

**TestAmerica**

## Chemical Analytical Support for Sediment

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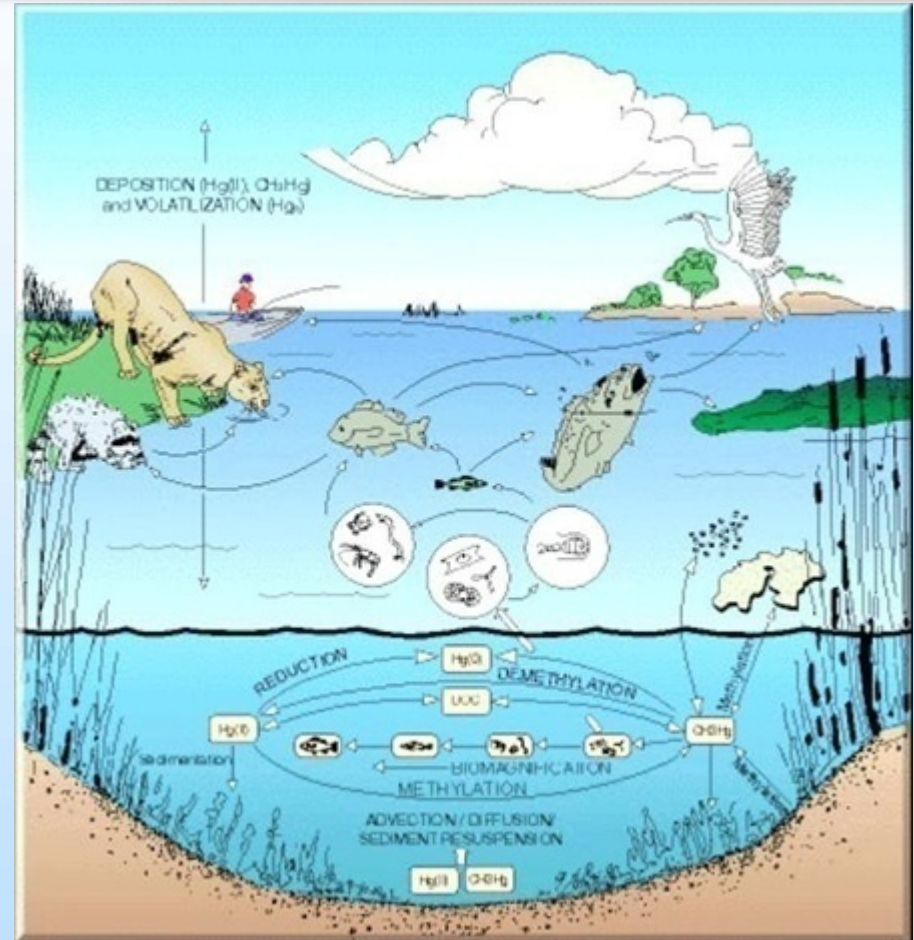
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## Why is sediment important?

- Contaminants in the sediment can directly harm aquatic organisms and/or accumulate in their tissues. These organisms can be consumed by humans.
- Contaminants in the sediment lead to the fish advisories.
- US EPA's National Listing of Fish Consumption Advisories in 2006 had 3,852 specific water bodies identified.



## Sediment is Controversial & Expensive

- Who is potentially responsible for the contamination?
- How can the sediment be remediated and to what level?
- How many governmental agencies can have oversight over sediment sites?
- Multiple political and technical issues abound.
- Costs can be in the millions of \$\$  
→ billions for proposed clean ups.



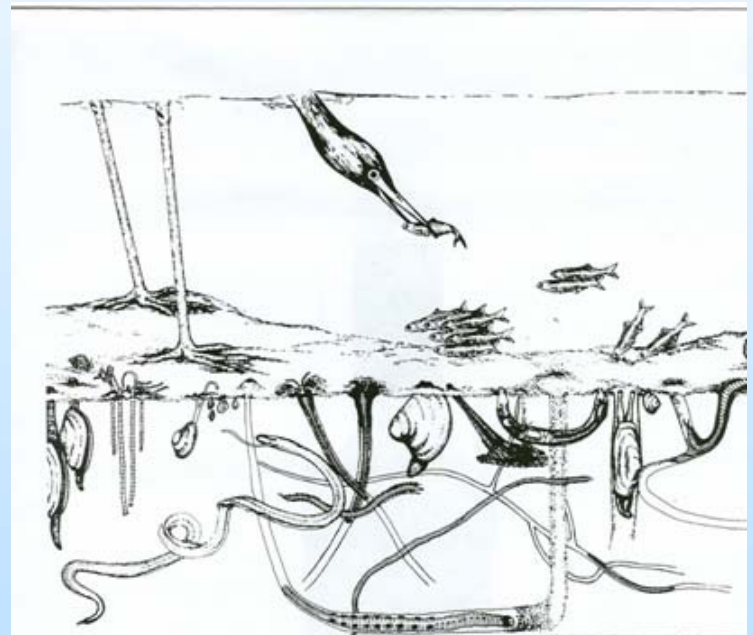
- Terrestrial Ecosystem
  - ~ Contaminant
    - Usually point source or non point source
    - Usually lower degree of transport away from source
    - Compounds of concern are generally 'conventional'
  - ~ Risk Assessment
    - Site boundaries are well defined
    - Food Webs are simple



