CHEMICAL ANALYSIS AND DREDGED MATERIAL

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KEY WORDS: Detection Limits, Analytical Chemistry, Target Analytes, QA/QC, Electronic Data Deliverables

Chemical Analysis for Sediment Evaluation

- Topics:
  - → Chemistry and DM
  - → Techniques
  - → Detection Limits
  - → QA/QC Samples
  - → Data Interpretation
  - → Electronic Data Deliverables

Chemistry and Dredged Material

- Involves analysis of sediment, water, and tissue.

→Review of existing chemical data on sediment, water, and/or tissue (Tier I): *Is there a problem?*

→Sediment analysis (Tier II): *How much and which COCs are present.*

→Analysis of elutriates and water from collection and disposal sites (Tier II): *Potential mobilization of DM COCs.*

→ Analysis of test organisms in bioaccumulation tests (Tier III) or tissue from fish/benthic organisms at site (Tier IV): *COCs ability to move from DM to living organisms.*

Sample Prep Techniques

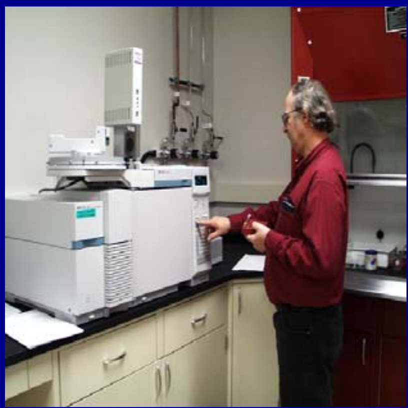
- **Extraction (Organics):**
  - **→ ASE or soxhlet (sediment)**
  - **→ Separatory funnel (water)**
  - **→ Sonication or ASE (tissue)**
- **Cleanup (Organics):**
  - **→ GPC**
  - **→ column chromatography**
  - **→ con. sulfuric acid (PCBs)**
  - **→ sulfur cleanup with Hg**
- **Digestion (Metals):**
  - **→ Heated block w/nitric acid**
  - **→ Microwave w/nitric acid**

Analytical Techniques

- Same basic techniques for sediment, water, tissue
- **Metals:** ICP-AES, ICP-MS, GFAAS, CVAFS
- **Organics:** GC, GC/MS, HPLC
- **Other Parameters:** IC, FT-IR, gravimetric, colorimetric, electrochemical

Chemical Analysis of Sediments

- **Sediments** are challenging analytical matrices
- **Contaminants** detected often drive target lists for water and tissue samples
- **Exhaustive target lists** may still miss key sediment contaminants
- **GC/MS & ICP/MS** techniques can cover broad spectrum of unknowns.



Chemical Analysis of Water

- **Freshwater** samples typically present fewer interferences and can yield low detection limits
- **Saltwater** often requires alternate techniques
- **Elutriate tests** measure potential release of sediment pollutants into site water

Chemical Analysis of Tissue

- **EPA** tested methods available
- **Organics** with Log $K_{ow} > 3.5$ & **Inorganics** with Log BCF > 3.0 should be evaluated
- **Select targets**: (1) found in sediment, (2) that may bioaccumulate, (3) are of toxicologic concern
- **Lipids** determination may be needed

Microscale Analysis of Tissue

- **Tier III bioaccumulation tests must be scaled to yield enough tissue for traditional analytical techniques**
  → Adds substantial cost burden to project.
- **Microscale techniques have been developed for PCBs and PAHs and are being developed for chlorinated pesticides.**
  → Enhanced extract volume reduction offsets reduced tissue amounts.
  → PAH & PCB Methods perform similar to traditional approaches although recoveries lower for PCBs.
- **Lipids may also be determined by a published microscale approach (Van Handel, 1985).**

Micromethod for PAHs

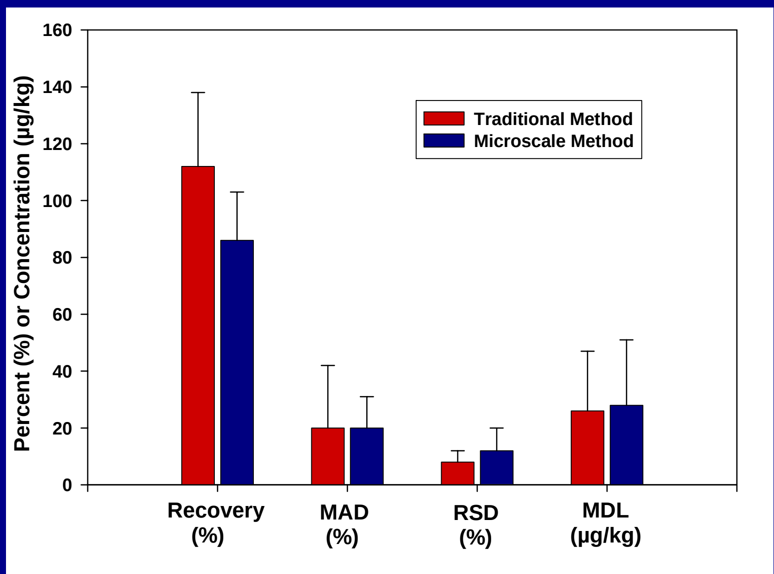


Figure 1. Comparison of traditional and microscale methods for PAH analysis in spiked cod.

