City of Coeur d'Alene IDAHO

CITY OF COEUR D'ALENE

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WASTEWATER UTILITY DEPARTMENT

765 W. Hubbard Ave.
Coeur d'Alene, ID 83814

December 20, 2017

Re: City of Coeur d'Alene (NPDES Permit No.: ID0022853), Toxics Management Plan Annual Report

Matthew Plaisted
Idaho Department of Environmental Quality
2110 Ironwood Parkway
Coeur d'Alene, ID 83814

Jason Rodriguez
United States Environmental Protection Agency
1200 6th Avenue, Suite 900, MS OCE-101
Seattle, WA 98101

Dear Mr. Plaisted and Mr. Rodriguez:

Please accept the attached annual report of the results and plan for the City of Coeur d'Alene's Toxics Management Plan. Included in this report are:

- A description and schedule for implementation of additional actions that may be necessary, based on monitoring results, to ensure compliance with applicable water quality standards.
- A summary of the actions the permittee plans to undertake to reduce discharges of PCBs and 2,3,7,8 TCDD during the next reporting cycle.
- A summary of actions taken to reduce discharges of PCBs and 2,3,7,8 TCDD during the previous 12-month period.

A supplement included in this submission is:

- Monitoring Results for PCBs and 2,3,7,8 TCDD for the previous 12 month period
- Copies of educational materials, ordinances (Ordinance No. 3558, Section 1.B.25), inventories, guidance materials, or other products produced as part of the TMP.

Should you have any need for additional information or comment please reach out to me at 208-769-2277.

Sincerely,

Michael Anderson
Wastewater Superintendent

City of Coeur d'Alene

PCB and TCDD Toxics Management Plan Annual Report

December 20, 2017

hdrinc.com River Quarry at Parkcenter, 412 E. Parkcenter Blvd. Suite 100, Boise, ID 83706-6659
(208) 387-7000

Table of Contents

1 Introduction 1

2 TMP: PCB Data Analysis 2

2.1 Coeur d'Alene PCB Monitoring 2

2.2 Characteristics of PCBs 3

2.3 PCB Congener Analytical Methods 4

2.4 Collection System Investigative Monitoring 5

2.4.1 Collection System Monitoring Results 5

2.5 Influent and Effluent PCB Congener Data 6

2.6 PCB Congener Patterns and Trends through the Wastewater Facility 10

2.7 PCB Congener Variability 13

2.8 PCB Congener Potential Sources and Relationships to Products 17

2.9 Spokane River PCB Congeners and Fish Tissue 19

2.9.1 Comparison of Effluent PCB Congeners and Biaccumulative PCBs 20

2.9.2 Comparison of Effluent PCB Congeners and Toxic Dioxin-like PCBs 23

2.10 PCBs Next Steps 25

2.10.1 PCB Congeners and Complex Analysis 25

3 TMP: TCDD Data Analysis 25

3.1 Coeur d'Alene TCDD Monitoring 26

3.2 Characteristics of TCDD 26

3.3 TCDD Methods 26

4 References 27

1 Introduction

The City of Coeur d'Alene (City) owns and operates the Advanced Wastewater Treatment Facility (AWTF), which provides treatment for municipal, commercial, and industrial wastewater prior to discharge to the Spokane River. The US EPA Region 10 issued the City's National Pollutant Discharge Elimination System (NPDES) permit (ID-0022853), effective December 1, 2014. Section II.I of the permit requires "Best Management Practices for PCBs and 2,3,7,8 TCDD", in addition to permit required influent, effluent, and receiving water monitoring. The permit requires monitoring, development of a Toxics Management Plan (TMP), and an update to the quality assurance project plan (QAPP) to reflect the PCB and TCDD sampling and monitoring. Following the first year of the permit, the City will be required to develop an Annual Report documenting the toxics reduction activities, sampling results, and program plan for the following years. For the purpose of this document and other references within the City's toxics management program, the use of the word 'toxics' is focused on PCBs and 2,3,7,8 TCDD, as defined in the NPDES permit.

The content and sections of this report that address the specific NPDES permit requirements in Section II. Special Conditions I.2.for content of the annual report are as follows:

> Beginning December 20, 2016, the permittee must submit an annual report to EPA and IDEQ as an electronic attachment to a DMR. Each annual report must contain the following information:
>
> a) Monitoring results for PCBs and 2,3,7,8 TCDD for the previous 12-month period, including laboratory data sheets.
>   a. See Appendix A.
>
> b) Copies of education materials, ordinances (or other regulatory mechanisms), inventories, guidance materials, or other products produced as part of the TMP.
>   a. See Appendix B.
>
> c) A description and schedule for implementation of additional actions that may be necessary, based on monitoring results, to ensure compliance with applicable water quality standards.
>   a. As described herein. See sections 2.10 PCB Next Steps and Section 3.
>
> d) A summary of the actions the permittee plans to undertake to reduce discharges of PCBs and 2,3,7,8 TCDD during the next reporting cycle.
>   a. As described herein. See sections 2.10 PCB Next Steps and Section 3.
>
> e) A summary of the actions taken to reduce discharges of PCBs and 2,3,7,8 TCDD during the previous 12-month period.
>   a. As described herein. Actions taken are described in detail in Sections 2.4, 2.5, 2.6, 2.7, 2.8, and 2.9 and Section 3 that demonstrate that the City's wastewater facility effectively reduces toxics discharges.

2 TMP: PCB Data Analysis

The City of Coeur d'Alene is authorized by the U.S. Environmental Protection Agency (EPA) to discharge treated water from the City's wastewater facility to the Spokane River. Requirements of this authorization are spelled out in the City's National Pollutant Discharge Elimination System (NPDES) Permit No. ID0022853. The permit was recently renewed and is effective from December 1, 2014 through November 30, 2019. The purpose of this section is to summarize the analysis of PCB data that are required to be collected by the permit. This includes examining changes in concentrations after passing through the wastewater facility.

2.1 Coeur d'Alene PCB Monitoring

One component of the permit is to conduct monitoring of the effluent (treated water prior to discharge) and the surface water (Spokane River). The monitoring requirements include sampling and testing for polychlorinated biphenyls (PCBs). As listed in the permit, the PCB monitoring requirements are shown in Table 1.

Table 1. NPDES Permit PCB Monitoring Requirements

Parameter	Units	Effluent Limits			Monitoring Requirements		
		Average Monthly Limit	Average Weekly Limit	Max. Daily Limit	Location	Frequency	Sample Type
Polychlorinated Biphenyl (PCB) Congeners	pg/L	Report	--	Report	Influent	½ months	24-Hr. Comp.
PCB Congeners	pg/L	Report	--	Report	Effluent	1/quarter	24-Hr.
Source: NPDES Permit ID0022853 Table 1: Final Effluent Limits and Monitoring Requirements for Outfall 001							

Parameter	Sample Locations	Sample Frequency	Sample Type	Maximum ML
PCB Congeners	Upstream and Downstream	2/year	Grab	Note 3
Source: NPDES Permit ID0022853 Table 4: Surface Water Monitoring Requirements				

Monitoring was conducted to the monitoring requirements and for the City to understand the characteristics of PCBs in the collection system and the effects of the wastewater facility. The locations and dates the City has collected PCB samples are summarized in Table 2. Sampling by the City included influent and effluent, either as a blend of the stream from secondary treatment and tertiary membrane filter, or the tertiary membrane filter alone.

Table 2. Summary of PCB Monitoring From January 2015 to September 2017

Location / Period	Influent	Effluent	Tertiary Membrane Filter	Spokane River
1	January-February 2015	January-March 2015	not sampled	not sampled
2	March-April 2015	not sampled	April 2015	not sampled
3	May-June 2015	April-June 2015	May 2015	April-June
4	July-August 2015	July-September 2015	July 2015	July-October
5	September-October 2015	not sampled	not sampled	not sampled
6	November-Dec. 2015	October-Dec. 2015	November 2015	not sampled
7	January-February 2016	January-March 2016	January 2016	not sampled
8	March-April 2016	not sampled	not sampled	not sampled
9	May-June 2016	April-June 2016	May 2016	April-June
10	July-August 2016	July-September 2016	July 2016	July-October
11	September-October 2016	not sampled	not sampled	not sampled
12	November-Dec. 2016	October-Dec. 2016	November 2016	not sampled
13	January-February 2017	January-March 2017	January 2017	not sampled
14	March-April 2017	not sampled	not sampled	not sampled
15	May-June 2017	April-June 2017	May 2017	April-June
16	July-August 2017	July-September 2017	July 2017	July-October
17	September-October 2017	not sampled	not sampled	not sampled

2.2 Characteristics of PCBs

PCBs are organic chlorine compounds with the formula $C_{12}H_{10-x}Cl_x$. A congener is any single, unique, well-defined chemical compound in the PCB category. The difference between congeners is the number and locations of the chlorine atoms on the PCB molecule. A "homologue" includes all congeners with an equal number of chlorines attached to the biphenyl ring. The name of a congener specifies the total number of chlorine substitutes and the position of each chlorine atom. There are a total of 209 PCB congeners. However, some congeners are grouped together as part of the laboratory analysis and results reported from monitoring.

