Use of the Triad Approach to Characterize PCB in a Riverine Sediment Site

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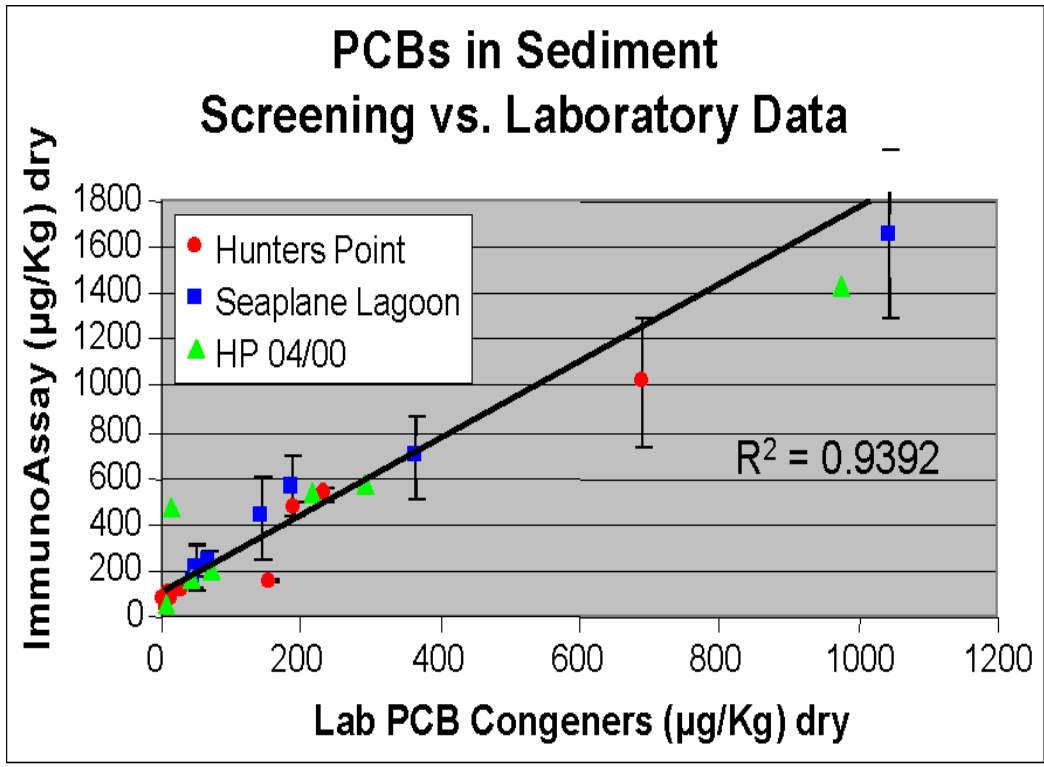
Objectives of Talk

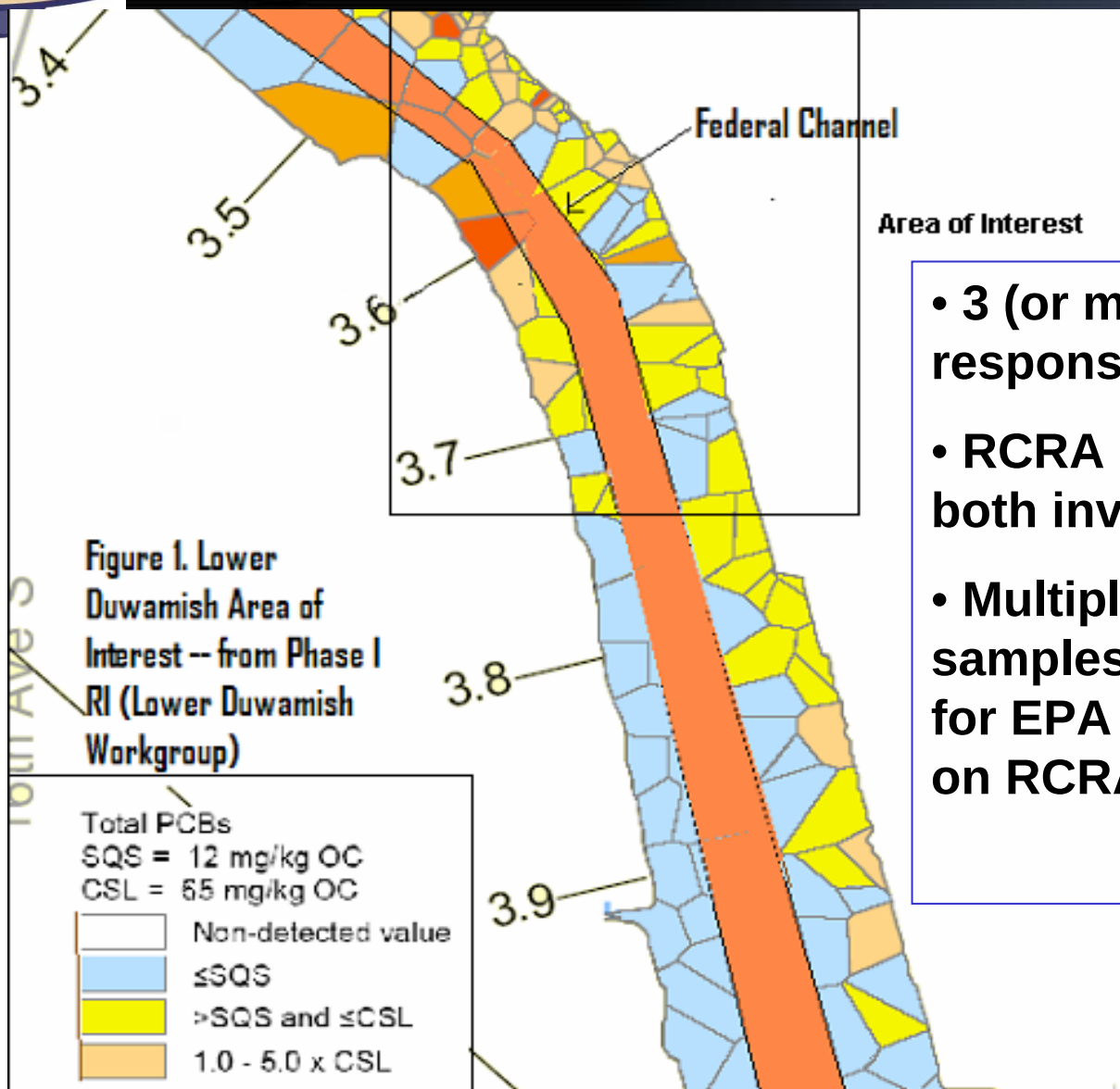
- Show applicability and reliability of the PCB ELISA immunoassay (EPA Method 4020) compared to GC/ECD (EPA Method 8082) in a sediment cleanup context
- M4020 previously used for sediment ->
- Emphasis on usability of this tool for total decision error management



Goals, Decisions

- Define patterns and determine source(s) of PCB in a reach of the Lower Duwamish River, Seattle
- Generate data usable for guiding RI/FS and Corrective Measures Study
- Assist EPA to move forward rapidly to remedial action, namely:
  - Whether to dredge/how deep to dredge are key project decisions
  - Extent of actionable area, responsibility