Micromethod for PCBs

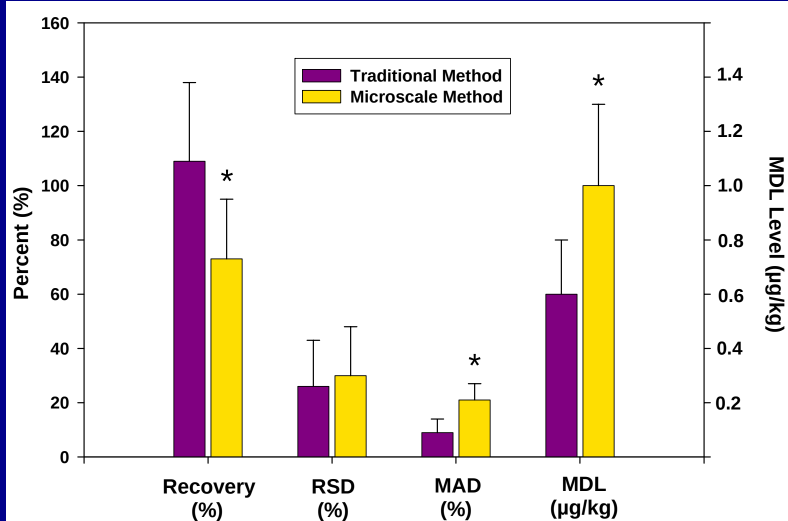


Figure 2. Comparison of traditional and microscale methods for PCB analysis in spiked cod. Asterisks indicate MM significantly different than TM ($P<0.001$).

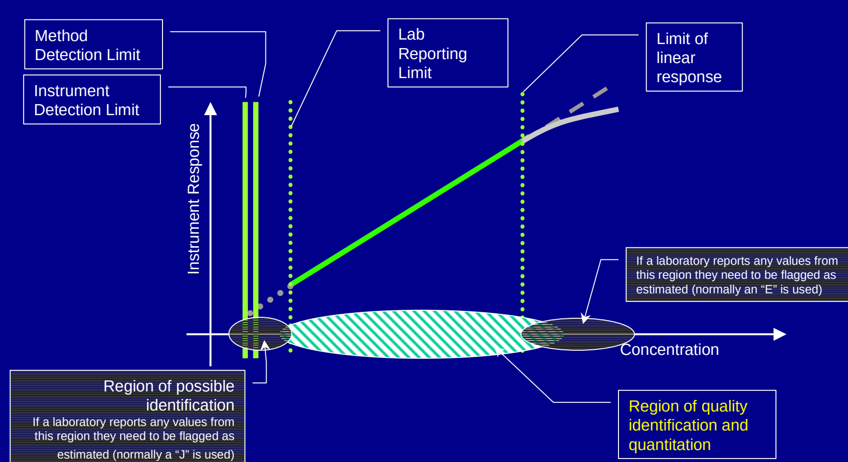
Detection Limits

- Determining presence/absence of contaminants of concern (COCs) is critical to evaluation of dredged sediments prior to disposal.
- With modern analytical techniques, COCs detected above threshold levels may be confirmed and quantified with a high degree of certainty.
- Unfortunately, the language we currently use to identify and discuss these threshold levels, generally termed "detection limits", is often poorly understood and consequently misused.

Detection Limit Terminology

- **Method Detection Limit (MDL)** – Statistically-derived minimum level that can be measured and reported with 99% confidence that it is greater than zero.
- **Lab Reporting Limit (LRL)** – Minimum level a lab will report with confidence in quantitative accuracy.
- **Target Detection Limit (TDL)** – Performance goal for project set to be lower than prevailing regulatory limits.
- **Project Action Level (PAL)** – Dictates decisions on disposal of dredged material (WQC, SQG, etc.).
- **MDL < LRL ≤ TDL < PAL**

Instrument Response and Analyte Detection and Quantitation



(Courtesy Dr. Rich Meyer, ERDC Env. Chem. Branch)

Factors That Influence Detection Limits

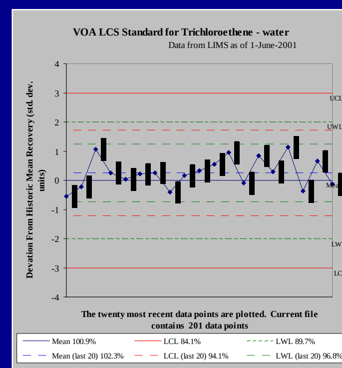
- Sample amount
- Sample matrix
- Interferences
- Dilution
- Injection volume
- Extract volume
- Analytical Technique