## Sediment Pose Unique Challenges

*Sediment is a complex dynamic system that often include biota.*

- Water and sediment move.
- Species can be highly mobile.
- Food webs can be highly complex.
- The fundamental elements of conducting terrestrial and aquatic investigations are similar.
- Sediment investigation are more complex.



## Sediment Pose Unique Challenges

### Aquatic Ecosystem

- Contaminants
  - ~ Multi-point source & non-point source
  - ~ Compounds of concern - PCBs, PST, PAHs, Dioxins/Furans & metals
  - ~ Bioaccumulate and bioamplify
- Risk Assessment
  - ~ Site boundaries can be extensive.
  - ~ Food Webs extremely complex and 'bioavailability' must be assessed.



***Sediment can be a reservoir for future source of contaminants.***

## ***Chemical Analytical Support For Sediment***

- General past and present data needs
- Greek mythology
- Achieving project specific analytical goals
- Variety of matrices
- Sediment specific analytical procedures
- Emerging techniques for measuring bioavailability
- Emerging compounds of interest
- Keys to success

Long ago & far away  
in the early years of  
environmental chemistry . . .

## *Routine Regulatory Environmental Chemistry*

~ **ND (Not Detected) = GOOD**

- Often ND was equated to the concentration being zero

~ **Detected = BAD**

Consistency of reporting limits over years and years...



***Data needs can be much different now.***

**Risk-based cleanup criteria → lower reporting limits**

**TestAmerica's Sediment & Tissue Laboratories  
have evolved from**

**routine regulatory environmental chemistry →  
project-specific environmental analytical support.**

**Risk-based clean up criteria can not generally be  
accomplished with routine analytical services.**

***Technically knowledgeable and flexible.***

For many projects, but not all, it is desirable to report  
**detected results at lower reporting limits**  
rather than  
**not detected at higher reporting limits.**

For example, a risk assessor may prefer to have Pyrene  
reported value at RL 2 ug/kg  
rather than  
ND at 330 ug/kg.

*Risk assessor may have to use ½ of the RL of the ND value.*

**Using method with higher reporting limits can lead to  
a conservative risk assessment.**

***All successful special projects start with . . .***

- **Pre-project communication** with the laboratory
  - ~ Support during the development of Data Quality Objectives & Quality Assurance Projects Plan
  - ~ Review of methods, reporting limits requirements and other project specific requirements
- **This is an iterative process** with the laboratory → **Partnering**

***If the laboratory is not aware of the special project needs...then the lab will keep providing their 'vanilla, standard, routine' services.***

*TestAmerica provides support utilizing our Sediment & Tissue Technical Laboratories.*

- TestAmerica has developed Minimum Standards to support sediment & tissue projects.
- Laboratories are familiar with the complexities associated with collecting sediment samples from waterways and managing tissue projects.
- Technical support for the development and review of project specific QAPjP
- Development of cost effective analytical approaches.



## Pandora's Jar Issues



- **Accurate sample volume/mass**
- **Water in sediment samples**
  - ~ Decant vs. reconstitute?
  - ~ % moisture
- **Homogenization assumptions & Sub-sampling**
- **QA/QC procedures on normalizing factors (Lipids, TOC, % moisture?)**
- **Dilution *Strategies?***

***Simple, defined project specific procedures can significantly improve the quality of the analytical data for the project.***

***Factors that effect achieving lower reporting limits are:***

- **Analyte Concentration**
- **Sample matrix**
- **Analyte interferants**
- **Sample processing/preparation**
- **Sample Size (both large and small sample size)**
- **Pre-injection volume**
- **Instrumental method**
- **Laboratory contaminants**

## How a laboratory can provide project-specific sediment support . . .

- **Pre-screen samples**
- ***Increase sample size***
- ***Perform Column Clean-up of extracts***
- **Decrease/increase injection volumes**
- ***Provide lower MDL studies***
- **Run instrument in different 'mode' such as SIM or SIM like**
- **Offer tiered analytical approach to analysis**
- **Offer different analytical approach to analysis**

## *Increased sample size can be used to provide lower reporting limits*

**Increased sample size can be used to overcome the high % moisture issues.**

- ~ **Most analytical results are reported on a dry weight basis**
- ~ **Sediment samples can have greater than 50% moisture**
- ~ **Reporting limits will be greatly increased due to high moisture content in the sample**

	RL	RL 20% Moisture	RL 50% Moisture	RL 80% Moisture
<b>Pyrene (ug/kg)</b>	2.0	2.5	4.0	10.0



*The purpose of clean-ups is to remove interferences and high boiling point compounds.*

- Non target compounds/ interferants can cause false positives, false negatives and errors in quantitation.

