

# **Rapid Screening and Real Time Monitoring of Petroleum Hydrocarbons**

**Marc A. Mills, PhD**  
**USEPA-Office of Research and Development**  
**National Risk Management Research Laboratory**  
**Cincinnati, OH**

# Sediment coring with rapid screening and forensic chemistry

- **Eagle Harbor, Washington to investigate freshwater upwelling through a capped layer above contaminated sediment. Funded by DOD-SERDP**



# Sediment/Cap Core Collection at Eagle Harbor, June 2006

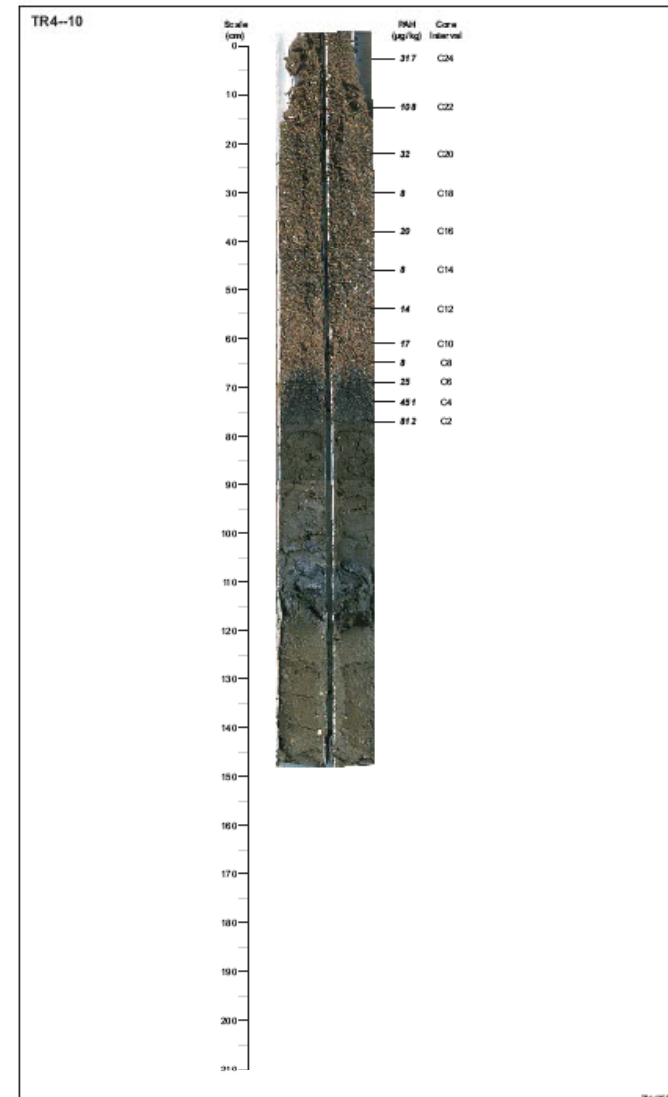
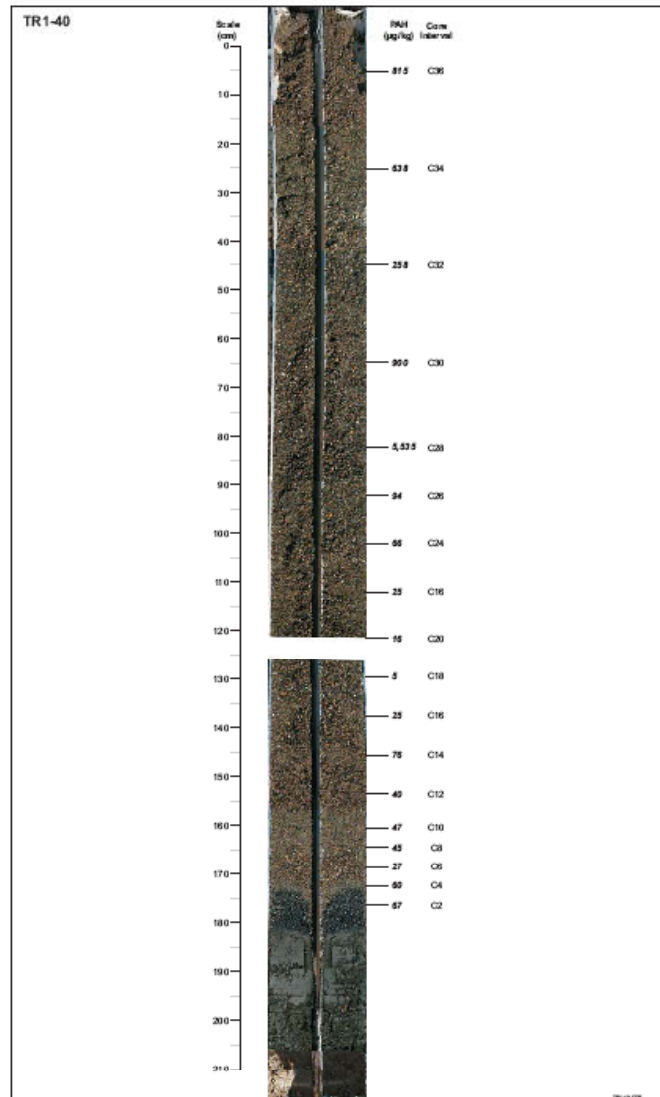