QA/QC - Quality Systems

- Positive and negative controls
- Demonstration of repeatability
- Measures of precision & accuracy
- Demonstration of capability
- Measures of method sensitivity
- Instrument calibration & dynamic range
- Analyst and lab proficiency
- Development and use of acceptance criteria
- On-going assessment of quality system
- Laboratory quality management manual

QA/QC - Samples and Spikes

- Surrogate
- Method Blank
- Trip Blank
- Lab. Control Sample (LCS)
- Laboratory Duplicate (LD)
- Matrix Spike (MS)
- Matrix Spike Duplicate (MSD)
- Performance Evaluation (PE) Samples



QA/QC - Common Data Flags

- B → Compound detected in method blank.
- D → Compound detected in analysis performed at a secondary dilution.
- E → Reported value exceeded calibration range or is an estimate.
- J → Compound detected but is below the Laboratory Reporting Limit.
- U → Compound analyzed but not detected above a specified limit.
- R → Data not usable according to QC; repeat analysis required.

Interpreting Data

- Are reported LRLs consistent with TDLs?
- Were sample holding times met?
- Is there evidence of blank contamination?
- Were corrective actions necessary?
- Is any data flagged?
- Were QC samples/spikes within limits?
- Are appropriate units reported?
- Does data pass the common sense test?

Interpreting Data – Non-Detects

- How do you use non-detect (<DL) data when performing statistical analyses?

→ May substitute <DL with numerical value of LRL, ½ LRL, MDL_{SA}, or Zero

→ As percentage of censored values increases, reliability of substitution techniques decreases

-- avoid substitution approach if censoring > 60%

→ Consider consulting a statistician when using substitution approach

Interpreting Data – Non-Detects

- How do you use non-detect (<DL) data when comparing individual sample data to the PAL?

  → May substitute <DL with numerical value of LRL, ½ LRL, MDL_{SA}, or Zero

  → Consider the range of possible values below the DL, especially if % censoring is high
  - -- LRL to Zero
  - -- ½ LRL to Zero
  - -- Sample-adjusted MDL to Zero

Interpreting Data – Case Study

- Elutriate Sample A from Dredging Channel X reported to have COC DNCW = 0.34 J ug/L.

(LRL = 0.50 ug/L; MDL = 0.10 ug/L; PAL = 0.3 ug/L)

- What's the problem with this data?

  → PAL < LRL

- More info: Method Blank DNCW = 0.32 J ug/L.

- Now what's wrong with the data?

  → Sample A DNCW reported incorrectly;

  - should be 0.50 U ug/L or 0.34 BJ ug/L

Interpreting Data – Case Study

- Sample A DNCW = 0.34 BJ ug/L; MB = 0.32 J ug/L (LRL = 0.50 ug/L; MDL = 0.10 ug/L; PAL = 0.3 ug/L)

- What about comparing data with PAL?
  → If Sample A = 0.50 U ug/L;
  - LRL to Zero = 0.00 - 0.50 ug/L (40% > PAL);
  - 1/2 LRL to Zero = 0.00 - 0.25 ug/L (100% < PAL);
  - MDL_{SA} to Zero = 0.00 - 0.10 ug/L (100%< PAL);

  → If Sample A = 0.34 BJ ug/L (> PAL);
  - J-value to Zero – 0.0 - 0.3 ug/L (100% ≤ PAL)

Electronic Data Deliverables

- EDDs now required by many Corps Districts when contracting chemistry services.
- EDDs are electronic "packages" allowing transfer of information from "A" to "B" (lab to user, etc.).
- Advantages:
  → allows comprehensive data review
  → content is complete and readily archived
  → easy data retrieval and report generation

EDDs - Approaches

- Two Formats: SEDD & ADR/EDMS
- **SEDD** – Staged Electronic Data Deliverables
  - → Application independent (more comprehensive)
  - → SEDD can used in concert with ADR/EDMS
  - → Specified for use in EPA CLP Program
  - → Proposed as long-term storage format
  - → www.epa.gov/superfund/programs/clp/sedd.htm
  - → POC – Joseph.F.Solsky@usace.army.mil

EDDs - Approaches

- Two Formats: SEDD & ADR/EDMS
- **ADR/EDMS** – Automated Data Review format for Electronic Data Review System
  - → Developed for Corps by Laboratory Data Consultants (Carlsbad, CA)
  - → Smaller and more specific than SEDD
  - → Not a long term storage platform
  - → Get Info at www.lab-data.com
  - → POC - Scott Denzer, sdenzer@lab-data.com

Final Remarks

- Analytical chemistry is a critical element in the evaluation of contaminated sediment.
- Be aware of differing terminology used is describing analytical detection limits.
- Quality control is a key element in chemical analyses of sediment and related matrices.
- When interpreting data, remember to consider all information provided in the data report.
- Consider requiring EDDs to improve data transfer, review, and storage.

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