Use of Solid-Phase Microextraction (SPME) to Investigate the Pacific Sound Resources Site Cap

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Objectives

- Illustrate preparation & use of Solid-Phase Microextraction (SPME) technique
- Answer specific questions regarding the remedial cap:
  - Do PAHs in sediment porewater currently exceed Ambient Water Quality Standards (AWQS)?
  - Are there upwelling trends suggesting groundwater advection and future cap failure?
  - What is the nature of cap recontamination, if any?
  - What does porewater imply for benthic toxicity?

Why Measure Porewater?

- To compare near-surface porewater to AWQS, required by Second PSR Five-Year Review that suggested based on increase in NAPL in wells along shoreline could indicate NAPL migration into adjacent Puget Sound

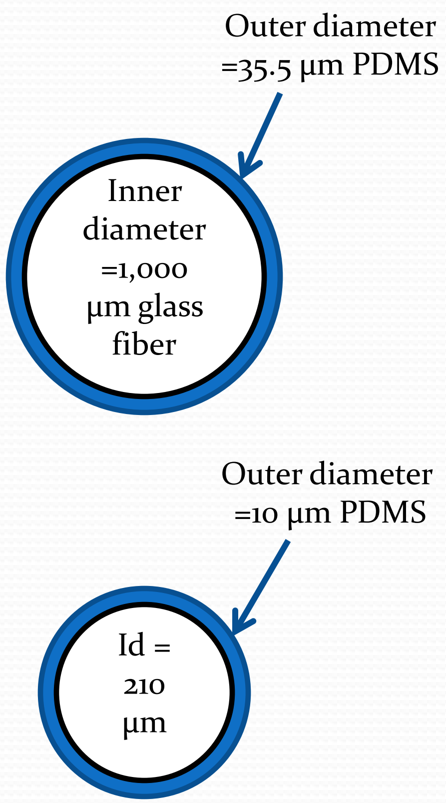
- To determine gradients in cap or in nearshore groundwater zones

- (Procedurally) to ascertain "non-steady state" adjustments for slow-to-uptake PAHs due to diffusion limitation in SPME device

- To gain an understanding of bioavailability of PAHs

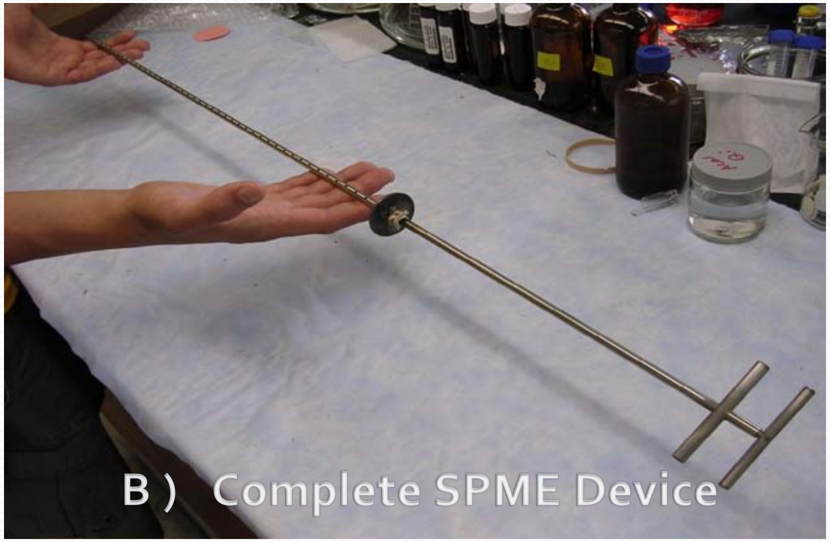
Sampling Strategy for PSR (1)

- *Prior Studies:*
  - EPA Diver Survey to ascertain sediment penetration
  - Univ. of Texas (UT) Calibration Study to develop fiber association constants
- Prepare SMPEs in pushpoint devices
  - Use both **1000/1071** µm and **210/230 µm** polydimethylsiloxane (PDMS) coated fibers (for nonequilibrium corrections)
  - Confirm fibers are free of PAH
  - Insert into push-point sampler
- Deploy and retrieve SMPEs using divers
- Clip fiber lengths, extract into acetonitrile
- Analyze with HPLC-FD



Solid Phase Microextraction (SPME) Sampler

A) SPME Fiber Close - up



B) Complete SPME Device

C) Insertion into Sediment

Sampling Strategy for PSR (2)

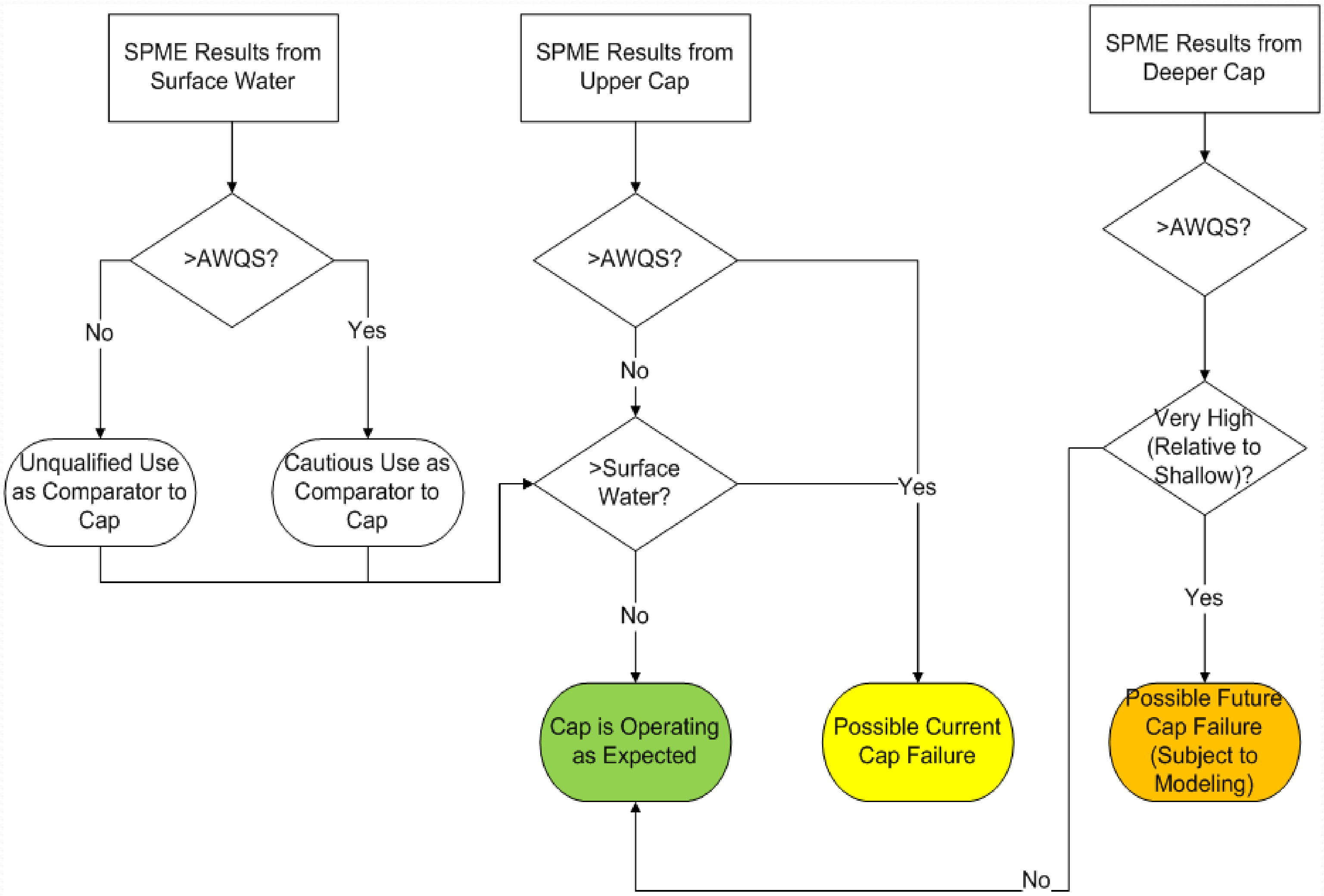
- SPME Deployment

SPME lengths (feet)	# Deployed in Sediment	# Deployed in Surface Water	# of Blanks (shipping and retrieval)
3	15	0	2
2	1	0	0
1	8	3	0

