Inland Empire Paper Company

Evaluation of Polychlorinated Biphenyl Reductions as a Basis for the Determination of IEP's Highest Attainable Condition

David Demers

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Terms and Abbreviations

Terms-

Blank censoring- The act of removing weak signals in a gas chromatography test that cannot be differentiated from a stated factor of levels measured in the Method Blank

Condition- Operating the mill under predetermined values for %Deink contribution and recycle mixture

Congener- The compositional distinction in a grouping of similar compounds; ie: PCBs have 209 unique congeners

Deink- Pulp derived from recycled materials

Event- Mill operations at a set Condition over a 48 hour window in order to collect samples and evaluate impact on the WWTS

Homolog- Congeners grouped by the number of chlorine atoms in the compound

%Deink contribution- The fraction or percentage of the pulp used in paper manufacturing sourced from recycled materials

Recycle mixture- The stated ratio of ONP to SOP used to produce Deink pulp

Abbreviations

IEP- Inland Empire Paper Company

ONP- old newsprint

PCBs- polychlorinated biphenyls

PTFE- polytetrafluoroethylene

QAPP- Quality Assurance Project Plan

SOP- sorted office paper

UF membrane- tertiary ultrafiltration membrane process

WWTS- wastewater treatment system

1.0 Introduction

Inland Empire Paper (IEP) completed the initial phase of a study of polychlorinated biphenyls (PCBs) treated by its wastewater treatment system (WWTS) in the spring of 2020. This study was founded upon IEP's original PCB Source Identification Study which concluded that recycled paper is the major source of PCBs to IEP's WWTS. IEP takes pride in the reuse of recycled material in its paper manufacturing. A significant degree of PCBs are removed from mill waste streams during wastewater treatment though a dedicated effort to quantify the overall degree of removal that can be expected and the installation of a new tertiary ultrafiltration process. The addition of this tertiary system makes IEP's WWTS the most advanced water quality treatment systems in the pulp and paper industry. This study provides a dataset to establish predictable PCB reductions across the water quality treatment system under typical operational conditions. The PCB reductions achievable under the system constitute the highest attainable condition, or HAC for PCB concentrations across IEP's WWTS. The design and objectives for this study were defined by a PCB Quality Assurance Project Plan (QAPP) proposal written in February of that year which is included in Appendix A for reference. The study objectives are:

1. Quantify the magnitude of PCBs fed into IEP's WWTS as a function of recycled (Deink) furnish.
2. Evaluate the efficacy of IEP's WWTS in removing PCBs from the final discharge stream.
3. Assess the impact of different levels of blank-censoring on the PCB samples.

IEP paper manufacturing is based on pulp from virgin wood fiber derived from wood chip residuals supplied by local sawmills and from old newsprint (ONP) and sorted office paper (SOP), two streams of recycled content which gets detrashed and pulped onsite to produce IEP's Deink supply. IEP's state-of-the-art paper machine can manufacture paper utilizing Deink contributions from 0 to 60% Deink contribution of the total pulp supply. With the expectation that ONP and SOP have distinct PCB fingerprints due to any number of characteristics unique to each source (which can include variables like trash content and different ink usage), the QAPP outlined the two prominent control variables for this study to be the percentage of Deink supplied for paper manufacturing as well as the percentage of SOP used for the recycled mixture in the Deink supply.

By altering these control variables, six unique operational Conditions were defined for the study as presented in Figure 1. The first objective of the study altered the percentage of Deink contribution to the pulp supply in Conditions A through D where Condition A contains 0% Deink contribution, Condition B contains 20% (which is IEP's current utilization for standard newsprint manufacturing), Condition C contains 40%, and Condition D contains 60% with a Deink mixture of 50/50 ONP to SOP. The other two Conditions, E and F, maintain 20% Deink contribution but alter the SOP fraction with Condition E using 100% ONP and no SOP and Condition F using no ONP and 100% SOP to further assess the influence of the sources for the Deink mixture on PCB concentrations in the feed stream at the head of the WWTS.