Prior “Known” Pattern of Surface PCB



- **3 (or more) potentially responsible parties**
- **RCRA and CERCLA both involved**
- **Multiple parties taking samples but not enough for EPA to make decision on RCRA “plume”**

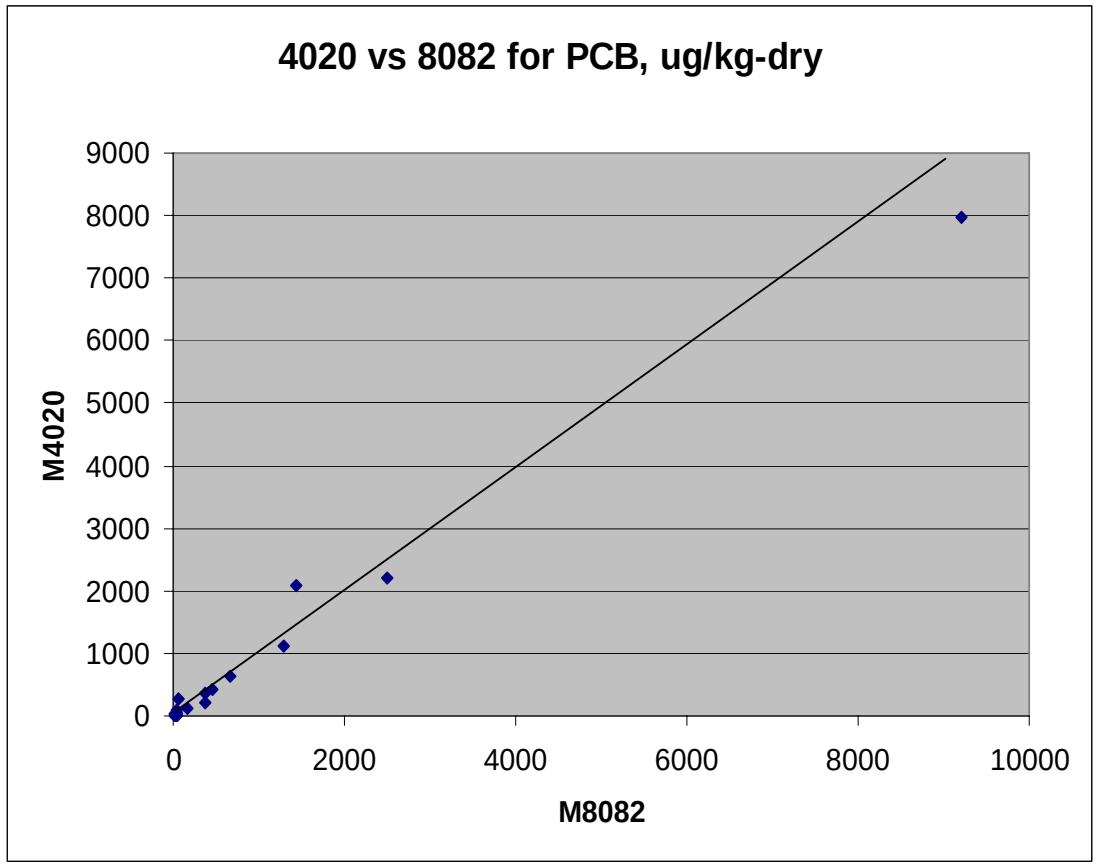
Approach/Assessment Tools

- **Demonstration of method applicability (DMA)** to make field decisions; large correspondence data set
- Key methodology questions:
  - Uncertainty associated with use of Method 4020 (ELISA) vs. Method 8082 (GC/ECD)
  - How do the “dredging plans” for the prospective action compare?
- Key Conceptual Site Model question:
  - Based on suspected riverine transport. Can we confirm this?
- Wished to become familiar with adaptive approach, acquiring M4020 results in 2-4 days in offsite lab; ***v.*** 4.5 months for M8082)

Preliminary DMA

- **Prior testing of 20 samples from the river using M4020 (SPAWAR) and M8082 (USACE and Boeing) showed linear correlation ($R^2 > 0.9$)**

- **Decision error rate versus dry weight decision (130 ug/kg) was 10%, e.g.,**
  - **1 false negative**
  - **1 false positive**



Cleanup Decision-making

- In Washington State, organic-carbon (OC) normalized sediment standards exist to protect benthic communities

  mg/kg-OC = μg/kg-dry /(OC*1000)

- State rule does not include an explicit tolerable uncertainty statement; should be developed for each investigation
- Presentation seeks to define uncertainty from M4020 versus M8082 for this Superfund Site

Regulatory Framework for PCB

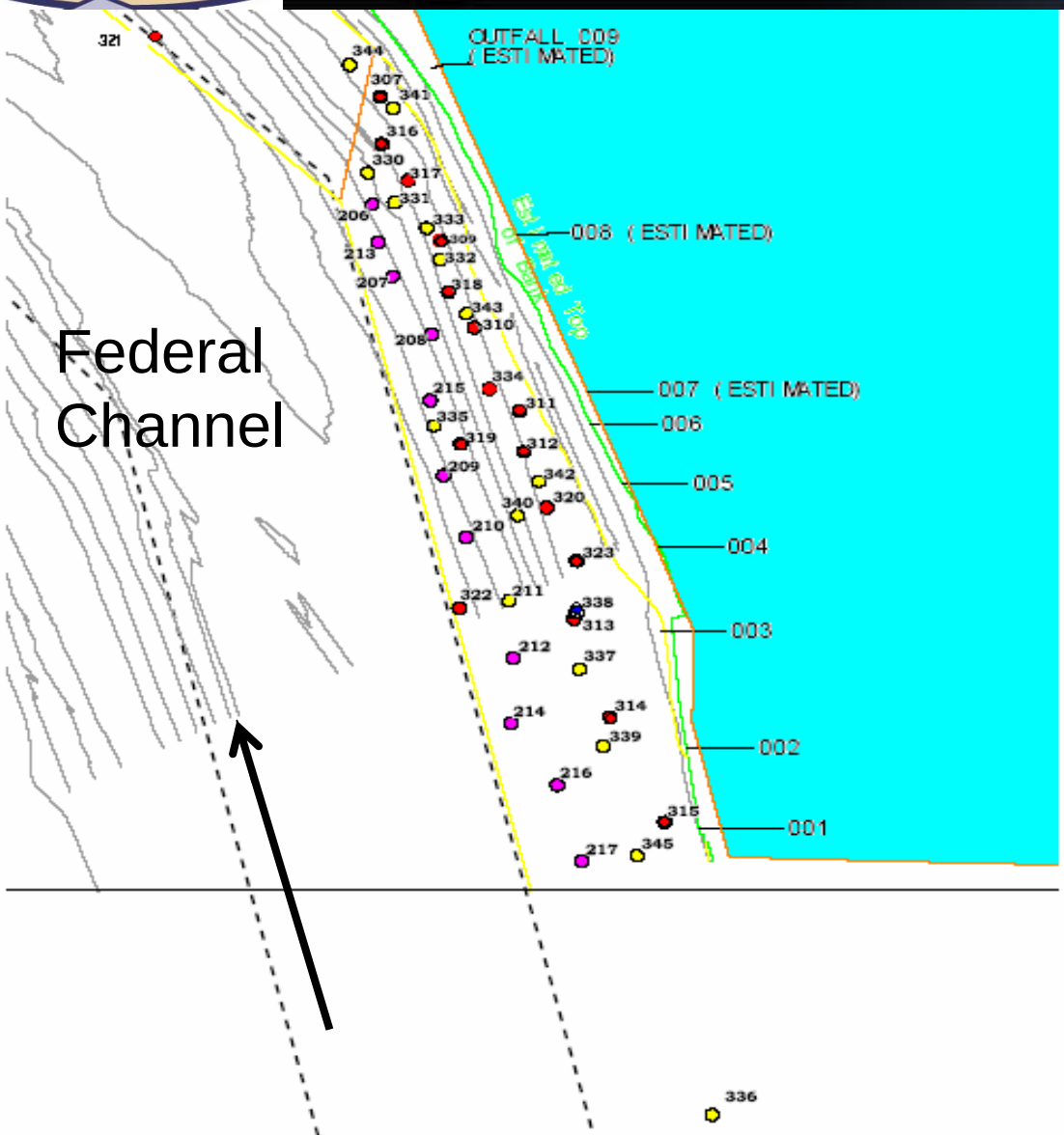
	Note	Organic Carbon
Pass		≤ 12 mg/kg-OC
Exceed SQS	A	12<X≤65 mg/kg-OC
Exceed CSL	B	>65 mg/kg-OC
		Unless < 0.5% OC:
Pass		≤130 ug/kg-dry
Exceed SQS		130<x<1000 ug/kg-dry
Exceed CSL		>1000 ug/kg-dry

