

## Determining Bioavailable PAHs in Sediment Pore Waters

Business of Brownfields Conference  
Pittsburgh

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## Objectives

- Compare traditional and emerging approaches to evaluating exposures of sediment-dwelling organisms
- Describe how the method is applied for ecological risk assessment
- Present information pertinent to method validity
- Describe method set-up and operation
- Report on the current status of the method
- Provide information on method performance
- Present advantages – challenges

- EPA - narcosis model predicts toxic effects to benthic wildlife from PAH-impacted sediments
- Toxicity is predicted when the sum of *bioavailable* concentrations expressed as toxic units exceeds the benchmark value
- Bioavailable Concentration = freely dissolved fraction. Given by equilibrium partitioning theory.
- $[\text{PAH}]_{\text{WATER}} = [\text{PAH}]_{\text{OC}} / K_{\text{oc}}$
- Assumes that OC / Water equilibrium position = Octanol / Water.

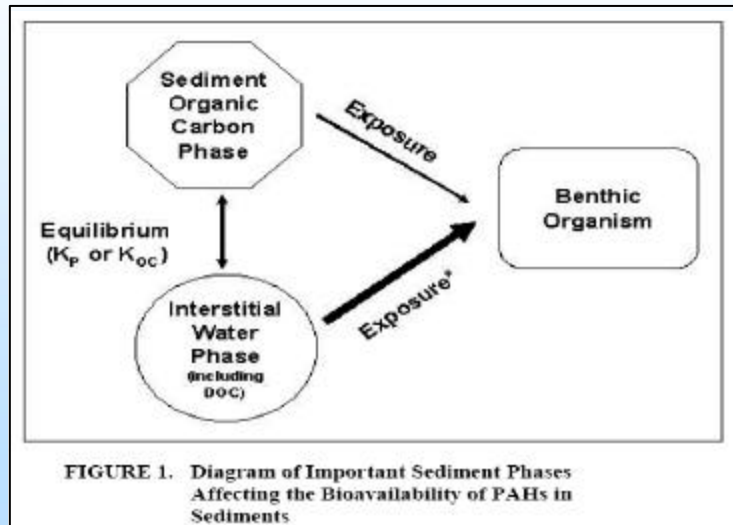
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### March 2007 - EPA Proposed Revised ERA Guidelines

- 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 (STU).

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## Where to Measure?



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## Why not simply perform direct analysis of pore water?

- Isolating 1 L porewater by centrifugation or pressing can require 5-10 L of wet sediment.
- Once isolated, the pore water can contain significant amounts of suspended particulate and colloidal agglomerates.
- Suspensions/dispersions can't be removed by centrifugation, due to ionic charges.
- Filtration is avoided due to two types of bias.
  - failure to remove colloids  $<0.1 \mu\text{m}$
  - "SPE phase" forms as oil sheen builds on filter

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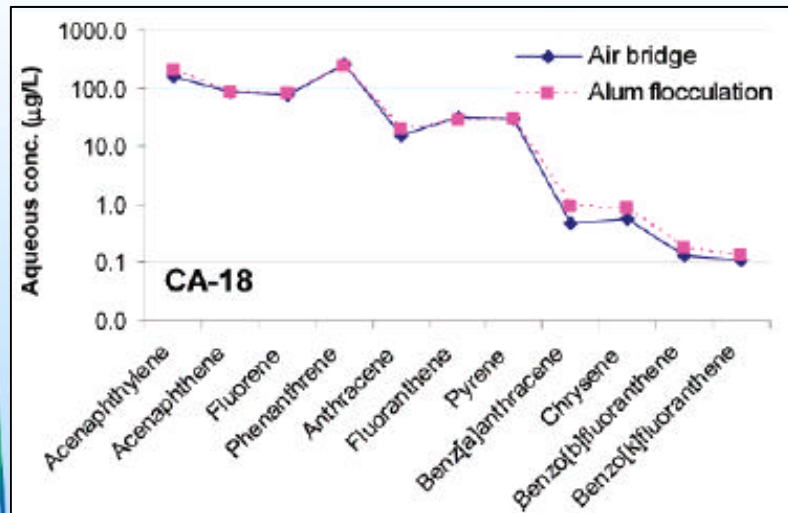
- Alum,  $\text{Al}_2(\text{SO}_4)_3$ . Is used within a controlled pH range. Other Al and Fe salts, including poly-aluminum chloride, ferric chloride, and ferric sulfate, may be used as well for flocculation processes.
- Salts react w/ cations on suspended clays, humates and OM-complexed cations, forming neutral solid precipitates
- Method as described by Hong, Ghosh & Hawthorne effective at removing colloids. But does it also remove dissolved PAHs?

