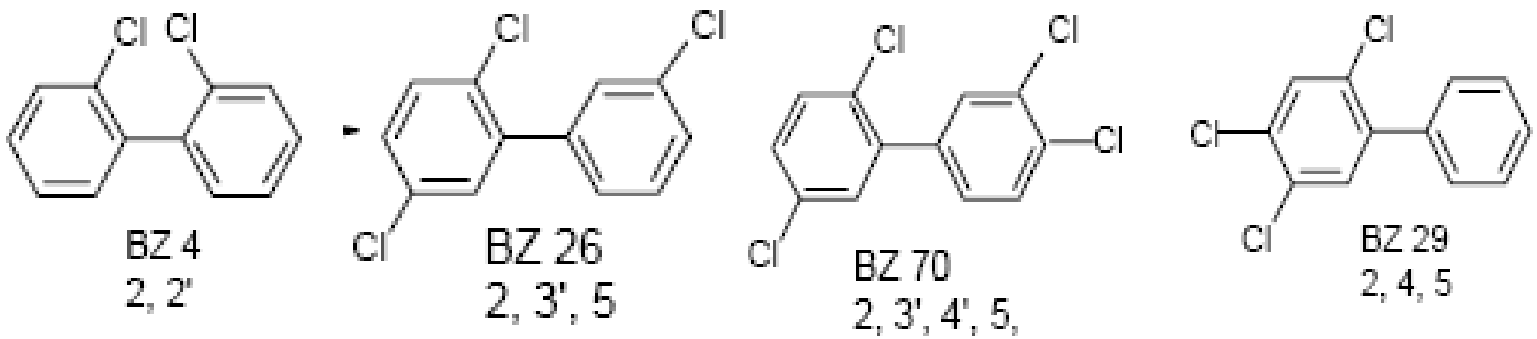
Polychlorinated Biphenyl Source Identification in Fish Tissue Using a Multivariate Statistical Evaluation of Congeners and Stable Isotope Ratio Mass Spectrometry.



Ed Corl, Ph.D
NAVSEA LQAO

Environmental Monitoring and Data Quality Workshop
St. Louis, MO
April 2016

SITE 49F BACKGROUND

U. S. Navy Photo

U. S. Navy Photo

- Contents located in pool (30 x 12 meters) at Site 49F
  - Construction debris and crushed drums.
  - Initial study indicated that the PCB contamination was confined to the concrete-lined pool.
  - Additional study located PCBs outside pool: at levels that presented risk.

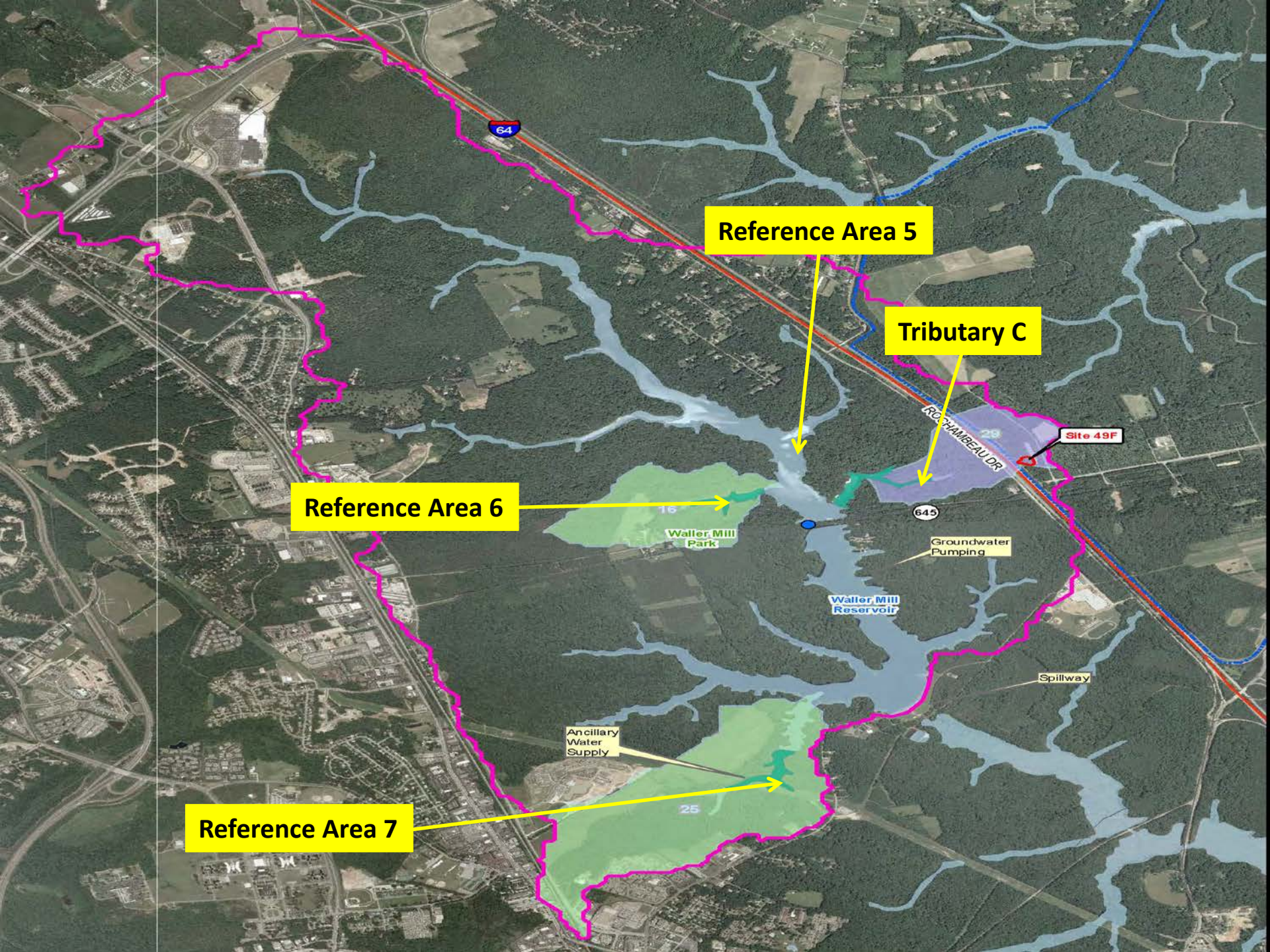
The Perfect Storm

- Area being investigated:

