Comparison of Multiple Bioassays to High-Resolution Gas Chromatography for Quantification of Polychlorinated Biphenyls and Dioxins/Furans in Sediment

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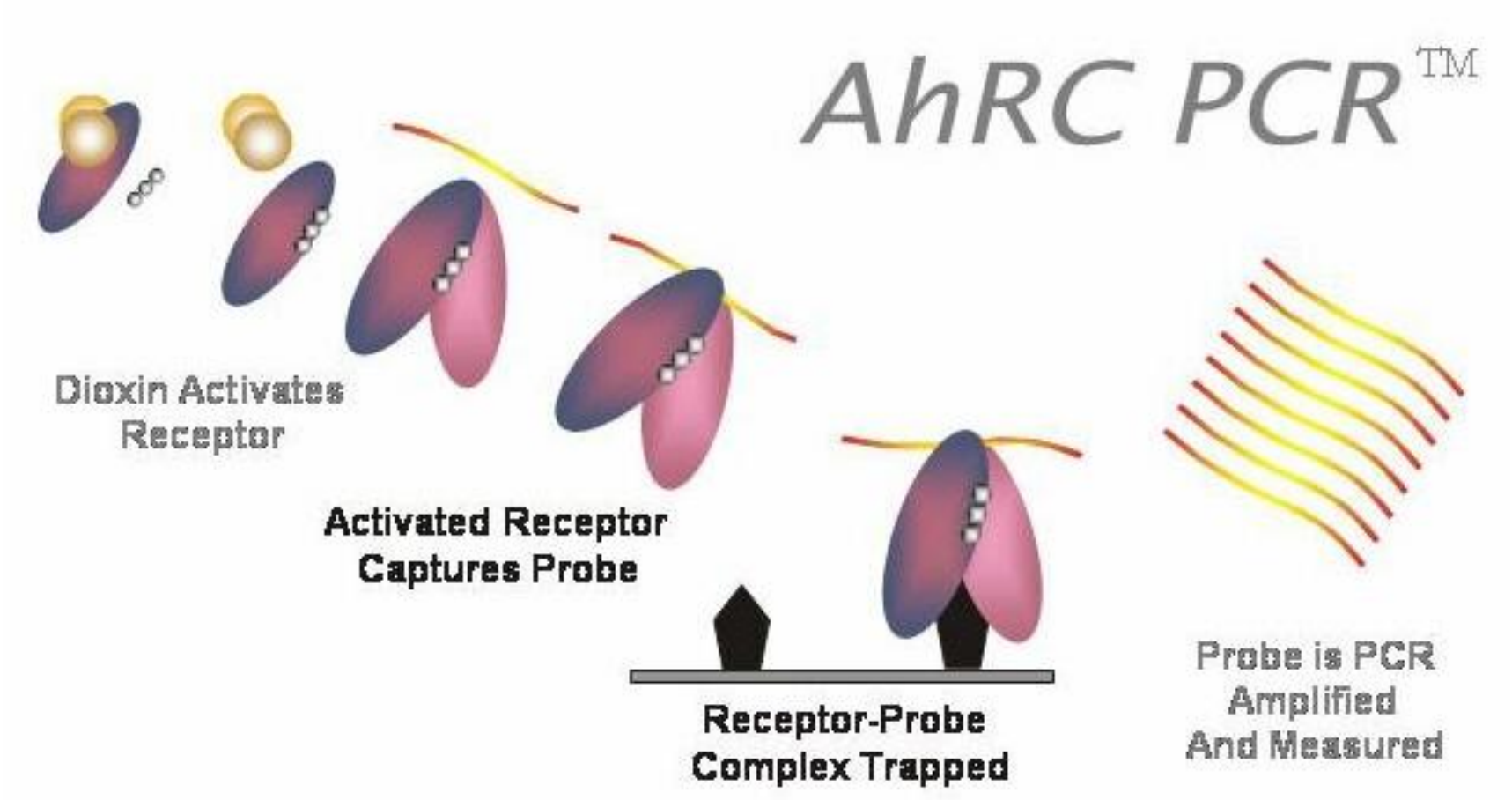
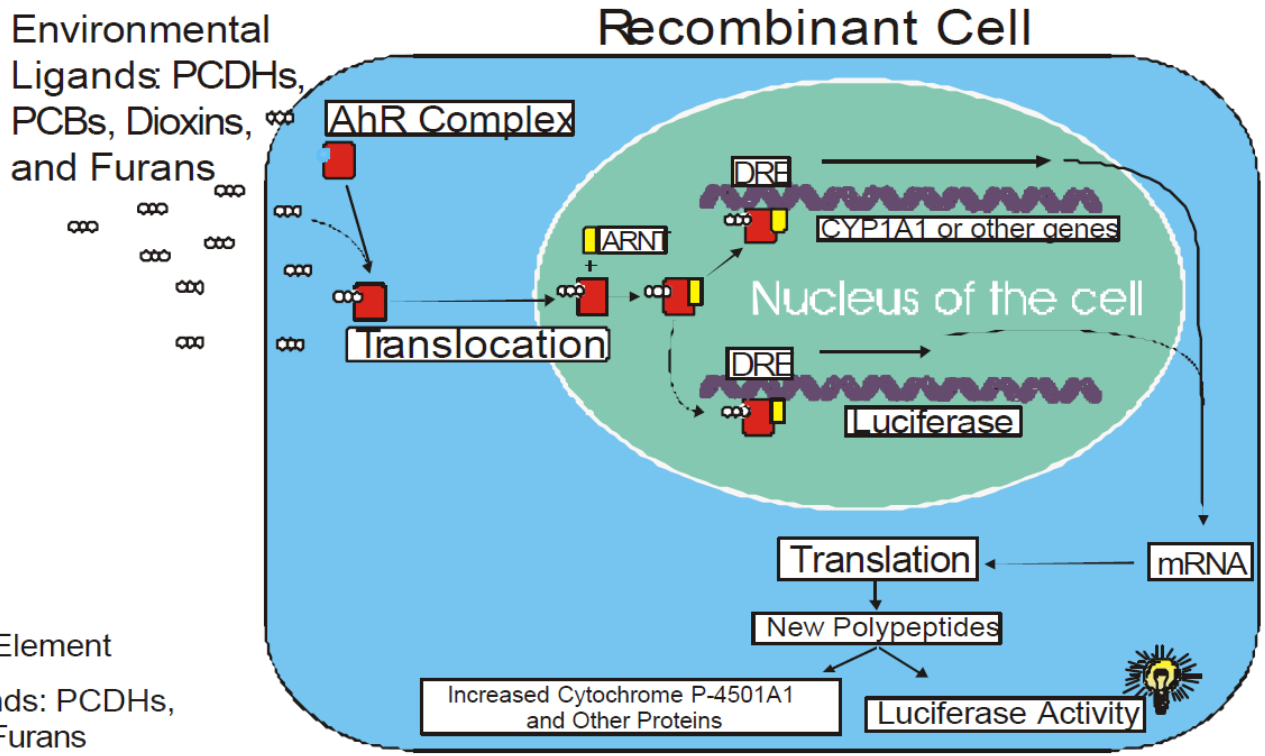
Dioxin in Sediment is Important, Costly Issue in the Pacific Northwest