PCBs were once widely deployed as dielectric and coolant fluids in electrical apparatus, carbonless copy paper and in heat transfer fluids. The manufacture of PCBs ended in the U.S. in 1977. While no longer produced in the United States, PCBs are still found in the environment. PCBs cause harmful health effects and are a probable carcinogen.

PCB congeners can be divided into the coplanar, the mono-ortho-substituted PCBs, and other non-dioxin-like PCBs. The significance of this designation is that the coplanar and some of the mono-ortho-substituted PCBs have dioxin-like toxic effects. The non-dioxin-like PCBs and their metabolites do not interact substantially with the aryl hydrocarbon receptor (AhR) and may act through different pathways than the dioxin-like chemicals, so their effects are not represented in the use of toxic equivalency factors (TEFs). Thus, groups of congeners behave differently in the environment and have different degrees of uptake into organisms with corresponding intensities of toxicity.

The toxicity of a PCB is dependent not only upon the number of chlorines present on the biphenyl structures, but the positions of the chlorines. High-chlorinated PCBs are often more resistant to degradation and volatilization and sorb more strongly to particulate matter. Some more-chlorinated PCBs tend to bioaccumulate to greater concentrations in tissues of animals than do low-molecular-weight ones. The more-heavily chlorinated PCBs can also biomagnify in food webs. Other high-molecular-weight congeners have specific structures that render them susceptible to metabolism by such species as fish, crustacea, birds, and mammals.

2.3 PCB Congener Analytical Methods

There are several methodologies for both total PCB Aroclor and PCB Congener specific laboratory analysis. Aroclors are a trade name for PCBs produced by Monsanto from 1930 to 1977. An Aroclor is a mixture of individual PCB congeners. Historically, PCB Aroclor analysis is the most commonly and widely used methodology for the testing of PCB. Improvements in laboratory techniques have allowed reporting of individual congeners. Test procedures for the presence of PCBs include Methods 608, 8082 and 1668 for water samples.

Method 608 is a method for organic chemical analysis of municipal and industrial wastewater including organochlorine pesticides and PCBs. This is a gas chromatographic (GC) method applicable to municipal and industrial discharges as provided under 40 CFR Part 136.1. The method reporting limits for PCB congeners is about 0.1 ug/L.

Method 8082 is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors or as individual PCB congeners in extracts from solid, tissue, and aqueous matrices, using open-tubular, capillary columns with electron capture detectors (ECD) or electrolytic conductivity detectors (ELCD). This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs (GC) and skilled in the interpretation of gas chromatograms. The method reporting limits for PCB congeners in water is 5.0 ng/L.

Method 1668 is for determination of chlorinated biphenyl congeners (CBs) in water, soil, sediment, biosolids, tissue, and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). This method is for use in data gathering and monitoring associated with the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Liability Act, and the Safe Drinking Water Act. The GC/MS portions of this Method are for use only by analysts experienced with HRGC/HRMS or under the close supervision of such qualified persons. This method is "performance-based." The laboratory is permitted to modify the method to overcome interferences or lower the cost of measurements, provided that all performance criteria are met. The method reporting limits for PCB congeners in water is 10 to 1,000 pg/L.

The analytical reports for these methods from the laboratory contain a significant amount of information and more than just a resulting value. Information in the reports includes the method detection limit (MDL) and method reporting limit (MRL). The MDL is the minimum concentration of a compound or analyte which can be measured using a specific method, including sample preparation steps. MDLs are statistically derived as the 99 percent confidence interval for detection of an analyte for a given method and matrix. The MRL is defined as the lowest level that can be reliably achieved with specified limits of precision and accuracy during routine laboratory operating conditions. The MRL is usually determined by multiplying the MDL by some factor which is decided upon by the laboratory. The MRL is supposed to represent the level where reliable quantitative information is routinely reported. It takes into account the sample size, matrix effects, and any dilutions made during the analysis of that particular sample. The MRL is always greater than or equal to the experimentally determined MDL. Therefore the MDL is what we really want to know, the practical quantitation level is where we can reliably measure, and the MRL is what the laboratory considers to be their lowest reportable value.

Given the laboratory methods, various data qualifiers may be attached to the resulting data. These qualifier flags indicate discrepancy issues with the laboratory analysis. Qualifier flags that are in the City's laboratory results are shown in Table 3.

Table 3. Description of Data Qualifiers

Qualifier Flag	Definition
B	Analyte found in sample and associated blank
C	Co-eluting congener
D	Dilution data. Result was obtained from the analysis of a dilution
G	Evidence of a disturbance with the lock-mass used during the analysis
J	The reported result is an estimate. The value is less than the minimum calibration level but greater than the detection limit
K	Peak detected but did not meet quantification criteria, result reported represents the estimated maximum possible concentration
T	Result recalculated against alternate labeled compound(s) or internal standard
U	The analyte was not detected in the sample at the detection limit
Data qualifier flags are used to flag analytes in the laboratory analytical report. The use of data qualifiers or flags is a common practice used by laboratories to highlight a potential concern with a reported result. Standardized flags set by the EPA and analytical laboratories are used.	

2.4 Collection System Investigative Monitoring

The City initiated the collection system monitoring program in 2015. The reason for collection system monitoring is where the permit requires, "From contaminated soils, sediments, storm water and groundwater entering the POTW collection system via inflow and infiltration." One goal of the collection system monitoring is to compare the collection system data with the influent data to see if there is a "hotspot" area contributing a higher than expected load of toxics to the treatment plant. Based on an evaluation of inflow through the City, a priority area was identified based on information presented in the Collection System Master Plan.

2.4.1 Collection System Monitoring Results

Three locations were identified for the first year in the main drainage basin that has the most inflow. Monitoring consisted of grab samples taken at approximately 9 a.m. as an estimate of peak flow conditions in the manholes. In June of 2016. Samples were analyzed using Method 8082 with a reporting limit of 0.8 ug/L. Table 4 summarizes the results of the monitoring with Non Detects reported for all Aroclors and Total PCBs at all three collection system locations.

Table 4. Collection System PCB Monitoring Results Using Method 8082, June 6, 2016

Parameter	PQL Reporting Limits	Collection System Manhole Location		
		BUS1-01	CEN1-01	SHR1-01
Aroclor 1016	0.8 ug/L	ND	ND	ND
Aroclor 1221	0.8 ug/L	ND	ND	ND
Aroclor 1232	0.8 ug/L	ND	ND	ND
Aroclor1242	0.8 ug/L	ND	ND	ND
Aroclor 1248	0.8 ug/L	ND	ND	ND
Aroclor 1254	0.8 ug/L	ND	ND	ND
Aroclor 1260	0.8 ug/L	ND	ND	ND
Total PCB	0.8 ug/L	ND	ND	ND

Dioxin (TCDD) analysis was not conducted on the collection system samples.

2.5 Influent and Effluent PCB Congener Data

Sample results are "corrected" to account for laboratory contamination. If a sample result is within a certain factor of the laboratory blank, it is removed from the total. A "10X" blank correction identifies congeners that are less than ten times the associated blank result and counts these congeners as zero when totaling. Equipment blanks were also run for the effluent sampler and corrected at the 10X level. An example is shown in Table 5 where the lab blank is multiplied by the blank factor, and when the multiplied value is greater than the sample value the correct value is zero instead of the sample value. The number of PCB congeners with K and B flags is shown in Table 6. A check of the laboratory B-flags to the methodology of 10 times the blank is also shown in Table 6. The reasons for the few differences are unknown but the values are shown in Table 7.

