Effect of Membrane Filtration on the Fate of Polychlorinated Biphenyls in Wastewater Treatment

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Prepared for:
Spokane River Regional Toxics Task Force

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Abstract

The Spokane River is impacted by levels of toxic polychlorinated biphenyls (PCBs) that have triggered fish consumption advisories and exceed water quality standards. Select wastewater treatment plants (WWTPs) on the river have been upgraded from secondary (biological) treatment to tertiary treatment in the form of membrane filtration to address phosphorus contamination in the river. Because membrane filtration is effective at removing particles, it is likely to reduce PCB concentrations in the effluent as well. In this work, PCBs measured in the influents and effluent of several WWTPs discharging to the river were examined. Implementation of membrane filtration reduced PCB concentrations in the effluent (and therefore PCB loads to the river) by 33% at a facility that produces recycled and virgin paper and by ~55% at municipal WWTPs, compared to secondary (activated sludge) treatment. Largest reductions in concentrations in effluent and loads were achieved for higher molecular weight (MW) PCB congeners, homologs, and formulations. The more modest reductions in effluent concentrations achieved at the paper WWTP may be due to the mix of PCBs in the wastewater there: it contained primarily the low MW Aroclor 1242 (presumably arising from its use in carbonless copy paper until 1974) and PCB 11 (3,3'-dichlorobiphenyl) possibly from pigments. PCBs that appear to be associated with silicone products such as caulk, tubing, and o-rings are relatively more abundant in the effluent of some plants compared to the influent, suggesting that these congeners arise from contamination during sampling. At some WWTPs, this contamination accounts for nearly a third of PCBs measured in the effluent.

Introduction

Polychlorinated biphenyls (PCBs) are toxic, persistent, and bioaccumulative chemicals that are regulated in the United States under several statutes including the Clean Water Act. The Spokane River is on the State of Washington's Clean Water Act 303(d) list for impairment by PCB contamination. The impairment is based on concentrations of PCBs in fish tissue that exceed a fish tissue equivalent concentration (FTEC) for applicable water quality standards (LimnoTech, 2016). Levels of PCBs in mountain whitefish and rainbow trout sampled in 2012 were sometimes more than ten times the FTEC of 5.3 ug/kg (Seiders et al., 2015). There is also a health advisory limiting the consumption of fish caught in the river due to PCB concentrations in fish tissue. PCB fingerprints in the fish are dominated by the higher molecular weight formulations, namely Aroclors 1254 and 1260 (Seiders et al., 2015). In contrast, the PCB signature in the water column contains more lower molecular weight congeners. In particular, PCB 11 is the single most abundant congener in a majority of water samples (Rodenburg et al., 2020). PCB 11 is virtually absent in the Aroclors. One potential source of PCB 11 is pigments, where is it sometimes present as an inadvertent by-product (Rodenburg et al., 2010b; Guo et al., 2014; Rodenburg et al., 2015b). However, many other processes may produce PCB 11 inadvertently (Vincent, 2020). PCB loads to the river must therefore be reduced to address the impairment, but low and high molecular weight PCBs might require different reduction strategies. PCB sources to the river have included treated effluent from municipal wastewater treatment plants (WWTPs), contaminated groundwater, stormwater, industrial discharges, and atmospheric deposition, many of which are being/have been addressed (LimnoTech, 2016).

One approach to reducing PCB loads is to upgrade WWTPs. The oldest WWTPs discharging to the Spokane River are Spokane City and Coeur d'Alene. Spokane City's WWTP was built in the 1950s with primary treatment, and later upgraded to secondary treatment. Coeur d'Alene was operational in 1939 with secondary treatment. Other treatment plants were originally built with secondary treatment except for the Spokane County facility with membrane filtration, completed in 2011. WWTP upgrades to membrane filtration are planned, and some have already been implemented, in order to address phosphorus loading (van der Graaf et al., 1999; Hjorth et al., 2010) as prescribed in the Spokane River and Lake Spokane Dissolved Oxygen Total Maximum Daily Load (Moore and Ross, 2010).

In recent decades, WWTPs across the US have upgraded to various forms of tertiary treatment, but little is known about how these upgrades will affect PCBs. Modern (or modernized) WWTPs employing conventional secondary treatment have been shown to remove >80% of total PCBs in most cases (Durell and Lizotte, 1998; Katsoyiannis and Samara, 2004; Bolzonella et al., 2010; Rodenburg et al., 2012; Yao et al., 2014; Capozzi et al., 2019), with higher MW congeners showing higher removal rates. Bolzonella et al. (2010) found that membrane bioreactors significantly enhanced PCB removal when employed as a tertiary treatment after conventional activated sludge secondary treatment. Other than this single study, there are no reports of the effects of tertiary treatment on PCB removal during wastewater treatment. It may be reasonably assumed that PCBs, especially high MW PCBs, are largely sorbed to particles, and therefore any treatment process that removes particles from the wastewater, including membrane filtration, will be effective at removing PCBs.

The purpose of this study was to examine the concentrations of PCBs in the influent and effluent of these WWTPs to understand the reduction in PCB loads to the Spokane River and to determine whether some PCB source types are more effectively removed by membrane filtration than others.

Methods

Sample collection

PCBs were measured in the influent and effluent of several WWTPs listed in Table 1 during 2012-2020. All but IEP (Inland Empire Paper) treat municipal sewage. Spokane City receives combined stormwater and wastewater; the remaining plants have separate sanitary sewers. The IEP WWTP treats waste from the paper production process via secondary (activated sludge) and tertiary (membrane filtration) processes. The IEP facility consumed between 57,000 and 201,000 tons of raw material per year during the period of sample collection, about 25% of which was post-consumer waste. The municipal plants are small to medium sized WWTPs with average daily flows less than 31 MGD (million gallons per day, where 1 MGD = 3.8×10^6 L/d). Samples were collected in accordance with Quality Assurance Project Plans prepared by the respective treatment facilities and approved by the appropriate regulatory agency. Samples of influent and effluent were collected using minimal tubing to limit contamination that might arise from silicone rubber tubing (Greyell and Williston, 2018; Rodenburg et al., 2020). Samples were shipped to the contract lab where they were analyzed for all PCBs using EPA methods 1668A and 1668C (EPA, 1999; U. S. EPA, 2010). In these methods, all 209 PCB congeners are measured in about 160 chromatographic peaks, each of which represents one or more PCB congeners. PCBs were measured using the SPB-octyl gas chromatography column for all samples except those from Liberty Lake, which used the SGE-HT8 column.

