Biofilm and Surface Water Fingerprinting of PCB Data ~~at~~ near GE Site

Prepared for:
Spokane River Regional Toxics Task Force

June 20, 2023
TTWG REDLINE REVIEW DRAFT

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Executive Summary

The Spokane River and Lake Spokane have been placed on the State of Washington's 303(d) list of impaired waters due to elevated concentrations of polychlorinated biphenyls (PCBs) in fish tissue, as specified by Washington's Water Quality Assessment Listing Methodology to Meet Clean Water Act Requirements (Water Quality Program Policy 1-11)[1]. To address these impairments, the Department of Ecology (Ecology) has been pursuing a toxics reduction strategy that included the establishment of a Spokane River Regional Toxics Task Force (Task Force). One of the key missions of the Task Force is to identify and remove sources of PCBs to the Spokane River. PCB contamination in groundwater is known to exist at the National Priorities List contaminated site known as the General Electric Co. Spokane Apparatus Service Shop ("GE Site"). Cleanup actions at the site were accepted as complete in 1999 when it was not ~~known~~ suspected that the site groundwater ~~was~~ could be a pathway for PCBs to reach surface water ~~(EPA, 2022)~~. However, recent fingerprinting of PCB loading to the Spokane River and PCB concentrations in regional groundwater found "a strong correlation between the homolog patterns at the GE site and the homolog patterns estimated by the mass balance assessment" for the affected reach of the river (LimnoTech, 2018a). The Washington State Department of Ecology's 1993 Cleanup Action Plan did not consider the potential for a complete groundwater to surface water pathway and no additional remedial actions have taken place since remedy implementation (WSDOE, 1993) ~~To date, the cleanup levels and remedies for the site have not been changed to reflect the apparent pathway to surface water (EPA, 2020).~~

This study describes the application of polytopic vector analysis (PVA) to support a determination of whether a PCB "signal" ~~from the GE groundwater~~ can be observed in Spokane River water column and biofilm in the vicinity of the GE Site and the similarity of this signal to patterns observed in GE groundwater. We recognize that sources of PCB contamination other than GE may exist in this area, and that presence of a PCB signal in the river is not definitive evidence that GE is the cause of this signal.

Surface water data from 2018 and 2022 and biofilm data from 2018 and 2019 were combined in a single data set and analyzed using PVA. The standard Task Force ~~C~~correction for ~~Blank~~ blank contamination (3x censoring) produced too many zeros in the sample compositions for PVA analysis so the data were used without blank correction. The PVA process starts with a principal components analysis step and recalculates the principal components such that the final components (called end-members, interpreted as source compositions) and their coefficients (called loadings, interpreted as source contributions) are positive while capturing the same data variability as the original principal components. The analysis yielded 10 end-members separating source end-members from blank contamination mixtures. We identified ~~as~~ Aroclor mixtures and

[1]Fish tissue PCB concentrations are considered as part of narrative water quality standards.

non-Aroclor mixtures which had contributions consistent with source locations or connected to samples on certain dates, and the composition of blank contamination on those dates. The end-member compositions were compared to GE groundwater well compositions as well as the congener increases in surface water downstream of GE calculated using a mass-balance analysis.

The PVA identified two end-members that can be linked to the composition of GE groundwater samples. One of these end-members resembles Aroclor 1260 and is present in biofilm located adjacent to where GE-impacted groundwater is expected to enter the Spokane River. This end-member is estimated to increase the total measured biofilm PCB concentrations at the GE left bank monitoring site by an average of 22% compared to upstream biofilm stations. The other GE-related end-member resembles a mixture of Aroclors 1260, 1254 and 1248. The congener pattern for this end-member is similar to the congener pattern calculated via mass balance assessment of the incremental loading required to explain the change in water column PCB concentrations between stations upstream and downstream of the GE site. These results strongly suggestadd weight to the hypothesis that a groundwater source with a composition similar to that seen in GE groundwater is present in transports PCBs from GE to the Spokane River affecting PCBs in the river downstream.

1 Introduction

The Spokane River and Lake Spokane have been placed on the State of Washington's 303(d) list of impaired waters due to elevated concentrations of polychlorinated biphenyls (PCBs) in fish tissue, as specified by Washington's Water Quality Assessment Listing Methodology to Meet Clean Water Act Requirements (Water Quality Program Policy 1-11)[2]. To address these impairments, the Department of Ecology (Ecology) has been pursuing a toxics reduction strategy that included the establishment of a Spokane River Regional Toxics Task Force (Task Force). One of the key missions of the Task Force is to identify and remove sources of PCBs to the Spokane River. PCB contamination in groundwater is known to exist at the National Priorities List contaminated site known as the General Electric Co. Spokane Apparatus Service Shop ("GE Site"). Cleanup actions at the site were accepted as complete in 1999 when it was not ~~known~~ suspected that the site groundwater was a pathway for PCBs to reach surface water ~~(EPA, 2022)~~. However, recent fingerprinting of PCB loading to the Spokane River and PCB concentrations in regional groundwater found "a strong correlation between the homolog patterns at the GE site and the homolog patterns estimated by the mass balance assessment" for the affected reach of the river (LimnoTech, 2018a). The Washington State Department of Ecology's 1993 Cleanup Action Plan did not consider the potential for a complete groundwater to surface water pathway and no additional remedial actions have taken place since remedy implementation (WSDOE, 1993) ~~To date, the cleanup levels and remedies for the site have not been changed to reflect the apparent pathway to surface water (EPA, 2020).~~

This study describes the application of polytopic vector analysis (PVA) to support a determination of whether a PCB "signal" ~~from the GE groundwater~~ can be observed in Spokane River water column and biofilm~~.~~ in the vicinity of the GE Site and the similarity of this signal to patterns observed in GE groundwater. We recognize that sources of PCB contamination other than GE may exist in this area, and that presence of a PCB signal in the river is not definitive evidence that GE is the cause of this signal.

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.

This report documents the analyses conducted and conclusions drawn. It is divided into sections of:

- Background: describes the scope of the current study and its relationship to previous similar studies.
- Methods - Polytopic Vector Analysis: describes the PVA method employed for PCB congener data analysis.

[2]Fish tissue PCB concentrations are considered as part of narrative water quality standards.

- Results: presents the final model selection, model output and interpretation ~~of GE impact~~with regard to ~~GE's hypothesized~~an observable impact on the river in the vicinity of the GE site..
- Conclusions: provides conclusions with regard to questions posed in the scope of work.

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2 Background

This section describes the purpose of this analysis in terms of the questions it was intended to address, previous related work and concludes with a description of the data used for the analysis.

2.1 Purpose of Fingerprinting Analysis

The purpose of this analysis is to support completion of the work originally scoped by US EPA to assess whether groundwater from the GE Site is delivering noticeable amounts of PCBs to the Spokane River and, if so, to provide an assessment of the magnitude of the load (US EPA, 202~~2~~0). The following relevant questions were identified in the October 18, 2022 Scope of Work:

1. How many distinct sources and processes contribute to the observed PCB congener compositions (i.e., number of end-members)?
2. What is the PCB congener composition of each end-member?
3. What is the identity of each end-member in terms of Aroclors and alteration mechanisms (degradation, weathering, uptake, etc.)
4. Can some of these end-members be linked uniquely to groundwater inputs, to the original groundwater composition at the GE source, or to the mass-balance changes by congener?
5. What is the magnitude of the contribution of the GE-linked end-members in the biofilm samples?
6. What is the trend of the ~~GE-linked~~ contributions from sources similar to GE downstream of the suspected input?
7. Can this contribution be used to estimate the significance of ~~GE~~ these PCB inputs to the river as a whole?

2.2 Related previous and concurrent analysis and their relationship to this effort

In 2022, Dr. Lisa Rodenburg reported on her study of Spokane River biofilm, SPMD, and fish tissue PCBs using Positive Matrix Factorization (PMF) (Rodenburg, 2022). The PMF method is closely related to PVA and these methods yield equivalent results (Johnson et al., 2015). The PMF analysis of biofilm and SPMD samples together yielded the presence of Aroclors 1242, 1248, 1254, 1260 and 1268 in biofilm, with an apparent enrichment of Aroclors 1254 and 1260 in biofilm samples downstream of GE. In addition, Dr. Rodenburg and collaborators conducted a PMF study on the sources of blank contamination as well and concluded that commercial Aroclor mixtures are sources of blank contamination (Rodenburg, 2019). Their study also indicated that aggressive censoring of samples with contaminated blanks is not necessary, and that **analysis of the uncorrected dataset is useful**.

The scope of the current work is narrower than the studies by Rodenburg et al., focusing on samples from a more limited reach around the GE site. We also explicitly include surface water and biofilm together in a single data set and use the newest surface water data collected in 2022. Overlap of results can be expected with greater resolution on the explicit question regarding the

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these methods yield equivale
we should consider all of the
Dr. Rodenburg's analysis of h
prior to completing PMF and

Conclusions:
Blanks and samples should b
examined for patterns prior t
2. Conducting PMF analysis c
concentrations
in the blanks proved to be ve
identifying the sources of PC
recommend that this be perf
of
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contamination.
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useful.
We recommend conducting
using the same analyte list as
3 above so that the results ma
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"

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impact of GE groundwater and a diminished emphasis on the interpretation of sources unrelated to GE except to the extent necessary for confidence in the model results.

LimnoTech (2018b) conducted a PVA analysis of Kaiser groundwater samples that found the presence of Aroclors 1242, 1248, 1254 and a PCB11 mix. The current work is expected to detect a Kaiser related PCB mixture, though the comparison to this previous study serves to bolster confidence rather than to explore ~~non-GE related~~ sources entering the river distant from the GE site.

The current PVA work parallels a concurrent mass-balance approach to determining the possible influence of GE groundwater on the Spokane River. The results of the mass-balance are explicitly included in the interpretation of PVA results, as they serve the same overall scope objectives.

