Microbial dechlorination of polychlorinated biphenyls, dibenzo-p-dioxins, and -furans in groundwater at the Portland Harbor superfund site, Oregon, USA

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Supporting information

Seven figures

One table

Figure S-1. Map of Portland Harbor superfund site showing major known contaminated sites.

Figure S-2. Map of Portland Harbor showing water sampling sites labeled by river mile (RM). Upstream sites at RM 11 and 15.9 are not shown for clarity. Map drawn with Google earth.

Table S-1. List of congeners used in PMF modeling and coelution patterns.

Sediment (DB-5 column)		Water column (SPB-octyl column)		
PCB004 & 010	PCB129	PCB 4	PCB 88	PCB 197+200
PCB011	PCB130	PCB 6	PCB 90+101+113	PCB 198+199
PCB016 & 032	PCB132 & 161	PCB 8	PCB 92	PCB 202
PCB017	PCB133 & 142	PCB 10	PCB 95+100+93+102+98	PCB 203
PCB018	PCB134 & 143	PCB 11	PCB 94	PCB 206
PCB019	PCB135	PCB 15	PCB 103	PCB 209
PCB020 & 021 & 033	PCB136	PCB 16	PCB 105	
PCB022	PCB137	PCB 17	PCB 110+115	
PCB026	PCB138 & 163 & 164	PCB 18+30	PCB 114	
PCB028	PCB139 & 149	PCB 19	PCB 123	
PCB031	PCB141	PCB 20+28	PCB 128+166	
PCB037	PCB144	PCB 21+33	PCB 138+163+129+160	
PCB041 & 064 & 071 & 072	PCB146 & 165	PCB 22	PCB 130	
PCB042 & 059	PCB151	PCB 25	PCB 132	
PCB043 & 049	PCB153	PCB 26+29	PCB 134+143	
PCB044	PCB156	PCB 27	PCB 151+135+154	
PCB047	PCB157	PCB 31	PCB 136	
PCB048 & 075	PCB158 & 160	PCB 32	PCB 141	
PCB052 & 069	PCB167	PCB 37	PCB 144	
PCB053	PCB170	PCB 40+41+71	PCB 146	
PCB056 & 060	PCB171	PCB 42	PCB 147+149	
PCB061 & 070	PCB172	PCB 44+65+47	PCB 153+168	
PCB066 & 076	PCB174	PCB 45+51	PCB 156+157	
PCB074	PCB176	PCB 46	PCB 158	
PCB077	PCB177	PCB 48	PCB 164	
PCB082	PCB178	PCB 49+69	PCB 169	
PCB084 & 092	PCB179	PCB 50+53	PCB 170	
PCB085 & 116	PCB180	PCB 52	PCB 171+173	
PCB087 & 117 & 125	PCB182 & 187	PCB 54	PCB 172	
PCB088 & 091	PCB183	PCB 56	PCB 174	
PCB090 & 101	PCB185	PCB 59+62+75	PCB 176	
PCB095 & 098 & 102	PCB189	PCB 60	PCB 177	
PCB097	PCB190	PCB 61+70+76+74	PCB 178	
PCB099	PCB193	PCB 64	PCB 179	
PCB105	PCB194	PCB 66	PCB 180+193	
PCB106 & 118	PCB195	PCB 77	PCB 183+185	
PCB107 & 109	PCB196 & 203	PCB 81	PCB 187	
PCB108 & 112	PCB199	PCB 82	PCB 189	
PCB110	PCB202	PCB 83+99	PCB 190	
PCB114	PCB206	PCB 84	PCB 194	
PCB128 & 162	PCB208	PCB 117+116+85	PCB 195	
	PCB209	PCB 108+119+86+97+125+87	PCB 196	

Data matrix details

PMF details

A major challenge in using this data was the absence of surrogate recoveries and sparse information about limits of detection (LOD), both of which are needed to construct accurate input matrices for PMF analysis. Where concentrations were below detection limit, the LOD was reported instead of the measured concentration in STORET but not in the RI database. Thus for the LOD matrixes for PMF analysis, the limited data on LODs were used to reconstruct what the LODs must have been for congeners that were detected, based on the assumption that LODs were the same for all congeners in a homologue in any given sample. In the concentration matrix, concentrations that were below detection limit were replaced with one-half of the inferred detection limit. LODs ranged from 0.1 to 358 pg/g for PCBs in sediment, from 0.00020 to 1.4 pg/L for PCBs in the water column, and from 0.00064 to 3.5 pg/L for PCDD/Fs in water.