Table 1. Details of the WWTPs sampled in this study.

WWTP	State	River Mile	Type	Flow (MGD)	Chemical P removal?	Year built	Year upgraded to tertiary treatment
Coeur d'Alene	ID	110.2	Municipal with separate sewers	3.6	Yes	1939	June 2018
Hayden	ID	108.7	Municipal with separate sewers	1.2	No	1986	
Post Falls	ID	100.5	Municipal with separate sewers	2.8	No	1985	
Liberty Lake	WA	93.4	Municipal with separate sewers	0.8	Yes	1982	November 2017
Spokane County	WA	78.5	Municipal with separate sewers	8.0	Yes	2011	
Spokane City	WA	67.4	Municipal with some combined sewers	30.7	Yes	1958	
IEP	WA	82.6	Industrial - recycled paper production	3.0	No	1988	January 2020

Laboratory method blanks were analyzed with each sampling event. Data were reported without blank correction, and subsequently the data was corrected by censoring at a level of one times the corresponding blank concentration, as per the recommendation of Rodenburg et al. (2020). Σ_{209}PCBs in blanks averaged (± standard deviation) 259 ± 252 pg/L at Coeur d'Alene, 211 ± 96 pg/L at Hayden, 253 ± 272 pg/L at Post Falls, 172 ± 376 pg/L at Liberty Lake, 152 ± 105 pg/L at Spokane County, and 306 ± 121 pg/L at Spokane City (non-detects set to zero). These blank concentrations are somewhat higher than those achieved during surface water sampling in the Spokane River (averaging 88 pg/L) (Rodenburg et al., 2020). Detection limits ranged from about 0.5 pg/L to 23 pg/L.

The final data set included 239 samples of influent and 162 samples of effluent. Notably, samples were collected both before and after upgrade to membrane filtration at Coeur d'Alene and Liberty Lake. The Spokane County plant included membrane filtration when it was built in 2011. At IEP, samples of effluent from secondary (conventional biological) and tertiary (membrane filtration) treatment were collected along with influent.

Positive Matrix Factorization (PMF)

The data were divided into two batches (influent and effluent) for PMF analysis. IEP data was not included in either of the data sets because as an industrial facility, PCBs levels and fingerprints were very different at this facility. Data from Liberty Lake were not included in the PMF analysis because these samples were measured using a different coelution pattern and had a high proportion of non-detects (89% of all data points). The final data sets therefore included 196 samples of influent and 120 samples of effluent. For both data sets, three inputs were constructed for analysis via Positive Matrix Factorization (PMF): the concentration matrix, the uncertainty matrix, and the Limits of Detection (LOD) matrix. The concentration matrix used the blank-censored concentrations. Concentrations below detection were replaced with half the LOD. The LOD matrix was constructed out of the LODs as provided. The uncertainty matrix was calculated by the method used previously (Du et al., 2008; Rodenburg et al., 2011;

Praipipat et al., 2013; Rodenburg and Meng, 2013; Rodenburg et al., 2015a), i.e. the relative standard deviation of the surrogate recoveries was used as the base uncertainty, which was applied to all detected concentrations. Three times this uncertainty was applied to non-detects.

Peaks were excluded from the input data sets when they were below detection in a majority of samples. As a result, the influent data set included 110 peaks representing 161 congeners and included 99% of the PCB mass (i.e. just 1% of mass was lost when peaks were excluded). The effluent data set included only 76 peaks (124 congeners, 92% of PCB mass) because high molecular weight (MW) PCBs are effectively removed during treatment, resulting in concentrations in the effluent that are not detectable. These input data sets were analyzed via the PMF2 software of Paatero and Tapper (1994).

Results

IEP influent and effluent

The IEP data is discussed separately since it was not included in the PMF analysis, because this industrial facility displayed distinct concentrations and fingerprints of PCBs. Σ_{209}PCB concentrations in the IEP influent were more variable than at the municipal plants, ranging from 30 ng/L to 4,000 ng/L with a relative standard deviation (RSD) of 132%.

Σ_{209}PCBs in samples from IEP effluent averaged 2,400 pg/L after secondary treatment and 1,600 after tertiary (membrane filtration) treatment, suggesting that membrane filtration significantly enhances PCB removal, which lowers the effluent PCB load by 33% over conventional secondary treatment. In both cases, the tri homolog dominated in the IEP effluent. PCB 11 concentrations were statistically identical in the secondary and tertiary effluent, averaging (±

standard deviation) 131 ± 23 pg/L and 141 ± 67 pg/L respectively, demonstrating that membrane filtration is not particularly effective at removing lower MW PCB congeners. PCB 11 was a greater fraction of Σ_{209}PCBs in the tertiary effluent (8.9%) than in the secondary effluents (5.5%), because membrane filtration was comparably more effective at removing the higher MW PCBs. Fang et al. (2012) measured nine indicator PCBs plus twelve dioxin-like PCBs in treated wastewater from pulp and paper mills in China and found concentrations ranging from 0.2 to 1.17 ng/L, i.e. similar to the levels detected in the IEP effluent.

Removal of PCBs during treatment was calculated as:

$$Removal = \frac{C_{in} - C_{out}}{C_{in}} \qquad \text{(Equation 1)}$$

Where C is the average concentration across all samples in influent (C_{in}) or effluent (C_{out}). Removal at IEP ranged from 98.9% for the monochlorobiphenyls to greater than 99% for all other homologues via tertiary treatment.

