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Memorandum

From:	Tim Towey, Dave Dilks	**Date:**	August 27, 2018
		Project:	SRRTTF7 Tasks 5C and 5D
To:	Spokane River Regional Toxics Task Force	CC:	

SUBJECT: Fingerprinting of Groundwater Samples in the Vicinity of the Kaiser Facility

Summary

LimnoTech used Polytopic Vector Analysis (PVA) to evaluate available groundwater samples analyzed using method 1668 to assess the likelihood that groundwater PCB levels upgradient of the Kaiser Trentwood facility are providing a PCB flux to the Spokane River through the Kaiser facility. A previous Task Force technical memorandum (LimnoTech, 2018a) had indicated that the Kaiser groundwater homolog pattern was a very good match to the observed increase in the PCBs in the Mirabeau to Trent reach of the river, which reasonably established that the Kaiser groundwater plume was reaching the Spokane River. The analysis described in this memorandum was intended to assess if the upgradient sources could also be reaching the river.

PVA is a factor analysis technique that has been demonstrated to be effective in “un-mixing” source fingerprints. In PVA, correlations between congeners observed across the entire data set are used to establish stable patterns that can be linked to sources. Each individual sample can then be decomposed into contributions from these patterns.

The groundwater samples were divided into four general regions: Upgradient, Kaiser “Plume”, West Discharge Ravine, and River Boundary wells. The well regions were based on designations provided Kaiser, but the analysis does not pre-suppose impacts or lack of impacts from Kaiser on any group of wells. The following provides additional context regarding the locations of these regions:

- Upgradient
    - Refers to wells generally located on the eastern (groundwater upgradient) side of the Kaiser facility
- Kaiser Plume
    - Refers to wells at the downgradient leading edge of PCB impacted groundwater from on-site sources at the Kaiser facility
- West Discharge Ravine (WDR)
    - Refers to wells located on the immediate north side of the former wastewater discharge ravine that has undergone Interim Actions for PCB in soil
    - Detailed groundwater elevation mapping during rising river conditions shows that these wells are downgradient of the WDR during these river rising events
- River Boundary Wells
    - Refers to wells generally located on the western (groundwater downgradient) side of the Kaiser facility near the property boundary
    - Does not include Plume or WDR wells

Key finding of this analysis are:

- The samples from Kaiser Plume and WDR wells are very similar in terms of their PCB source composition, and are dominated by the contribution of a pattern that resembles Aroclor 1248.
- The samples from the Upgradient and River Boundary also have a similar source composition, that is different from the Plume and WDR source composition. The Upgradient and River Boundary well samples are primarily composed of a pattern dominated by PCB-11 and a pattern that resembles Aroclor 1254.
- The Aroclor 1254 pattern is also present in the Plume and WDR well samples but, on average, contributes less than 10% of the PCBs in the WDR well samples.
- The analysis provides an additional line of evidence that the PCB sources found in the Upgradient wells are reaching the Spokane River. However, the analysis cannot refine the upgradient load estimate of 14 to 55 mg/day provided in a separate analysis conducted by LimnoTech (2016).

This memorandum summarizes the PVA analysis. It is divided into sections of:

- Available Data, Data Validation, and Data Handling
- PVA Method Overview
- PVA Results

Available Data, Data Validation, and Data Handling

Available Data

For the fingerprinting analysis, Kaiser provided 212 sample results for 27 groundwater wells (Figure 1).

As noted previously, the wells were divided into four regions by Kaiser: Upgradient wells (4 locations), Plume wells have the greatest magnitude of Kaiser PCB impact near the river (5 locations), the WDR wells located between the former Kaiser West Discharge Ravine and the Plume wells (2 locations) and the River Boundary Wells (14 locations). An additional two wells were included in the analysis to develop the PCB source patterns, but were excluded from the group evaluations: RM- MW-05S and the North Supply Well. These wells did not fit with any of the designated groups. RM-MW-05S may be inside the Kaiser plume and is too close to Kaiser operations to be considered completely upgradient. The North Supply Well draws water from deeper than the other wells included in the analysis.

All sample were analyzed by AXYS Analytical using method 1668A, which provides congener-specific PCB values.

