PCB Alternative Analysis

Comparison of Aroclor to low and high-resolution GCMS

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Introduction

- Aroclor analysis is standard for sediments, but has its issues
  - Weathering and mixtures: impact to identification of Aroclors
  - Detection limits (Ecology background issue)
  - Cannot calculated dioxin-like TEQs
- High resolution gas chromatograph/mass spectra (HR-GCMS) is the "gold standard" of analysis, but is expensive. Is an alternative available?
- This study investigated low resolution GC-MS (LR-GCMS) methods and its potential as a surrogate for total PCB and for calculating dioxin-like PCB TEQs

Approach

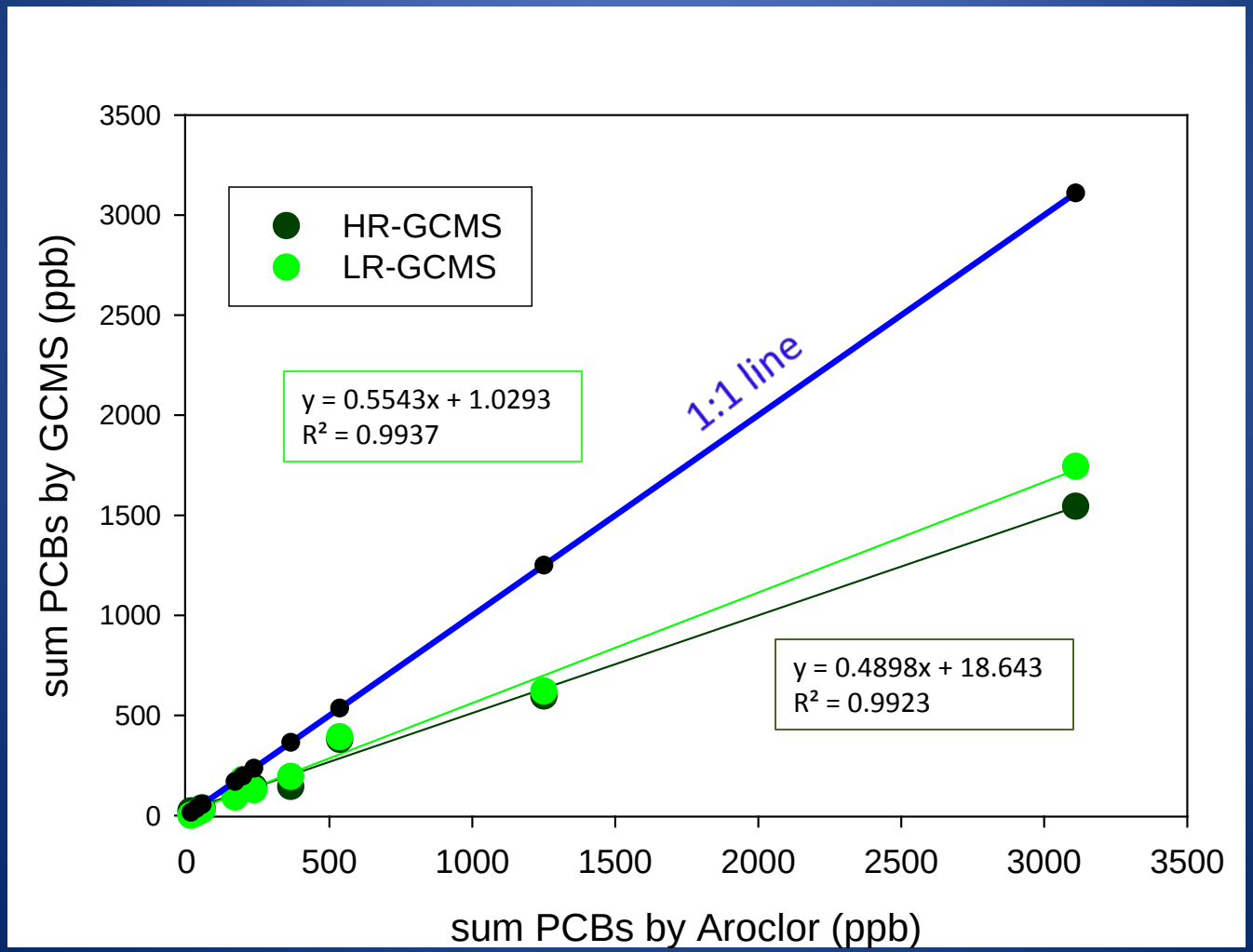
- Two different studies were initiated in 2012.
  - USACE Duwamish
    - 9 samples from the Duwamish plus PS-SRM
    - HR-GCMS (EPA 1668), LR-GCMS (EPA 680), and Aroclor
    - Total PCB HR-GCMS concentration range 12-1744 ppb
  - Ecology Study: freshwater and marine sediments from region
    - 3 marine samples from 3 different locations, 5 FW samples from 2 locations, plus PS-SRM
    - HR-GCMS (EPA 1668), LR-GCMS (EPA 8270C/D GC/LRMS), and Aroclor
    - Total PCB HR-GCMS concentration range from 4-191 ppb