Washington State Sediment Management Standards.

A: Sediment Quality Standard (SQS) -- May affect benthic community

B: Cleanup Screening Level (CSL) -- Likely to affect benthos

Sampling Schema for Reach



- **Two stages of sampling: specified and adaptive**
- **Purple stations sampled by Boeing Company by specification**
- **Red stations specified sampling this study—surface, also 16 subsurface cores**
- **Purple and yellow (24) adaptive surface stations added to address areas of greatest uncertainty**
- **Adaptive coring was not possible due to budget constraints**

QA Expectations for M4020 Met

Initial Calibration, 3 point	**Every batch of 20**	**$R^2 \geq 0.95$**	**MET**
Reference Material; Known Standard (NRCC HS-1)	**Once**	**% Recovery = 70-130%**	**MET**
Continuing Calibration Verification	**Aroclor 1254 std. every batch of 20**	**$R^2 \leq 0.95$**	**MET**
Method Blank (Methanol Extractant)	**Every batch of 20**	**$\leq$ RL**	**MET**
Lab Duplicates	**Every batch of 20**	**% RPD $\leq$ 30%**	**MET**

Regression VS Decision Analysis

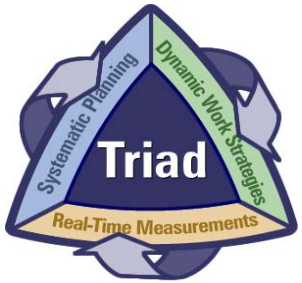
- R^2 of 0.9 postulated in QA Project Plan
- Organic carbon relationship:

[M4020, mg/kg OC] = 0.377 * [M8082 mg/kg OC] + 13.61

(SE=0.037) (SE=4.9)

R^2 = 0.549, p <0.01, Durbin-Watson D = 2.03

- Regression predictions worked poorly for predicting actual M8082 concentrations; however--
- For this analysis, in decisionmaking, data are being placed in “bins” compared to numeric standards



Evaluation Approach

- Determine decision error rates (correct, false positive error *[FPE],* false negative error *[FNE]*)
- Compare *pair-wise* samples against regulatory criteria. Focus on Organic Carbon normalized (also evaluated dry weight, with similar results).
- Because of OC data, sample turnaround would become about 4-5 days
- Compare decisions carried out using regulatory criteria (*e.g.*, how deep to dredge to remove sediments above cleanup level)