Table 5. PCB Blank Correction Example

Laboratory Results			3X Blank Correction		10X Blank Correction	
Congener	Lab Blank	Sample	3X	Corrected	10X	Corrected
1	ND	100	ND	100	ND	100
2	5	100	15	100	50	100
3	25	100	75	100	250	0
4	50	100	150	0	500	0
5	100	100	300	0	1000	0

Table 6. Summary of PCB Qualifier Flags

Period*	Influent			Effluent			TMF		
	K Flags	B Flags	Check	K Flags	B Flags	Check	K Flags	B Flags	Check
1	5	1	2	16	61	62	n/a	n/a	n/a
2	10	2	2	n/a	n/a	n/a	20	62	62
3	5	4	4	26	63	63	23	51	51
4	16	10	10	25	71	71	12	49	49
5	9	6	3	n/a	n/a	n/a	n/a	n/a	n/a
6	14	5	5	9	58	58	16	57	57
7	5	4	4	11	45	44	5	43	43
8	5	8	8	n/a	n/a	n/a	n/a	n/a	n/a
9	10	4	4	26	46	46	12	46	46
10	10	5	5	12	37	37	8	38	38
11	23	4	4	n/a	n/a	n/a	n/a	n/a	n/a
12	28	8	8	31	58	58	35	62	62
13	2	13	13	17	55	55	11	52	52
14	12	7	7	n/a	n/a	n/a	n/a	n/a	n/a
15	13	6	6	30	55	55	30	51	51
16	16	9	9	41	63	63	24	61	61
17	27	7	7	n/a	n/a	n/a	n/a	n/a	n/a
Total	210	103	101	244	612	612	196	572	572
*Period – See Table 2									

Table 7. PCB Blank Correction Subset

Period*	**Congener**	**Matrix**	**Lab Blank (pg/L)**	**10X (pg/L)**	**Sample (pg/L)**	**Flags**
1	1	Influent	1.43	14.3	13.4	
5		Influent	2.31	23.1	32.7	B
5	15	Influent	2.64	26.4	50.7	B
5	19	Influent	0.739	7.39	13.6	B
1	11	Effluent	5.03	50.3	48.5	
7	153+168	Effluent	2.13	21.3	21.9	B
*Period – See Table 2						

The influent and effluent PCB totals, both blank corrected and unaltered, are shown in Table 8. Table 8 provides a comparison of the reported results. The effluent and TMF data show that the blank correction results in significantly lower effluent concentrations.

The PCB congeners with at least 50 percent of the samples qualified with a B-flag are shown in Table 9. There is no readily apparent pattern in the specific blanks that they are contaminated by the same congeners.

Table 8. PCB Totals in Coeur d'Alene Wastewater 2015-2017

Period*	Condition	Influent	Effluent (Secondary + TMF)	TMF
1	Total PCBs without Exclusions	19,947	1,398	n/a
	Minus K-Flag estimates	19,942	1,386	n/a
	Minus B-Flag less 10X blank	19,937	1,066	n/a
2	Total PCBs without Exclusions	9,851	n/a	239
	Minus K-Flag estimates	9,808	n/a	225
	Minus B-Flag less 10X blank	9,788	n/a	16
3	Total PCBs without Exclusions	11,508	712	452
	Minus K-Flag estimates	11,484	625	388
	Minus B-Flag less 10X blank	11,032	28	40
4	Total PCBs without Exclusions	10,058	607	229
	Minus K-Flag estimates	9,787	547	203
	Minus B-Flag less 10X blank	9,565	15	0
5	Total PCBs without Exclusions	25,403	n/a	n/a
	Minus K-Flag estimates	25,223	n/a	n/a
	Minus B-Flag less 10X blank	25,078	n/a	n/a
6	Total PCBs without Exclusions	10,980	701	312
	Minus K-Flag estimates	10,921	691	290
	Minus B-Flag less 10X blank	10,808	72	8
7	Total PCBs without Exclusions	8,864	723	402
	Minus K-Flag estimates	8,804	660	391
	Minus B-Flag less 10X blank	8,724	84	2
8	Total PCBs without Exclusions	10,567	n/a	n/a
	Minus K-Flag estimates	10,535	n/a	n/a
	Minus B-Flag less 10X blank	10,269	n/a	n/a
9	Total PCBs without Exclusions	9,564	408	184
	Minus K-Flag estimates	9,483	357	165
	Minus B-Flag less 10X blank	9,421	62	24
10	Total PCBs without Exclusions	9,792	1,283	1,202
	Minus K-Flag estimates	9,710	988	1,034
	Minus B-Flag less 10X blank	9,528	569	750
11	Total PCBs without Exclusions	9,034	n/a	n/a
	Minus K-Flag estimates	8,781	n/a	n/a
	Minus B-Flag less 10X blank	8,724	n/a	n/a
12	Total PCBs without Exclusions	9,430	560	239
	Minus K-Flag estimates	9,115	493	177
	Minus B-Flag less 10X blank	8,970	122	5
13	Total PCBs without Exclusions	7,332	557	408
	Minus K-Flag estimates	7,312	524	386
	Minus B-Flag less 10X blank	6,326	20	6
14	Total PCBs without Exclusions	6,636	n/a/	n/a/
	Minus K-Flag estimates	6,567	n/a	n/a
	Minus B-Flag less 10X blank	6,111	n/a	n/a
15	Total PCBs without Exclusions	8,336	372	213
	Minus K-Flag estimates	8,209	322	163
	Minus B-Flag less 10X blank	7,590	4	1
16	Total PCBs without Exclusions	8,585	540	200
	Minus K-Flag estimates	8,474	391	169
	Minus B-Flag less 10X blank	8,278	9	2

17	Total PCBs without Exclusions	7,863	n/a	n/a
	Minus K-Flag estimates	7,674	n/a	n/a
	Minus B-Flag less 10X blank	7,525	n/a	n/a
*Period – See Table 2				

Table 9. PCB Congeners B-Flag Qualified[a] in 50-Percent or more Samples

Influent	Effluent	TMF
1	1	1
2	2	2
3	3	3
	4	4
	6	6
7		
	8	8
	11	11
15	15	15
	16	16
	17	17
	18+30	18+30
	19	19
	20+28	20+28
	21+33	21+33
	22	22
	25	25
	26+29	26+29
	31	31
	32	32
	37	37
	40+41+71	40+41+71
	42	42
	44+47+65	44+47+65
	45+51	45+51
	48	48
	49+69	49+69
	50+53	50+53
	52	52
	56	56
	60	60
	61+70+74+76	61+70+74+76
	64	64
	66	66
	77	
	83+99	83+99
	84	84
	86+87+97+109+119+125	86+87+97+109+119+125
	90+101+113	90+101+113
	93+95+98+100+102	93+95+98+100+102
	105	105
	110+115	110+115
	118	118
	129+138+160+163	129+138+160+163

	132	132
	135+151+154	135+151+154
	147+149	147+149
	153+168	153+168
	156+157	
	180+193	180+193
	187	187
	209	209
[a]Qualifier Flag B: Analyte found in sample and associated blank		

2.6 PCB Congener Patterns and Trends through the Wastewater Facility

Patterns and trends in PCB congener concentrations were examined. In doing so, the City sought to understand the impacts of the wastewater facility on PCBs including the following:

- Which congeners have the greatest concentrations in the collection system influent coming into the wastewater facility?
- Are those congeners transformed or reduced in the effluent after passing through the wastewater facility?
- Which congeners have the greatest concentrations in the effluent?

Using the City's sampling results dataset, the median concentration of the influent samples gathered from January-February 2015 through September-October 2017 was calculated. The median was selected as a statistical representation of the central tendency or average of the data which would dampen the effect of outlying samples. Whereas the average or mean may be skewed to by higher concentrations and the mode may not be appropriate for a small dataset. The median concentrations were then ranked from largest to smallest for PCB congeners with a median concentration greater than 100 pg/L in the influent wastewater. The results using the uncorrected data are shown in Table 10 and the blank corrected results are shown Table 11.

This shows the difference between examining the uncorrected and blank corrected data. The corresponding concentrations of the effluent, secondary + TMF and TMF are also shown in Tables 10 and 11. The list of PCB congeners captures the effluent with the greatest concentrations. The percent reduction from influent to effluent (secondary + TMF and TMF) along with the reduction from secondary +TMF to TMF were calculated and are shown in the Tables 10 and 11.

From data presented in Table 10 that has not been blank corrected, the results show that the wastewater facility reduces the influent PCB congeners by 88-percent or greater, with most PCB congeners reduced by 97-percent or greater. The TMF provides an additional significant reduction in PCB congener concentrations. There are only 4 PCB congeners with median concentrations greater than 10 pg/L after TMF.

From Table 11, the blank corrected results show that the wastewater facility reduces the influent PCB congeners by 93-percent or greater, with most PCB congeners reduced by 98-percent or greater in the effluent of the wastewater facility. The TMF provides an additional significant reduction in PCB congener concentrations. There are only 6 PCB congeners with median concentrations greater than 1 pg/L following TMF at the wastewater facility.