The PCB signatures in the IEP influent and secondary effluent were very similar to Aroclor 1242: when PCB 11 is removed from the correlation, the similarity (R^2) ranged from 0.87 to 0.98 when compared with the Aroclor profile of Rushneck et al. (2004) (Figure S-1). Aroclors therefore account for more than 90% of PCBs in the influent and effluent from this plant. The dominance by Aroclor 1242 suggests these PCBs are probably from carbonless copy paper, which was impregnated with Aroclor 1242 only (Kuratsune and Masuda, 1972; Agency for Toxic Substances and Disease Registry (ATSDR), 2000). This is somewhat surprising since Aroclors have not been used for this purpose in the US since 1971 (Gorsuch et al., 1982). Aroclor 1242 was reportedly used in the de-inking process itself (State of Oregon Department of

Environmental Quality), but a 1977 EPA report on PCB sources in the pulp and paper industry (Carr et al., 1977) does not mention this use, suggesting that it had ceased by 1977. Paperback books produced in the 1950s and 1960s often contained Aroclors in their binding, although the Aroclors were typically 1248 and 1254 (Parker and Mayer-Blackwell, 2019). Waste paper used to make recycled paper arrives at the mill contaminated with every other imaginable type of waste, so there is potential for contamination of the paper from many sources of Aroclors, and Aroclor 1242 was used for many other purposes (Agency for Toxic Substances and Disease Registry (ATSDR), 2000), raising the possibility that other sources/processes contribute Aroclors to the IEP influent. However, the absence of the other Aroclors in the influent suggests that the source of Aroclor 1242 is a process unique to the pulp and paper industry.

Based on the (quite variable) influent concentrations and a typical flow of 3 MGD, the load of Σ_{209}PCBs entering the IEP WWTP ranges from about 300 mg/d to as high as 45 g/d. Carbonless copy paper reportedly contained 2-6% PCBs by weight (Kuratsune and Masuda, 1972). De Voogt et al. (1989) report that PCBs constituted and average of 3.4% of the weight of carbonless copy paper, at which level just 8.8 to 1,300 g/d of carbonless copy paper contains enough PCBs to account for all of PCB load to the IEP WWTP. Given that a sheet of 8.5” by 11” paper weights about 4.5 g, this represents between 2 and 300 sheets of carbonless copy paper per day in a facility that uses 150 to 550 tons raw material per day, 61% to 24% of which is previously used paper.

There is evidence that paper produced from post-consumer waste after 1971 also contained PCBs, such that the recycling of this paper could contribute PCBs to the IEP facility. The very fact that PCBs are found at IEP suggests that the paper they produce contains some low levels of PCBs. Stone (2016) found PCBs in a variety of US paper samples at ppb (ug/kg) levels. Similarly, Pivnenko et al. (2014) found an average concentration of 3.9 ug/kg of the sum of seven PCB congeners (PCBs 28, 52, 101, 118, 138, 153 and 180) in household waste paper from Denmark. The authors suggest that this sum of seven congeners can be converted to the sum of 209 PCBs by multiplying by 5.6, implying a Σ_{209}PCB concentration of about 22 ug/kg. Paper of this concentration would contribute about 1-4 mg/d of PCBs to the IEP facility.

Rigby et al. (2021) measured 21 PCB congeners in kiln-dried paper sludge from recycled paper processing in the U.K. When their measured congener patterns are compared to the Aroclor patterns of Rushneck et al. (2004), they are most similar to Aroclor 1242. Despite the differences in the coelution patterns between the two data sets), the correlation coefficient (R^2) ranges from 0.53 to 0.58 in the dried paper sludge and is 0.72 in the paper sludge ash. PCB-containing carbonless copy paper was used in the U.K. (Kuratsune and Masuda, 1972; CDC, 2000), and Monsanto produced Aroclors in the U.K. until 1977 (De Voogt et al., 1989). Total concentrations of the 21 congeners measured by Rigby et al. (2021) ranged from 41 to 56 ug/kg in these samples. Carr et al. (1977) observed that “the PCB concentration in the waste sludge might reasonably be assumed to be at the same concentration as in the product.” The kiln drying process probably causes some PCBs to evaporate, so the measurements of Rigby et al. (2021) are a lower bound on concentrations in the recycled paper materials used as inputs to plants such as IEP. If the concentrations measured by Rigby et al. (2021) are representative of the inputs to the IEP facility, then the incoming load of these 21 PCB congeners to the facility would be between 6 g/d and 30 g/d, i.e. enough to explain the measured PCB loads entering the plant. Therefore, the PCBs entering the IEP facility could plausibly come from paper with recycled content and not from original carbonless copy paper that has been stored since 1971.

PCB concentrations in municipal influents

Because the data from Liberty Lake was very different from all other municipal plants, it is discussed separately below. For the remaining municipal plants, average Σ_{209}PCBs in the municipal influent ranged from 7,800 pg/L at Post Falls to 13,500 pg/L at Spokane County (Figure 1). These levels were relatively stable with RSD values ranging from 80% at Hayden to 21% at Post Falls. The homolog patterns of PCBs in the municipal influent were dominated by tetra and penta PCBs. These levels are similar to those observed recently in other locations (Rodenburg et al., 2010a; Rodenburg et al., 2012; Capozzi et al., 2019). For example, data from at least 20 WWTPs discharging to the Delaware River sampled circa 2000, Σ_{209}PCBs show similar influent PCB concentrations from plants as small as 0.01 MGD and as large as 100 MGD, i.e. those treating waste from Philadelphia, PA with a population of about 1.5 million (Rodenburg et al., 2010a). This indicates that these PCB levels are universal in wastewater from the United States.

Average concentrations of the 12 dioxin-like PCBs (non-detects set equal to zero) ranged from 330 pg/L at Hayden to 910 pg/L at Spokane County. Of these, PCB 118 had the highest concentrations in the influent at all WWTPs, followed by PCB 105 and then by PCB 156+157. Toxic Equivalency (TEQ) values ranged from 0.013 pg/L at Hayden to 0.13 pg/L at Spokane City. PCB 126 dominated the TEQ in the influents.

Non-Aroclor or inadvertent PCBs are present in the influents. PCB 11 (3,3'-dichlorobiphenyl), was detected in all influent samples at concentrations ranging from 20.5 to 5,970 pg/L and averaging 542 pg/L. As a percent of Σ_{209}PCBs, PCB 11 ranges from 3.2% at the Spokane City to 7.2% at Post Falls. PCB 68 is thought to be a tracer for PCBs from silicone (and possibly other polymers) that has been cured using chlorinated peroxides (Perdih and Jan, 1994; Anezaki and Nakano, 2015; Herkert et al., 2018). It was detected in 94% of the influent samples at concentrations averaging 13 pg/L (maximum 95 pg/L). PCB 68 accounts for between 0.07% of Σ_{209}PCBs at Spokane City to 0.39% at Hayden. PCB 209 was detected in 92% of wastewater samples. It can be an impurity in some pigments (Du et al., 2008; Hu and Hornbuckle, 2009), but in the Spokane River basin, it appears that PCB 209 is primarily associated with Aroclors (see PMF results below).