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- Air bridge studies allow direct measures of freely dissolved concentrations.
- Air bridge studies provide standard against which to evaluate impact of flocculation on dissolved concentrations.
- Allowed empirical determination of sediment-specific  $K_{OCs}$ .
- Observed partitioning behavior was very different from predicted on some sediments.
- SEM imaging of sediment components.

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### Dissolved Concentrations Unaffected by Flocculation



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Hong, Ghosh *et al.*, 2003

### Now that freely dissolved concentration can be measured, some dissolved concentrations observed 100 to 1000 times below predicted

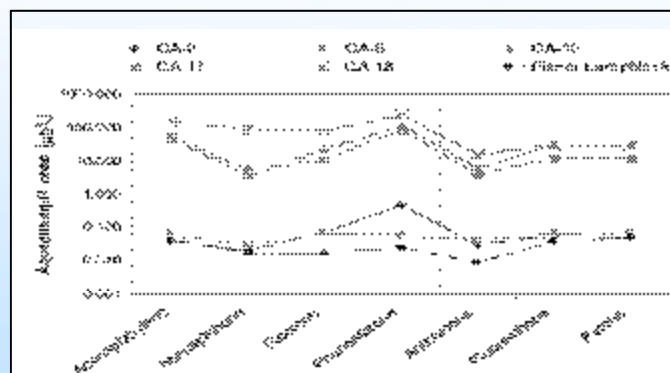
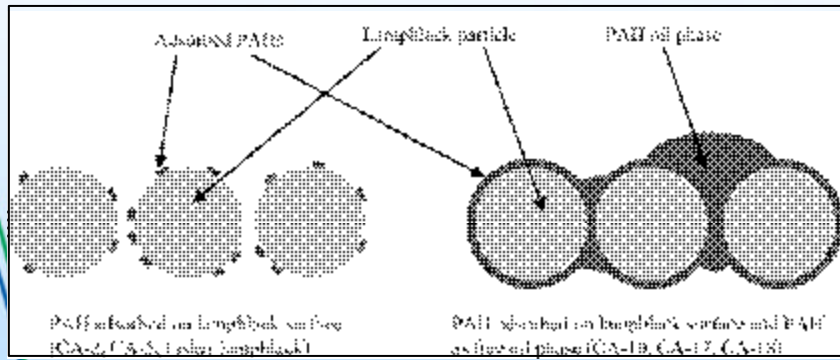


FIGURE 7. Aqueous equilibrium concentrations of PAHs for the six study materials as measured by the microdye technique. CA-2, CA-4, and Endor (unpolluted) show nearly 2–3 orders of magnitude lower PAH concentrations in the aqueous phase as compared to the other (polluted) unpolluted soils including CA-18, CA-12, and CA-18.

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Hong, Ghosh *et al.*, 2003

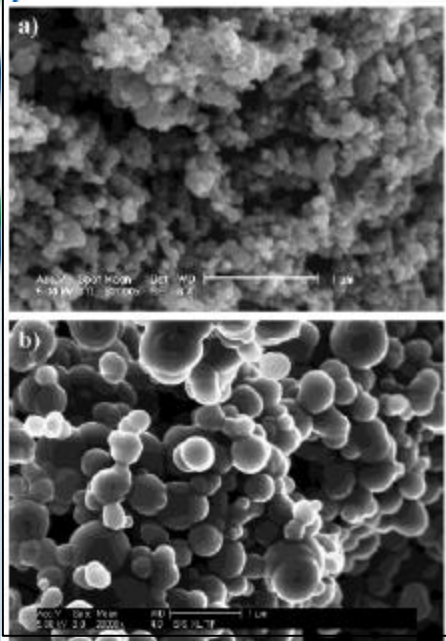
Is this why observed  $K_{OC} \gg K_{OW}$ ?



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Hong, Ghosh *et al.*, 2003

Scanning Electron Microscopy



← Standard black carbon vs.