Table 10. PCBs with the Highest Influent Median Concentration and Resulting Effluent Concentrations using the Uncorrected Data Set (January-February 2015 through September-October 2017)

PCB	Influent	Effluent (Secondary + TMF)		Effluent (TMF)		
	Median (pg/L)	Median (pg/L)	Reduction[A] (%)	Median (pg/L)	Reduction[A] (%)	Reduction[B] (%)
11	467	83	82%	59	87%	29%
129+136+160+163	418	14	97%	4	99%	71%
61+70+74+76	402	18	96%	8	98%	56%
110+115	400	16	96%	6	99%	64%
90+101+113	390	17	96%	6	98%	65%
153+168	383	12	97%	3	99%	73%
52	332	26	92%	14	96%	45%
147+149	321	11	97%	3	99%	72%
118	318	13	96%	5	99%	65%
93+95+98+100+102	299	17	94%	6	98%	64%
44+47+65	273	22	92%	14	95%	36%
86+87+97+109+119+125	262	2	95%	5	98%	59%
180+193	238	7	97%	2	99%	76%
83+99	207	9	95%	3	98%	64%
20+28	199	122	89%	12	94%	44%
31	174	16	91%	9	95%	41%
66	169	8	95%	4	98%	54%
187	165	5	97%	1	99%	86%
135+151+154	148	7	96%	2	99%	75%
132	128	5	96%	1	99%	70%
21+33	121	8	94%	4	97%	53%
105	121	5	96%	2	98%	63%
49+69	114	8	93%	4	96%	48%
18+30	110	11	90%	8	93%	28%
84	101	5	95%	2	98%	57%

A – Reduction is influent to effluent
B – Reduction is effluent (secondary + TMF) to effluent (TMF)

Table 11. PCBs with the Highest Influent Median Concentration and Resulting Effluent Concentrations using the Blank Corrected Data Set (January-February 2015 through September-October 2017)

PCB	Influent	Effluent (Secondary + TMF)		TMF		
	Median (pg/L)	Median (pg/L)	Reduction[A] (%)	Median (pg/L)	Reduction[A] (%)	Reduction[B] (%)
11	476	49	90%	--	--	--
129+136+160+163	418	--	--	--	--	--
61+70+74+76	402	--	--	--	--	--
110+115	400	--	--	--	--	--
90+101+113	390	--	--	--	--	--
153+168	383	--	--	--	--	--
52	328	--	--	--	--	--
147+149	321		--	--	--	--
118	318	--	--	--	--	--
93+95+98+100+102	300	20	93%	--	--	--
44+47+65	273	--	--	--	--	--
86+87+97+109+119+125	262	--	--	--	--	--
180+193	238	8	96%	--	--	--
83+99	207	--	--	--	--	--
20+28	199	16	92%	10	95%	37%
31	174	--	--	--	--	--
66	169	8	96%	3	98%	64%
187	165	8	95%	--	--	--
135+151+154	148	7	95%	1	99%	88%
132	128	3	98%	3	98%	13%
21+33	121	--	--	--	--	--
105	121	2	98%	1	99%	51%
49+69	114	--	--	--	--	--
18+30	110	--	--	--	--	--
84	101	5	95%	--	--	--

A – Reduction is influent to effluent
B – Reduction is effluent (secondary + TMF) to effluent (TMF)

To further the analysis, the City's sampling results dataset, with the median concentrations, was then reordered to identify those PCB congeners that are potentially the most persistent. The results using the data are shown in Table 12 and the corrected results are shown Table 13. This shows the difference between examining the uncorrected and blank corrected data.

Most persistent PCB congeners included those with high concentrations and those with low reduction percentages. Some of the PCB congeners with high influent concentration are also persistent. Many of the PCB congeners that are persistent are generally those with low or single digits indicating that they are lower molecular weight congeners, either from the original source or degraded from legacy higher molecular weight congeners. These PCB congeners have fewer chlorine atoms. Biotransformation of the less chlorinated congeners can occur; however, molecules with four or more chlorine atoms (PCB-40 and greater) are considered persistent.

Anaerobic conditions allow the dechlorination of the highly chlorinated PCBs to less chlorinated, degradable forms as described in Environmental Toxicology and Risk Assessment, Third Volume, Issue 1218.

Table 12. Potentially Most Persistent PCBs from Influent to Effluent using the Uncorrected Data Set

PCB	Influent	Effluent (Secondary + TMF)		Effluent (TMF)		
	Median (pg/L)	Median (pg/L)	Reduction[A] (%)	Median (pg/L)	Reduction[A] (%)	Reduction[B] (%)
11	467	83	82%	59	87%	29%
20+28	199	22	89%	12	94%	44%
18+30	110	11	90%	8	93%	28%
31	174	16	91%	9	95%	41%
44+47+65	273	122	92%	14	95%	36%
52	332	26	92%	14	96%	45%
49+69	114	8	93%	4	96%	48%
21+33	121	8	94%	4	97%	53%
93+95+98+100+102	299	17	94%	6	98%	64%
66	169	8	95%	4	98%	54%
84	101	5	95%	2	98%	57%
83+99	207	9	95%	3	98%	64%
86+87+97+109+119+125	262	12	95%	5	98%	59%

A – Reduction is influent to effluent
B – Reduction is effluent (secondary + TMF) to effluent (TMF)

Table 13. Potentially Most Persistent PCBs from Influent to Effluent using the Blank Corrected Data Set

PCB	Influent	Effluent (Secondary + TMF)		TMF		
	Median (pg/L)	Median (pg/L)	Reduction[A] (%)	Median (pg/L)	Reduction[A] (%)	Reduction[B] (%)
11	476	49	90%	--	--	--
20+28	199	16	92%	10	95%	37%
93+95+98+100+102	300	20	93%	--	--	--
84	101	5	95%	--	--	--
187	165	8	95%	--	--	--
135+151+154	148	7	95%	1	99%	88%

A – Reduction is influent to effluent
B – Reduction is effluent (secondary + TMF) to effluent (TMF)

2.7 PCB Congener Variability

There is significant variability of PCB congeners in the environment and thus the collection system and influent. The variability can be described in many ways including various statistics. Simply comparing the minimum and maximum concentration of a congener in the sample dataset shows some congeners with ranges of hundreds to thousands of pg/L. This variability is greatly reduced in the effluent concentrations. Four PCB congeners were selected as examples. The variability for the uncorrected data is shown in Figure 1 and for the corrected data is shown in Figure 2. The vertical scale is a factor of 10 greater for the influent than the effluent, demonstrating the significant reduction in concentration in the effluent of the wastewater facility.