PCB concentrations in municipal effluents

Average Σ_{209}PCBs in the municipal effluent range from as low as 200 pg/L at Spokane County, which is the newest of the WWTPs and uses both membrane filtration and chemical precipitation to remove phosphorus, to 660 pg/L at Spokane City, which also uses chemical precipitation to remove phosphorus but has not yet been upgraded to include membrane filtration. For most of the WWTPs, the homolog pattern in the effluent is shifted toward lower MW homologs relative to the influent (Figure 1).

Average concentrations of the 12 dioxin-like congeners in effluent ranged from 8.3 pg/L at Spokane County to 43 pg/L at Spokane City. TEQ in the effluent ranged from 0.002 pg/L at Spokane City to 0.032 pg/L at Post Falls and was dominated by PCB 126 (when detected). At Coeur d'Alene, the average concentrations of dioxin-like PCBs dropped to 9.3 pg/L after upgrade from 23 pg/L before, a 60% decrease. TEQ dropped by over 90% at Coeur d'Alene because PCB 126 was not detectable in the effluent after the upgrade to membrane filtration.

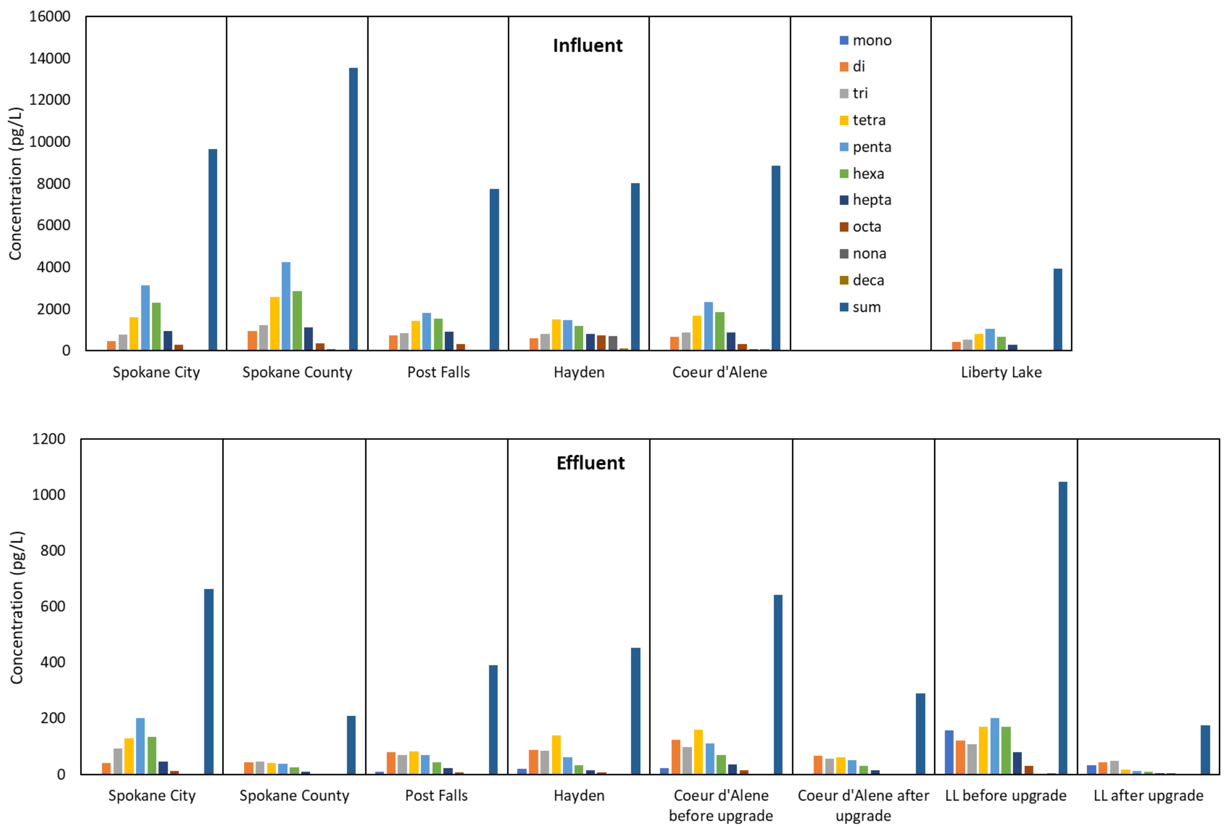

Figure 1. Average Σ_{209}PCBs and homologs in the influent and effluent of the WWTPs, including the Coeur d'Alene and Liberty Lake effluents both before and after their upgrade to membrane filtration. Note the difference in the y-scale between the influent and effluent.

Percent removal of PCBs

Removal of Σ_{209}PCBs ranged from 93% at Spokane City to 98% at Spokane County. Thus, even plants without membrane filtration achieved high removal of PCBs. Membrane filtration at Spokane County increases Σ_{209}PCB removal by about 5% compared to Spokane City. This may seem like a small percentage, but it represents a 55% reduction in Σ_{209}PCB loads to the Spokane

River and reductions of between 43% (for tri) to 92% (for nona) in homolog loads.