2.3 Data Sources

The analyses were conducted on PCB congener data from surface water, wastewater effluent discharged to the river, and biofilm samples from the Spokane River and groundwater monitoring well samples from the GE site. The surface water and biofilm data span the reach between Mirabeau Point and Greene Street, selected to include information about upstream "baseline" such as known point sources and locations just downstream of the ~~suspected~~ GE ~~groundwater input~~site. The goal was to ensure sufficient resolution of variability to distinguish ~~GE~~ groundwater near GE from other sources without unnecessary additional variability that could mathematically dilute the signal. The data were drawn from the 2018 and 2019 biofilm data sets, the 2018 and 2022 synoptic survey of the Spokane River (these years lack effluent data for Kaiser Aluminum) and GE groundwater monitoring data from 2016. Figure 1 shows sample locations. Table 1 below shows the locations and years included along with reason for inclusion in the analysis. Tables A.1 and A.2 in Attachment A list additional sample information.

Table 1. Summary of Sample Locations.

Station Descriptor	Station ID	Media Sampled	Sample Dates	Purpose
Plante's Ferry	PF-BF	Biofilm	2018	PVA Analysis
Plante's Ferry	PF	Biofilm	2019	PVA Analysis
Barker Rd.	SR9	Spokane R. Water	2018	PVA Analysis
Mirabeau Point	SR8a	Spokane R. Water	2018	PVA Analysis
Trent Bridge	SR7	Spokane R. Water	2018, 2022	PVA Analysis
Inland Empire Paper	SR6	WWTP Effluent	2018, 2022	PVA Analysis
Downstream of Upriver Dam	SR5a	Spokane R. Water	2018, 2022	PVA Analysis
Upriver Dam – Right Bank	URD	Biofilm	2018, 2019	PVA Analysis
Upriver Dam – Left Bank	URD_LB	Biofilm	2019	PVA Analysis
Upriver Dam – Right Bank	GEM_LB	Biofilm	2018, 2019	PVA Analysis
Upriver Dam – Left Bank	GEM_RB	Biofilm	2018, 2019	PVA Analysis
Spokane County WRF	SR5	WWTP Effluent	2018, 2022	PVA Analysis
Greene Street	SR4	Spokane R. Water	2018, 2022	PVA Analysis
Greene Street – Left Bank	GR_LB	Biofilm	2018, 2019	PVA Analysis

Greene Street – Right Bank	GR_RB	Biofilm	2018	PVA Analysis
Groundwater at GE	MW22	Groundwater	2016	Interpretation
Groundwater at GE	MW18	Groundwater	2016	Interpretation
Groundwater at GE	MW11	Groundwater	2016	Interpretation
Groundwater at GE	MW21	Groundwater	2016	Interpretation
Groundwater at GE	MW19	Groundwater	2016	Interpretation
Groundwater at GE	MW10	Groundwater	2016	Interpretation
Groundwater at GE	MW20	Groundwater	2016	Interpretation
Groundwater at GE	MW01	Groundwater	2016	Interpretation

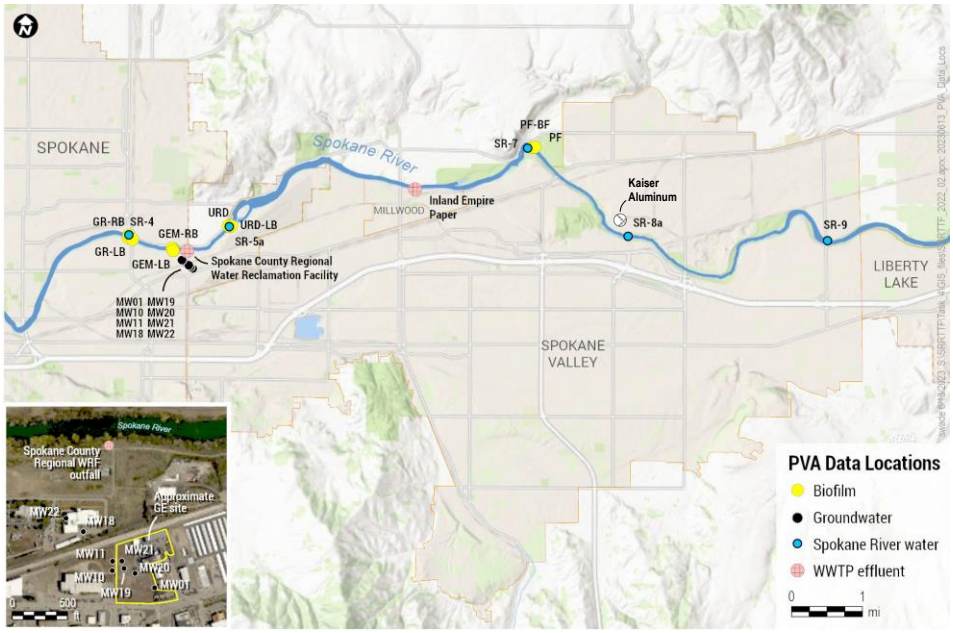

Figure 1. Sample locations

3 Methods - Polytopic Vector Analysis

This section describes how the PVA method works and how the data were prepared for analysis. 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).

3.1 The 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. This is possible because mixing in the environment is incomplete and original associations among congeners are preserved as spatial and temporal gradients. PVA is described by Johnson and Ehrlich (2002) and is comparable to other statistical fingerprinting methods (Johnson et al., 2015).

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 initial principal component 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 represent real world sources.

Figure 2 shows the conceptual relationship between characteristics of real-world source releases into the environment and the steps and outputs of PVA. Panel (A) shows that each source releases a "fingerprint" mixture that is unique and results from their own unique operations. Panel (B) demonstrates that the *composition* of a sample depends on where the sample was located with respect to the sources, and along transport pathways. The sample *composition* comes about during the mixing in the environment after all sources released their mixtures. The *composition* reflects how much each source *contributed* to the sampled medium (water or biofilm) at that location. Panel (C) shows how PVA evaluates *sample compositions* variability based on what chemicals tend to occur together in certain proportions. Panel (D) demonstrates that PVA unmixes the *sample*

compositions into possible original *source mixture compositions* (EMs) and simultaneously estimates the relative importance of the sources as coefficients, i.e., *EMs contributions* within each sample. The original fingerprints or sources are usually unknown, so *EM compositions* have to be compared against *documented compositions* for site-specific processes, and if available, on-site samples near the industrial processes in question. The identity is verified on the basis of the spatial distribution of the *contributions*. *Contributions* from an individual source are higher near the source's release location(s) and lower at a distance. This information allows interpretation of *end-members* with respect to the nature of the sources while the *contributions* allow mapping of a source's footprint of influence in the sampled environment.

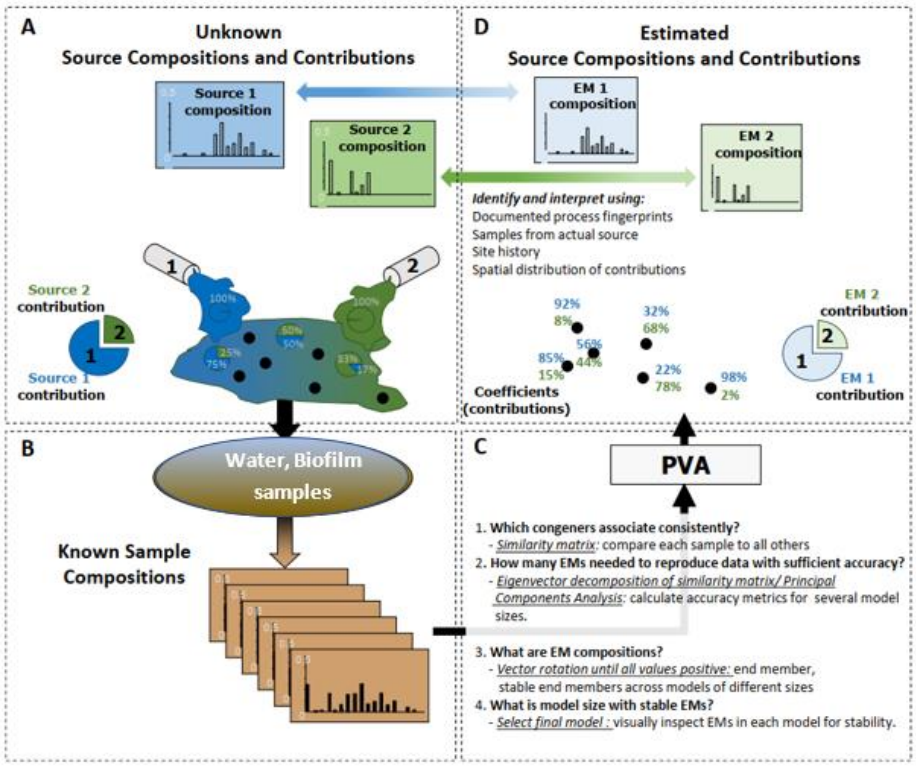

Figure 2. Conceptual diagram of the relationship between source releases, sampled mixtures, and PVA results.

In the case of PCBs, the interpretation of results includes comparing EM compositions to the composition of commercial Aroclor mixtures as reported by Frame et. al (1996). There are also sources of PCB congeners from industrial processes as also identified in Rodenburg et al. (2022). In addition, once in the environment, the original mixtures may be altered by dechlorination, chromatographic separation (removing heavy congeners and generating lighter congeners), volatilization (removing lighter congeners and enriching heavier congeners), phase partitioning

(heavier congeners with higher octanol-water partitioning coefficients sorb more strongly and desorb less readily than lighter congeners) and during the biological uptake process.

