

Spokane River Regional PMF Analysis -- Blank Influence Analysis

Conceptual Scope of Work

This report details the results of the first phase of a project to utilize Positive Matrix Factorization (PMF) to identify sources of PCBs to the Spokane River. Upon completion of Summer 2018 sampling activities and receipt of the analytical data a scope of work for the second phase will be developed. The second phase scope of work will identify the data sets to be used in the PMF analysis and detailed approach to PCB source characterization in the Spokane River.

In the first phase of the project, we investigated the influence of blank contamination on the source apportionment of PCBs in the ambient surface water of the Spokane River via conducting factor analysis using Positive Matrix Factorization Model (PMF2) software on a number of permutations of the Spokane River Regional Toxics Task Force (SRRTTF) Spokane River water column data set.

PROJECT GOALS

The purpose of this study was to determine whether PMF could be successfully used on this data set despite the blank contamination issues, and if so, to identify which approach (or combination of approaches) best addresses the impact of blank contamination on the analysis of low levels of PCB measured in the Spokane River water column.

What is Positive Matrix Factorization?

Positive Matrix Factorization (PMF) is a mathematical receptor model developed by Paatero and Tapper (1994) who developed the PMF2 software. PMF is used to quantify the contribution of sources to samples based on the composition or fingerprint of the sources. The PMF model can analyze a wide range of environmental sample data on sediments, wet deposition, surface water, ambient air, and indoor air. It reduces the large number of variables in complex analytical data sets to combinations of species called source types and source contributions. The source types are identified by comparing them to measured profiles. Source contributions are used to determine how much each source contributed to a sample. Algorithms used in the various PMF versions have been peer reviewed by leading air and water quality management scientists.

BACKGROUND

It has been proposed to conduct factor analysis on PCB data from the Spokane River watershed using PMF2 in order to characterize the sources of PCBs to the watershed. This approach involving the PMF2 software has been used successfully in many watersheds, including the Green-Duwamish River (Rodenburg and Leidos 2017, Rodenburg and Leidos 2017), the Delaware River (Du, Belton et al. 2008, Praipipat, Rodenburg et al. 2013), the Portland Harbor Superfund Site (Rodenburg, Krumins et al. 2015), and the NY-NJ Harbor (Rodenburg, Du et al. 2011, Rodenburg and Ralston 2017). PMF analysis has revealed the relative importance of different types of PCB sources, including stormwater and treated wastewater, and has in some cases been able to identify previously unknown PCB sources (Du, Belton et al. 2008, Rodenburg, Krumins et al. 2015).

In all of these previous cases, the concentrations of PCBs in the affected water bodies were generally greater than 1,000 pg/L and blank masses were therefore negligible. In the Spokane River, by contrast, the sum of 209 PCB congeners (Σ PCBs) was 171 pg/L in the data set analyzed here (ND = 0, no blank correction), with an average of 88 pg/L found in the blanks. Thus contamination introduced during or after sample collection as represented by blank samples may constitute a large fraction of the PCB mass in the samples.

EPA guidance on how to handle blank contamination in method 1668 is unclear. Method 1668 (USEPA 2003) notes that "The recommended procedure for blank correction (Reference 20) is that a result is significantly above the blank level, and the level in the blank may be subtracted, if the result is greater than the mean plus 2 standard deviations of results of analyses of 10 or more blanks for a sample medium." Reference 20 is a peer-reviewed paper (Ferrario, Byrne et al. 1997) that specifically discusses the difficulties associated with obtaining low or zero concentrations of PCBs in blanks when using high resolution mass spectrometry. These authors note that blank contamination frequently consists of Aroclor-type congeners. However, in our experience, non-Aroclor congeners are frequently abundant in blanks as well. For other methods, EPA guidelines suggest that blank subtraction is not recommended. For example, EPA method 8270D (EPA 2017) for measurement of semivolatiles by gas chromatography/mass spectrometry states that "The laboratory should not subtract the results of the [method blank] from those of any associated samples. Such "blank subtraction" may lead to negative sample results." It is important to note that the procedure for handling blank contamination might be different depending on how the data is to be used. For example, when the data is to be used for assessing absolute concentrations, i.e. whether they are above detection, blank subtraction might be appropriate. In contrast, the procedure for dealing with blank contamination might be different when the data is to be used for fingerprinting and source apportionment, as in the present work. In their Hazard Ranking System Guidance Manual, EPA states that, for purposes of establishing a release of a chemical, the concentration detected in the release sample should

be compared to background: “If the background level is greater than or equal to its DL, the minimum requirement for an observed release is that the concentration in the release sample is at least three times greater than the background level.” (US EPA 1992). To our knowledge, there is no specific guidance from EPA concerning blank correction in scenarios involving fingerprinting or source apportionment.

In our previous experience, we have faced two situations in which blank contamination was problematic. The first case concerned PCBs in the effluent of the Spokane County Regional Water Reclamation Facility (SCRWRF). This data set included measurements of PCBs in both the influent and effluent of the plant. PCB concentrations in the influent were high enough that blank masses (median 130 pg/L) were negligible, but blank contamination was a significant issue for the effluent where the median PCB concentrations were about 200 pg/L. Notably, the non-Aroclor congener PCB 11 was the most abundant congener in the majority of blanks. This is problematic because one of the issues to be investigated in the Spokane River is the extent to which PCB sources are associated with Aroclors versus non-Aroclor sources. It will be difficult to determine the true impact of PCB 11 if it is abundant in the blanks.

In consultation with the SCRWRF, we decided to blank correct the data by subtracting the average concentration of each congener across all blanks (field, lab, rinsate) collected for each sampling event. The results of this blank subtraction were not noticeable when the influent and effluent were analyzed together in a combined data set, probably because the concentrations in the influent were so much higher and ‘swamped’ the effluent, dominating the resolved source profiles. However, when the effluent was analyzed separately via PMF2, a factor was generated that contained high proportions of PCBs 44+47+65, 45+51, and 68, and it became clear that one sample of effluent was dominated by these three peaks, which are known to be associated with silicone. This sample was then discarded from further analysis, and the final PMF2 solution for the effluent contained four factors that resembled the four main Aroclor formulations (1016, 1248, 1254, and 1260). It is not clear whether the discarded sample reflected a real PCB source in the sewage of Spokane County, or if it became contaminated during sampling, handling, or analysis.

The second scenario in which we have faced the issue of blank contamination concerned the ambient water data from the Green River, which flows into the Duwamish River in Washington State (Rodenburg and Leidos 2017). The Green River is relatively remote and therefore has low PCB concentrations. The sum of 209 PCB concentrations in these samples ranged from 5 to 450 pg/L, but the concentrations of PCBs 44+47+65 plus 45+51 plus 68 made up between 0% and 91% of the PCBs in the samples. It was subsequently confirmed that silicone rubber tubing had been used for sample collection (Greyell and Williston 2018). Blank data was not available, but

the concentrations of these three peaks in the samples ranged from non-detect to 270 pg/L. Taking an average of this wide range of values and subtracting it from each sample would not have solved the contamination problem. Instead, it would have resulted in roughly half of the samples continuing to display high concentrations of congeners associated with contamination. Therefore, it was decided to exclude these three peaks from the PMF2 analysis. Due to the large number of non-detects, only 42 PCB peaks representing 69 congeners were included in the final PMF2 model runs. This highlights another problem related to measuring low concentrations of PCBs: large numbers of non-detect values mean that only a few congeners can be included in the PMF2 analysis. These peaks contained only about 60% of the total PCB mass detected across all 209 congeners. Of the 'missing' 40% of mass, about 15% was explained by the three peaks that were excluded due to silicone contamination. Thus, the final model explained about 75% of the PCB mass detected in the samples. The results yielded four factors which resembled the four main Aroclors, although for the factor that was most similar to Aroclor 1248, the correlation coefficient between the congener patterns of the Aroclor and the factor was just 0.44.