## Types of Clean Up Procedures

- |                         |                              |
|-------------------------|------------------------------|
| ~ Adsorption Gel        | Alumina, Florisil and Silica |
| ~ Size Separation (GPC) | Gel Permeation Cleanup       |
| ~ Acid/Base Partioning  |                              |
| ~ Sulfur Cleanup        |                              |
| ~ Sulfuric Acid         |                              |

- **40 CFR Part 136 Part B requires all laboratories to perform MDL studies.**
- **Laboratories can support a variety of reporting limits for project from 'routine' to low level.**
- **Laboratories support Low Level MDL studies.**
- **Laboratories can support MDL studies with smaller sample sizes.**
- **The laboratory needs to document and demonstrate that they can support the low level reporting limits.**
  - ~ MDL determination
  - ~ Special project requirement
  - ~ MDLVs (MDL verification standards)

**Other matrices can be associated with sediment projects.**

- **Water and Soil**
- ***Ambient Air***
- ***'Different' Matrix***
  - Biota /Tissue*
- ***Generated Matrix***
  - Pore Water*
  - Variety of Elutriates*
  - Amended Sediment*

*Sediment programs can have  
Biota / tissue components.*

These programs require  
specialized preparation  
techniques :

- Tissue handling
- Filleting
- Dissecting
- Preparation (homogenization,  
washing)
- Specialize analytical clean up  
procedures
- Lipid analysis for animals

Not for the faint of heart

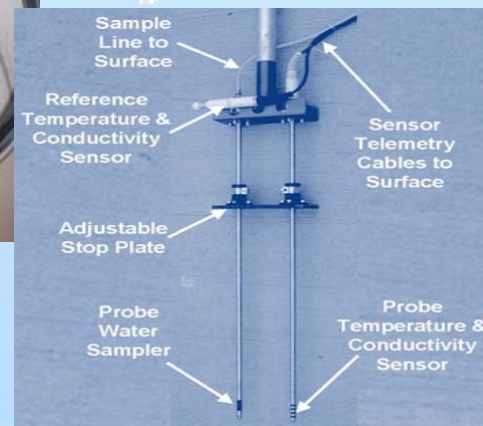
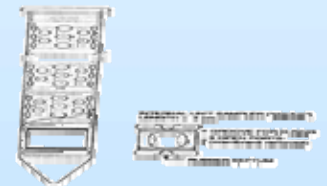
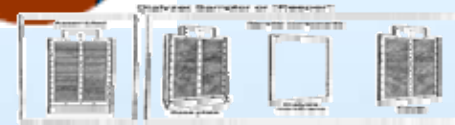
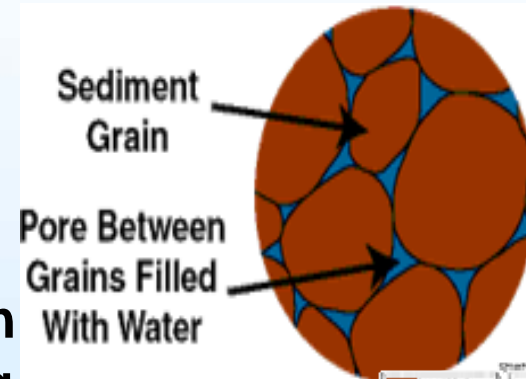
EHS concerns



**Pore water is the water in between the interstitial space of sediment.**

**The bioavailability of chemicals in sediment is often estimated using sediment pore water.**

- In situ Pore water - peepers
- Ex situ Pore water - laboratory centrifugation (pressing or suction)
- Trident Probe



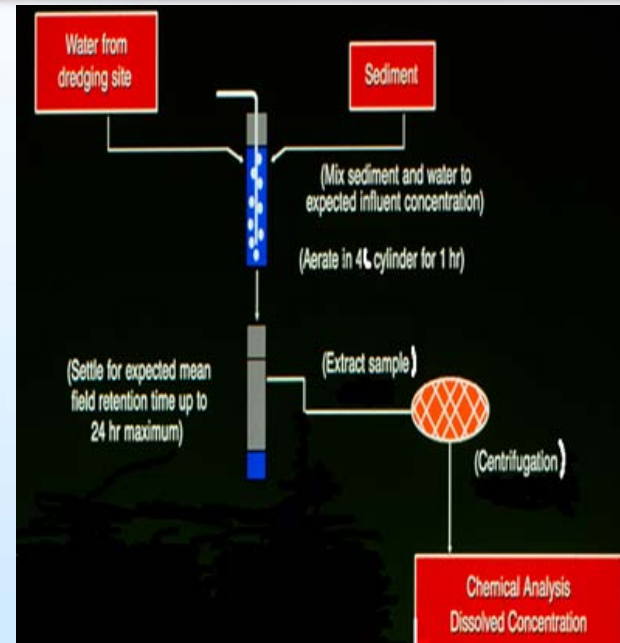
**Elutriates** are associated with various dredged material programs.