# Processing Core Tubes



# Split Core Tubes



# ELISA Rapid Screening

- Rapid screening with the ELISA immunoassay method was used to measure total PAH concentrations in over 150 samples
- Inexpensive (<\$50/sample including labor), accurate within pre-defined data ranges, and offers fast turn-around (~4-hrs)
- Avoid missing PAHs or expending resources measuring non-detects in the cap
- Dr. Jim Leather (Navy, SPAWAR): experience and expertise in the sediment RSC assay—Dr. Leather's team refined the RSC analyses for PAH and PCB contaminants under a SERDP project

# ELISA Rapid Screening





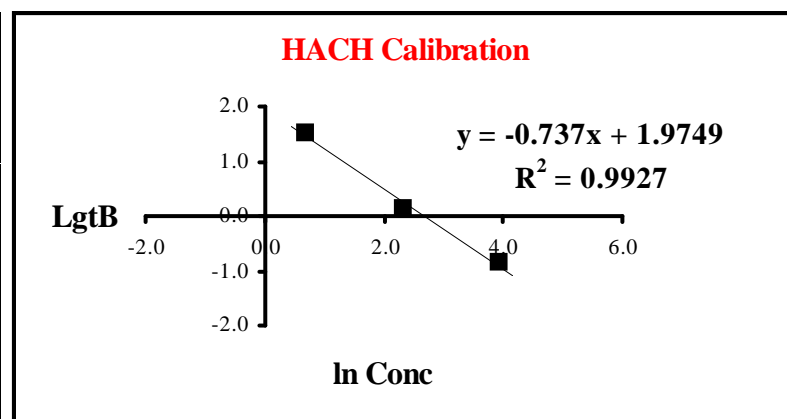
## ELISA Rapid Screening

- **Cores were cut into centimeter-thick segments and analyzed using the ELISA immunoassay analysis technique to characterize total PAH concentrations.**
- **Results were used to determine contamination profiles in sediment cores and to identify portions of sediment cores for detailed PAH and TPH analyses.**
- **Selected segments of cap material and native sediment were sent to Battelle's laboratory for detailed PAH chemistry.**
- **Additional cores were collected for UMBC studies**



# ImmunoAssay (IA) Method Calibration for PAHs Using a Direct-Reading (DR) Spectrophotometer [HACH]

LABEL ID	abs	x	conc	% recov	pah	pah <sub>corr</sub>
control [Phe]	0.559	3.23707	25.46	101.84%		
TR1 -10A C1	0.606	3.04969	21.11		33816	4734
TR1 -10A C2	0.936	1.73334	5.66		9067	1269
TR1 -10A C3	0.972	1.57304	4.82		7724	1081
TR1 -10A C4	0.949	1.67623	5.35		8563	1199
TR1 -10A C5	1.054	1.17606	3.24		5193	727
TR1 -10A C6	0.932	1.75075	5.76		9226	1292
TR1 -10A C7	1.019	1.35191	3.86		6191	867
TR1 -10A C8	0.940	1.71585	5.56		8909	1247
TR1 -10A C9	0.628	2.96327	19.36		31017	4342
TR1 -10A C10	0.356	4.14206	62.93		100818	14114
TR1 -10A C11	0.563	3.22094	25.05		40133	5619
TR1 -10A C12	0.326	4.29988	73.69		118052	16527
TR1 -10A C13	0.294	4.47983	88.22		141327	19786
TR1 -10A C14	0.505	3.45916	31.79		50928	7130
TR1 -10A C15	0.600	3.07338	21.61		34627	4848
TR1 -10A C16	0.647	2.88911	17.98		28800	4032
TR1 -10A C17	0.638	2.92419	18.62		29828	4176
TR1 -10A C18	0.838	2.14238	8.52		13649	1911
TR1 -10A C19	0.700	2.68352	14.64		23448	3283
TR1 -10A C20	0.762	2.44291	11.51		18433	2581
BL1-MeOH	1.444	#NUM!	#NUM!		0	0