Taken together, EPA guidance and our experience lead to several conclusions regarding PMF2 fingerprinting of PCB data for which blank contamination may be significant:

- It is important to have blank data available for examination.
- Blank subtraction has in the past resulted in data sets in which factor analysis identified Aroclors.
- Absence of blank correction can sometimes lead to factors that are presumed to resemble the blank contamination.
- It is difficult to perform factor analysis on data sets with low concentrations not only because of blank contamination issues, but also because many of the congeners have to be excluded from the PMF model because they are not detected in enough samples (even when they are not detected in the blanks).
- Non-Aroclor congeners are often prevalent in blanks, making a determination of their true levels in the sample difficult.

METHODS

The Spokane River ambient water data set included 139 Spokane River water column samples collected in conjunction with the SRRTTF 2014 synoptic sampling, 2015 synoptic sampling and the 2016 monthly sampling. PCBs were measured in these samples via method 1668 in which all 209 PCB congeners were measured in 159 peaks using the SPB-octyl gas chromatography column. Of these 159 peaks, 20 were never detected in any sample (which is typical). In general, it is preferable for the PMF input to have at least as many samples as analytes, but

stable solutions can sometimes be obtained even when the number of analytes exceeds the number of samples. Given that 139 samples were available, the PMF input could therefore have included all of the 139 detected peaks. Despite this, most PMF modeling work that we have performed utilizes only about 90 to 100 peaks even when detection limits are not a problem. The remaining 60-70 peaks are discarded because they are rarely detected and are not particularly useful in identifying PCB sources. In the present work, the maximum number of peaks included in any model was 73, because the remaining peaks were below detection limit in too many samples to be included in the PMF input.

Two different types of blank samples are utilized in this analysis: Batch specific laboratory blanks, or method blanks, that are run during the same batch as the sample, and associated field blanks which refers to the field blank collected on the same day as the sample. The associated field blank is often run in the same batch as the sample, but that is not always the case. These blanks were used two ways: 1. The max of all blanks is the maximum value on a per congener basis of the batch specific lab blank and associated field blank. 2. The measured value of the congener-specific concentration in the method blanks was also used. In most instances there is only one lab blank, but there are some instances where the lab ran three lab blanks with each batch. In those cases the average of the three lab blanks on per congener basis was used to represent the batch specific lab blank.

We analyzed several permutations of the ambient water data set with the following modifications:

- Approach A: No blank correction. Interpret the output of the model with the assumption that one or more of the resolved factors may represent blank contamination. These model runs are labeled 'Uncor'.
- Approach B: Censor (exclude) concentrations of peaks that were present in the method blanks. We initially intended to censor concentrations that are within 3x the blank level, 5x the blank level, and 10x the blank level. The results of this approach left too few congeners with enough data above the censor limit to construct a useful PMF model. Therefore, we also investigated a 1x blank level censored data set. Censored concentrations were designated as ND and therefore assigned a higher uncertainty in the PMF2 model. Dr. Rodenburg worked with SRRTF to determine the exact censoring procedure to be consistent with the approaches used to censor this data set for other purposes. Two sets of values were used for the censoring: either the batch-specific blank concentrations (approach 2 above; these runs are called 'BatchCensor') or the maximum of all blank concentrations (approach 1 above; called 'MaxCensor').

- Approach C: Subtract blank masses from sample masses. Dr. Rodenburg again worked with SRRTTF to determine the exact blank subtraction procedure to be consistent with the approaches used to censor this data set for other purposes. When such a subtraction resulted in a zero or negative concentration, the data point was designated as ND. As with the censoring, two sets of values were used: the batch-specific blank concentrations (these runs are called 'BatchSub') or the maximum of all blank concentrations (called 'MaxSub').
- Approach D: Exclude from the PMF2 analysis specific congeners that are often present in the blanks, as, for example, in the Green River ambient water data in which PCBs 68, 44+47+65, and 45+51 were excluded. This may underestimate the importance of non-Aroclor sources in the Spokane River. These runs are identified by the number of peaks included in each run, which is the number appended at the end of each data set label (for example, Uncor73 is a data set that was not corrected for blanks and included 73 peaks). Runs with 59 peaks excluded PCBs 44+47+65, and 45+51. PCB 68 was never included in any of the data sets analyzed because it was not detected in enough samples.

We analyzed Spokane River ambient water column data collected by the SRRTTF by the above approaches and compared the various model outputs to determine which approach (or combination of approaches) yielded the most useful information about PCB sources to the river.

PMF analysis

PMF is an advanced factor analysis method developed by Paatero and Tapper (1994). All factor analysis techniques, including PMF and principle components analysis (PCA), define the sample matrix as a product of two unknown factor matrices with a residue matrix:

$$X = GF + E \quad (1)$$

The sample matrix (X) is composed of 'n' observed samples and 'm' chemical species. 'F' is a matrix of chemical profiles of 'p' factors or sources. The 'G' matrix describes the contribution of each factor to any given sample, while 'E' is the matrix of residuals. The PMF solution (i.e., 'G' and 'F' matrices) is obtained by minimizing the objective function 'Q' through the iterative algorithm:

$$Q = \sum_{i=1}^n \sum_{j=1}^m (e_{ij} / s_{ij})^2 \quad (2)$$

The calculated 'Q' is the sum of the squares of the difference (e_{ij}) between the observations (X) and the model (GF), weighted by the measurement uncertainties (s_{ij}). As a result, lower

calculated 'Q' values are desirable as they indicate a better fit to the input data. There is also a theoretical value of 'Q' equal to $m \cdot n - p \cdot (m+n)$, where 'm' is the number of samples, 'n' is the number of PCB congeners, and 'p' is the number of factors requested (Polissar and Hopke 2001).

PMF analysis of any data set therefore yields two matrices: the F matrix, which consists of the fingerprints of the factors (source terms), and the G matrix, which consists of the concentration of each factor in each sample (in the same units used in the input data set). In this report, we evaluate the success of the analysis of each permutation of the data set mostly by evaluating whether the PMF model converges on a stable solution, and whether it produces fingerprints (F matrix) that resemble known PCB sources. For purposes of this report, then, we mostly ignore the G matrix. However, the G matrix will become vital in the next phase of this project, in which we attempt to identify specific PCB sources (such as industrial facilities, groundwater inputs, discharges, etc.). The G matrix will indicate where and when the highest concentrations of each factor were found.

Full details of the methods used to construct the PMF input matrixes, run the PMF model, choose the optimal number of factors, and evaluate the output are given in Rodenburg and Leidos (2017) and are briefly summarized here.

The PMF2 program requires three input data sets: concentration, limits of detection (LOD), and uncertainty. All three of these inputs have the same dimensions, i.e. the same number of peaks and samples.

- Concentration matrix: Analyte concentrations were provided by SRRTTF. When concentrations were designated as ND, they were replaced with a random proxy value between 1 and 100 percent of the LOD. In order to eliminate this proxy value as a confounding variable, a set of values was generated that was used for all permutations of the data set described above, i.e. the exact value of this random proxy did not change from one data set to the next.
- LOD matrix: LODs were provided all data points.
- Uncertainty matrix: The uncertainty matrix is difficult to derive and requires the user to exercise judgment. As in previous analysis of EPA Method 1668 data (Du, Belton et al. 2008, Rodenburg, Du et al. 2011, Praipipat, Rodenburg et al. 2013, Rodenburg and Meng 2013, Rodenburg, Delistraty et al. 2015), the relative standard deviation of the surrogate recoveries (RSDSR) was used as the uncertainty. These generally range from approximately 10 to 15%.