USACE Study, Total PCBs

- Initial LRMS results confounded by sulfur
- Sulfur clean-up added and samples re-analyzed.
- Total PCB HR-GCMS concentration range
  12-1744 ppb
- Aroclor results always higher than GC-MS results.
- HR and LR-GCMS methods correlated well
  ($y = 1.13x – 19.417$; $R^2 = 0.998$)

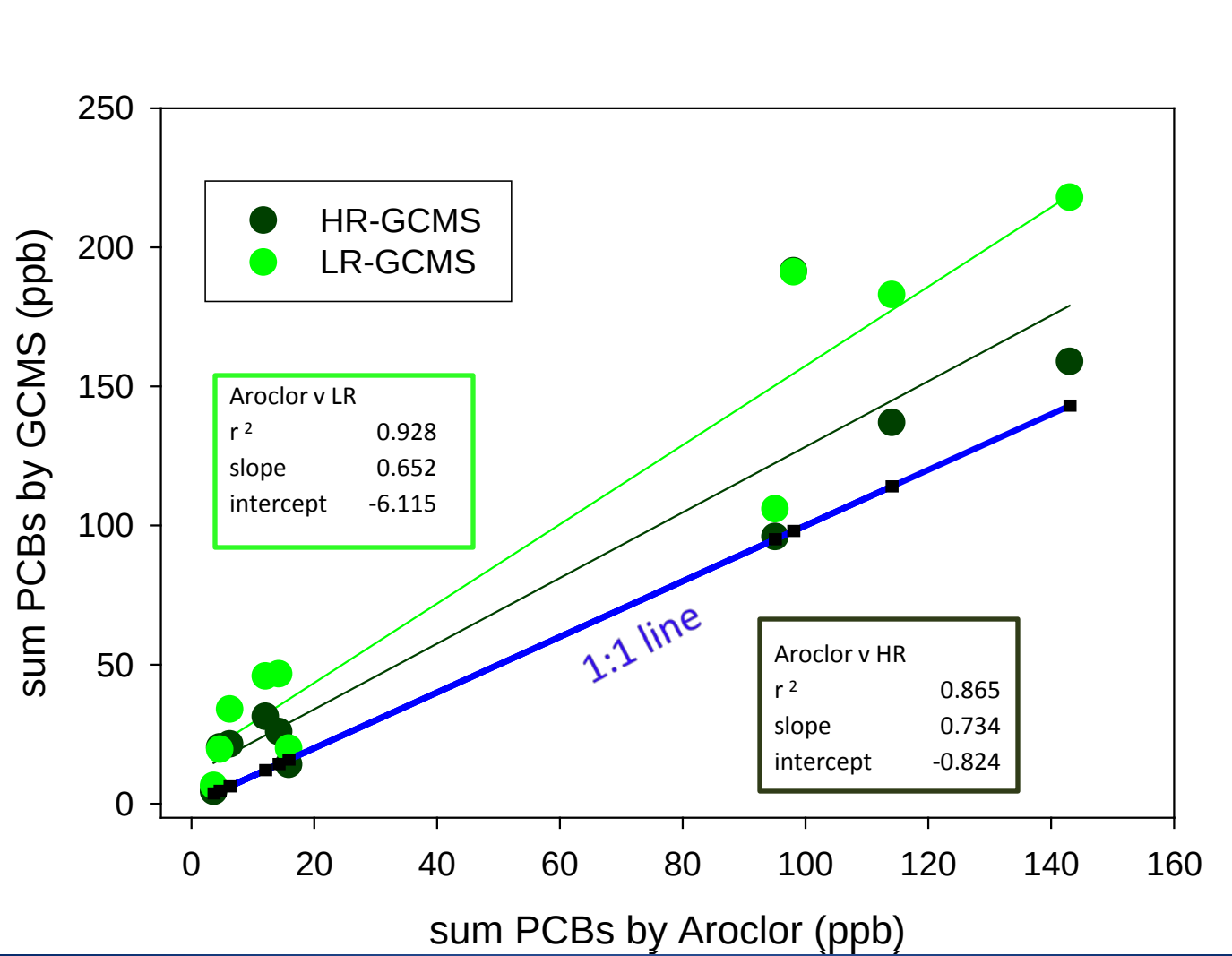
USACE Total PCB Results

Regression of (1) sum of the HR-congeners (U=1/2 RL) vs. total Aroclors and (2) sum EPA 680 LR-homologs vs. total Aroclors