← impacted sediment black carbon

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## 2005, 6 – Hawthorne Reports PAH Partitioning Behavior Using New Method

- Isotope Dilution-Solid Phase Microextraction performed on flocculated pore waters.
- Measures only freely dissolved PAHs.
- Addresses EPA 34 list, uses homolog-RRFs rather than RFs from parent.
- Method requires only a 4 oz jar of slurry.

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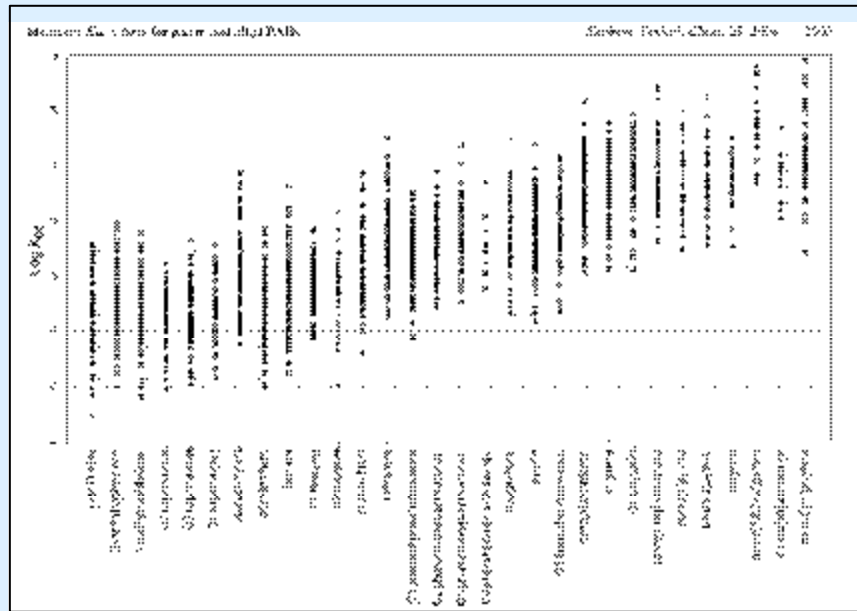
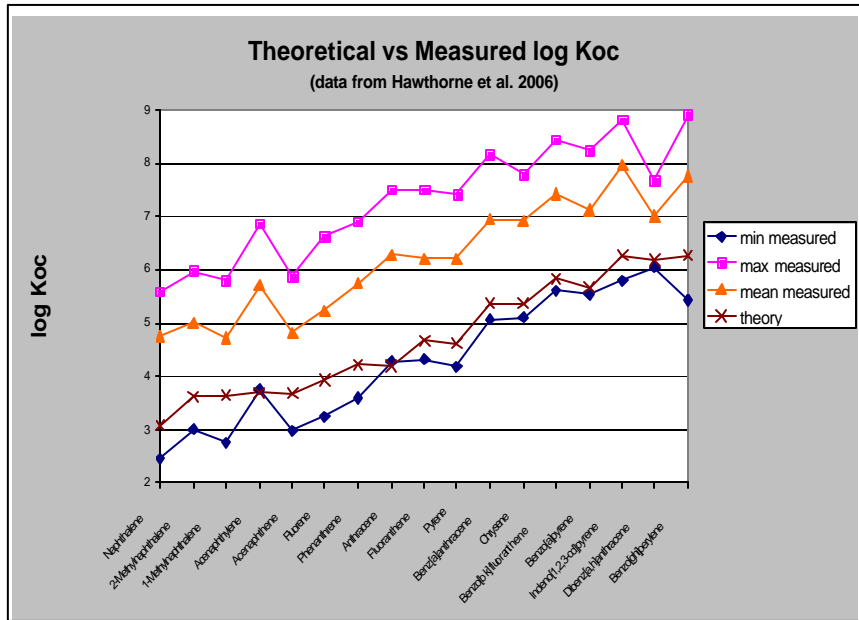


Fig. 1. Log K<sub>ow</sub> values for parent and alkyl PAHs.

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Hawthorne et al., 2006



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## Method shows better specificity, and overall prediction efficiency for toxicity to *H. azteca*.