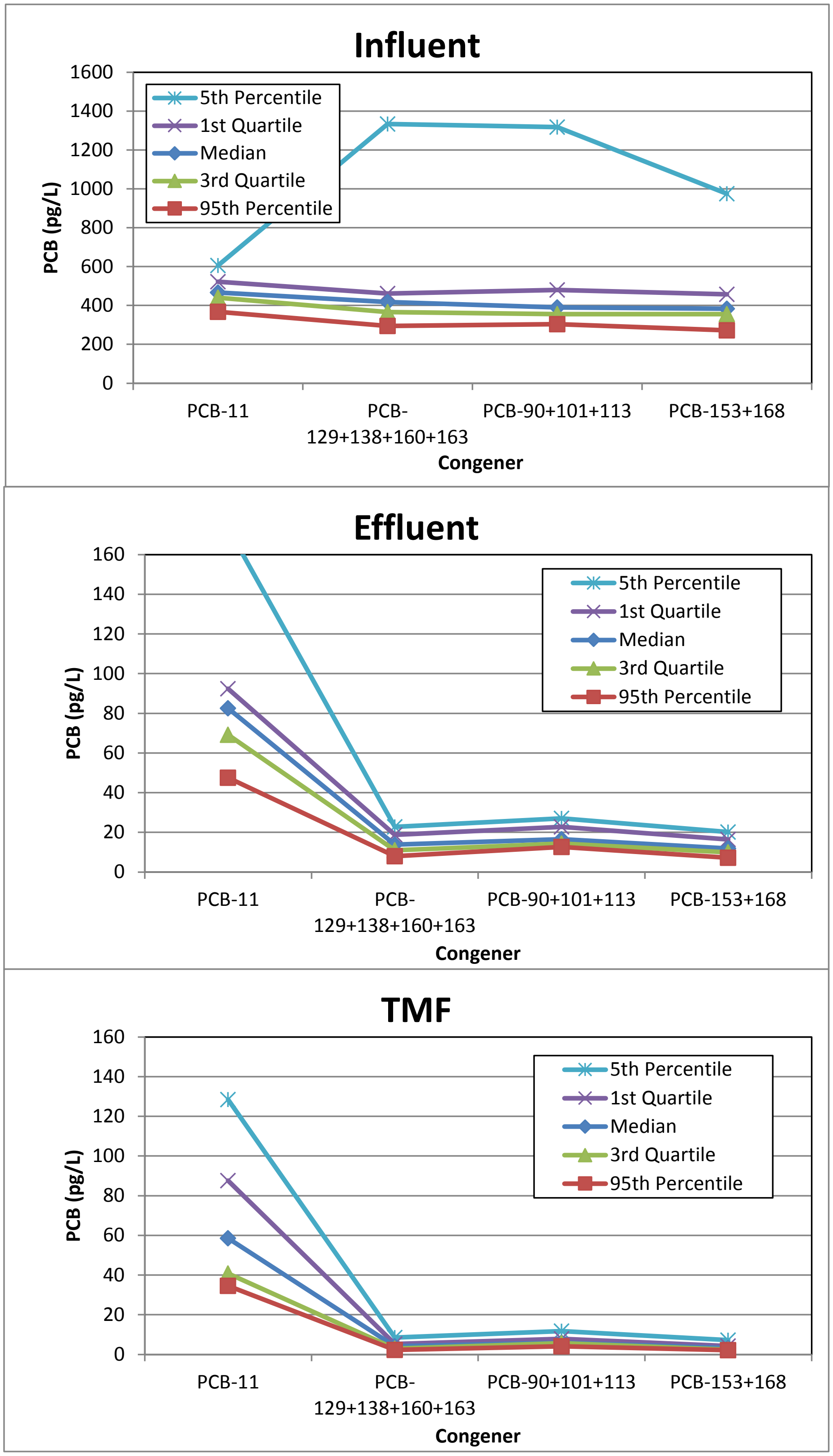

Figure 1. Example of PCB Congener Variability in Influent and Effluent using the Uncorrected Data Set

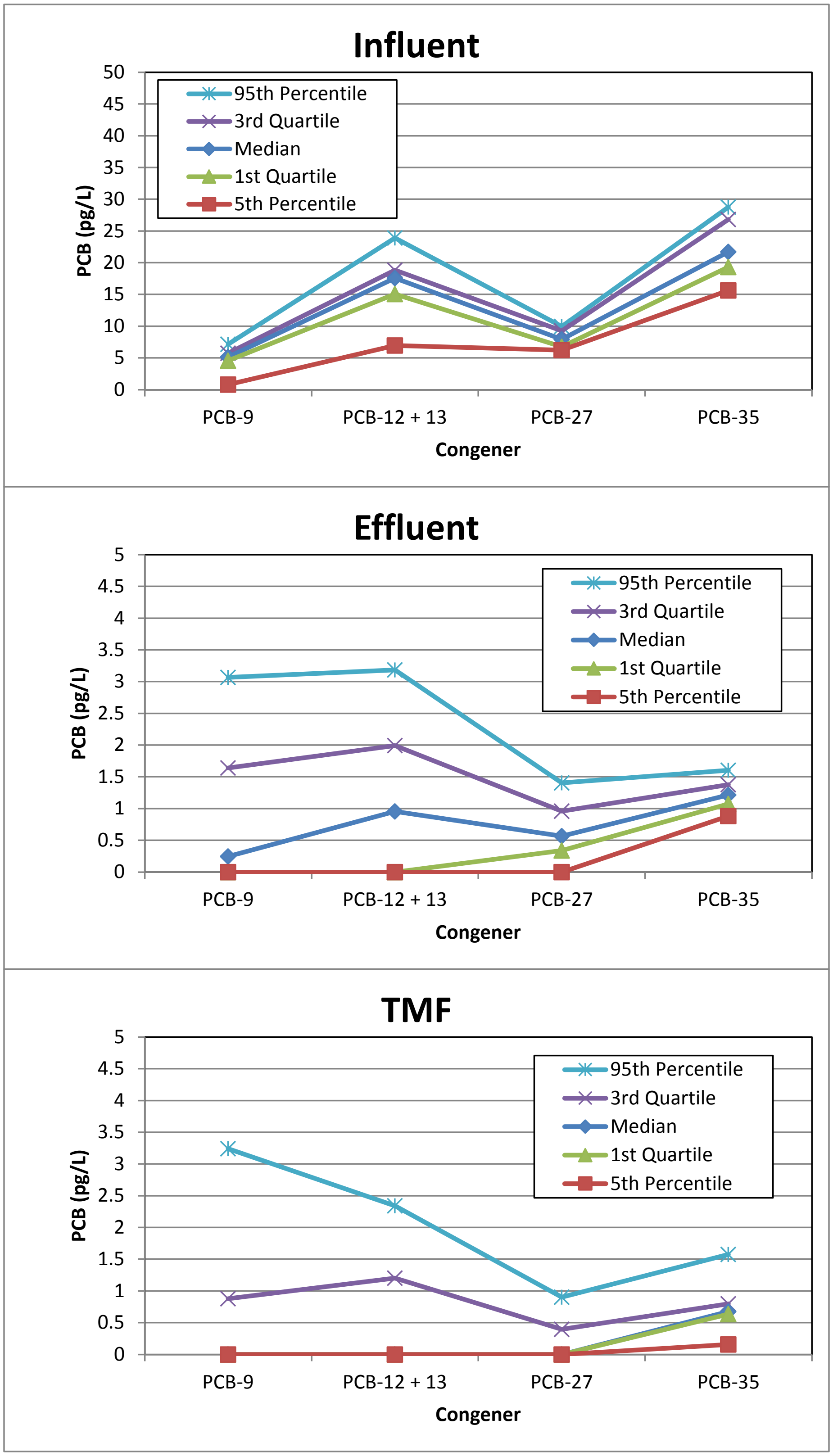

Figure 2. Example of PCB Congener Variability in Influent and Effluent using the Blank Corrected Data Set

2.8 PCB Congener Potential Sources and Relationships to Products

One of the issues to be addressed in the Spokane River watershed is the source of PCBs. The City of Spokane prepared a report titled PCBs in Municipal Products (City of Spokane 2015) to investigate the PCB content of commercial products currently in use. The report includes a range of products and identifies the major PCB congeners present in them. An example from the report is the PCB congeners for crack sealer and hand soap / toothpaste, as shown in Figure 3. If the pattern of PCB congeners from the City matched the pattern shown for crack sealer, then the source is potentially crack sealer. If the pattern of PCB congeners from the City also had concentrations of PCB-95 and PCB-194, then the source is potentially a combination of crack sealer and hand soap / toothpaste. Notice that both products have PCB-18 but some percentage could be from crack sealer and another percentage from hand soap / toothpaste. This approach was expanded to use the products provided in the PCBs in Municipal Products report.

The percentages of PCB congeners in these products were used with the percentages of PCB congeners in the City of Coeur d'Alene monitoring dataset. This is a complex analysis to create a reverse estimate of the mixture of congeners present in the City's influent samples. An initial estimate was completed to investigate what clues it might provide to potential PCB sources.

The results of correlating the products identified in the City of Spokane report and the percent potentially present in the City of Coeur d'Alene's samples are shown in Table 14. Of the 16 commercial products examined for a match with Coeur d'Alene influent congeners in Table 14, only 4 products show a match with 5 percent or more of the influent wastewater: Paints, Asphalt, Hydroseed, and Fire Foam. By far and away, the influent characteristics matched up better with the "Other" product category. By comparison, the effluent characteristics only matched Paints and Deicer more than 1 percent of the time.

Some of the PCB sources in the influent wastewater suggested by this correlation analysis seem plausible, while others are not so easily explainable. Paints seem to generally be a contributing source and given the ubiquitous presence of paints, they seem to be a plausible source. Deicer could potentially be a source and seems to move through the wastewater facility and show presence in the effluent. Hydroseed and firefighting foam are occasionally high and could be occasionally used in high volume somewhere that potentially enters the collection system. Everyday products should as soaps, shampoos, and toothpaste also seem to be a constant source and would be anticipated to be present in the collection system. The results suggest that none of these products are key contributors and other sources of PCBs may need to be investigated.