The uncertainty matrix is usually constructed from the relative standard deviation of the percent recoveries of the surrogate that is applied to each analyte. In the total absence of surrogate recovery information, the uncertainty matrix was borrowed from previous studies that used the same analytical methods and the same matrixes i.e. Du et al. [1] for the water column PCBs, Rodenburg et al.[2] for the water column PCDD/Fs, and Praipipat et al. [3] for the sediment PCBs. Note that uncertainties are input as a fraction for the PMF2 software, but as absolute concentrations in the PMF 5.0 software.

Justification for selection of the number of factors

PCBs in sediment

PMF2: Three, four, five, and six factor solutions were generated. The four factor model was selected. For the four-factor model, all nine seed runs were similar with an RSD of the G matrix of 1.8%. All four of these factors had positive and significant coefficients when the G matrix was regressed against the measured sum of PCBs. In contrast, this regression for the five-factor model revealed one factor with a coefficient that was not significant. Also, for the five factor model, two of the nine seed runs were very different from the other seven. The G-space plots indicated that all factors of the four-factor solution were independent of each other. The agreement (R^2) between measured and modeled concentrations was greater than 0.77 for 80 of 83 peaks. The three peaks/congeners with low R^2 were PCB 206 (0.38), PCB (0.34) and PCB 209 (0.53). However, the good agreement between measured and modeled concentrations for PCBs 4+10 and 19 (which are markers of dechlorination) were driven by the two data points with the highest concentrations of these congeners, both collected at RM 8.8. When these two samples are discarded, the agreement between measured and modeled concentrations is much worse for these congeners due to several outliers with high measured concentrations.

PMF 5.0: Bootstrapping of the 4- and 5-factor models confirmed that 4 was the correct number of factors. Out of 100 bootstrap runs, at least 86 mapped correctly when 5 factors were requested. When 6 factors were requested, the new factor was 'smeared' across five of the six factors, with 21, 4, 24, 6 and 1 of the bootstrap runs mapped across the five. This indicates that the new factor was not meaningful.

PCBs in water column

PMF2: Four, five, six, and seven factor solutions were generated. The five factor model was selected. The five factor solution had low RSD of the G matrix (0.43%). The six factor model had two outliers

among the nine seed runs. Although both the five and six factor models gave positive and significant coefficients for all factors when the G matrixes were regressed against the measured sum of PCBs, two of the factors in the six-factor model were similar in fingerprint (both resembled Aroclor 1260). Therefore the five factor model was selected. The agreement (R^2) between measured and modeled concentrations was greater than 0.7 for 85 of 90 peaks. The peaks/congeners that were not well modeled were PCB 11 (R^2 = 0.51), PCB 81 (0.24), PCB 123 (0.18), PCB 169 (0.027), and PCB 209 (0.40). Note that PCBs 81, 123, and 169 were included in the data matrix despite low concentrations because they are dioxin-like congeners. The G space plots for the five factor model showed strong correlation between factors W2 and W5, but this was because the regression was dominated by the seven samples with the highest PCB concentrations, all of which were collected at Willamette Cove. When the nine samples collected at Willamette Cove were removed, all of the factors were independent of each other.