When constructing these input data sets, it is necessary to exercise judgement about which peaks to include and which to exclude. (In some cases it is also necessary to exclude some samples, but in this work, all 139 samples were included in all permutations.) For the present work, we included PCB peaks when the peak was designated as detected in at least half of the 139 samples. Relaxing this restriction can result in data sets that have high proportions of ND data points. The PMF program sometimes cannot converge on a stable model solution when the proportion of ND values is too high. The data set of PCB concentrations in the blank violated this rule: it included congeners that were detected in at least 68 of the 162 blanks (not to be confused with the 139 *samples*). As a result, 27% of the data points were designated as ND. Nevertheless, the PMF program was able to converge on a stable solution. Throughout this report, we have indicated how much of the total mass of all 209 PCB congeners detected in all samples was included in each permutation of the data set. This percentage ranges from 96.6% in the uncorrected data set with 73 peaks (Uncor73) to just 51.4% in the data set generated from blank subtraction using the maximum concentration detected across all blanks and excluding peaks 44+47+65 and 45+51 (MaxSub59). One of the goals of this study was to determine which combination of approaches to blank correction is best for analysis of the data by PMF. One of the criteria used to make this determination was that the approach should retain as much of the PCB mass as possible.

RESULTS

PCB 68

Before conducting source apportionment analysis, it is always useful to examine the raw data. We commonly investigate concentrations of PCB 68 in raw data, because this congener is usually not included in PMF analysis because it is not detected in enough samples. PCB 68 is virtually absent in the Aroclors. It has been detected in silicone products (Perdih and Jan 1994) and is therefore considered a marker for contamination from silicone. Throughout this report we have used the term 'silicone' to refer to any use of silicone. Silicone rubber is one particular use of silicone. PCBs, especially congeners 47, 51 and 68) can be present in silicone that is produced using bis(2,4-dichlorobenzoyl) peroxide as a cross-linking agent (Perdih and Jan 1994). This congener pattern was found in water samples collected using silicone rubber tubing in the Green River (Greyell and Williston 2018). PCBs 1, 2, 3 and others can be present whenever the silicone is produced from chlorophenylsilanes (i.e. the phenyl type of silicone as opposed to the methyl type) and these congeners have been found in raw dichlorodiphenylsilane, diphenylsilanediol, and chlorotriphenylsilane (i.e. feedstocks for phenyl silicone production) as well as in finished silicone products such as silicone-based adhesives (Anezaki and Nakano 2015). Phenyl-based silicones are more resistant to heat than the methyl

type. Such phenyl silicones can be used in a wide variety of products, including sealants, adhesives, lubricants, medicine, cooking utensils, and thermal and electrical insulation. Some common forms include silicone oil, silicone grease, silicone rubber, silicone resin, and silicone caulk. Thus PCB contamination from silicone can come from many sources, not just silicone rubber tubing that might be used for water sampling.

In the present data set, PCB 68 was detected in 7 of the 50 blanks. In those seven, the congeners most strongly correlated with 68 were: PCBs 44+47+65 ($R^2 = 0.962$), 45+51 (0.846), 18+30 (0.841), 8 (0.679), 32 (0.564), 48 (0.539), 6 (0.527), 17 (0.527), and 16 (0.518). All of these congeners were detected in silicone rubber by Perdih and Jan (1994). (Note that Perdih and Jan did not detect PCBs 30 and 65 in silicone rubber. They are listed here as co-eluters, but were resolved by Perdih and Jan.) Anezaki and Nakano (2015) also found these congeners (except 45+51) in silicone feedstocks and adhesives.

PCB 44+47+65 was detected in 48 of 50 blanks, and PCB 45+51 was detected in 34. When these congeners were detected in blanks, they averaged 3.6 pg/L for PCB 44+47+65 and 1.0 pg/L for PCB 45+51. These results suggest that silicone is a significant contributor of PCBs to blanks. The congeners thought to be associated with silicone (6, 8, 16, 17, 18+30, 32, 44+47+65, 45+51, 48, and 68) comprised about 11% of total PCBs detected in all blanks, although it is important to note that many of these congeners are also present in the Aroclors.

PCB 68 was detected in 29 of the 139 samples (uncorrected for blanks). PCB 68 concentrations in samples are strongly correlated with concentrations of PCBs 44+47+65 ($R^2 = 0.75$) and 45+51 ($R^2 = 0.72$) in 28 of the 29 samples in which PCB 68 was detected. The outlier sample (HC1-082014-1515) contained the highest concentration of Σ PCBs in the data set at 2,461 pg/L (uncorrected for blanks, ND=0). Concentrations of PCBs 44+47+65 averaged 14.2 pg/L in these 28 samples, versus 5.5 pg/L in the other 110 samples in which PCB 68 was not detected. Similarly, PCB 45+51 concentrations averaged 3.7 pg/L when 68 was detected and 1.3 pg/L when it was not. These concentrations are higher than those observed in the blanks.

These results suggest that a substantial fraction of the concentrations of PCBs 44+47+65 and 45+51 measured in ambient water samples arise from silicone. It is not clear whether this represents blank contamination or a real influence of silicone on water quality in the Spokane River. The fact that concentrations of these congeners found in the ambient water samples are 4 to 5.5 times greater than the blanks suggests that there may be a measurable influence of silicone on PCB levels in the Spokane River. In our investigations of PCBs in the influent and effluent of the Spokane County Regional Water Reclamation Facility (SCRWRF), we also noted meaningful correlations between PCBs 68, 44+47+65 and 45+51.

The sum of congeners thought to be associated with silicone in the blanks averages about 21 pg/L in the ambient samples (uncorrected for blanks, ND=0), but it should be noted that all of these congeners (with the exception of PCB 68) are also present in the Aroclors.

WHAT'S IN THE BLANKS?

Approach A asks us to interpret the results of PMF analysis with no blank correction by assuming that some of the factors generated might represent blank contamination. In order to do so, we must know what is in the blanks. For that purpose, we analyzed a data set on PCB concentrations in the blanks. The data set provided for this work included 48 blanks (26 method blanks and 22 field blanks). To this relatively small number of blanks was added 114 blanks from the SCRWRf study of PCBs in the influent and effluent of this plant. These blanks were collected in the same geographic area as the ambient water blanks, generally during the same years, and were analyzed by the same contract lab (Axys Analytical Services). The average (\pm standard deviation) concentrations of PCBs in the Spokane River blanks was 88 ± 148 pg/L, versus 168 ± 132 pg/L in the SCRWRf blanks.

For this analysis, 42 peaks were used (1, 2, 3, 4, 8, 11, 15, 16, 17, 18+30, 20+28, 21+33, 22, 26+29, 31, 32, 37, 40+41+71, 44+47+65, 45+51, 49+69, 52, 56, 60, 61+70+74+76, 64, 66, 68, 83+99, 86+87+97+108+119+125, 90+101+113, 93+95+98+100+102, **105**, 110+115, **118**, 129+138+160+163, 135+151+154, 147+149, 153+168, 180+193, 187, 209) (dioxin-like congeners in bold). 41 of these were chosen because they were above detection in at least 68 of the 162 blanks analyzed. The final congener was PCB 68, which was included in order to investigate whether it varied in tandem with PCBs 44+47+65 and 45+51 even though it was detected in only 41 of the 162 blanks. Of the 6,804 data points in this matrix, 1,868 (27%) were ND. The data set contained 89.9% of the PCB mass detected in all 209 congeners in all 162 blanks (ND = 0).