Across all plants, Removal was always lowest for the mono homolog at each plant, ranging from 40% at Hayden to 94% at Spokane County. For homologs with 5 or more chlorines, Removal was greater than 94% at all five municipal plants. Removal for individual congeners was calculated only for peaks/congeners that were detected in both the influent and the effluent (Figure 2). The two plants employing membrane filtration (Spokane County and Coeur d'Alene after upgrade) had higher removal of congeners than the other plants ($p < 0.05$ via paired two-tailed t-test). Notably, PCB congeners that are associated with silicone and peroxide-cured polymers, such as PCBs 1, 2, 3, 44+47+65, 45+51 and 68 (Perdih and Jan, 1994; Anezaki and Nakano, 2015; Herkert et al., 2018), show particularly poor removal at some plants. This may indicate that these PCBs were introduced into the samples during sample collection, in the laboratory, or during the analytical procedure. If these PCBs were truly present in the influent, they should be removed with similar efficiency as other PCB congeners of the same homolog. Notably, PCB 11 is removed efficiently at all plants, with Removal ranging from 77% at Coeur d'Alene before their upgrade to 96% at Spokane County. This removal is mostly due to secondary treatment. Upgrading to tertiary treatment/membrane filtration had little impact on the PCB 11 removal. This suggests that PCB 11 is not an artifact of blank contamination in the effluent. In the only other peer-reviewed study to examine PCB 11 removal during wastewater treatment, Yao et al. (2014) found that PCB 11 was not well removed (R ~ 10%) by the conventional activated sludge process when this congener was present at high levels (~10 ng/L) in industrial wastewater from pigment manufacture. In contrast, at the lower levels present in the Spokane River basin, PCB 11 is efficiently removed.

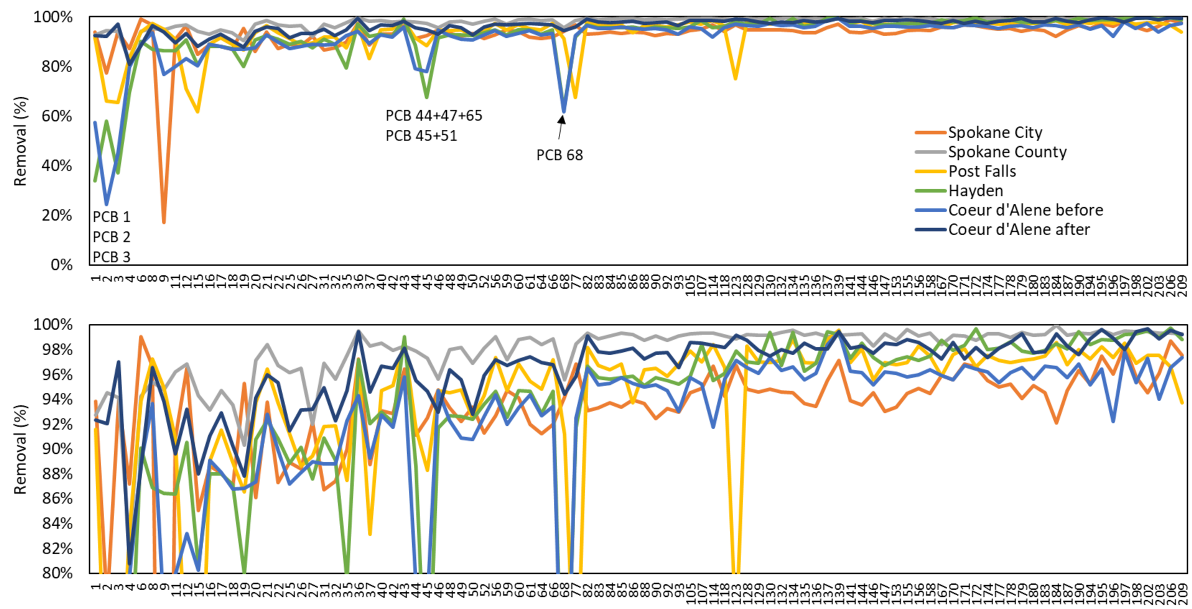

Figure 2. Removal of PCBs during wastewater treatment. PCB congeners shown on the x-axis represent the first congener of any co-eluting groups (co-elutions are listed in Supporting Information). Removal was calculated only for congeners detected in both the influent and effluent. Spokane County and Coeur d'Alene after represent treatment via membrane filtration. All others represent conventional secondary treatment. Lower panel displays the same information with a zoomed y axis. Liberty Lake is not shown due to the high number of non-detects.

Liberty Lake

The Liberty Lake data was markedly different from the other municipal plants. As noted above, samples from Liberty Lake were analyzed by a different contract laboratory using a different gas chromatography column than all other samples, so it is impossible to determine whether the differences are real or related to methodology. The average Σ_{209}PCBs in the Liberty Lake influent was 3,900 pg/L, half of the average concentration at the lowest of the other plants, Post Falls. This may be a result of the large number of non-detects or may reflect the history of the Liberty Lake area: the vast majority (~90%) of the residential construction in the Liberty Lake sewershed has occurred since 2000, long after PCBs were banned. Similar to the other municipal plants, dioxin-like PCBs averaged 200 pg/L in the influent with PCB 118 dominating the concentrations while PCB 126 dominated the TEQ.

Σ_{209}PCBs in the Liberty Lake effluent averaged 1050 pg/L before the upgrade to membrane filtration and 177 pg/L after, suggesting that the load of PCB to the Spokane River from this plant decreased by 83%. Removal of Σ_{209}PCBs was 73% before the upgrade to membrane filtration and 95% after.

In part, the decrease in effluent concentrations after the upgrade reflects the prevalence of non-detects, which make up 86% of data points in samples collected before the upgrade and 94% after. Measuring PCBs at these extremely low levels required that the limits of detection decrease from a median of about 10 pg/L before the upgrade to 1.6 pg/L after. In addition, the concentrations in the method blanks decreased from an average of 255 pg/L before the upgrade to 33 pg/L after. Since all data was censored at one time the concentration in associated method blank, very few congeners would have been detectable in the effluent after the upgrade without this decrease in method blank concentrations.

PMF results: Influent

The PMF analysis of the influent (Figure 3) yielded six factors (denoted Inf1 through Inf6) that mostly resemble Aroclors (Rushneck et al., 2004). Fingerprints of these factors are shown in figure S-2. Inf1 resembles Aroclor 1242 (R^2 = 0.85), Inf3 resembles Aroclor 1254 (R^2 = 0.96), and

Inf6 resembles Aroclor 1268 (R^2 = 0.97). When PCB 11 is excluded from the correlation, Inf2 resembles Aroclor 1254 (R^2 = 0.76), Inf5 resembles a ~50/50 mix of Aroclors 1254 and 1260 (R^2 = 0.83) and Inf4 resembles a mix of Aroclors 1248 and 1260 (R^2 = 0.72). PCB 11 is present in large proportions in Inf2 (11% of the fingerprint) and Inf4 (11%). Therefore, the PMF analysis does not separate PCB 11 into a separate factor, although it is certainly present in the influent. Inf1 through Inf6 explain 12%, 20%, 34%, 14%, 16%, and 3.3% of the PCB mass in the influent data set, respectively. Thus, Aroclors are the main source of PCBs to municipal wastewater throughout the Spokane River basin.