PMF 5.0: Bootstrapping of the 5- and 6-factor models confirmed that 5 was the correct number of factors. Out of 100 bootstrap runs, at least 92 mapped correctly when 5 factors were requested. When 6 factors were requested, the new factor was 'smeared' across four of the six factors, with 6, 37, 42, and 1 of the bootstrap runs mapped across the four, and 14 'unmapped' runs. This indicates that the new factor was not meaningful. For the 5-factor model, 74 of the 90 congeners were modeled more accurately by the PMF2 model. The same five congeners (R^2) were not well modeled by PMF 5.0: PCB 11 (R^2 = 0.31), PCB 81 (0.27), PCB 123 (0.21), PCB 169 (0.088), and PCB 209 (0.31). However, two additional congeners were not well modeled by PMF 5.0: PCB 6 (R^2 = 0.42 via PMF 5.0 vs. 0.84 via PMF2), PCB 8 (0.17 vs. 0.94).

PCBs and PCDD/Fs in the water column

PMF2: Four, five, six, seven, and eight factor solutions were generated. The seven factor model was selected. The six and eight factor models did not converge on a robust solution, with the nine seed runs generating at least three distinct solutions. In contrast, for the seven factor solution, eight of the nine seed runs were in good agreement with each other (RSD of the G matrix = 1.4%). All seven factors yielded positive and significant coefficients in the regression of the G matrix versus the sum of analytes, and all seven were independent of each other. The agreement between measured and modeled concentrations was greater than 0.7 for 73 of 77 analytes. Analytes with low R^2 values were 1,2,3,7,8,9-HxCDD, 1,2,3,7,8-PCDD, and 2,3,4,6,7,8-HxCDF, all of which had R^2 values greater than 0.65, and PCB 126, a dioxin-like congener. As with the solution for PCBs in the water column, the seven factors were independent of each other when the nine samples from Willamette Cove were excluded.

PMF 5.0: PMF 5.0 was not able to generate a useful solution for this data set. When the original uncertainty matrix was used, none of the base runs converged on a solution. The PMF 5.0 User Guide[4] suggests that this might be caused by underestimation of uncertainty, so the uncertainty matrix was increased by 50% for all data points. With this higher uncertainty, a small number (perhaps 4 out of 20) of the base runs converged when 3 to 6 factors were requested, but none converged when 7 factors were requested. Despite the fact that PMF 5.0 could not corroborate the PMF2 results, the PMF2 results were deemed reliable because the PCB portion of each factor resembled one of the factors generated by the PCB-only data matrix above.