- Dioxins are primary risk drivers in Puget Sound and are key to the Puget Sound Cleanup Initiative
- The Dredge Material Management Program has proposed revised background-based guidelines for suitability determination for in-water dredge material disposal, which likely means more sediment dioxin testing will be required
- High-Resolution Gas Chromatography/Mass Spectrometry (HRGC/MS, EPA 1613b) is “gold standard” for sediment dioxin testing but costly with long turn around times
- Bioassays have potential to provide much cheaper, quicker quantitative dioxin results for sediments but have not been evaluated for sediment in low, dredge material-relevant concentration range of 4 and 10 ppt TEQ

qPCR-Based Assay: Procept (EPA 4430)



Cell-Based Assays: CALUX (EPA 4435) and 101-L



Induction of light is directly proportional to concentration of dioxin TEQ in the sample.

DRE =Dioxin Responsive Element

=Dioxin-like compounds: PCDHs, PCBs, Dioxins and Furans

ARNT =AhR Nuclear Translocator protein

AhR Complex =Aryl hydrocarbon Receptor Complex

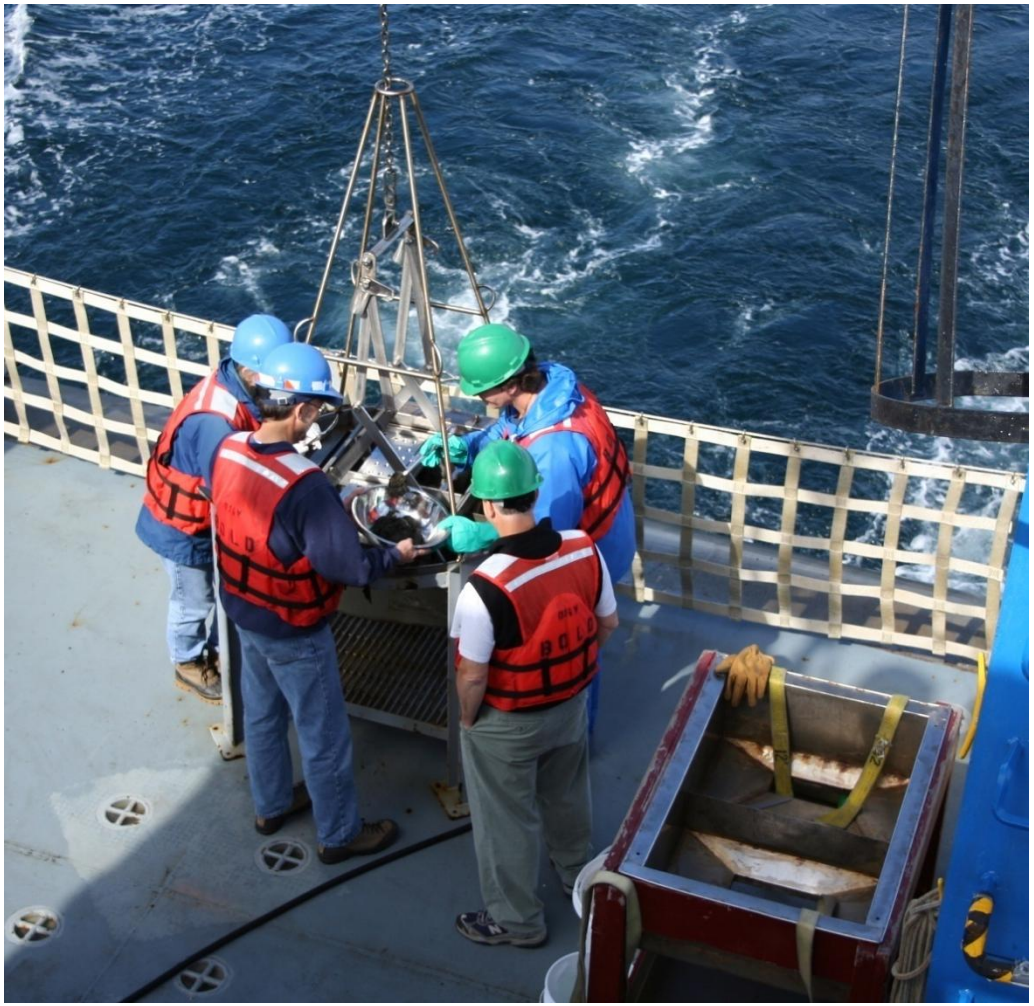
http://www.dioxins.com/pdf/downloads/downloads02.pdf

OSV Bold Research Cruise

Collective effort of multiple State and Federal Agencies to characterize non-urban influenced sediment samples throughout the sound for determination of natural background contaminant concentrations to support DMMP revised sediment management guidelines

An additional 21 urban influenced samples were retrieved from project archives and included in the data set