  Waller Mill Reservoir

  - 360-acre water supply municipal reservoir for Williamsburg.
  - Recreational boating & fishing

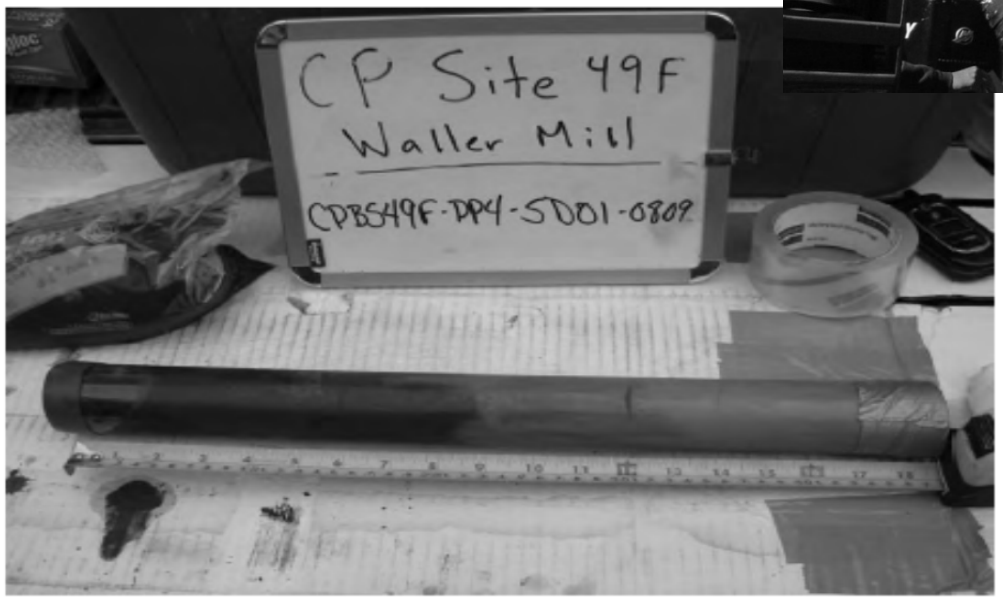
Primary Objective: The ability to use the information to determine the Navy's ultimate cleanup responsibility, liability reduction, and or cost recovery.


Reference Area 5
Tributary C
Reference Area 6
Reference Area 7
64
ROCHAMBEAU DR
Site 49F
645
Waller Mill Park
Groundwater Pumping
Waller Mill Reservoir
Spillway
Ancillary Water Supply
16
25

Sampling

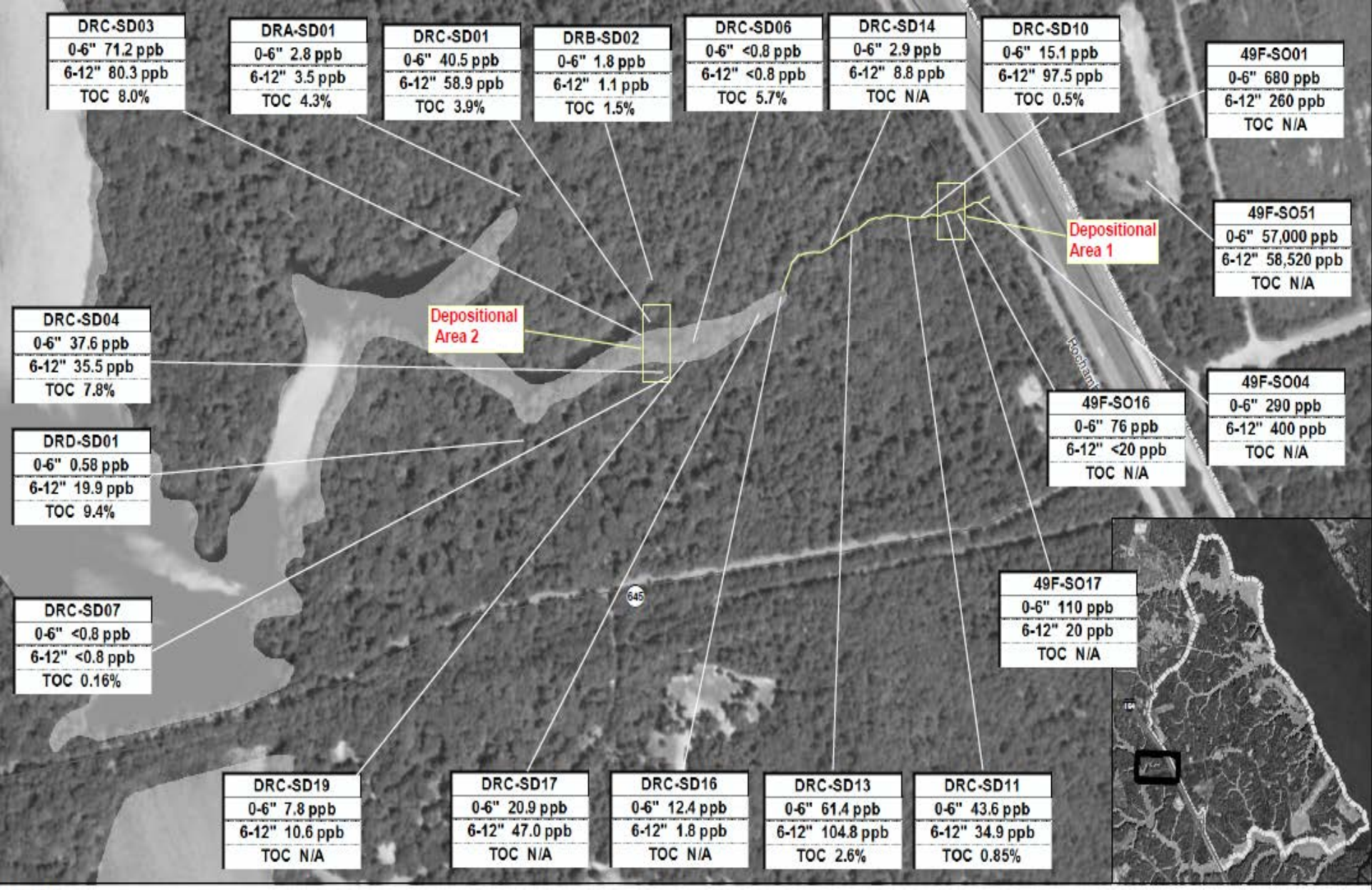
- **Soil and Sediment**
  - 153 samples total
  - 49F soil samples
  - Sediments in transport pathway (0-6", 6-12")
  - Sediments in Reservoir (lexan tube & ponar)
    - 0-6, 6-12, 12-refusal
    - 49F inlet and reference locations