3.2 Data Preparation

The input data set for PVA has certain constraints that must be satisfied, and the data have to be prepared accordingly. Mathematically, the data matrix must be complete with no missing values. Too many non-detects and censoring can skew results as well as diminish the number of samples and/or congeners that can be included. We eliminated congeners from the input data that were never or very rarely detected in any medium. The blank correction was not applied for reasons summarized in the next section. ~~because it generated too many zeros for meaningful analysis.~~ Detection limits were not always available so all non-detect results were set to zero. The final data consisted of results for 128 congeners in 39 surface water, 12 effluent and 12 biofilm samples for a total of 63 samples. We also determined that the surface water and effluent data were variable, and each individual sample represented a potentially unique relative composition. Thus, we did not average samples at the same location, but used the original individual samples.

3.3 Considerations of Blank Contamination for Surface Water Samples

The low concentrations of PCBs in surface water make water samples susceptible to the effects of contamination from uncontrolled sources, as captured in the contamination detected in blanks (biofilm concentrations are 1-2 orders of magnitude above blank concentrations). We made the decision to use the sample results at face value and to evaluate the possible effects on the interpretation based on an understanding of the PVA process, composition of contaminated blanks and the nature of available correction methods. PVA fundamentally detects covariation, i.e., the tendency of certain congener groups to vary together. Thus, any source of variance can be detected by PVA, whether that variance stems from the input of PVA sources into the sampled medium, the input of unknown sources at unknown steps into the final sample (i.e., blanks, or sampling or laboratory error). As long as there is sufficient differentiation among the sources of variance and representation in the data (statistical signal) these different sources are separable by the PVA procedure. Having different, even if unknown causes, we expected contamination of blanks to vary differently from sample to sample and date to date than contamination due to Spokane River sources. At the resolution of a larger number (10, as reported below) of end-members used here we also expected the signal (the magnitude of variability) to be detectable. Due to these two factors, it is likely that the effect of confounding sources of variability such as that captured in blanks is separable into different end-members. If PVA does indeed separate the variance from the sources, then the impact of blank contamination on the objective of this study will be minimal and interpretable.

Figure 3. shows the composition of the 8/7/2018 sample at SR4, a key location downstream of GE, where we look for possible signs of GE impact in water. The congener distributions in the blank and the sample are similar, and the concentration ranges are comparable. Subtracting the blank concentrations from the sample concentrations shifts the composition towards the tri- and tetrachlorobiphenyls (negatives occur in the mono- and di- range), while the concentration range

remains similar. This subtraction shows more precisely where the impact of blank contamination occurs among the congeners: the impact is most pronounced in the range of the mono-, di-, and trichlorobiphenyls.

The blank correction method, however, is not a subtraction, rather it is a censoring (setting to zero) of only those congeners whose blank concentration exceeds the sample concentration by a certain pre-determined factor. Other congener concentrations are not altered even if blank contamination is present. We consider a sample to blank comparison at 1:1 (1x correction) and at 1:3 (3x correction) and determine the impact on the composition of the corrected sample at SR4.

Figure 3 also shows that both correction levels result in the removal of some congeners from consideration, without altering the relative composition of the remaining congeners. The 3x scenario removes many more congeners than the 1x scenario (the 3x scenario also generates too many zeros for conducting PVA with the surface water data). The implication for conducting PVA on censored data compared to uncensored data as we have chosen, is that the impact of censoring on congeners that are not consistently removed will be small, because the relationship between the retained congeners does not change, on the other hand, congeners that are sometimes removed and sometimes not, will alter to some extent the light end of PVA end-member compositions, while end-members dominated by light congeners will not be detectable. Whether this effect is beneficial or introduces artifacts depends on a few factors but is ultimately difficult to discern. What is certain is that blank correction affects the congeners unequally because of the censoring rules, which is itself a potentially confounding factor. (Interestingly, the composition of blank contamination is frequently very similar to the composition of the sample itself, as in the case of SR4, but the explanation is unknown.)

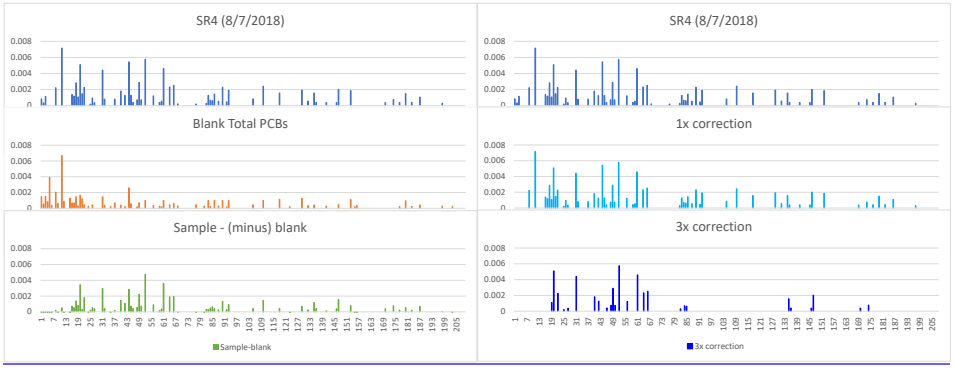

Figure 3. Concentrations in sample, blank, and effect of blank correction method on final sample concentration and composition (the sample SR4 is repeated to facilitate comparison to the profiles below).

The above example is on the basis of a single sample. To evaluate the larger context, Figure 4. shows the frequency of blank contamination in all surface water samples on a normalized scale (summing to 100%). This confirms the observation that blank contamination affects the lighter congeners much more than the heavier congeners in this dataset.

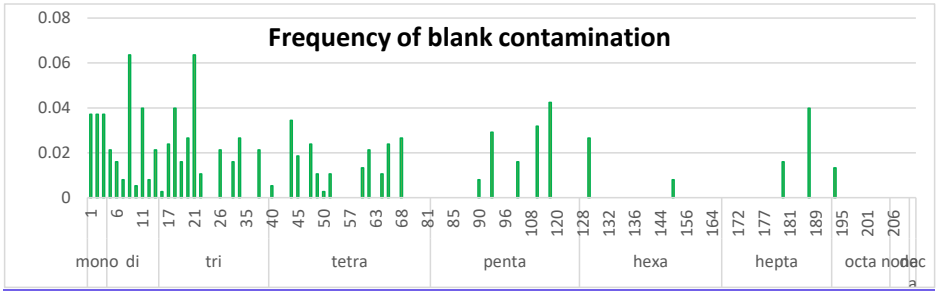

Figure 4. Frequency of blank contamination by congener included in the PVA analysis

By using an uncensored dataset, PVA can likely isolate the influence of blank contamination based on their differential impact on variability. This will likely manifest in separate end-members, apart from end-members representative of Spokane River PCB sources. The possibility of the other end-member compositions shifting relative to the "true" sources is also present, though this possibility is also present for a censored dataset.

Given that the possibility of confounding is present (and would be with censoring as well), it is particularly important to examine the spatial and temporal patterns of the PVA results, and consider their meaning in light of additional lines of evidence, which is best practice for any forensic fingerprinting technique.

4 PVA Results

In PVA, the modeler determines the most 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. The composition of the end-members stabilizes in the 10 EM model, and additional EMs do not result in interpretable additional EMs. Thus, the 10 EM model was selected as the final model, explaining 94% of the total variance in the data.

Figure 5 shows the end-members of the 10-EM model derived from the data set. The EMs are arranged in groupings corresponding to what type of source they represent on the basis of both composition and spatial patterns, discussed below. The group with orange or yellow labels (A-C) relates to biofilm and is consistent with GE patterns. The group with blue labels (D-F) relates to point sources. The group with grey labels (G-J) relates to mixtures that occur sporadically in single events and at single locations. Candidate matching Aroclor congener patterns as described by Frame et al (1996) are shown as grey bars on the same graph as the EM.

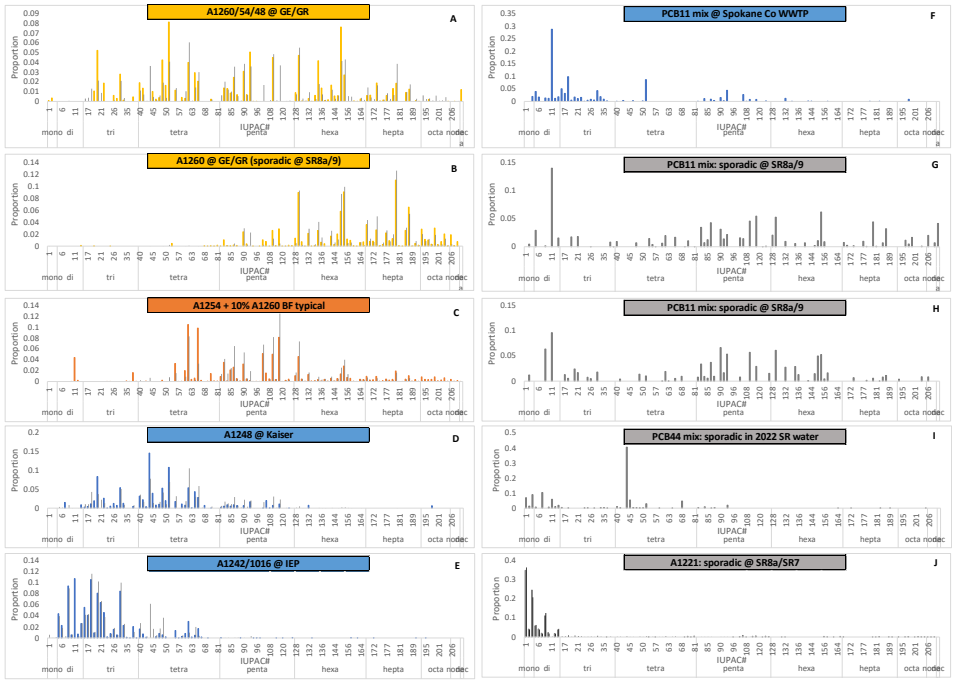

Figure 5. EMs of the 10 EM model and their corresponding interpreted identity and spatial or source association. Colored bars represent the EM composition and the matching pattern, where applicable, are represented by grey bars.