Sediment Sampling Methods



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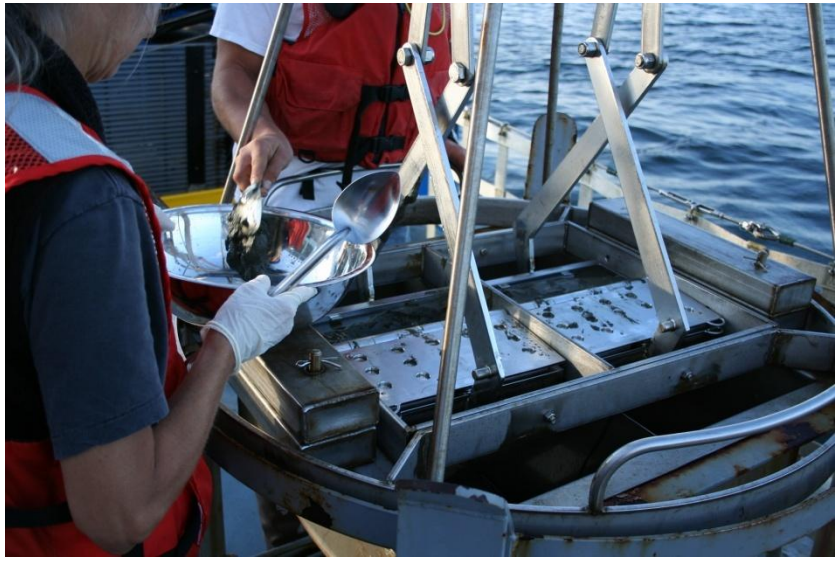


Sediment Sampling Methods

Sediment Analysis Methods

- High-Resolution Gas Chromatography/Mass Spectrometry (HRGC/MS)
  - SGS Laboratories, Wilmington, NC
- XDS-CALUX®
  - Xenobiotic Detection Systems Laboratory, Durham, North Carolina
- 101-L & Procept
  - Engineering Research & Development Center Laboratory, US Corps of Engineers, Vicksburg, MS

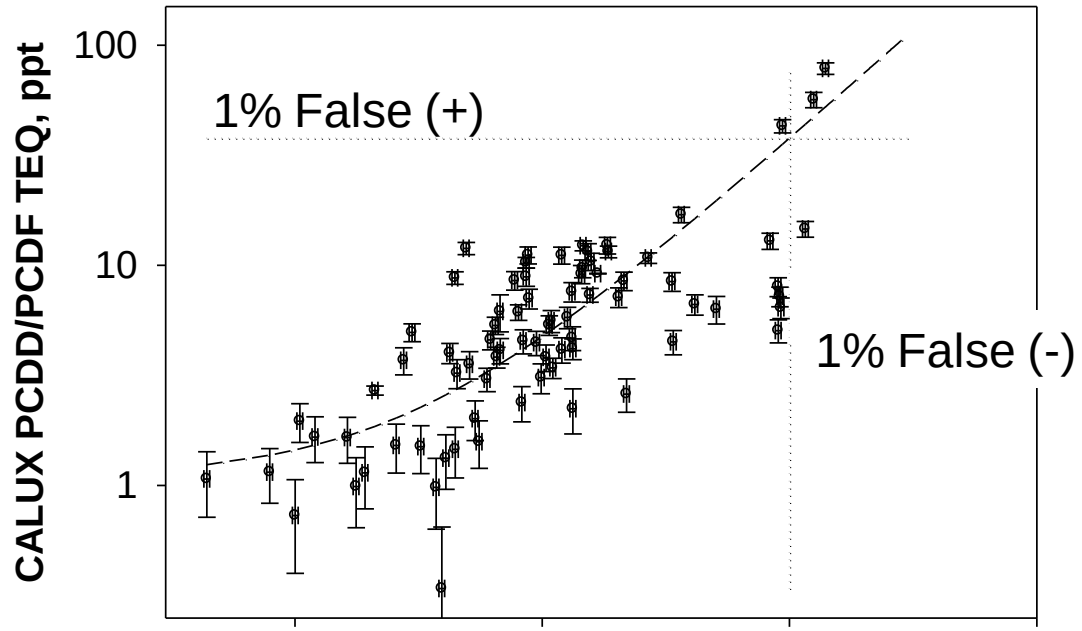
Bioassay vs. HRGC/MS Evaluation Methods

- Bioassay performance was evaluated against HRGC/MS by
  - Bivariate Least-Squares Regression
    - Does not assume error-free independent variable
    - Considers variances of both independent and dependant variables simultaneously
    - Sample-specific variances were estimated for HRGC/MS and bioassay results by extrapolating calibration standard variances based on sample concentrations
  - Relative percent differences
  - False positive/false negative rates