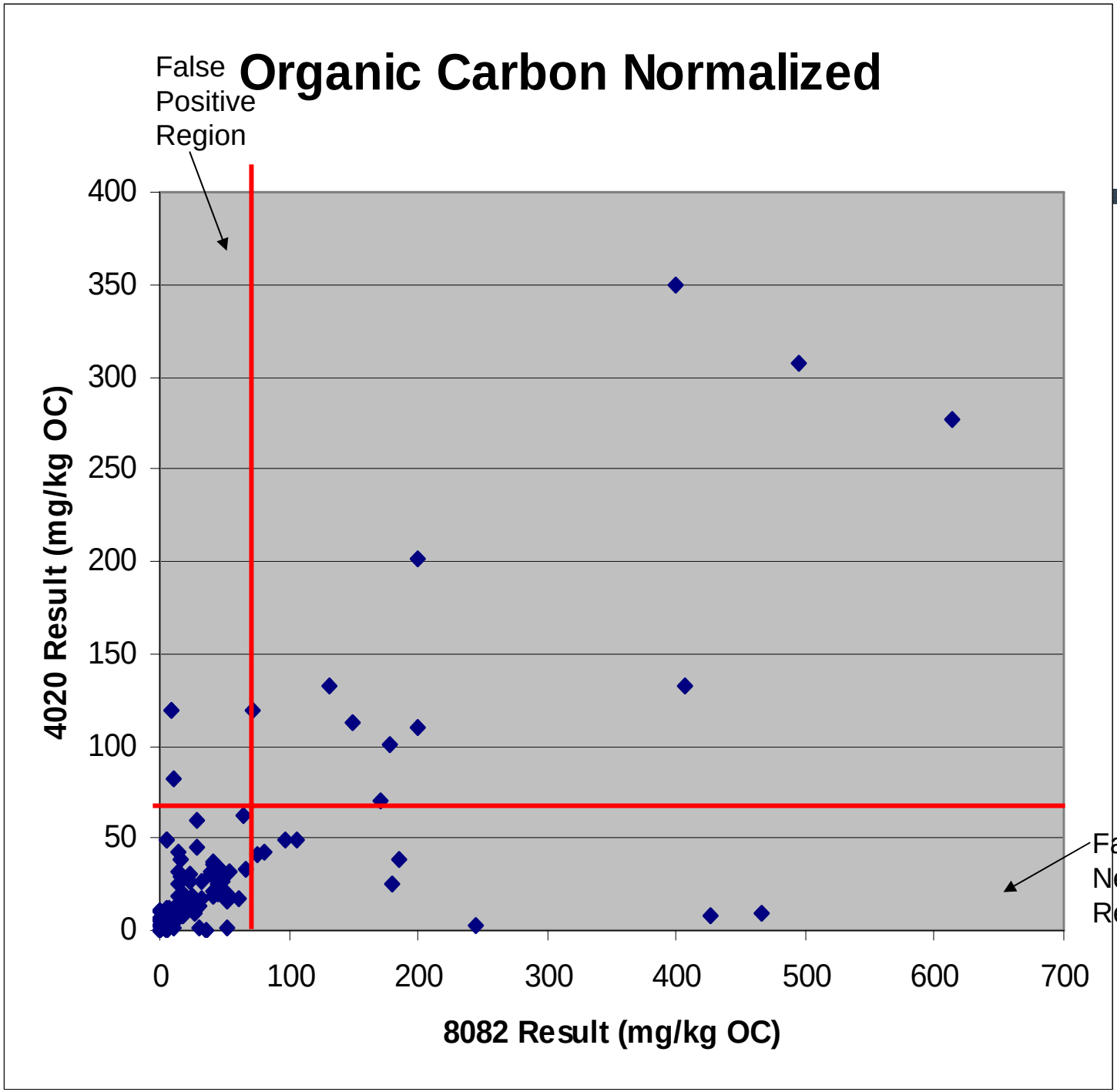
Pairwise Evaluation of Error Rate

8082 OCN	Q	4020 OCN	Q	8082 OCN	Q	4020 OCN	Q	8082 OCN	Q	4020 OCN	Q
0.1	J	3.3	U	14.7		42.4		45.4		19.9	
0.2	U	2.9	U	15.9		38.3		46.5		19.8	
0.3	J	5.9		16.1		19.0		49.1		26.5	
0.4	JC	10.8	UC	16.2	J	29.0		50.7		30.7	
0.7	U	6.0	J	16.6		11.7		51.1		18.9	
0.8	U	0.5	U	16.8		8.3	J	51.6		15.4	
1.3	U	3.5	U	17.8	J	9.7		51.8		19.5	
1.6	U	1.9	U	18.3		11.4		52.3	C	0.7	UC
2.9		7.7		18.7		19.7		52.9	J	118.9	
3.0	J	8.8		20.2		12.0		53.7		31.4	
3.5		4.1	J	22.2	C	60.3	C	61.5		17.4	
4.7	JC	49.3	UC	23.3		30.3		64.5		62.5	
4.9		7.1		23.8		26.2		66.1		33.3	
5.2	UC	0.1	UC	25.8		19.0		71.7		118.9	
5.4		9.2		27.2		9.5	J	76.5		41.2	
6.0		5.5	J	28.1		13.4		80.6	C	42.9	JC
6.2	U	12.3		28.2		15.5		105.4		48.4	
6.7		9.3		28.2		11.5		130.9		132.3	
6.9	J	12.3		28.3	J	12.9		149.6		113.2	
8.6		7.4	UC	28.3		44.9		171.5		69.8	
8.8		9.6	J	29.8	UC	1.0	UC	178.2		100.8	
10.2	U	1.4	U	31.0		13.5		179.3	J	25.1	
10.2		7.0	U	31.6	J	16.7		200.3		201.9	
11.4		82.0		32.0		26.2		200.4		110.0	
12.0		12.7		36.6	UC	0.0	UC	244.7	UC	2.5	UC
12.4		9.6		40.0		31.3		251.0		48.6	
13.1		6.3	J	40.4		30.4		399.2		349.8	
13.3		38.8		40.8		36.8		405.9		132.3	
13.5		18.4		41.7		35.9		426.4		8.4	
13.5		31.3		41.7		21.7		465.3	J	9.2	
14.3	J	25.8		41.8		18.0		494.7		307.3	
14.3		38.5		44.3		34.0		613.2		276.3	
				44.5		25.1					

	N	Error Rate
Total	**97**	
Correct	**73**	***73%***
FNE	**17**	***17.5%***
FPE	**6**	***6.2%***

C qualifiers are for low organic carbon

Nondetect based on elevated DL for an aroclor not seen in any sample

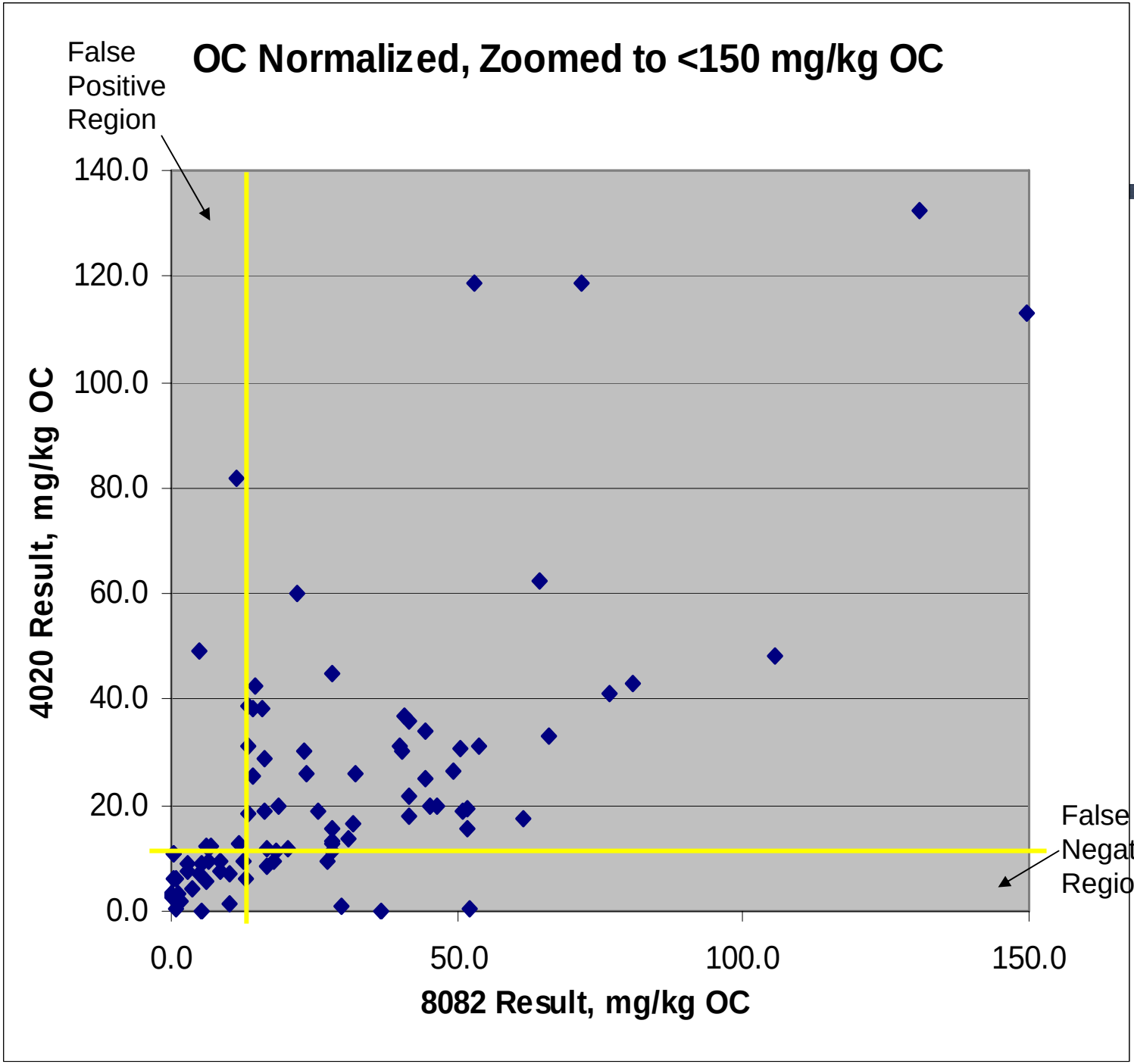


Entire OC Data Set

Comparison to 65 mg/kg OC (red line)

