

# **Port Gardner Regional Background Characterization**

Summary of Validated Data Results

August 6, 2013

Department of Ecology

Toxics Cleanup Program

This validated package has been submitted to interested stakeholders for their review and comment.

Comments must be received by August 21, 2013. Ecology will consider all comments received by this date to develop the draft data report. You may submit comments to:

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Will Hafner



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# Study Design and Spatial Distribution of Bioaccumulative Contaminants of Concern (BCOC)

# Study Design



50 locations were randomly selected from the AOI, including:

- 25 baseline locations.
- 20 secondary locations.
- 5 additional secondary locations were selected from the south end of the AOI during field sampling to obtain more samples with higher fines.

Chemical and physical analyses were conducted on:

- All baseline samples.
- Selected secondary samples (see slides 18-20).
- All baseline and secondary for mercury due to short holding times.

# Data Quality Objectives

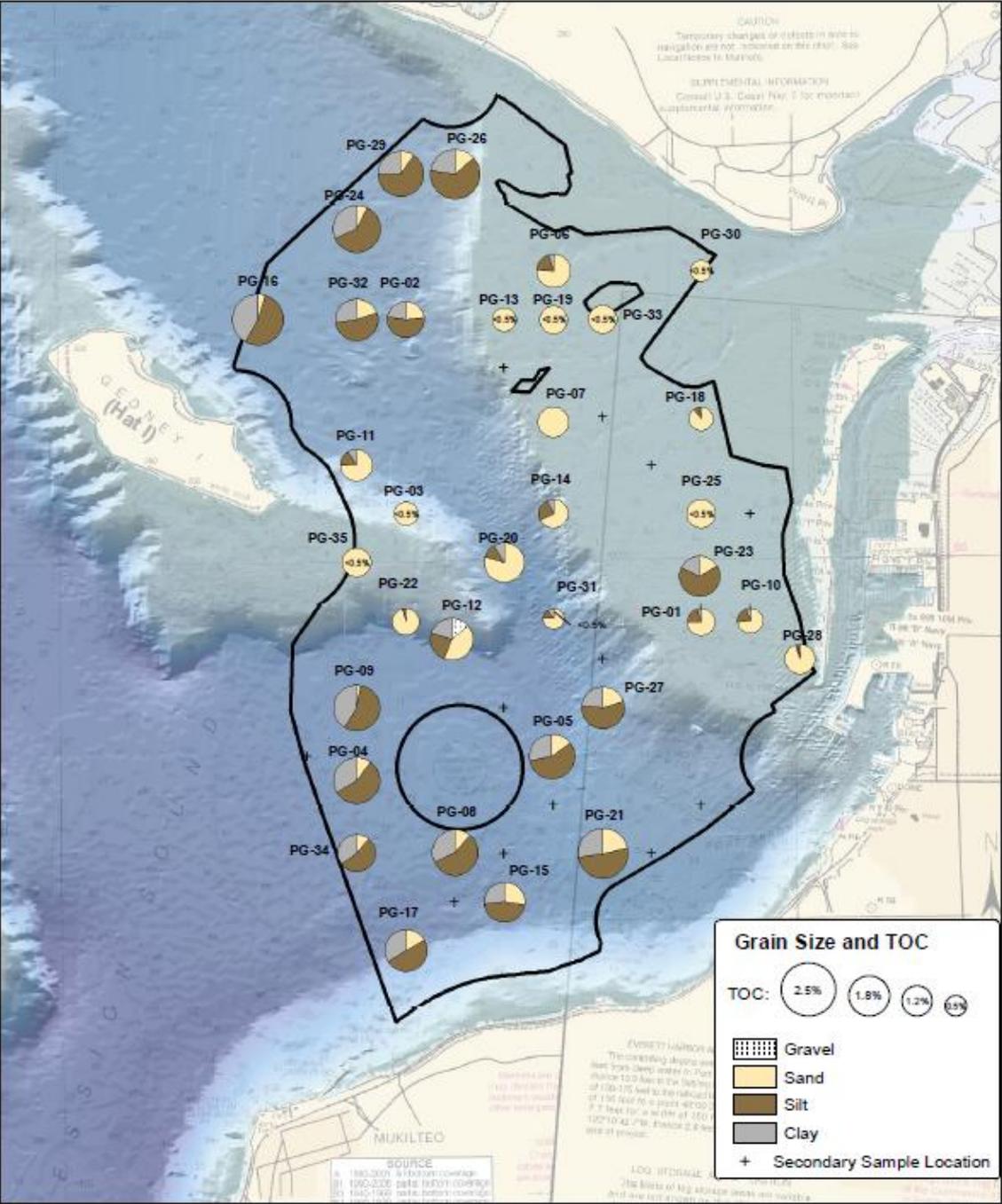
- Low PQLs were targeted to assure as few non-detects and as many unqualified results as possible (target PQLs listed below).
- All results have undergone a QA2 (USEPA Stage 3/4) independent data validation by EcoChem, Inc.

Analyte	Method	PQL	Units	# of Results Below PQL
Arsenic	EPA 200.8	0.5	mg/kg	0/25
Cadmium	EPA 200.8	0.1	mg/kg	10/25
Mercury	EPA 7471A	0.025	mg/kg	14/50
cPAH*	EPA 8270 SIM LL	0.76	ug/kg	4/25
PCB congeners*	EPA 1668	0.052	ng/kg	13/35†
Dioxin/Furan*	EPA 1613B	2.3	ng/kg	14/25

