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Strategic Information Memorandum (SIM 04-02)

TO: Canadian Corporate Correspondents

FROM: Kirsten Vice

SUBJECT: Independent Analysis of PCB Data Collected Through Quebec Attestations Development

The Quebec Ministry of Environment (MENV) has required all bleached kraft mills and mills with recycle capacity in the province to sample effluent monthly for one year for the purpose of determining levels of polychlorinated biphenyls (PCBs). For this special permit condition, the samples were analyzed by the Ministry's laboratory using a high resolution analytical procedure. To our knowledge, this represents the first application of this specific methodology to pulp mill effluents; thus, the industry has had essentially no knowledge as to what these analyses might reveal. In this memorandum and the attached report, we provide the results of NCASI's independent analysis of the data. This analysis was undertaken to provide the industry with an understanding of the levels of PCBs found in these effluents, as well as the distribution characteristics of the various PCB congeners ("fingerprinting").

<u>This material will interest Quebec pulp and paper companies and other pulp and paper companies following the development of PCB regulations.</u>

Quebec's activity on PCBs is part of the government's development of effluent discharge permits for a suite of substances potentially released by pulp and paper mills (a provincial initiative to develop effluent, air, and residual permits known as "*les attestations d'assainissement*"). PCBs were detected in virtually all samples, some at concentration levels that could lead to a requirement for certain mills to carry out a source identification or reduction study. NCASI is currently undertaking preparations for a 2005 in-plant sampling project at two facilities, representing the pulping categories implicated in the initial PCB sampling for *les attestations d'assainissement*. It is anticipated that the results of these sampling projects will enable the industry to derive further clarification as to the source(s) of PCBs measured during Quebec's permit development process.

The lack of a correlation of the PCB results with bleached pulp production is consistent with the hypothesis that PCBs are not being formed in the process. It also suggests that PCBs are not being introduced into the process by furnish or by pulping or bleaching chemicals. Further

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clarification will be made during subsequent NCASI studies as to whether these vectors or historic uses of PCBs in carbonless paper, electrical equipment, hydraulic fluids, paints, insulation for underground cables, or ink formulations may be sources of the PCBs identified through this sampling program.

In addition to the PCB activities being undertaken by the Quebec MENV, Environment Canada will soon be releasing new federal PCB regulations, which will likely go into effect in 2005. These regulations will apply to PCBs both in service and in storage, significantly limiting the ability to use them in either capacity. The regulations will limit the concentration of PCBs in products at the time they are imported, manufactured, or offered for sale, as well as limit the amounts of PCBs that may be released into the environment. NCASI will prepare a Corporate Correspondent Memorandum for NCASI members once these regulations have been published, to provide you with more information as to how these regulations may affect the forest products industry.

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NCASI Analysis of Quebec
Pulp and Paper Effluent PCB Congener Data

December 22, 2004

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NCASI ANALYSIS OF QUEBEC
PULP AND PAPER EFFLUENT PCB CONGENER DATA

INTRODUCTION

As part of the Industrial Waste Reduction Program (Programme de réduction des rejets industriels, PRRI) of the Quebec Ministry of Environment (MENV), pulp and paper mills must request an "attestation d'assainissement" (environmental permit), which is valid for five years. The attestation program is a progressive process by which mills can be gradually subjected to more stringent environmental requirements. In the first attestation, mills have to characterize their air, water, and solid discharges. Using effluent characterization data and water quality criteria, MENV then determines a set of objectives for environmental releases that are based on the assimilative capacity of the specific receiving waterbody for each mill. Depending on how these objectives compare with actual releases, the mill can be subjected to a discharge limit set at or below its current releases, or be requested to carry out a source identification or reduction study for certain parameters.

In the first attestation, all bleached kraft mills and mills with recycle capacity were asked to perform three days of sampling for PCBs using a new high resolution analytical method. Based on an examination of these PCB results, MENV then asked 23 of the 38 facilities to do monthly effluent sampling for a period of one year.

All the analyses in this program were performed by the MENV laboratory (at the expense of the mills) using an ultra-trace high resolution GC/MS PCB congener method. The method reports individual PCB congener concentrations in the low parts per quadrillion range for 41 congeners and provides concentrations for total PCB homologue class concentrations. NCASI reviewed this methodology and discussed some aspects of it with MENV scientists. The method was found to have many features that are consistent with state-of-the-art, ultra-trace methodology being used elsewhere in the world. Although the primary objective of the monitoring was to measure levels in mill effluents, the mills were given the option of submitting river water samples for analysis as well. Some mills elected to submit these additional samples.