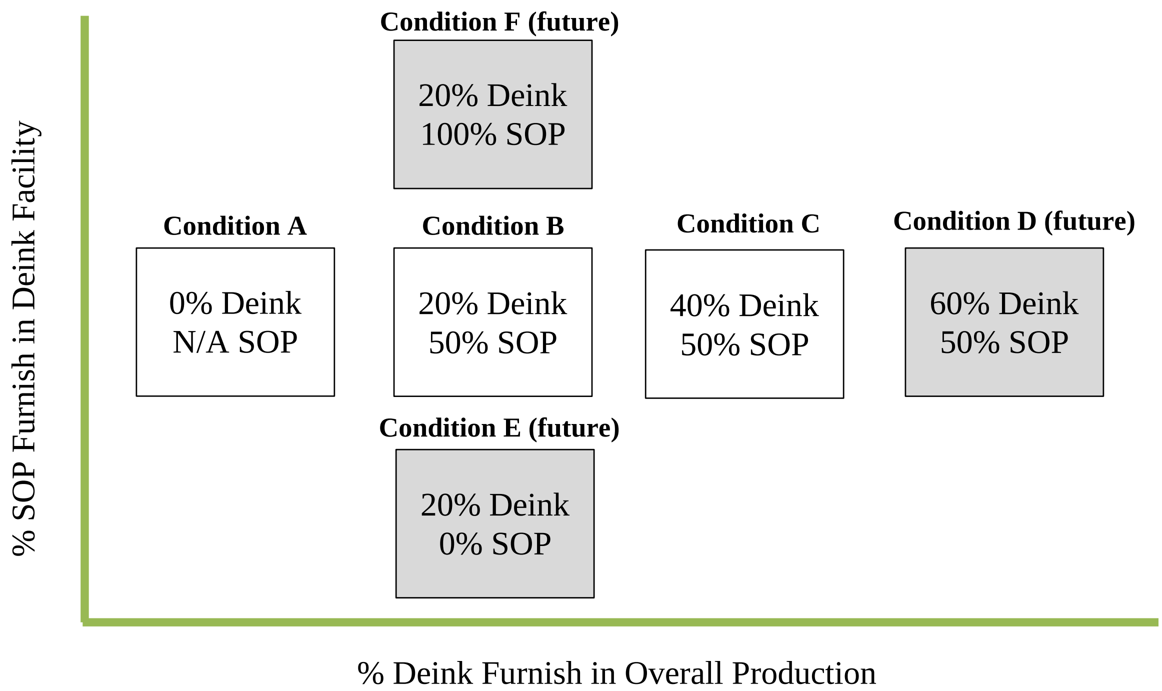

Figure 1- Condition Diagram- The six study Conditions as outlined by the QAPP.

This report relays the findings of Phase 1, Conditions A, B, and C, as presented in the QAPP iterative approach that suggests Phase 1 data to be compiled and evaluated before continuing with subsequent phases of study. The conclusions reached from this initial input will help inform and determine whether any alterations to either the design or implementation of the study are warranted and whether proceeding with Phase 2, including Conditions D, E, and F and any alterations, continue to be considered necessary and beneficial.

2.0 Method

An in-depth explanation of the design of this study is provided in the QAPP and can be referenced in Appendix A. In brief, the mill would operate under the specified parameters of %Deink contribution and recycled mixture (%SOP) unique to each Condition for a period of 48 hours. For identification, this will be considered a singular Event. Twenty four hours into each Event, composite sampling would be initiated at the head of the WWTS to collect the Pump House samples. Once initiated, sampling would continue over a 24-hour period. After 48 hours into the Event, composite sampling would be initiated at two additional locations and similarly composited over a 24-hour period. The first, Secondary Effluent sample is collected from the outfall of the secondary clarifier. A tertiary ultrafiltration membrane process (UF membrane) was installed and commissioned in January of 2020. While still considered to be in the start-up and commissioning phase, the UF membrane process was fully operational throughout the study, treating 100% of WWTS effluent. The permeate stream off the UF membrane process is the source for the Tertiary Effluent samples. While the Secondary Effluent samples represent the final outfall of IEP's WWTS at the time the study was conducted, there was significant interest in quantifying the advanced capability in PCB reductions that will be achieved with the inclusion of the UF membranes. The additional delay in starting the composite sampling for these latter two samples compensates for residence time across the WWTS. A layout of IEP's WWTS is shown in Figure 2.

Each Condition was duplicated by operating two distinct and separate Events. When possible, these Events were staggered and not run consecutively. Each Event yielded the three composite samples which are then labelled by identifying first the Condition, then the Event, followed by the sample type. For instance, A.2 Tertiary Effluent signifies that this is the sample composite collected from the UF membrane permeate stream during the second Event of Condition A (which utilized 0% Deink.) The composite samplers use collection vessels which contained PTFE liners that were changed out at the conclusion of each Event to prevent cross-contamination. Each sample was transferred from the collection vessels into new, clean 1-liter amber glass jars using the EPA prescribed clean hands/dirty hands procedure. As outlined in the QAPP, certain samples were selected for quality control purposes to have their measurements duplicated. This process entailed filling two separate 1-liter jars from the same original composite sample and having each jar analyzed individually. For data presentation, the results of both jars are averaged to better represent the specific sample in question. The PCB analysis for every sample was performed by SGS Axys Analytical Services, Ltd in Sidney, British Colombia.