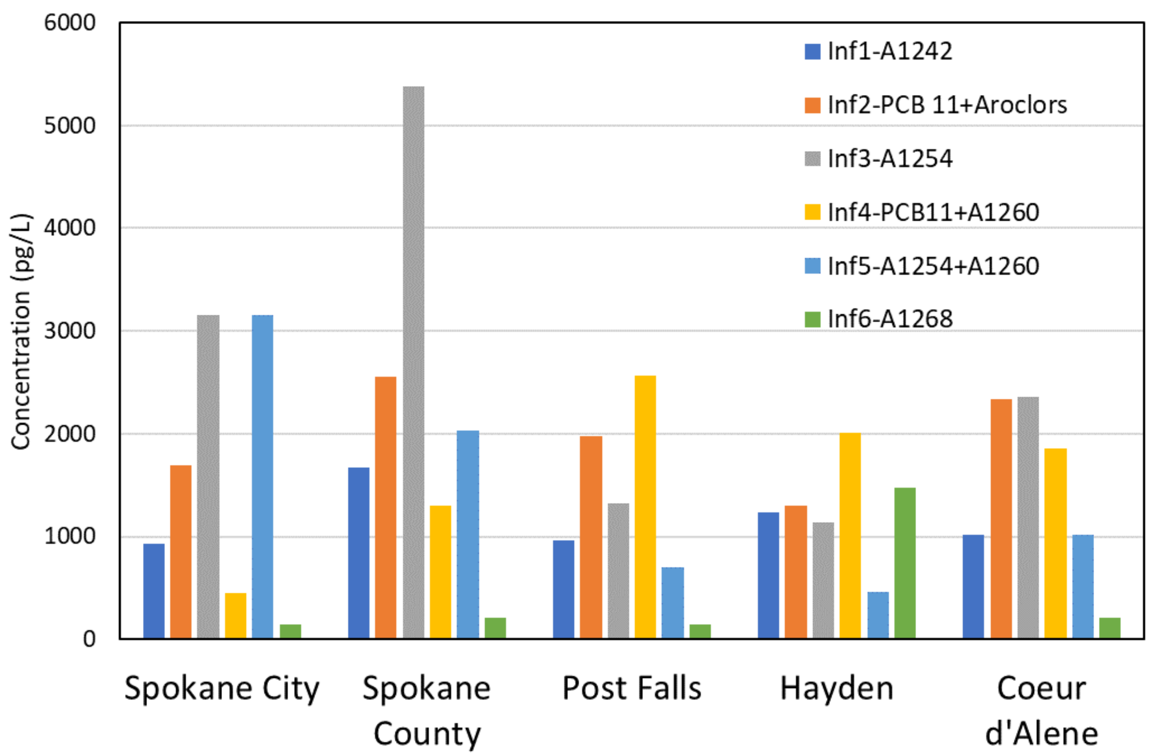

Figure 3. PCBs sources in the influent as explained by the PMF-derived factors (Inf1 through Inf6).

Notably, the PMF analysis of the influent does not identify a factor associated with silicone.

Congeners often associated with silicone are present in the effluent, as revealed by the removal calculations (Figure 2). The absence of a silicone factor in the PMF results for the influent suggests that the presence of these congeners in the effluent may be due to blank contamination (Greyell and Williston, 2018; Rodenburg et al., 2020). It is also notable that PMF does not identify any factors associated with microbial dechlorination of PCBs. PCB congeners resulting from this process have been observed at high levels in many WWTP influents and effluents (Rodenburg et al., 2010a; Rodenburg et al., 2012; Capozzi et al., 2019), especially those serving combined sewers. Despite the combined sewers present in parts of the city of Spokane, dechlorination was not observed there, nor at any of the WWTPs considered here.

The identification of Aroclor 1268 in the influent is surprising since it accounted for less than 1% of the total Aroclor production by Monsanto (Brown, 1994). The PMF results indicate that Inf6 (Aroclor 1268) accounts for >99% of PCBs in the influent sample from Hayden with the highest Σ_{161}PCBs of 32,000 pg/L. Inf6 explains 21% of PCBs in a sample from Coeur d'Alene, and up to 9% of PCBs in samples from Spokane County. Traces of Aroclor 1268 have also been detected in stormwater from the city of Spokane (data not shown). This indicates that Aroclor 1268 was used or disposed at locations throughout the Spokane River basin. Aroclor 1268 has been observed as a contaminant in other environmental media in the United States (Cantwell et al., 2006; Robinson et al., 2015). Aroclor 1268 was used in pipeline valve grease, insulation and other building materials (Agency for Toxic Substances and Disease Registry (ATSDR), 2000; Erickson and Kaley, 2011). Aroclor 1268 was used in a building material called galbestos manufactured by the H. H. Robertson Company from the 1950s to the 1970s (Erickson and Kaley, 2011). Galbestos was used at the Kaiser Aluminum facility in Mead, WA (https://response.epa.gov/site/site_profile.aspx?site_id=14546), which is now a superfund site and lies within the Spokane River watershed about 16 km northeast of Spokane Valley. This facility is not in the service area of any of the WWTPs discussed here, but it does demonstrate that galbestos was used in the watershed. Across the data set, Inf6 explains 3.3% of PCB mass and 82% of PCB 209 mass. Most of the remaining PCB 209 mass (15%) is explained by Inf2, which contains a high percentage of PCB 11. This fraction of PCB 209 may therefore arise from non-Aroclor (inadvertent) sources.

