?
- Does he procedure communicate detection/quantitation concepts?



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Methods with numerical blank results

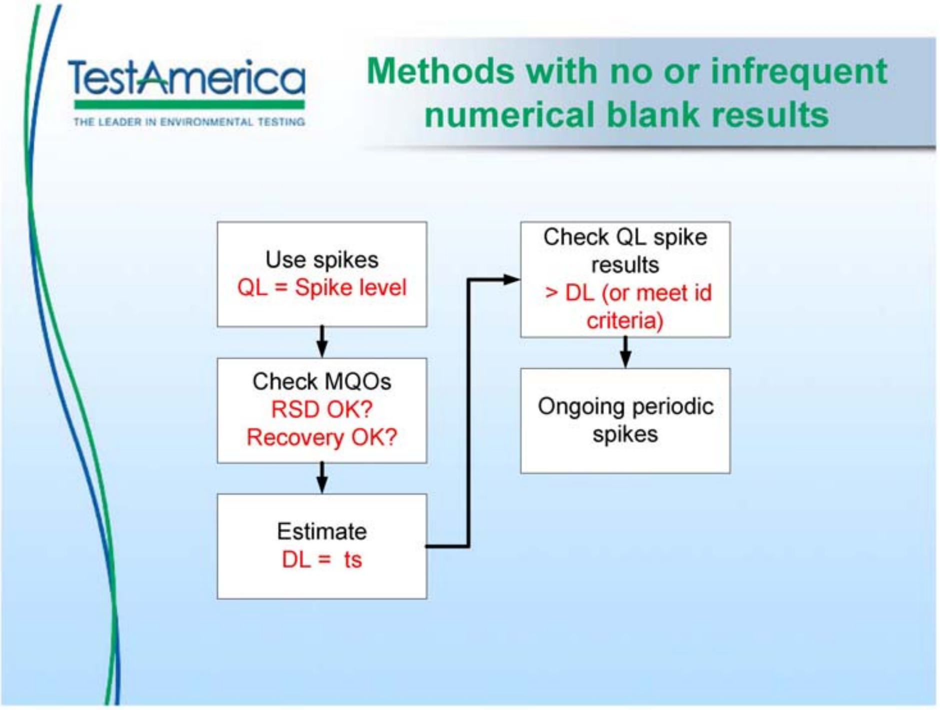
Use method blanks
DL = Mean + ts

Estimate QL
At least 2X DL

Check QL with spikes

Check QL
All results > DL?
RSD OK?
Recovery OK?

Ongoing Quarterly QL verification
Periodic reassessment of <X> + ts



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Methods with no or infrequent numerical blank results

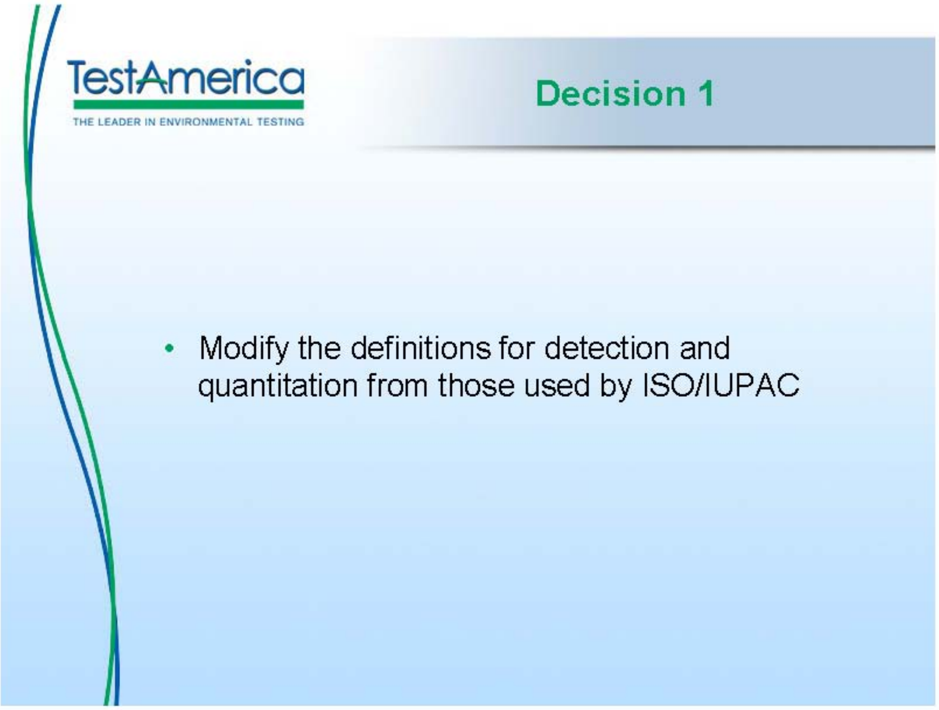
Use spikes
QL = Spike level

Check MQOs
RSD OK?
Recovery OK?