Data Validation

The laboratory results were validated by LimnoTech in a manner consistent with the Quality Assurance Project Plan (QAPP) prepared for the data collected as part of SRRTTF monitoring (LimnoTech, 2014). A total of 31 lab reports were analyzed for the following data quality indicators evaluated for PCBs:

- Analytical method
- Detection limits
- Daily calibration verification
- Method blank concentrations
- Sample and method blank surrogate recoveries
- Lab Control Sample Recoveries

- Matrix Spike Sample Recoveries (not specified in the QAPP)
- Duplicate sample RPDs
- Completeness

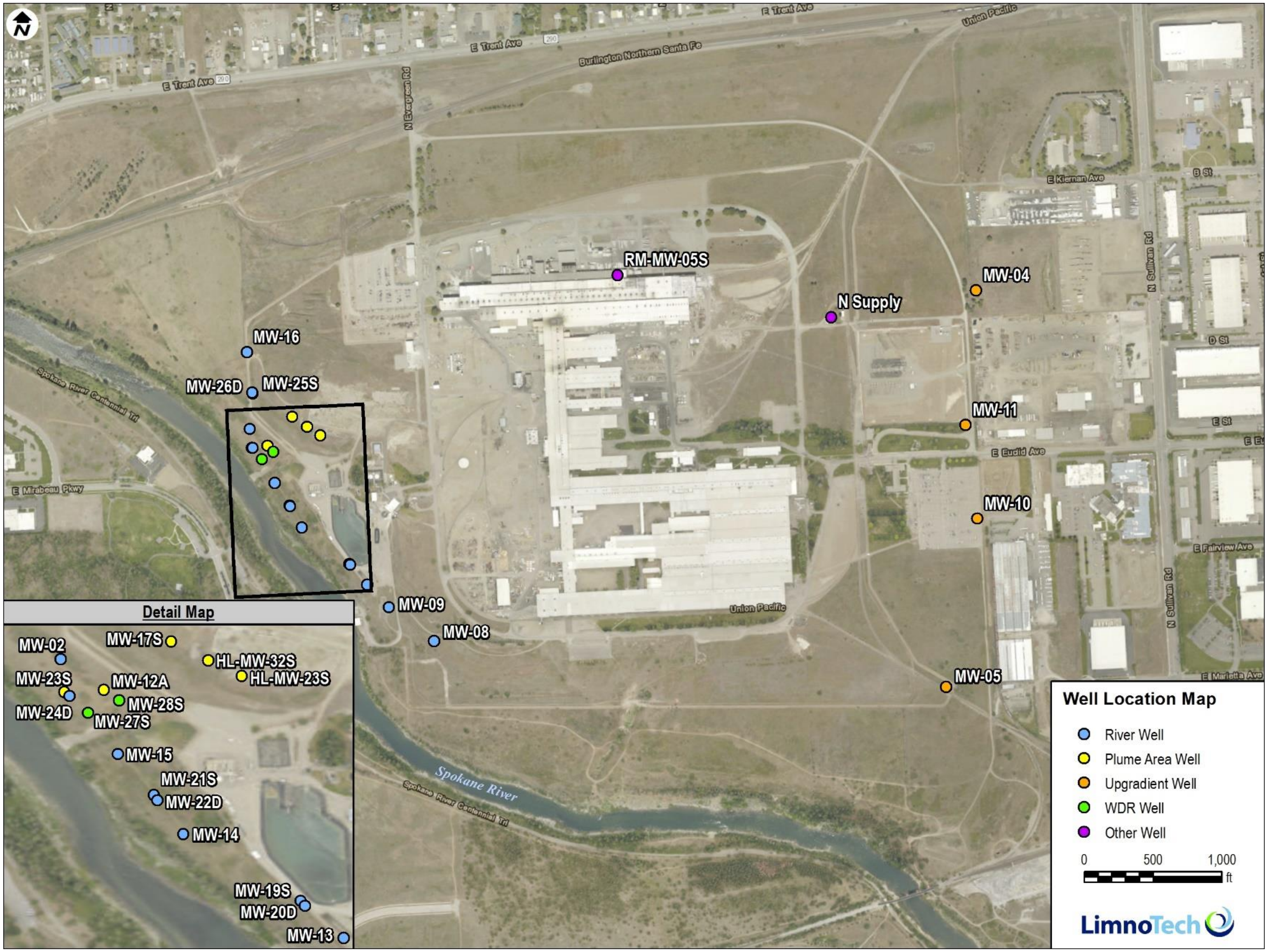

Figure 1. Location of wells used in Kaiser fingerprinting evaluation.