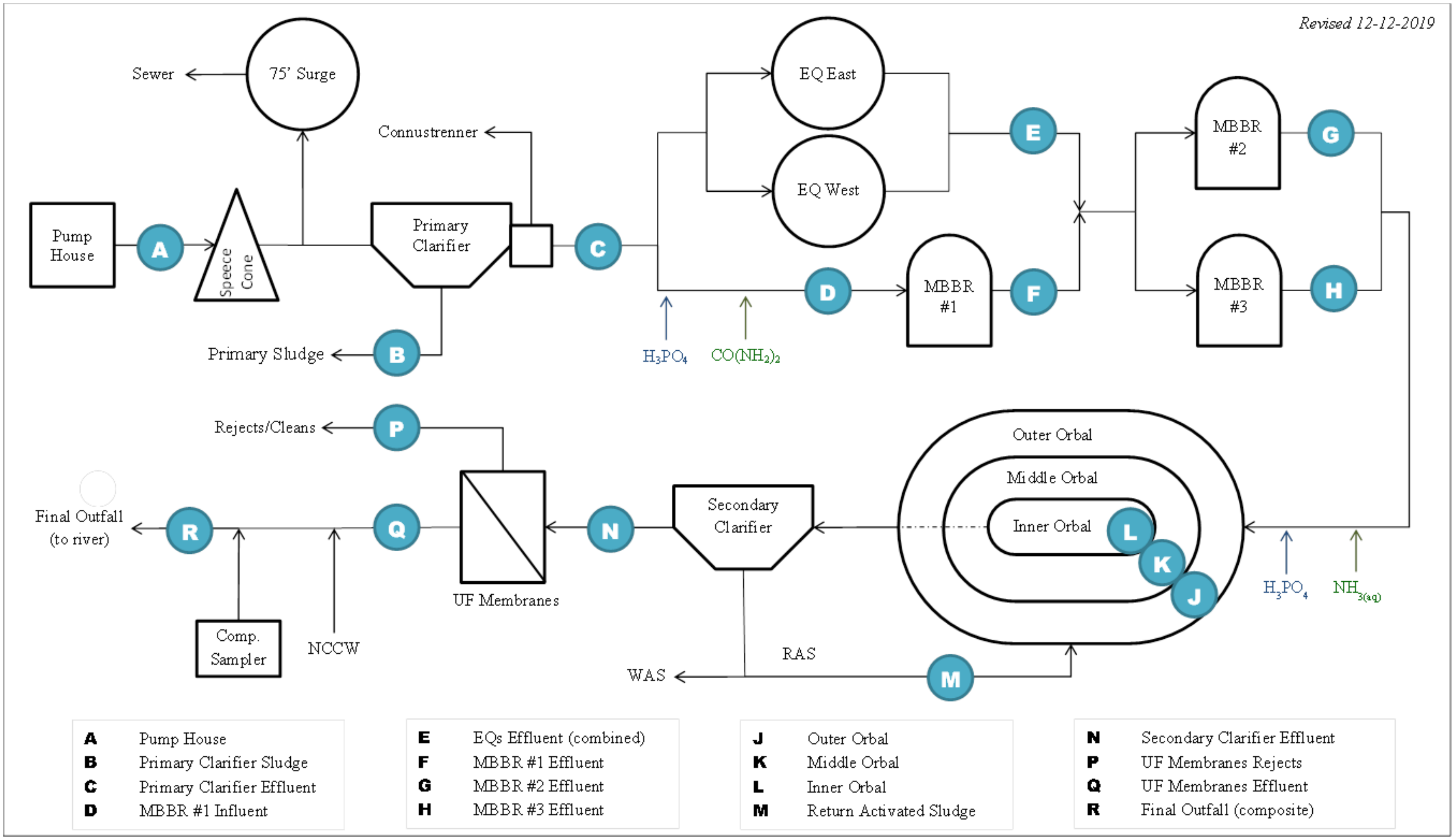

Figure 2- IEP's WWTS with Sampling Locations- Samples for this study were collected at locations A, N, and Q

3.0 Results and Discussion

The data are presented in their entirety in the Appendices. Appendix B groups the data results by homolog in a series of Results Tables with Appendix B.1 displaying the homolog totals that do not incorporate any blank censoring. Appendix B.2 through B.4 display the Results Tables reflecting totals after the application of 3x blank censoring, after 7x blank censoring, and after 10x blank censoring in that order. Appendix C lists the raw data for all samples by individual congener with homolog and overall totals at the end. This data is not blank censored, but includes the blank results used for censoring determinations. Appendix D presents the individual sample results by homolog in a graphical pie depiction listing both the total and percentage of the whole that each homolog represents. The Appendix E charts continue with the pie graphs but shift the focus towards blank correction impacts on each sample.