PMF analysis of this data set yielded seven factors, here denoted Blank42F1 through Blank42F7. In keeping with the lower overall PCB concentrations in the Spokane River blanks, the concentrations of all factors except Blank42F7 are lower in the Spokane River blanks than in the SCRWRf blanks ($p < 0.05$ based on a two-tailed t-test with unequal variances). Notably, however, the proportions of the seven factors are not different between the Spokane River blanks and the blanks from the SCRWRf study (Figure 1; $p < 0.05$).

Several of the factors isolated from the blanks represent Aroclors. Blank42F2 resembled Aroclors 1016 ($R^2 = 0.72$) and 1242 ($R^2 = 0.61$). Blank42F6 strongly resembled Aroclor 1254 (R^2

= 0.90). Blank42F7 resembled Aroclor 1260 ($R^2 = 0.77$). Blank42F5 somewhat resembled Aroclor 1248 ($R^2 = 0.43$). Together, these four factors explain 66% of PCBs in the Spokane River blanks.

Blank42F3 was dominated by PCB 11 (77% of the fingerprint) and accounted for 18% of PCBs in the blanks. The second-most abundant congener in this factor is PCB 52 (3.6%). Hu and Hornbuckle (2010) and Anezaki and Nakano (2014) observed PCB 52 with PCB 11 in some organic pigments.

Blank42F1 explained 8% of the PCB mass in the blank data sets and was dominated by mono- and di-chlorinated congeners: PCBs 1 (19% of the fingerprint), 2 (8%), 3 (19%), 4 (6%), 8 (9%), and 15 (6%). This factor is quite similar to Aroclor 1232 ($R^2 = 0.76$). This Aroclor represented only 0.24% of total US PCB production (Brown 1994), and therefore we deem it unlikely that Aroclor 1232 is the source of this fingerprint. We argue that it is more likely that this factor represents PCBs from silicone products. Anezaki and Nakano (2015) found all of these congeners in silicone-based adhesives as well as in chlorophenyl silane feedstocks.

Blank42F4 is dominated by PCBs 44+47+65 (59% of the fingerprint) and 45+51 (12%). It also contains some PCB 68 (2.9%). This factor therefore represents PCBs from silicone products, probably those cured using bis(2,4-dichlorobenzoyl) peroxide. Note that the PMF analysis separates this signal into a different factor than the PCBs thought to be related to phenylsilanes (Blank42F1).

This analysis suggests that Aroclors are the dominant source of PCBs in the blanks considered in this study. If our interpretation is correct and Blank42F1 represents PCBs from silicone-based products, then silicone is the second-most important source of PCBs in the blanks. Pigments are the third most important source.

Sources of PCBs to blanks

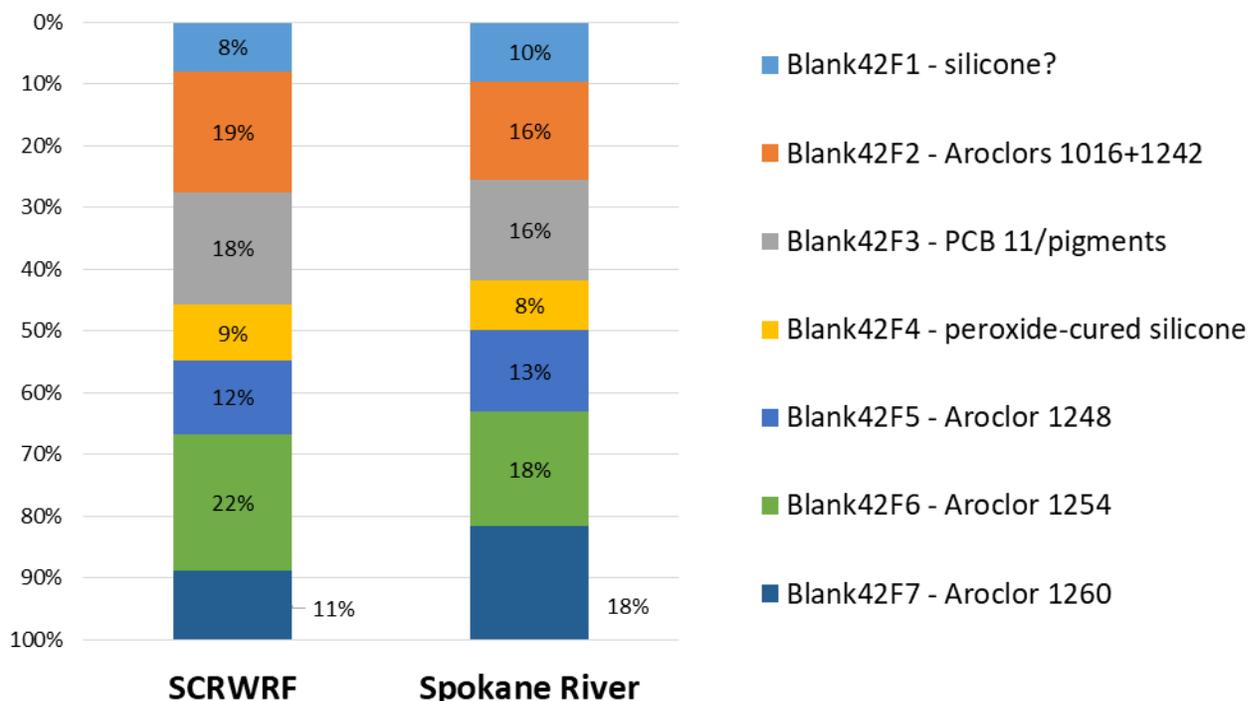


Figure 1. Distribution of the seven factors isolated from the blank data set (Blank42) across blanks collected as part of the Spokane River ambient water studies (48 blanks) versus the blanks collected by the SCRWRf (114 blanks).

EFFECT OF BLANK CENSORING AND SUBTRACTION ON DATA SET

Table 1 shows the results of censoring and blank subtraction on the number of data points that were designated as non-detect (ND). For clarity, this table does not include congeners that were ND in 80 or more samples even in the uncorrected data set, because these congeners would never have been candidates for inclusion in the PMF model. The exception to this rule is PCB 68, which is included here because it is important to the story of blank contamination.

Peaks that were never detected were: 38, 58, 73, 78, 80, 106, 111, 112, 120, 121, 127, 142, 145, 148, 150, 152, 161, 165, 186, and 204. Additional peaks that were ND in 80 or more samples and were never included in any PMF model were: 5, 7, 9, 10, 12+13, 14, 23, 24, 34, 36, 39, 43, 54, 55, 57, 63, 67, 68, 72, 79, **81**, 89, 94, 96, 103, 104, 108, **114**, 122, **123**, **126**, 130, 131, 133, 134+143, 137, 139+140, 144, 155, 159, 162, 164, **167**, **169**, 171+173, 172, 175, 176, 178, 181, 182, 184, 188, 189, 190, 191, 192, 195, 196, 197+200, 201, 202, 205, 206, 207 and 208. (Dioxin-like congeners shown in bold).

Blank subtraction and censoring at 1x the blank value (whether the max of all blanks or the batch specific blanks is used) result in the same numbers of ND values and are therefore listed in the same columns in this table.