**TABLE 2. Survival Predictions for *H. azteca* using Total Extractable, SFE Rapidly Released, and Pore Water PAH<sub>34</sub> Concentrations from 97 Field Sediments**

method	15–85% survival range (μmol/g of lipid) <sup>a</sup>	no. of sediments in 15–85% range	prediction efficiencies			Goodman–Kruskal γ
			sensitivity <sup>b</sup> (%)	specificity <sup>c</sup> (%)	overall <sup>d</sup> (%)	
PAH <sub>13</sub> concn > 1.6 mg/kg (TEC) <sup>e</sup>			100	6	30	0.73
PAH <sub>13</sub> concn > 22.8 mg/kg (PEC) <sup>f</sup>			96	32	48	0.75
PAH <sub>34</sub> concn	36–315	26	80	81	80	0.78
SFE rapidly released PAH <sub>34</sub>	0.9–43	40	92	64	71	0.80
pore water PAH <sub>34</sub>	15–75	17	92	89	90	0.95

<sup>a</sup> Lower 95% confidence interval for 95% survival and upper 95% confidence interval for 15% survival. <sup>b</sup> Sensitivity is the extent to which a test correctly classifies a toxic sample as toxic and is therefore protective of the environment. <sup>c</sup> Specificity is defined as the rate at which a test correctly classifies a nontoxic sample as nontoxic. <sup>d</sup> Overall efficiency is the fraction of correct predictions for all samples. <sup>e</sup> TEC is the sum of 13 parent PAH concentrations below which toxicity is considered unlikely (1). <sup>f</sup> PEC is the sum of 13 parent PAH concentrations above which toxicity is considered likely (1).

Hawthorne, Azzolina, Neuhauser & Kreitinger ES&T Aug 4, 2007

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## Sediment Contaminant Bioavailability Alliance

- Formed in 2004, is a multi-industry group being led by Alcoa, Central Hudson Gas and Electric, National Grid, New York State Electric and Gas Company, the Northeast Gas Association, and their consultants
- Also Supported by Dow, NiSource and US Steel.
- Bioavailability Research Team Participants include representatives of University of ND Energy and Environment Research Center, USACE ERDC, AquaTox, University of Maryland Baltimore County, ENSR, TestAmerica

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## SCBA Purpose

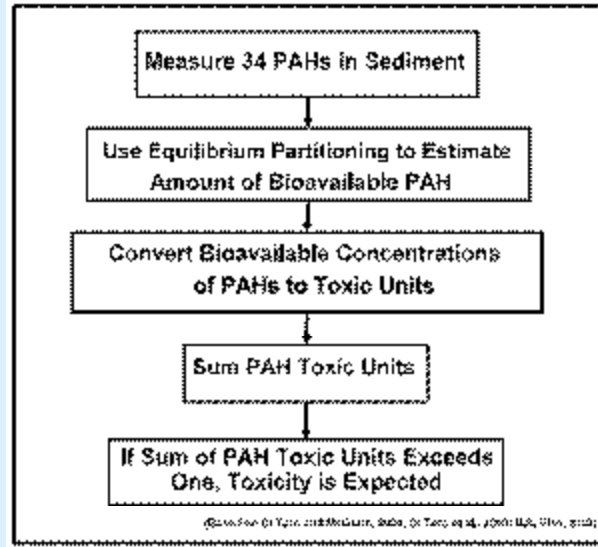
Increase scientific understanding of chemical exposure to aquatic organisms in sediments

Develop site-specific chemical measures that estimate the bioavailability of sediment-bound organic chemicals to these organisms