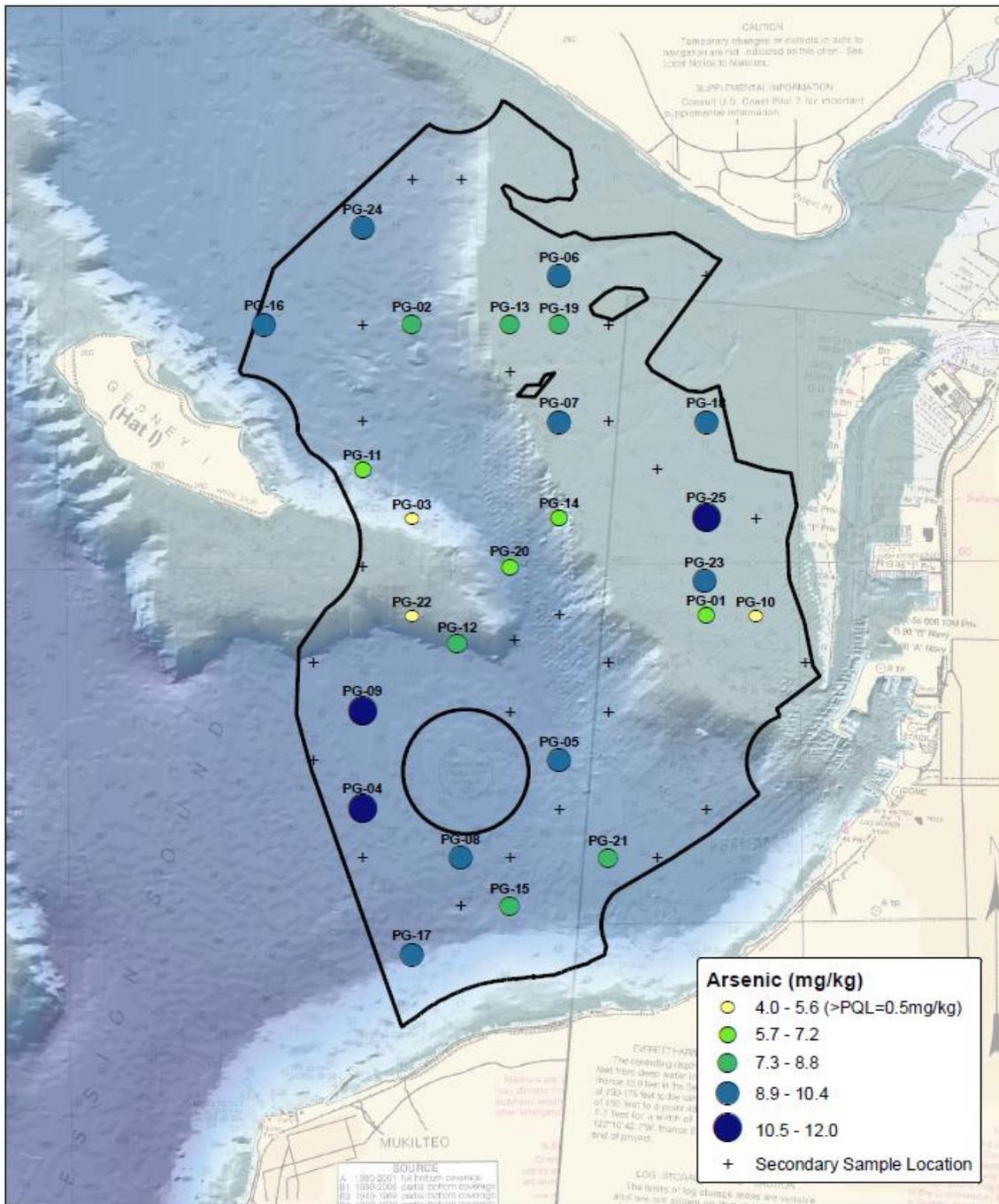
\* total PQLs represent a TEQ value calculated by multiplying the congener specific PQL by the TEF value from Ecology 2007 (Evaluating the Toxicity and Assessing the Carcinogenic Risk of Environmental Mixtures Using Toxicity Equivalency Factors)

† see slides 18-20 for selection of secondary locations for analysis

# Percent Fines/Total Organic Carbon (TOC)



- The Snohomish River Delta and the SE side of Hat Island consisted of sandy sediments, with low TOC.
- 7 locations had TOC less than 0.5 percent.
- The NW corner of the AOI and the southern side of the AOI near the disposal site consisted of fine sediments.



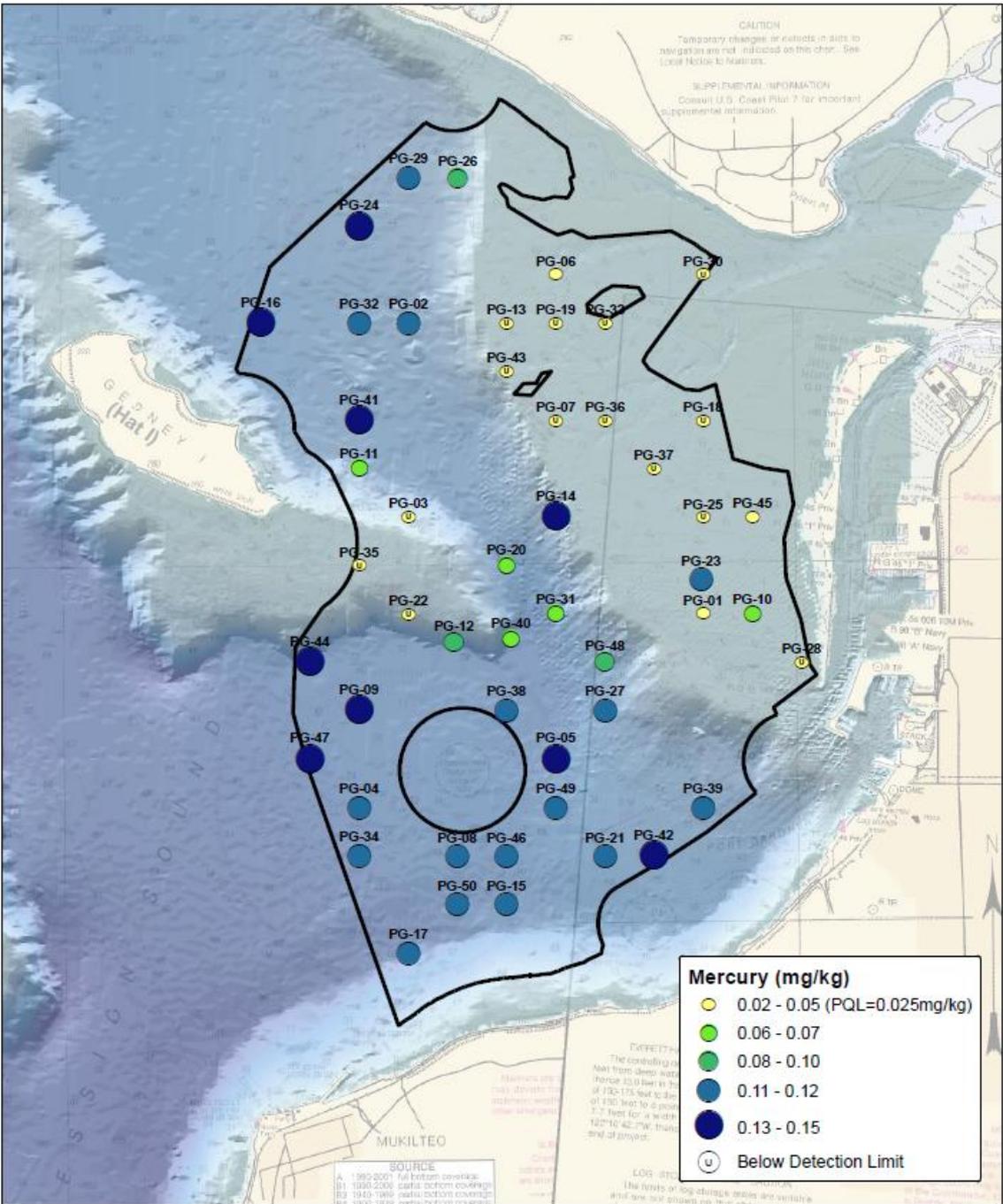
# Arsenic

- Correlated to %fines with an  $r^2$  of 0.223 and p-value of 0.017.
- This is the lowest correlation to fines of the target analytes due to elevated concentrations on the Snohomish Delta.