$$x = \ln(\text{conc})$$

$$b = \text{intercept}$$

$$m = \text{slope}$$

$$x = (y - b) / m$$

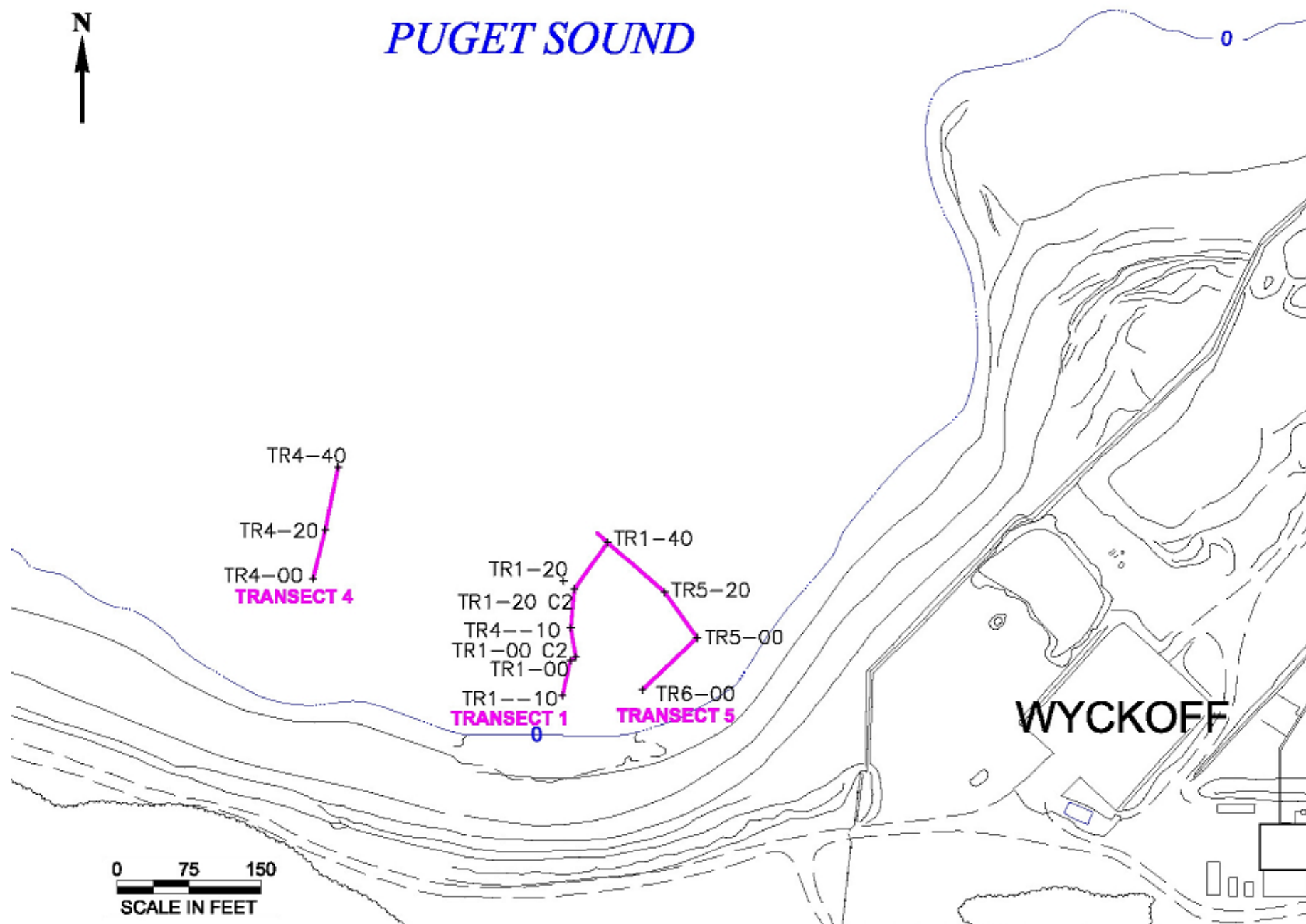
$$y = \ln(r/r_0)/(1-r/r_0)$$