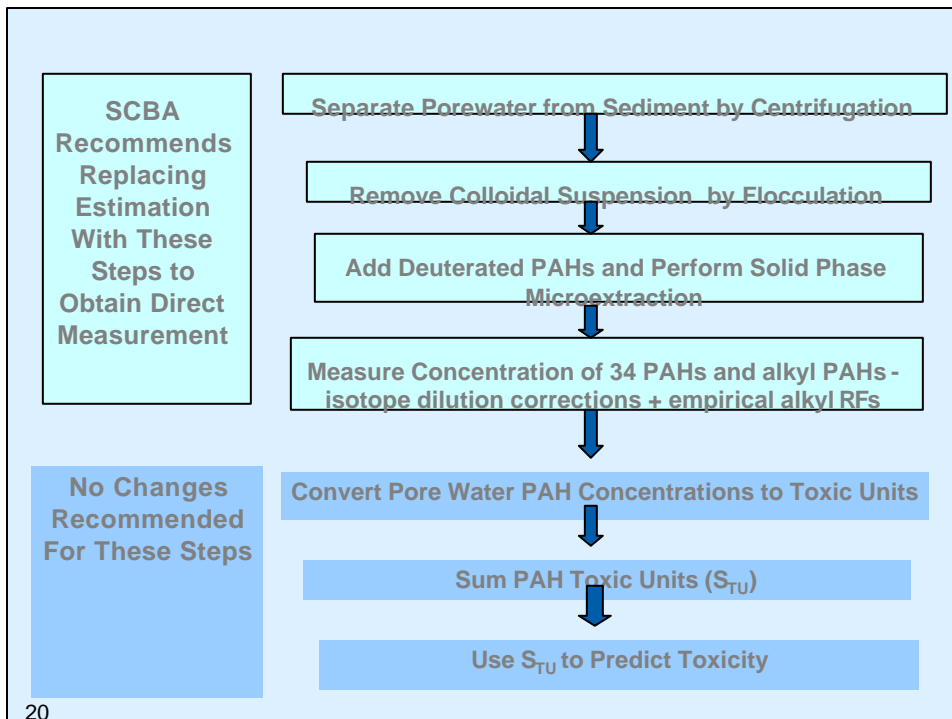
Use this improved scientific understanding within existing regulatory frameworks to make more informed sediment management decisions

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## March 2007 Proposed Guidance



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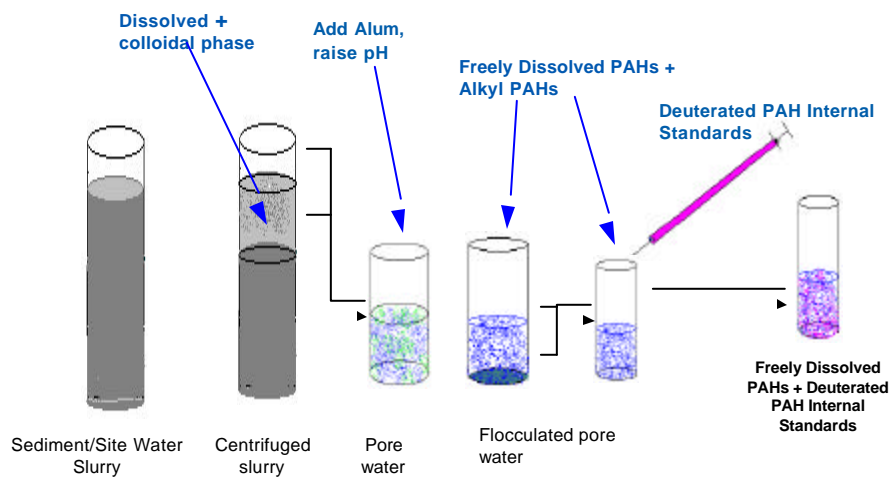
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## Regulatory Situation

- Proof of Concept Study, completed in October 2006. TestAmerica served as non-development lab. (~**500 data points - 1 outlier**).
- ASTM has approved the provisional method **WK10122**. To publish it as a full standard with limited validation data - 2008 Annual Book of Standards Section 11.
- Following publication of that standard, 5 years is allowed to complete the full interlab study with 7 labs.
- EPA Interlab Validation study as **EPA Draft Method 8272** was completed in summer 2007 under the guidance of Mr. Barry Lesnik. Three non-development labs participated. (TestAmerica, UMBC, Meta)
- Results will be published in a peer reviewed paper as well as presented in the next NEMC conference. (**1512 Data points - 2 outliers**).
- Posted by EPA in Jan 2008 as SW-846 Method 8272. <http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8272.pdf>

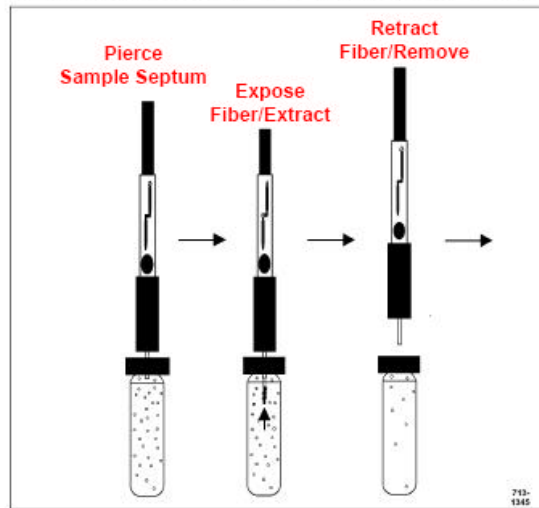
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## Centrifuge, Flocculate, Separate, Spike w/ Isotopically Labeled PAHs