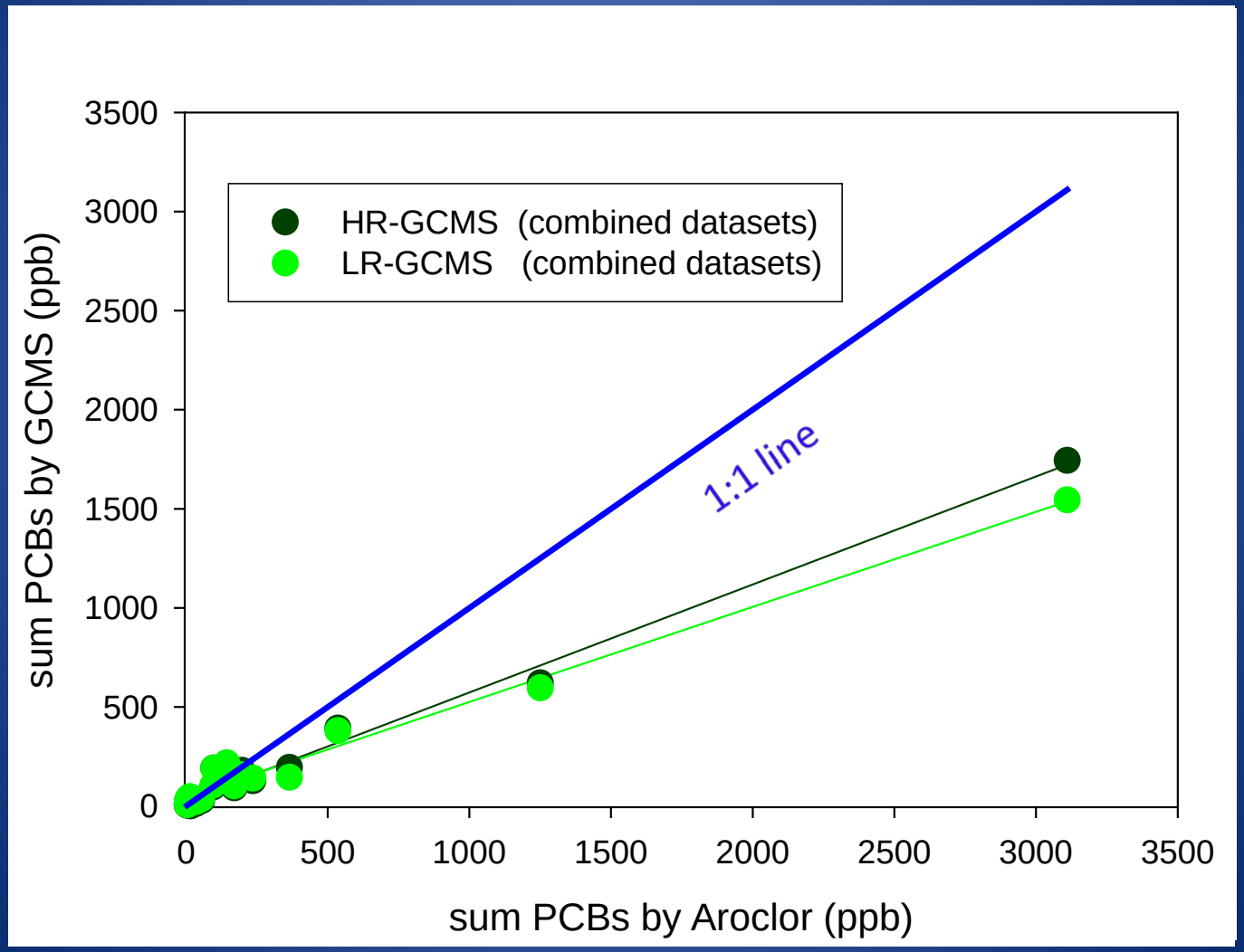


Ecology Study, Total PCBs

Sum PCBs, Aroclors v HR-GCMS congeners and LR-GCMS homologs



Combined Studies, Total PCBs



Ecology Study, Total PCBs