PMF results: Effluent

PMF analysis of the effluent resolved four factors, denoted Eff1 through Eff4, which explain 33%, 14%, 30%, and 23% of PCB mass in the effluent data set (Figure 4). Fingerprints of these factors are show in figure S-3. The physical, chemical, and microbial processes of treatment are likely to alter the PCB fingerprints, causing them to be less similar to the Aroclors. Despite this, most of the factors still resembled Aroclors. PCB 11 constituted 23% of Eff1, but the remainder of this fingerprint resembled Aroclors 1016 and 1242 (R^2 = 0.81 and 0.71 respectively). Eff1 consists mostly of low MW PCBs, suggesting that it may represent the dissolved phase. Eff4 resembled Aroclor 1260 (R2 = 0.76). Eff3 resembled a ~50/50 mix of Aroclors 1248 and 1254 (R2 = 0.65 with PCB 11, 0.73 without). PCB 11 is 6% of Eff3. Notably, a factor resembling Aroclor 1268 is not observed in the effluent, suggesting that this high MW PCB formulation is virtually completely removed during treatment.

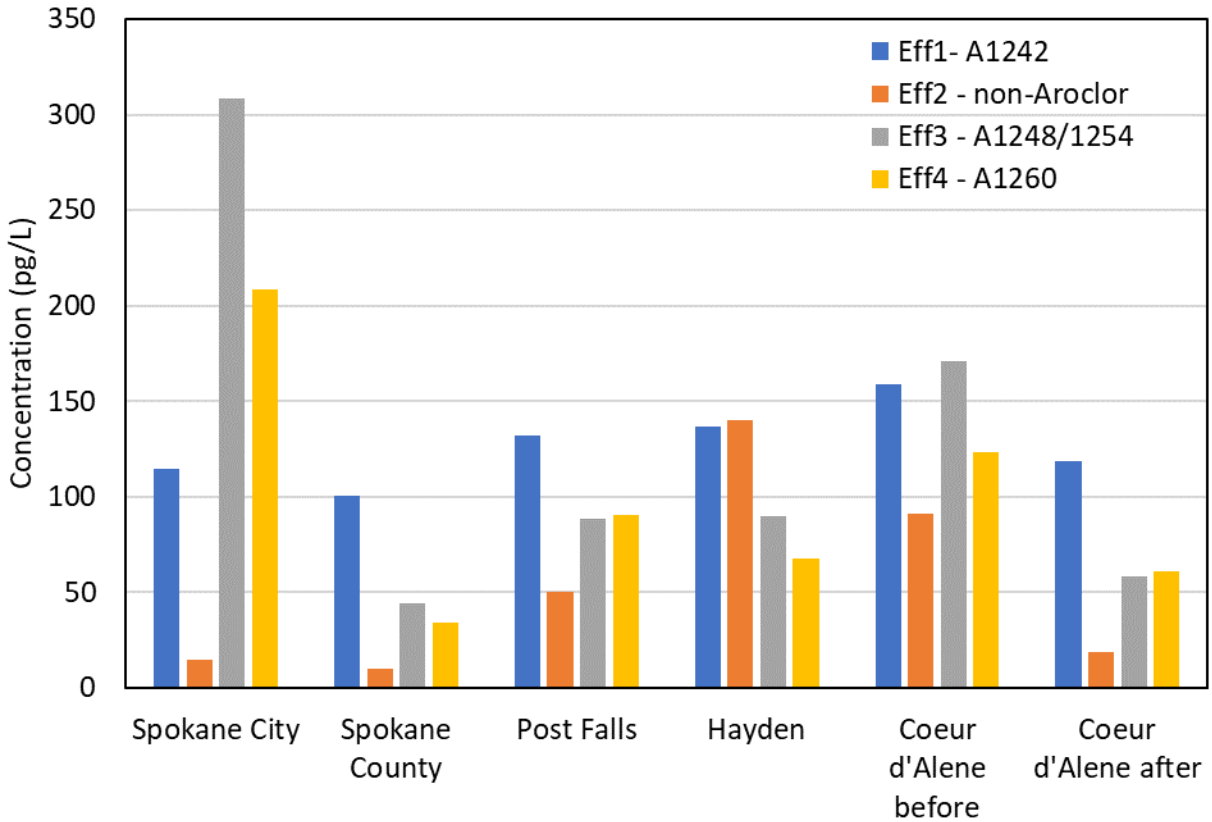

Figure 4. PCBs sources in the effluent as explained by the PMF-derived factors (Eff1 through Eff4). Eff2 may represent blank contamination.

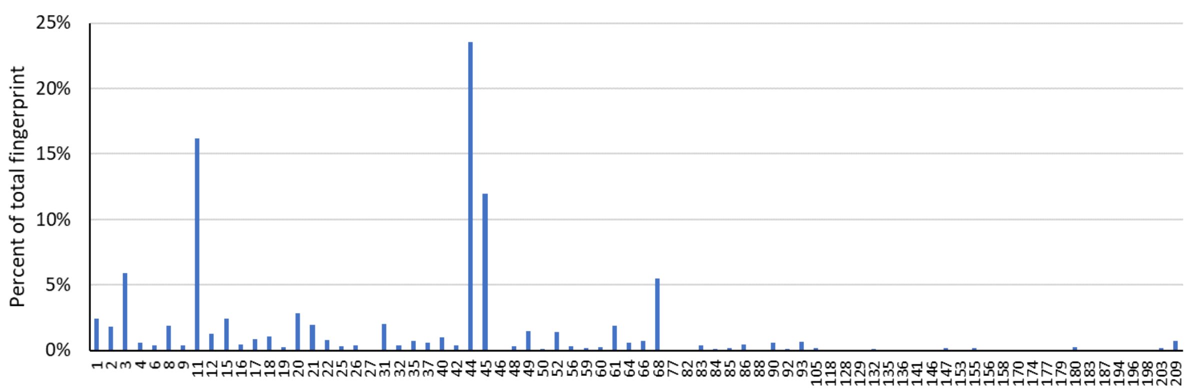

Figure 5. Fingerprint of Eff2 (PMF factor derived from effluent analysis) that is thought to be related to silicone products.