- **Fish Tissue**
  - Striped bass, catfish, gizzard shad, carp
    - 93 samples total
    - Gill net & hoop net (VDGIF)
    - Skin-on fillet
  - Small class (5-10 cm) electroshocking
    - Bluegill, sunfish, yellow perch
    - Whole body composites

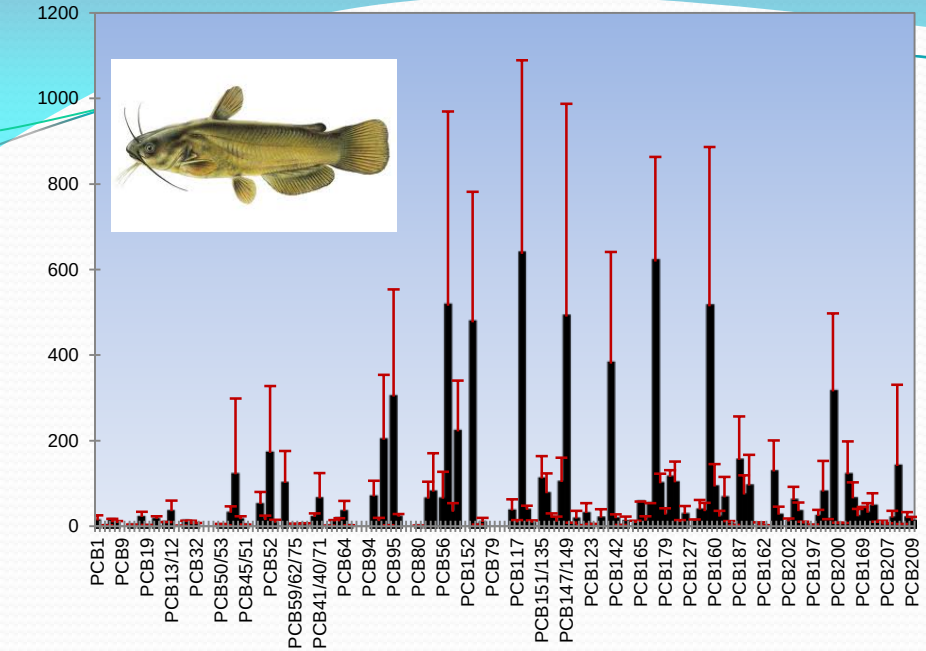


Photograph of CP Offsite 49F (Waller Mill) – PP4-SD01

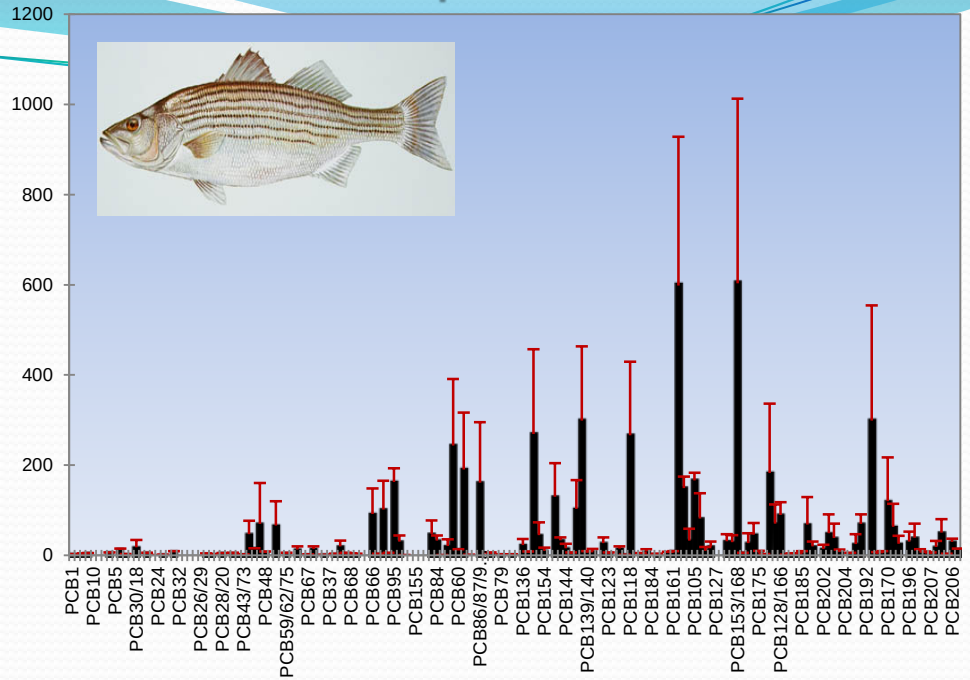
- 70-80g sample
- Hydromatrix® pulverized in stainless blender
- ASE & Soxhlet Ch_2Cl_2/Hexane
- Solid Phase Extraction & GPC
- 60m x 0.25 DB-XLB column
- Siltek® liners & Thermogreen® septa
- I.S. Quantification by (5971) MSD using SIM
- All 209 congeners used in 5 point calibration (15% RSD)
- 133 minute run time -187 congener (groups) resolved
- Detection limits in mid ppt range
- QC: CCC, Blanks, 0.05 RRT, Surrogates, NIST-1947 Reference Material/batch, and Spikes (all 209)/batch