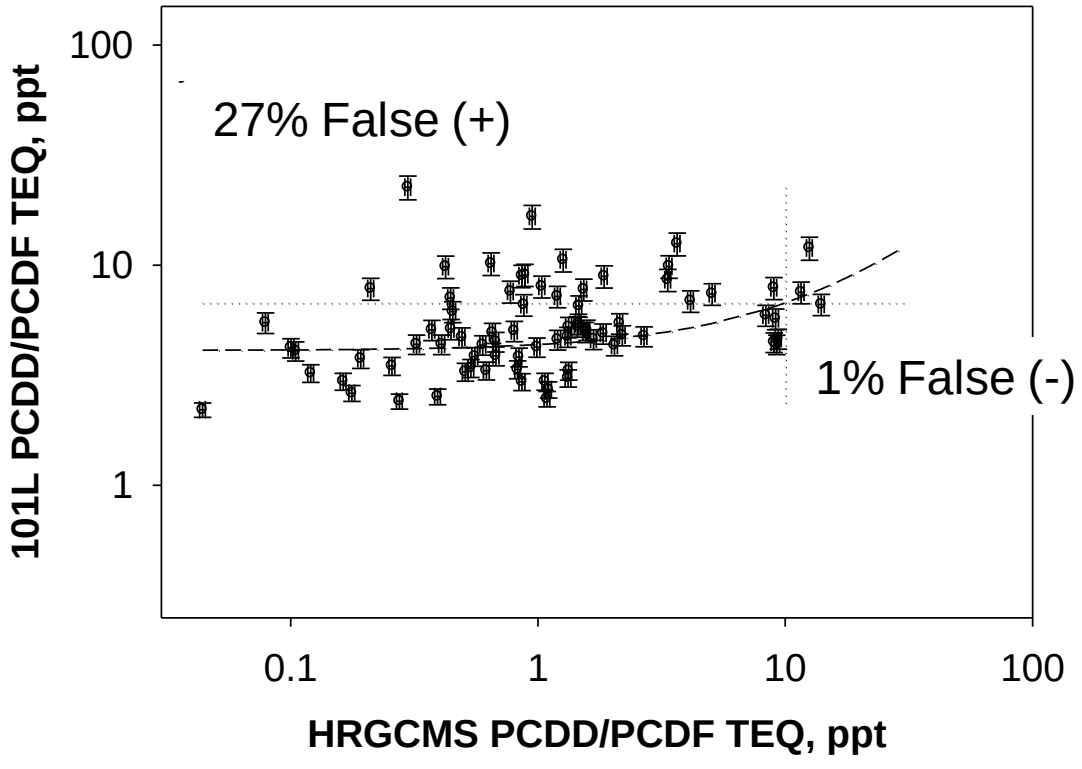
Results

	HRGCMS	CALUX	101L	Procept
min	0.0440	0.340	0.893	-0.136
max	11.6	17.0	22.6	184
Correlation coefficients		**0.708**	0.166	-0.162