Estimate
DL = ts

Check QL spike results
> DL (or meet id criteria)

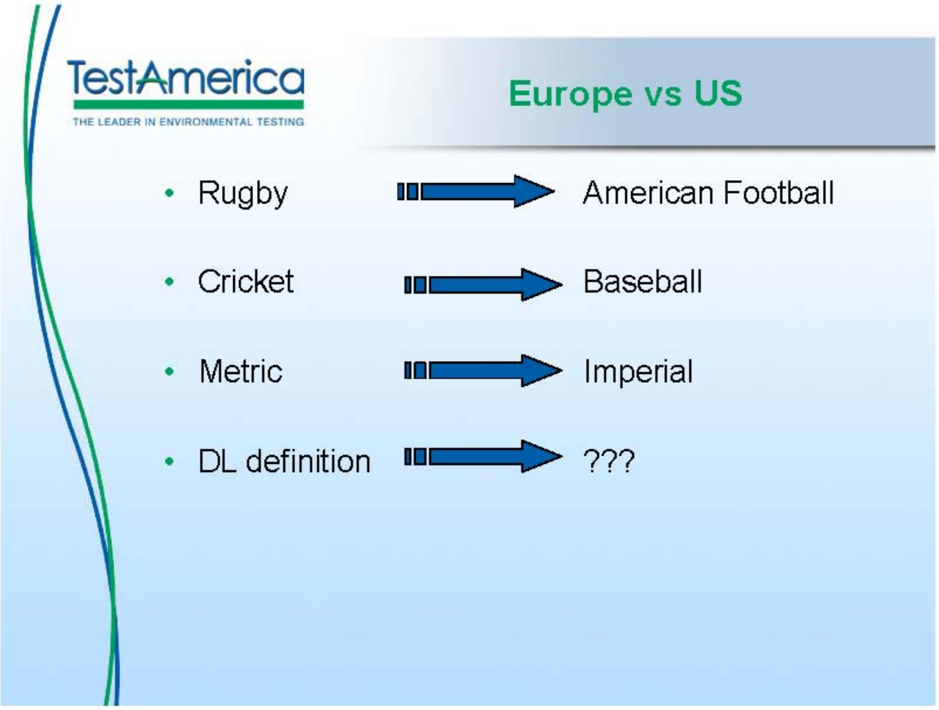
Ongoing periodic spikes



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Decision 1

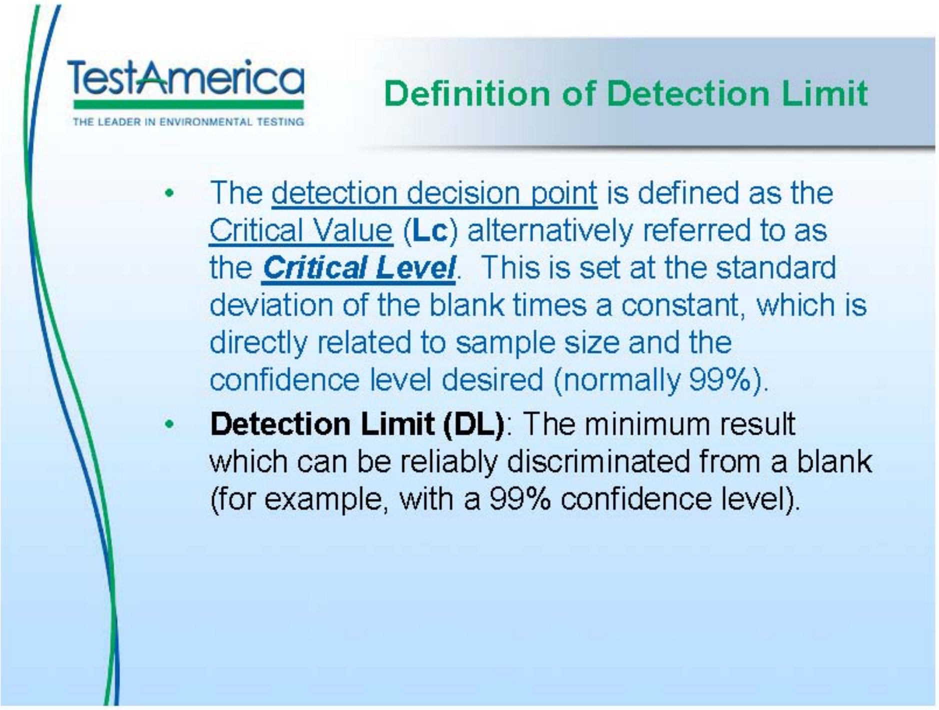
- Modify the definitions for detection and quantitation from those used by ISO/IUPAC



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Europe vs US

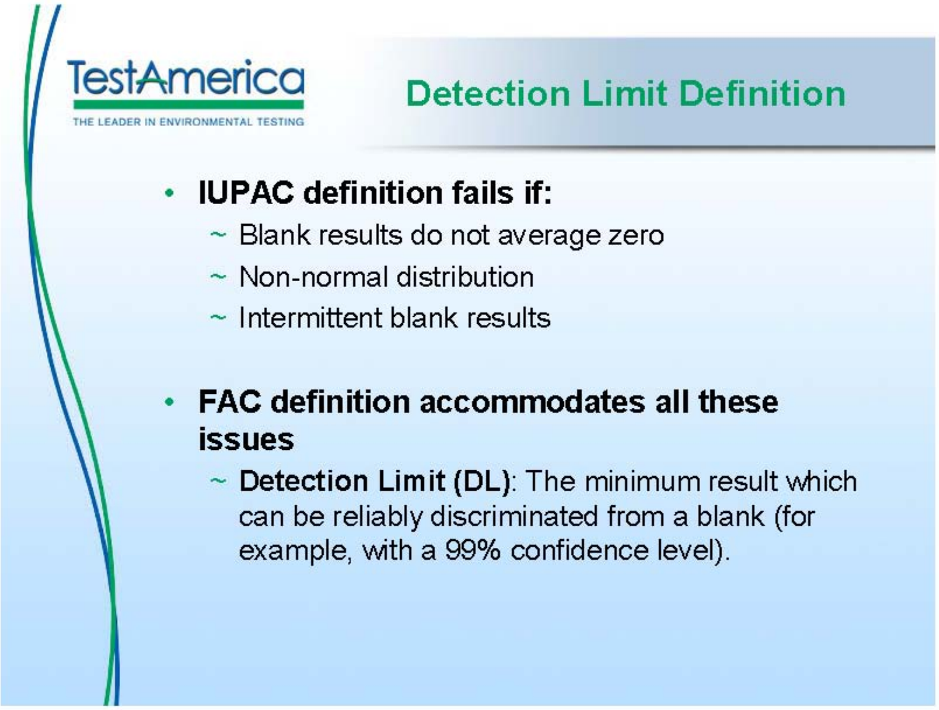
- Rugby → American Football
- Cricket → Baseball
- Metric → Imperial
- DL definition → ???