Condition A					Condition B				
0% De-Ink N/A SOP					20% De-Ink 50% SOP				
Event	Pump House	Secondary Effluent	Tertiary Effluent	Date of Event	Event	Pump House	Secondary Effluent	Tertiary Effluent	Date of Event
A.1	39,000	2,398	1,384	27-Apr	B.1	220,000	1,584	1,281	23-Mar
A.2	30,000	2,118	1,777	4-May	B.2	3,975,000	3,201	1,548	6-Apr

Condition C				
40% De-Ink 50% SOP				
Event	Pump House	Secondary Effluent	Tertiary Effluent	Date of Event
C.1	818,000	1,757	1,076	30-Mar
C.2	2,029,000	2,994	1,793	20-Apr

Figure 3- Results Matrix for Total PCBs- The numbers in the chart represent the sum of all 209 PCB congeners measured in each sample and stated in pg/L as determined by Method 1668C.

Figure 3 presents the total PCB concentrations found in each sample of each Event along with the date in 2020 that each Event commenced. As nearly one-quarter of all mill waste streams sent to the WWTS are returned to the mill for reuse after primary treatment, the subsequent recirculation of PCBs initially introduced through the Deink process cannot be entirely voided leading to the residual concentrations seen in the Pump House samples under Conditions A.1 and A.2. There remains significant difference, though, in those Conditions not involving recycled content as opposed to those that do when looking at PCB concentrations at the head of the WWTS. The very lowest PCB concentrations in Pump House samples for any Event under either Conditions B or C remain more than five times higher than concentrations measured in the two Events for Condition A.

The Pump House samples under Conditions B and C display a wide variability with respect to the total PCBs measured. The significant difference in total PCBs at the head of the WWTS even between two separate Events under the same Condition suggests that the first objective of the study may not be attainable in a practical way, at least with regard to proving overall PCBs as a direct function of %Deink contribution. Though further Events carried out under each Condition should gradually clarify this relationship (as an infinite number of Events per Condition can be expected to generate a bell curve of total PCB concentrations in Pump House samples), proving this relationship is a lesser priority of this study and likely would require more Events than scope and resources permit. The greater point is that this high variability suggests that resulting PCBs in Pump House samples are more dependent upon the composition of the recycled content being used in the Deink supply and less dependent on the increase of the %Deink contribution, though this is still likely a minor factor.

0% De-ink		mono	di	tri	tetra-deca	Total
A.1	PH	257	6734	15304	17046	39,340
A.1	2^o Effl	31	437	987	943	2,398
A.1	3^o Effl	53	389	568	375	1,384
Pump House --> 3^o Effluent		**79.49%**	**94.23%**	**96.29%**	**97.80%**	**96.48%**
A.2	PH	229	4618	9495	15701	30,043
A.2	2^o Effl	33	376	855	854	2,118
A.2	3^o Effl	54	355	590	778	1,777
Pump House --> 3^o Effluent		**76.59%**	**92.31%**	**93.78%**	**95.04%**	**94.10%**

20% De-ink, 50% SOP		mono	di	tri	tetra-deca	Total
B.1.	PH	1452	34071	87634	96919	220,076
B.1.	2^o Effl	31	454	672	427	1,584
B.1.	3^o Effl	81	424	555	220	1,281
Pump House --> 3^o Effluent		**94.40%**	**98.75%**	**99.37%**	**99.77%**	**99.42%**
B.2.	PH	7749	414810	1994795	1557291	3,974,644
B.2.	2^o Effl	40	744	1463	954	3,201
B.2.	3^o Effl	86	458	624	380	1,548
Pump House --> 3^o Effluent		**98.89%**	**99.89%**	**99.97%**	**99.98%**	**99.96%**