The quality control results for PCBs comply with QAPP data quality indicators and there were no changes to the reported PCB result values. However, additional J (estimated value) flags were added to some results.

Data Handling

The data was manipulated to prevent zero values for concentration of individual PCB congeners, which create errors in the PVA algorithm:

- Blank contamination was corrected by subtracting the blank value from the sample result, as opposed to excluding congener values less than a given multiple of the blank value
- Congeners with greater than 75 non-detects (35% of the samples) were eliminated.
    - The eliminated congeners represented 6% of the total detected PCB concentrations
- Concentrations at the detection limit were substituted for the remaining non-detects

The resulting dataset included 48 congeners (or congener combinations) for 212 samples. A summary of the concentrations for each well is presented in the Table 1 below. Additional summary statistics using the congeners included in the fingerprinting analysis (substituting the detection limit for non-detects and subtracting black contamination) are presented in Table 2. The same statistics are presented in Table 3 using the standard SRRTTF blank correction approach of using all congeners, censoring values within a factor of 3 of the concentration found in the blank, and excluding non-detect values. The differences in mean concentrations between the two blank correction methods are generally 10% or less.

Table 1. Summary of samples used in Kaiser fingerprinting evaluation.

Region	Well	Samples	Mean PCB Sum* (pg/L)	Min PCB Sum* (pg/L)	Max PCB Sum* (pg/L)
Upgradient	MW-10	19	349	22.1	5240
Upgradient	MW-11	20	136	24.1	641
Upgradient	MW-4	19	156	25.7	1, 030
Upgradient	MW-5	19	185	24.2	1,450
Plume	HL-MW-23S	9	7,580	1920	12,200
Plume	HL-MW-32S	8	10,100	1130	23,500
Plume	MW-12A	10	16,800	2270	56,900
Plume	MW-17S	11	3,600	822	10,000
Plume	MW-23S	7	7,570	514	42,800
WDR	MW-27S	16	2,300	24.1	12,600
WDR	MW-28S	16	8,220	486	34,200
River Boundary	MW-13	1	22.2	22.2	22.2
River Boundary	MW-14	1	79.7	79.7	79.7
River Boundary	MW-15	7	339	64.6	1630
River Boundary	MW-16	1	22.5	22.5	22.5
River Boundary	MW-19S	1	22.4	22.4	22.4
River Boundary	MW-2	1	25.5	25.5	25.5
River Boundary	MW-20D	1	21.4	21.4	21.4
River Boundary	MW-21S	1	45.7	45.7	45.7
River Boundary	MW-22D	1	24.7	24.7	24.7
River Boundary	MW-24D	1	118	118	118
River Boundary	MW-25S	1	83.4	83.4	83.4
River Boundary	MW-26D	1	20.9	20.9	20.9
River Boundary	MW-8	1	27.3	27.3	27.3
River Boundary	MW-9	1	28.5	28.5	28.5
Other	N. Supply Well	19	48.2	24.1	167
Other	RM-MW-5S	19	319	48	1,260

*Represents the sum of the 48 PCB congeners used in the analysis, substituting the detection limit for non-detects.

Table 2. Summary statistics by region based on sum of congeners used in fingerprinting evaluation, blank subtraction, and substitution of the detection limit for non-detects.

Region	Mean PCB sum (pg/L)	25th %ile PCB sum (pg/L)	Median PCB sum (pg/L)	75th %ile PCB sum (pg/L)
Upgradient	206	37.8	67.9	126
Plume	8,910	1,440	4,800	10,500
West Discharge Ravine	5,260	622	2,150	8,370
River Boundary	165	24.7	64.6	101

Table 3. Summary statistics by region based on all detected congeners with 3X blank censorship.