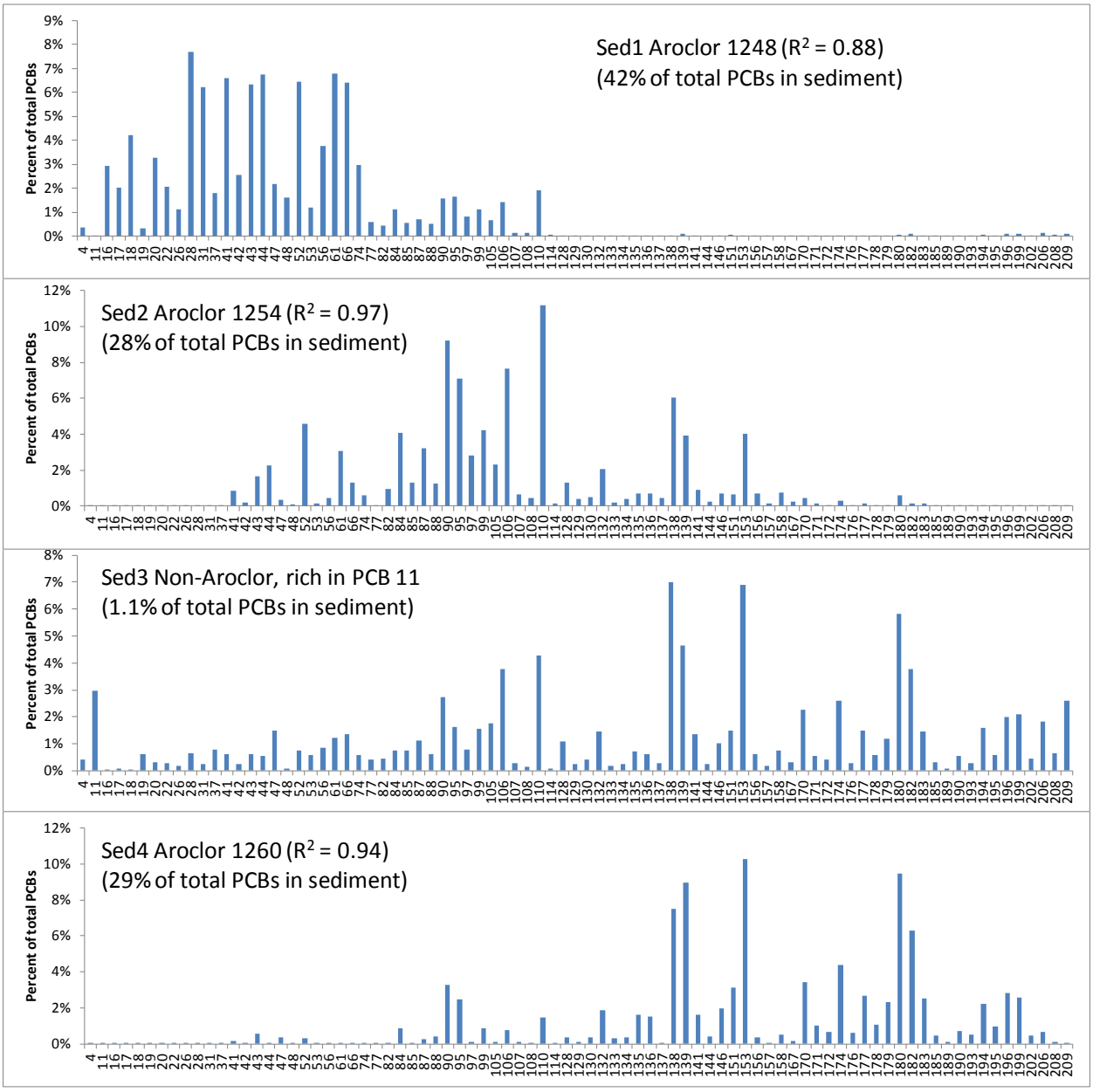

Figure S-3. Four factors resolved from the data matrix on PCBs in sediment.