DRC-SD03
0-6" 71.2 ppb
6-12" 80.3 ppb
TOC 8.0%
DRA-SD01
0-6" 2.8 ppb
6-12" 3.5 ppb
TOC 4.3%
DRC-SD01
0-6" 40.5 ppb
6-12" 58.9 ppb
TOC 3.9%
DRB-SD02
0-6" 1.8 ppb
6-12" 1.1 ppb
TOC 1.5%
DRC-SD06
0-6" <0.8 ppb
6-12" <0.8 ppb
TOC 5.7%
DRC-SD14
0-6" 2.9 ppb
6-12" 8.8 ppb
TOC N/A
DRC-SD10
0-6" 15.1 ppb
6-12" 97.5 ppb
TOC 0.5%
49F-SO01
0-6" 680 ppb
6-12" 260 ppb
TOC N/A
49F-SO51
0-6" 57,000 ppb
6-12" 58,520 ppb
TOC N/A
Depositional Area 1
Depositional Area 2
DRC-SD04
0-6" 37.6 ppb
6-12" 35.5 ppb
TOC 7.8%
DRD-SD01
0-6" 0.58 ppb
6-12" 19.9 ppb
TOC 9.4%
DRC-SD07
0-6" <0.8 ppb
6-12" <0.8 ppb
TOC 0.16%
49F-SO16
0-6" 76 ppb
6-12" <20 ppb
TOC N/A
49F-SO04
0-6" 290 ppb
6-12" 400 ppb
TOC N/A
49F-SO17
0-6" 110 ppb
6-12" 20 ppb
TOC N/A
645
DRC-SD19
0-6" 7.8 ppb
6-12" 10.6 ppb
TOC N/A
DRC-SD17
0-6" 20.9 ppb
6-12" 47.0 ppb
TOC N/A
DRC-SD16
0-6" 12.4 ppb
6-12" 1.8 ppb
TOC N/A
DRC-SD13
0-6" 61.4 ppb
6-12" 104.8 ppb
TOC 2.6%
DRC-SD11
0-6" 43.6 ppb
6-12" 34.9 ppb
TOC 0.85%
Legend
Base Boundary
N
W
E
S
0 150 300 600
Feet