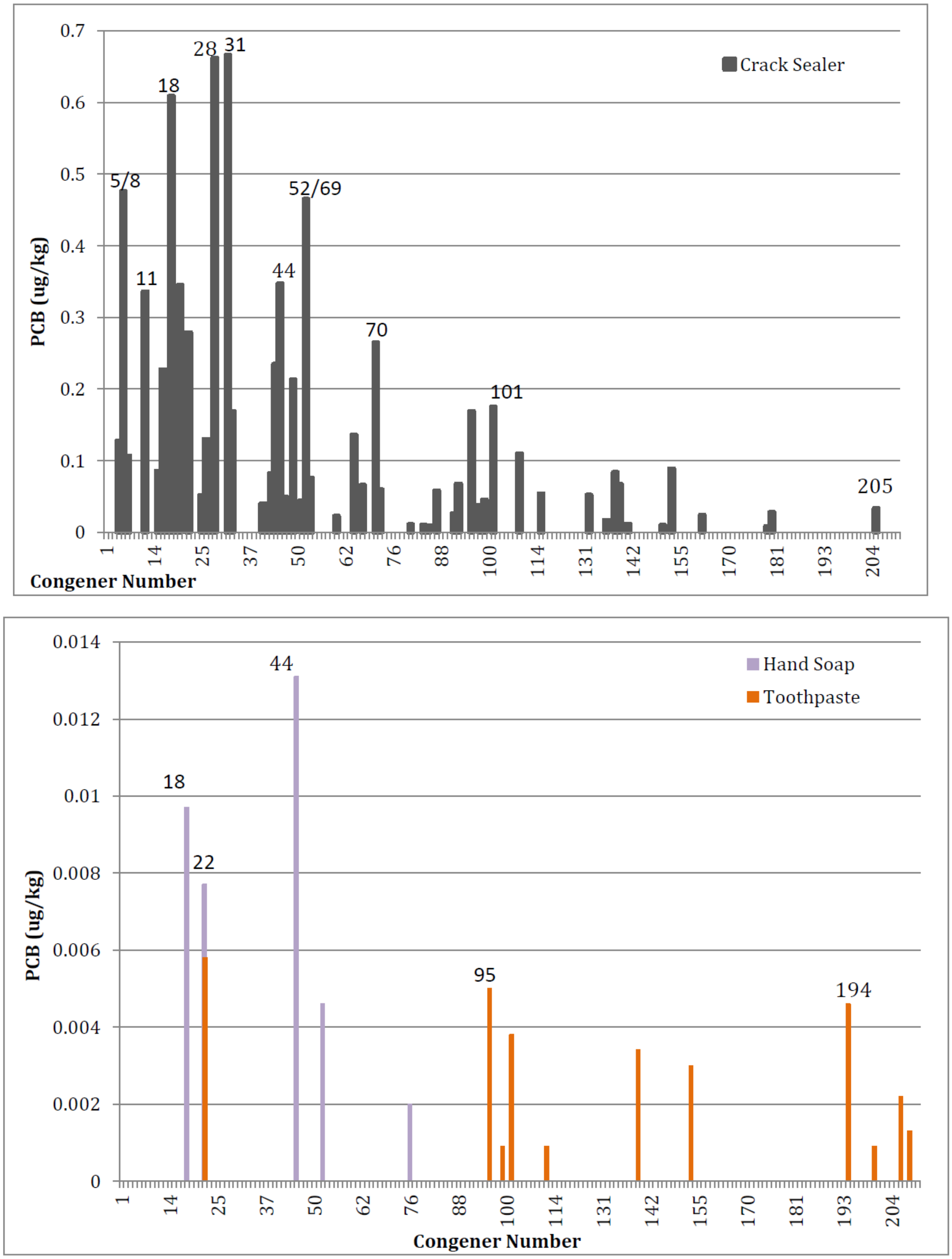

Figure 3. Examples of PCB Congeners from PCBs in Municipal Products Report (City of Spokane 2015)

Table 14. Influent PCBs compared to PCBs Present in Municipal Products

Source	Influent								Effluent				
	Jan Feb '15	**Mar Apr '15**	**May Jun '15**	**Jul Aug '15**	**Sep Oct '15**	**Nov Dec '15**	**Jan Feb '16**	**Mar Apr '16**	**Jan Mar '15**	**Apr Jun '15**	**Jul Sep '15**	**Oct Dec '15**	**Jan Mar '16**
Paints	3%	6%	6%	3%	3%	10%	7%	9%	<1%	<1%	<1%	4%	<1%
ThermoTape	2%	2%	<1%	4%	1%	2%	3%	<1%	<1%	<1%	<1%	1%	<1%
Deicer	1%	2%	2%	2%	1%	1%	2%	2%	<1%	<1%	2%	2%	2%
Antifreeze	1%	<1%	<1%	<1%	<1%	<1%	<1%	<1%	<1%	<1%	<1%	1%	<1%
Pesticide	2%	<1%	2%	<1%	<1%	<1%	<1%	<1%	<1%	<1%	<1%	1%	<1%
Motor Oil	<1%	1%	1%	<1%	<1%	<1%	1%	<1%	<1%	<1%	<1%	1%	<1%
EADA	1%	3%	3%	<1%	<1%	<1%	3%	3%	<1%	<1%	<1%	1%	<1%
Dustgard	<1%	<1%	<1%	<1%	<1%	<1%	<1%	<1%	<1%	<1%	1%	1%	<1%
Asphalt	<1%	2%	<1%	3%	1%	2%	6%	<1%	<1%	<1%	<1%	1%	<1%
Crack Sealer	<1%	<1%	<1%	3%	2%	<1%	<1%	<1%	<1%	<1%	1%	1%	<1%
Hydroseed	5%	6%	<1%	5%	2%	3%	2%	4%	<1%	<1%	<1%	1%	<1%
Pipe Material	<1%	<1%	<1%	<1%	1%	1%	<1%	<1%	<1%	<1%	<1%	1%	<1%
Fire Foam	6%	<1%	5%	<1%	<1%	3%	<1%	2%	<1%	<1%	<1%	1%	<1%
SimpleGreen	1%	3%	2%	4%	1%	2%	2%	<1%	<1%	<1%	<1%	1%	<1%
Soaps Shampo	<1%	1%	1%	1%	<1%	1%	1%	<1%	<1%	<1%	<1%	1%	<1%
Hand Soaps Toothpaste	<1%	<1%	1%	<1%	<1%	2%	<1%	5%	<1%	<1%	<1%	<1%	<1%
Other	78%	74%	74%	74%	88%	72%	72%	75%	99%	99%	97%	81%	98%

2.9 Spokane River PCB Congeners and Fish Tissue

PCBs enter the bodies of fish from water, sediment, and from eating prey that have PCBs in their bodies. PCBs bind especially well with clay-silt sediment, soils and the fat tissue of living creatures. PCBs build up in fish and can reach levels hundreds of thousands of times higher than the levels in water. Larger, older fish will have had more time to accumulate more PCBs in its fat tissue.

A dataset of Spokane River specific fish tissue data that has congener information is available to be able to assess fish tissue values to those in effluents. Several studies over have indicated that elevated concentrations of PCBs in the Spokane River. To help address these concerns, fish have been collected from the Spokane River and analyzed for PCBs. These studies include ones by the U.S. Geological Survey (as part of the National Water-Quality Assessment Program) and the Washington State Department of Ecology (USGS 2001). Ecology has analyzed over 200 fish tissue samples from the Spokane River. Total PCB concentrations greater than 1,000 µg/Kg have been measured in some species (Ecology 2001).

Additional studies are being conducted including the Quality Assurance Project Plan: Spokane and Troutlodge Fish Hatchery PCB Evaluation. This study should provide another indication of the potential connection between effluent and river concentrations along with concentrations of PCBs in sediments and fish tissue in the river. Older fish that have had a greater potential to bioaccumulate PCBs will be studied.

2.9.1 Comparison of Effluent PCB Congeners and Biaccumulative PCBs

PCB Congeners that bioaccumulate in fish tissue are of particular interest because it is those constituents that contribute to the potential human health risk. Controlling fish tissue concentrations is at the foundation of the human health water quality criteria for PCBs. The National Toxics Rule human health criterion for fish tissues is 5.3 µg/kg. Since the composition of the total PCBs in influent wastewater has been measured, as well as the effluent following the advanced treatment process, the congeners removed and those remaining in the effluent can both be characterized. The congeners remaining in the effluent are those that the aquatic organisms are exposed to in the receiving waters.

In a 2001 report, Washington Ecology reported on PCB levels in Spokane River fish (Ecology 2001). Table 15 presents a comparison of the PCB congeners present in Spokane River fish and the congeners present in Coeur d'Alene wastewater. Of the 23 PCB congeners tested for in fish tissue from 1999 samples at Plante Ferry Park, only 9 were congeners that are present in influent wastewater in Coeur d'Alene. Only 3 PCB congeners tested for in fish tissue were present in the blank corrected Coeur d'Alene effluent; PCB-28, PCB-66, and PCB 180.