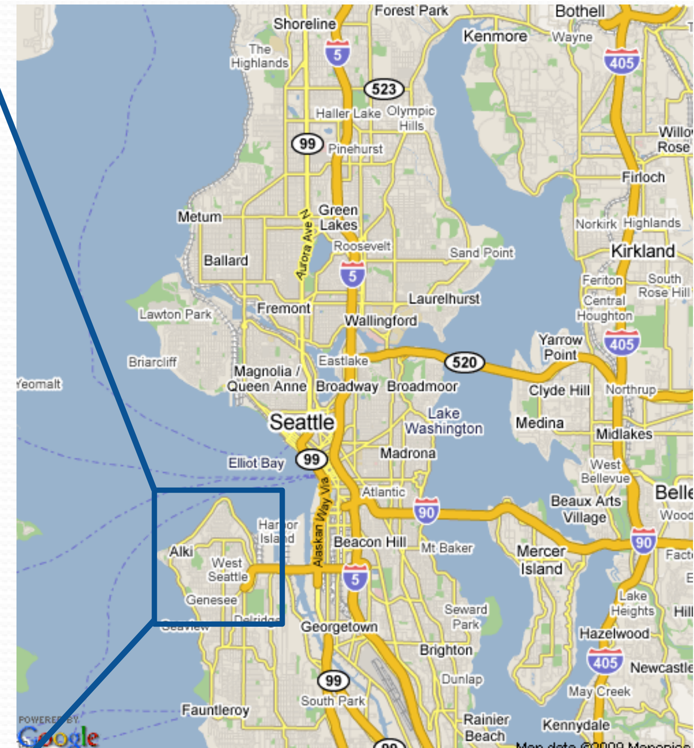
- 7 day equilibration period before recovery
- Subsamples collected immediately – Intervals:

Target Depth (cm)	Sample intervals (cm)
0 – 10	3 – 5 and 5 – 7
10 – 20	13 – 15 and 15 – 17
20 – 24	53 – 55 and 55 – 57
27 - 30	70 – 72 and 72 – 74