Location ID	Arsenic
Units	mg/kg
<b>Summary Statistics</b>	
Sample Size	25
Minimum	4
Average	8.3
Median	8.2
Maximum	12

# Mercury

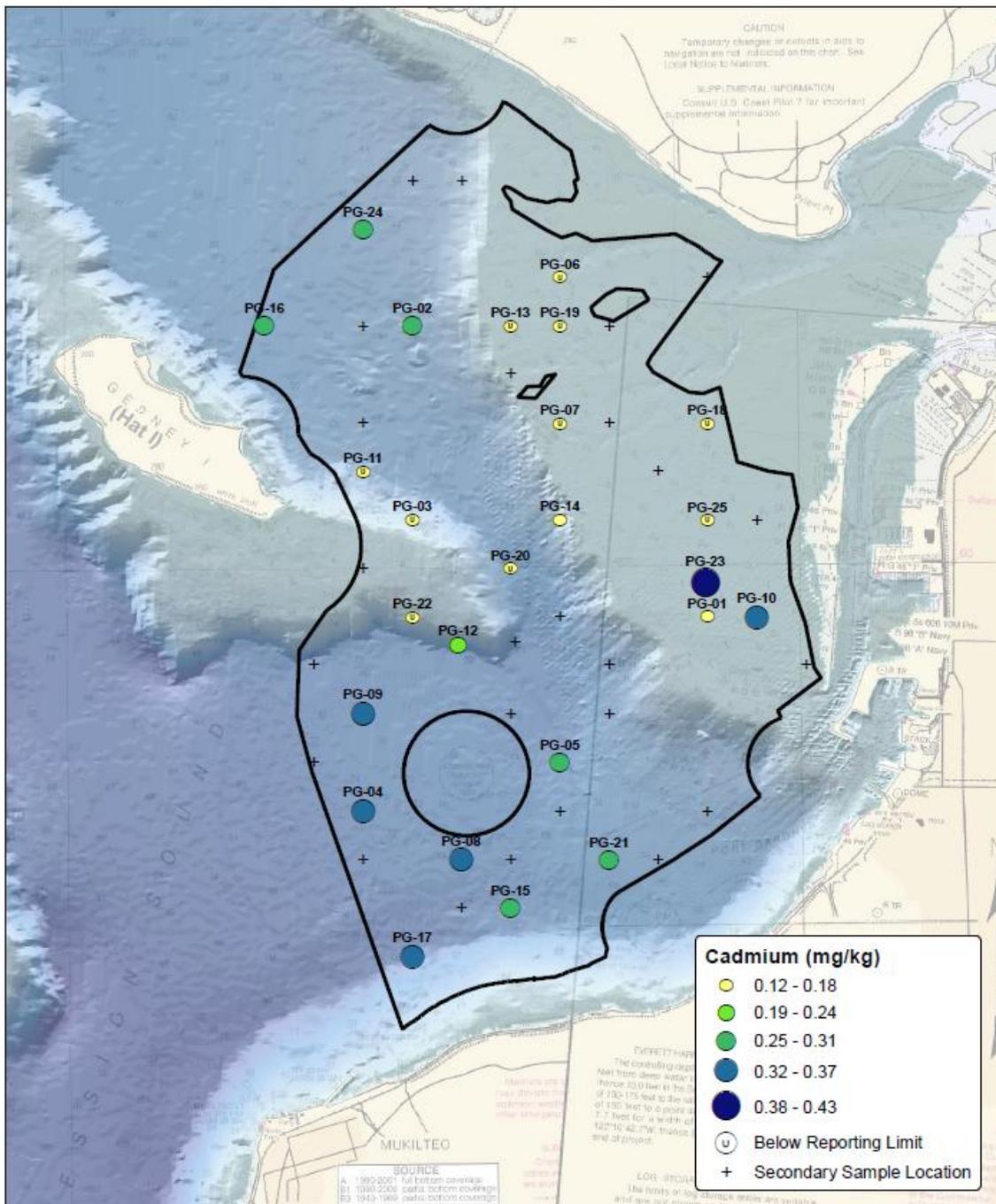
- Correlated to %fines with an  $r^2$  of 0.728 and p-value of  $<0.001$ .
- All 50 samples were analyzed for mercury due to short holding times.



Location ID	Mercury
Units	mg/kg
<b>Summary Statistics</b>	
Sample Size	50
Minimum	0.02
Average	0.095
Median	0.079
Maximum	0.15

# Cadmium

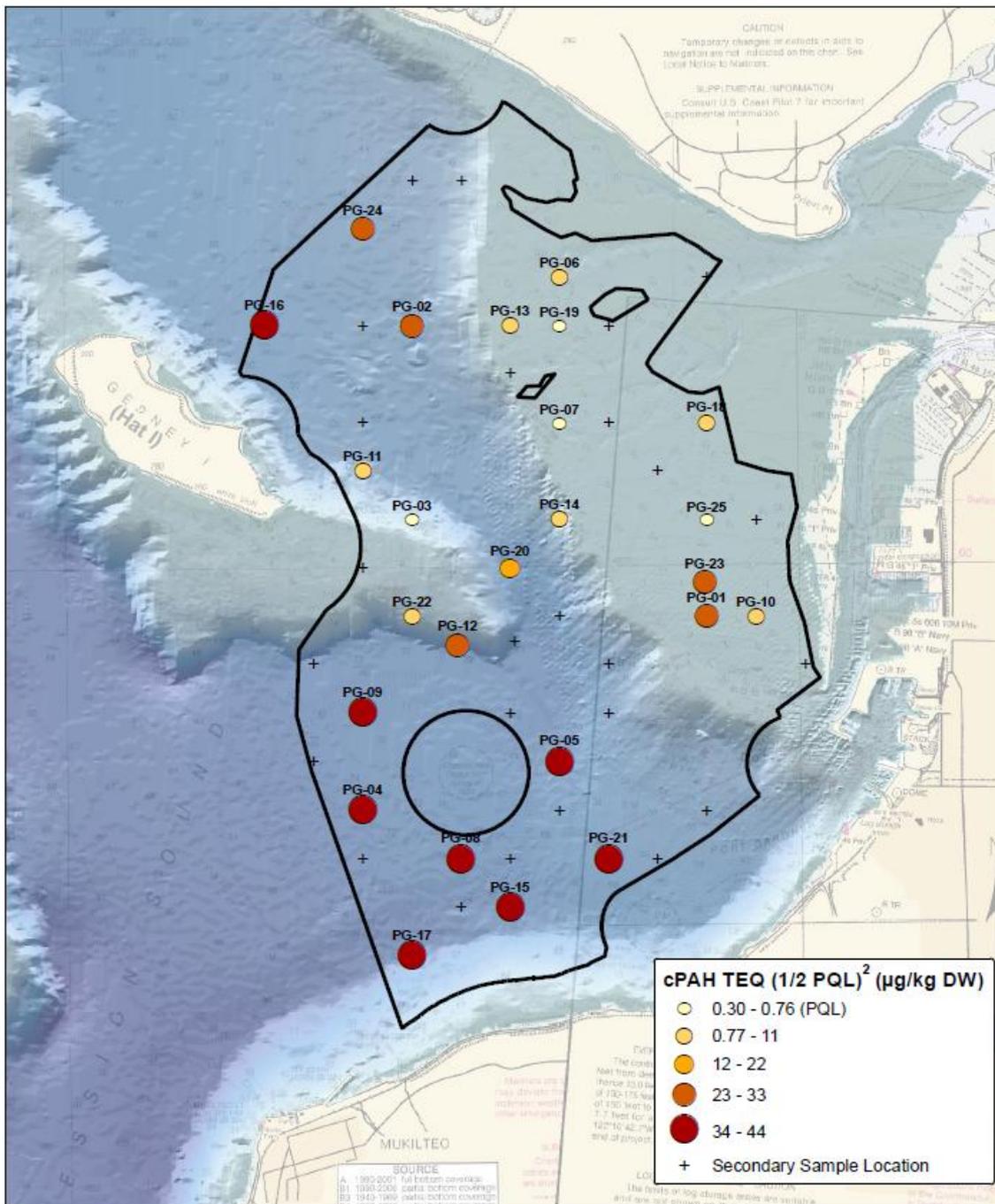
- Correlated to %fines with an  $r^2$  of 0.822 and p-value of  $<0.001$ .
- The majority of samples from sandy sediments were non-detects.