Batch-specific blank concentrations

The least aggressive blank correction method uses the batch-specific method blank concentrations, which is used either to censor or subtract from the sample concentrations. Where the lab had run multiple method blanks for a specific batch, the average of the method blank concentrations was used. This method leaves 68 peaks with enough detections for PMF analysis. Therefore the congeners that are most affected by blank correction are those that are lost between the 73 and 68 peak lists: 1, 3, 6, 35, and 209. Most of these can be considered non-Aroclor congeners. Only PCB 6 is found in reasonable amounts in Aroclors 1016 and 1242 (about 1.5%), PCBs 1, 3, and 6 were found in silicone products by Anezaki and Nakano (2015). PCB 35 is often associated with PCB 11 in pigments (Litten, Fowler et al. 2002), and PCB 209 is associated with pigments (Du, Belton et al. 2008, Hu and Hornbuckle 2010).

The most severe level of blank correction that yields enough data for PMF analysis is censoring using three times the batch-specific method blank concentration. This approach leaves 43 peaks and involves discarding PCBs 2, 4, 11, 16, 17, 18+30, 20+28, 21+33, 22, 31, 32, 37, 44+47+65, **77**, 86+87+97+119+125, 90+101+113, 107+124, **118**, 129+138+160+163, 153+168, **156+157**, 177, 179, 180+193, 183+185, 187, 194, 198+199, and 203. Most of these congeners are abundant in the Aroclors. Censoring the data at higher levels (i.e. 5x or 10x blank levels) leaves insufficient data for PMF analysis.

Maximum blank concentrations across all blanks

We also investigated using the maximum concentration of PCBs across all blanks associated with a sample for blank censoring/subtraction. This is more aggressive than using the batch-specific method blank only. Using one times the max of all blanks to censor/subtract blank concentrations yields a data set for PMF analysis that includes 61 peaks. Additional peaks that are discarded between the 68 and 61 peaks lists are PCBs 8, 15, 27, 107+124, **156+157**, and 158. Of these, 8 and 15 are relatively abundant in Aroclors 1016 and 1242, and 156+157 as well as 158 are somewhat abundant in Aroclors 1254 and 1260. Censoring at 3x the maximum blank level leaves too few peaks for a meaningful PMF analysis. Censoring the data at higher levels (i.e. 5x or 10x blank levels) similarly leaves insufficient data for PMF analysis.

Table 1. Effect of blank subtraction and censoring on the peaks with enough detections to be included in the PMF model runs in 139 samples of ambient water from the Spokane River.

Uncorrected	censor/subtract 1x batch	3x batch censor	censor/subtract 1x max all blanks	1x max blank and discard silicone congeners
73 peaks	68 peaks	43 peaks	61 peaks	59 peaks
1				
2	2			
3				
4	4		4	4
6				
8	8			
11	11		11	11
15	15			
16	16		16	16
17	17		17	17
18+30	18+30		18+30	18+30
19	19	19	19	19
20+28	20+28		20+28	20+28
21+33	21+33		21+33	21+33
22	22		22	22
25	25	25	25	25
26+29	26+29	26+29	26+29	26+29
27	27	27		
31	31		31	31
32	32		32	32
35				
37	37		37	37
40+41+71	40+41+71	40+41+71	40+41+71	40+41+71
42	42	42	42	42
44+47+65	44+47+65		44+47+65	
45+51	45+51	45+51	45+51	
46	46	46	46	46
48	48	48	48	48
49+69	49+69	49+69	49+69	49+69
50+53	50+53	50+53	50+53	50+53
52	52	52	52	52
56	56	56	56	56
59+62+75	59+62+75	59+62+75	59+62+75	59+62+75
60	60	60	60	60
61+70+74+76	61+70+74+76	61+70+74+76	61+70+74+76	61+70+74+76
64	64	64	64	64
66	66	66	66	66
77	77		77	
82	82	82	82	82
83+99	83+99	83+99	83+99	83+99
84	84	84	84	84
85+116+117	85+116+117	85+116+117	85+116+117	85+116+117
86+87+97+119+125	86+87+97+119+125		86+87+97+119+125	86+87+97+119+125
88	88	88	88	88
90+101+113	90+101+113		90+101+113	90+101+113
92	92	92	92	92
93+95+98+100+102	93+95+98+100+102	93+95+98+100+102	93+95+98+100+102	93+95+98+100+102
105	105	105	105	105
107+124	107+124			
110+115	110+115	110+115	110+115	110+115
118	118		118	118
128+166	128+166	128+166	128+166	128+166
129+138+160+163	129+138+160+163		129+138+160+163	129+138+160+163
132	132	132	132	132
135+151+154	135+151+154	135+151+154	135+151+154	135+151+154
136	136	136	136	136
141	141	141	141	141
146	146	146	146	146
147+149	147+149	147+149	147+149	147+149
153+168	153+168		153+168	153+168
156+157	156+157			
158	158	158		
170	170		170	170
174	174	174	174	174
177	177		177	177
179	179		179	179
180+193	180+193		180+193	180+193
183+185	183+185		183+185	183+185
187	187		187	187
194	194		194	194
198+199	198+199		198+199	198+199
203	203		203	203
209				

PMF RESULTS

Many permutations of the data set were analyzed. The results are summarized in Table 2. One of the central difficulties of factor analysis is determining the optimal number of factors that adequately describes the data set without over-fitting. In this study, we have followed the approach outlined in Rodenburg and Leidos (2017) to determine the optimal number of factors for each data set. The number ranged from five to seven. In all cases, the PMF model converged on a solution that was interpretable. Thus, we conclude that PMF analysis can be performed on the Spokane River ambient water data and yield useful results.

Due to the large number of data sets (permutations) analyzed, it is cumbersome to discuss each one individually. Therefore, we will discuss the general features of each PMF solution, with the full results presented in the appendix.

All of the permutations of the data set yielded the following five factors:

- a factor strongly resembling Aroclor 1254 with similarity (R²) values ranging from 0.80 to 0.98
- a factor very similar to Aroclor 1260 with R² values ranging from 0.70 to 0.81
- a factor similar to Aroclor 1248 with R² values ranging from 0.63 to 0.89
- one (or sometimes two) factors that were similar to low molecular weight Aroclors 1016 and/or 1242 with R² values ranging from 0.35 to 0.84
- a factor dominated by PCB 11

Furthermore, all permutations generally agreed on the contribution of these factors to the total mass of PCBs *in the data set* (keeping in mind that different data sets contain differing amounts of mass, based on how much mass is discarded during censoring/subtraction; see “% of PCB mass included” in table 2).

When the PMF model converged on more than five factors, the additional factors fell into four categories:

1. Aroclors. As noted above, sometimes the PMF model generated two factors that both resemble lower MW Aroclors.
2. Monochlorinated PCBs probably associated with phenyl-based silicone. As noted above, silicone contamination fell into two groups. The first was dominated by PCB 1, 2, and 3 (labeled ‘mono’ in table 2) and appears to represent PCBs from silicone caulks, lubricants, etc. This factor was only generated from the data set employing no blank correction and utilizing the maximum number of peaks (Uncor73). All other data sets

discarded these three congeners because they were frequently detected in blanks, and therefore did not generate this factor.