Interpretation Logic



Surface Water Sampling Locations



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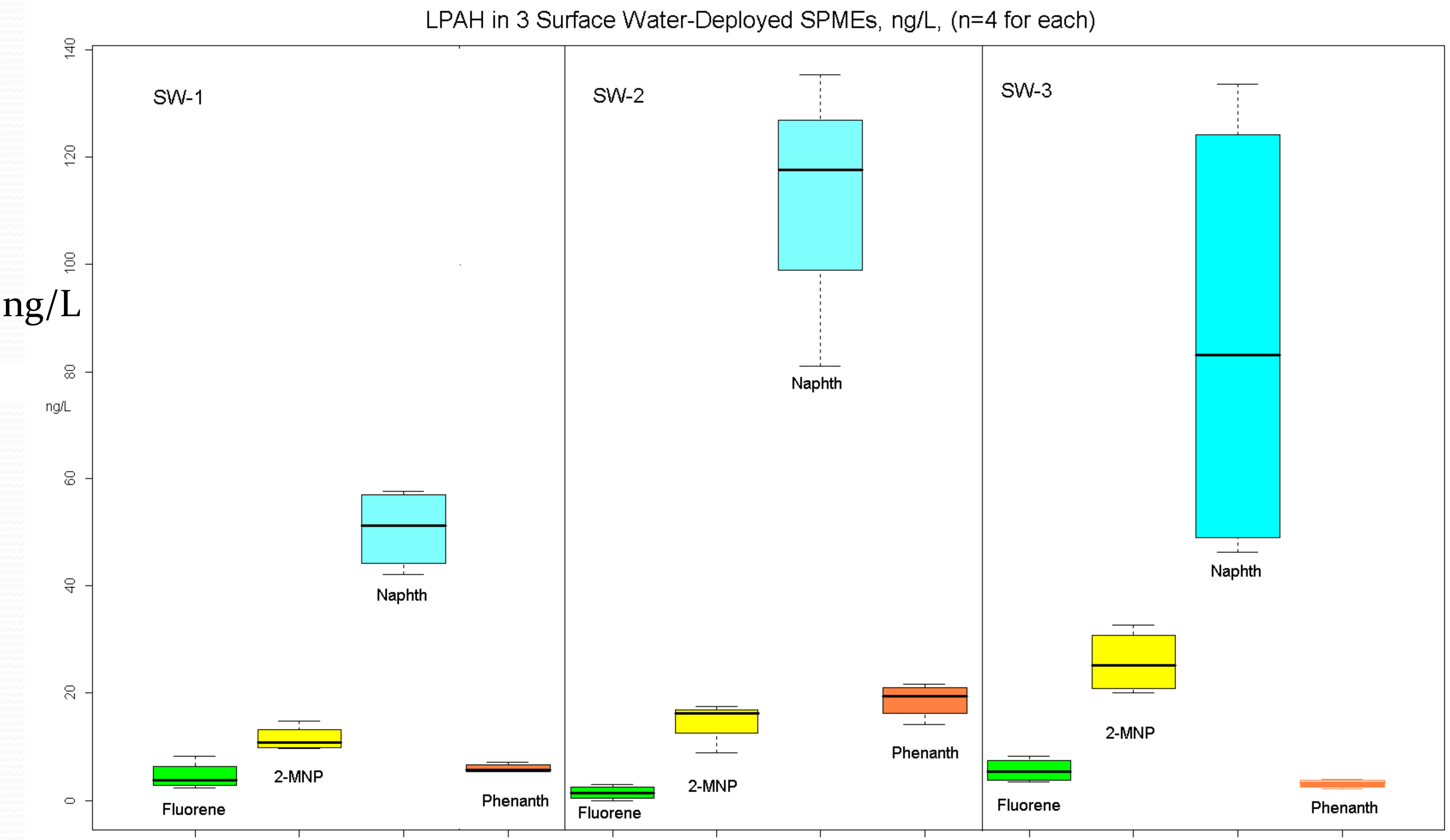
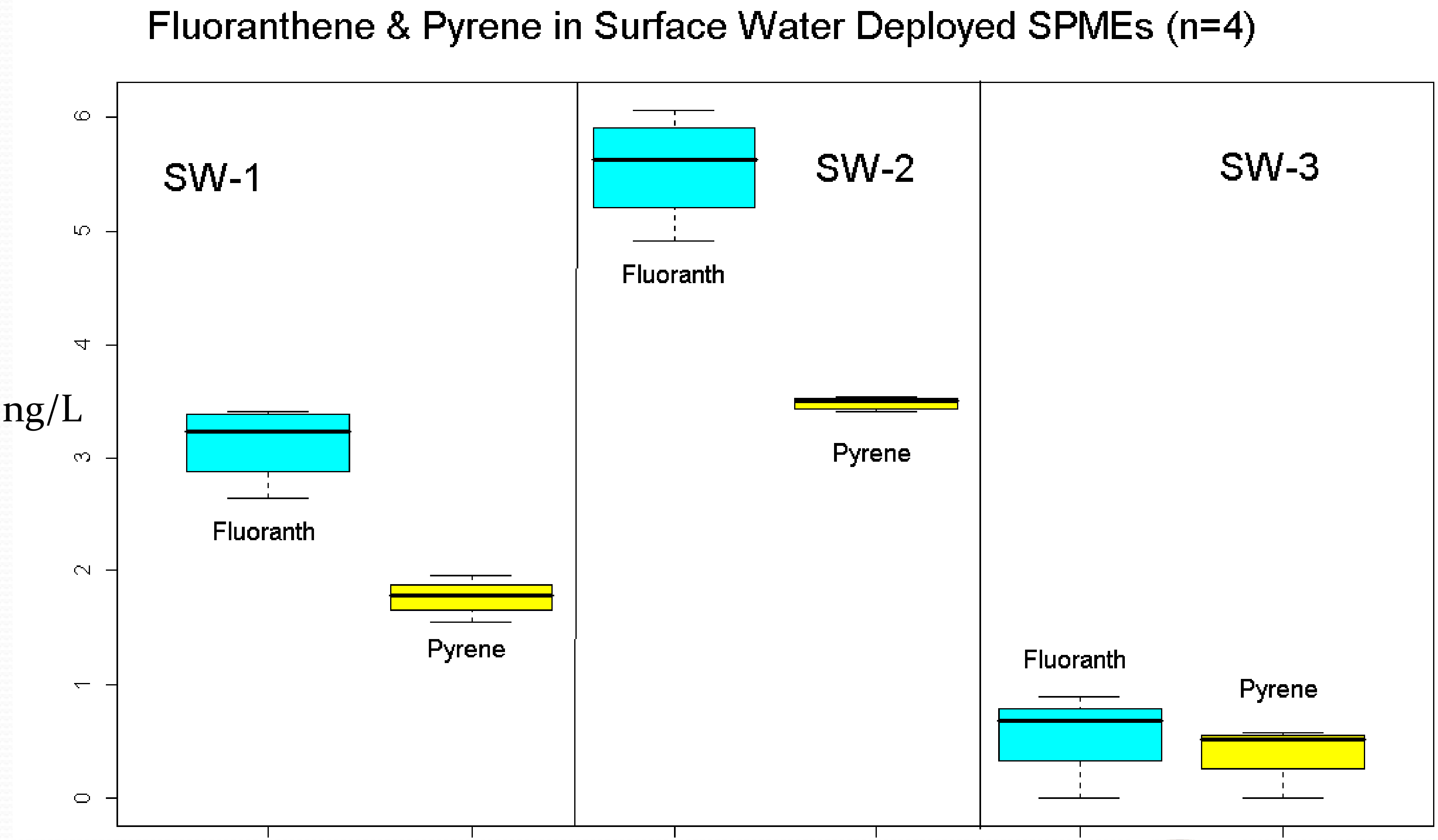
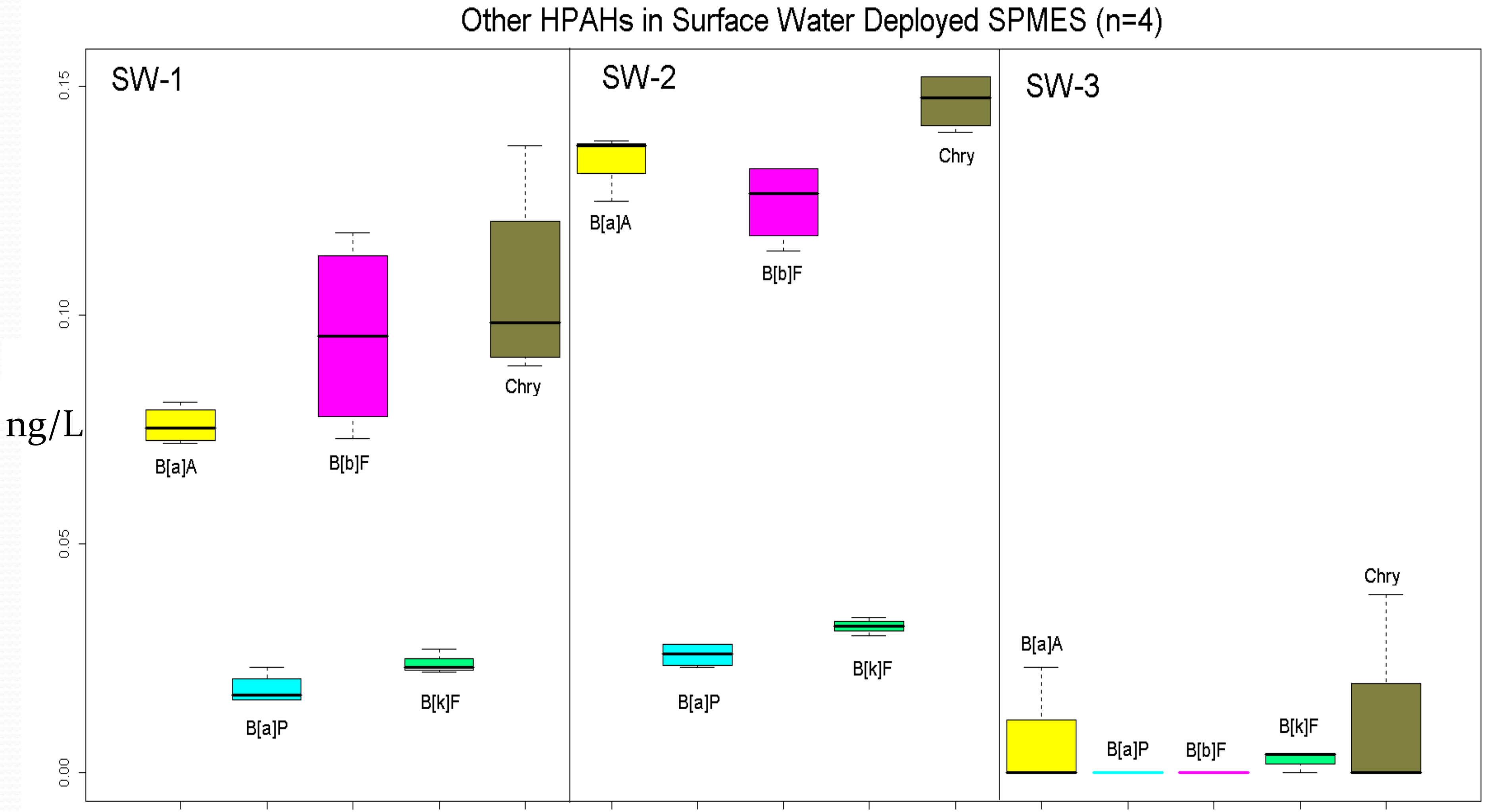
Surface Water LPAH



Surface Water HPAH (1)



Surface Water HPAH (2)