An **elutriate** is the supernatant (liquid phase) produced after mixing of the sediment and site water and allowing it to settle for a specified period of time.

Multiple types of elutriates: Standard, Modified, Effluent and DRET elutriates

Data is used to evaluate water column compliance with applicable Water Quality Standards.

Dredged Material evaluation can include other types of leachate testing.



The concept of **bioavailability** stems from :

- some chemicals in soil or sediment appear to be less available for uptake by humans or other ecological receptors than is suggested by the total concentration present.
- cleanup levels expressed as bulk concentration may not necessarily correlate with the actual risk.

Emerging areas for PAH's using SPME and other methods for the evaluation of pore water concentrations of constituents of concern.

## **Various Approaches being investigated**

Pore water generation

Dissolved vs freely dissolved

SPME for PAHs

US EPA Method 8272 – ID SPME

In situ SPME

‘Virtual Fish’ - Semi-permeable Membrane Device (SPMD)

Polyoxymethylene (POM) passive sampler



## Pore water

### Acid Volatile Sulfides/Simultaneous Extracted Metals (AVS/SEM)

AVS/SEM provides insight to the bioavailability of metals in anaerobic sediment.

AVS appears to affect the divalent metals (Ag, Cd, Cu, Ni, Pb, and Zn) since sulfides have an affinity for divalent metals.

AVS/SEM is reported as a ratio.

- AVS>SEM - metals are bound to sulfide complex limiting bioavailability; metals are in-soluble and not available.
- AVS<SEM - metals may be toxic.

Redox issues are critical to manage.

- Samples are to be collected with zero headspace
- Other option is the use of N<sub>2</sub> glove box for sediment cores.

# Sediment Specific Analytical Procedures

To successfully support sediment projects requires a commitment from the laboratory to support the array of sediment procedures.

- Geotechnical support  
Grain Size by D422 and D4464
- TOC and Black Carbon (BC)



## TOC (Lloyd Kahn TOC)

- Measure of nonionic organic chemical bioavailability.
- Used to normalize dry weight sediment concentration of chemical.
- TestAmerica's Sediment Laboratories follow our minimum standard for TOC
- New TOC Instruments require **5-25 mg** of sample for each analysis and the samples are analyzed in duplicate.
- **Dixon's Q-test** is an outlier test. It is used in analytical chemistry in the data treatment of replicate measurements

## Black Carbon (Soot Carbon)

- Black Carbon can have an effect on the partitioning and bioavailability of organic contaminants.

- Methyl Mercury
- Dioxins/Furans – additional congeners
- Polybrominated Biphenyl Ethers (PBDEs)
- Polybrominated Biphenyls
- PFC- PFOA/PFOS and other compounds
- Polychlorinated Naphthalenes (PCNs)
- Polychlorinated Terphenyls (PCTs)
- Pharmaceuticals and Personal Care Products (PPCP)
- Endocrine Disrupting Compounds (EDC)

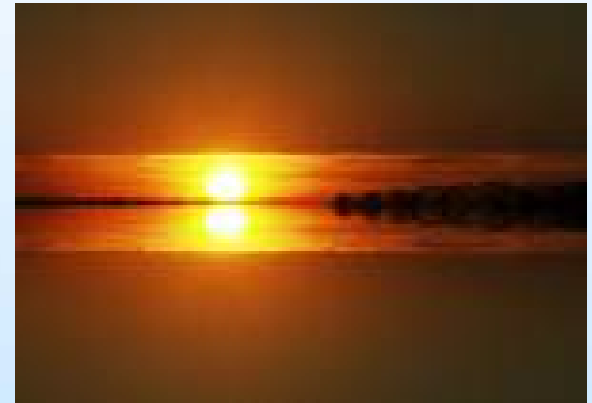
## TestAmerica's Sediment & Tissue Laboratories

- TestAmerica Pittsburgh
- TestAmerica Burlington
- TestAmerica Knoxville
- TestAmerica Mobile
- TestAmerica Seattle
- TestAmerica West Sacramento
- TestAmerica Richland (radiodating only)

These are the TestAmerica Laboratory who support our Sediment as well as Tissue Program Minimum Standards.

***Sediment Projects = Experiments with many variables.***

***Have a strategy,  
Plan,  
Communicate,  
Communicate, and  
Communicate more...***



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