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Definition of Detection Limit

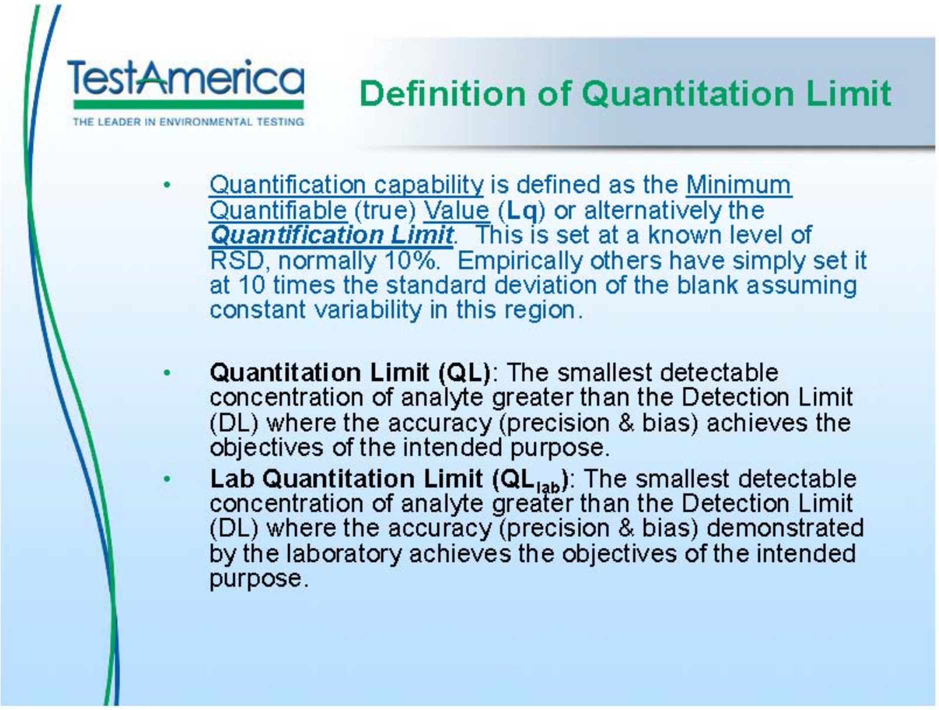
- The detection decision point is defined as the Critical Value (**Lc**) alternatively referred to as the ***Critical Level***. This is set at the standard deviation of the blank times a constant, which is directly related to sample size and the confidence level desired (normally 99%).
- **Detection Limit (DL)**: The minimum result which can be reliably discriminated from a blank (for example, with a 99% confidence level).



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Detection Limit Definition

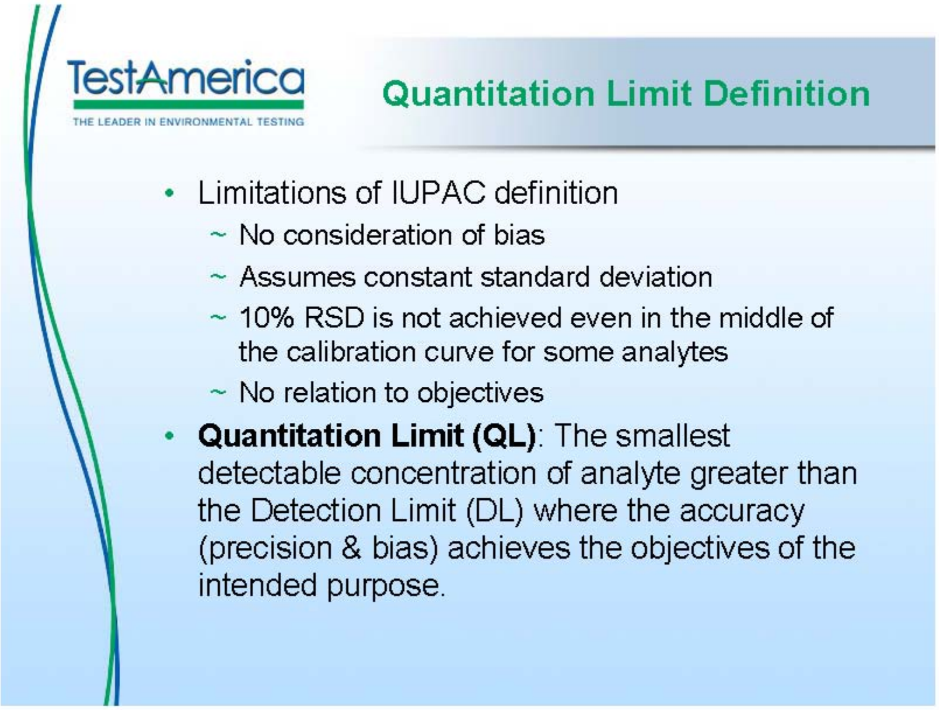
- **IUPAC definition fails if:**
  - Blank results do not average zero
  - Non-normal distribution
  - Intermittent blank results
- **FAC definition accommodates all these issues**
  - **Detection Limit (DL)**: The minimum result which can be reliably discriminated from a blank (for example, with a 99% confidence level).