In the biofilm group of EMs, end-member A matches most closely a 35:35:30 mixture of Aroclors 1248:1254:1260. Contributions of this EM are highest in samples at and downstream of GE, seen in Figure 6. End-member B is a near-perfect match with Aroclor 1260. While EM B is present to some extent in all samples, its highest contributions are in surface water samples far upstream and in biofilm samples downstream of GE. Sporadically very high contributions (at SR9 2018-08-07 and SR4 2022-08-30) may be influenced by blank contamination. Excluding the one-time increase at SR4 2022-08-30, this EM does not increase in surface water downstream of GE. It increases in biofilm only. End-member C most closely matches Aroclor 1254 mixed with 10% Aroclor 1260. Its congener composition is slightly shifted from penta and hexachlorinated congeners towards di, tri and tetra chlorinated congeners, likely caused by biotic dechlorination. This EM is a defining component of biofilm samples. Biofilm compositions in other studies have been found to best reflect (biomagnify) components in surrounding water with a log K_{ow} value between 5 and 7 (Frouin et al., 2013; Hobbes et al., 2019). Aroclors 1254 and 1260 have overall log K_{ow} of 6.5 and 6.8 respectively (Table 4-3 in https://www.atsdr.cdc.gov/toxprofiles/tp17-c4.pdf), and they may be enriched in biofilm samples due to their optimal K_{ow} values for sorption. While being a defining component of biofilm PCB patterns, the relative contribution of this EM decreases in samples downstream of GE, due to being displaced by the increased contribution of EMs A and B.

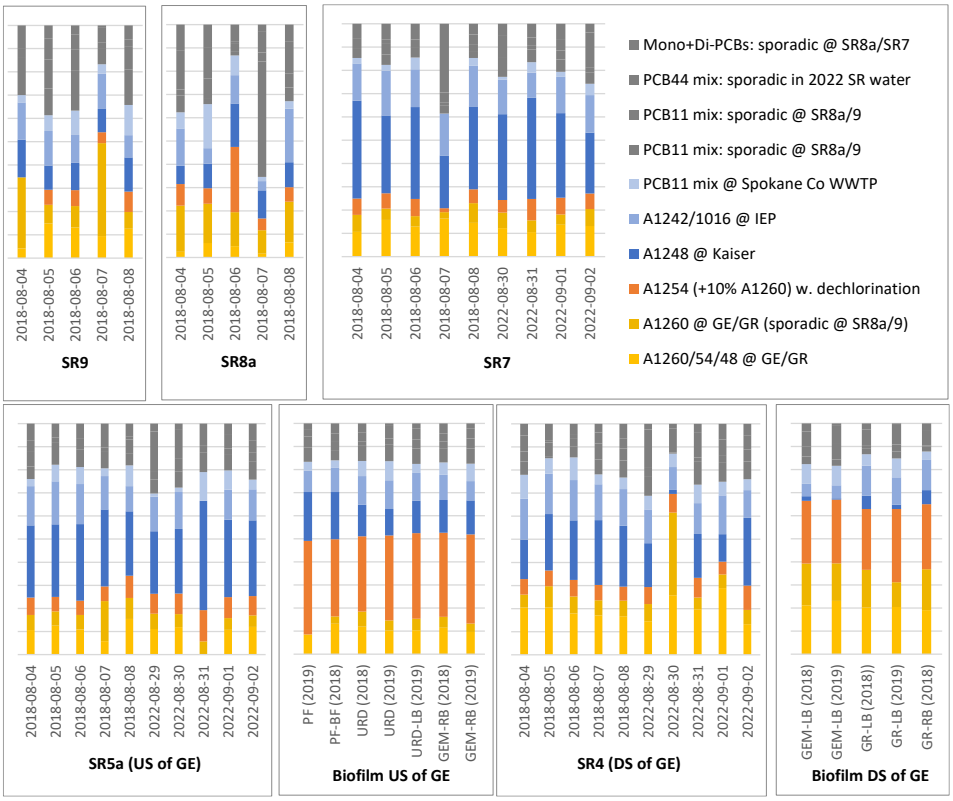

Figure 6. EM contributions in surface water and biofilm samples from upstream to downstream.

In the point source group, EM D matches Aroclor 1248 and EM E matches Aroclor 1016, both displaying a compositional shift towards lighter congeners. EM D's contributions increase 3 to 4-fold in samples downstream of SR8a, all of which are downstream of the Kaiser facility that is known to contribute PCB contaminated groundwater to the Spokane River (LimnoTech, 2018). EM E's contributions are elevated only in the effluent of the IEP WWTP (Figure 7). The outfall is located between locations SR7 and SR5a, however, no discernible impact is visible at the SR5a location, i.e. the contributions of this EM do not increase downstream relative to upstream. End-member F is a non-Aroclor mixture of PCB11 along with mostly other lighter congeners, and low levels of penta-chlorinated congeners, possibly from an Aroclor 1254 source. This EM has highest contributions in the effluent of the Spokane County WRF. The outfall is located upstream of SR4, where no discernible impact can be seen, i.e. the contributions of this EM do not increase downstream relative to upstream.

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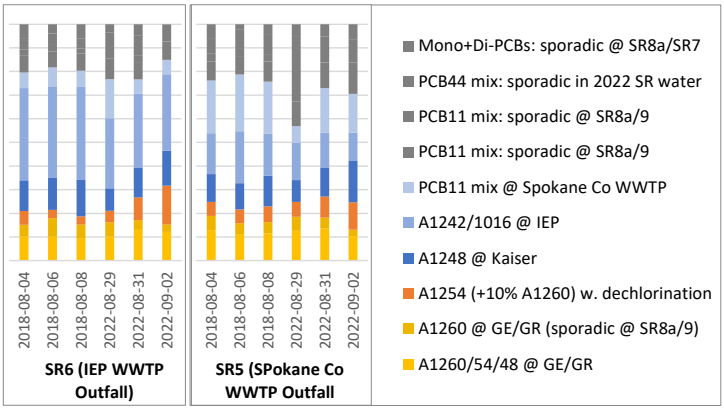
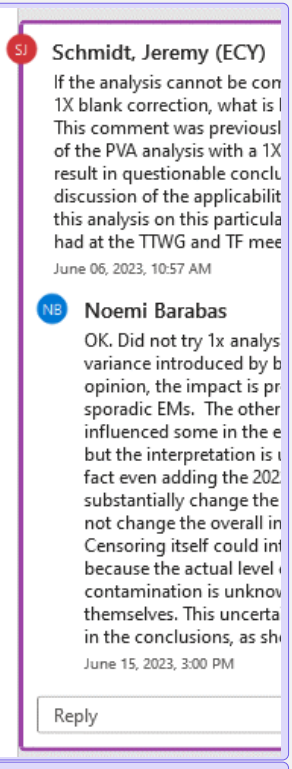


Figure 7. EM contributions in sampled point sources from upstream to downstream.

The final group of EMs are characterized by their sporadic elevated contribution at single locations on single dates. End-members H and I are compositions dominated by either PCB11 or PCB44 mixed with Aroclor 1254-like components. End-member J consists of mono and di-chloro PCBs that are a near-perfect match to Aroclor 1221. Given the sporadic association with dates/locations, as well as their composition being dominated by light congeners, we hypothesize that the source of these EMs is related to blank contamination. This is a highly probable interpretation given that these four EMs closely resemble the composition of blanks themselves. Determining the origin of this contamination is outside of the scope of the current study. ~~, the source of these EMs cannot be discerned without further consultation of additional information sources, in addition determining their identity is outside of the scope of the current study~~Dr. Rodenburg's blank study found blanks to be contaminated by compositions similar to the ones found here as well as Aroclors. ~~studies suggest several possibilities, of which blank contamination is one plausible explanation. It appears~~ We conclude that contaminated blanks minimally influence the composition of EMs, rather they might lead to additional EMs. Thus, the analysis with uncorrected sample data fulfills the scope's objectives even in the presence of uncertainties regarding EM compositions.



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5 Impact of Groundwater Seepage ~~from~~ near GE~~'s~~ Facility

The driving question for this study is whether and to what extent groundwater ~~contaminated by activities at~~ possessing pattern's similar to those observed in the GE~~'s facility~~ plume contributes to PCBs in the biofilm and in surface water. The purely spatial evidence presented above identified two mixtures that display a gain in contribution at and downstream of the approximate groundwater seepage location/reach. One of these mixtures is composed of congeners found in Aroclors 1248, 1254 and 1260. The other mixture has a pure Aroclor 1260 composition. In order to ~~verify~~ examine their interpretation as related to GE, we compare these compositions to two additional sources of information: the PCB congener composition measured in monitoring wells at the GE facility and the PCB pattern derived from mass balance calculations LimnoTech performed on a subset of the data used in the PVA. The groundwater well data are independent of the PVA results, as they were excluded from the dataset.

5.1 PCB Congener Composition of the GE Groundwater Source

Figure 8 shows the composition of the samples from the GE monitoring wells in comparison to the composition of Aroclor 1260 and the two ~~GE-related~~ PVA EMs most similar to the well samples (A and B in Figure 5). The composition of all well samples downgradient from the source are clearly derived from Aroclor 1260. MW20 has a heavier profile than Aroclor 1260 and likely represents a pattern shifted by volatilization of lighter components. MW10 has low total PCB concentration and it's composition is closer to 1254. It approximates a mixture of 60% 1254 and 40% 1260, with additional congeners also present in MW01, known to be upgradient of the source zone. MW10 is likely in proximity to but outside of the plume perimeter. WSDOE (2003) states that the "lateral extent of PCB bearing groundwater is limited due to the velocity of groundwater in this area, and the relatively narrow source area, grouted during 1997." MW10 may represent background, as seen in MW01, mixed with PCBs occasionally dispersed laterally from the source zone. In this case, it is interesting that its composition is shifted towards Aroclor 1254. We are not aware of the Aroclor use practices at GE, however, among a total of 70 samples over time (1997-2002), 6 samples contained Aroclor 1254 detections, with the rest being identified as Aroclor 1260 WSDOE (2003).