$$x = ((\ln((r/r_0)/(1-r/r_0)))-b)/m$$

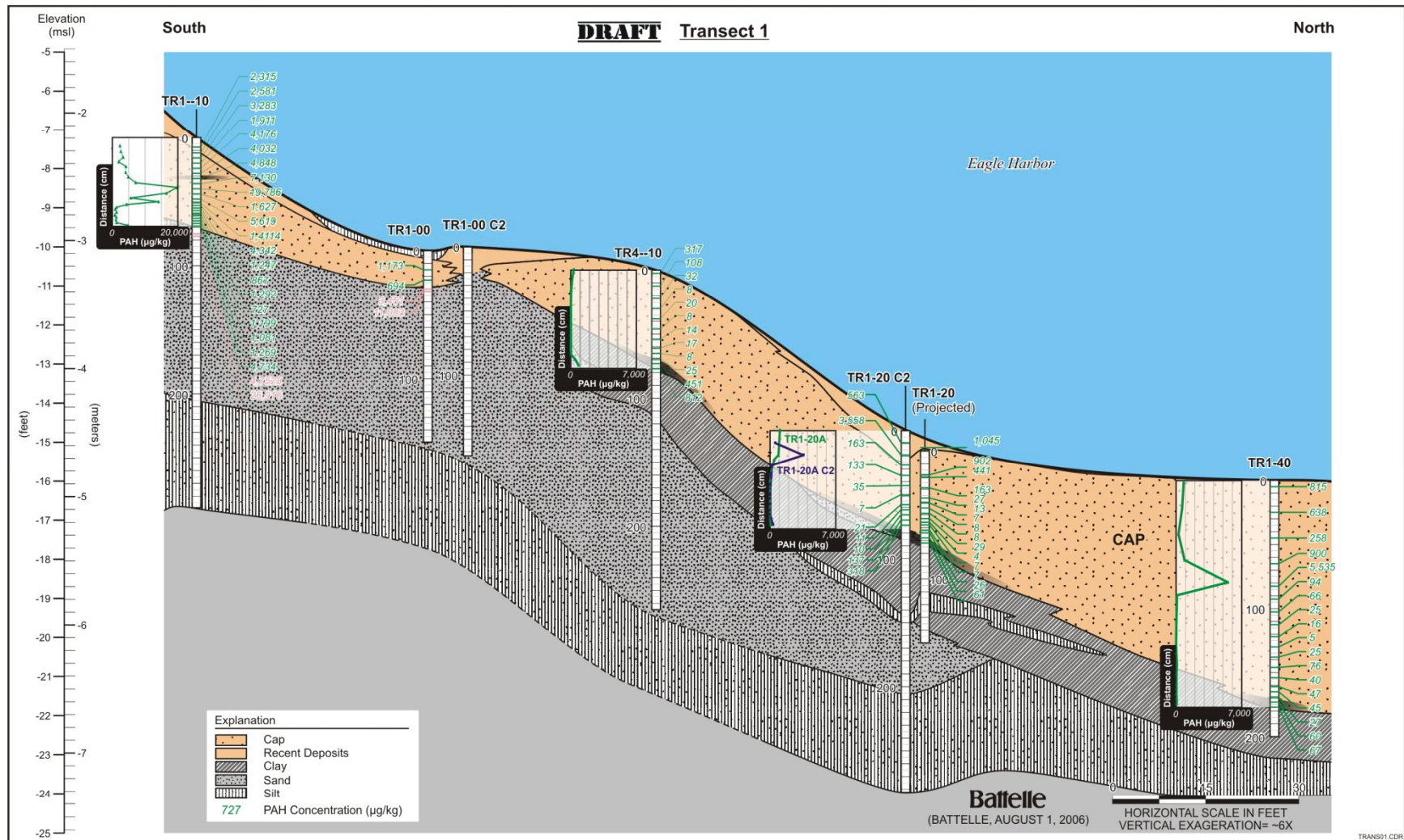
$$\text{conc} = \exp(x) = \exp(((\ln((r/r_0)/(1-r/r_0)))-b)/m)$$