Location ID	Cadmium
PG-01	0.38 - 0.43
PG-02	0.19 - 0.24
PG-03	Below Reporting Limit
PG-04	0.32 - 0.37
PG-05	0.19 - 0.24
PG-06	Below Reporting Limit
PG-07	Below Reporting Limit
PG-08	0.32 - 0.37
PG-09	0.32 - 0.37
PG-10	0.38 - 0.43
PG-11	Below Reporting Limit
PG-12	0.19 - 0.24
PG-13	Below Reporting Limit
PG-14	Below Reporting Limit
PG-15	0.19 - 0.24
PG-16	0.19 - 0.24
PG-17	0.32 - 0.37
PG-19	Below Reporting Limit
PG-20	Below Reporting Limit
PG-21	0.19 - 0.24
PG-22	Below Reporting Limit
PG-23	0.38 - 0.43
PG-24	0.19 - 0.24
PG-25	Below Reporting Limit

# carcinogenic PAH TEQ

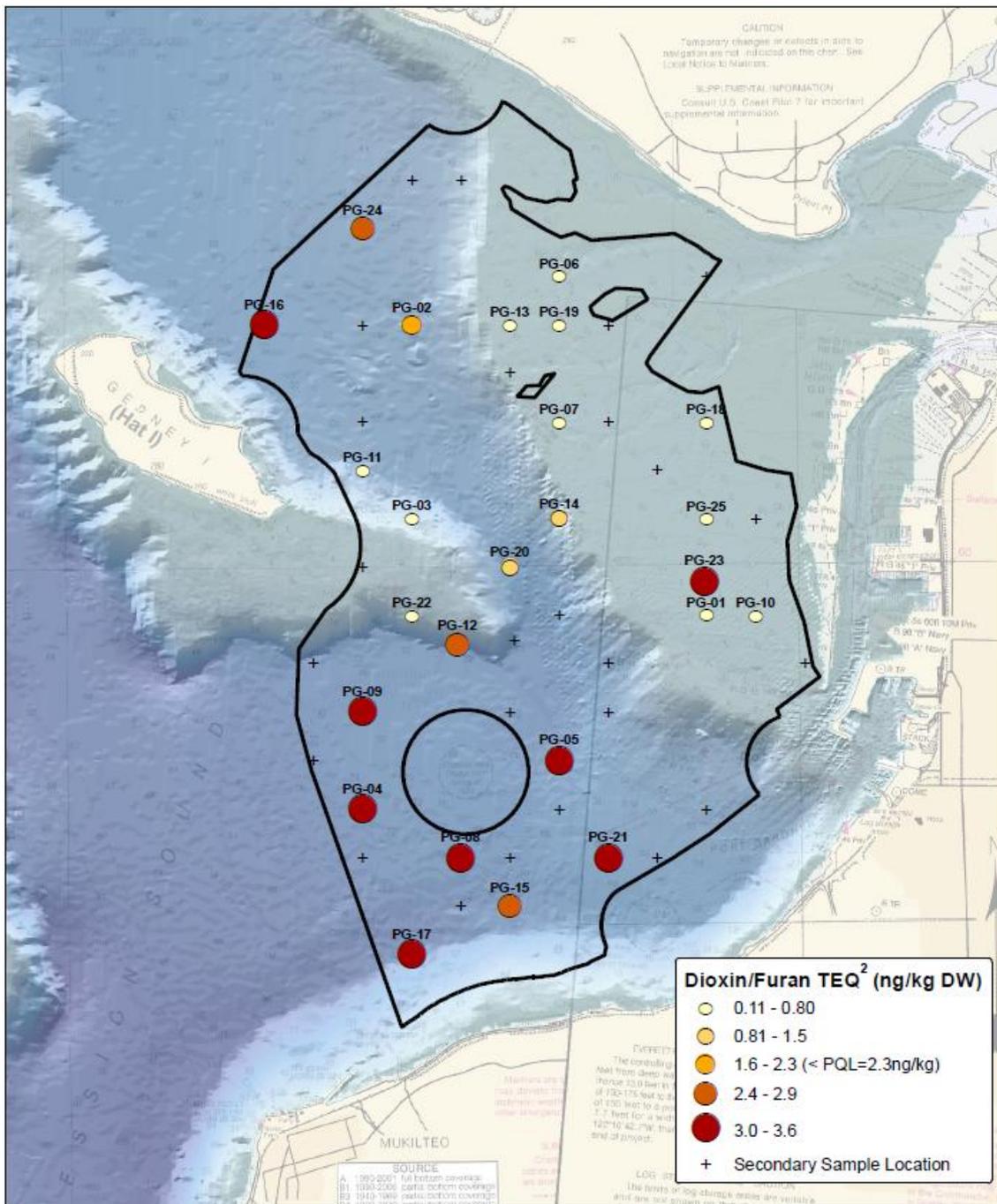
- Correlated to %fines with an  $r^2$  of 0.889 and p-value of <0.001.



Location ID	cPAH TEQ
Units	ug/kg
Summary Statistics	
Sample Size	25
Minimum	0.296
Average	23
Median	19.5
Maximum	43.6

# Dioxin/Furan TEQ

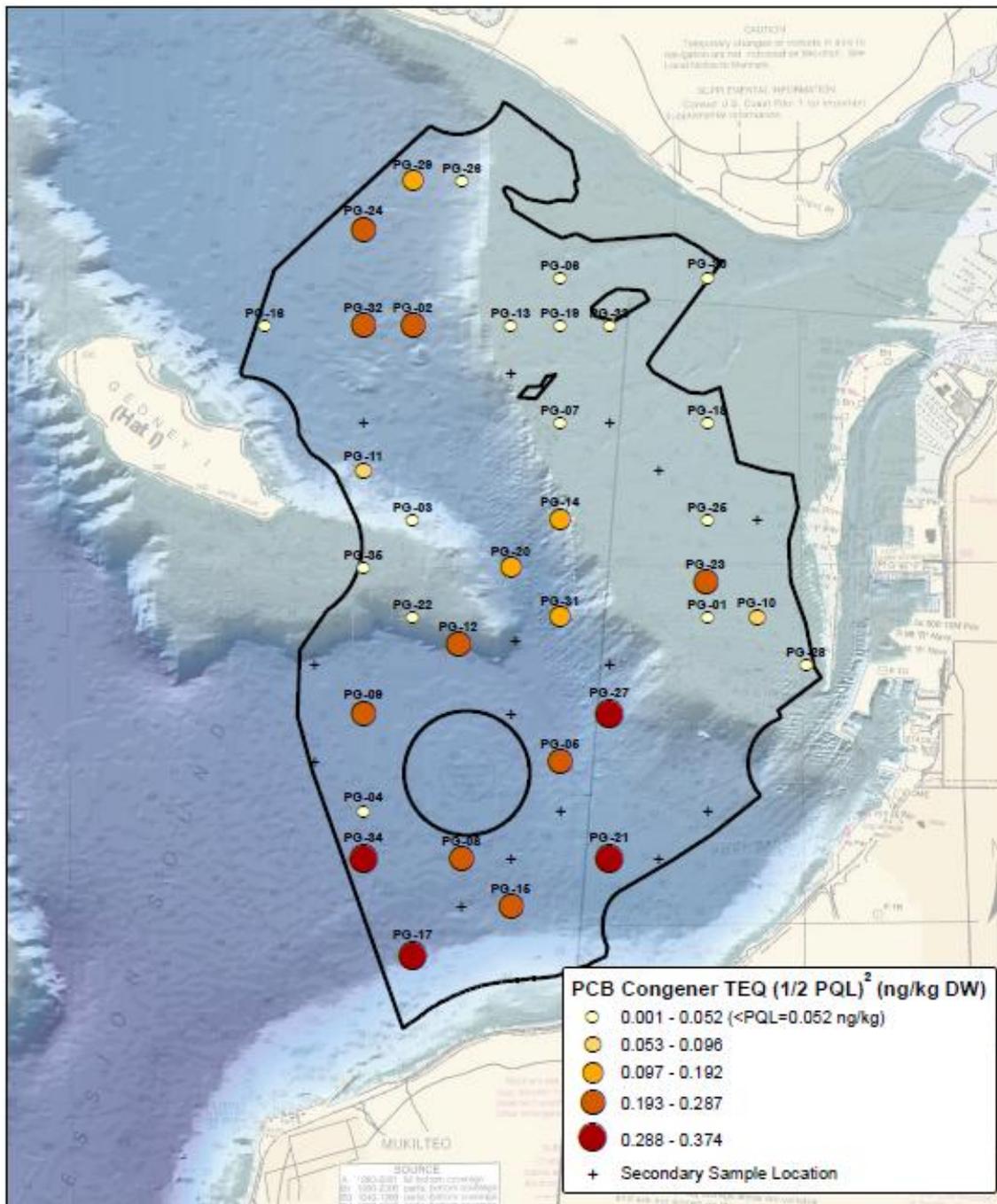
- Correlated to %fines with an  $r^2$  of 0.945 and p-value of  $<0.001$ .