- Total PCB HR-GCMS concentration range 4-191 ppb
- Aroclor results always equal to or lower than GC-MS results.
- HR and LR-GCMS methods correlated well

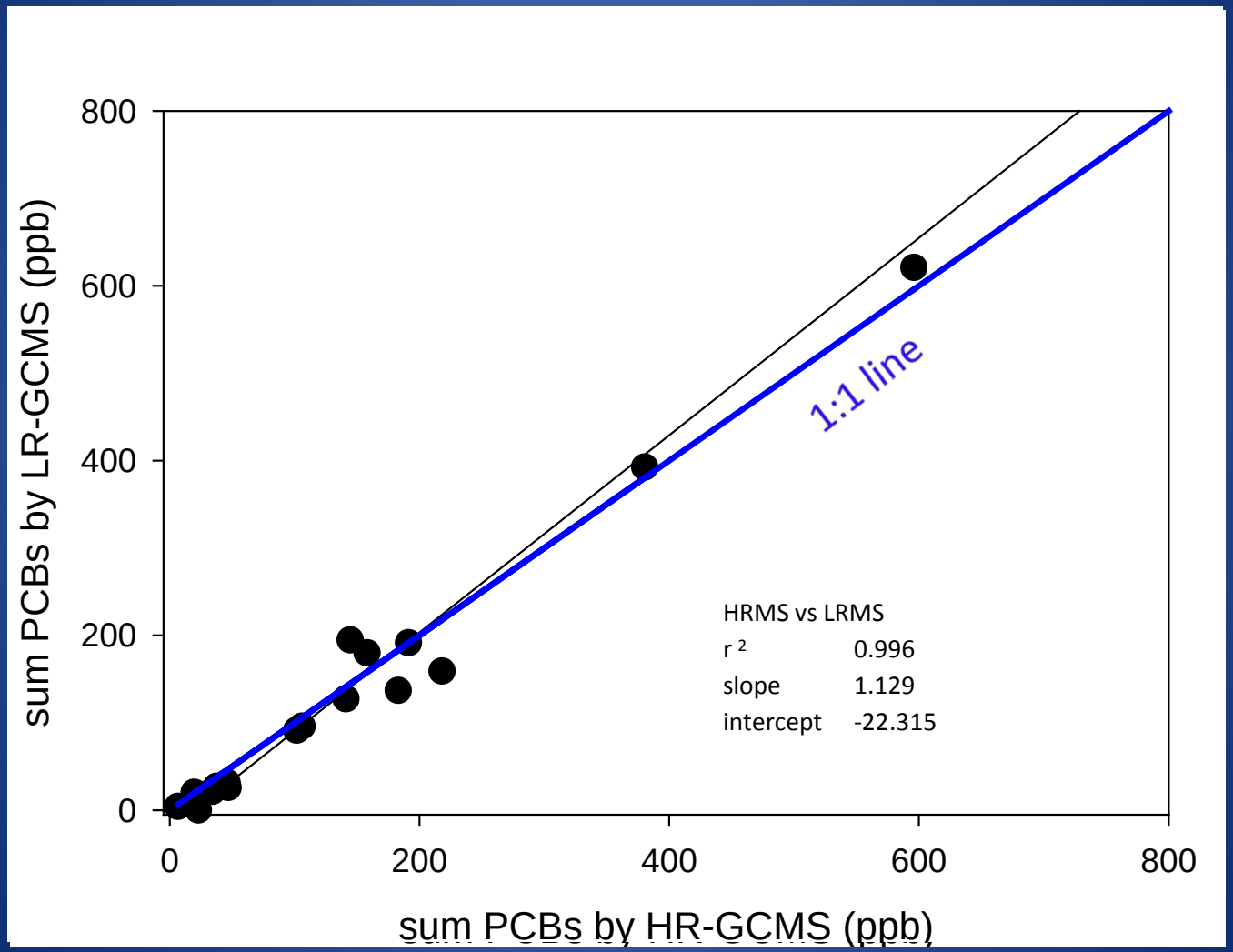
  ($y = 1.1384x - 7.27$; $R^2 = 0.952$)