3. Tetrachlorinated PCBs associated with peroxide-cured silicone. The second type of silicone factor was dominated by PCBs 44+47+65 and 45+51 (labeled 'tetra' in table 2) and represents PCBs from silicones that have been cured using bis(2,4-dichlorobenzoyl) peroxide. This factor was isolated in uncorrected data sets in which these congeners were present, and in BatchCensor61, a data set in which the batch-specific method blank(s) was used to censor the data. Note that this factor could not be produced in any of the data sets with 59 peaks, because these data sets specifically excluded these two peaks.
4. Data sets generated via blank subtraction sometimes produced a factor that was not interpretable (labeled "Mystery factor" in table 2). It contained congeners that are present in Aroclors, but in proportions that do not match the Aroclors: PCBs 31, 52, 66, and 118. For example, MaxSub61F4 consisted of 8%, 16%, 13% and 13% of these congeners, respectively. Perdih and Jan (1994) found PCBs 52 and 66 in silicone, but not PCBs 31 and 118. Anezaki and Nakano (2015) found PCB 31, 52, and 66 in silicone-based products. However, this mystery factor contained almost no contribution from PCBs 44+47+65 and 45+51, suggesting it is not related to silicone. We speculate that the process of subtracting blank masses introduced a pattern to the data that the PMF program recognized. This pattern may be merely an artifact of the blank subtraction procedure, not an indicator of a unique source of PCBs.

Table 2. Summary of the results of analyzing several permutations of the Spokane River ambient water data set (139 samples) using PMF2.

Name	Correction method	Which blanks?	Approach	Congeners /peaks	% of PCB mass included	# factors	Silicone factor?	Mystery factor?	Low MW Aroclors	Aroclor 1254	Aroclor 1260	PCB 11 factor	Other
Uncor73	none	none	A	73	96.6%	7	mono + tetra	no	38%	24%	16%	11%	11%
Uncor68	none	none	A + D	68	94.4%	7	tetra	no	46%	21%	15%	14%	5%
Uncor61	none	none	A + D	61	90.9%	7	tetra	no	45%	21%	15%	13%	6%
Uncor59	none	none	A + D	59	85.2%	6	no	no	47%	22%	15%	15%	0%
BatchCensor68	cancel	batch	B	68	90.7%	5	no	no	41%	24%	23%	12%	0%
BatchCensor61	cancel	batch	B + D	61	87.7%	7	tetra	no	47%	16%	20%	10%	7%
BatchSub68	subtract	batch	C	68	68.3%	6	no	no	51%	22%	19%	8%	0%
BatchSub61	subtract	batch	C + D	61	66.4%	5	no	no	43%	25%	22%	10%	0%
MaxCensor61	cancel	all	B	61	78.9%	5	no	no	47%	21%	19%	13%	0%
MaxCensor59	cancel	all	B + D	59	74.2%	5	no	no	45%	21%	21%	13%	0%
MaxSub61	subtract	all	C	61	54.2%	6	no	yes	37%	23%	25%	9%	5%
MaxSub59	subtract	all	C + D	59	51.4%	6	no	yes	38%	25%	19%	10%	8%

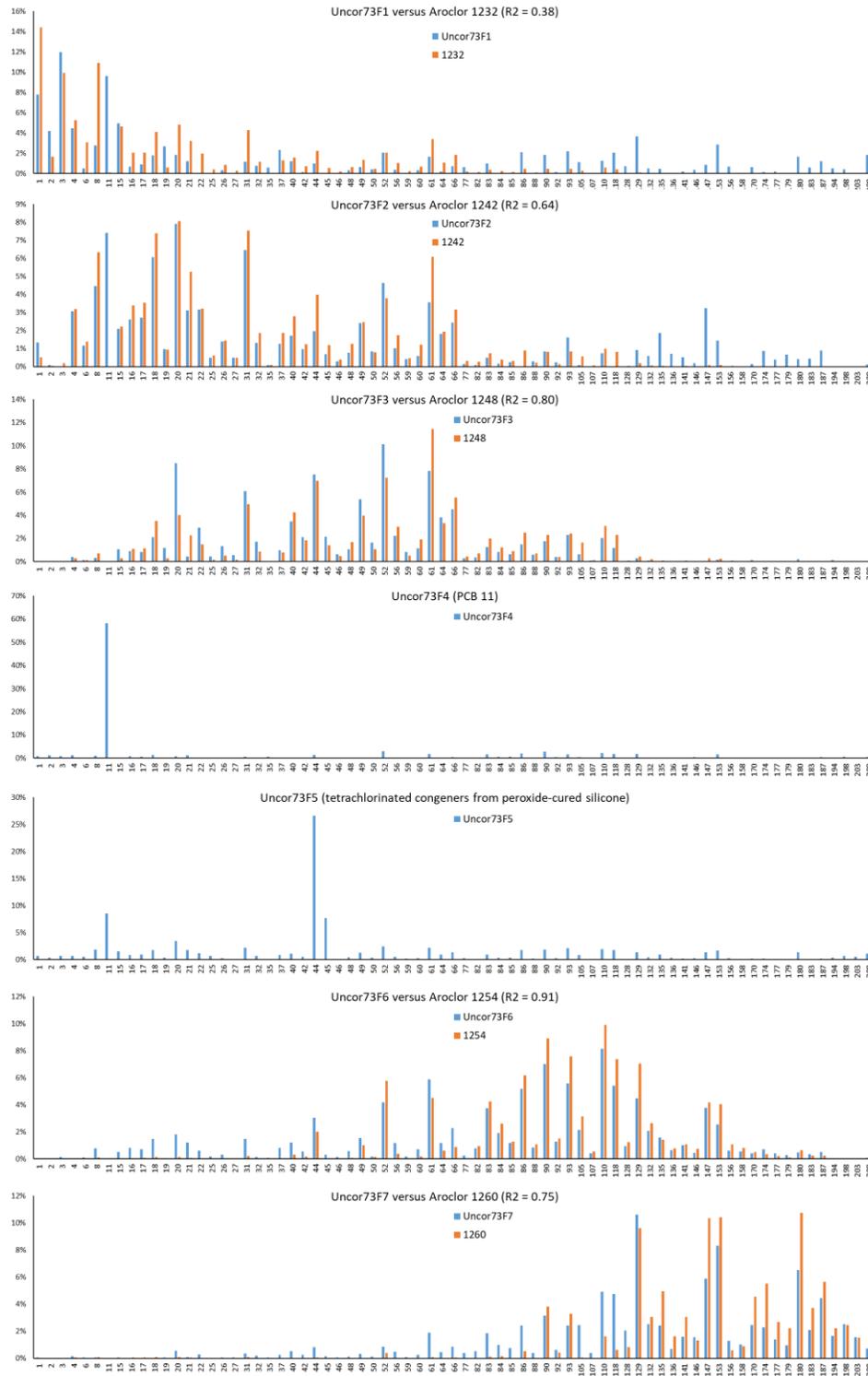


Figure 2. The seven factors isolated by PMF analysis for the Uncor73 data set, compared with their best-match Aroclors. Uncor73F1 is thought to be related to phenylsilanes, but is compared with Aroclor 1232 here.

Approach A: uncorrected data, 73 peaks (Uncor73)

The uncorrected data was analyzed using PMF to determine whether factors representing blank contamination would be isolated. This data set contained 73 peaks with 13% of all data points ND (see table 1). This data set contains 96.6% of all the PCB mass measured in all samples/peaks, i.e. the discarded congeners contain only 3.4% of the mass (ND=0). PMF analysis suggested that the optimal number of factors was seven (Figure 2). The five basic factors were produced plus two representing silicone. Uncor73F1 contained high proportions of PCBs 1, 2, 3, 11, and 209 and therefore represents phenylsilanes, though it is compared to Aroclor 1232 in Figure 2. It probably arises from blank contamination. It explains 6% of the PCB mass. Uncor73F5 contains high proportions of PCBs 11, 44+47+65 and 45+51, suggesting that it is related to peroxide-cured silicone, either as a blank contaminant or from use of silicone in the watershed. It explains 6% of the PCB 11 mass, 34% of the PCB 44+47+65 mass, and 39% of the mass of PCB 45+51. It explains 5% of the total PCB mass.