Location ID	cPAH TEQ
Units	ng/kg
<b>Summary Statistics</b>	
Sample Size	25
Minimum	0.118
Average	1.08
Median	1.76
Maximum	3.61

# PCB Congener TEQ

- Correlated to %fines with an  $r^2$  of 0.713 and p-value of  $<0.001$ .
- 10 secondary samples were analyzed (slides 18-20).



Location ID	PCB TEQ
Units	ng/kg
Summary Statistics	
Sample Size	35
Minimum	0.00755
Average	0.112
Median	0.142
Maximum	0.383



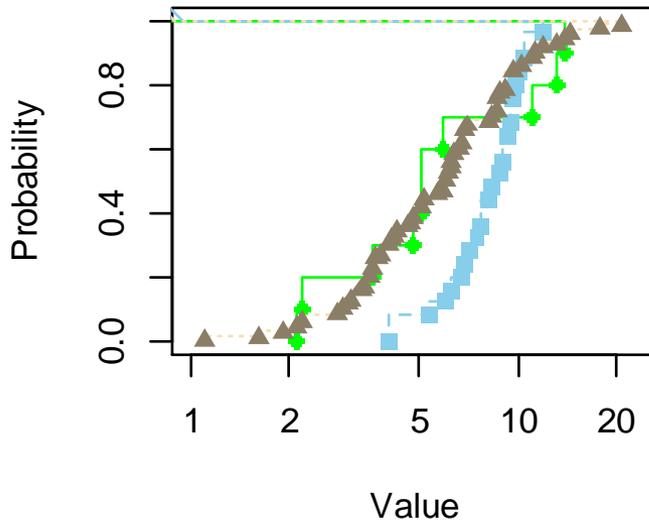
# Statistical Analysis of Results

# Analysis of Results from Baseline Locations

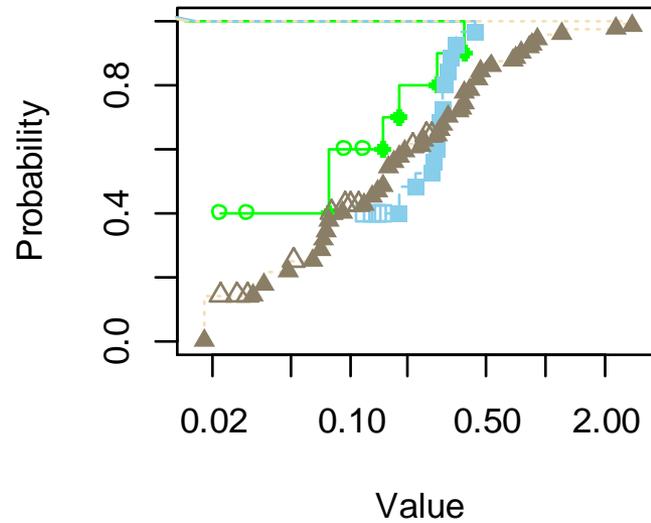
- **Initial results were evaluated using Empirical Cumulative Distribution Functions (ECDF) plots.**
- **Some Notes on Interpreting ECDF Plots:**
  - The concentration is shown on the x-axis.
  - The cumulative probability is shown on the y-axis.
  - The shape of the curve describes the distribution of the data:
    - Curves shifted to the right indicate higher concentrations.
    - Steeper curves have less variance (i.e., many samples within small concentration range).
    - Flatter or skewed curves have larger variance (i.e., fewer samples across a large concentration range).
  - Port Gardner results were compared to the OSV Bold data-set using ECDF plots.

# ECDF Plots for Metals

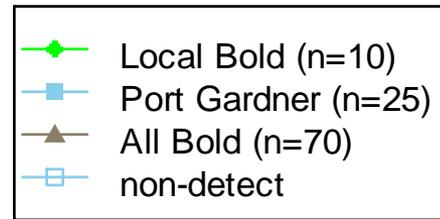
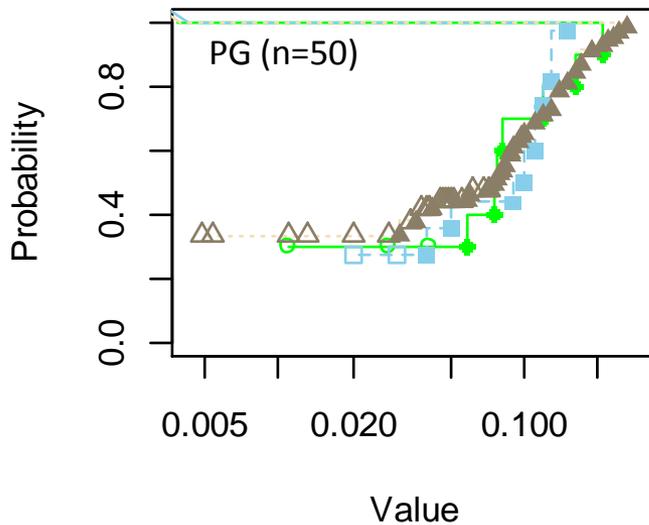
## Arsenic



## Cadmium



## Mercury



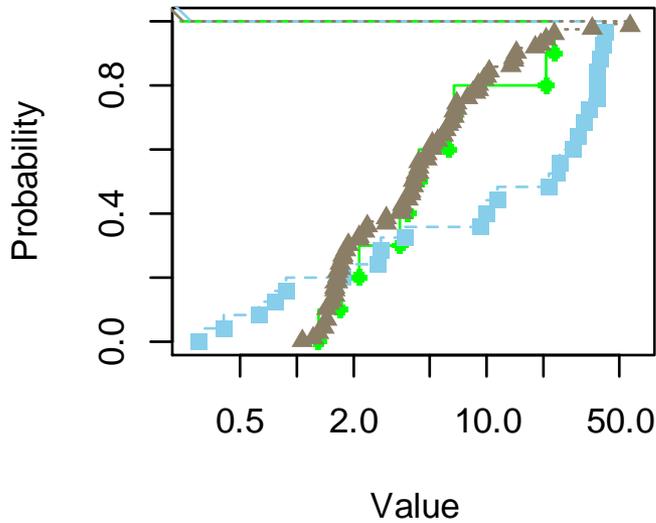
\*The 'Local Bold' data set is comprised of 5 samples from Port Susan (PSPS) and 5 samples from North Central Puget Sound (NCPS) – a subset of the Bold dataset. These values are shown here for a local comparison to the Port Gardner Regional data.