## PUGET SOUND

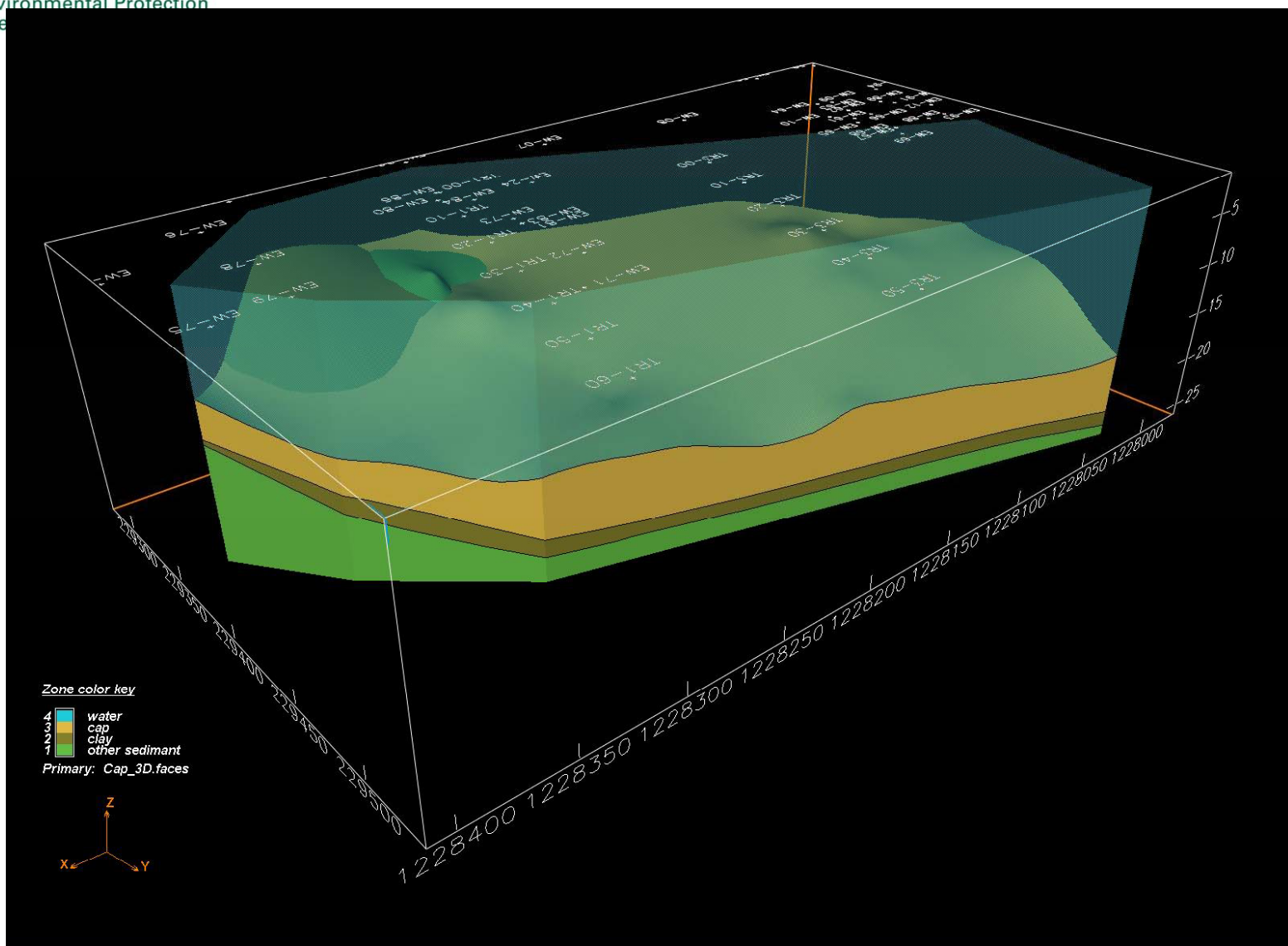


# Total PAH Profile of Transect 1





# 3-D Model of Sampling Area



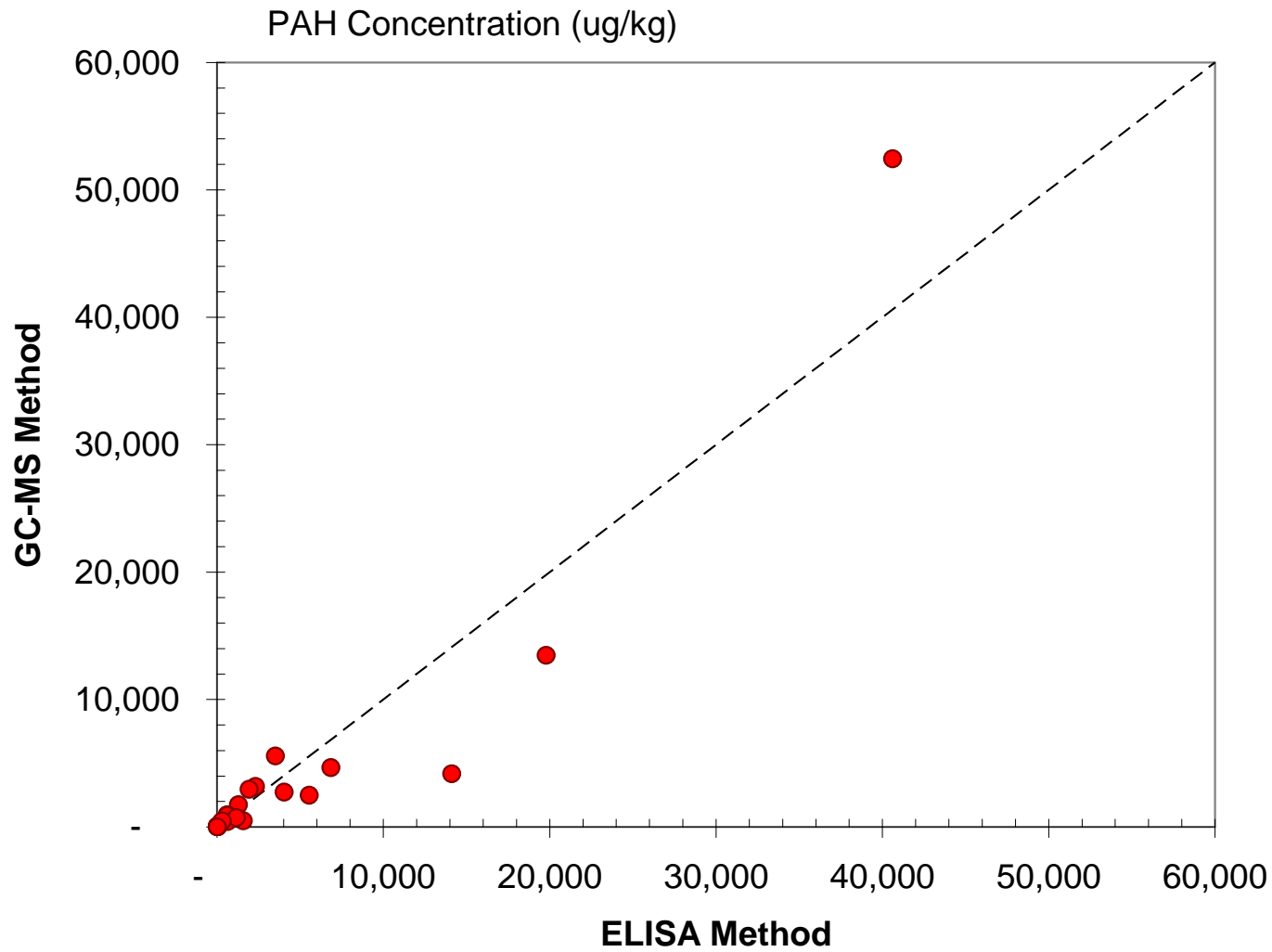


## 27 Segments Were Analyzed for PAHs and Petroleum Hydrocarbons

		TR5-(+)20A-C12	
		TR5-(+)20A-C14	TR5-00A-C10
TR1-(-)10A-C10		TR5-(+)20A-C18	TR5-00A-C14
TR1-(-)10A-C13	TR1-(+)40A-C12	TR5-(+)20A-C2	TR5-00A-C20
TR1-(-)10A-C16	TR1-(+)40A-C28	TR5-(+)20A-C22	TR5-00A-C24
TR1-(-)10A-C21	TR1-(+)40A-C20	TR5-(+)20A-C26	TR5-00A-C28
TR1-(-)10A-C6	TR1-(+)40A-C34	TR5-(+)20A-C4	TR5-00A-C4
TR1-(-)10A-N1	TR1-(+)40A-N1	TR5-(+)20A-N1	TR5-00A-N1