40% De-ink, 50% SOP		mono	di	tri	tetra-deca	Total
C.1.	PH	4724	98084	340729	374112	817,649
C.1.	2^o Effl	36	478	737	506	1,757
C.1.	3^o Effl	44	397	426	209	1,076
Pump House --> 3^o Effluent		**99.07%**	**99.59%**	**99.88%**	**99.94%**	**99.87%**
C.2.	PH	6493	226260	886452	909635	2,028,840
C.2.	2^o Effl	45	543	1263	1142	2,994
C.2.	3^o Effl	77	606	674	437	1,793
Pump House --> 3^o Effluent		**98.82%**	**99.73%**	**99.92%**	**99.95%**	**99.91%**

Figure 4- Abbreviated Results Table without Blank Censoring

From the Pump House to the secondary clarifier's outfall stream, PCB removals exceeded 99% in every Event with Deink. This is seen in blue in the rightmost column in Figure 4. Even the two Events of Condition A that were carrying residual recirculating PCBs due to water reuse without any direct PCB introduction due to Deink pulp exhibited a minimum 94% reduction. This minimum percentage of reduction occurred under Condition A.2 (0% Deink) where the lower mono-, di-, and tri-chloro biphenyls collectively achieved 93% reduction. This may be important in HAC determinations considering that theoretically the longer operations without Deink are conducted, the higher likelihood that PCB values in the effluent would gradually be decreased by dilution and removal over time. Under those conditions, lower homologs may persist in the system longer than the heavier homologs due to their being more soluble. If so, there is potential that the minimum reduction efficiency may be lower than reported under Condition A.2..

Remaining PCB concentrations in the Secondary Effluent samples that did not settle out in primary treatment or get taken up biologically in secondary treatment, ranged from 1,600 to 3,200 pg/L, a significant reduction as Pump House samples measured as high as 3,975,000 pg/L in Event B.2. Considering that this effluent then passes through the UF membrane system and all residual total suspended solids are filtered out of the stream, total PCBs are further reduced to between 1,000 and 1,800 pg/L with residual concentrations consisting in greater measure of the lower homologs of mono-, di-, and trichloro biphenyls.

		Homologue	
		mono-tri	tetra-deca
A.1	PH	56.7%	43.3%
A.1	SE	60.7%	39.3%
A.1	TE	72.9%	27.1%
A.2	PH	47.7%	52.3%
A.2	SE	59.7%	40.3%
A.2	TE	56.2%	43.8%
B.1	PH	56.0%	44.0%
B.1	SE	73.1%	26.9%
B.1	TE	82.8%	17.2%
B.2	PH	60.8%	39.2%
B.2	SE	70.2%	29.8%
B.2	TE	75.4%	24.6%
C.1	PH	54.2%	45.8%
C.1	SE	71.2%	28.8%
C.1	TE	80.5%	19.5%
C.2	PH	55.2%	44.8%
C.2	SE	61.8%	38.2%
C.2	TE	75.6%	24.4%

Figure 5- Homolog Breakdown in Samples

In every Event, the fraction of total PCBs consisting of mono-, di-, and trichloro biphenyls was greater in the Secondary and Tertiary Effluent samples than the fraction that these homologs comprised in the Pump House sample for that Event. This is displayed in Figure 5. On average, 55.1% of the composition of Pump House samples consisted of these lower homologs, whereas in the Secondary Effluent samples this average fraction grew to 66.1% further reaching 73.9% in Tertiary Effluent samples. The heavier homologs appear to be either more particulate in nature or more likely to get bound up in particulate matter rather than pass easily through the WWTS as strictly soluble matter would behave. For example, the total PCB concentrations in the Condition B.1 Pump House sample was 56.0% mono-, di-, and trichloro biphenyls and only 44.0% of tetrachloro on up. By the Tertiary Effluent sample for Condition B.1, 82.8% of the PCBs remaining after treatment by the wastewater system in the sample were the lower homologs and only 17.2% consisted of tetrachloro on up. Before considering any impact of blank censoring, IEP's WWTS has demonstrated a proven capacity not only to reduce PCB concentrations fed at the head of the process by a significant margin, but also naturally remove those heavier homologs suspected of being the more persistent, bioaccumulative and toxic.

SGS Axys analyzes a reference matrix Method Blank alongside of each batch of samples received and includes the blank data results with the batch. To differentiate between a clear signal for an individual PCB congener from background noise, a comparison will typically be made between the sample and the blank as either a blank censor or a blank correction. With a blank correction a stated factor will be multiplied against the measurement of a specific congener determined in the blank and the resulting product will be subtracted from the sample results for that congener. This is applied to every individual congener in the sample. A blank censor is more passive in that the congener measurement in the sample is compared against the product of factor times congener presence in the blank. If the congener in the sample is greater than that in the product, that congener is determined to present a clear signal and is not adjusted in any way. If the converse is true, the congener in the sample is determined to be indifferentiable from noise in the blank and is ‘censored’, or excluded, from the finalized data results.