In autumn 2003, NCASI agreed to solicit data from participating mills and to review them to determine if any trends were apparent. A total of 16 mills responded to this solicitation, providing results for between 3 and 26 sampling events that took place between 2001 and 2004. Table 1 summarizes the PCB data that were received from these 16 mills, grouped by type of mill.

Table 1. Summary of PCB Data

Type of Mill	No. of Mills in Category	No. of Samples	No. of Detects	Concentration Range (ppq)
Bleached kraft mills	5	37	35	ND – 31,400
TMP and semi-chemical mills with recycle capacity	7	95	91	ND – 12,419
Secondary fibre and paper mills	4	42	40	ND – 270,000

The purpose of this report is to summarize NCASI's findings regarding these PCB data.

ANALYTICAL PROCEDURE AND QA/QC CONSIDERATIONS

Examination of Laboratory Blank Data

One of the most significant analytical challenges in ultra-trace PCB congener analyses is control of spurious contamination. Due to the ubiquitous nature of PCBs, it is very difficult to obtain consistently clean laboratory blanks. Because PCBs are often detected in laboratory blanks, it is very important to assess how this contamination may impact the interpretation of sample results. Generally, there are two factors to consider. The first is the potential bias spurious laboratory contamination can introduce into low level sample results. The second is the effect variable detections in the blanks may have on the detection limit of the sample measurements.

Some of the analytical reports provided to NCASI included information on MENV laboratory blanks However, data were only provided for the 41 individual congeners, not for the congener totals. In the future, it would be highly desirable to obtain blank data for the congener totals results along with the data for the individual congeners, as this would enable a more robust evaluation of analytical results. NCASI examined the available data to attempt to determine the impact blank contamination may have had on the levels of PCBs found in samples.

The Quebec Ministry of the Environment analytical protocol (MENV 2001) stipulates that the analyst must subtract the level of a congener detected in the blank from the concentration measured in the sample if the blank level exceeds 20% of the measured value in any sample analyzed within the batch of analyses. According to MENV scientists, there is always one sample that fits this criterion; thus, the blank correction is essentially uniformly applied.

The practice of blank subtraction is an unusual approach to handling the laboratory blank bias issue. Most analytical procedures either restrict allowable levels of blank contamination to levels which are not likely to adversely affect interpretation of the results, or require reporting of the result measured in the sample with a data qualifier indicating that contamination for the analyte was found in the blank. The latter approach is usually accompanied by a full report of the blank findings and essentially puts the decision of how to handle the results in the hands of the data user. The data user may (a) choose to perform a simple background subtraction in the context of a sensitivity analysis to determine if the blank levels would render the data unusable for their intended purpose; (b) apply parametric or non-parametric statistical analysis techniques; or (c) elect to undertake a more nuanced interpretation of the results, based on the relative pattern of the blanks versus the sample results.

The implementation of background subtraction of laboratory blank results can result in significantly increased uncertainty in the results. One should first consider the variability of the blank and whether a single blank is representative of potential contamination of the samples. Blanks are run only once for every nine samples. If blank contamination is highly variable, subtracting the results from a single blank may actually increase the uncertainty in all nine sample results or cause a negative bias. Another source of potential increased variability is the propagation of error associated with the inherent measurement variability of each blank analysis. For these reasons, it is recommended that any data where blank subtractions have been

performed should be flagged or qualified and every effort should be made to provide data users with information about how large the blank corrections were relative to the sample results.

The second data analysis and interpretation problem encountered when dealing with frequent detections in the laboratory blank is the increased uncertainty that the analyte has actually been detected in the sample. The American Chemical Society has defined the detection limit as "the lowest level that can be determined that can be statistically different from a blank" (Keith et al. 1983).

The MENV PCB analytical method implements this by requiring a minimum signal to noise ratio of 3:1 and describing a procedure to calculate a sample-specific detection limit. However, that approach only addresses the criteria for determining if an analyte has been detected in that particular sample. Where sporadic and/or frequent laboratory contamination occurs, one must assess whether the analyte found in the sample is statistically different from the analyte found in the blanks. Two approaches to this problem are described herein.