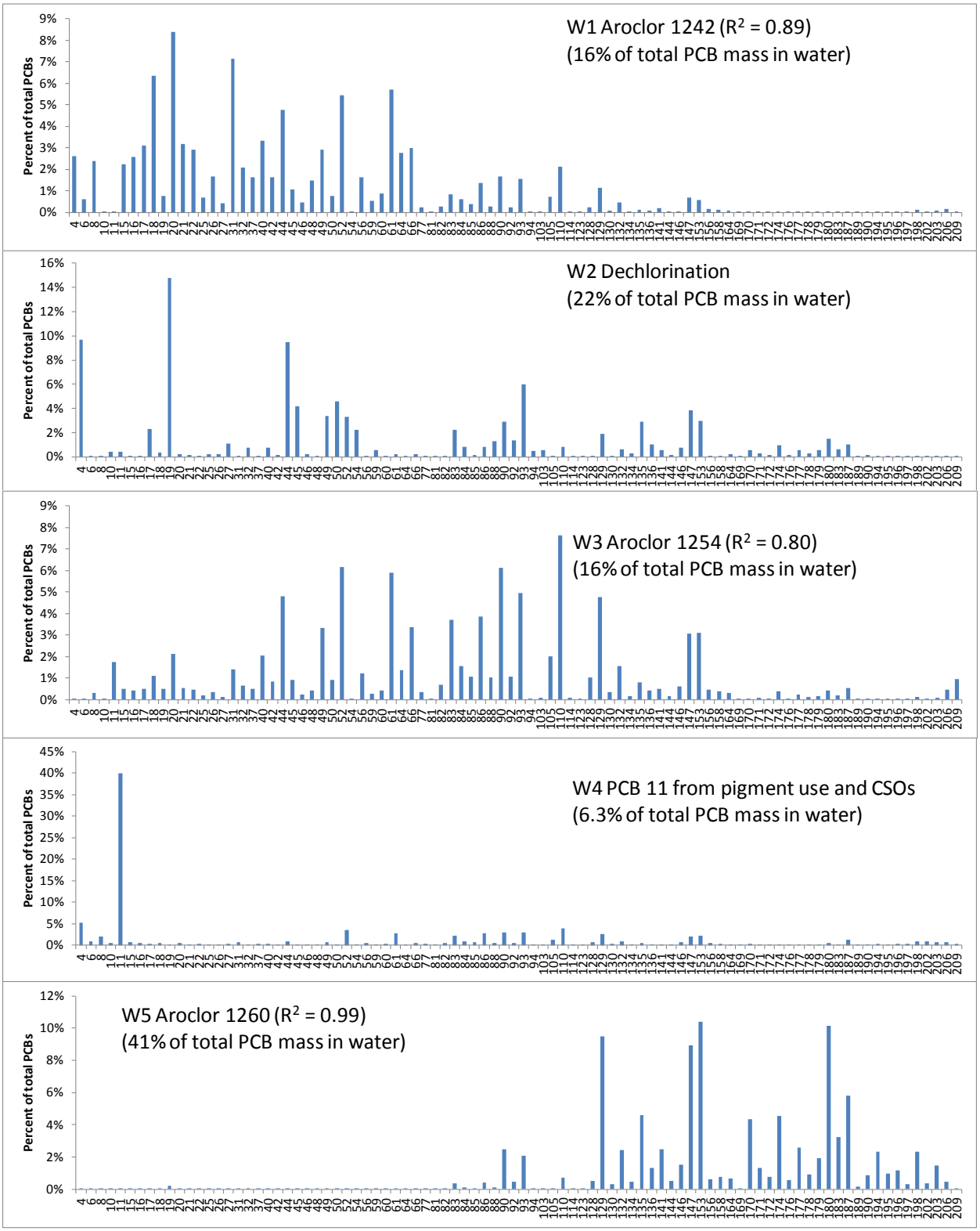

Figure S-4. Five factors resolved from the data set on PCBs in the water column.