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Definition of Quantitation Limit

- Quantification capability is defined as the Minimum Quantifiable (true) Value (**Lq**) or alternatively the ***Quantification Limit***. This is set at a known level of RSD, normally 10%. Empirically others have simply set it at 10 times the standard deviation of the blank assuming constant variability in this region.
- **Quantitation Limit (QL)**: The smallest detectable concentration of analyte greater than the Detection Limit (DL) where the accuracy (precision & bias) achieves the objectives of the intended purpose.
- **Lab Quantitation Limit (QL_{lab})**: The smallest detectable concentration of analyte greater than the Detection Limit (DL) where the accuracy (precision & bias) demonstrated by the laboratory achieves the objectives of the intended purpose.



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Quantitation Limit Definition

- Limitations of IUPAC definition
  - ~ No consideration of bias
  - ~ Assumes constant standard deviation
  - ~ 10% RSD is not achieved even in the middle of the calibration curve for some analytes
  - ~ No relation to objectives
- **Quantitation Limit (QL)**: The smallest detectable concentration of analyte greater than the Detection Limit (DL) where the accuracy (precision & bias) achieves the objectives of the intended purpose.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

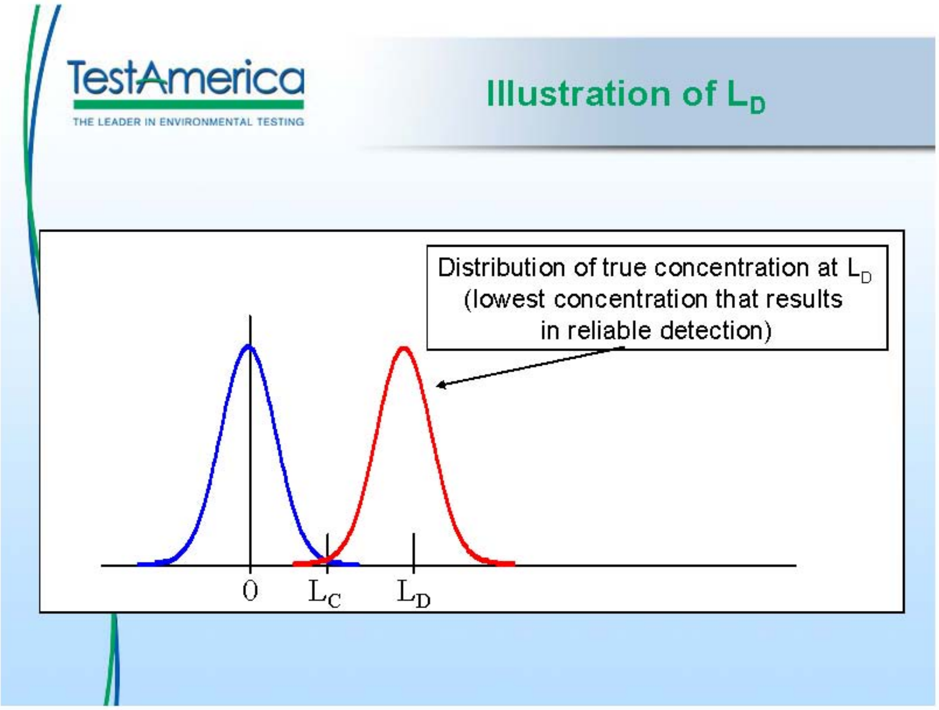
Decision 2

- Use a 2 level detection / quantitation scheme with a critical level and a quantitation limit
- Do not use a three level detection / quantitation scheme with a critical level, a limit of detection and a quantitation limit

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Why use a 2 level DL/QL rather than a 3 level DL/QL?

- Currie defined three levels, L_C, L_D and L_Q
- L_C = Critical level
  - Lowest result that can be reliably distinguished from a blank
- L_D = Limit of Detection
  - Lowest true concentration that can be reliable detected (ie lowest true concentration that reliable returns a result greater than L_C
- L_Q = Limit of Quantitation
  - The lowest true concentration at which the precision of result is adequate for quantification (often considered to be 10%RSD)