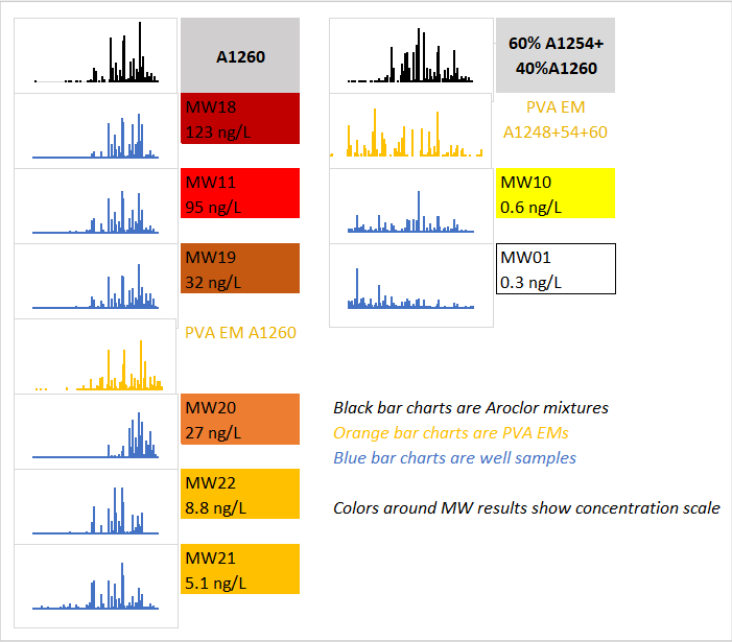

Figure 8. Composition of GE groundwater monitoring wells, with concentrations and in comparison to Aroclor mixtures and PVA EMs. PVA EMs are positioned relative to the well pattern they most closely resemble.

When considering groundwater as a potential source via seepage to a river, it is important to consider that the varying molecular weight of the congeners, retardation processes, dechlorination and potentially volatilization may shift the original contaminating composition during transport through the aquifer matrix. The aquifer material in this location is known to be very low in organic carbon so sorption/desorption dynamics are unlikely to shift the composition. For the same reason, biotic processes are not expected to dechlorinate PCBs significantly. Volatilization can affect compositions in the vadose zone. Retardation due to varying molecular weights is a possibility. The extent to which any one of these processes affect PCB patterns in the aquifer can be tested by plotting PCB composition in monitoring well samples against a measure of time since release or distance traveled. We assumed that the source zone has high concentrations which represent shorter travel distances and low concentrations represent longer travel distances. Figure 9 shows a plot of average chlorination level in the sample PCB mixture vs. the total PCBs in the corresponding sample. As expected, the lowest concentration samples have a lighter composition than samples of higher concentrations. Monitoring wells 11, 18 and 19 have chlorination levels close to that of pure Aroclor 1260.

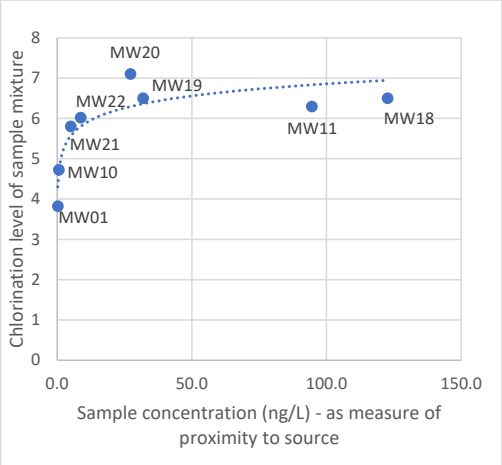

Figure 9. Average PCB congener chlorination level of monitoring well samples vs. sample concentration. Sample concentration here is an approximation of travel time from the source, except in the case of well MW01 which is upgradient and represents background conditions.

Based on the groundwater well monitoring data and their spatial patterns, the ~~GE site groundwater plume~~ composition of groundwater ~~at~~ in the seepage zone, if impacted by the GE PCB plume, is expected to ~~be~~ contain a slightly shifted Aroclor1260 mix~~tures~~ with the possibility of Aroclor 1254 in smaller proportion and any other congeners from background sources. ~~In this respect, t~~ As seen in Figure 8, the GE groundwater sample compositions are a near-perfect match to ~~at least one of the two~~the Aroclor 1260 -PVA EM~~M~~s. The ~~other~~ PVA EM consisting of a mix of 1248, 1254 and 1260 is a partial match to the available monitoring well data and is consistent with additional information about Aroclor 1254 detections in the groundwater. Given the above information about GE groundwater composition, it is possible that the mixed 1248/54/60 EM is a composite of biofilm uptake/absorption of PCBs from a groundwater source with 1260 and 1254, and uptake/absorption of lighter PCBs (such as Aroclor 1248) from the river water. In this latter case, only part of this EM represents groundwater contribution. The ~~is~~ match/s~~s~~imilarity of these two EMs to the GE groundwater PCB patterns is congruent with the result that ~~verifies that~~ the ~~GE EM spatial pattern of~~ in-river and biofilm contributions of these two EMs increase downstream of GE. In combination, the EM compositions and the spatial pattern of their sample contributions ~~indicates~~ add weight to the hypothesis that ~~impact by the~~ PCBs in GE groundwater ~~PCB plume~~ contribute to PCBs in~~on~~ the Spokane River. We recognize, however, that the GE site is located in a heavily industrialized area and that other sources of PCB may exist in this area. These other sources likely include Aroclor 1260, and colud contain compositions similar to that observed in the GE plume.

5.2 PCB Congener Composition Derived from In-River Mass-Balance

Mass balance profiles represent the change in PCB congener masses between stations SR5a and SR4, subtracting the contribution of Spokane County WWTP effluent. Mass balance was performed for each congener, and the increase/decrease of all the congeners constitutes a profile against

which the Aroclor 1260 and Aroclor 1248/54/60 ~~PVA GE~~ EMs can be compared. In this way, the purely statistical PVA process can be compared against measured physical changes to further ~~verify~~ strengthen interpretations. The mass balance was performed for ~~2~~ two scenarios for the sampling years 2018 and 2022: without blank correction as consistent with PVA, and with 3x blank correction as consistent with previous Spokane River mass balances. In addition, due to ~~the~~ some unusually high concentrations measured in 2022, an additional calculation was done for the 3x blank correction with outliers removed. This yields 5 mass-balance profiles to be compared against the ~~GE~~ PVA EMs. Figure 10 shows the 5 mass balance profiles in direct comparison to each other. As can be seen, ~~each of these scenarios weights certain chlorination levels differently~~the impact of the blank correction is greater in 2018 than in 2022. ~~In common between them is the presence of a region of heavy congeners corresponding to Aroclor 1260.~~ Blank correction (3x) ~~shifts the emphasis away from some hexachloro- and heavier congeners prevalent in Aroclor 1260 towards tetra- and pentachloro-CBs more prevalent in Aroclor 1254~~removes most mono- through tri-congeners~~. In addition,~~and Outlier correction impacts the heavy congeners the most, leaving a residual resemblance to Aroclor 1260. PCB11 with other mono-, di- and some trichloro-CBs appear only in the uncorrected profiles, particularly in 2018. These profiles suggest that even with the uncertainty due to blank contamination, the river gains congeners present in Aroclor 1254 and Aroclor 1260 in the reach that includes the possible GE groundwater plume seepage zone. This is consistent with the PVA results.

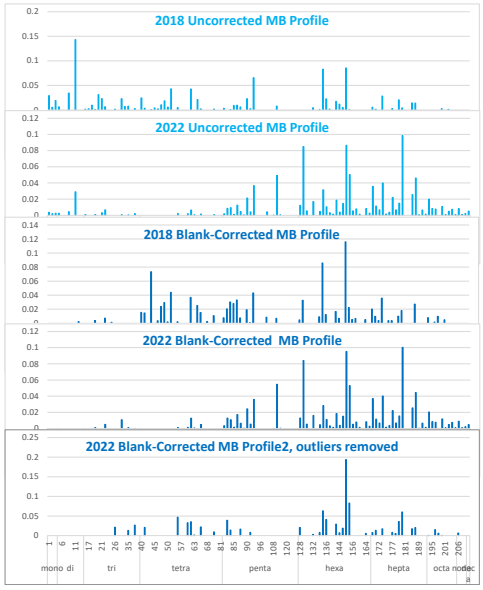

Figure 10. PCB congener profiles based on the mass balance calculations. Lost mass, indicated by negative numbers are not shown, as they cannot be directly compared to the PVA EMs.

Figure 11 shows the comparison between each of the mass balance profiles and the two~~2 GE~~ EMs. The best matches for both EMs are to blank-corrected mass-balance profiles. The mixed Aroclor 1248/54/60 ~~GE~~ EM matches best the 2018 blank-corrected mass balance profile~~s~~, followed by the blank corrected 2022 profile. ~~All scenarios yield similarity in the region of Aroclor 1260 congeners and Aroclor 1254 congeners when considered separately. The Aroclor 1260 overlaps in the corresponding heavy congener regions.~~ The Aroclor 1260 EM ~~The best match is~~matches best with the blank~~un~~-corrected ~~2022 mass balance profile~~and also the uncorrected 2022 mass balance profile, since the difference between these mass-balance profiles is slight. ~~Blank correction deemphasizes the heavy congeners of Aroclor 1260, suggesting the possibility that this EM is influenced more strongly by blank contamination. In the blank corrected mass balance scenarios the Aroclor 1260 EM still overlaps well with the mass balance profile in the heavy congener region~~ The fact that these EMs best match blank-corrected profiles supports the informed assumption we made that the PVA end-members of interest are relatively robust to the influence of contaminated blanks. The "true" composition of the PVA end-members is somewhat uncertain but not to the point of impacting their interpretation.