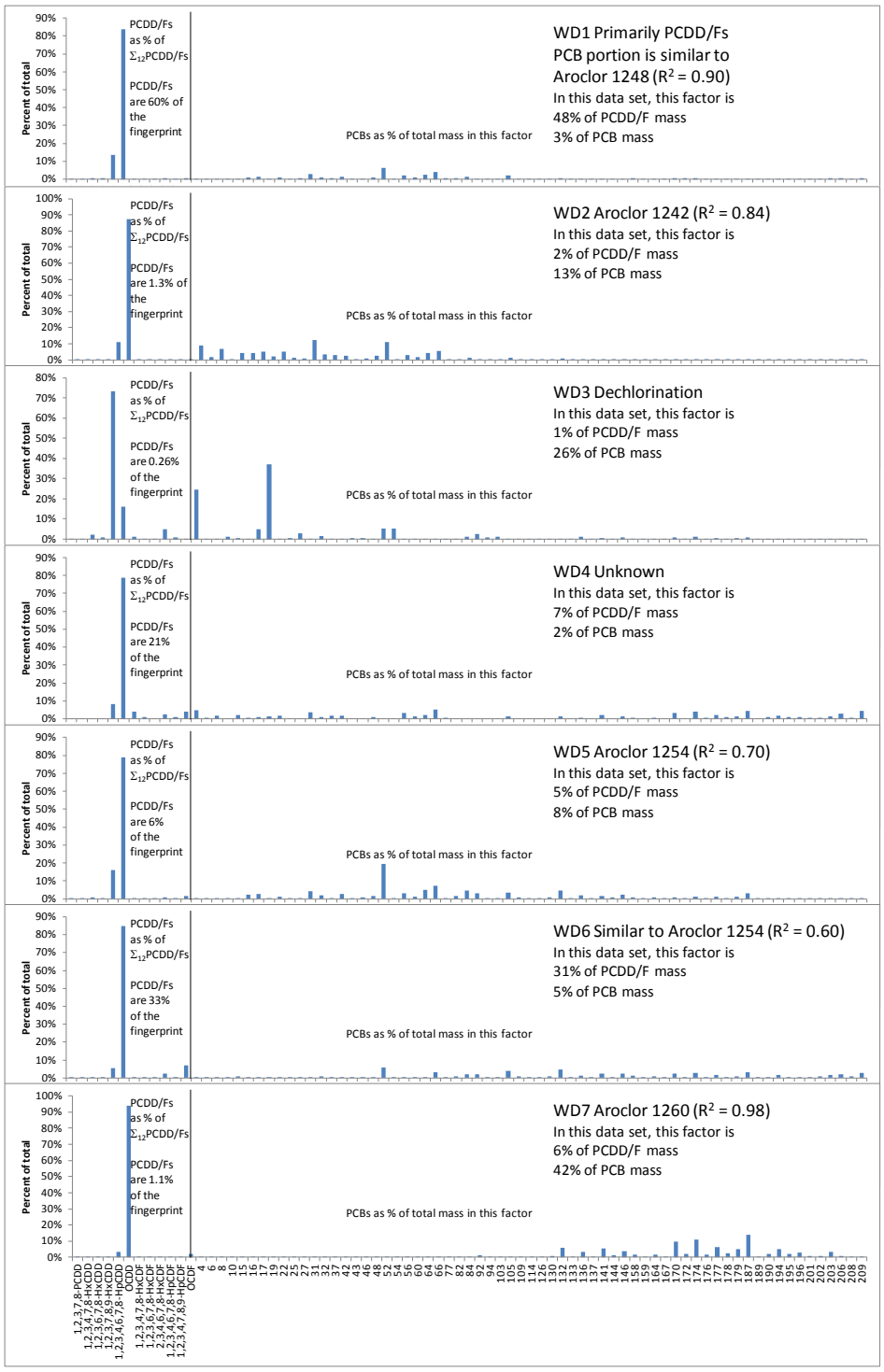

Figure S-5. Seven factors resolved from the data matrix of 12 PCDD/Fs congeners and 65 PCB congeners in the water column. Note that the % of the total mass in the data set represented by each factor is not a reliable indicator of the % of total PCBs in the water column, since this data set includes only a fraction of the PCBs measured.