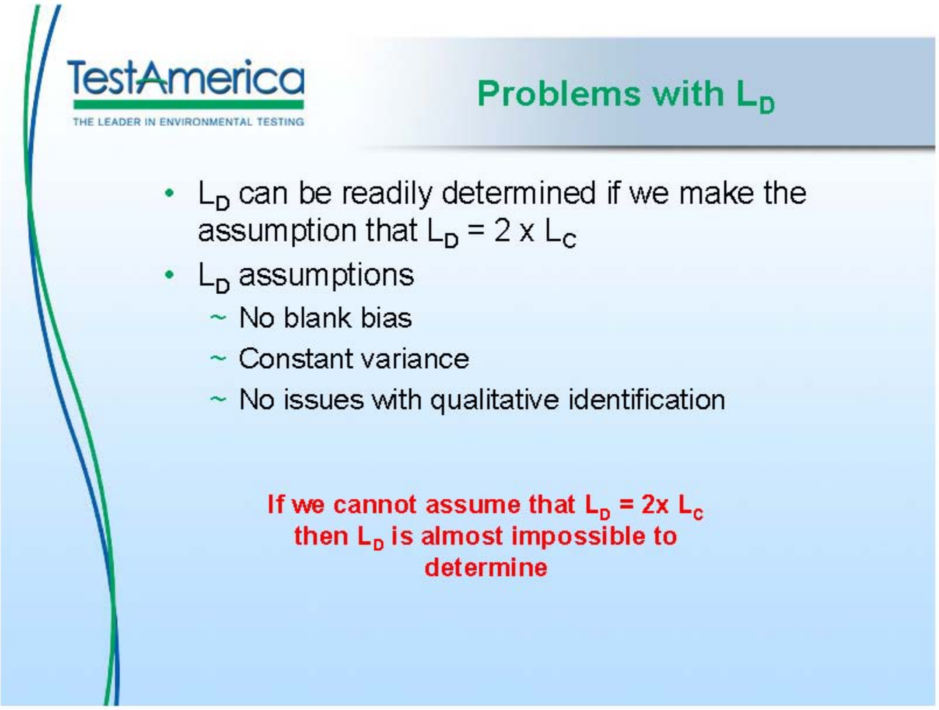


TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Illustration of L_D

Distribution of true concentration at L_D (lowest concentration that results in reliable detection)



TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Problems with L_D

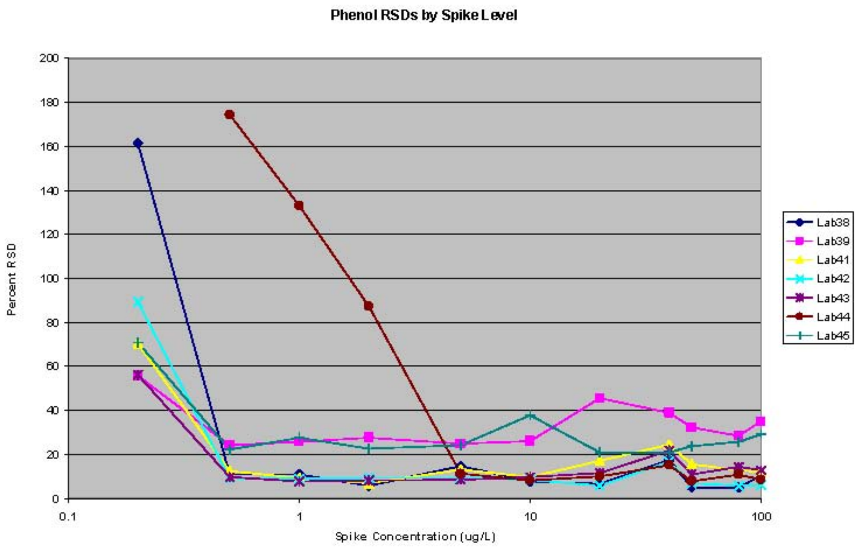
- L_D can be readily determined if we make the assumption that $L_D = 2 \times L_C$
- L_D assumptions
  - ~ No blank bias
  - ~ Constant variance
  - ~ No issues with qualitative identification

If we cannot assume that $L_D = 2x\ L_C$ then L_D is almost impossible to determine

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Reasons for the 2 level procedure

- L_D turns out to be close to L_Q in most cases
- The current MDL/ML process is a two level scheme
- Critical level (MDL)
- Quantitation limit (ML)
  - ~ Changing to a three level scheme would have severe implementation problems for laboratory reporting and regulatory use of data