Results

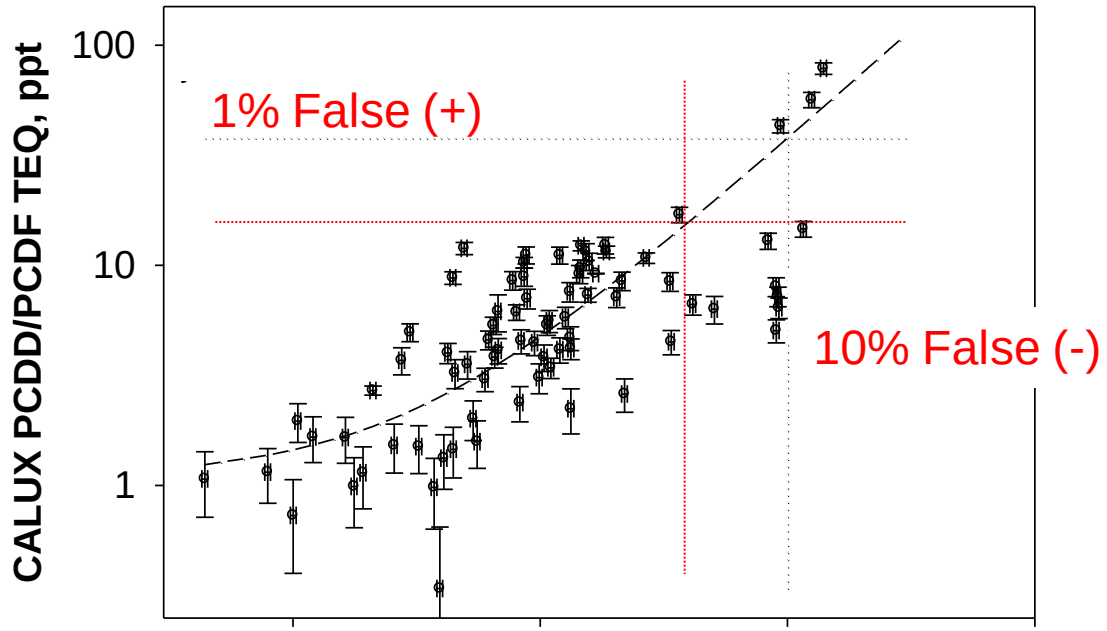


CALUX
BLS Regression Results
Y = 3.67x + 1.08, R = 0.59



101-L
BLS Regression Results
Y = 0.265x + 4.09, R = 0.02

Results