Dry Weight Concentrations

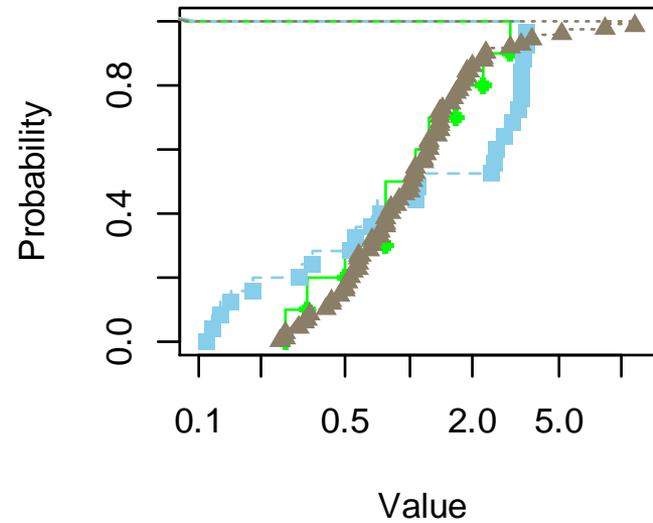
# ECDF Plots for Organics

Dry Weight Concentrations

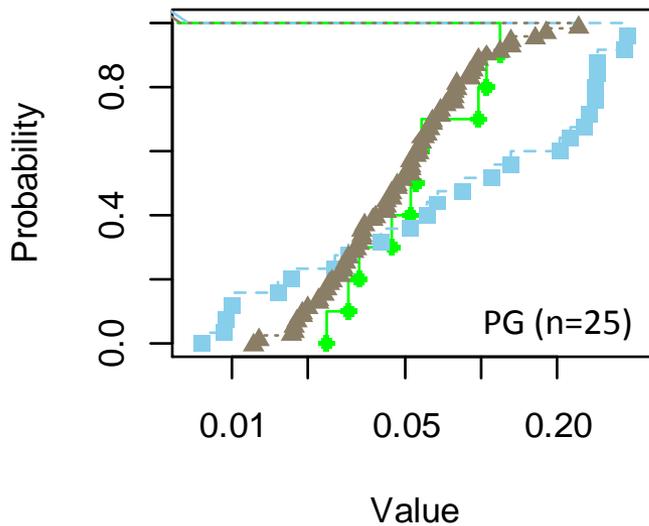
### cPAH TEQ (half DL)



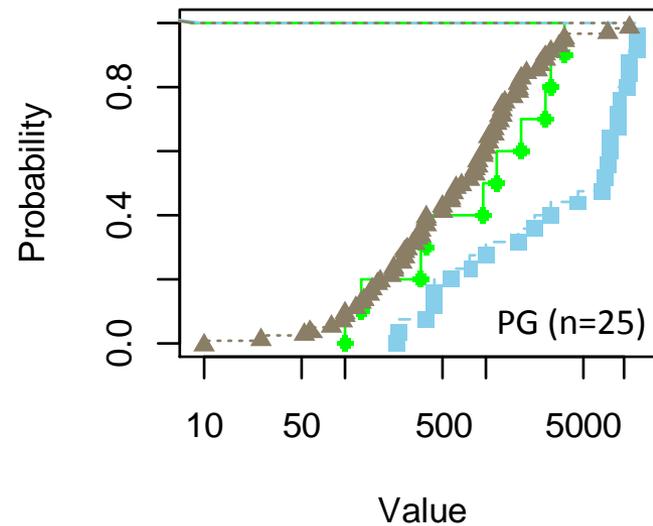
### Dioxin/Furan TEQ (half DL)