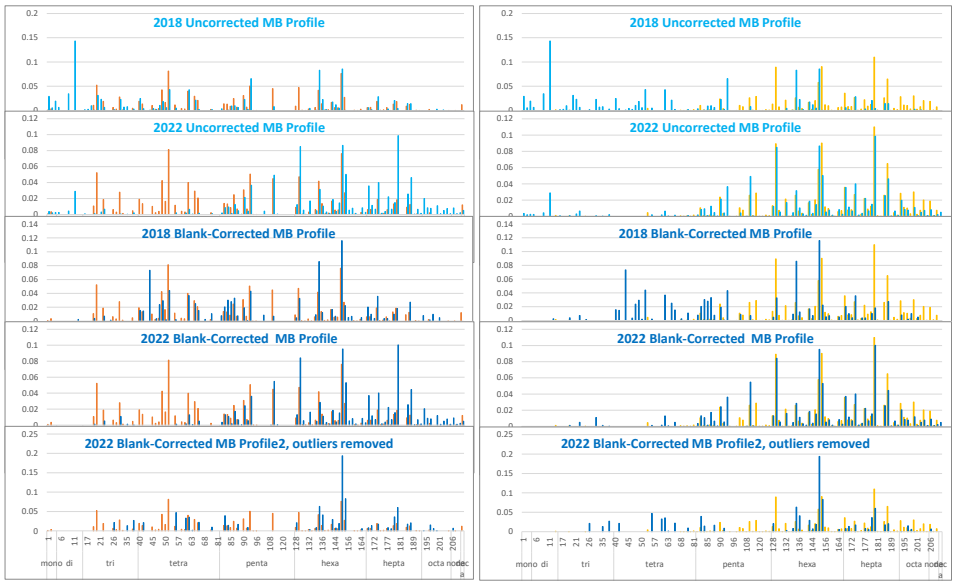

Figure 11. Comparison of MB profiles (light blue is uncorrected, dark blue is corrected) to PVA EMs (dark orange is the Aroclor 1248/54/60 mixture and light orange/yellow is the Aroclor 1260 EM).

Both, the spatial distribution, and the sampling over multiple consecutive days add power. The repetition in time reveals that the impact of certain EMs is limited to specific dates, re-enforcing that the undesired contamination can be isolated in certain end-members.

5.3 The Spatial Signature of ~~possible GE~~ Impact in Surface Water and Biofilm near GE

~~In order to~~We next visualize and evaluate the extent to which the identified ~~GE~~ possible groundwater EM inputs contribute to the measured total PCBs in the biofilm. Surface water compositions are variable from day to day and may not represent a long-term distribution of impact, whereas biofilm integrates PCB inputs over the growing season. ~~and surface water, w~~We grouped the PVA EMs into 4 categories: (1) the sum of all upstream contributions (Kaiser EM, IEP WWTP EM, all sporadic EMs), (2) Spokane County WWTP EM contributions alone to separate its contribution because it occurs between the GE source zone and the first available downstream water and biofilm sample locations, (3) the biofilm Aroclor 1254 EM contributions because it represents a ~~non-GE~~ background input to biofilm PCBs, and (4) the sum of the Aroclor 1260 and Aroclor 1248/54/60 possible groundwater ~~both GE~~ EMs. Within each of these groups, upstream and downstream results were averaged together separately to give a single representation of upstream vs. downstream source contributions in each of the 4 categories. Figure 12 shows the results of these contributions as vertical bars, capturing the same information as in Figure 6 but separated into up- and downstream of GE and averaged. ~~These are shown in panels A (biofilm) and C (surface water).~~ For each of the colored categories in the vertical bars panel B shows the absolute magnitude of increase or decrease in downstream samples over the contribution in upstream samples. We call an increase a "gain" and a decrease a "loss" in order to be clear that this isn't a ratio or percent increase relative to the upstream contribution in the denominator. The percentages in this case refer to the percent of measured sample tPCBs that are sourced from each of the source categories.

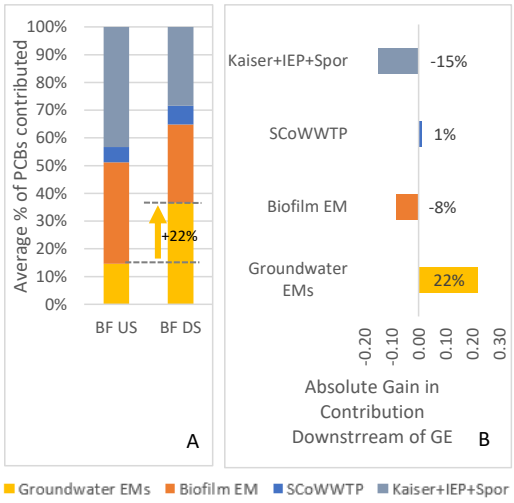

Figure 12. Magnitude of increase in total sample PCBs in biofilm due to contribution of Aroclor 1260 and Aroclor 1248/1254/1260 downstream of GE.

~~Panel A in~~ Figure 12 shows that in biofilm samples, the possible groundwater~~GE~~ EMs ~~is~~ are responsible for a 22% gain in measured sample PCBs. ~~In surface water, the corresponding gain is 12%.~~ This does not translate directly to mass loading to the river. Discharge and spatial over/under-representation and temporal variation must be accounted for to translate these numbers into mass loading from the groundwater input.

In terms of the other sources, there is a loss of contribution from the group of upstream sources because they are mathematically displaced by the gain due to the ~~GE~~ groundwater group ~~of sources~~. The situation is similar for the biofilm background group. There is a very small gain in measured total PCBs due to the Spokane County WWTP.

The following section discusses the conclusions possible to be drawn based on this work, distinguishing between what can be concluded with confidence and remaining questions and uncertainties.

6 Conclusions

The above analyses identified two separate signatures that may be associated with groundwater loading, which ~~may be impacted by~~are also present in GE groundwater. The Aroclor 1248/54/60 ~~GE~~ EM has increased contributions downstream of GE in both biofilm and surface water. The Aroclor 1260 ~~GE~~ EM has increased contributions in downstream biofilm samples but not in surface water (except at SR4 2022-08-30, which is an outlier). Overall, the link to ~~the~~ a groundwater ~~plume~~ contribution is well-supported. The confidence in the magnitude of contribution is limited by the time period the data represent, given the observed variability. In these samples, on average, the two groundwater ~~GE~~ EMs lead to 22% more total PCBs in downstream biofilm samples ~~and 12% more tPCBs in downstream surface water samples~~. However, this number cannot be broadly generalized beyond the time period and locations sampled. ~~Both mass balance calculations and PVA suggest that the contribution of Aroclor 1260 in the river water is slight and that most of the increase is driven by a mixture of Aroclor 1248/1254/1260. It is important to note that the biofilm PCBs integrate the PCBs that are transported in the river over the growing season, while the surface water data are snapshots on 3-5 days in two different years, and this snapshot applies to the mass balance as well.~~ The surface water concentration variability ~~suggests that it may be necessary to capture a longer time interval with surface water samples to complete a mass balance calculation representative of the year~~is too great to provide a credible quantitative estimate of contribution to the water column, consistent with the findings of the recent Spokane-area PCB mass balance assessment (LimnoTech, 2023).

Whereas the PVA work affirms and strengthens the hypothesis that groundwater loadings in this reach lead to biofilm impacts, true test and verification of this hypothesis ~~It also appears beneficial to~~ requires characterizatione of the PCBs in the groundwater transition zone along the river bank. This is ~~because~~ recommended also because the ~~GE~~ groundwater monitoring well data ~~,~~ support a ~~GE contribution~~ link of primarily Aroclor 1260, whereas the PVA supports a greater contribution of Aroclor 1254 along with Aroclor 1260 and also Aroclor 1248. Thus, it is uncertain if all the Aroclor 1254 in the mixed Aroclor 1248/54/60~~GE~~ EM can be attributed to GE-like sources and if any of the Aroclor 1248 in the biofilm can be attributed to groundwater from this reach. It is possible that the biofilm, via uptake and sorption, would mix~~es~~ a part of the Aroclors 1248 and 1254 from surface water with Aroclor 1260 from ~~GE~~ groundwater and partly eliminates some of the signal of separate sources. Given that only 5 biofilm samples are from the likely plume impacted zone, this is a possible explanation. An alternative explanation is that the Aroclor 1260 pattern is shifted toward Aroclor 1254 during migration through the groundwater-surface water transition zone combined with uptake/sorption processes. This is less likely given the low organic carbon content of the substrate and that uptake/sorption would favor the higher K_{ow} of Aroclor 1260, when in fact it is Aroclor 1254 that is enriched.

Overall, this work justifies further pursuing the hypothesis of ~~GE~~the nature and extent of groundwater impact. A large part of the uncertainty and data gap relates to which environmental

compartments are well-represented by the data. While blank contamination and data censoring decisions as well as modeling decisions influence the results, the biggest benefit would come from contemporary groundwater data along the probable seepage zone.

The table below summarizes the answers to the questions posed in the Scope of Work.