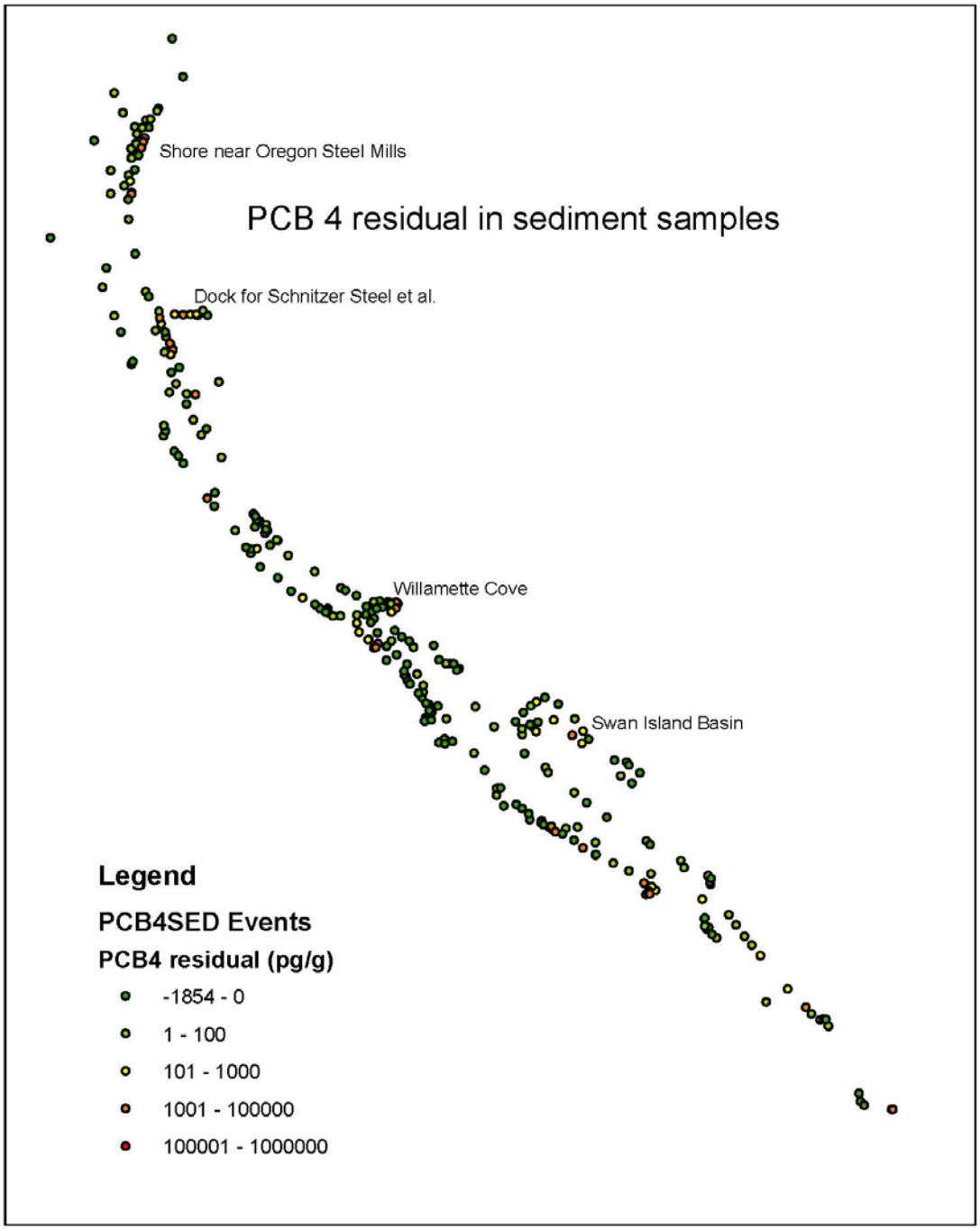

Figure S-6. Map of PCB 4 residual (measured minus modeled) in sediment.