FPE: 2 (2.1%)

FNE: 9 (9.3%)



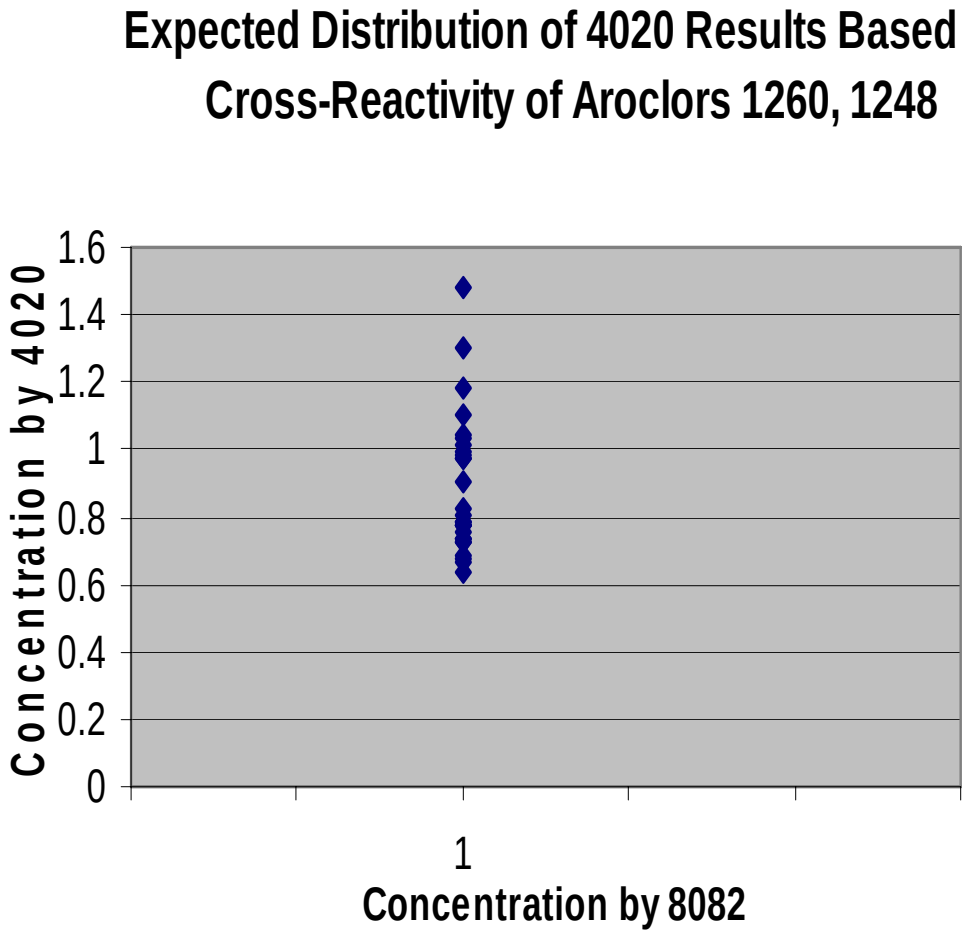
Entire OC Data Set

Comparison to 12 mg/kg OC (yellow line)

FPE: 4 (4.1%)

FNE: 8 (8.2%)

Sensitivity Contributes to FPE

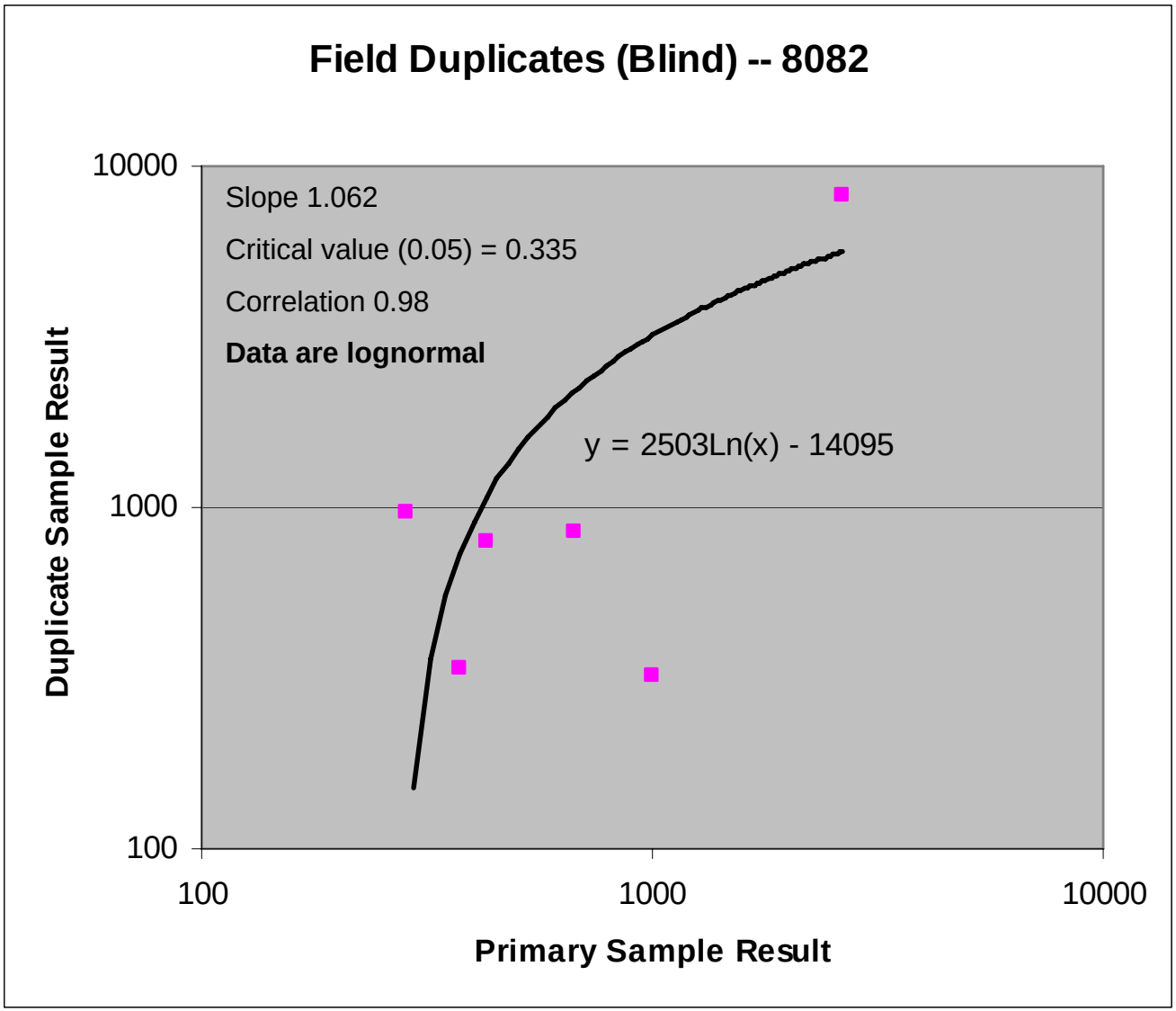


Cross Reactivity to 1254:
Aroclor 1248 111.1%
Aroclor 1254 100.0%
Aroclor 1260 55.6%