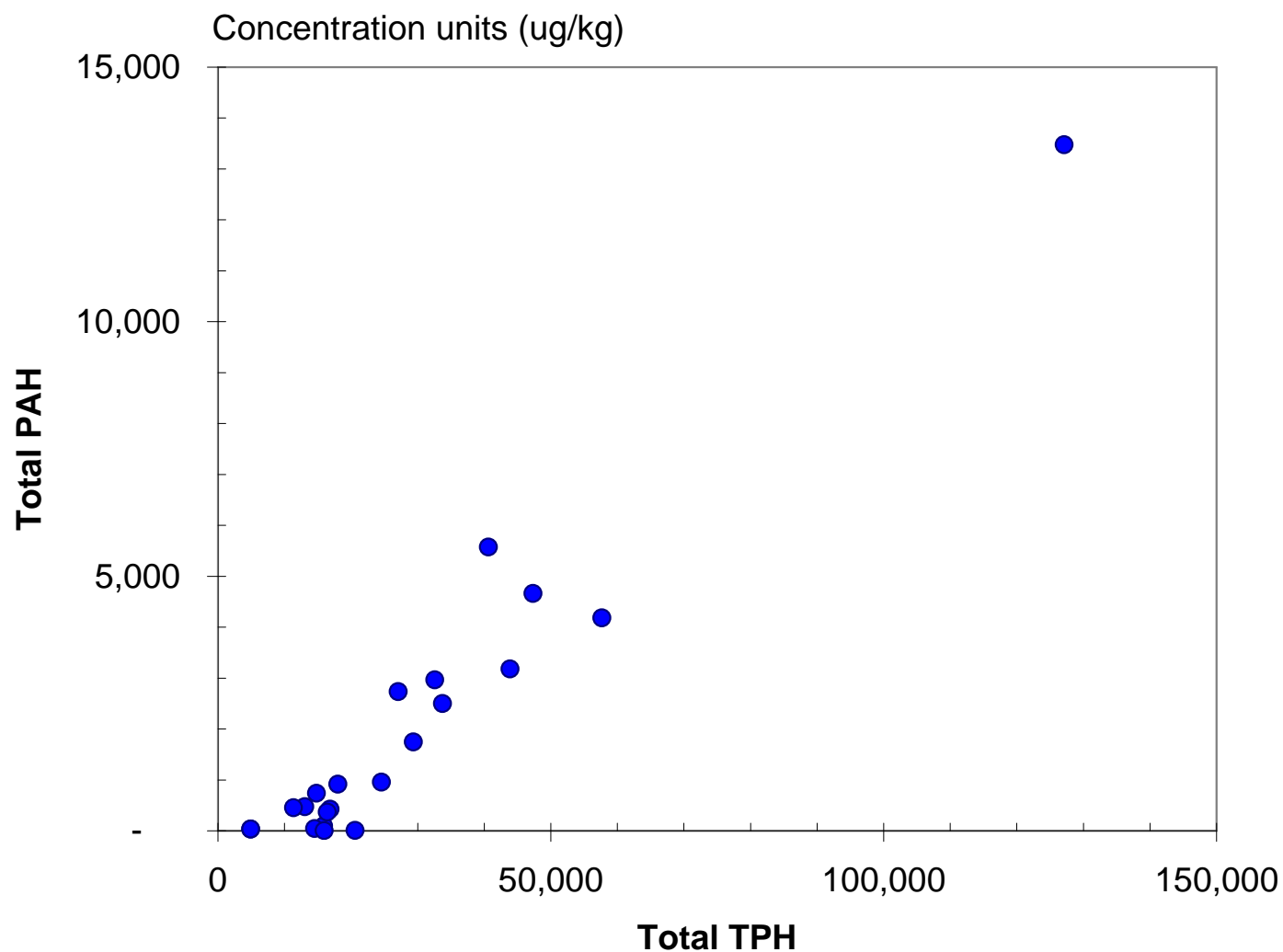


# Results of ELISA Method are Consistent with those of the Fixed Lab





# Total PAH is Proportional to Total TPH





# Water Quality Monitoring Tools to Detect Hydrocarbon Contamination

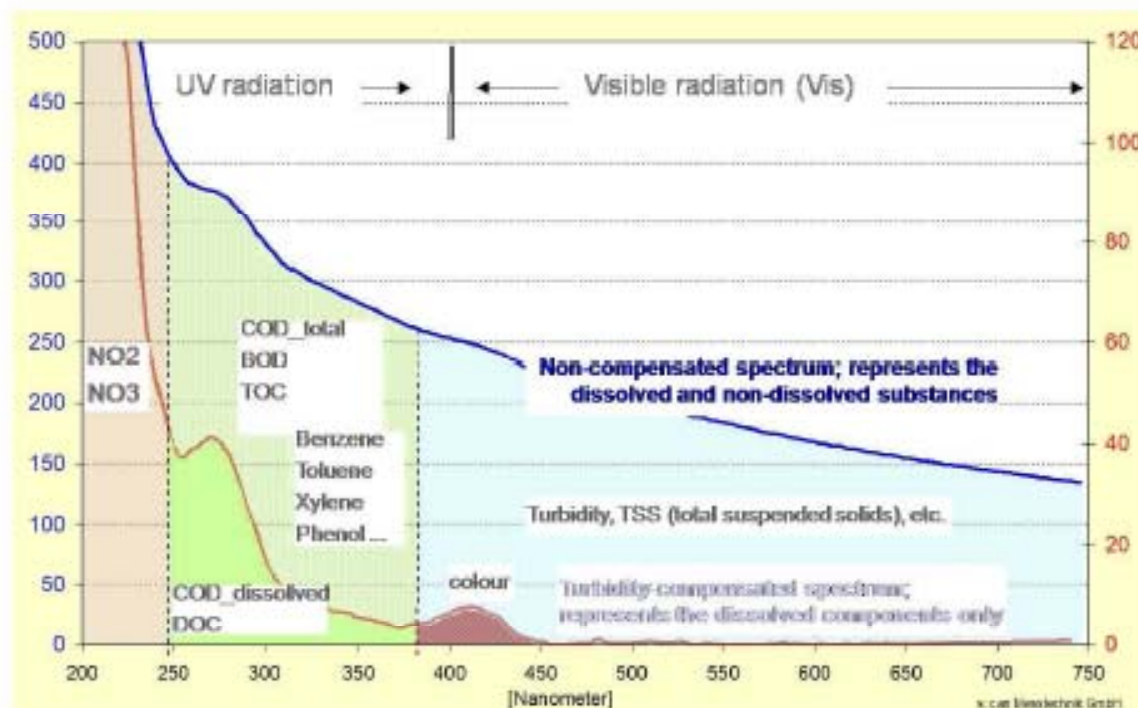
- **Potential sensors for detecting changes in water quality (currently being used in research on water supply early warning)**
  - **Physical/Chemical Sensors**
    - **S:Can UV/Vis Spectrometer**
      - ❖ Organic carbon
      - ❖ Contaminants
      - ❖ Nutrients
    - **Multiparameter Sondes**
  - **On-line Toxicity Monitoring**
    - **Bivalve Gape/Behavior**
    - **Bacterial Luminescence**
    - **Fish Behavior/Mortality**
- **S:Can is the most promising for dredging related real-time monitoring but other approaches may be applicable from a broader WQ standpoint**