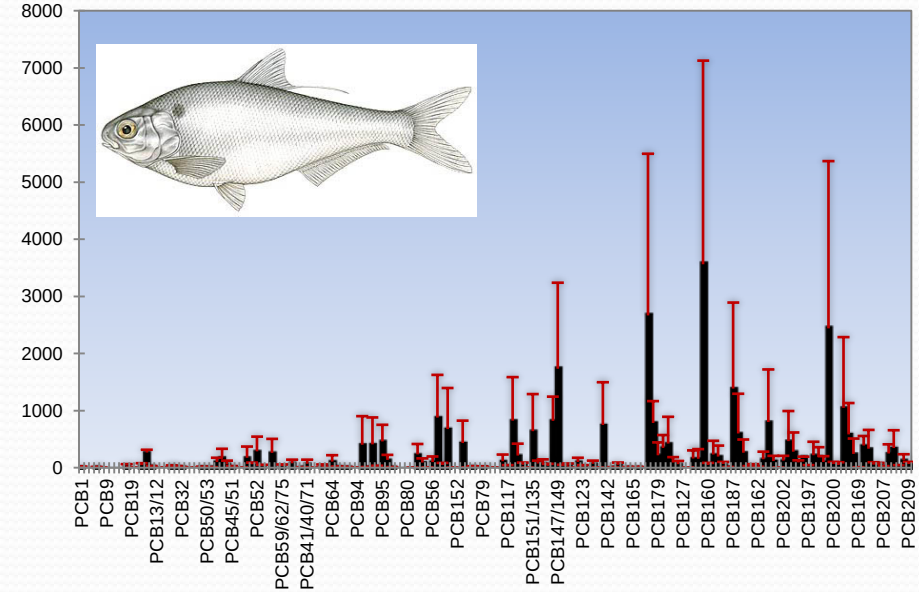
Catfish



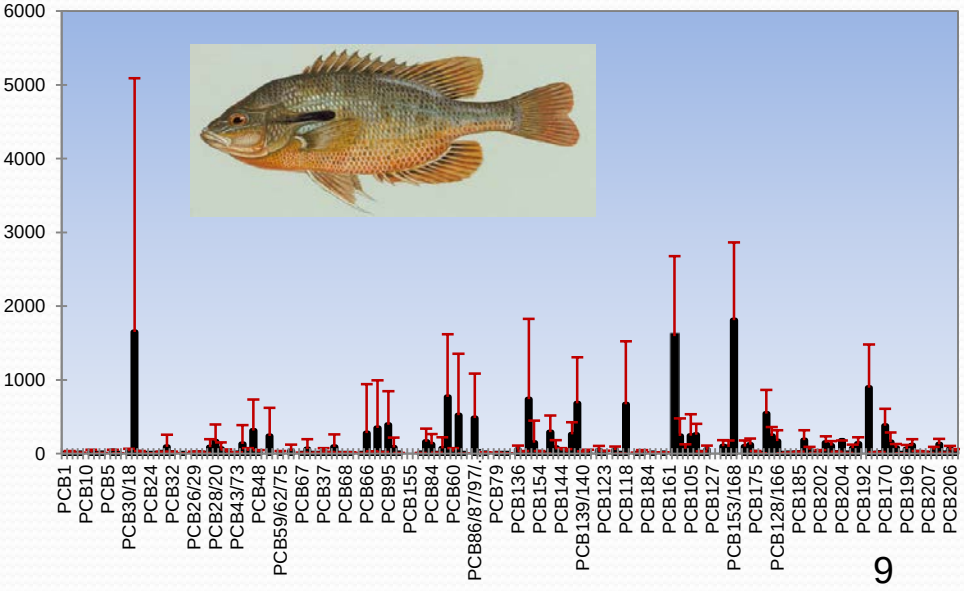
Striped Bass



Gizzard Shad



Blue Gill



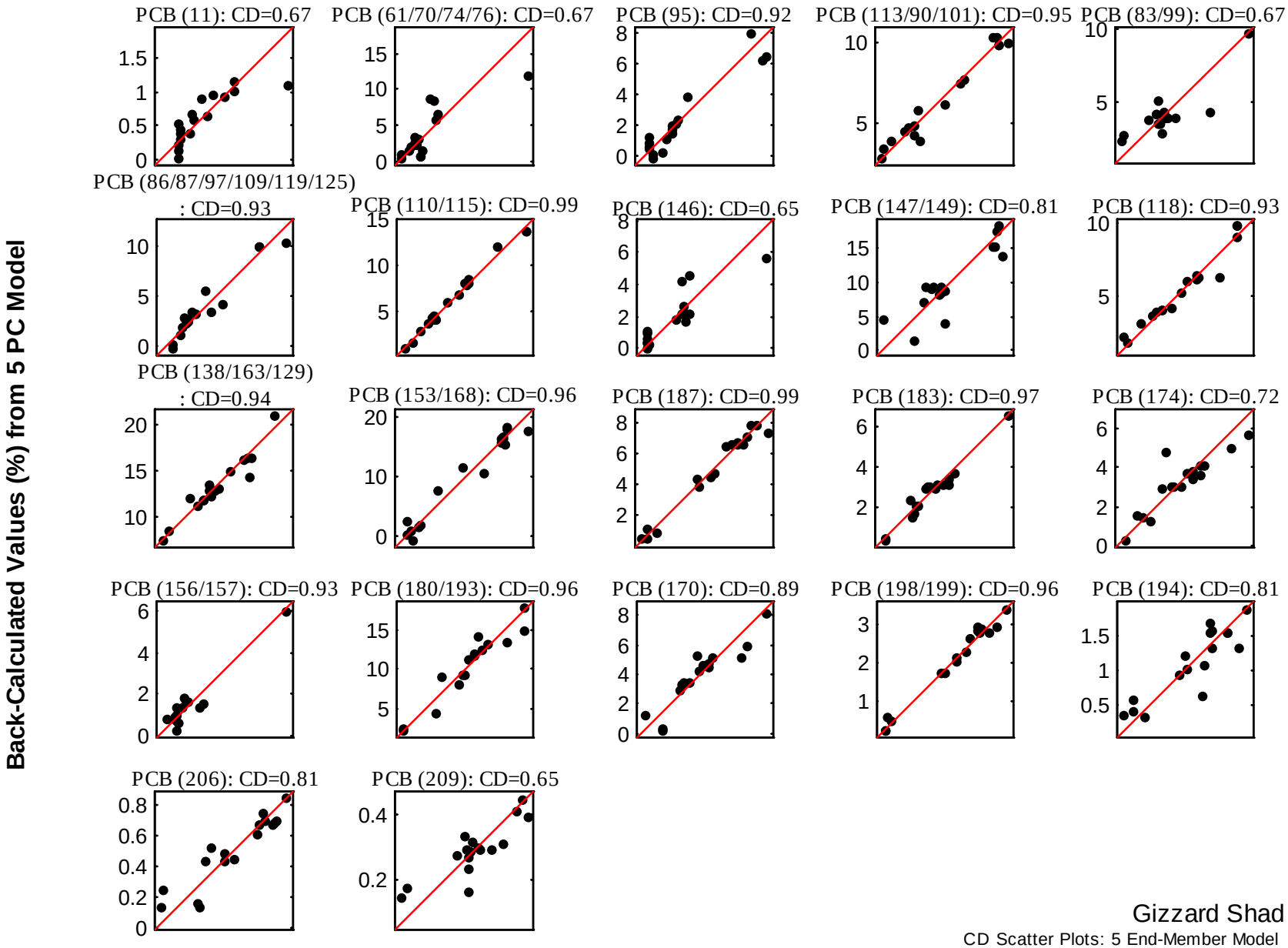
Polytopic Vector Analysis (PVA)

$$X_{(m*n)} = A_{(m*k)} F_{(k*n)} + \varepsilon_{(m*n)}$$

- Careful screening of data
- 22 Diagnostic Congeners selected
- Multivariate Statistical Process (Heuristic)
- Normalized Data Matrices
- Principal Component Analysis
- Sensitivity Analysis on EM mixing
- Oblique Rotation of Axes
- Back calculated proportions in samples