One approach to addressing laboratory contamination was presented by Ferrario et al. (1997). The authors reviewed data from method blanks where selected PCB congeners were always encountered. They computed the standard deviation for 18 method blanks and used the mean blank concentration plus two standard deviations to background correct the study sample results. This approach attempts to address the bias issue associated with chronic laboratory blank contamination. The authors then used one standard deviation of the blanks above the background-corrected concentration as a reporting threshold. This latter consideration was intended to attempt to define the minimum amount of each congener that can be reliably distinguished from the blank background. However, the limited validation study was insufficient in that the proposed reporting threshold corresponds to the <1% false positive rate generally accepted as the definition of the limit of detection.

Of the sixteen mills that submitted data to NCASI, six included at least some laboratory reports summarizing the laboratory blank data for the 41 target PCB congeners. No data were provided for total PCB homologues detected in laboratory blanks. NCASI compiled the data into a single database for review. It was found that many of the target PCB congeners were frequently detected in the laboratory blanks. Specifically, 30 congeners were detectable in between 1 and 28 of the laboratory blanks. This represents a degree of censoring (with censoring referring to the occurrence of non-detects) that precludes the technique described by Ferrario et al. (1997), even if one attempts to use statistical procedures specifically designed to handle data censoring.

Another non-parametric approach that may be useful in this instance involves estimating the 99th percentile for each congener's blank data. This would be a reasonable estimate of the concentration level above which one could be assured of a <1% false positive rate. Unfortunately, one cannot calculate the 99th percentile concentration without making some assumptions about what type of distribution best represents the data when the data set is so highly censored. In this instance, the best estimate is the highest concentration encountered in all the method blanks. Table 2 summarizes the frequency at which a given PCB congener was detected and the maximum concentration that was measured. NCASI could only perform this analysis using the blank data provided by the participating companies. This analysis could be improved if the Ministry laboratory has additional laboratory blank data.

This approach is simple, does not require any distributional assumptions, and provides a conservative estimate of the concentration level below which one would expect a >1% chance of a false positive. Thus, when the individual sample data are interpreted, the concentrations should be compared on a congener-specific basis to the corresponding congener data in Table 2. Concentrations below the levels in Table 2 should not be considered representative of levels in the samples and should be viewed as having a high potential for being a false positive and/or being biased by laboratory contamination.

Table 2. Summary of Laboratory Blank Data

Analyte	Number of times Analyte was Detected	Maximum Concentration Detected (pg/L)	Analyte	Number of times Analyte was Detected	Maximum Concentration Detected (pg/L)
Tri - Cl			**Tetra - Cl**		
IUPAC - 18	5	110	IUPAC - 52	24	140
IUPAC - 17	0	0	IUPAC - 49	20	110
IUPAC - 31	4	46	IUPAC - 44	18	67
IUPAC - 28	10	66	IUPAC - 74	7	54
IUPAC - 33	3	39	IUPAC - 70	18	150
Penta - Cl			**Hexa - Cl**		
IUPAC - 95	14	160	IUPAC - 151	11	59
IUPAC - 101	20	270	IUPAC - 149	28	190
IUPAC - 99	7	84	IUPAC - 153	20	98
IUPAC - 87	7	210	IUPAC - 132	12	70
IUPAC - 110	20	180	IUPAC - 138	21	200
IUPAC - 82	1	82	IUPAC - 158	2	6.7
IUPAC - 118	12	92	IUPAC - 128/167	4	36
IUPAC - 105	3	30	IUPAC - 156	2	21
			IUPAC - 169	0	0
Hepta - Cl					
IUPAC - 187/189	8	30	**Octa - Cl**		
IUPAC - 183	6	15	IUPAC - 199	1	8
IUPAC - 177	3	17	IUPAC - 195	0	0
IUPAC - 171	4	24	IUPAC - 194	10	40
IUPAC - 180	10	44	IUPAC - 205	0	0
IUPAC - 191	0	0			
IUPAC - 170	4	88			
Nona - Cl			**Deca - Cl**		
IUPAC - 208	2	7	IUPAC - 209	25	71
IUPAC - 206	0	0			
Total:		2915			

Lower Calibration Level

The MENV PCB analytical method describes its standard sample volume, the concentration of its lowest calibration standards, and the final volume injected on the GC/MS for analysis. Using this information, NCASI calculated the sample concentrations which represent the lowest concentrations within the calibration range. These are summarized in Table 3. Although the MENV PCB protocol does not require it (and the MENV laboratory does not practice it), it is widely accepted that all data outside the calibration range be flagged or qualified. Many laboratory accreditation standards also prescribe qualification of the data. Thus, it is recommended that all results below the concentration levels shown in Table 3 be flagged or qualified as outside the calibration range of the method.