About 6% (1/3) of FNE due to Aroclor variations

Little difference for FPE

Heterogeneity –Large Contribution to Uncertainty

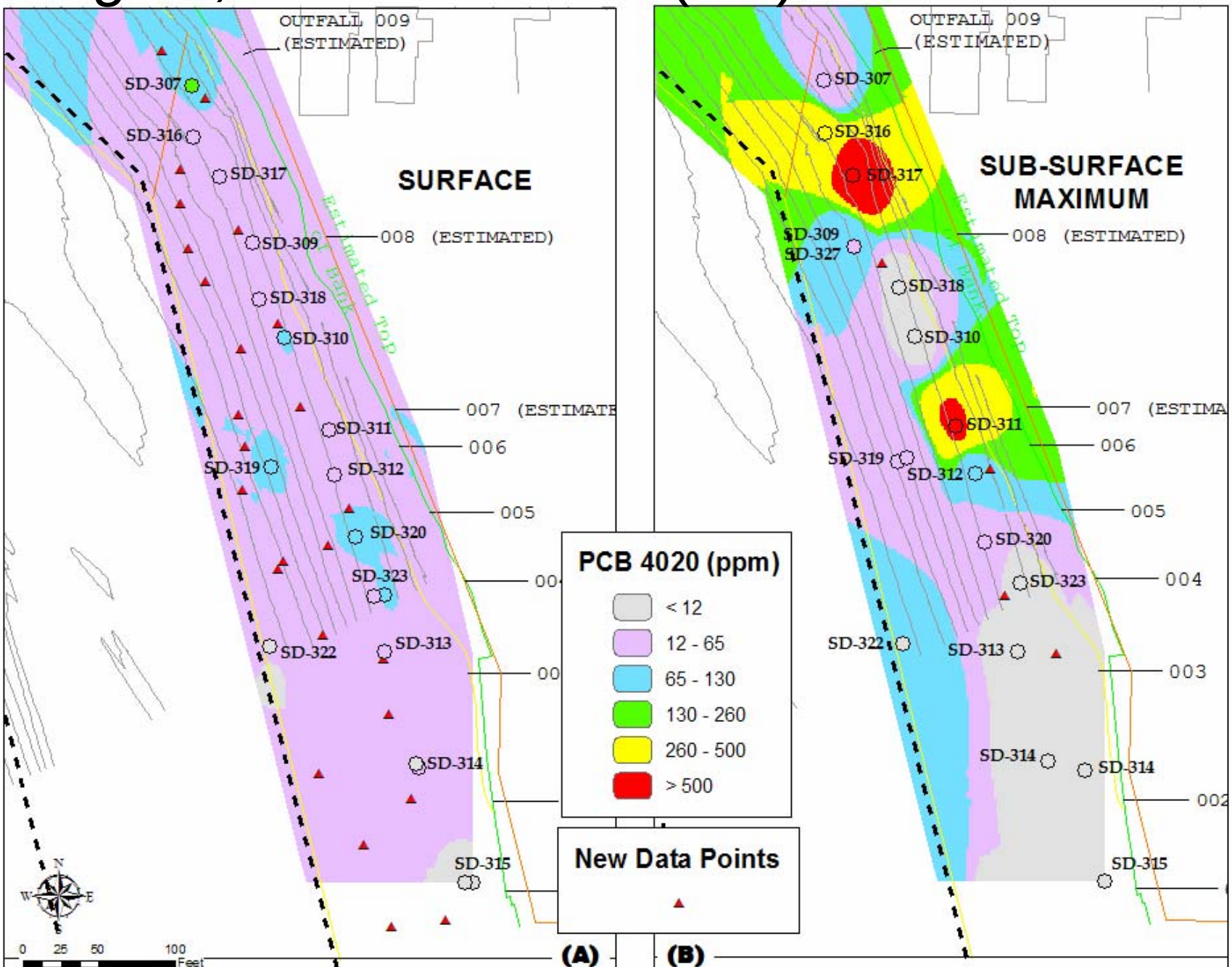


M8082 Field duplicates had RPDs up to 109%, with a mean of 66%

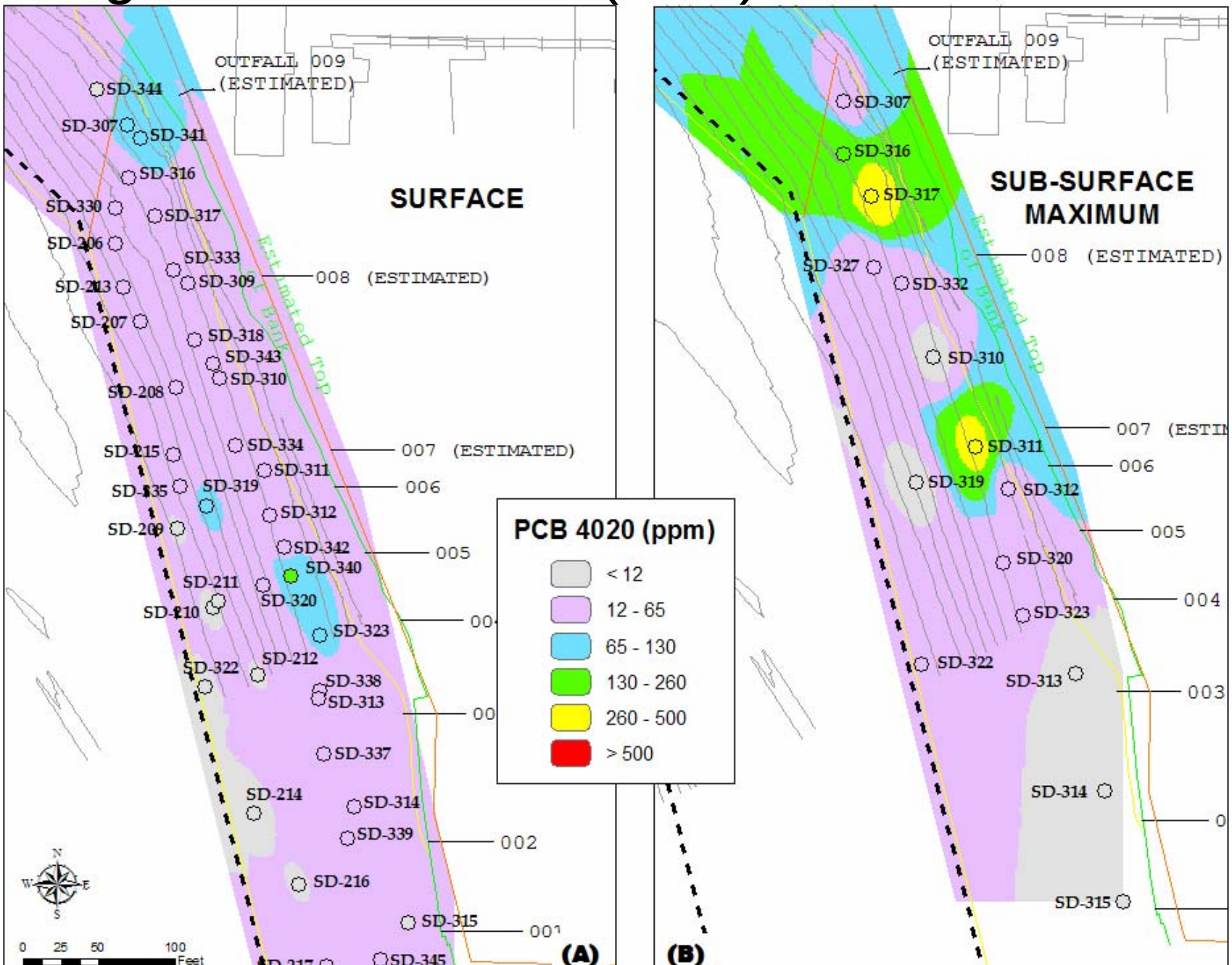
Use of M4020 to Visualize Site

- *First view*: stage 1—assumed OC; results used to establish Stage 2 locations; time is 3 days
- *Second view*: stages 1&2, known OC; time is 10 days
- *Third view*: M8082 view (“correct answer); time is 4-5 months
- Display of “full knowledge” 8082 Dredge Plan and difference plot from 4020 Dredge Plan