Principal Component Evaluation for Gizzard Shad				
PC Number	Eigenvalue	Cumulative Percent Variance	Normalized Varimax Loadings	Henry's Signal-to-Noise ratio
1	11.63	72.9388	Factor 1: 16 of 17 samples.	33.7573
2	2.991	87.7913	Factor 2: 14 of 17 samples.	14.519
3	2.34	91.1464	Factor 3: 13 of 17 samples.	4.4621
4	2.101	94.0534	Factor 4: 5 of 17 samples.	3.6182
5	1.325	96.3233	Factor 5: 3 of 17 samples.	2.2189
6	0.749	97.9188	Factor 6: 2 of 17 samples.	1.7589
7	0.265	98.756	Factor 7: 1 of 17 samples.	1.0924
8	0.230	99.2134	Factor 8: 1 of 17 samples.	0.5663
9	0.198	99.5451	Factor 9: 1 of 17 samples.	0.471
10	0.067	99.7708	Factor 10: 1 of 17 samples.	0.3329
11	0.046	99.9034	Factor 11: 0 of 17 samples.	0.1063
12	0.023	99.9402	Factor 12: 0 of 17 samples.	0.0564
13	0.012	99.9703	Factor 13: 0 of 17 samples.	0.0464
14	0.007	99.9875	Factor 14: 0 of 17 samples.	0.0317
15	0.001	99.997	Factor 15: 0 of 17 samples.	0.0152
16	0.001	99.9987	Factor 16: 0 of 17 samples.	0.0041
17	0.001	100	Factor 17: 0 of 17 samples.	0

Table 7.1: Criteria-Based Index Evaluations for Estimating the Number of Critical Components (End-Members) for Gizzard Shad. Selection Criteria Was Set at 95% Cumulative Percent Variance, Inflection in the Normalized Varimax Loadings, and a Henry's S:N of 2.



Gizzard Shad

CD Scatter Plots: 5 End-Member Model

Testing Eds Data(59x25 matrix)(59x22 matrix)(17x22 matrix)

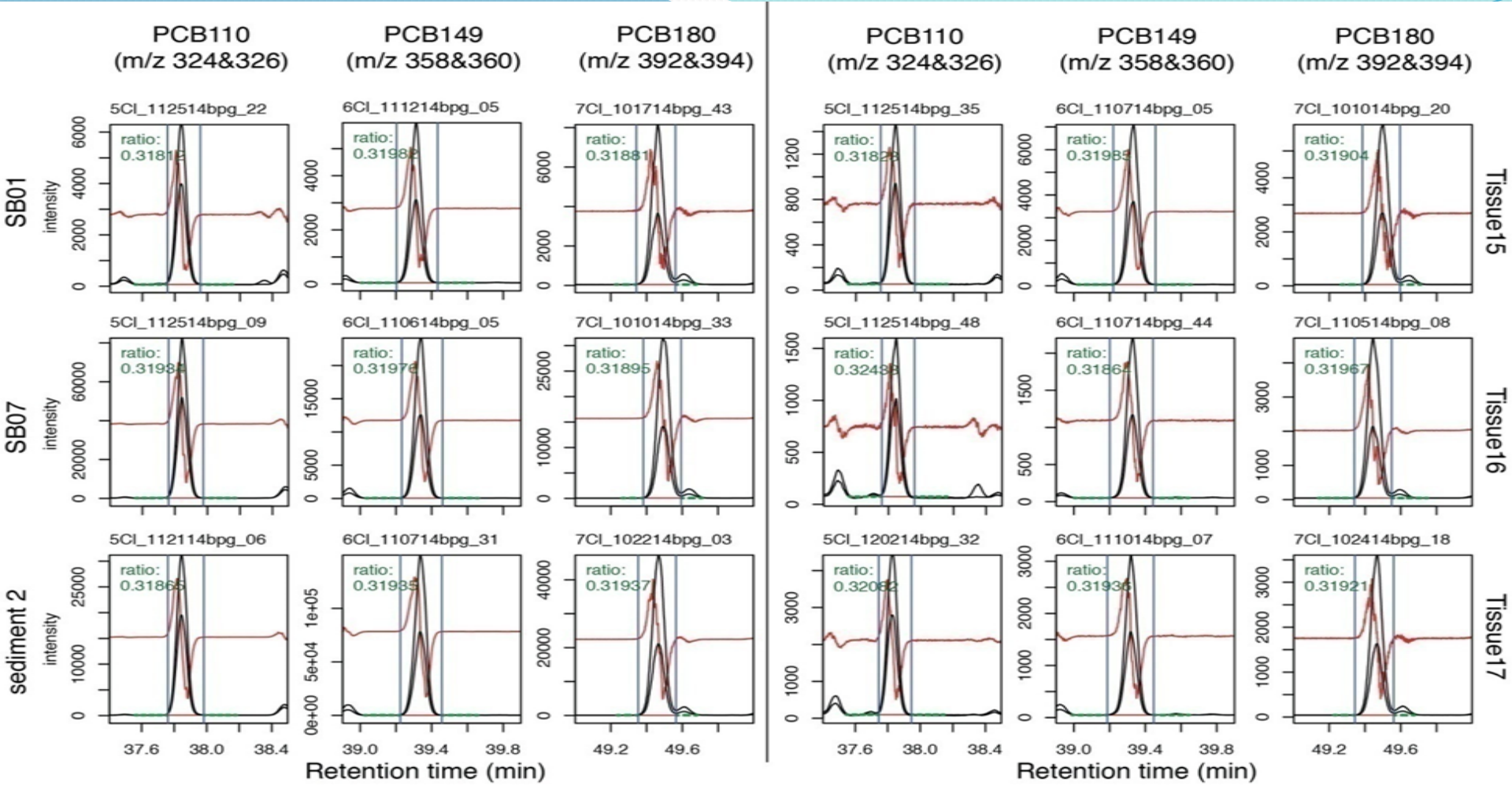
Bluegill	EM1	EM2	EM3	EM4	EM5
PCB (11)	0	0	0	0	85.81
PCB (61/70/74/76)	1.2014	0.6564	4.1969	0	0
PCB (95)	1.2332	0.6006	4.664	0	0
PCB (113/90/101)	5.5948	0.0542	7.8613	0	0
PCB (83/99)	0.9767	0	10.284	1.0646	0
PCB (86/87/97/109/119/125)	0	0	11.562	1.1791	0
PCB (110/115)	0	0	20.101	2.2234	0
PCB (146)	3.8396	0.3709	1.3954	0.5392	0.7749
PCB (147/149)	6.4679	0.1765	5.5828	0	0
PCB (118)	0.7688	0	15.72	2.6073	0
PCB (138/163/129)	18.485	0	16.662	3.7372	5.4145
PCB (153/168)	30.36	0	0	0	5.2065
PCB (187)	10.082	0	0.218	0.6922	1.7109
PCB (183)	4.4662	0.6354	0	0.1231	0.7214
PCB (174)	2.4828	0.7823	0.5495	0.2595	0.1495
PCB (156/157)	0	0.053	1.2033	14.256	0
PCB (180/193)	11.06	0	0	28.233	0
PCB (170)	2.0358	0	0	24.607	0
PCB (198/199)	0.947	34.947	0	2.0369	0
PCB (194)	0	0.3098	0	14.507	0
PCB (206)	0	46.389	0	3.9345	0
PCB (209)	0	15.026	0	0	0.2126