From Ken Miller, CSC

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

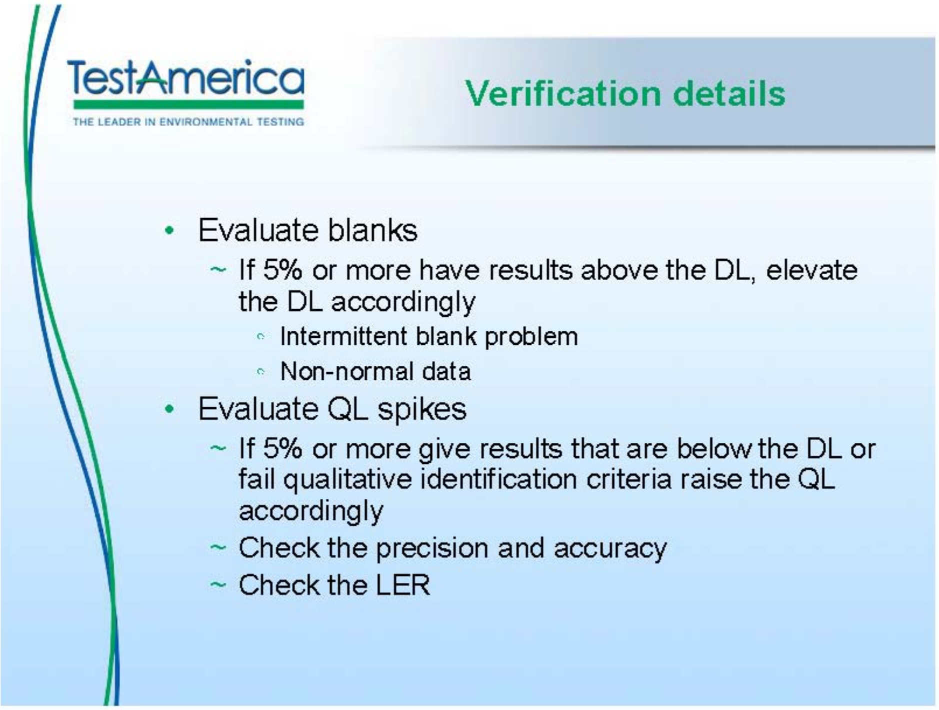
Decision 3

- Use method blanks to determine the detection limit wherever possible
  - ~ The level of contamination or instrument bias has a very significant impact on the detection limit, and the degree of impact can only be determined with blanks
  - ~ A large population of routine blanks is available, since they are analyzed along with every preparation batch
  - ~ No problems regarding selection of the correct spiking level
  - ~ Blanks work best!

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Decision 4

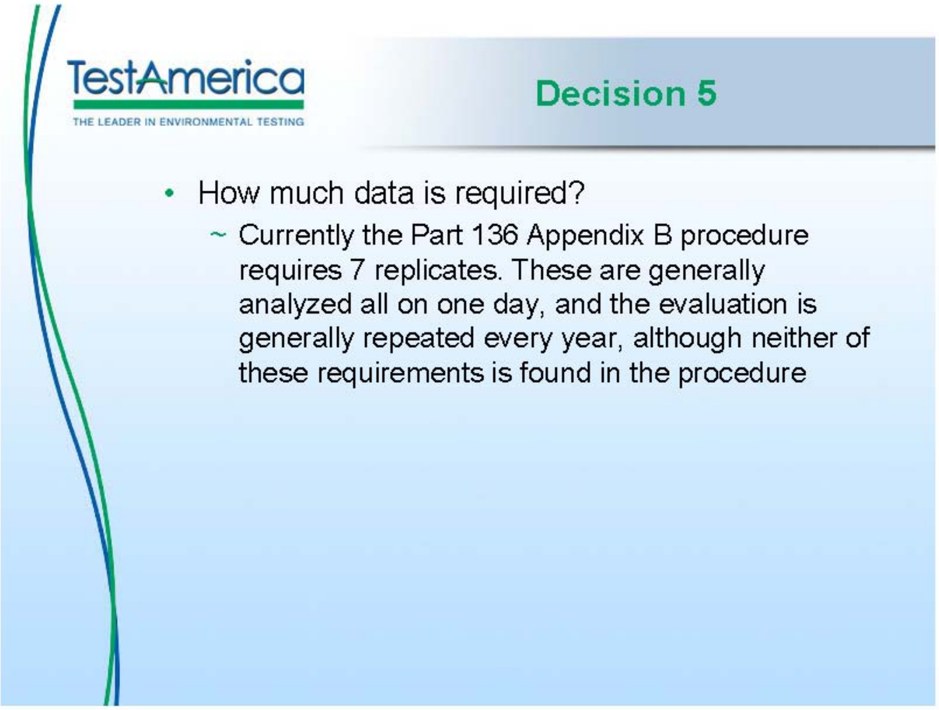
- Include a process for verifying the determined detection and quantitation limits
  - ~ There is no requirement to verify MDL or ML in the current Part 136 Appendix B, but….
  - ~ The need for verification is widely recognized
    - ◦ Requirements for DL and QL verifications in NELAC
    - ◦ Requirements in recent methods



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Verification details

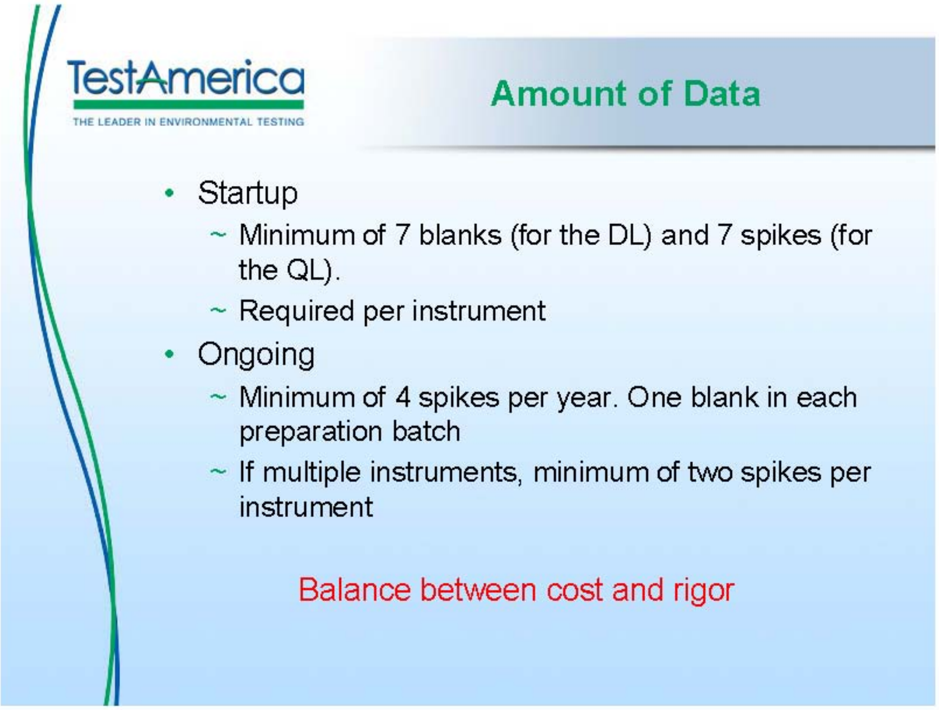
- Evaluate blanks
  - If 5% or more have results above the DL, elevate the DL accordingly
    - Intermittent blank problem
    - Non-normal data
- Evaluate QL spikes
  - If 5% or more give results that are below the DL or fail qualitative identification criteria raise the QL accordingly
  - Check the precision and accuracy
  - Check the LER