Table 3. Summary of Lower Calibration Levels

Analyte	Concentration of Lower Calibration Limit (pg/L)	Analyte	Concentration of Lower Calibration Limit (pg/L)
Tri - Cl		**Tetra - Cl**	
IUPAC - 18	1000	IUPAC - 52	1000
IUPAC - 17	250	IUPAC - 49	1000
IUPAC - 31	750	IUPAC - 44	1000
IUPAC - 28	1000	IUPAC - 74	1000
IUPAC - 33	1000	IUPAC - 70	1000
Penta - Cl		**Hexa - Cl**	
IUPAC - 95	500	IUPAC - 151	1000
IUPAC - 101	1000	IUPAC - 149	1000
IUPAC - 99	1000	IUPAC - 153	1000
IUPAC - 87	1000	IUPAC - 132	1000
IUPAC - 110	1000	IUPAC - 138	1000
IUPAC - 82	250	IUPAC - 158	250
IUPAC - 118	1000	IUPAC - 128/167	1000
IUPAC - 105	250	IUPAC - 156	1000
		IUPAC - 169	1000
Hepta - Cl			
IUPAC - 187/189	1000	**Octa - Cl**	
IUPAC - 183	1000	IUPAC - 199	750
IUPAC - 177	1000	IUPAC - 195	1000
IUPAC - 171	1000	IUPAC - 194	1000
IUPAC - 180	1000	IUPAC - 205	1000
IUPAC - 191	1000		
IUPAC - 170	1000		
Nona - Cl		**Deca - Cl**	
IUPAC - 208	1000	IUPAC - 209	1000
IUPAC - 206	1000		

Field Duplicates

In the data received by NCASI, only one sample was analyzed in duplicate. The mean concentration for the duplicate and the relative percent difference (RPD = range divided by the mean expressed as a percentage) for each analyte are summarized in Table 4.

Table 4. Summary of Field Duplicate

Analyte	Mean Concentration Detected (pg/L)	Relative Percent Difference (%)	Analyte	Mean Concentration Detected (pg/L)	Relative Percent Difference (%)
Tri - Cl			**Tetra - Cl**		
IUPAC - 18	155 B(30)	6	IUPAC - 52	200	20
IUPAC - 17	60	66	IUPAC - 49	180 B(27)	11
IUPAC - 31	145 B(19)	7	IUPAC - 44	175 B(17)	17
IUPAC - 28	130 B(29)	0	IUPAC - 74	84 B(9)	19
IUPAC - 33	93 B(13)	10	IUPAC - 70	195 B(20)	15
Penta - Cl			**Hexa - Cl**		
IUPAC - 95	85 B(36)	27	IUPAC - 151	22 B(14)	18
IUPAC - 101	155 B(59)	6	IUPAC - 149	79 B(37)	6
IUPAC - 99	72	7	IUPAC - 153	73 B(28)	19
IUPAC - 87	47 B(36)	0	IUPAC - 132	34 B(16)	65
IUPAC - 110	88 B(31)	0	IUPAC - 138	109 B(44)	21
IUPAC - 82	19	16	IUPAC - 158	NA	ODO
IUPAC - 118	83 B(20)	11	IUPAC - 128/167	NA	ODO
IUPAC - 105	54	22	IUPAC - 156	NA	ODO
			IUPAC - 169	ND	NA
Hepta - Cl					
IUPAC - 187/189	18	40	**Octa - Cl**		
IUPAC - 183	NA B(6)	ODO	IUPAC - 199	ND	NA
IUPAC - 177	10 B(9)	32	IUPAC - 195	ND	NA
IUPAC - 171	NA	ODO	IUPAC - 194	ND	NA
IUPAC - 180	49 B(16)	27	IUPAC - 205	ND	NA
IUPAC - 191	ND	NA			
IUPAC - 170	36	0			
Nona - Cl			**Deca - Cl**		
IUPAC - 208	ND	NA	IUPAC - 209	NA	ODO
IUPAC - 206	ND	NA			
Total:	5270	16			