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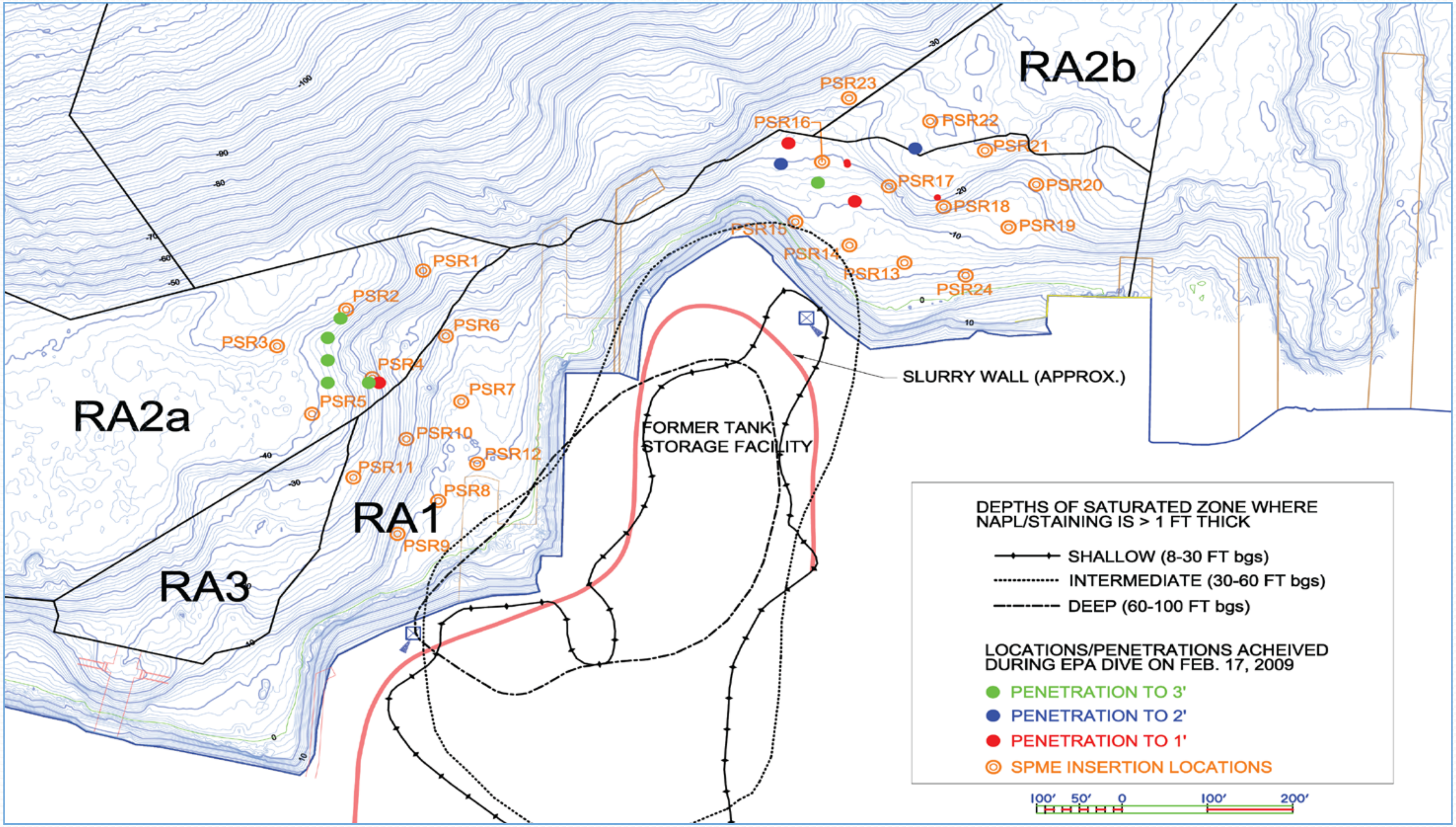
Surface Water Conclusions

- Elliott Bay has higher HPAHs in surface water than a nearby ambient Puget Sound station
- No AWQS were exceeded
  - Elliott Bay surface water results are suitable comparators to the SPME results