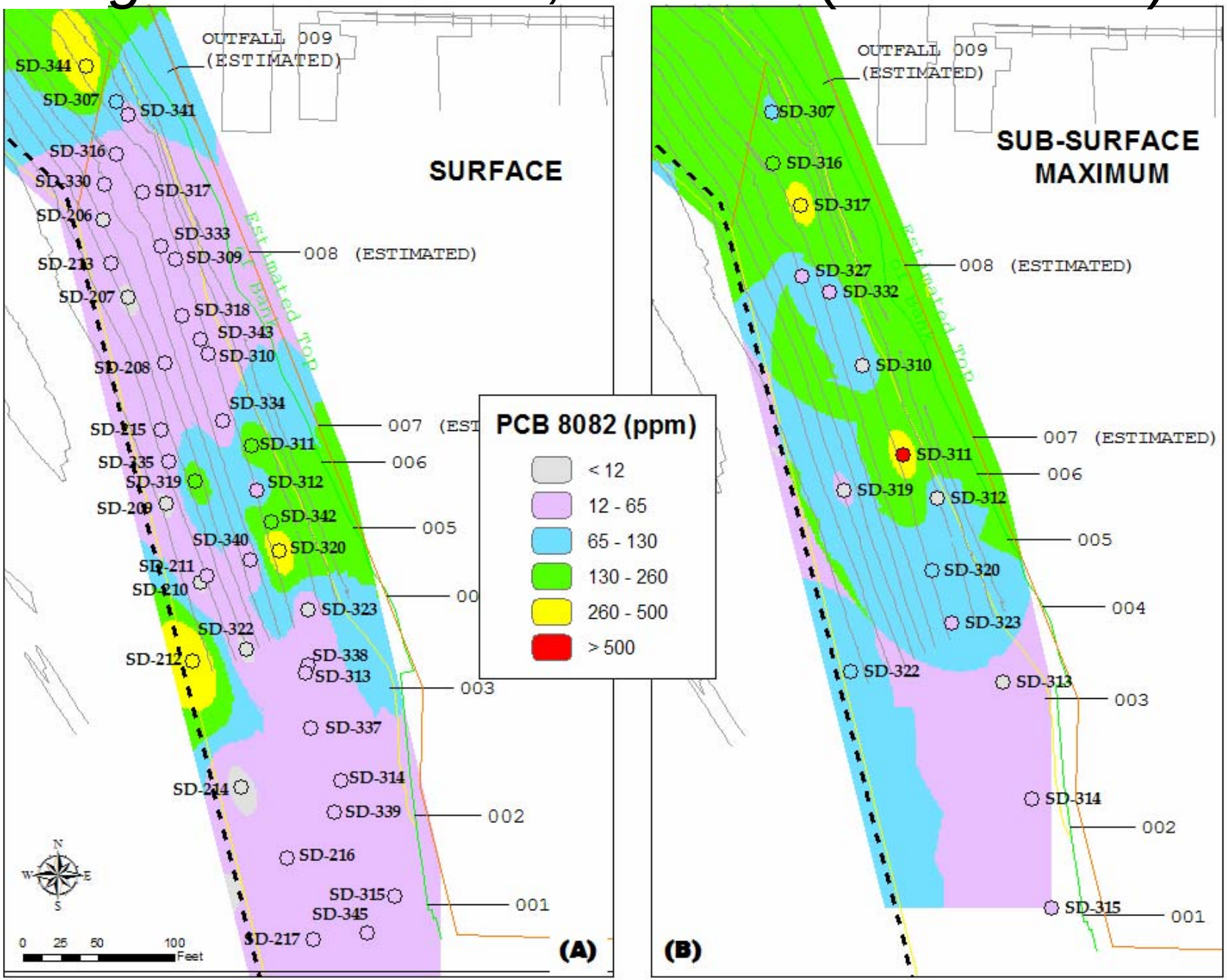
Stage 1, Estimated OC (3 d)



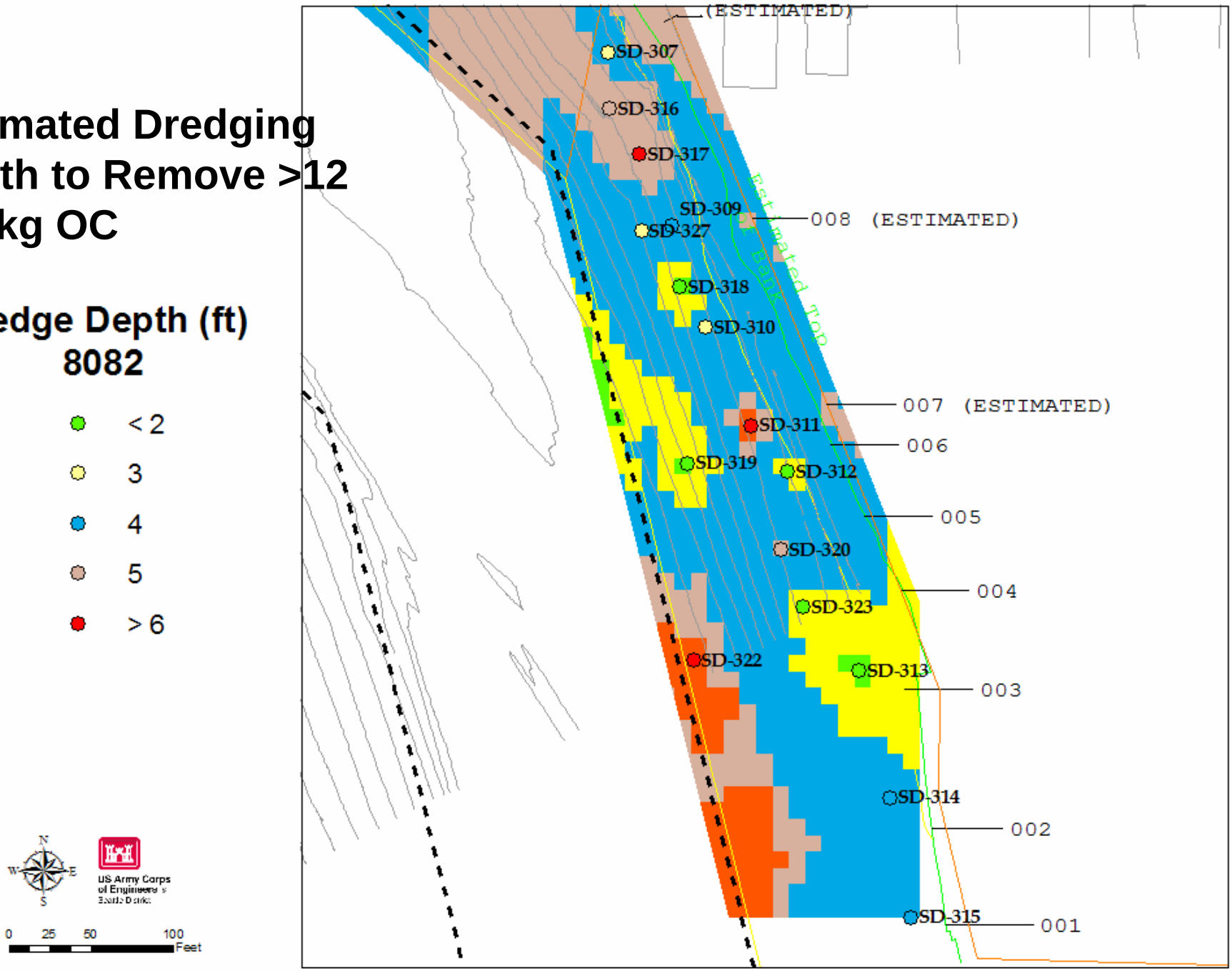
Stages 1&2, Lab OC (10 d)