In a 2012 report, Washington Ecology reported on PCB level in Spokane River fish (Ecology 2012). Table 16 presents a comparison of the PCB congeners from the Ecology studies present in Spokane River fish and the congeners present in Coeur d'Alene wastewater. Fish tissue data on PCBs are commonly reported in units of mass/mass. Water column data on PCBs are commonly reported in units of mass/volume. A translation can be performed using published bioaccumulation factor for PCBs in fish tissue (EPA 4440/5-80-068, October 1980). The water column concentration that resulted in the fish tissue contamination can be estimated using the equation shown below (EPD 2002)

WC= TC/BCF

Where WC = Water column concentration (mg/L)
TC= Fish tissue (mg/kg)
BCF = EPA bioaccumulation Factor (31,200 L/kg)
4.48 X 10-6 mg/L = (0.14 mg/kg) / 31,200 L/kg
WC = 4.5 X 10-3 µg/L

The BCF was used with the fish tissue data from the Spokane to estimate the concentrations for comparison with the wastewater facility concentrations. The results suggest that the effluent concentrations are much lower than the fish concentrations for the higher weight molecular PCBs and similar for some of the lowest weight molecular PCBs. However, some of the assumptions may not be accurate. The results are based on summing the entire fish tissue mass for the three species for the entire reach of river. Also the same BCF was used for all fish types and all congeners which may not be correct. However, the results align with other findings that suggest that PCBs in the effluent may not be the main source of PCBs in fish in the Spokane River.

Table 15. Comparison of PCB Congeners Present in Spokane River Fish Tissue with Coeur d'Alene Influent and Effluent

PCB Congener	Fish Tissue Samples from Plante Ferry Park[a] (River Mile 85) µg/Kg wet weight basis		Coeur d'Alene Wastewater Congeners (2015-2017 Median Concentration) pg/L				
				Effluent			
				Uncorrected		Blank Corrected	
	Rainbow Fillet 485013	Sucker Fillet 485019	Influent	Secondary	TMF	Secondary	TMF
PCB-8	0.89 U	1.5 U	89	8	4		
PCB-18	3.0	1.9	110	11	8		
PCB-28	37	6.5	199	22	12	16	10
PCB-44	27	8.0	273	22	14		
PCB-52	80	7.1	328	26	14		
PCB-66	130	13	169	8	4	8	3
PCB-77	0.89 UJ	1.5 UJ	15	1		1	
PCB-81	0.89 UJ	1.5 U					
PCB-101	48	7.1	390	17	6		
PCB-105	46	4.3	121	5	2	2	1
PCB-114	5.3	1.5 U	9				
PCB-118	70	7.5	318	13	5		
PCB-126	0.78 NJ	1.5 U					
PCB-128	4.4	0.71 J	54	2		1	
PCB-138	4.6 NJ	2.8	418	14	4		
PCB-153	17	2.7	383	12	3		
PCB-156	3.6	1.5	52	2		1	
PCB-169	0.89 UJ	1.5					
PCB-170	4.4	0.65 J	82	2	1	2	
PCB-180	8.9	1.3 J	238	7	2	8	
PCB-187	4.6	0.83 J	165	5	1		
PCB-195	0.85	1.5 U	19				
PCB-206	0.89	1.5 U	39	1			

[a]Ecology 2001

Table 16. Comparison of PCB Congeners Present in Spokane River Fish Tissue

PCB Congener	Fish Tissue Samples from the Spokane River[a]				Estimated Concentration	Coeur d'Alene Wastewater Congeners (2015-2017 Median Concentrations)					Coeur d'Alene Blank Corrected Secondary + TMF / Fish Tissue Estimated Concentration
	ng/g weight basis				pg/L	pg/L					
	Largescale Sucker	Mountain Whitefish	Rainbow Trout, Redband Trout, Steelhead	Total	Conversion BCF 31,200 L/kg	Influent	Effluent				
							Uncorrected		Blank Corrected		
							Secondary + TMF	TMF	Secondary + TMF	TMF	
PCB-4	0.030	0.068	0.137	0.236	7.6	28	5	4	2	2	26%
PCB-6	0.013	0.042	0.117	0.172	5.5	28	3	2	1	1	18%
PCB-8	0.066	0.229	0.503	0.798	25.6	89	8	4			0%
PCB-9	0.007	0.015	0.040	0.062	2.0	5	1	1			0%
PCB-12	0.007	0.031	0.016	0.055	1.8	18	2	1	1		56%
PCB-15	0.022	0.284	0.117	0.424	13.6	51	8	5			0%
PCB-18	0.598	0.693	2.160	3.452	110.6	110	11	8			0%
PCB-28	4.118	4.720	12.268	21.106	676.5	199	22	12	16	10	2%
PCB-44	4.980	2.296	17.772	25.049	802.8	273	22	14			0%
PCB-52	6.230	0.784	17.271	24.285	778.4	328	26	14			0%
PCB-66	8.174	6.893	25.353	40.420	1295.5	169	8	4	8	3	0.6%
PCB-77	2.187	1.417	6.419	10.024	321.3	15	1		1		0.3%
PCB-81	1.682	0.059	5.224	6.964	223.2						0%
PCB-101	10.795	9.373	37.070	57.238	1834.6	390	17	6			0%
PCB-105	8.259	9.305	26.873	44.436	1424.2	121	5	2	2	1	0.1%
PCB-114	2.769	8.051	7.398	18.218	583.9	9					0%
PCB-118	16.978	15.651	44.818	77.448	2482.3	318	13	5			0%
PCB-126	1.822	13.425	12.672	27.919	894.8						0%
PCB-128	3.938	6.563	9.166	19.667	630.4	54	2		1		0.2%
PCB-138	20.416	20.373	50.778	91.567	2934.9	418	14	4			0%
PCB-153	17.141	54.508	54.610	126.259	4046.8	383	12	3			0%
PCB-156	10.200	46.242	40.874	97.316	3119.1	52	2		1		0.03%
PCB-169	1.925	12.040	30.344	44.309	1420.2						0%
PCB-170	9.231	13.891	37.750	60.872	1951.0	82	2	1	2		0.1%
PCB-180	13.883	45.993	52.459	112.335	3600.5	238	7	2	8		0.2%
PCB-187	8.368	31.833	39.968	80.170	2569.5	165	5	1			0%
PCB-195	5.791	21.066	25.377	52.234	1674.2	19					0%
PCB-206	0.608	2.347	2.250	5.205	166.8	39	1				0%

[a]Ecology 2012

2.9.2 Comparison of Effluent PCB Congeners and Toxic Dioxin-like PCBs

Some PCB Congeners are especially toxic to mammals, including humans, and toxicity equivalency factors (TEFs) have been used to estimate the toxicity of the so called dioxin-like congeners. Table 17 presents an analysis of 9 different Aroclors using Method 1668 to determine the content of 12 dioxin-like congeners (Rushneck 2004). Table 17 presents the dioxin-like congener analysis of Aroclors, along with the World Health Organization (WHO) toxicity equivalency factors and identification of some of the products that used these congeners.

The dioxin-like congener content of Arolors is compared with the results of congener analysis of influent and effluent wastewater from Coeur d’Alene in Table 17. The units presented in Table 17 for the Aroclor content (ug/g) and the concentration of Coeur d’Alene wastewater (pg/L) are not comparable, however there is an opportunity identify the presence or absence of the especially toxic dioxin-like congeners in the City’s wastewater. The only one of the 12 dioxin-like congeners present in Coeur d’Alene wastewater in 2015-1016 monitoring is PCB-105. The median concentration of PCB-105 in influent wastewater was 121 pg/L, with no reportable concentration remaining in the blank corrected effluent data. Further, the most toxic of the dioxin-like congeners, based on the World Health Organization toxicity equivalency factors, do not appear to be present in Coeur d’Alene wastewater.