Cap SPME Locations



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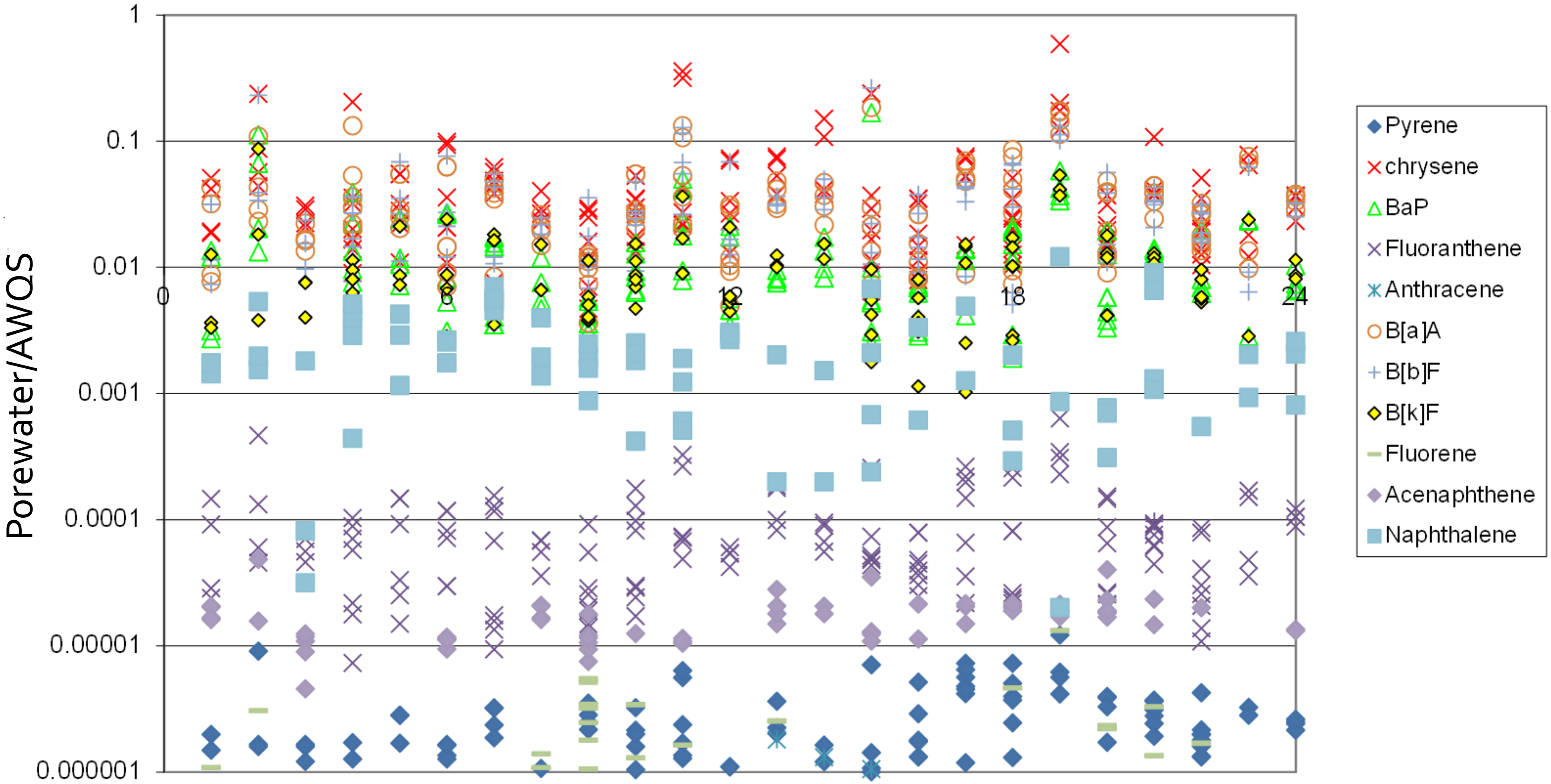
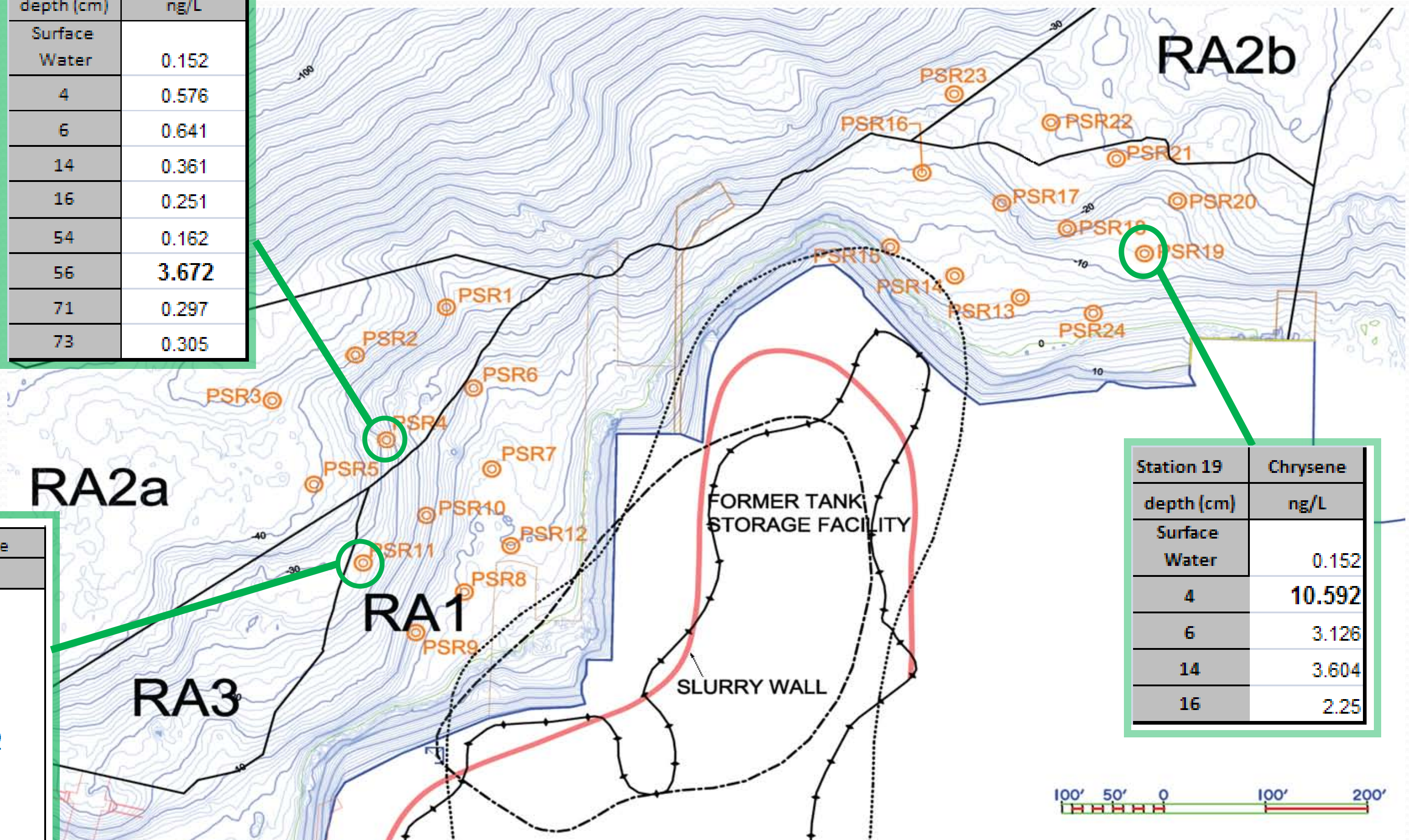
Cap SPME Results Compared to AWQS



Maximum Chrysene Stations: AWQC 18 ng/L

Station 4	Chrysene
depth (cm)	ng/L
Surface Water	0.152
4	0.576
6	0.641
14	0.361
16	0.251
54	0.162
56	**3.672**
71	0.297
73	0.305

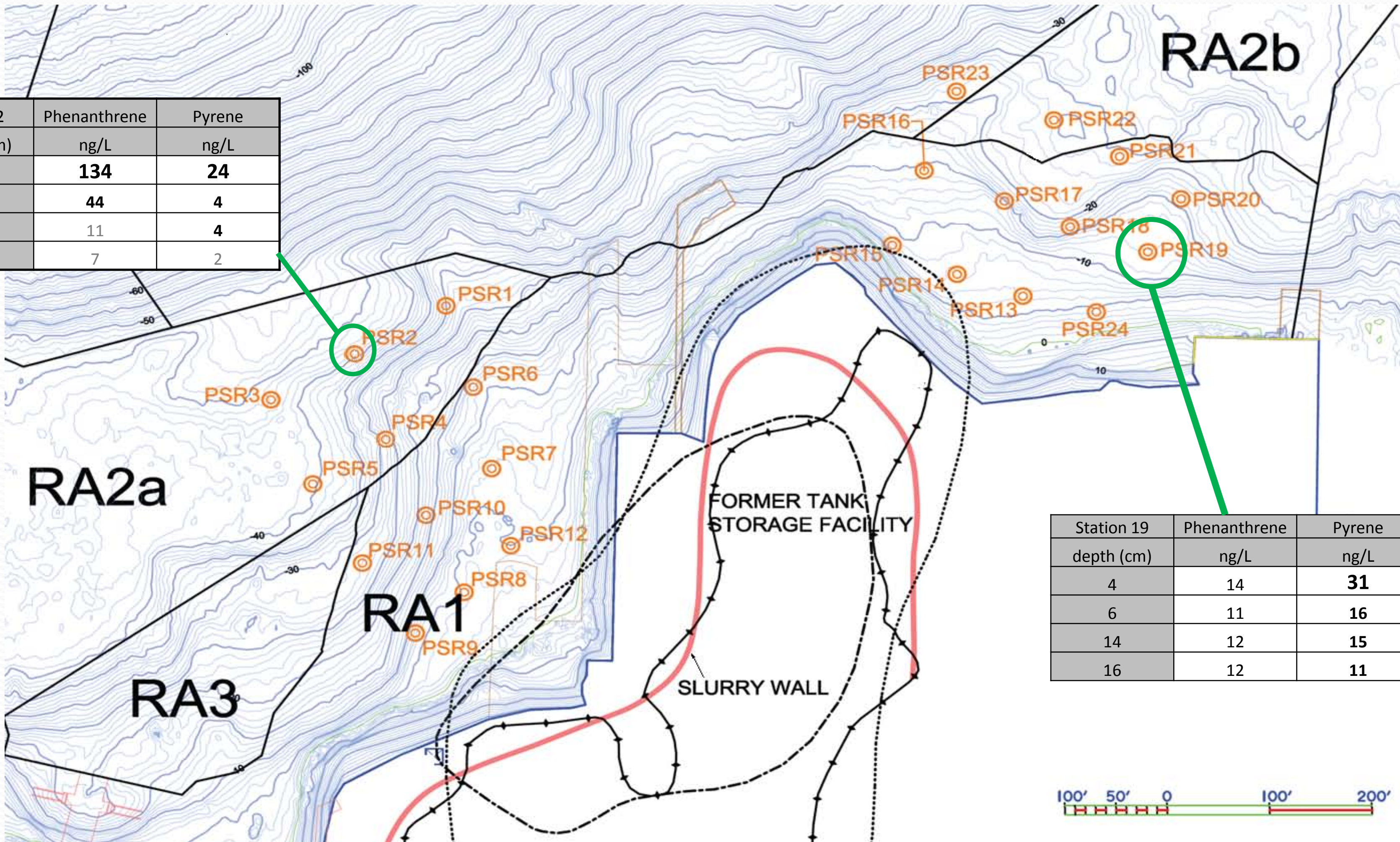


Station 11	Chrysene
depth (cm)	ng/L
Surface Water	0.152
4	5.68
6	0.405
14	0.389
16	**6.442**
54	0.779
56	0.49
71	0
73	0