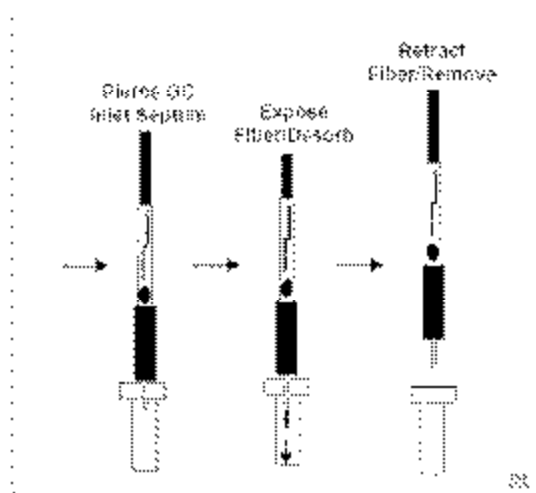


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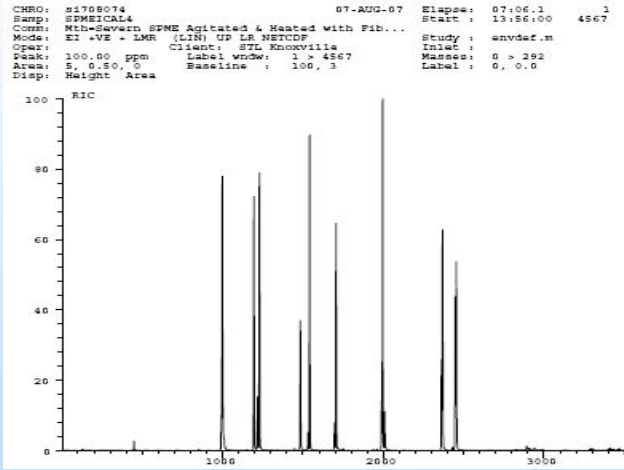
**Fig. 1 - Extraction Procedure for SPME**