Blank censoring was found to have a significant impact upon PCB concentrations in both the Secondary and Tertiary Effluent samples. This is not the case for the Pump House samples as PCB concentrations are in sufficient strength, even at the levels seen in Condition A, to present a clear signal for every congener determined to be present in the sample. For these Pump House samples, even a 10x blank censoring application had effectively no impact upon the PCB concentrations. In Tertiary Effluent samples, however, 3x blank censoring created an average reduction in accepted congener signals by 13% across the samples, 7x increased that reduction to 35%, and 10x blank censoring resulted in an average reduction in accepted congener signals by 52% across the samples. Put another way, the residual PCB concentrations in Tertiary Effluent samples, as previously mentioned, ranged from 1,000 to1,800 pg/L before considering blank censoring. Applying censoring to the data to qualify stronger signals causes a reduction the range of total PCBs to between 460 and 910 at a factor of 10x for those same results. More significantly, blank censoring displayed a disproportionate impact across the homolog totals with heavier homologs being censored more aggressively. Tetrachloro through decachloro biphenyls were reduced by at least 92.4% (and as much as 99.6%) when applying 10x blank censoring to Tertiary Effluent samples. After physical treatment across IEP’s holistic WWTS and after filtering weak signals out of the data results with 10x blank correction, Tertiary Effluent PCB concentrations predominantly consist of residual mono-, di-, and trichloro biphenyls making up between 94.0 to 99.7% of the total residual PCB concentrations measured in each sample.

The second Event of Condition B is an illustrative example. Figure 6 shows the progression of PCB totals and composition as the water is treated across IEP’s WWTS. Condition B.2 generated the largest PCB concentrations at the head of the WWTS of any other Event with a total of nearly 3,975,000 pg/L, of which 1,557,000 pg/L consisted of tetrachloro through decachloro biphenyls. The WWTS reduces these total PCB concentrations to 3,200 pg/L in the Secondary Effluent sample and by half yet again to 1,550 pg/L in the Tertiary Effluent, with 380 pg/L of tetrachloro through decachloro biphenyls remaining. The application of blank censoring to the data results continues to alter the picture as seen with Figure 7. Applying a minimum 3x blank censoring to the data further reduces the total PCB concentration to 1,188 pg/L with 200 pg/L of tetrachloro through decachloro biphenyls cutting the heavier homologs nearly in half even with this minimal factor. By the 10x factor, the total PCB concentrations have been reduced to 462 pg/L with only 22 pg/L of tetrachloro through decachloro biphenyls remaining. With the application of 10x blank censoring, the total PCB concentration reduction across the WWTS which was 99.961% prior is increased to a reduction of 99.988% with the heavier homologs (tetrachloro on up) increasing from 99.976% to 99.999% reduction.