Station 19	Chrysene
depth (cm)	ng/L
Surface Water	0.152
4	**10.592**
6	3.126
14	3.604
16	2.25

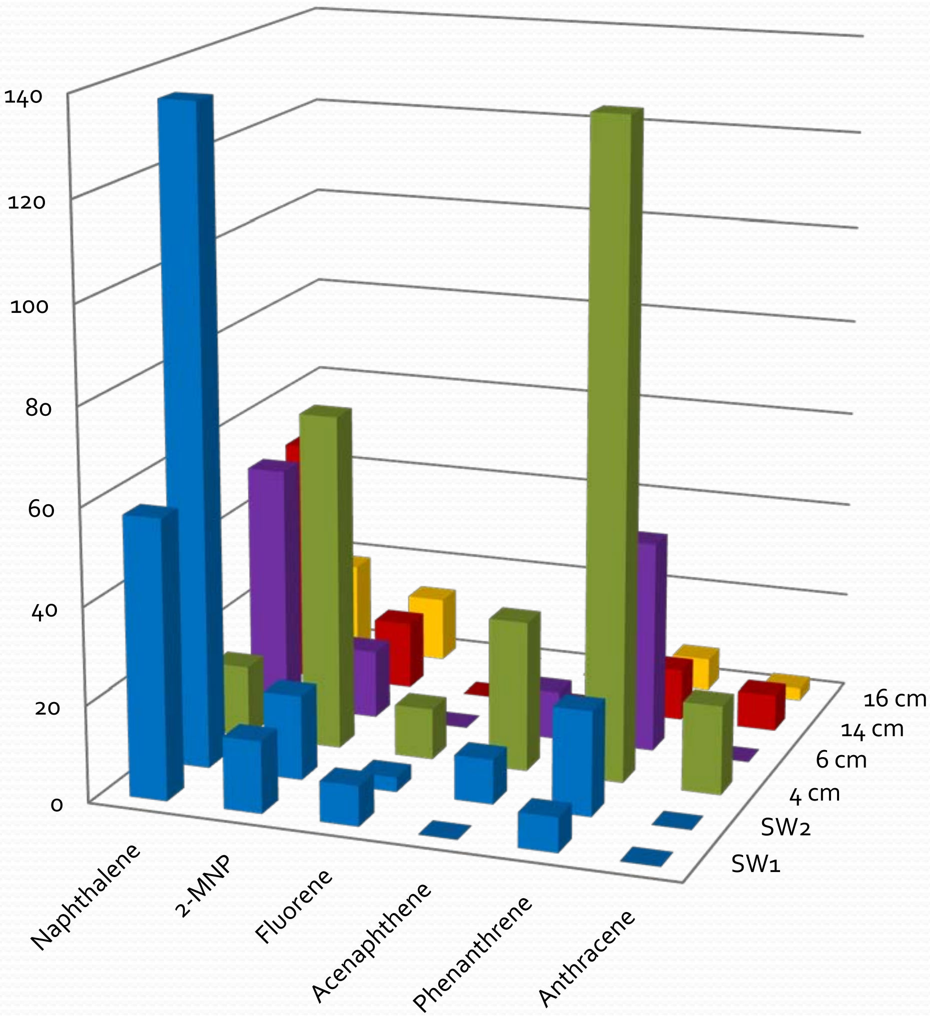
Maximum Phenanthrene & Pyrene Stations

Station 2	Phenanthrene	Pyrene
depth (cm)	ng/L	ng/L
4	**134**	**24**
6	**44**	**4**
14	11	**4**
16	7	2

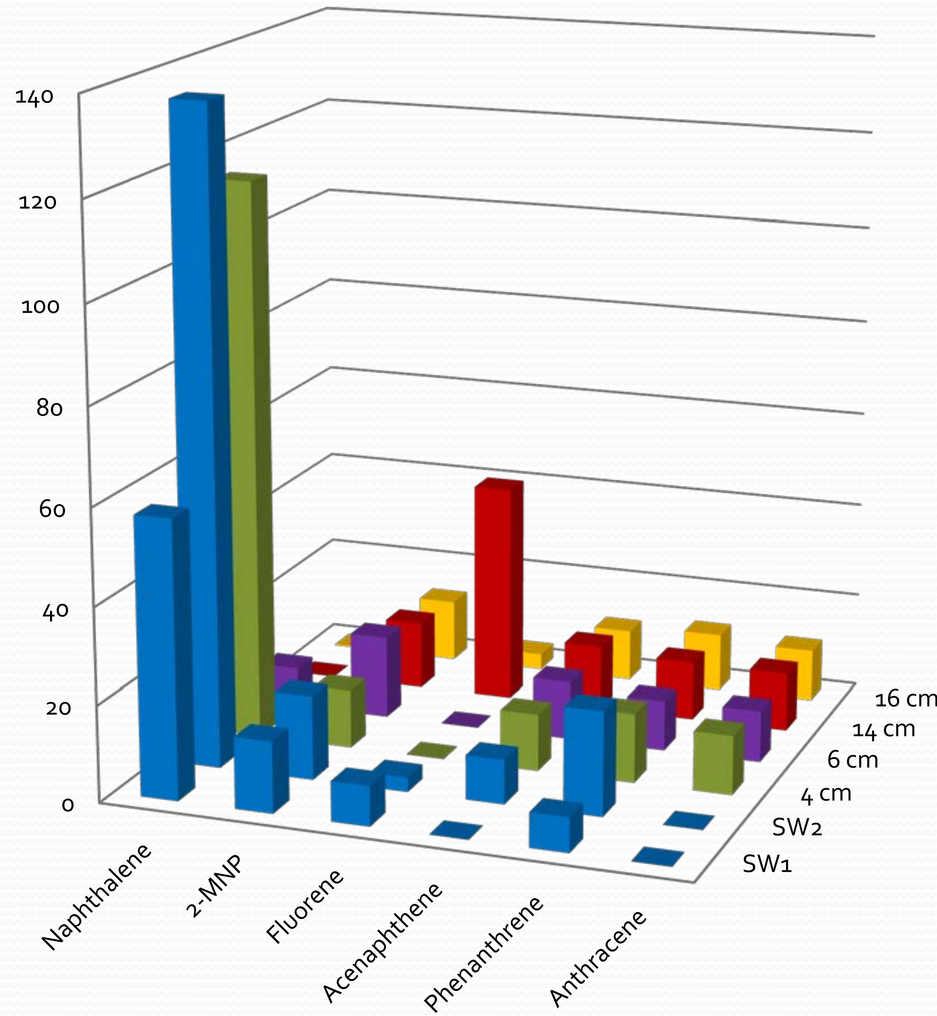


Station 19	Phenanthrene	Pyrene
depth (cm)	ng/L	ng/L
4	14	**31**
6	11	**16**
14	12	**15**
16	12	**11**