**Fig. 2 - Desorption Procedure for SPME**

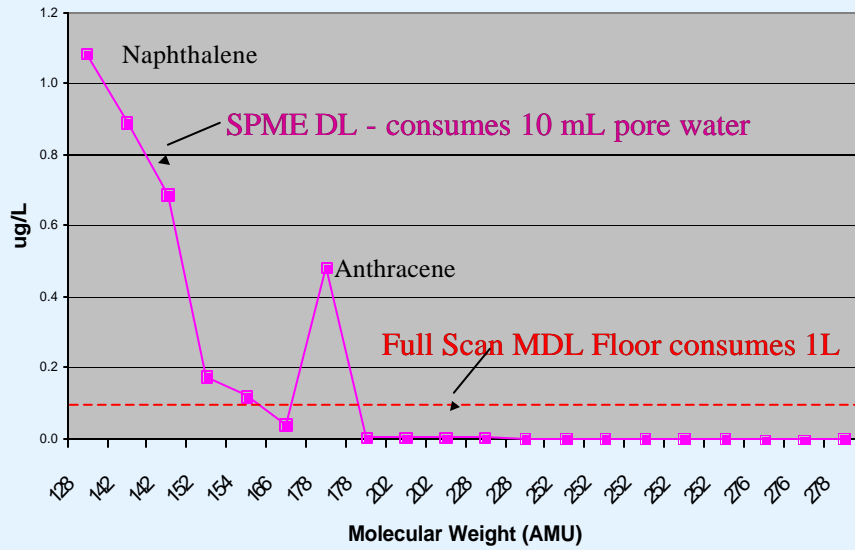


**Signal to Noise Enhanced by Flocculation, SIM + Good Peak Shape**

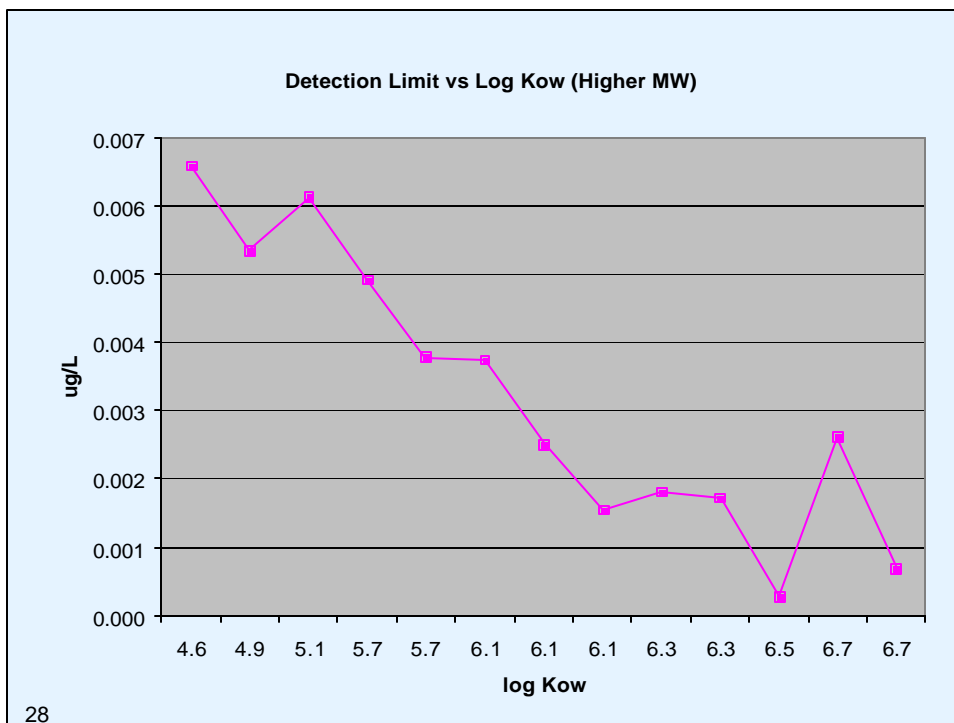
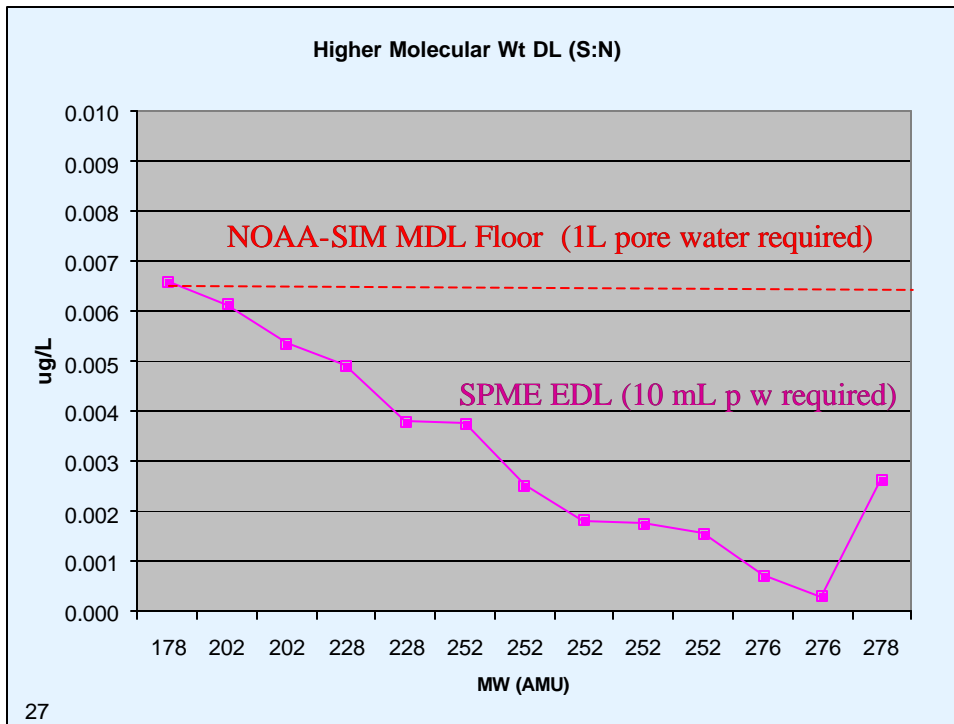