Uncor73F4 contains 40% PCB 11 and therefore represents the amount of PCB 11 that is not well correlated with the congeners in Uncor73F1 such as PCBs 1, 2, and 3. Uncor73F4 explains 17% of the total PCB mass. Uncor73F1 explains 7% of the PCB 11 mass, while Uncor73F4 explains 85%. This suggests that the vast majority of the PCB 11 mass arises from the water samples themselves, not from blank contamination.

The results of the analysis of this data set (uncorrected for blanks and containing the largest number of peaks possible) suggest that Aroclors are the dominant source of PCB contamination in the Spokane River, and that PMF analysis can generate factors that resemble blank contamination.

In order to make direct comparisons between the uncorrected data and the blank censored and subtracted data, we analyzed additional data sets containing uncorrected data with 68, 61, and 59 peaks (refer to table 1 for peak lists).

Uncor68 and Uncor61 each generated seven factors: the basic five plus an additional Aroclor factor and a factor representing tetrachlorinated congeners related to peroxide-cured silicone. The tetra silicone factor also contained some PCB 11. The extra Aroclor factor allowed these solutions to isolate two factors that resembled mixtures of Aroclors 1016, 1242, and 1248.

Uncor59 did not isolate a tetra silicone factor, because these two peaks (44+47+65 and 45+51) were excluded. Similar to Uncor68 and Uncor61, the Uncor59 model isolated an extra Aroclor factor.

These data sets (uncorrected for blanks, containing shorter congener lists) corroborate the findings from the Unc73 data set: Aroclors are the dominant source of PCB contamination in the Spokane River, and PMF analysis can generate factors that resemble blank contamination.

Approach B: Censored data

Censoring was performed using one times either the batch-specific blank(s) or the maximum of all blanks. Using batch-specific blanks was a less aggressive form of blank correction that allowed 68 peaks and 90.7% of the total PCB mass to be used in the PMF model (BatchCensor68). This approach yielded a solution containing only the five basic factors.

For purposes of comparison, we analyzed the same data set with just 61 peaks (BatchCensor61), which yielded 7 factors: the basic five plus an additional Aroclor factor and a tetra silicone factor. Although it seems counter-intuitive, this is not an unusual result: Sometimes smaller data sets actually yield more factors. The reasons for this are unknown, but we speculate that the exclusion of more data, especially when many of the data points that are eliminated are ND, reduces the noise in the data and makes it easier for the PMF program to identify the signal. BatchCensor 61 was the only censored data set that produced the tetra silicone factor. Thus censoring of the data usually but not always eliminated all factors related to silicone.

Using the maximum concentration across all method blanks to censor the data set was a more aggressive form of blank correction: it resulted in a greater loss of mass than censoring using the batch-specific blank(s). For example, the BatchCensor61 data set contained 87.7% of the PCB mass detected in all samples, while the MaxCensor61 data set contained just 78.9%. This approach yielded five factors for both the MaxCensor61 and MaxCensor59 data set, i.e. factors representing blank contamination were no longer identified.

Approach C: Blank subtraction

Blank subtraction resulted in a loss of mass greater than censoring. For example, BatchSub61 contained just 66.4% of the PCB mass detected in all samples. In contrast, BatchCensor61 contained 87.7%. In both cases, 18% of the data points were designated as ND. Note that the same data points are designated as ND in both the censored and subtracted data sets. The difference lies in the subtraction of mass from data points that are designated as detected. The

difference was even more pronounced when the maximum of all blank concentrations was used for subtraction. MaxSub61 contained just 54.2% of the PCB mass detected in all samples, versus 78.9% for MaxCensor61.

When the batch-specific method blank(s) was used for subtraction, the model converged on either six factors (BatchSub68) or five (BatchSub61). The sixth factor isolated from the BatchSub68 data set represented a mix of low molecular weight Aroclors. Thus blank subtraction always eliminated the factors related to silicone products.

When the maximum concentration across all blanks was used for subtraction, determining the optimal number of factors was difficult, but this is presumably not due to the high number of ND data points, since the same number of ND values yielded a stable solution in the censored data set. Eliminating peaks or samples with high number of ND values would almost certainly help the stability of the model, but information is lost when samples/peaks are discarded. One way to assess the stability of the model is to compare the various seed runs. Our common practice, followed here, is to originate the model at ten random starting points, i.e. 'seed values'. If the model is finding a global minimum (i.e. lowest value of E from equation 1), then all ten seed runs should give virtually identical model solutions. The four factor model was stable with all ten seed runs agreeing (RSD = 0.2%). The five factor model was bifurcated: four of the ten seed runs agreed with each other, and the other six also agree with each other. This is often a sign that the model wants to create two new factors, but can't decide which one to create first, and therefore indicates that the model solution with one additional factor (in this case, six) will be stable. The six factor solution was reasonably stable: nine of the ten seed runs agreed with each other (RSD = 5.7%). Here we will interpret the six factor model. It contained the five basic factors, but the additional factor was difficult to identify. This factor was described above as the 'mystery' factor, and contained high proportions of PCBs 31, 52, 66, and 118. Perdih and Jan (1994) found PCBs 52 and 66 in silicone, but not PCBs 31 and 118. This factor contains almost no contribution from PCBs 44+47+65 and 45+51, suggesting it is not related to silicone. We speculate that the process of subtracting blank masses introduced a pattern to the data that the PMF program recognized. This pattern may be merely an artifact of the blank subtraction procedure, not an indicator of a unique source of PCBs.

Approach D: Exclude problematic congeners

Approach D was applied to the uncorrected, max blank censored, and max blank subtracted data sets. In all cases, PCBs 44+47+65 and 45+51 were excluded from the data sets, leaving 139 samples and 59 peaks. Elimination of these two PCB peaks meant that the PMF program was unable to produce a factor related to peroxide-cured silicone. This was only important for the

uncorrected data set (Uncor59) because Uncor61 had produced a tetra silicone factor. Since MaxCensor61 and MaxSub61 did not produce the tetra silicone factor, eliminating these congeners had little effect on the model solution. Notably, MaxSub59 continued to produce a factor that is dominated by PCBs 31 (5%), 52 (13%), 66 (16%), and 118 (14%), i.e. the 'mystery' factor.

CONCLUSIONS

The purpose of this study was to determine whether PMF could be successfully used on this data set despite the blank contamination issues, and if so, to identify which approach (or combination of approaches) best addresses the impact of blank contamination on the analysis of low levels of PCB measured in the Spokane River water column.

Regarding the first goal, PMF was successfully applied to these data sets and told a consistent story about PCB contamination in the Spokane River. All of the various PMF models suggested that Aroclors are the dominant source of PCBs to the Spokane River. All suggest that PCB 11 is present in the river at levels that cannot be accounted for by blank contamination, and that sources of PCB 11, probably pigments, are responsible for a small fraction of the PCB problem in the Spokane River. It is important to note that while the factor containing most of the PCB 11 mass accounts for 8% to 15% of total PCB mass in these data sets, this does not imply that 8% to 15% of PCBs in the Spokane River come from non-Aroclor sources. In other systems, PCB 11 has been associated with secondary sources such as stormwater. For example, in the Delaware River, the factor containing most of the PCB 11 mass was thought to be associated with stormwater and combined sewer overflows because it was more prevalent at high river flow (Du, Belton et al. 2008). If the same is true in the Spokane River, the other PCBs in this factor may arise from Aroclors, but have undergone a great deal of weathering. In other words, these congeners may be moving with PCB 11 via the same transport mechanism even though they have a different primary source. This possibility will be fully explored in the second round of the project, when the full ambient water data set is available.