Cos Theta angles between small class fish end members and potential sources in measurement space

	EM1	EM2	EM3	EM4	EM5	REF7 ASD03 0-6"	REF7 ASD03 6-12"	REF6 BSD02 0-6"	REF6 BSD02 6-12"	REF5 SD02 0-6"	REF5 SD02 6-12"	49F inlet 0-6"	49F PP1 BSD02 12-24"	49F DRC SD03 6-12"	49F PP2 SD04 0-6"	49F PP2 SD04 6-12"	49F PP4 SD01 0-6"	49F PP4 SD01 6-12"
EM1	1.000	0.018	0.297	0.258	0.082	0.446	0.589	0.586	0.578	0.897	0.603	0.913	0.868	0.857	0.843	0.317	0.570	0.519
EM2		1.000	0.004	0.100	0.001	0.020	0.030	0.036	0.078	0.106	0.072	0.077	0.165	0.075	0.086	0.016	0.031	0.026
EM3			1.000	0.122	0.029	0.848	0.928	0.849	0.803	0.475	0.837	0.419	0.554	0.384	0.604	0.470	0.883	0.833
EM4				1.000	0.006	0.138	0.223	0.187	0.181	0.510	0.245	0.441	0.473	0.547	0.478	0.103	0.201	0.167
EM5					1.000	0.037	0.071	0.325	0.303	0.112	0.300	0.071	0.186	0.065	0.200	0.854	0.283	0.279
Ref7 surf						1.000	0.919	0.882	0.924	0.570	0.901	0.525	0.626	0.457	0.680	0.537	0.886	0.941
Ref7 ssurf							1.000	0.935	0.904	0.716	0.931	0.664	0.768	0.614	0.810	0.536	0.952	0.909
Ref6 surf								1.000	0.966	0.706	0.953	0.665	0.765	0.605	0.829	0.745	0.996	0.958
Ref6 ssurf									1.000	0.696	0.981	0.665	0.777	0.596	0.811	0.749	0.957	0.992
Ref5 surf										1.000	0.728	0.975	0.972	0.971	0.978	0.416	0.695	0.635
Ref5 ssurf											1.000	0.691	0.820	0.630	0.832	0.735	0.956	0.978
49F inlet-surf												1.000	0.952	0.979	0.946	0.366	0.649	0.602
49F PP1-ssurf													1.000	0.936	0.972	0.512	0.759	0.722
49F DRC														1.000	0.935	0.327	0.591	0.531
49F PP2-surf															1.000	0.549	0.818	0.761
49F PP2-ssurf																1.000	0.713	0.735
49F PP4-surf																	1.000	0.957
49F PP4-ssurf																		1.000

$$\cos \emptyset_{nm} = \frac{\sum_{j=1}^{p} x_{nj} x_{mj}}{\sqrt{\sum_{j=1}^{p} x_{nj}^2 \sum_{j=1}^{p} x_{mj}^2}}$$

S. BASS END MEMBER MIXING PROPORTIONS					
Sample	EM1	EM2	EM3	EM4	EM5
SB1	0.1429	0.2843	0.0338	0.1783	0.3607
SB2	0.0939	-0.0525	0.1095	0.3076	0.5415
SB5	0.1751	0.35	0.0765	0.1783	0.22
SB3	0.3906	0.3817	0.1503	0.0897	-0.0123
SB6	0.1861	-0.0968	0.6261	-0.0136	0.2982
SB7	0.0954	0.5063	0.1207	-0.0136	0.2912
SB9	-0.0223	0.154	0.0891	0.1137	0.6655
SB4	0.3949	0.2033	-0.0149	0.0507	0.366
SB4a	0.4271	0.3026	0.1102	0.0663	0.0938
SB8	0.044	0.2375	0.0251	-0.0091	0.7025
Cos Theta Similarity	**0.890 Ref7**	**0.783 49F**	**0.531 49F**	**0.718 49F**	**0.789 49F**