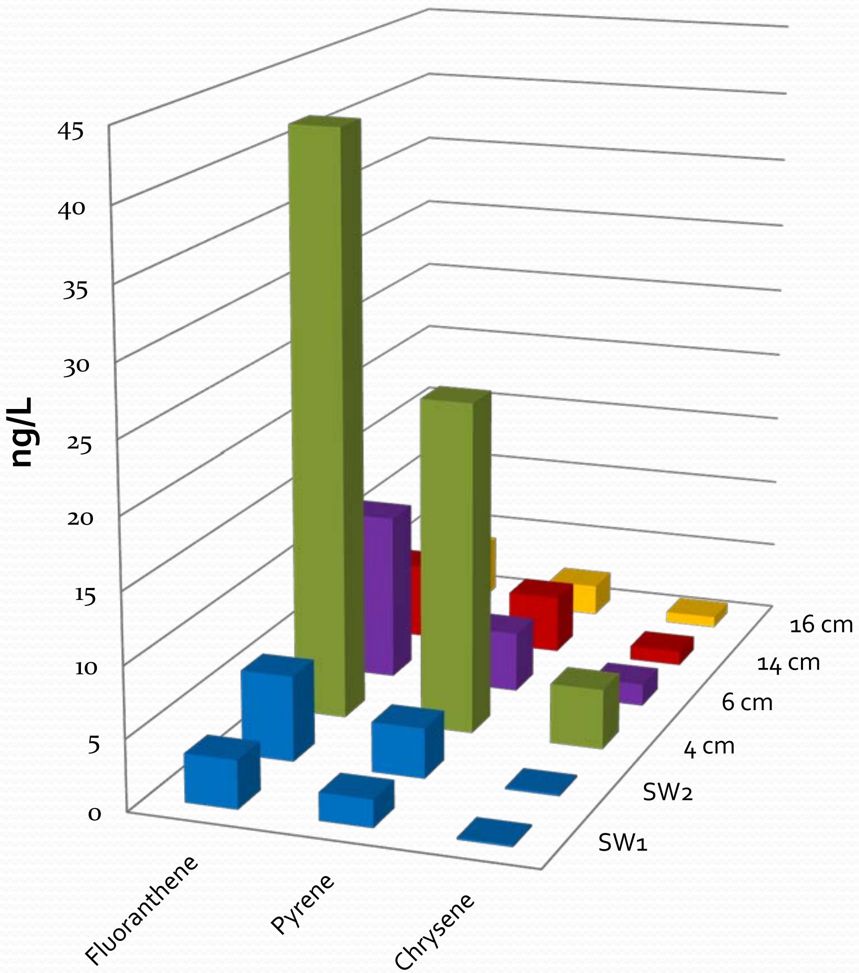
LPAH in Station 2
Compared to Surface Water (ng/L)



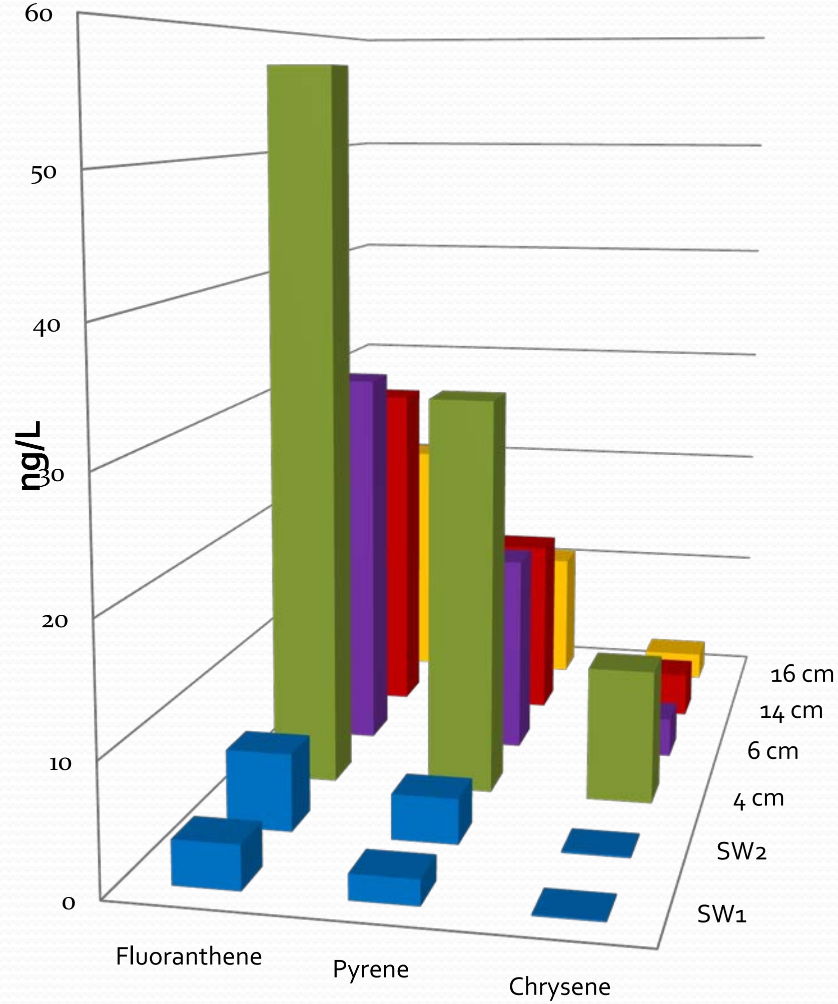
LPAH in Station 19
Compared to Surface Water (ng/L)