The various data sets analyzed by PMF paint a remarkably consistent picture of PCB sources to the Spokane River (Table 2). In this table, 'other' represents either PCBs from silicone or the unidentified factor. These are typically present when the data set is not corrected for blank contamination, other than the removal of some congeners. When censoring is performed, these other factors usually disappear, suggesting that they are associated with blank contamination, instead of representing real sources of PCBs to the Spokane River. This issue of whether certain factors are 'real' or artifacts of blank contamination is discussed in more detail

below. Subtraction introduces the 'mystery' signal into the PMF results, resulting in a non-zero percentage in the 'Other' category in table 2.

All data sets indicate that low molecular weight Aroclors (1016, 1242, and 1248) are the largest source of PCBs to the Spokane River, accounting for about 45-47% of total PCB mass. Aroclor 1254 is the second largest PCB source, accounting for 21-22% of PCB mass, and Aroclor 1260 is responsible for 15-21% of PCB mass in the Spokane River.

Selection of best approach(es)

The criteria used to evaluate the success of each approach were as follows:

1. The approach should generate a stable model solution.
2. The model solution should be interpretable, i.e. the results make sense based on everything we know about PCB contamination in general and in the Spokane River in particular.
3. Other criteria being met, the bias should be towards using the approach that includes the largest amount of mass and the largest number of peaks possible.

Based on the first criterion, all data sets converged on a solution. In some cases (Uncor73, BatchCensor68, MaxSub61), the optimal solution was a product of only nine of the ten seed runs, but this is not unusual and did not prevent us from identifying the optimal solution. Thus all approaches met the first criterion.

In order to evaluate the approaches under criterion two, we need to determine whether the factors produced by the PMF analysis are 'real', i.e. they reflect the actual conditions in the river, or are 'artificial', i.e. they are due to blank contamination. The fact that the same five basic factors are produced by all model runs suggests that these five factors at least are 'real'. Note that this implies that PCB 11 contamination in the Spokane River is real. There is no method of blank correction that makes the PCB 11-dominated factor disappear.

The approaches using blank subtraction generated a 'mystery' factor that is uninterpretable and did not appear in any other model runs. Therefore, blank subtraction fails under criterion #2. The preponderance of evidence suggests that the mono silicone factor is an artifact, since it does not appear in any model run except those for which no blank correction of any kind is performed.

The tetra silicone factor is a bit more robust, but this is likely due to the fact that PCBs 44+47+65 and 45+51 are present in the Aroclors, such that these congeners are real contaminants in the river, and blank correction does not, and should not, eliminate them. The

tetra silicone factor was not produced by the vast majority of data sets that included 68 or 61 congeners (i.e. that included these two peaks). However, when the model produced a factor that was dominated by these two congeners, it did a better job of reproducing their concentrations. When the tetra silicone factor is generated, the model fit (R^2 between the measured and modeled concentrations) for PCBs 44+47+65 and 45+51 ranges from 0.938 to 0.999. When the tetra silicone factor is not generated, R^2 values are lower, ranging from 0.617 to 0.877. This suggests that there is some variation in the concentrations of these two peaks that cannot be explained without the tetra silicone factor.

To estimate the size of this anomaly, the G matrix of the model solution for the largest data set that did not generate the tetra silicone factor was investigated (BatchCensor68). In this solution, the average residual (measured minus modeled concentration) for all PCB peaks was 0.025 pg/L. (The average residual is small but positive due to PMF's robust mode, which down-weights high concentrations, causing the modeled concentration to be lower than the measured concentration.) The average residual for PCB 44+47+65 was the largest among all peaks at 0.59 pg/L, i.e. this is the average amount of PCB 44+47+65 in the water samples that is not explained by the basic five factors and is not eliminated by blank censoring. It therefore might be due to silicone. The next-highest average residuals are for PCBs 61+70+74+76 (0.26 pg/L), 45+51 (0.23 pg/L), 11 (0.21 pg/L), and 21+33 (0.21 pg/L). These congeners have all been detected in silicone-based products or feedstocks (Perdih and Jan 1994, Anezaki and Nakano 2015). Summing these residuals suggests that the impact of silicone on water quality in the Spokane River is at most about 1.5 pg/L, which is within the noise. (In this work, we estimated the uncertainty in the surface water PCB measurements to be roughly equal to the standard deviation of the surrogate recoveries, or about 10% to 15%. The averaged measured Σ PCB concentrations were 171 pg/L (ND = 0), so the uncertainty is about 17 to 26 pg/L.) Thus, we conclude that silicone is not a significant contributor to PCB water pollution in the Spokane River.

Assuming that the tetra silicone factor is mostly a result of blank contamination, we can conclude that model runs that do not generate this factor are acceptable. Since all of the runs utilizing blank censoring produced the same basic five factors, they are all acceptable under criterion #2.

Criterion #3 calls for the model to incorporate as much of the data as possible. This criterion suggests that we should utilize the batch-specific blank concentration(s) instead of the maximum concentration across all blanks. Further, this criterion suggests that we should use the longest congener list possible. In this study, BatchCensor68 satisfies criterion #3 the best. Retaining PCBs 44+47+65 and 45+51 allows us to use the PMF model to determine whether

silicone contamination is significant. Eliminating these congeners may leave us blind to this source of contamination and is not recommended for the data set considered here. Note that this conclusion may change once the full data set is available if clear evidence of contamination from silicone rubber tubing is found.

The second goal of this study was to determine which approaches are most useful for accounting for blank contamination when conducting source apportionment in the Spokane River. My recommendations are as follows.

1. Blanks and samples should both be carefully examined for patterns related to silicone PCBs via some of the methods described above under the section on PCB 68, i.e. prior to PMF analysis.
2. Conducting PMF analysis on the PCB concentrations in the blanks proved to be very useful in identifying the sources of PCBs to blanks. We recommend that this be performed again when the full data set becomes available.
3. Blank censoring should be performed on the data at one times the batch-specific blank concentration (approach B), but congeners should not be discarded solely because they may be associated with silicone (approach D).
4. PMF analysis of the uncorrected data set was useful. We recommend conducting such an analysis using the same congener list as in recommendation 3 above.

FUTURE DIRECTIONS

This report has recommended an approach for analyzing the full data set on PCB concentrations in the Spokane River that should become available in 2019. The results of this study also point to some future directions to be pursued in the next stage. We expect that the results from the full data set will be similar to those obtained in this study, i.e. the PMF results will contain the five basic factors (four Aroclor factors and a factor related to PCB 11). The results might also contain a factor associated with peroxide-cured silicone (i.e. tetra silicone). To investigate whether the PCB 11 factor (and any tetra silicone factor) is related to blank contamination or is a real indicator of Spokane River contamination, we will investigate the spatial and temporal variations in the concentrations of these factors using the G matrix output of the PMF model. For example, if the PCB 11-dominated factor is related to stormwater/treated wastewater/CSOs, it should be more abundant just downstream of discharge points for these sources. Process water from Inland Empire Paper also likely contains significant amounts of PCB 11, so PCB 11 concentrations in the river should be higher downstream of their discharge. Also, PCB 11 concentrations would be expected to increase during high flow events related to recent rains, but decrease in high flow events related to the spring freshet. In the more limited

data set examined here, nearly all of the samples were collected a low river flow, which might make it difficult for us to examine the changes in factor concentrations with river flow.

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