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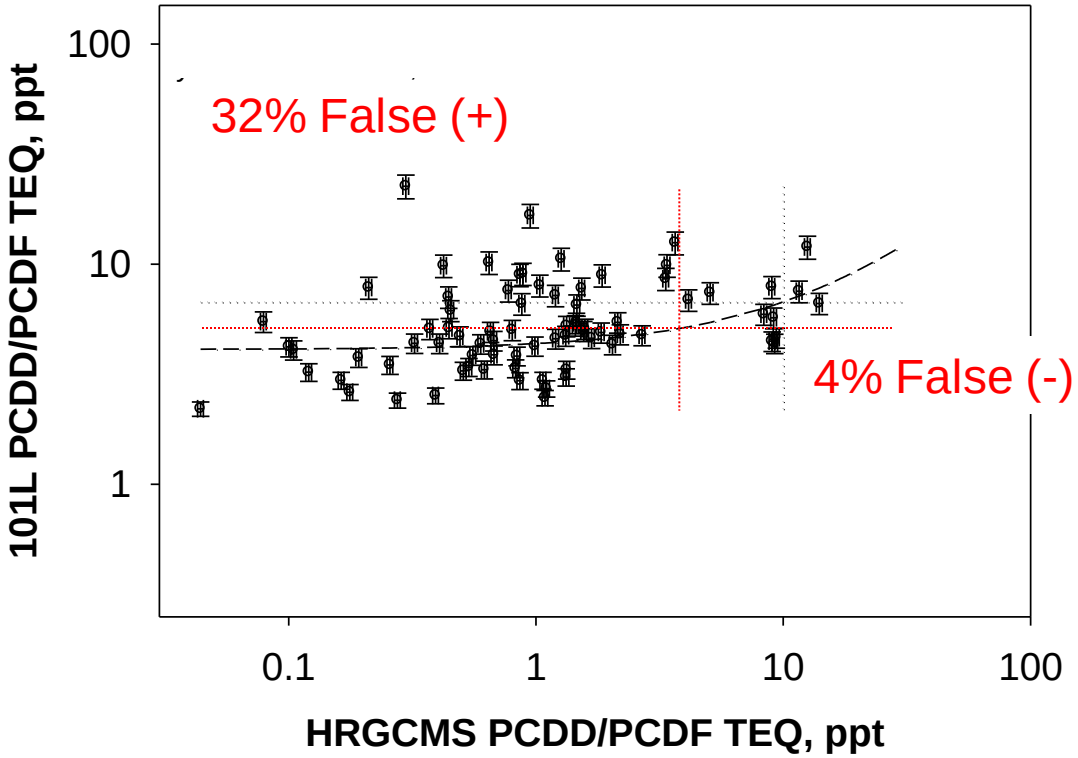
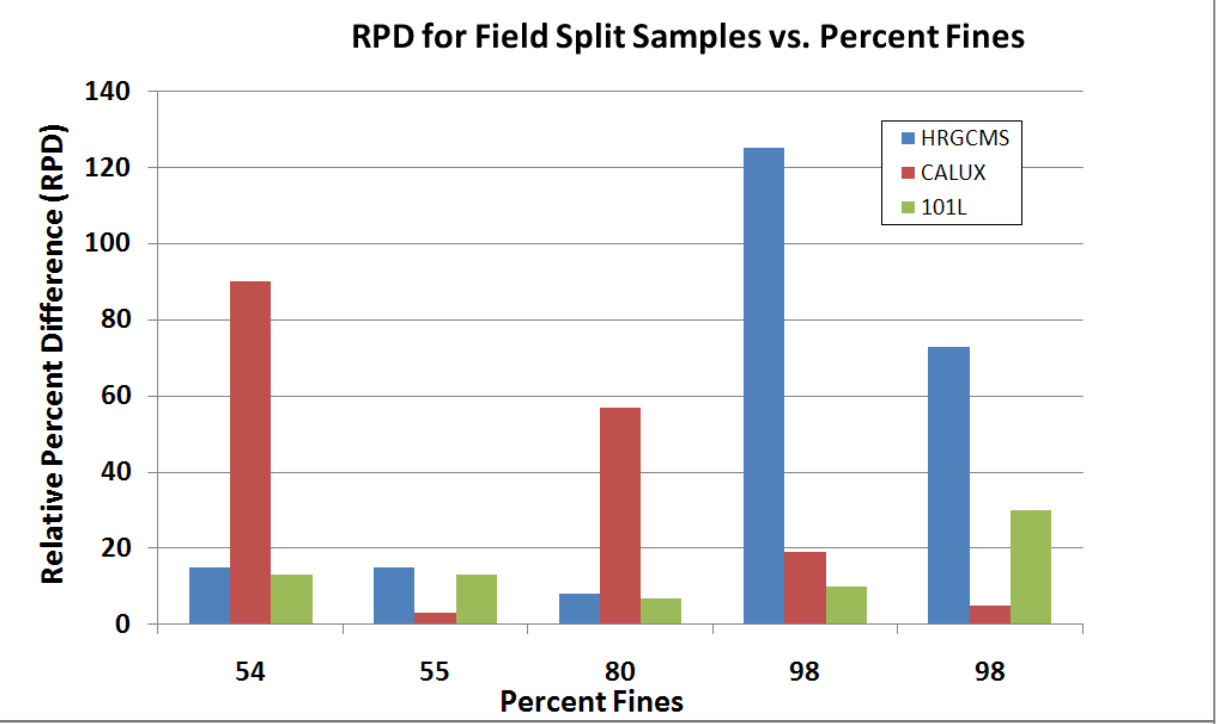
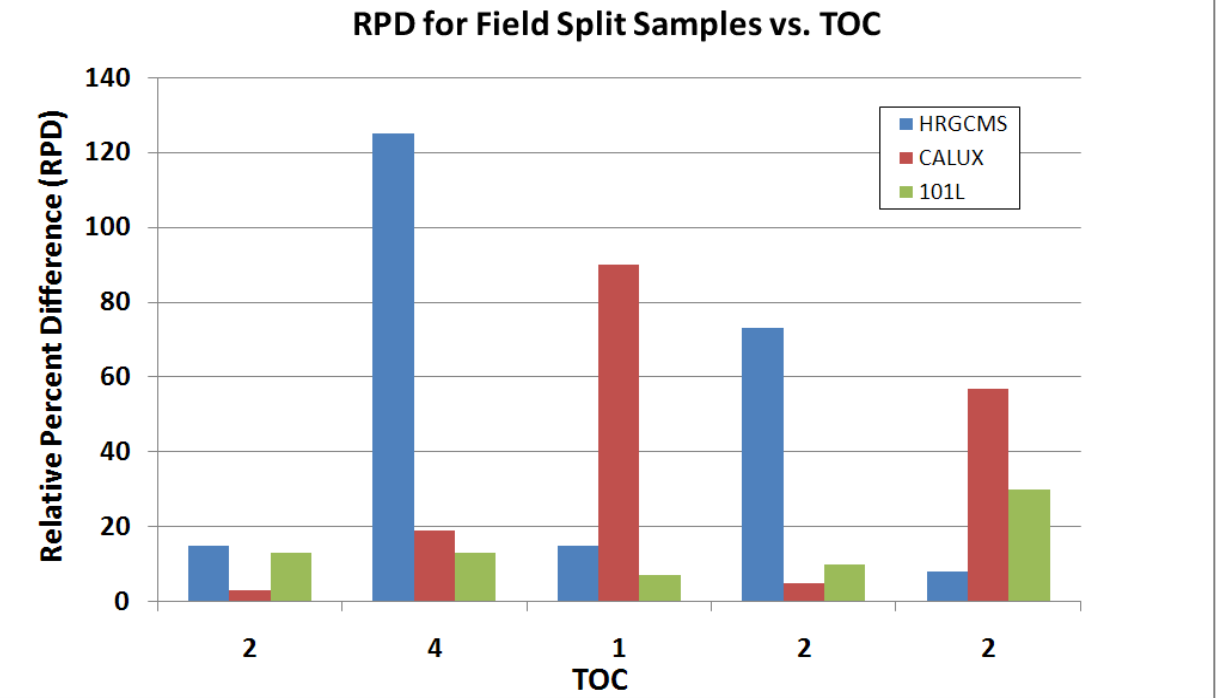