# S:Can Spectrolyzer

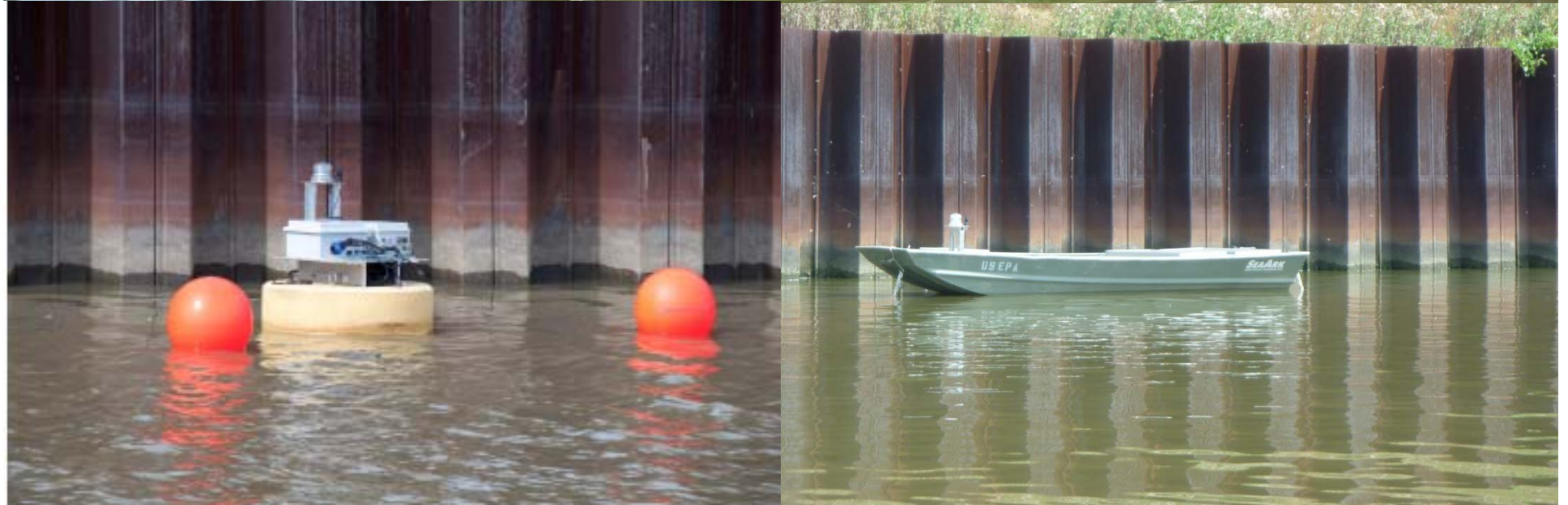
## Advantages of S:Can

- Entire UV-Vis spectrum is measured. This provides endpoints such as:
  - Hydrocarbons
    - ❖ BTEX
    - ❖ TOC
    - ❖ DOC
  - Turbidity/Suspended Solids
  - H<sub>2</sub>S
  - NO<sub>2</sub>-NO<sub>3</sub>
- Profiling for temporal analysis
- Can be deployed quickly for immediate or long term monitoring
- No consumable reagents
- No calibration





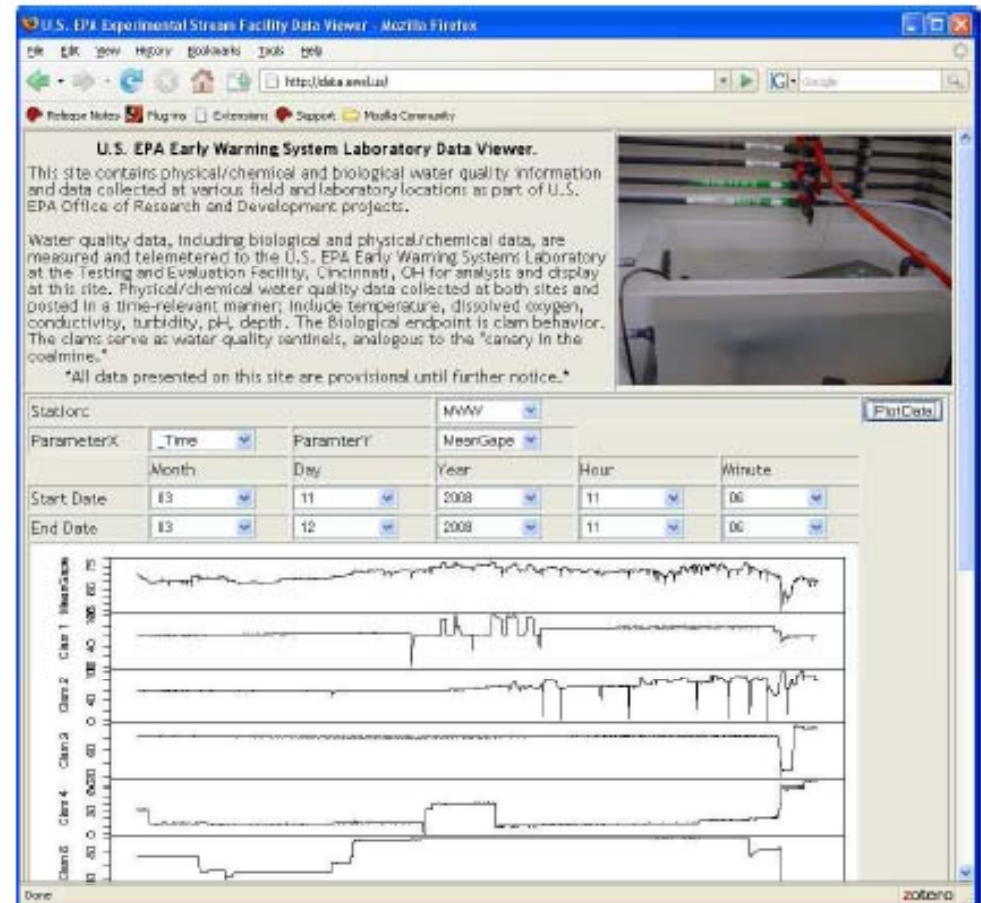
# Real-time and S:Can monitoring at GLLA Ottawa River – Environmental dredging project





# Information Management and Dissemination

- Data from Ottawa River deployments are accessed via web-base GUI interface and are available for review/processing/action as soon as they are received
- Can also be obtained or accessed by direct SQL queries





# Questions?