Comparison of Studies, Total PCBs

COE: Aroclor > GC-MS ECY: Aroclor $\leq$ GC-MS

- Different concentrations ranges?
- Differences in lab Aroclor analysis?
- Differences in sample mixture composition?

Combined Studies, Total PCBs



Total PCBs summary

- Sulfur cleanup is essential for EPA680
- Both studies showed good correlation between HRMS and LRMS.
- Even though different LRMS methods were used, combined comparison of Aroclor vs HRMS and HRMS vs LRMS resulted in good correlations.
- When samples have lower concentrations, Aroclor NDs become an issue. This becomes problematic if a large part of the dataset is ND (i.e. background determinations).

Developing PCB Homolog TEFs

- Given HRMS and LRMS results are well correlated, can TEFs be developed for homologs?
    - All dioxin-like PCBs fall into 4 homolog groups
- Overview development of homolog TEFs based on HR-GCMS dioxin-like congeners, and sum homologs for tetra, penta, hexa, and heptachlorinated PCBs.

TEQ definition

Congener-based TEQ:

$$TEF_{cong} \times Conc_{cong} = TEQ$$

Homolog-based TEQ:

$$TEF_{homo} \times Conc_{homo} = TEQ_{homo}$$

Homolog-TEF derivation

Since

$$TEF_{homo} \times Conc_{homo} = TEQ_{homo}$$

and from HR-GCMS, we can obtain

$Conc_{homo}$ and TEQ_{homo}

then we can solve for TEF_{homo} using

$$TEF_{homo} = TEQ_{homo} / Conc_{homo}$$

Sample-specific homolog TEF calculations: ECY HRMS data

1. For each sample, sum all congeners (both dioxin-like and non-dioxin like) for each homolog group.

1. gather HR homolog data

	HRMS
	RM01
Monochlorobiphenyl	43.9
Dichlorobiphenyl	5710
Trichlorobiphenyl	11000
Tetrachlorobiphenyl	32600
Pentachlorobiphenyl	62800
Hexachlorobiphenyl	44900
Heptachlorobiphenyl	15600
Octachlorobiphenyl	1010
Nonachlorobiphenyl	99.2
Decachlorobiphenyl	739
SUM	171502

Sample-specific homolog TEF calculations: ECY HRMS data

2. For each sample, HR-MS TEQs summed for each homolog group with dioxin-like PCBs (tetra, penta, hexa, and heptachlorinated PCBs). Can't use KM, so used ND=DL, which was closest to KM sum.

2. Gather the HRMS dioxin-like PCB congeners, calculated TEQs, and sum based on homolog groups.

HRMS	# chlorines	Actual TEQs RM
77	4	0.012
81	4	0.001
105	5	0.034
114	5	0.002
118	5	0.095
123	5	0.013
126	5	1.380
167	6	0.010
169	6	0.570
156/157	6	0.022
189	7	0.005

Sample-specific homolog TEF calculations: ECY HRMS data

3. For each homolog group and each sample, the sample-specific TEF is calculated for each homolog group by dividing the homolog congener-based TEQ by the sum homologs.