101-L
BLS Regression Results
Y = 0.265x + 4.09, R = 0.02

Laboratory Duplicate Results

Sample ID	% fines	% organic carbon	CALUX Results	CALUX RPD	101L Results	101L RPD	HRGCMS Results	HRGCMS RPD
CPS_3	55%	1.55	4.18	3%	5.23	13%	1.33	15%
QC_1 (CPS_3 split)		1.49	4.07		4.59		1.55	
HC_2	98%	3.65	8.54	19%	7.59	10%	0.774	125%
QC_2 (HC_2 split)		4.33	7.05		8.40		3.33	
NCPS_2	54%	0.640	5.35	90%	2.96	13%	1.07	15%
QC_3 (NCPS_2 split)		0.949	2.03		3.38		0.923	
PSPS_1	98%	2.31	7.16	5%	4.31	30%	2.04	73%
QC_4 (PSPS_1 split)		2.03	6.82		5.86		0.947	
SPSB_0	80%	2.24	9.68	57%	5.41	7%	1.46	8%
QC_5 (SPSB_0 split)		2.07	5.36		5.79		1.57	
			average:	35%		15%		47%





Laboratory Duplicate Results for Other Parameters

Results

Sample ID	HRGCMS	CALUX	101L
*FBA3-32-2**	41.0	18.6 ✓	11.1 x
*T115-S1-CS-0803**	19.2	88.7 ✓	6.06 x
*T115-S2-01-ZA-0803**	31.5	71.0 ✓	18.2 ✓
*T115-S2-02-ZA-0803**	24.1	104 ✓	12.5 x
*T115-S2-CS-0803**	23.3	75.7 ✓	20.6 ✓
*T18-S1-C5**	22.3	60.2 ✓	20.5 ✓
*PO-BA-25-SS-A**	23.6	14.1 x	7.65 x
*PO-BA-25-SC-Z**	67.2	16.3 ✓	13.4 x
*PO-UP-22-SC-A**	40	11.4 x	9.61 x
*PO-UP-22-SC-B**	28.2	3.90 x	18.7 ✓
*PO-UP-20-SC-A**	39.2	15.4 ✓	12.6 x
*PO-UP-20-SC-B**	54.1	8.64 x	11.9 x
		67%	33%

notes
Urban samples are shown in itallics
* Urban samples used for screening evaluation purposes only not included in regression or correlation analysis. Check marks indicate assay >15 ppt TEQ and x's indicate assay <15 ppt TEQ.
a. value was truncated to zero for correlation analysis
b. estimated value below lowest calibration standard concentration
c. estimated variance value for this datapoint was negative for 101L so it was not included in the analysis.

Discussion

- Assays performed well in the concentration range of interest
  - False positive errors for CALUX and 101-L < 27 percent
  - False negative errors for CALUX and 101-L < 10 percent
- RPDs indicate that sampling error may have contributed significantly to total error in this study
- Assays performed poorly for urban samples containing concentrations > 15 ppt TEQ; however, samples originated from separate studies
- Factors contributing to poor performance may include
  - Presence of co-contaminants
  - Proximity to known sources
  - Variations in sample percent moisture
  - Sample heterogeneity and differences in sample preparation
- Recommend assay performance be evaluated on site-specific basis considering uniformity of sediment, presence of co-contaminants and known sources

Acknowledgements

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