Region	Mean PCB sum (pg/L)	25th %ile PCB sum (pg/L)	Median PCB sum (pg/L)	75th %ile PCB sum (pg/L)
Upgradient	197	7.33	24	87
Plume	9,500	1,560	5,020	11,100
West Discharge Ravine	5,660	678	2,350	9,000
River Boundary	147	5.09	14.5	96.4

PVA Method

Polytopic vector analysis (PVA) is a multivariate statistical technique that uses the observed relationships among congeners in a given data set to extract source profiles and their relative contributions, assisting in the identification of sources. PVA is described by Johnson and Ehrlich (2002), and is comparable to other statistical fingerprinting methods.

The initial step of PVA is the normalization of the data. There are two normalization steps. First, each sample is represented by the ratio of each congener's concentration to the total sample concentration. This focuses the analysis on relative concentrations of congeners, and prevents very large concentrations in one sample from overwhelming the presence of concentrations in another sample. Second, an additional scaling is then performed with respect to the range of the normalized concentration of each congener, so that each normalized congener varies from 0.0 to 1.0. This serves a similar purpose, making sure that high variability in some congeners does not mask the existence of smaller but also important variability in other congeners that can be used to identify common patterns among congeners. Following data normalization, the dataset is decomposed into discrete congener patterns called end-members using Principal Components Analysis and subsequent rotations. The axes are iteratively rotated until a non-negativity constraint is satisfied. Both the congener end-members (EMs) and the contribution of each EM to each sample must satisfy the non-negativity constraint. The additional rotations and the non-negativity constraint in PVA differentiate it from principal components analysis and allow the resulting EMs to better represent real world sources.

LimnoTech used MATLAB code developed as part of a dissertation project at the University of Michigan to perform PVA (Barabas, 2003). Several peer reviewed publications have been based on analysis using this code (Barabas et al, 2004a, 2004b; Towey et al, 2012).

PVA Results

In PVA, it is up to the user to determine the appropriate number of end-members. A number of criteria may be used to evaluate the number of EMs, including the amount of variability explained and interpretability of results. While use of a large number of end-member may explain more variability in the observed data, use of too many end-members can result in an over-parameterization similar to curve-fitting.

Figure 2 shows the end-members of the 2-, 3- , and 4-EM models derived from the Kaiser data set. The bottom row shows candidate matching Aroclor congener patterns as described by Frame et al (1996). The Frame et al congener patterns in Figure 2 were limited to the congeners included in this analysis, after eliminating congeners with high incidence of non-detects.

The percent variance explained, shown on the right-hand side of each row in Figure 2, does not increase substantially by increasing the number of end-members. In the 2-EM model, one EM resembles a modified or dechlorinated Aroclor 1248 and the other EM resembles Aroclor 1254 with a substantial additional contribution of PCB-11. In the 3-EM model, the Aroclor 1254 pattern and PCB-11 pattern were separated into two separate end-members, though the Aroclor 1254 pattern (EM3) still has a contribution from PCB-11. When the model is expanded to 4 EMs, an additional EM that may be related to Aroclor 1242 is extracted.

The extracted end-members were compared to known Aroclor patterns (Frame et al, 1996) using the cosine similarity metric (also referred to as cosine theta or cos-θ). The cos-θ parameter is similar to a correlation coefficient or Spearman correlation, and has been used for other Task Force pattern comparisons (LimnoTech, 2018a). Table 4 shows the results of the cosine similarity analysis.

For the three EM model: EM1 is not similar to any Aroclor as PCB-11 is a common incidentally produced congener, EM2 is comparable to both Aroclor 1248 and Aroclor 1242, and EM3 has a strong similarity with Aroclor 1254. In expanding to a four EM model, EM2 has a much stronger correlation with Aroclor 1248. It is not clear that EM4 is directly related to a specific Aroclor, as the maximum cos- θ to a direct Aroclor is 0.47. EM4 was also compared to a range of mixtures of Aroclor 1242 and Aroclor 1260. The cos-θ value comparing EM4 to the most similar mixture, a 70/30 mix of Aroclor 1242 and 1260, is 0.55, still a fairly weak relationship. EM4 may represent a dechlorination pattern of an Aroclor – likely Aroclor 1242 due to the high level of PCB-18. Alternately, it could be an Aroclor fragment. However, because expanding to four end-members improves the interpretability of EM2, the four EM-model was selected as the preferred model.