HRMS	Step 1 Homolog	Step 2 Sum TEQ
	RM01	RM01
Tetrachlorobiphenyl	32600	0.013
Pentachlorobiphenyl	62800	1.52
Hexachlorobiphenyl	44900	0.602
Heptachlorobiphenyl	15600	0.0049

3. Divide sum homolog TEQ (step 2) by sum homolog PBC (step 1) to generate sample-specific TEF.

	HRMS Homolog TEF calculations RM
Tetrachlorobiphenyl	4.0E-07
Pentachlorobiphenyl	2.4E-05
Hexachlorobiphenyl	1.3E-05
Heptachlorobiphenyl	3.1E-07

Average homolog TEF : ECY HRMS data

5. After generating sample-specific homolog TEFs for all 10 samples, generate AVERAGE TEFs for each of the four homolog groups by averaging sample-specific homolog TEFs.

Sample ID	Tetrachlorobiphenyl	Pentachlorobiphenyl	Hexachlorobiphenyl	Heptachlorobiphenyl
RM01	4.0E-07	2.4E-05	1.3E-05	3.1E-07
MC01	6.3E-07	4.2E-05	7.7E-06	2.7E-08
FWA01	7.8E-07	3.0E-05	1.5E-05	1.1E-07
FWA02	1.1E-06	5.6E-05	1.3E-05	1.2E-07
FWA03	4.5E-07	4.2E-05	8.4E-06	1.4E-07
FWA03dup	5.2E-07	3.0E-05	9.6E-06	1.0E-07
MA01	8.2E-07	3.1E-05	7.4E-06	1.2E-07
MA02	8.2E-07	3.5E-05	1.0E-05	9.2E-08
MB01	1.4E-06	8.5E-05	8.9E-06	6.5E-08
FWB01	1.8E-06	9.8E-05	2.0E-05	1.2E-07
FWB02	1.1E-06	5.6E-05	1.0E-05	1.6E-07
average TEF	9.0E-07	4.8E-05	1.1E-05	1.2E-07