Table 2. Summary Conclusions

Scope Objective	Confident Conclusions	Remaining Questions and Uncertainties
1. How many distinct sources and processes contribute?	Three point-sources (Kaiser, IEP, Spokane Co WWTP)	
	Two ~~GE groundwater~~ mixtures attributable to groundwater and ~~in part at least~~ similar to what is seen in the ~~to~~ GE~~sources~~ plume.	Are Aroclors 1248 and 1254 derived from surface water or groundwater?
	~~Five non-Aroclor mixtures at SR7, SR8a, SR9 with sporadic contribution on certain dates.~~	~~Blank contamination may in part cause some of the sporadic variation. The number of associated sources may be less than 5, as these end-members could capture variable composition at a source rather than distinct sources/processes.~~ Five non-Aroclor mixtures at SR7, SR8a, SR9 with sporadic contribution on certain dates likely due to blank contamination. The number of true PCB sources to the river may be represented by the three point sources and two groundwater sources.
2. What is the PCB congener composition of each end-member? 3. What is the identity of each end-member in terms of Aroclors and alteration mechanisms (degradation,	A1260 at ~~GE-LB~~left bank biofilm station downstream of GE.	A1248 and A1254 components in ~~BF~~ biofilm at GE could be groundwater or uptake from river. Source of A1248- and A1254-like components within end-member mixtures could be Kaiser (A1248), and background (A1254). ~~and may be in part affected by blank contamination.~~

weathering, uptake, etc.)	A1242/1016 @ IEP, A1248 @ Kaiser, PCB11 mix @ Spokane Co WWTP.	Compositions may in part be affected by blank contamination- and also by ~~dechlorination~~27ichlorination, although this uncertainty may not be large given the spatial consistency with point sources~~.~~
	~~Mixtures dominated by PCB11, PCB44 or mono/di PCBs contribute to Spokane River PCBs on certain dates.~~	Mixtures dominated by PCB11, PCB44 or mono/di ~~Some PCB11/44 mixtures could be affected or driven by~~represent blank contamination. ~~Mono and di homologs may be derived from dechlorination~~27ichlorination ~~processes also, and not necessarily be Aroclor 1221.~~
4. Can some of these end-members be linked uniquely to groundwater inputs, to the original groundwater composition at the GE source, or to the mass-balance changes by congener?	Two ~~Ems~~ EMs can be linked to ~~GE~~ groundwater, and are consistent in composition to . ~~One of them consistently also affects surface water downstream, the other one only the biofilm. They can also be linked to GE on the basis of~~ GE groundwater well data. ~~These links are strong hypotheses, that need further sampling for verification.~~	A1260 ~~GE~~ end-member does not contribute to surface water below GE except for one sample in 2022/08/30. What could cause such a temporary contribution to surface water at this location? ~~GE? GE groundwater? Variation in groundwater flow direction? Non-GE source~~? The impact on biofilm alone may be due to the snapshot nature of the surface water data. It is possible that the biofilm better captures the range of contributions and the selected sampling dates did not fully characterize the possible groundwater load to the river. How much of the groundwater contamination is due GE vs. other possible PCB inputs to groundwater?
5. What is the magnitude of the contribution of the GE-linked end-members in the biofilm samples?	Higher by an additional 22% in biofilm ~~and by 12% in surface water~~.	This increase is specific to the samples and cannot be interpreted in terms of mass of PCBs entering the river via ~~GE~~ groundwater.

6. What is the trend of ~~the GE-linked~~ contributions from sources similar to GE downstream of the suspected input?	Overall increase.	Unknown significance of the transient increase in downstream contribution to surface water by the A1260 ~~GE~~ end-member. It could be a sample cross-contaminated by Aroclor 1260 on that date.
7. Can this contribution be used to estimate the significance of ~~GE~~ these PCB inputs to the river as a whole	Blank-corrected composition from the mass balance is a reasonable representation of groundwater impact on surface water for the reach at and downstream of GE.	This increase is specific to the samples and cannot be interpreted in terms of the whole river. Day to day variability in surface water PCB concentrations and end-member contributions indicates that river PCB levels may not be fully characterized in terms to estimate GE groundwater PCB load over a longer time period. Such an estimate needs verification based on contemporary groundwater samples closer to the groundwater-surface water transition zone.

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Attachment A – Data Used for Fingerprinting Analysis

Table A.1 Samples used for fingerprinting analysis

Colors indicate media:

Biofilm	Surface Water	Effluent	Groundwater

Locations are in order from upstream to downstream.

Media	Station ID	Station Descriptor	Location relative to GE	Sample Date	Sample total PCB congeners (Water: ng/L, BF: pg/g)	Data used for:
Biofilm	PF-BF	~~Post Falls~~Plante's Ferry	Upstream	2018-08-27	617.491	PVA
Biofilm	PF	~~Post Fall~~Plante'sFerrys	Upstream	2019-08-06	804.140	PVA
Surface Water	SR9	Barker Rd	Upstream	2018-08-04	0.102	PVA
Surface Water	SR9	Barker Rd	Upstream	2018-08-05	0.061	PVA
Surface Water	SR9	Barker Rd	Upstream	2018-08-06	0.049	PVA
Surface Water	SR9	Barker Rd	Upstream	2018-08-07	0.097	PVA
Surface Water	SR9	Barker Rd	Upstream	2018-08-08	0.049	PVA
Surface Water	SR8a	Mirabeau Point	Upstream	2018-08-04	0.047	PVA
Surface Water	SR8a	Mirabeau Point	Upstream	2018-08-05	0.042	PVA
Surface Water	SR8a	Mirabeau Point	Upstream	2018-08-06	0.060	PVA
Surface Water	SR8a	Mirabeau Point	Upstream	2018-08-07	0.428	PVA
Surface Water	SR8a	Mirabeau Point	Upstream	2018-08-08	0.043	PVA
Surface Water	SR7	Trent Bridge	Upstream	2018-08-04	0.116	PVA
Surface Water	SR7	Trent Bridge	Upstream	2018-08-05	0.122	PVA
Surface Water	SR7	Trent Bridge	Upstream	2018-08-06	0.127	PVA
Surface Water	SR7	Trent Bridge	Upstream	2018-08-07	0.245	PVA
Surface Water	SR7	Trent Bridge	Upstream	2018-08-08	0.138	PVA
Surface Water	SR7	Trent Bridge	Upstream	2022-08-30	0.147	PVA
Surface Water	SR7	Trent Bridge	Upstream	2022-08-31	0.121	PVA
Surface Water	SR7	Trent Bridge	Upstream	2022-09-01	0.129	PVA
Surface Water	SR7	Trent Bridge	Upstream	2022-09-02	0.173	PVA
Effluent	SR6	Inland Empire Paper WWTP	Upstream	2018-08-04	1.945	PVA
Effluent	SR6	Inland Empire Paper WWTP	Upstream	2018-08-06	1.720	PVA
Effluent	SR6	Inland Empire Paper WWTP	Upstream	2018-08-08	1.126	PVA
Effluent	SR6	Inland Empire Paper WWTP	Upstream	2022-08-29	0.600	PVA
Effluent	SR6	Inland Empire Paper WWTP	Upstream	2022-08-31	1.656	PVA

Effluent	SR6	Inland Empire Paper WWTP	Upstream	2022-09-02	1.593	PVA
Surface Water	SR5a	Downriver of Upriver Dam	Closest Upstream	2018-08-04	0.133	PVA
Surface Water	SR5a	Downriver of Upriver Dam	Closest Upstream	2018-08-05	0.130	PVA
Surface Water	SR5a	Downriver of Upriver Dam	Closest Upstream	2018-08-06	0.108	PVA
Surface Water	SR5a	Downriver of Upriver Dam	Closest Upstream	2018-08-07	0.147	PVA
Surface Water	SR5a	Downriver of Upriver Dam	Closest Upstream	2018-08-08	0.154	PVA
Surface Water	SR5a	Downriver of Upriver Dam	Closest Upstream	2022-08-29	0.134	PVA
Surface Water	SR5a	Downriver of Upriver Dam	Closest Upstream	2022-08-30	0.116	PVA
Surface Water	SR5a	Downriver of Upriver Dam	Closest Upstream	2022-08-31	0.153	PVA
Surface Water	SR5a	Downriver of Upriver Dam	Closest Upstream	2022-09-01	0.098	PVA
Surface Water	SR5a	Downriver of Upriver Dam	Closest Upstream	2022-09-02	0.117	PVA
Biofilm	URD	Upriver Dam - Right Bank	Upstream	2018-08-28	1410.707	PVA
Biofilm	URD	Upriver Dam - Right Bank	Upstream	2019-08-06	831.442	PVA
Biofilm	URD-LB	Upriver Dam - Left Bank	Upstream	2019-08-06	708.731	PVA
Biofilm	GEM-RB	GE - Right Bank	Across from GE	2018-08-28	947.692	PVA
Biofilm	GEM-RB	GE - Right Bank	Across from GE	2019-08-06	794.366	PVA
Biofilm	GEM-LB	GE - Left Bank	At GE	2018-08-28	2040.628	PVA
Biofilm	GEM-LB	GE - Left Bank	At GE	2019-08-06	1851.784	PVA
Effluent	SR5	Spokane County WWTP	Downstream	2018-08-04	0.254	PVA
Effluent	SR5	Spokane County WWTP	Downstream	2018-08-06	0.279	PVA
Effluent	SR5	Spokane County WWTP	Downstream	2018-08-08	0.237	PVA
Effluent	SR5	Spokane County WWTP	Downstream	2022-08-29	0.301	PVA
Effluent	SR5	Spokane County WWTP	Downstream	2022-08-31	0.212	PVA
Effluent	SR5	Spokane County WWTP	Downstream	2022-09-02	0.233	PVA
Surface Water	SR4	Greene Street	Closest Downstream	2018-08-04	0.108	PVA
Surface Water	SR4	Greene Street	Closest Downstream	2018-08-05	0.121	PVA
Surface Water	SR4	Greene Street	Closest Downstream	2018-08-06	0.101	PVA
Surface Water	SR4	Greene Street	Closest Downstream	2018-08-07	0.096	PVA
Surface Water	SR4	Greene Street	Closest Downstream	2018-08-08	0.108	PVA
Surface Water	SR4	Greene Street	Closest Downstream	2022-08-29	0.125	PVA
Surface Water	SR4	Greene Street	Closest Downstream	2022-08-30	0.501	PVA
Surface Water	SR4	Greene Street	Closest Downstream	2022-08-31	0.111	PVA
Surface Water	SR4	Greene Street	Closest Downstream	2022-09-01	0.101	PVA
Surface Water	SR4	Greene Street	Closest Downstream	2022-09-02	0.110	PVA
Biofilm	GR-LB	Greene Street - Left Bank	Downstream	2018-08-28	1057.055	PVA
Biofilm	GR-LB	Greene Street - Left Bank	Downstream	2019-08-06	618.446	PVA
Biofilm	GR-RB	Greene Street - Right Bank	Downstream	2018-08-28	1069.176	PVA