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Decision 5

- How much data is required?
  - Currently the Part 136 Appendix B procedure requires 7 replicates. These are generally analyzed all on one day, and the evaluation is generally repeated every year, although neither of these requirements is found in the procedure



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Amount of Data

- Startup
  - Minimum of 7 blanks (for the DL) and 7 spikes (for the QL).
  - Required per instrument
- Ongoing
  - Minimum of 4 spikes per year. One blank in each preparation batch
  - If multiple instruments, minimum of two spikes per instrument

Balance between cost and rigor

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Decision 6
Lowest Expected Result

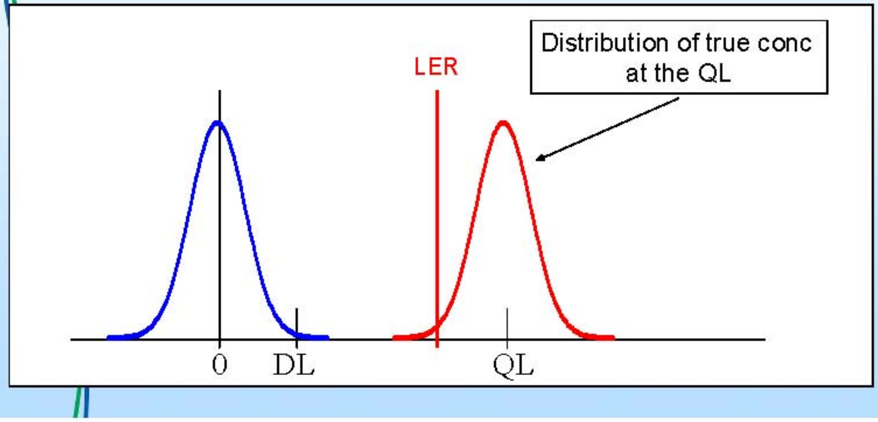
$$\text{LER} = \frac{\overline{X}_s * QL}{SL} - \left(s \times t_{(n-1,1-\alpha=0.95)}\right)$$

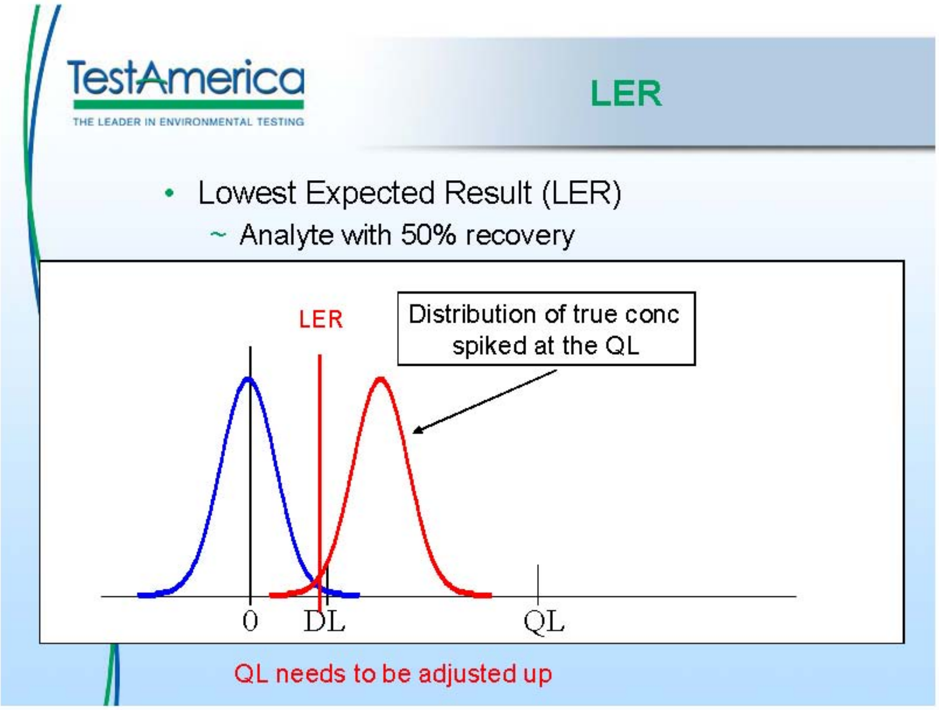
- Where *s* is defined in std dev of spikes
- Where X is the mean concentration result from the QL spikes.
- t is the 95th percentile of a *t* distribution with n-1 degrees of freedom.
- *SL* is the spike level used for the QL spike sample.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