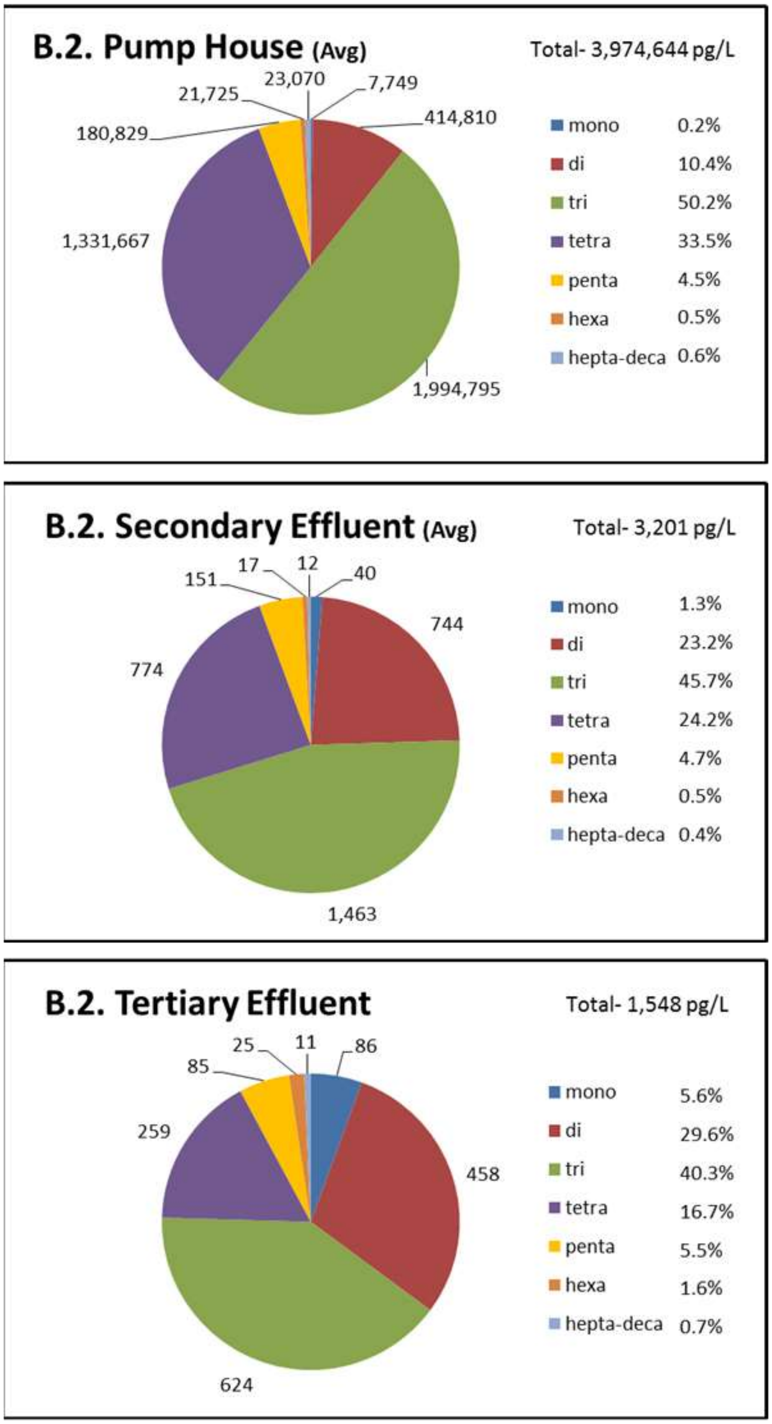

Figure 6- WWTS Impact on Condition B.2

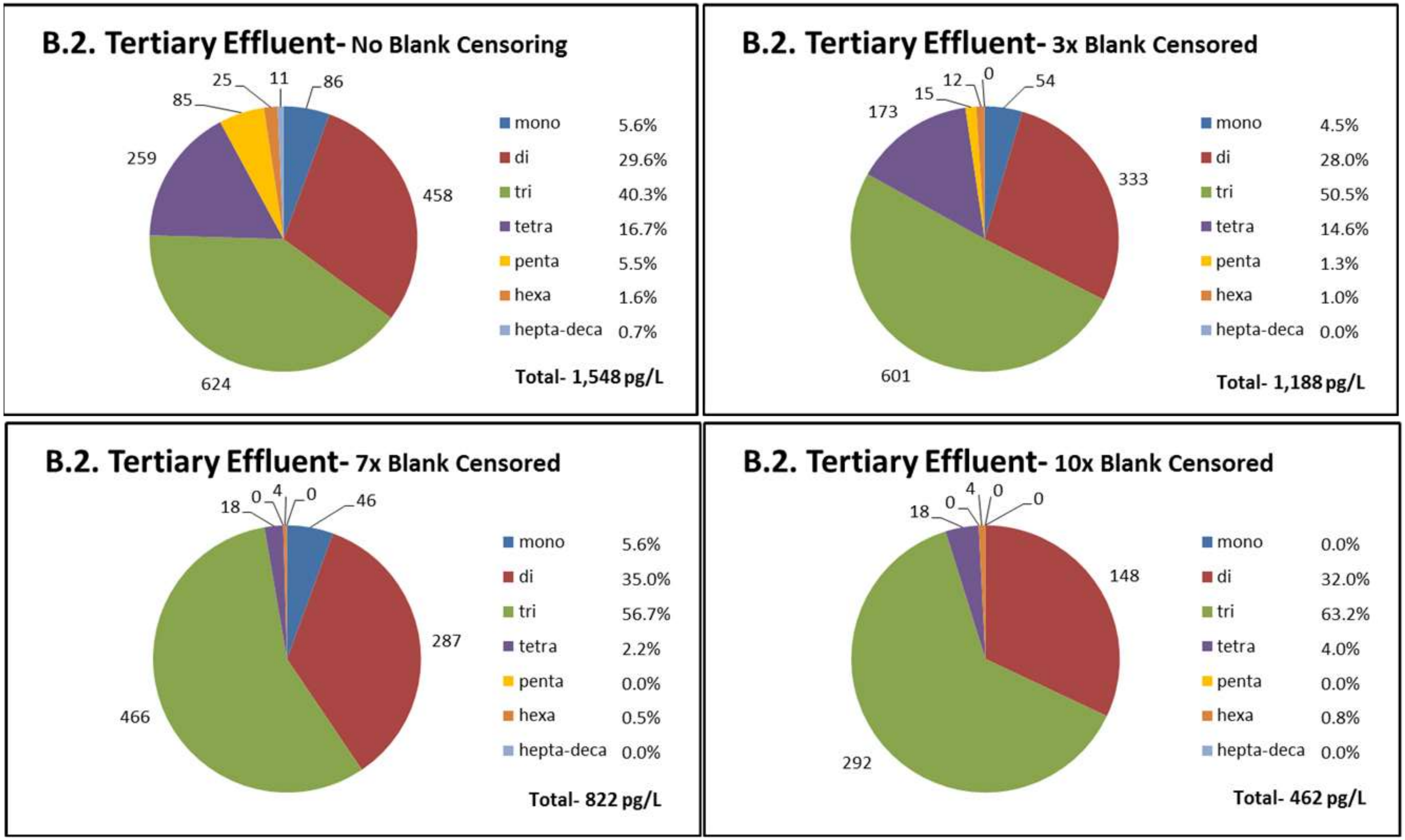

Figure 7- Impact of Different Blank Censoring Factors on Condition B.2

4.0 Conclusion

Revisiting the objectives of this study, a clear distinction was evident in PCB concentrations at the headworks of the WWTS when recycled content was utilized in paper manufacturing as opposed to when it was not. A clear correlation of increased concentration as a function of increased recycle utilization was not readily apparent which points to the variable nature of recycled content as a greater factor in PCB loading than the degree of utilization. The use of Deink in paper manufacturing produced a wide range of PCB concentrations feeding into the WWTS varying between 200,000 pg/L and nearly 4,000,000 pg/L in total PCBs.

Phase 1 of this study demonstrates the efficacy of IEP's WWTS in treating PCB contamination. Whether total PCB concentrations at the head of the WWTS were 30,000 pg/L or 4,000,000 pg/L, residual totals after secondary clarification did not exceed 3,400 pg/L and after tertiary ultrafiltration did not exceed 1,800 pg/L without blank censoring. In every case where Deink was utilized overall PCB removals exceeded 99%. These PCBs are permanently destroyed once they are processed through IEP's fluidized bed combustor thus assuring that they are removed from the environment and eliminating the potential for future contamination. Furthermore, the heavier homologs were removed with greater efficiency across the WWTS and constituted a smaller fraction of the whole in the Tertiary samples collected after the UF membrane process.