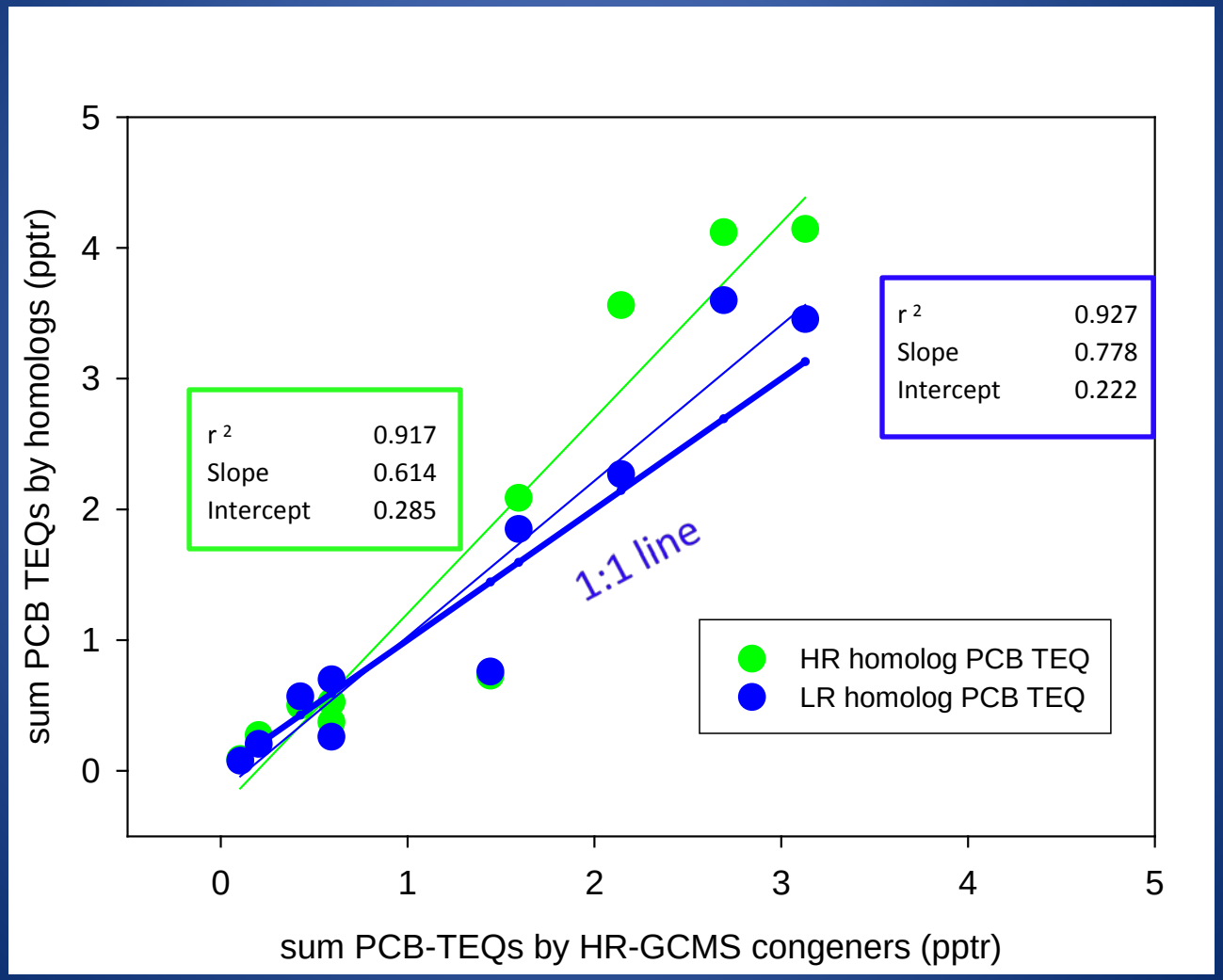
TEF_{homo} Analysis

Compare TEQs for:

1. HRMS congeners, using congener-specific TEFs
2. HRMS homologs, using average homolog TEF
3. LRMS homologs using average homolog TEF

	congener TEF	homolog TEFs	
	HRMS sum TEQ	HRMS sum TEQ	LRMS sum TEQ
RM01	2.1	3.6	2.3
MC01	0.4	0.5	0.6
FWA01	0.2	0.3	0.2
FWA02	0.1	0.1	0.1
FWA03	3.1	4.1	3.5
MA01	2.7	4.1	3.6
MA02	1.6	2.1	1.8
MB01	0.6	0.4	0.3
FWB01	1.4	0.7	0.8
FWB02	0.6	0.5	0.7

HR-GCMS congener sum TEQ vs sum TEQ from homolog TEF



How Robust is the Homolog TEF?

- Use other datasets to compare actual HRMS TEQ to homolog generated TEQ
- Comparison with Corps data difficult due to high DLs for PCB 169 and PCB 126, the highest TEF congeners.
- PS SRM analyzed in both COE and ECY studies
- Compare sum TEQ from both studies using HR and LR data

Homolog TEF and PS-SRM results:

- Comparison of PS-SRM for Ecology and USACE study.

Ecology data	
HR-GCMS congener (KM sum)	2.1
LR-GCMS using homolog TEF	2.3
Corps data	
HR-GCMS congener (KM sum)	8.4
LR-GCMS using homolog TEF	2.1

Homolog TEF summary

- Used a set of 10 samples from ECY study of widely distributed water bodies.
- Sum TEQ calculated using average homolog TEFs correlate well with HR-GCMS sum TEQs (R^2>0.9)
- Need more samples from different areas to check performance (N=10 is insufficient)

So What?

DMMP disposal sites in the dawn of the new sediment rule.