Table 4. Similarity (cos Θ) of end-members to Aroclor patterns (Frame et al, 1996).

	3 EM Model			4 EM Model			
Aroclor	EM1	EM2	EM3	EM1	EM2	EM3	EM4
A1242	0.28	0.64	0.26	0.23	0.66	0.20	0.47
A1248 (1)	0.20	0.65	0.53	0.16	0.85	0.43	0.43
A1248 (2)	0.18	0.60	0.52	0.15	0.84	0.42	0.38
A1254 (1)	0.16	0.06	0.92	0.09	0.32	0.90	0.10
A1254 (2)	0.22	0.22	0.93	0.10	0.41	0.89	0.23
A1260	0.40	0.01	0.46	0.20	0.04	0.53	0.30

Note: analysis of two lots of Aroclor 1248 and 1254 are presented in the Frame manuscript. Both lots are included here.

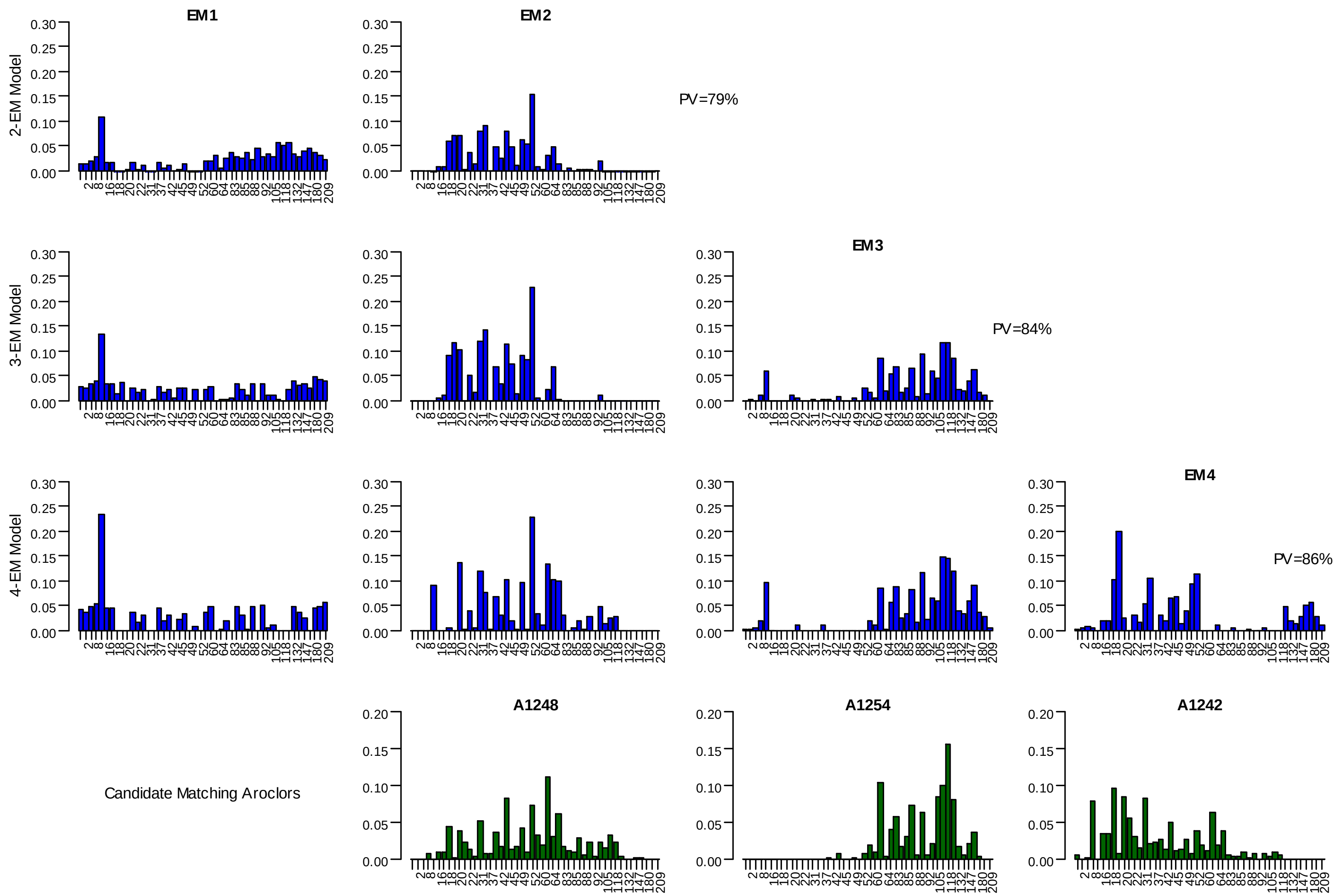

Figure 2. PVA end-members for 2-, 3-, and 4-EM models and candidate matching Aroclors (PV represents percent variance explained).

The interpretation of the EMs in the four EM model is as follows:

- EM1: primarily PCB-11
- EM2: resembles Aroclors 1248
- EM3: resembles Aroclor 1254
- EM4: possibly dechlorinated A1242

The percentage contributions of each EM (called "loadings" in PVA terminology) were assessed based on their contributions to the samples from each of the well groups. Figure 3 shows a box and whisker plot of the distribution of EM loadings for the 4-EM model.

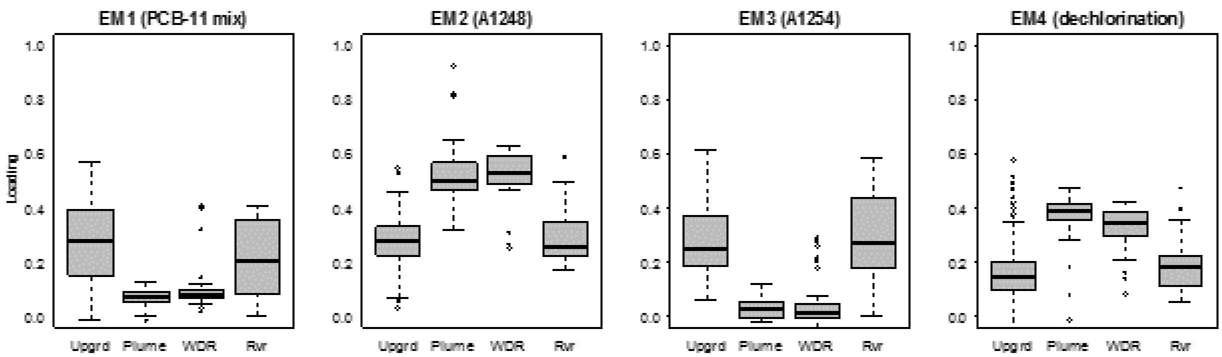

Figure 3. Distribution of EM loadings by geographic area for the 4-EM model.

The loading distributions for the Plume and WDR wells are very similar, suggesting similar PCB source contributions for both locations. The largest contributor is EM2 - the pattern resembling Aroclor 1248. These areas also have a substantial contribution from the EM that may be an Aroclor 1242/1260 mix. The median contribution from the other EMs is less than 10%.

The loading distributions for Upgradient and River Boundary wells are also similar. The EM dominated by PCB-11 and the EM resembling Aroclor 1254 are the largest contributors to these samples.

The results of this fingerprinting analysis suggest that the PCBs observed in the Upgradient wells are reaching the river. In the WDR wells along the river, where Kaiser Plume PCBs are also present, the Upgradient PCBs are a minor contributor. However, outside of the WDR, the same sources that influence the Upgradient appear to be the primary sources of PCBs reaching the river.

Although the analysis shows that the PCBs present in the Upgradient wells are very likely reaching the Spokane River, the PCB sums in the River Boundary wells are approximately two orders of magnitude lower than those in the Plume and WDR wells. While this analysis provides an additional line of evidence that the sources of PCBs upgradient of Kaiser are reaching the Spokane River, the best (albeit still highly uncertain) estimate for the quantification of that load is still the 14 to 55 mg/day range as provided by LimnoTech (2016).

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