The lowest removal efficiency occurred under Condition A.1 and A.2 where no Deink was utilized in paper manufacturing. Condition A.2 yielded an average 94.1% reduction across all 209 congeners though the lower mono-, di-, and trichloro biphenyls were reduced across the WWTS at a rate of 93%. The least impact by the WWTS on A.2 congeners was seen on monochloro biphenyls where only a 76% reduction was achieved. This is likely due to the fact that lower homolog PCBs tend to be more soluble than higher homologs that also have a greater affinity for solids attachment. This focus on the lower homologs may be an important consideration in the determination of a HAC as it remains untested as to whether the lower homologs would remain in circulation and how long it may take for their eventual removal. It is suggested that further testing under the "no Deink" scenario be performed as part of future studies to substantiate the HAC based on efficiency of removal.

The application of blank censoring to the analytical results had very little impact upon the Pump House as congeners in those samples were present in large enough concentrations to yield strong, clear signals during the testing exceeding that of the signal found in the blank when increased ten-fold with virtually no exceptions. Conversely, the Secondary Effluent and even more so the Tertiary Effluent samples are significantly impacted by blank censoring which demonstrates the importance of censoring at very low concentrations using this test method. PCB concentrations of all congeners were reduced from 13% to over 50% depending on the degree of blank censoring applied. Heavier homologs of tetrachloro biphenyls on up were reduced as much as 99.999% with 10x blank censoring. Even at a blank censoring of 7x, Tertiary Effluent samples consist nearly entirely of the lower mono-, di-, and trichloro biphenyls.

5.0 Appendix A: Quality Assurance Project Plan Proposal

6.0 Appendix B: Results Tables Grouped by Homolog

7.0 Appendix C: Raw PCB Data

8.0 Appendix D: Homolog Composition of Samples (Pie Graphs)

9.0 Appendix E: Blank Censoring Impact on Samples by Homolog (Pie Graphs)