### PCBs TEQ (half DL)

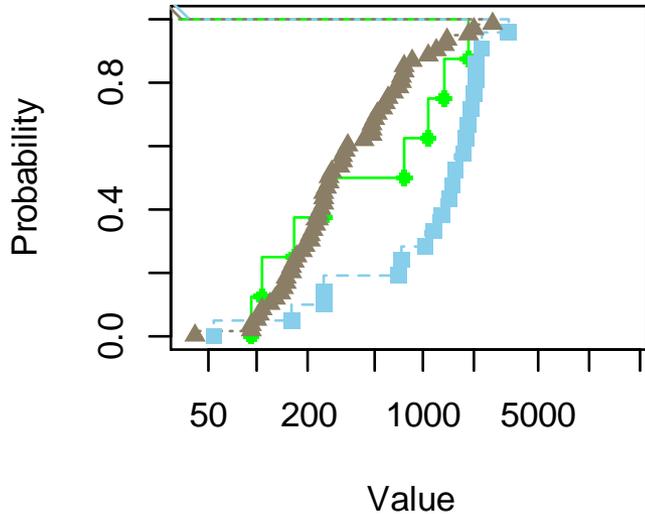


### Total PCBs (detected congeners)

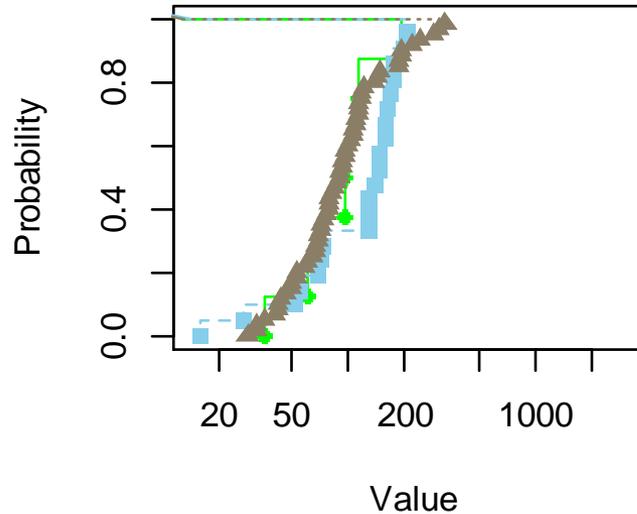


# TOC Normalized ECDF Plots for Organics\*

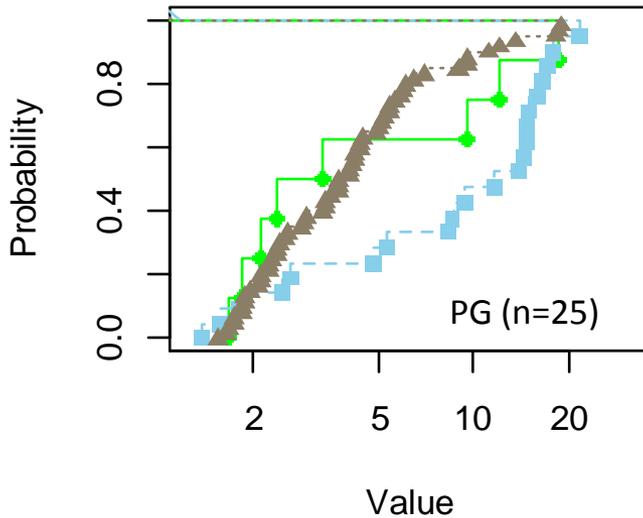
**cPAH TEQ-TOC norm  
(TOC > 0.5%)**



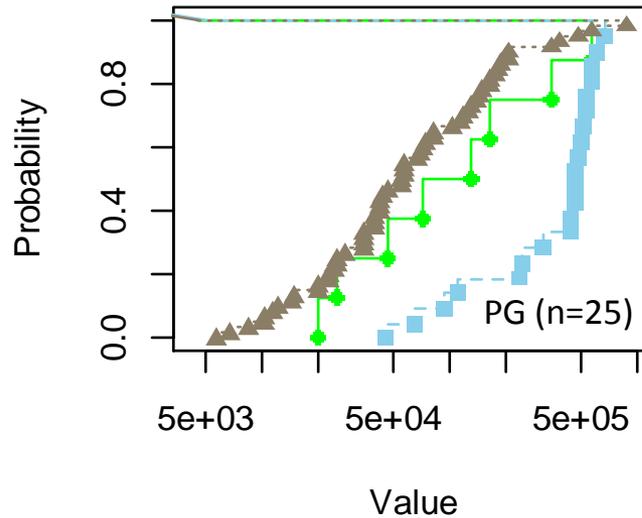
**Dioxin TEQ-TOC norm  
(TOC > 0.5%)**



**PCBs TEQ-TOC norm  
(TOC > 0.5%)**

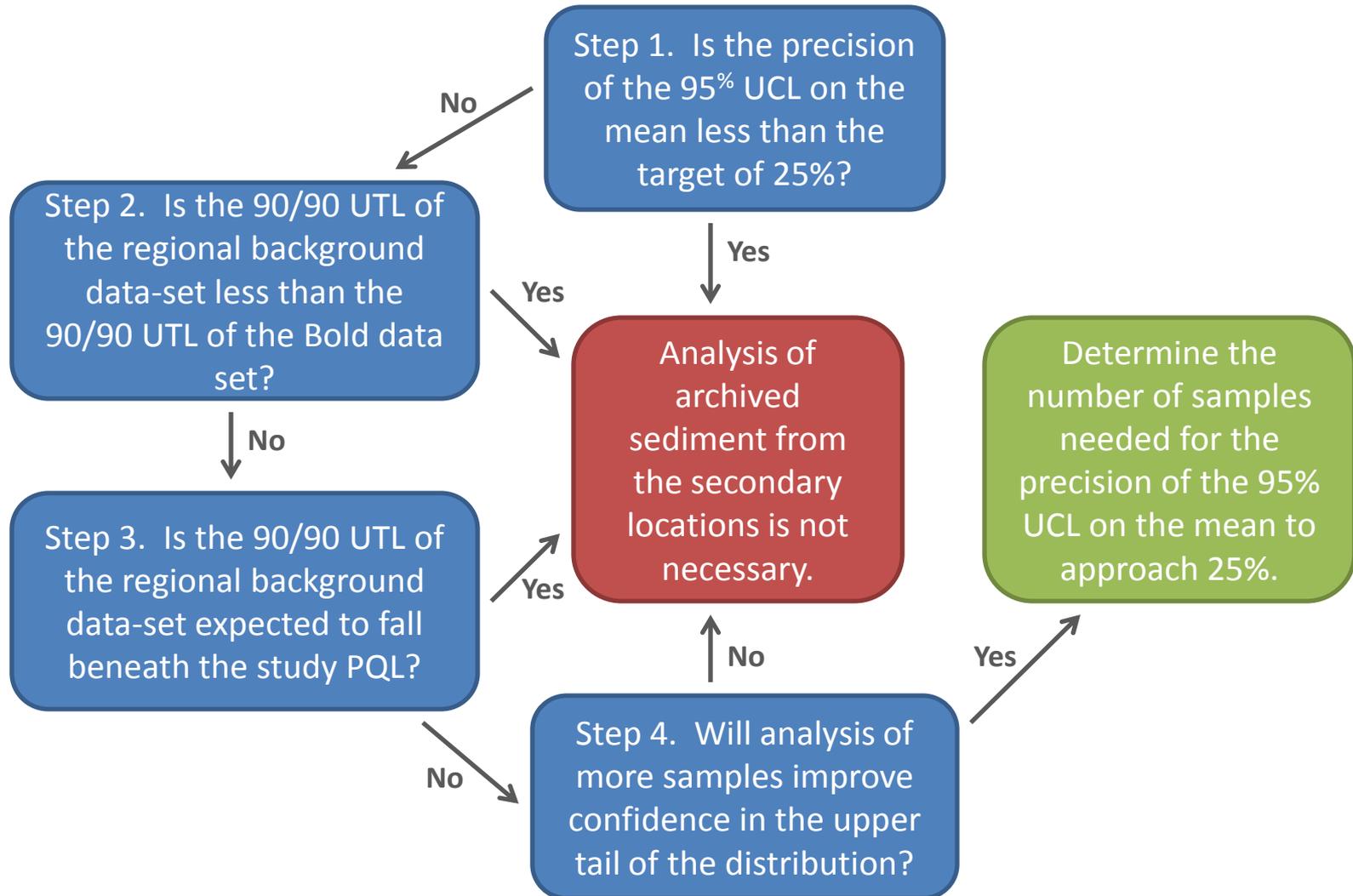


**Total PCBs-TOC norm  
(TOC > 0.5%)**



\*included for reference purposes only to show the difference between the Port Gardner and the Bold data was similar for normalized data. The regional background was not calculated from TOC normalized data.

# Process for the Selection of Secondary Samples for Analysis



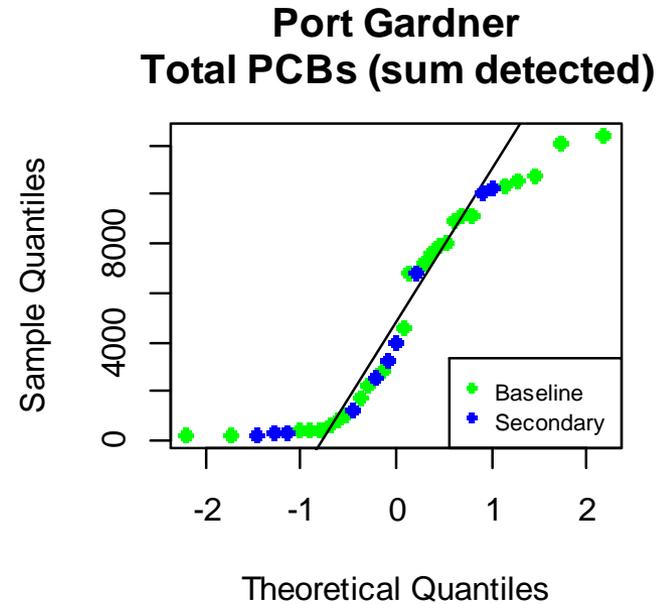
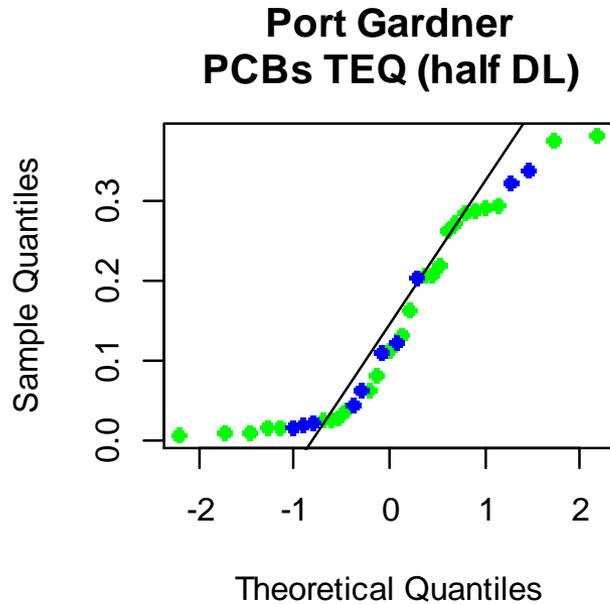
# Decision Process for Secondary Sample Analysis