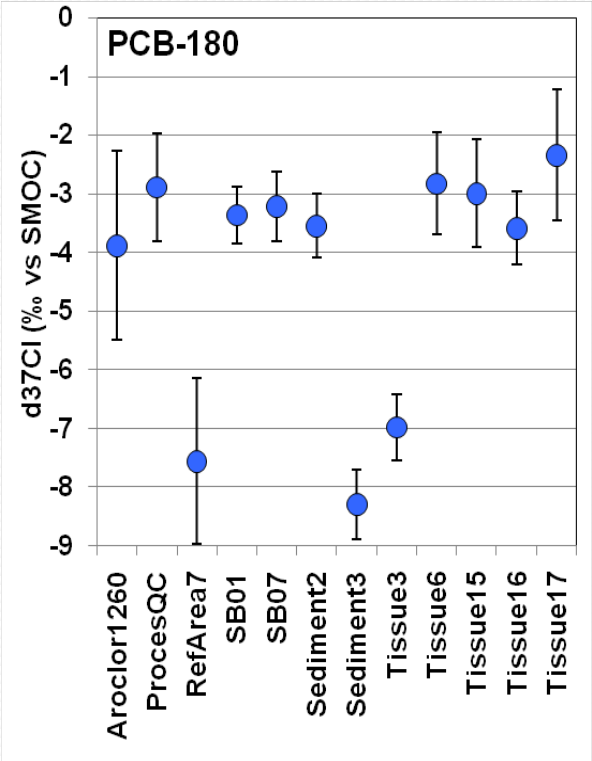


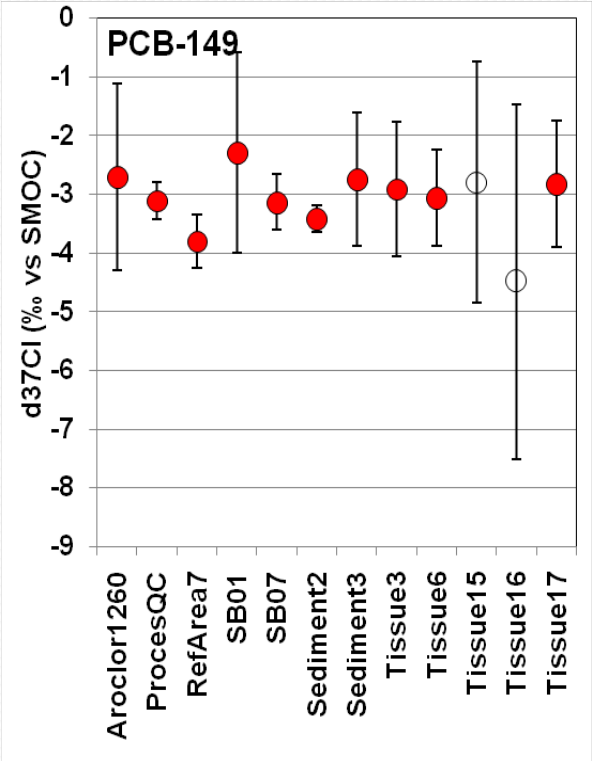
- Multiple sample injections bracketed by isotopologue of known $^{\delta 37}Cl$
- Peak integration routine (in R) based on peak slopes w/background subtraction

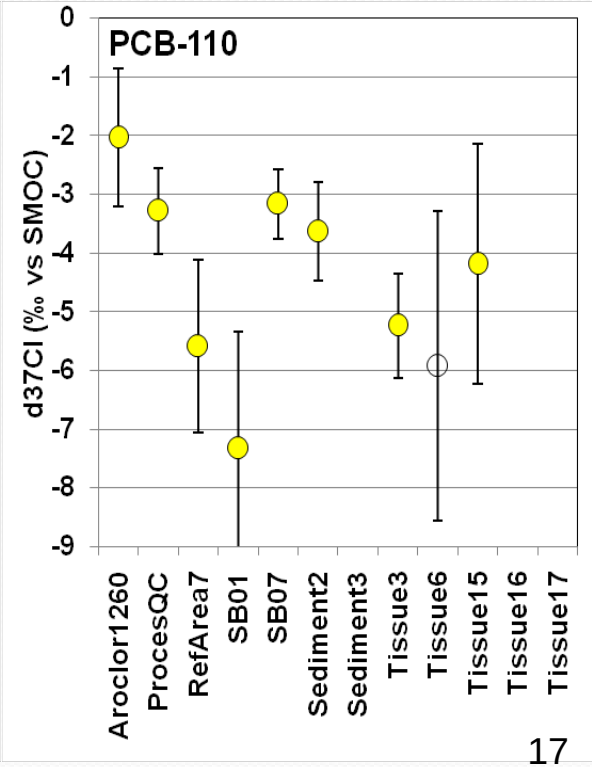
$$R_{Cl}^{180} = \frac{1}{7} * \frac{A_1^{m/z394}}{A_0^{m/z392}}$$

Direct Compound-Specific Stable Chlorine Isotope Analysis of Organic Compounds with Quadrupole GC/MS Using Standard Isotope Bracketing. **Christoph Aeppli,† Henry Holmstrand,*,† Per Andersson,‡ and O¨ rjan Gustafsson†,** *Analytical Chemistry, Vol. 82, No. 1, January 1, 2010.* *(Bigelow labs)*

Isotope	Protons	Neutrons	Abundance	"Form"
^{35}Cl	17	18	75.8%	Stable
^{37}Cl	17	20	24.2%	Stable
^{12}C	6	6	98.9%	Stable
^{13}C	6	7	1.07%	Stable
^{14}C	6	8	Trace (10^{-12})	Radioactive*







Conclusions

- Arochlor signatures in 49F and Ref 5 locations similar Profiles (1260)
- Ref 6/7 locations are different (1254) and likely “capped” – Sedimentation
- PCBs from 49F more readily re-suspended and transported to reservoir proper-(Bioavailable)
- Once downstream from PP2-Profile similarities w/reference areas increase
- Highest PCB concentrations in Ref.7 sediments

Conclusions

- PVA Results:
  - 3-5 End-Members (sources)
  - End-members from each species show 49F and reference area influences
  - Mixing Proportions in fish samples suggest predominance of source signatures that are consistent with 49F and Reference Area 5
  - Numerous End-Members in Fish that have low similarities to sampled sediments

Conclusions

- Isotopic Results:
  - Lack of ^{13}C Data
  - ^{37}Cl- inconclusive but not inconsistent with PVA
  - $\delta^{37}Cl$ - Results consistent with earlier research using TIMS suggesting a viable method (loss of precision)
  - Fractionation during extraction/analysis for PCB-180 & PCB-110
  - No fractionation PCB-149