Groundwater	MW22	GE Monitoring Well	Groundwater at GE	2016-10-24,25	8.786	Interpretation
Groundwater	MW18	GE Monitoring Well	Groundwater at GE	2016-10-24,25	122.669	Interpretation
Groundwater	MW11	GE Monitoring Well	Groundwater at GE	2016-10-24,25	94.530	Interpretation
Groundwater	MW21	GE Monitoring Well	Groundwater at GE	2016-10-24,25	5.081	Interpretation

Groundwater	MW19	GE Monitoring Well	Groundwater at GE	2016-10-24,25	31.891	Interpretation
Groundwater	MW10	GE Monitoring Well	Groundwater at GE	2016-10-24,25	0.619	Interpretation
Groundwater	MW20	GE Monitoring Well	Groundwater at GE	2016-10-24,25	27.188	Interpretation
Groundwater	MW01	GE Monitoring Well	Groundwater at GE	2016-10-24,25	0.272	Interpretation

Table A.2 PCB congeners used for fingerprinting analysis

Homologue	IUPAC #	COMPOUND	Coellutants
mono	1	2-MoCB	
mono	2	3-MoCB	
mono	3	4-MoCB	
di	4	2,2'-DiCB	
di	6	2,3'-DiCB	
di	7	2,4-DiCB	
di	8	2,4'-DiCB	
di	9	2,5-DiCB	
di	11	3,3'-DiCB	
di	12	3,4-DiCB	12 + 13
di	15	4,4'-DiCB	
tri	16	2,2',3-TriCB	
tri	17	2,2',4-TriCB	
tri	18	2,2',5-TriCB	18 + 30
tri	19	2,2',6-TriCB	
tri	20	2,3,3'-TriCB	20 + 28
tri	21	2,3,4-TriCB	21 + 33
tri	22	2,3,4'-TriCB	
tri	24	2,3,6-TriCB	
tri	25	2,3',4-TriCB	
tri	26	2,3',5-TriCB	26 + 29
tri	27	2,3',6-TriCB	
tri	31	2,4',5-TriCB	
tri	32	2,4',6-TriCB	
tri	35	3,3',4-TriCB	
tri	36	3,3',5-TriCB	
tri	37	3,4,4'-TriCB	
tri	39	3,4',5-TriCB	
tetra	40	2,2',3,3'-TeCB	40 + 41 + 71
tetra	42	2,2',3,4'-TeCB	
tetra	43	2,2',3,5-TeCB	
tetra	44	2,2',3,5'-TeCB	44 + 47 + 65
tetra	45	2,2',3,6-TeCB	45 + 51
tetra	46	2,2',3,6'-TeCB	
tetra	48	2,2',4,5-TeCB	
tetra	49	2,2',4,5'-TeCB	49 + 69
tetra	50	2,2',4,6-TeCB	50 + 53
tetra	52	2,2',5,5'-TeCB	
tetra	54	2,2',6,6'-TeCB	
tetra	56	2,3,3',4'-TeCB	
tetra	57	2,3,3',5-TeCB	
tetra	59	2,3,3',6-TeCB	59 + 62 + 75
tetra	60	2,3,4,4'-TeCB	
tetra	61	2,3,4,5-TeCB	61 + 70 + 74 + 76
tetra	63	2,3,4',5-TeCB	
tetra	64	2,3,4',6-TeCB	
tetra	66	2,3',4,4'-TeCB	
tetra	67	2,3',4,5-TeCB	
tetra	68	2,3',4,5'-TeCB	
tetra	72	2,3',5,5'-TeCB	
tetra	77	3,3',4,4'-TeCB	
tetra	79	3,3',4,5'-TeCB	
tetra	81	3,4,4',5-TeCB	
penta	82	2,2',3,3',4-PeCB	
penta	83	2,2',3,3',5-PeCB	83 + 99
penta	84	2,2',3,3',6-PeCB	
penta	85	2,2',3,4,4'-PeCB	85 + 116 + 117
penta	86	2,2',3,4,5-PeCB	86 + 87 + 97 + 109 + 119 + 125
penta	88	2,2',3,4,6-PeCB	88 + 91
penta	89	2,2',3,4,6'-PeCB	
penta	90	2,2',3,4',5-PeCB	90 + 101 + 113
penta	92	2,2',3,5,5'-PeCB	
penta	93	2,2',3,5,6-PeCB	93 + 95 + 98 + 100 + 102
penta	94	2,2',3,5,6'-PeCB	

Homologue	IUPAC #	COMPOUND	Coellutants
penta	96	2,2',3,6,6'-PeCB	
penta	103	2,2',4,5',6-PeCB	
penta	105	2,3,3',4,4'-PeCB	
penta	107	2,3,3',4',5-PeCB	
penta	108	2,3,3',4,5'-PeCB	108 + 124
penta	110	2,3,3',4',6-PeCB	110 + 115
penta	114	2,3,4,4',5-PeCB	
penta	118	2,3',4,4',5-PeCB	
penta	120	2,3',4,5,5'-PeCB	
penta	122	2',3,3',4,5-PeCB	
penta	123	2',3,4,4',5-PeCB	
penta	126	3,3',4,4',5-PeCB	
hexa	128	2,2',3,3',4,4'-HxCB	128 + 166
hexa	129	2,2',3,3',4,5-HxCB	129 + 138 + 160 + 163
hexa	130	2,2',3,3',4,5'-HxCB	
hexa	131	2,2',3,3',4,6-HxCB	
hexa	132	2,2',3,3',4,6'-HxCB	
hexa	133	2,2',3,3',5,5'-HxCB	
hexa	134	2,2',3,3',5,6-HxCB	134 + 143
hexa	135	2,2',3,3',5,6'-HxCB	135 + 151 + 154
hexa	136	2,2',3,3',6,6'-HxCB	
hexa	137	2,2',3,4,4',5-HxCB	
hexa	139	2,2',3,4,4',6-HxCB	139 + 140
hexa	141	2,2',3,4,5,5'-HxCB	
hexa	144	2,2',3,4,5',6-HxCB	
hexa	146	2,2',3,4',5,5'-HxCB	
hexa	147	2,2',3,4',5,6-HxCB	147 + 149
hexa	153	2,2',4,4',5,5'-HxCB	153 + 168
hexa	156	2,3,3',4,4',5-HxCB	156 + 157
hexa	158	2,3,3',4,4',6-HxCB	
hexa	159	2,3,3',4,5,5'-HxCB	
hexa	162	2,3,3',4',5,5'-HxCB	
hexa	164	2,3,3',4',5',6-HxCB	
hexa	167	2,3',4,4',5,5'-HxCB	
hepta	170	2,2',3,3',4,4',5-HpCB	
hepta	171	2,2',3,3',4,4',6-HpCB	171 + 173
hepta	172	2,2',3,3',4,5,5'-HpCB	
hepta	174	2,2',3,3',4,5,6'-HpCB	
hepta	175	2,2',3,3',4,5',6-HpCB	
hepta	176	2,2',3,3',4,6,6'-HpCB	
hepta	177	2,2',3,3',4',5,6-HpCB	
hepta	178	2,2',3,3',5,5',6-HpCB	
hepta	179	2,2',3,3',5,6,6'-HpCB	
hepta	180	2,2',3,4,4',5,5'-HpCB	180 + 193
hepta	181	2,2',3,4,4',5,6-HpCB	
hepta	182	2,2',3,4,4',5,6'-HpCB	
hepta	183	2,2',3,4,4',5',6-HpCB	183 + 185
hepta	187	2,2',3,4',5,5',6-HpCB	
hepta	189	2,3,3',4,4',5,5'-HpCB	
hepta	190	2,3,3',4,4',5,6-HpCB	
hepta	191	2,3,3',4,4',5',6-HpCB	
octa	194	2,2',3,3',4,4',5,5'-OcCB	
octa	195	2,2',3,3',4,4',5,6-OcCB	
octa	196	2,2',3,3',4,4',5,6'-OcCB	
octa	197	2,2',3,3',4,4',6,6'-OcCB	197 + 200
octa	198	2,2',3,3',4,5,5',6-OcCB	198 + 199
octa	201	2,2',3,3',4,5',6,6'-OcCB	
octa	202	2,2',3,3',5,5',6,6'-OcCB	
octa	203	2,2',3,4,4',5,5',6-OcCB	
octa	205	2,3,3',4,4',5,5',6-OcCB	
nona	206	2,2',3,3',4,4',5,5',6-NoCB	
nona	207	2,2',3,3',4,4',5,6,6'-NoCB	
nona	208	2,2',3,3',4,5,5',6,6'-NoCB	
deca	209	2,2',3,3',4,4',5,5',6,6'-DeCB	

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