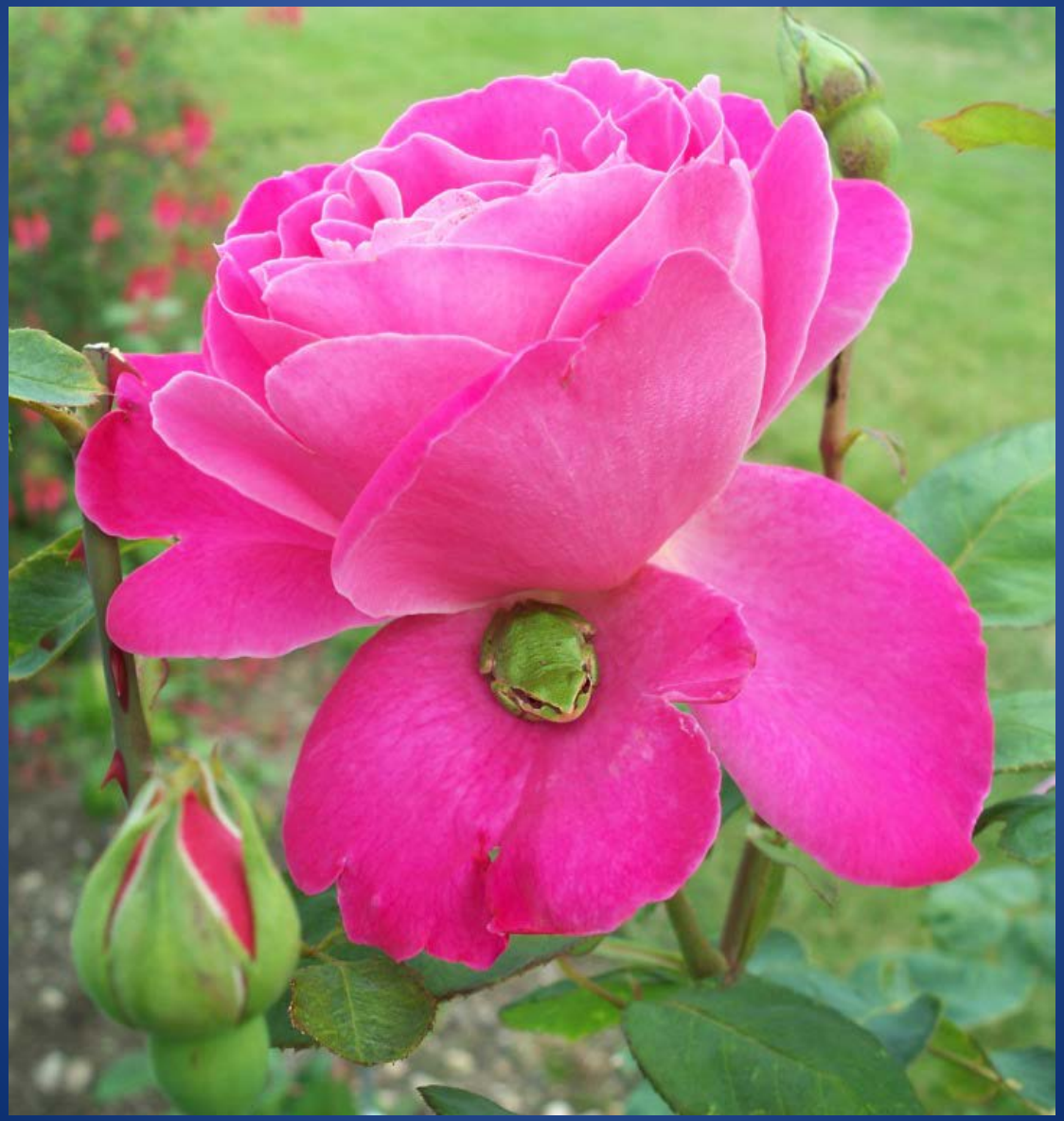
- Need to stay below CSL
- Regional and natural background: what does it look like?
- No answers now, but if PCBs are below standard Aroclor analytical limits, GCMS may be required and LRMS may offer a lower cost alternative to HRMS.

So What?

Summed PCB and dioxin TEQ approach

- PCB contribution to TEQ
  - Preliminary Port Gardner Regional Background dataset:
    - PCB = 0.008 to 0.38 pptr TEQ
    - Dioxin = 0.1-3.6 pptr TEQ.
    - PCB % of total TEQ ranges from 4-11%
  - Port Angeles Regional Background dataset
    (90/90UTL, 5 areas)
    - PCB = 0.12 – 0.39 pptr TEQ
    - Dioxin = 1.9-6.0 pptr TEQ.
    - PCB % of total TEQ ranges from 4-8%
- Other concerns- non-dioxin-like PCB carcinogenicity

Next Steps

- NO PROPOSAL AT THIS TIME, but potential approaches are being discussed
  - If no “reason to believe” PCBs would be detected, use Aroclor analysis.
  - If “reason to believe” use LRMS and the sum PCB dioxin TEQ approach.
- Initial studies are promising, but we need more information for the homolog TEF approach

COMMENTS? QUESTIONS?