Table 17. Comparison of Dioxin-Like PCB Congeners[1] with Congeners Present in Coeur d'Alene Influent and Effluent[2]

Dioxin-Like PCB Congeners and Aroclor Composition from Rushneck[1] (ug/g; ppm)											Coeur d'Alene Wastewater Congeners (2015-2017 Median Concentration pg/L)				
											Influent	Effluent			
												Uncorrected		Corrected	
PCB Congener	WHO Toxic Equivalency Factor (TEF)	Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Aroclor 1268		Secondary + TMF	TMF	Secondary + TMF	TMF
		Common Uses of Aroclors[3]													
		Capacitors	Hydraulic Fluid	Capacitors	Transformers	Hydraulic Fluid	Transformers	Transformers	Synthetic Resins	Rubbers					
77	0.0001	12.6	2150	40.9	2590	4440	174	33.8	84.6	36.1	15	1		1	
81	0.0001	0.51	111	1.96	156	221	16.4	3.33	4.63	1.35					
105	0.0001	55.9	3030	69.5	4840	17300	33800	434	764	107	121	5	2	2	1
114	0.0005	4.04	248	6.03	443	1320	1930	17.0	46.0	5.86	9				
118	0.0001	88.1	4460	110	6980	24200	78900	5610	1980	101	318	13	5		
123	0.0001	3.33	164	4.72	277	806	1150	5.02	27.8	3.24	22				
126	0.1	0.28	21.0	0.56	33.6	98.0	37.3	2.13	2.28	1.76					
156	0.0005	7.49	90.7	3.72	255	654	8440	4860	946	17.6	52	2		1	
157	0.0005	1.46	22.0	1.03	70.9	171	1870	252	63.8	R 7.92					
167	0.00001	2.52	32.4	1.10	80.7	207	3100	1990	278	4.96	14				
169	0.01	U 0.08	U 0.17	0.13	R 0.11	0.21	0.81	U 0.82	0.40	U 0.32					
189	0.0001	1.17	4.36	0.12	4.53	11.0	246	1290	451	4.4	3				
Aroclor total TEQ[4]		0.05	3.3	0.09	5.2	15	21	3.5	1.1	0.21					

[1] PCB congener composition of Aroclors and TEF from Rushneck 2004.

Notes from Rushneck, 2004:

U = Not Detected at given detection limit

R = Peak deleted, but did not meet identification criteria

If congener qualified with U or R, concentration is estimated maximum, but Aroclor TEQs are minimum values (i.e. U and R values were included in TEQ calculations)

[2] Coeur d'Alene influent and effluent PCB congener data form 2015 – 2016 monitoring.

[3] Oregon DEQ Fact Sheet: Sources of Polychlorinated Biphenyls

[4]Rushneck the dioxin equivalent concentration (TEQ) by multiplying the concentration of each dioxin-like congener by its 2,3,7,8-TCDD TEF from WHO and adding the products to yield the Aroclor TEQ.

2.10 PCBs Next Steps

While the current sample size is statistically insignificant, it does provide some insights for next steps in the source tracing. PCB congeners with the highest influent concentrations could be pursued further. However, many of these show significant reductions in the wastewater treatment process and little remains present in the effluent. Pursuing these may not be very beneficial to reducing the total effluent PCB discharge to the Spokane River. A relatively easily identifiable source, such as paints could be pursued. Paints are commonly used throughout the City for many purposes and on variety of surfaces. However, there may not be many, if any, best practices available to reduce this source. Further, the findings suggest that there are many other sources that may be potentially much greater contributors. The PCB congeners that are persistent in the effluent may be the best PCB congeners to pursue for source tracing. Many of these are lower molecular weight congeners that may be best eliminated at the source.

However, the challenge is some of these may be the result of higher molecular weight congeners breaking down in the environment, or in the wastewater facility, rather than from a source in the collection system. This may necessitate some sampling at various steps in the wastewater facility processes to understand the possible breakdown and transformation of PCBs at the wastewater facility.

2.10.1 PCB Congeners and Complex Analysis

PCBs are subject to microbial dechlorination in the sewer collection system and wastewater treatment process. The literature includes studies of wastewater treatment plant influents and effluents where PCBs were analyzed to look for evidence that these compounds underwent dechlorination. Tools used for analysis include the Positive Matrix Factorization (PMF) (Soonthornnonda et.al. 2011) and advanced chemical fingerprinting (ESTCP 2012). PMF is an advanced source apportionment tool that has been used to identify PCB sources in water, sediment, and air. PCB fingerprinting refers to a method of identifying types of sources by comparing PCB congener or homologue patterns in samples to those of Aroclors or congeners in products with inadvertently produced PCBs. The EPA (2014) has published a PMF User’s Guide. An overview of the model includes: “Receptor models are mathematical approaches for quantifying the contribution of sources to samples based on the composition or fingerprints of the sources” (EPA 2014). The PCB and TCDD Toxics Management Plan included a recommendation for future investigation of congener analysis and fingerprinting that may warrant further consideration.

3 TMP: TCDD Data Analysis

The City of Coeur d’Alene is authorized by the U.S. Environmental Protection Agency (EPA) to discharge treated water from the City’s wastewater facility to the Spokane River. Requirements of this authorization are spelled out in the City’s National Pollutant Discharge Elimination System (NPDES) Permit No. ID0022853. The permit was recently renewed and is effective from December 1, 2014 through November 30, 2019. The purpose of this section is to summarize the analysis of TCDD data that are required to be collected by the permit. This includes examining changes in concentrations after passing through the wastewater facility.

3.1 Coeur d'Alene TCDD Monitoring

One component of the permit is to conduct monitoring of the effluent (treated water prior to discharge) and the surface water (Spokane River). The monitoring requirements include sampling and testing for tetrachlorodibenzo-p-dioxin (TCDD). As listed in the permit, the TCDD monitoring requirements are shown in Table 18.

Table 18. NPDES Permit PCB Monitoring Requirements

Parameter	Units	Effluent Limits			Monitoring Requirements		
		Average Monthly Limit	Average Weekly Limit	Max. Daily Limit	Location	Frequency	Sample Type
2,3,7,8 tetrachloro-dibenzop-dioxin (TCDD)	pg/L	Report	--	Report	Effluent	1/quarter	24-Hr. Comp.
Source: NPDES Permit ID0022853 Table 1: Final Effluent Limits and Monitoring Requirements for Outfall 001							

The dates, locations and results of the City TCDD samples are summarized in Table 19. Sampling by the City included influent and effluent, with the effluent being a blend of the stream from secondary treatment and tertiary membrane filter.

Table 19. TCDD Monitoring Results

Date	2,3,7,8 TCDD (pg/L)	
	Influent	Effluent
January 6, 2015	< 0.191	< 0.212
May 4, 2015	< 0.191	< 0.212
July 8, 2015	< 0.515	< 0.513
November 3, 2015	< 0.516	< 0.503
January 5, 2016	< 0.500	< 0.502
May 3, 2016	< 0.499	< 0.500
July 12, 2016	< 0.504	< 0.502
November 1, 2016	< 0.510	< 0.511
January 10, 2017	< 0.510	< 0.509
May 2, 2017	< 0.858	< 0.507
July 18, 2017	< 0.510	< 0.509

3.2 Characteristics of TCDD

TCDD was not mass produced and has no commercial applications. TCDD is primarily found as a contaminant or byproduct. It occurred as a contaminant in some herbicides, especially ones used in the 1960s and 1970s to control weeds. It also can be formed during the chlorine bleaching process used by pulp and paper mills, and as a by-product from the manufacture of certain chlorinated organic chemicals. TCDD can also occur as a result of metal-processing, the combustion of fossil fuels (including motor vehicles) and wood, and during incineration processes. TCDD has a high persistence and toxicity in the environment.

3.3 TCDD Methods

The following is discussion of various laboratory analysis methods potentially useful for evaluating TCDD.

Method 613 covers the determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). This is a gas chromatographic/mass spectrometer (GC/MS) method applicable to the determination of 2,3,7,8-TCDD in municipal and industrial discharges as provided under 40 CFR Part 136.1. Method 625 may be used to screen samples for 2,3,7,8-TCDD. The method reporting limits for TCDD in water is 0.002 ug/L.

Method 1613 is for determination of tetra- through octa-chlorinated dibenzo-p-dioxins (CDDs) and dibenzofurans (CDFs) in water, soil, sediment, sludge, tissue, and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The method is for use in EPA's data gathering and monitoring programs associated with the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Liability Act, and the Safe Drinking Water Act. This method is "performance-based". The analyst is permitted to modify the method to overcome interferences or lower the cost of measurements, provided that all performance criteria in this method are met. The method reporting limits for TCDD in water is 5.0 pg/L.

Method 8280 is appropriate for the detection and quantitative measurement of 2,3,7,8-tetrachlorinated dibenzo-p-dioxin (2,3,7,8-TCDD), 2,3,7,8-tetrachlorinated dibenzofuran (2,3,7,8- TCDF), and the 2,3,7,8-substituted penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in water (at part-per-trillion concentrations). The analytical method requires the use of high resolution gas chromatography and low resolution mass spectrometry (HRGC/LRMS).

Method 8290 provides procedures for the detection and quantitative measurement of polychlorinated dibenzo-p-dioxins (tetra- through octachlorinated homologues; PCDDs), and polychlorinated dibenzofurans (tetra- through octachlorinated homologues; PCDFs) in a variety of environmental matrices and at part-per-trillion (ppt) to part-per-quadrillion (ppq) concentrations.

4 References

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