HPAH(1) in Station 2
Compared to Surface Water



HPAH(1) in Station 19
Compared to Surface Water



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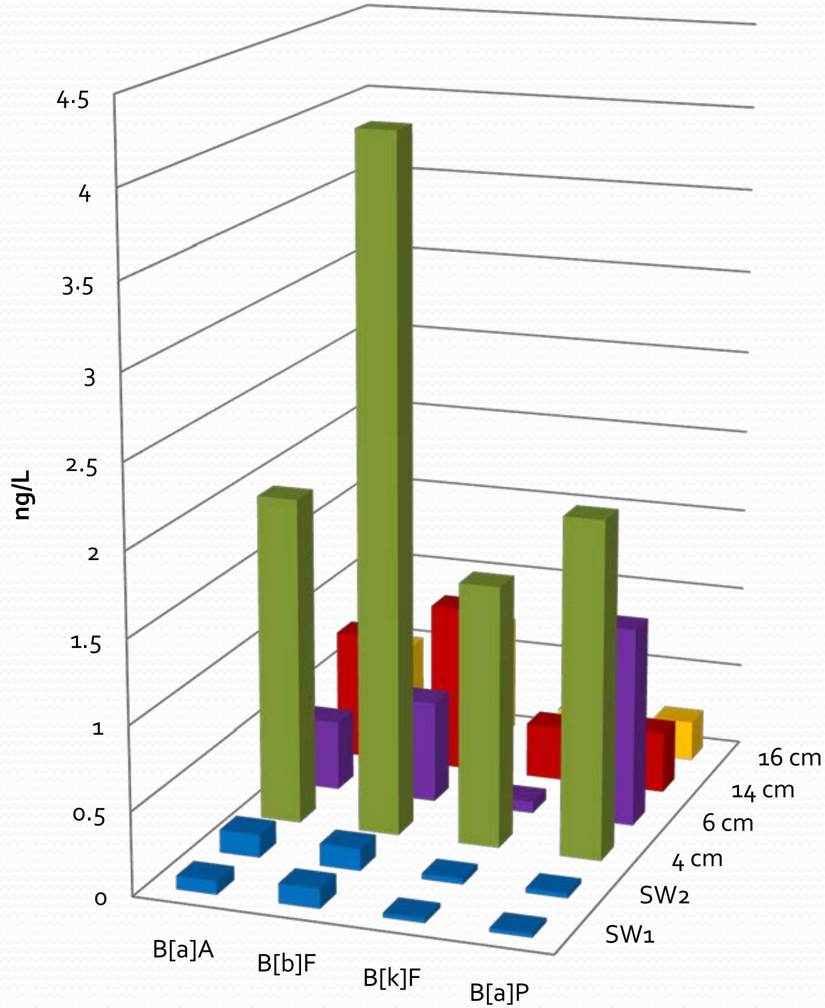
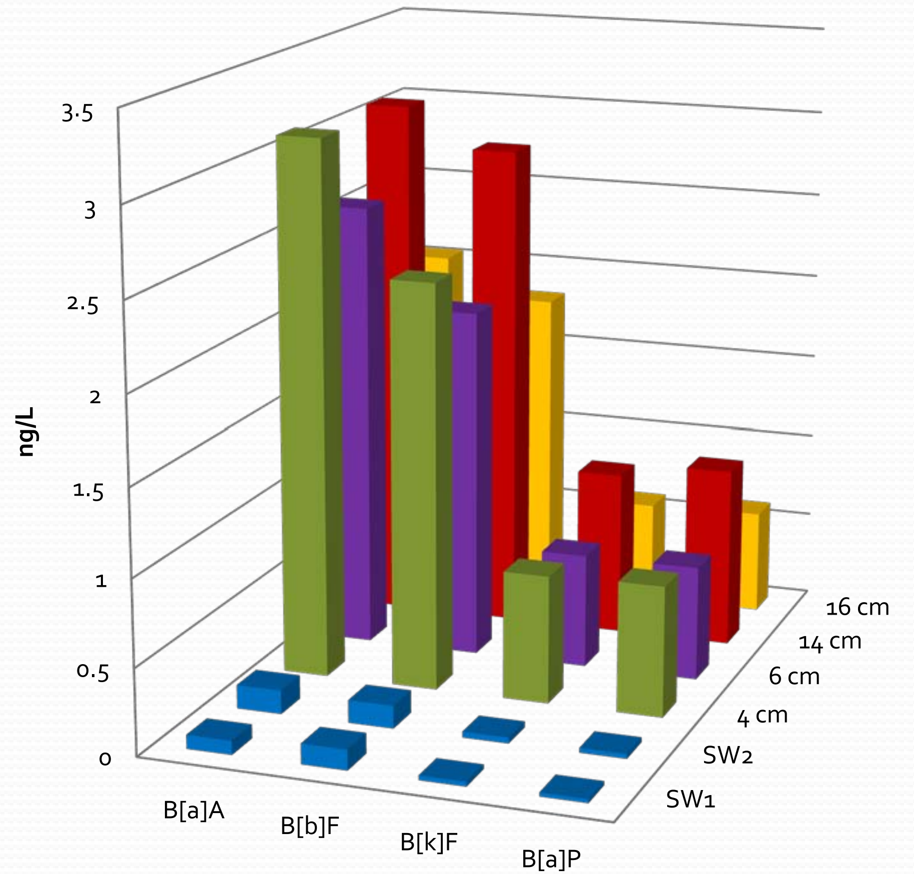
Four More HPAH in Station 2

Compared to Surface Water



Four More HPAH in Station 19

Compared to Surface Water



Conclusions for PSR Cap

- All compounds below AWQS
  - SPMEs capable of very low levels of resolution
  - Chrysene
    - Maximum concentration at 59% of the AWQS; apparently related to incoming sediment (not deep upwelling)
  - Most other compounds in porewater :
    - 1-4 orders of magnitude below AWQS
  - Surface water was below AWQS
    - Near-surface cap (4 - 6 cm) were higher than surface water but below AWQS
- No *upward* trend
  - Thus, no evidence of a bottom-up contamination
  - Possible top-down contamination pattern from incoming sediment
    - Trend is not critical at this time given the magnitude of dissolved PAH

Why Use Passive Samplers?

Measuring Bioavailability <u>without</u> SPME

- Prediction of toxicity – from EPA (2003) and EPA (2007):
  - Use Equilibrium Partitioning (EqP) to determine concentration
  - Calculate the ratios of individual PAHs to their Final Chronic Values ("Toxicity Units", TU)
  - Add these to determine ΣTU
  - Compare to a ΣTU of 1.0 – the probable effect level using the narcosis model
- Caveats:
  - EqP overestimates toxicity by c 100x.
  - Also, "black carbon" adjusted EqP tends to underpredict toxicity (Gschwend, et al. 2010)

Why Use Passive Samplers?

Measuring Bioavailability with SPME

- SPME measures porewater directly
  - SPMEs are better benthic toxicity estimators than bulk sediment PAH
  - Usually, results are within a factor of 2, as opposed to 100 for EqP alone
- Total Toxicity of all surface stations are far below 1.0
  - Stations with highest sediment surface concentrations evaluated on next slide
- Other passive samplers are quite comparable to SPME (the main differences are the logistics of deployment – SPME are better for penetrating a cap)

Toxicity Units Calculation, Stations 2 and 19

Sampler 2, 4 cm	ng/L	FCV	TU	Uncertainty Adjusted TU		*Sampler 19, 4 cm*	ng/L	FCV	TU	Uncertainty Adjusted TU
Naphthalene	14.792	193500	7.64E-05	7.64E-05		Naphthalene	116.03	193500	6.00E-04	6.00E-04
2-MNP	69.644	72160	9.65E-04	9.65E-04		2-MNP	12.197	72160	1.69E-04	1.69E-04
Fluorene	10.597	39300	2.70E-04	2.70E-04		Fluorene	0	39300	0.00E+00	0.00E+00
Acenaphthene	31.036	306900	1.01E-04	1.01E-04		Acenaphthene	11.865	306900	3.87E-05	3.87E-05
Phenanthrene	134.153	19130	7.01E-03	7.01E-03		Phenanthrene	14.372	19130	7.51E-04	7.51E-04
Anthracene	18.42	20730	8.89E-04	8.89E-04		Anthracene	12.331	20730	5.95E-04	5.95E-04
Fluoranthene	41.794	7109	5.88E-03	5.88E-03		Fluoranthene	57.033	7109	8.02E-03	8.02E-03
Pyrene	23.519	10110	2.33E-03	2.33E-03		Pyrene	31.408	10110	3.11E-03	3.11E-03
Chrysene	4.263	2042	2.09E-03	2.09E-03		Chrysene	10.592	2042	5.19E-03	5.19E-03
B[a]A	1.964	22270	8.82E-05	8.82E-05		B[a]A	3.119	22270	1.40E-04	1.40E-04
B[b]F	4.141	677.4	6.11E-03	1.22E-02		B[b]F	2.355	677.4	3.48E-03	6.95E-03
B[k]F	1.566	641.5	2.44E-03	4.88E-03		B[k]F	0.744	641.5	1.16E-03	2.32E-03
B[a]P	2.02	957.3	2.11E-03	4.22E-03		B[a]P	0.76	957.3	7.94E-04	1.59E-03
TU Sum			**0.030**	**0.041**		TU Sum			0.024	**0.029**

Questions?