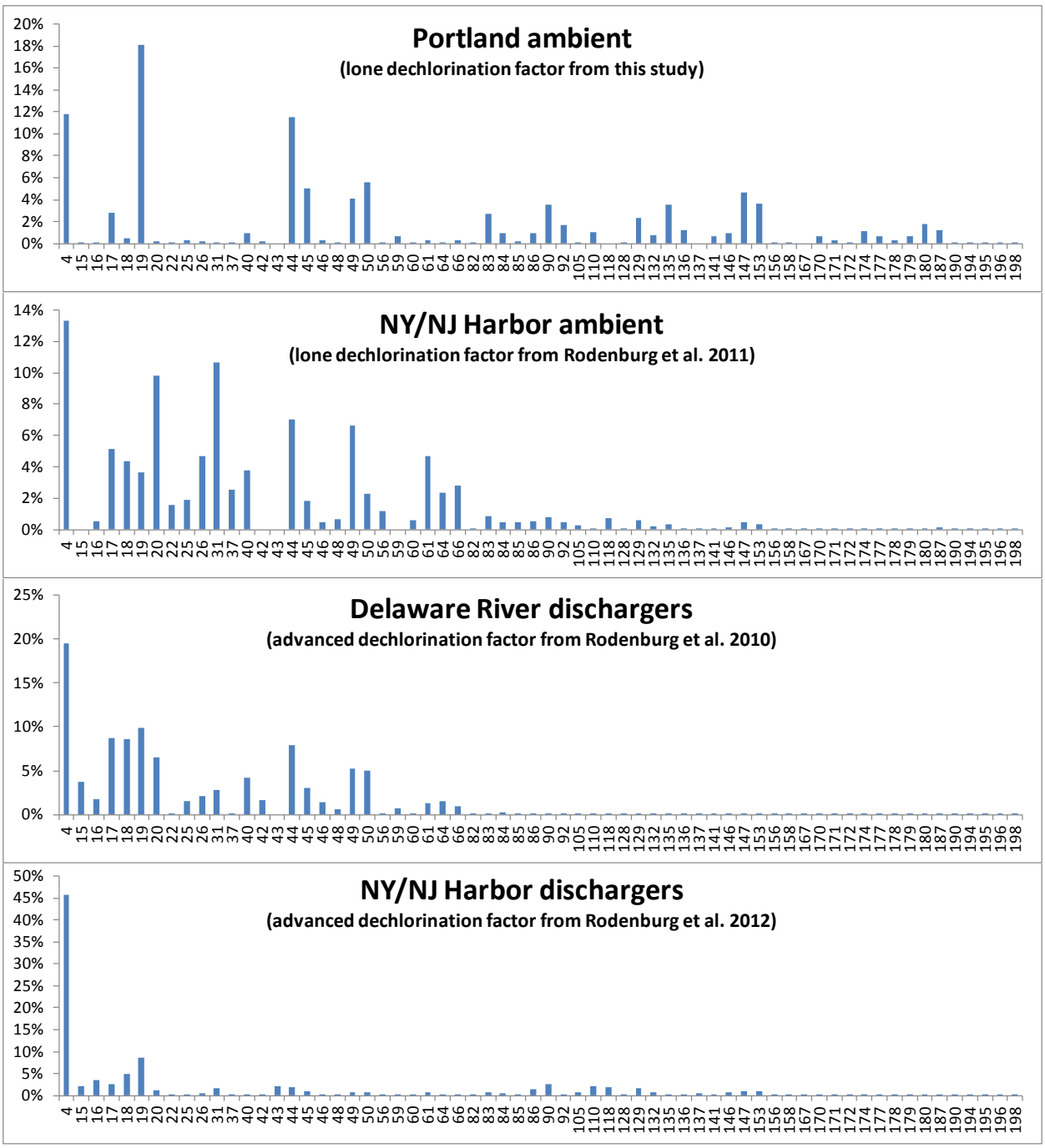

Figure S-7. Dechlorination factors resolved from factor analysis using various data sets. Because each data set utilized slightly different congener lists, only congeners common to all four data sets are shown. Note that co-eluting congeners are labeled using the lowest IUPAC congener number. All of these data sets utilized an SPB octyl GC column, so information about co-elutions is provided in Table S-1.

References

1. Du, S.; Belton, T. J.; Rodenburg, L. A., Source Apportionment of PCBs in the Tidal Delaware River. *Environ. Sci. Technol.* **2008,** *42*, 4044–4051.
2. Rodenburg, L. A.; Du, S. Y.; Lui, H.; Guo, J.; Oseagulu, N.; Fennell, D. E., Evidence for Dechlorination of Polychlorinated Biphenyls and Polychlorinated Dibenzo-p-Dioxins and -Furans in Wastewater Collection Systems in the New York Metropolitan Area. *Environmental Science & Technology* **2012,** *46*, (12), 6612-6620.
3. Praipipat, P.; Rodenburg, L. A.; Cavallo, G. J., Source Apportionment of Polychlorinated Biphenyls in the Sediments of the Delaware River. *Environ. Sci. Technol.* **2013,** *47*, 4277−4283.
4. Norris, G.; Duvall, R.; Brown, S.; Bai, S. *EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide. EPA/600/R-14/108*; U.S. Environmental Protection Agency Office of Research and Development: Washington, DC, 2014.