- Arsenic, cadmium, and mercury had excellent precision (<25%, step 1, previous slide). No additional analyses were required.
- cPAH, Dioxin/Furan, PCB TEQs, and total PCBs all had higher precision than desired (>25%, step 1, previous slide).
  - cPAH and Dioxin/Furan TEQs were elevated above the Bold survey and above the study's PQLs (steps 2 and 3, previous slide). However, the Port Gardner distributions were well-defined, particularly at the high-end (step 4, previous slide). Additional data were not expected to affect the background statistics. No secondary analyses were required.

# Decision Process for Secondary Sample Analysis (cont.)

- cPAH, Dioxin/Furan, PCB TEQs, and total PCBs all had higher precision than desired (>25%, step 1, previous slide).
  - PCB TEQ were elevated above the Bold survey and above the study's PQLs (steps 2 and 3, previous slide). But PCBs had two semi-extreme values (high concentration, but not statistical outliers) that impacted the confidence in the distribution (step 4, previous slide).
  - It was determined additional samples may help confirm the upper tail of this distribution. Ten secondary samples were submitted for analysis of PCB congeners.

# Normal Probability Plots for Port Gardner PCBs



The probability plots include results from the 25 baseline and 10 secondary locations, demonstrating that results from the secondary analysis:

- Fill in both the upper and lower tails of the distribution.
- Confirm the higher concentrations measured during baseline sampling.

# Port Gardner Statistical Summary

Parameter	N	% Detect	Min	Median	Mean	Max	CV	Precision	outliers	90/90 UTL	Dist'n
<b>Arsenic (ppm, dw)</b>											
Baseline	25	100%	4.0	8.3	8.2	12	0.25	8%	none	11.6	N
<b>Cadmium (ppm, dw)</b>											
Baseline	25	60%	0.12	0.22	0.25	0.43	0.31	10%	none	0.37	N
<b>Mercury (ppm, dw)</b>											
Baseline	25	72%	0.020	0.090	0.082	0.15	0.50	--	--	--	--
Secondary	25	72%	0.020	0.100	0.084	0.13	0.44	--	--	--	--
Baseline + Secondary	50	72%	0.020	0.090	0.083	0.15	0.46	11%	none <sup>1</sup>	0.14	NP
<b>cPAH TEQ (1/2 DL; ppb, dw)</b>											
Baseline	25	na	0.30	23.0	19.5	43.6	0.85	29%	none <sup>1</sup>	41.8	NP
<b>Dioxin/Furan TEQ (1/2 DL; ppt, dw)</b>											
Baseline	25	na	0.118	1.08	1.76	3.61	0.81	29%	none <sup>1</sup>	3.58	NP
<b>PCBs TEQ (1/2 DL; ppt, dw)</b>											
Baseline	25	na	0.0076	0.131	0.153	0.383	0.83	29%	none <sup>1</sup>	0.38	NP
Baseline+Secondary	35	na	0.0076	0.112	0.145	0.383	0.86	37%	none <sup>1</sup>	0.43	G
<b>Total PCBs (detects only; ppb, dw)</b>											
Baseline	25	na	0.231	6.79	5.46	12.4	0.80	29%	none <sup>1</sup>	12.1	NP
Baseline+Secondary	35	na	0.231	3.92	5.01	12.4	0.84	25%	none <sup>1</sup>	11.4	NP

<sup>1</sup> These distributions look more bimodal; there are extremes, but these are masked by concentrations in the subset of stations with the higher modal concentration.

Precision column shows the half-width of the 95% UCL on the mean relative to the mean [for example, for a normal distribution this is:  $t \cdot \text{std.dev.} / \sqrt{n} / \text{mean}$ ]; the target value is 25%.

Outlier tests included Dixon's (normal data,  $n < 25$ ), Rosner's (normal data,  $n \geq 25$ ), or Tukey's rule of  $2 \cdot \text{IQR}$  from median (non-parametric). *Multivariate outliers not assessed.*

Distribution column shows N (normal), G (gamma), or NP (non-parametric). Best distribution determined by goodness-of-fit tests in ProUCL (detected concentrations only).

# Bold Survey Statistical Summary

Parameter	N	% Detect	Min	Median	Mean	Max	CV	Precision	outliers	90/90 UTL	Dist'n
Arsenic (ppm, dw)	70	100%	1.1	5.9	6.51	21	0.58	12%	none	12.5	G
Cadmium (ppm, dw)	70	67%	0.018	0.15	0.30	2.8	1.56	14%	none	0.79	G
Mercury (ppm, dw)	70	59%	0.0048	0.076	0.086	0.26	0.73	17%	none	0.18	N
cPAH TEQ (1/2 DL; ppb, dw)	70	na	1.1	4.1	6.7	57	1.30	67%	yes <sup>2</sup>	19.4	NP
Dioxin/Furan TEQ (1/2 DL; ppt, dw)	70	na	0.24	1.02	1.4	12	1.22	41%	two <sup>3</sup>	3.4	NP
PCBs TEQ (1/2 DL; ppt, dw)	70	na	0.012	0.046	0.057	0.25	0.73	14%	none	0.12	G
Total PCBs (detects only; ppb, dw)	70	na	0.010	0.65	1.2	11	1.41	27%	none	3.3	G

<sup>2</sup> up to 10 outliers, statistically (values range from 13.3 to 57.1)

<sup>3</sup> Stations SS\_0 and SS\_9.

Precision column shows the half-width of the 95% UCL on the mean relative to the mean [for example, for a normal distribution this is:  $t \cdot \text{std.dev.} / \sqrt{n} / \text{mean}$ ]; the target value is 25%.

Outlier tests included Dixon's (normal data,  $n < 25$ ), Rosner's (normal data,  $n \geq 25$ ), or Tukey's rule of  $2 \cdot \text{IQR}$  from median (non-parametric). *Multivariate outliers not assessed.*

Distribution column shows N (normal), G (gamma), or NP (non-parametric). Best distribution determined by goodness-of-fit tests in ProUCL (detected concentrations only).

# Regional Background & Bold Survey

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<b>BCOC</b>	<b>Units</b>	<b>Port Gardner</b>	<b>Bold Survey</b>
Arsenic	(ppm)	11.6	12.5
Cadmium	(ppm)	0.37	0.79
Mercury	(ppm)	0.14	0.18
cPAH TEQ	(ppb)	41.8	19.4
Dioxin/Furan TEQ	(ppt)	3.58	3.40
PCB TEQ	(ppt)	0.43	0.12
Total PCBs	(ppb)	11.4	3.3

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- Bold survey is slightly higher for metals.
- Regional background is higher for organics, particularly cPAH and PCBs.
- Regional background (Port Gardner) and Bold survey are represented by the 90/90 upper tolerance limit (UTL) from the previous two slides.