Eff2 appears to represent PCBs from silicone and other non-Aroclor/inadvertent sources (Figure 5). PCB 11 constitutes 16% of this factor, along with congeners probably arising from silicone (PCBs 1, 2, 3, 44+47+65, 45+51, and 68). PCB 209 constitutes 0.7% of Eff2. Despite rigorous protocols to limit blank contamination, this factor explains 14% of Σ_{124}PCBs and 20% of PCB 11 in the effluent (Figure 3). The fact that no such factor is found in the influent suggests that it arises from blank contamination, or at least from some process that affects the wastewater after it enters the plant. The highest concentrations of Eff2 (averaging 140 pg/L) are found at the smallest WWTP, Hayden, while the lowest concentrations (averaging 10 and 14 pg/L respectively) are found at the two largest plants, Spokane County and Spokane City. It is not clear whether this is a coincidence or an indication of some source of contamination affected by size or flow rate. Σ_{209}PCB concentrations in laboratory blanks are lowest at Spokane County. At Hayden, the concentrations of Eff2 show little variability (average = 140 pg/L, standard deviation = 40 pg/L, RSD = 28%), and Eff2 accounts for 32% of PCBs in the effluent, suggesting that this contamination could be a significant issue at some facilities. If unrecognized, this contamination could significantly affect decisions about how to manage PCB contamination at impacted WWTPs. It is not clear where the contamination in the Hayden samples arises, since only a 6-12 inch piece of silicone rubber tubing is used in the peristaltic pump of the samplers used by all of the WWTPs (and there is no viable replacement for this piece). It seems unlikely that such a small piece of tubing could have such a large influence on the results.

Another indicator that Eff2 is an artifact comes from Coeur d'Alene: Eff2 concentrations are reduced by nearly 80% upon the implementation of membrane filtration, but the reduction in the higher MW factors, Eff3 and Eff4, is much smaller (Figure 3). It is unlikely that membrane filtration would have a greater impact on a factor consisting of lower MW congeners. Notably, two samples of effluent from Coeur d'Alene, both collected before the upgrade, have the highest concentrations of Eff2 (749 and 772 pg/L).

The effects of membrane filtration on the treated effluent are best observed at Coeur d'Alene, where samples were collected before and after the upgrade. Average concentrations of Eff1 were reduced by 26%, a relatively small improvement that probably reflects the dissolved nature of Eff1. In contrast, Eff3 and Eff4 are reduced by 66% and 51%, respectively, reflecting their tendency to reside in the particle phase which is effectively removed by membrane filtration. The PMF results suggest that even though about 20% of the PCB 11 in the effluent comes from Eff2 and therefore might be associated with contamination, PCB 11 is still a significant contributor to PCBs in the effluent. The PMF results suggest that although PCB 11 averages 50 pg/L in the effluent, a fraction of this is due to contamination, and the 'real' amount of PCB 11 in the effluent averages 36 pg/L. This calculation is most extreme at Hayden, where PCB 11 was measured to average 59 pg/L, but 39% of this amount is due to Eff2, so the 'real' amount is only about 36 pg/L.

Discussion

Even without membrane filtration, conventional secondary treatment of municipal wastewater removed at least 93% of PCBs in the WWTPs of the Spokane area, similar to plants in other locations (Rodenburg et al., 2012). Membrane filtration is effective at enhancing removal of PCBs, especially high MW PCBs, from the wastewater stream. Implementation of membrane filtration reduced concentrations of total Σ_{209}PCBs in the effluent at the Coeur d'Alene WWTP by over 50% to 289 pg/L from 644 pg/L, which reduced loads to the river by nearly 5 mg/d, a significant reduction for the Spokane River where total loads of PCBs from municipal WWTPs is estimated to be 51-125 mg/d (LimnoTech, 2016). These reductions in load are compounded when the upgrades are implemented at larger WWTPs. For example, if installation of membrane filtration at the Spokane City plant reduces its PCB load by a similar percentage, the load would drop by more than 40 mg/d, equivalent to eliminating all of the other municipal WWTPs on the river.

Membrane filtration is more effective at removing high MW PCBs that are present in the particle phase. Fish data from the Spokane River suggest that although much weathering of the PCB fingerprints has occurred, higher MW Aroclors such as 1254 and 1260 are the source of most of the PCBs in the fish (data not shown). Therefore, reduction in the loads of high MW PCBs is likely to have the largest impact on PCB levels in the fish of the Spokane River. Conversely, PCB 11 is negligible in the fish tissue: it is frequently not detected and when detected, is much less than 1% of total PCBs (Seiders et al., 2015). Therefore, the lesser ability of membrane filtration to remove this congener may have little impact on the fish.

Aroclor 1268 contributed a significant load of PCBs to the influents, but it was virtually completely removed by all WWTPs. In contrast, at the IEP facility, Aroclor 1242 is the dominant source of PCBs. This is unfortunate for IEP since membrane filtration is less effective at removing lower MW congener such as those found in Aroclor 1242. Recycling of paper has obvious environmental benefits, so reducing the use of post-consumer paper at the IEP facility to reduce PCB loads to the Spokane River is counterproductive. Unfortunately, IEP has been decreasing the use of post-consumer feed due to a variety of concerns from a high of 61% of total feedstock in 2008 to just 24% in 2020.

Contamination of effluent samples with PCBs appears to be a significant issue. This is not obvious from the blanks, which contained similar amounts and fingerprints of PCBs across all of the WWTPs, suggesting that the contamination may not be coming from the sampling equipment or analysis laboratory. It might be due to the use of silicone products (caulk, tubing, o-rings) in the WWTP. Although it should be possible to drive levels of PCBs in the blanks lower (Rodenburg et al., 2020), it is not clear whether these efforts would necessarily lower PCB concentrations in the samples arising from this kind of contamination. It is not clear whether the silicone-type PCBs found in the samples are truly in the effluent (perhaps leaching out of silicone products in the piping within the WWTP, for example) or if they are truly a sample contaminant and therefore do not impact the river.

We recently undertook an extensive examination of blank correction methods (Rodenburg et al., 2020) and concluded that the method followed here of censoring at one times the level in the corresponding method blank was the least aggressive method that would achieve the desired goal of eliminating blank-related fingerprints from the PMF results. The present work suggests that this approach may not be aggressive enough. An alternate method of blank correction can be to analyze the analytical results via PMF and exclude any fingerprints that appear to be related to some kind of contamination from consideration in interpreting the results. This is, de facto, the procedure followed here. One of the conclusions of the blank study was that silicone-type PCBs are not present in the water column of the Spokane River, at least not at meaningful levels (Rodenburg et al., 2020). Therefore, it is justifiable in this case to treat Eff2 as contamination, but in other studies at other locations, this issue should be carefully examined.

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