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**Detection Limit (S:N) - Naphthalene through Indeno (1,2,3-C,D) Pyrene**



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## Data Reduction

- The concentrations for 18 parent PAHs is obtained using isotope dilution quantitation (15 labeled analogs).
- The concentrations for 16 groups of alkyl PAHs are determined using relative response factors provided by Hawthorne (2005) .
- Each concentration is converted to Toxic Units (TU), (TU = Conc/FCV).
- The TU for each of the 34 concentrations is summed, to provide STU.
- Alternatively, the results can be expressed in terms of ?mole/g lipid.

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## Advantages

- Improved predictive efficiency for narcosis
- Reduces uncertainty about partitioning – allows site-specific  $K_{OCs}$  to be developed
- Very Sensitive: Working with 10 mLs, similar to sensitivity to 1L 8270 for 2-3 rings.
- Much lower sensitivity for 4-6 ring PAHs. Comparable to NOAA-SIM at 1 L.
- Requires 4 oz jar of sediment site water slurry.
- Turnaround time can be short. For 8 samples, sample receipt to data acquisition can be done in 2 days, with advance notice.

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## Challenges

- Lab had to upgrade a good Agilent 5973. New electronics, new inert source ~\$15K.
- Specialized autosampler required unless instrument is to be continually staffed. ~\$34K.
- Special standards must be formulated, with native and deuterated standards adjusted for solubility.
- Background air sources must be controlled.
- Requires change in liner, septum, very clean ion source.
- Learning curve - senior analyst and instrument 3-wks - 1 month to get going for low molecular weight targets.
- 1-2 add'l months for high molecular weight targets.
- Multiple runs required, separated by multiple blanks - minimum 4 runs per sample. Almost 1h per run.

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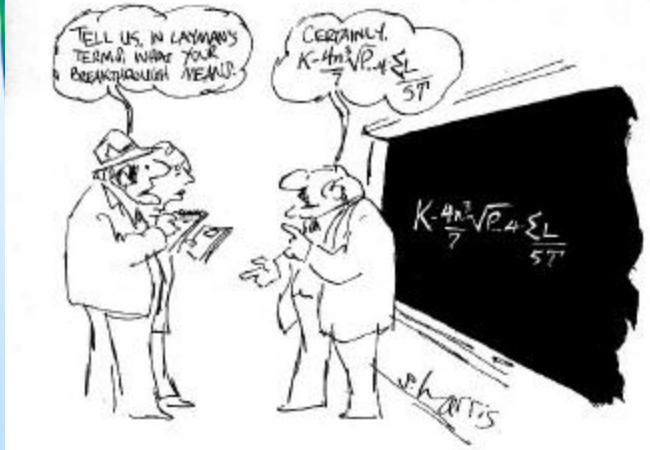
## Summary

- ✍ Narcosis model predicts narcosis toxicity
- ✍ Literature/Modeled  $K_{OW}$ s can overestimate bioavailable concentrations by several orders of magnitude.
- ✍ EPA is considering a revision of PAH ecological risk assessment to include 34 alkyls and parents.
- ✍ Flocculation is a useful analytical tool for removing colloids & suspensions.
- ✍ ID-SPME is a new way to directly measure dissolved phase on flocculated pore waters.
- ✍ Used in concert, these techniques provide an important new line of evidence for site specific KOCs.
- ✍ Methodology is being taken through necessary steps for regulatory acceptance. Now an EPA method.

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“ Method 8272 covers the separation of pore water from PAH-impacted sediment samples, the removal of colloids, and the subsequent measurement of dissolved concentrations of the 10-parent PAHs and two alkylated daughter PAHs in the pore water samples. **This method directly determines the concentrations of dissolved PAHs in environmental sediment pore water, groundwater, and other water samples.**”

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- Hawthorne, S.B., Azzolina, N., Neuhauser, E., Kreitinger, J.P., Predicting Bioavailability of Sediment Polycyclic Aromatic Hydrocarbons to *Hyalella Azteca* Using Equilibrium Partitioning, Supercritical Fluid Extraction and Pore water Concentrations. *Environ. Sci. Technol.* 2007, online edition Aug 4 2007.



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