LER

- Lowest Expected Result (LER)
  - ~ Analyte with 100% recovery





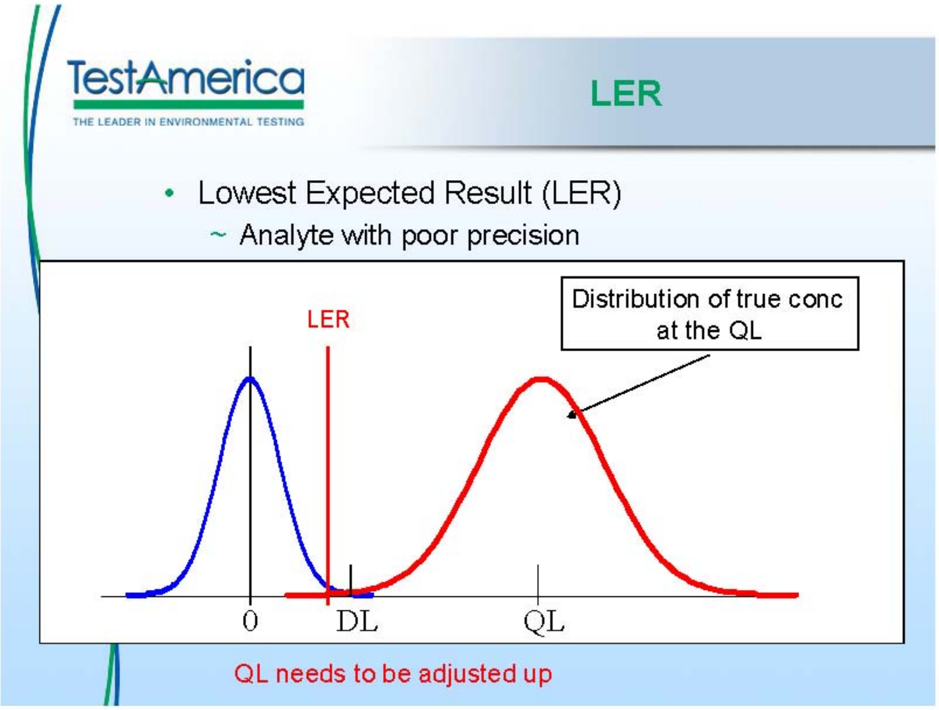
TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

LER

- Lowest Expected Result (LER)
  - ~ Analyte with 50% recovery

Distribution of true conc spiked at the QL

QL needs to be adjusted up



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

LER

- Lowest Expected Result (LER)
  - ~ Analyte with poor precision

Distribution of true conc at the QL

QL needs to be adjusted up

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

LER check, method 524.2

- 13 samples, spiked at QL
- No false negatives for any analyte that passes the LER test
- 10 analytes that failed the LER test had between 1 and 13 false negatives

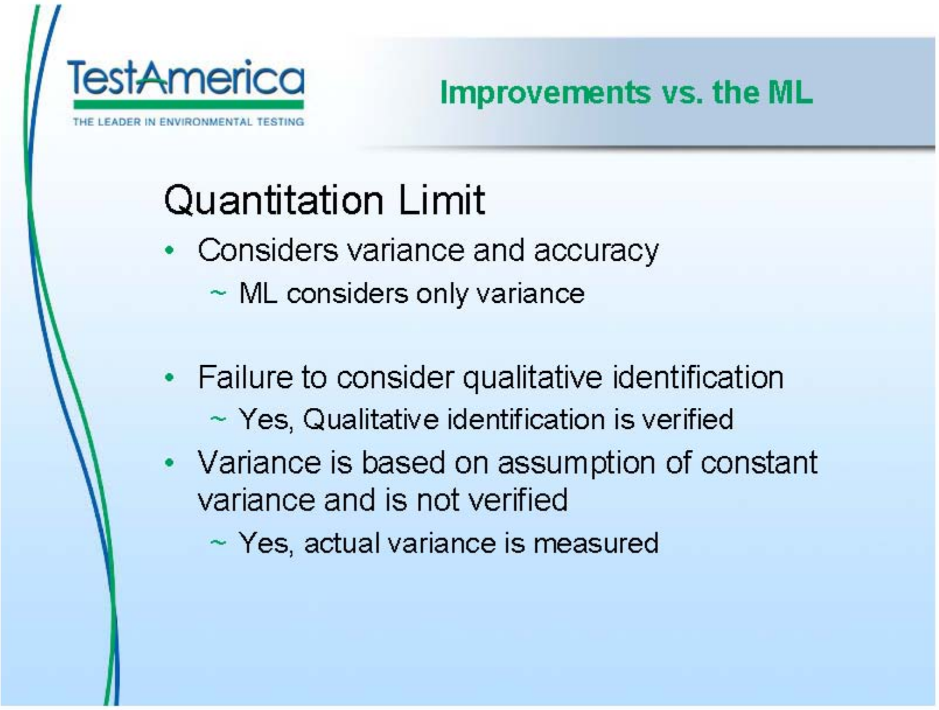
---

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Improvements vs. the MDL

Detection Limit

- Uses ongoing routine data
  - ~ MDL was a snapshot in time
- Blank bias explicitly included
  - ~ MDL calculation does not involve blank bias
- Verification a key part of the procedure
  - ~ MDL does not require verification



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Improvements vs. the ML

Quantitation Limit

- Considers variance and accuracy
  - ~ ML considers only variance
- Failure to consider qualitative identification
  - ~ Yes, Qualitative identification is verified
- Variance is based on assumption of constant variance and is not verified
  - ~ Yes, actual variance is measured

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Next Steps

- Pilot test of the procedure
- Procedure modifications, if indicated by Pilot results
- Proposed rule
- Public Comment
- Final rule

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

- All opinions expressed are those of the author, not necessarily of the FAC

Questions?

AUTHOR INDEX

NATIONAL ENVIRONMENTAL MONITORING CONFERENCE PROCEEDINGS 2008

AUTHOR INDEX