Stages 1&2 M8082, Lab OC (4.5 months)



Estimated Dredging Depth to Remove >12 mg/kg OC



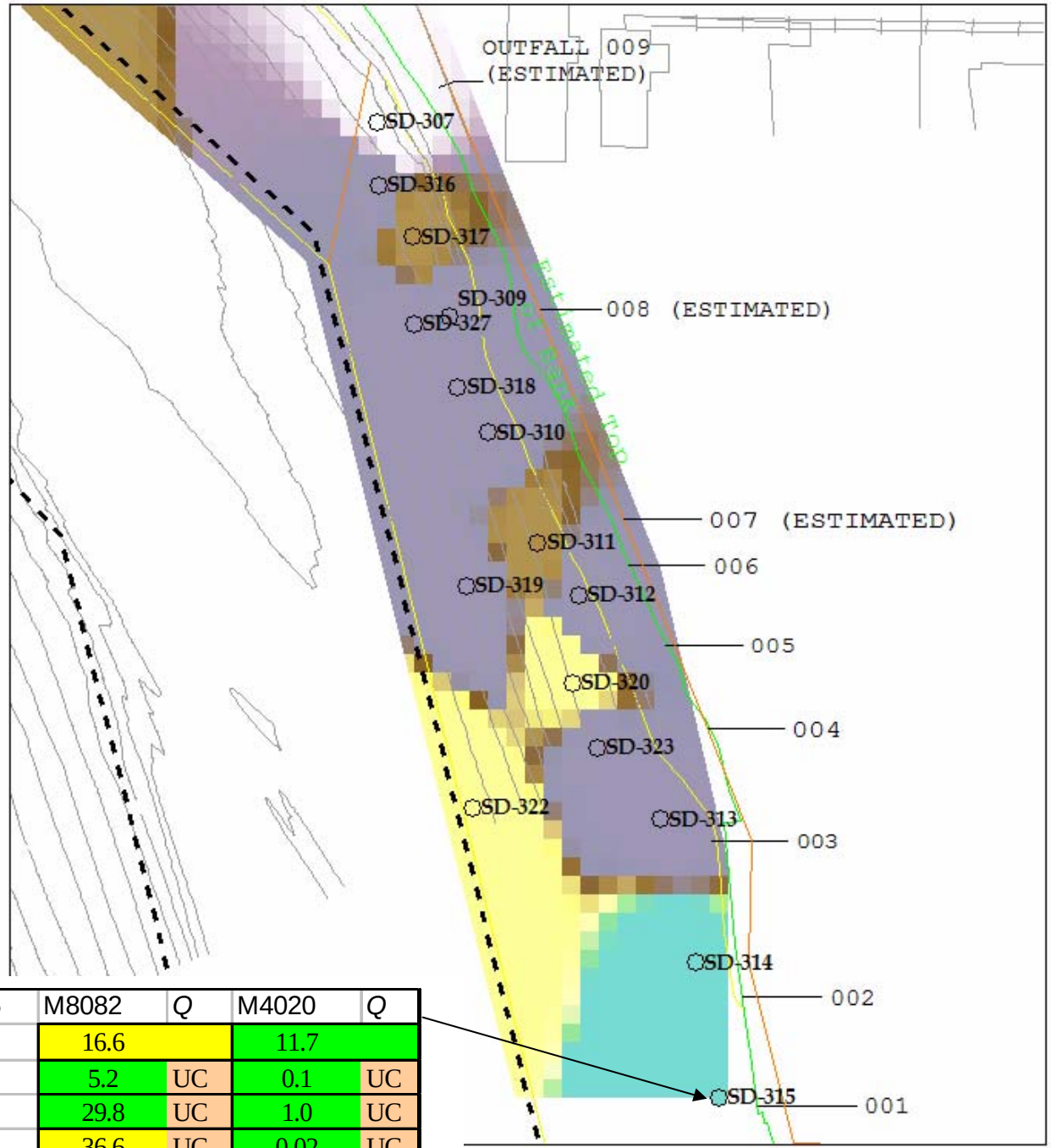
Difference Plot

M8082 – M4020

Differences in Dredge Depths (ft) 8082 - 4020

High : 4

Low : -1



SD 315	M8082	Q	M4020	Q
0-0.3 ft	16.6		11.7	
1-2 ft	5.2	UC	0.1	UC
2-3 ft	29.8	UC	1.0	UC
3-4 ft	36.6	UC	0.02	UC

US Army Corps of Engineers Seattle District

0 25 50 100 Feet

Discussion

- **Method Applicability of M4020:**
  - Suitable for placement of adaptive surface samples, selecting samples to analyze using M8082
    - In Dyes Inlet, Puget Sound,US Navy used M4020 to triage samples for submission to lab
  - Less efficient predictor at 12 than 65 mg/kg OC
  - Selection of M4020 should consider data use
    - Differential sensitivity due to various Aroclor mixtures
    - “Threshold” versus scalar determination of concentration
    - Need for near-real-time info
- **Conceptual Site Model.** For southern 2/3 of reach, we rejected the river-transport hypothesis, based on presence of deep hotspots, visible through M4020 (assumed OC)

Conclusions/Recommendations

- M4020 can give information rapidly and permit near-real-time assessment of a Conceptual Site Model
- Estimates (in our case) have a somewhat low bias which, when known, can be considered.
  - E.g., application of a 27% M4020 escalation factor decreased FNE ~4%, to 14%, but increased FPE by about the same amount
- Major cost avoidance is in not in cheapness of method, but in use for triage of samples and gaining time in lab sequencing, e.g.,
  - Testing all cored intervals by M4020, and targeting lab analysis by M8082 for critical intervals
  - Reduces the inherent 12.5% error rate of sequential 8082 sampling (2/16 cores)