NA = not applicable
ND = not detected in either sample
B = congener detected in laboratory blank (concentration detected given in parentheses), blank correction has been applied to sample results
ODO = detected in only one of the two replicates

It should be noted that all concentrations reported are below the lower calibration limit and should be so qualified. Laboratory blank results were reported along with the sample results, so the data in Table 4 have been qualified (designated by the letter B) and the concentration levels reported in the blank are given in parentheses. All samples results in Table 4 have been corrected for blank contamination where detectable levels of a given congener were found in the blank. By comparing the reported values to the levels detected in the blank, one can get a sense of how significant those corrections were.

In some instances, an average and a relative percent difference could not be calculated because the analyte was detected in only one of the two replicates. Although the method specifies RPDs should be less than 30%, this was only intended to apply for analyte levels that are greater than ten times the method detection limit. Despite the fact that all the analyte concentrations measured in these samples were lower than that cut off level, the RPD criteria were met for all but three of the detected congeners. This generally indicates good precision.

STATISTICAL ANALYSIS TECHNIQUES

Detailed statistical analyses of the congener data were undertaken in order to (a) potentially characterize final effluent sample PCB contents with respect to their relative Aroclor composition; and (b) identify, to the extent practical, systematic deviations from original Aroclor congener compositions due to chemical or physical "weathering" or other factors. These fingerprinting analyses were intended to provide data that may be useful in characterizing potential PCB sources to a mill's final effluent.

Following some preliminary exploratory work, it was determined that the techniques described herein would only be applied to samples with total PCB concentrations in excess of 2000 pg/L. There were several reasons for this. First, laboratory blank issues are more apparent at lower concentrations and, at some point, might bias or adversely affect the statistical analyses. Next, at lower concentrations some of the PCB congeners with lower percentages in the Aroclor formulations may begin to drop out due to limitations in analytical sensitivity. To the extent that these lower concentration congeners may provide vital fingerprinting information indicating the presence of a particular Aroclor, their absence (due to non-detects) may bias the statistical analysis techniques, causing them to indicate that the Aroclor was not represented in the effluent. It was determined that these potential interpretation difficulties could be minimized if the analyses were only performed on samples with total PCB concentrations in excess of 2000 pg/L. Because many of the sample levels were below this threshold, whatever insights the fingerprinting analyses provide are not available for all mill sites. However, it was felt that it was better to accept this limitation, rather than risk the potential for incorrect or misleading interpretations.

Relative Aroclor composition was assessed by comparing effluent congener proportions derived from congener-specific concentration data to congener compositions reported for common commercial Aroclor mixtures (Frame et al. 1996). To conduct statistical analyses of congener composition, the concentrations of all 41 congeners reported by MENV were summed and the relative amount contributed by each individual congener (weight percent) was calculated. All non-detects were assumed to be 0. Although the laboratory data contain some co-elutions and

some differences between the expected proportions based on the Frame et al. data, the impact on characterization of Aroclor proportions is expected to be minor.

Preliminary data review indicated that many samples contained either Aroclor 1016 or 1242, along with Aroclor 1254 and Aroclor 1260 in varying proportions. As a result, two sets of candidate Aroclor combinations were typically evaluated: Aroclors 1242/1254/1260 and Aroclors 1016/1254/1260. Two statistical approaches were used to quantitatively assess Aroclor composition. Both methods are based on the hypothesis that the PCB congener composition of each effluent sample could be described as a combination of original or altered Aroclor mixtures. Similar approaches are published in the literature (Sather et al. 2003; Sather et al. 2001). The first method, referred to as the "unique congener" (UC) method, used the relative proportions of a subset of congeners indicative of certain Aroclor mixtures to estimate relative Aroclor proportions. In the UC method, the ratio of the observed congener weight percent to the weight percent expected in the original Aroclor was calculated for several congeners indicative of that Aroclor. Once the ratios for all unique congeners were calculated, the proportion of each Aroclor in the sample was estimated from the average of the estimates obtained for each of the congeners in an indicator group.

The second method involved a multiple linear regression (MLR) procedure in which the independent variables were the congener proportions of multiple candidate Aroclors. Because the weight percent values in each sample or Aroclor mixture equal 100%, the coefficients of the independent variables in the regression equation provided an estimate of the proportion of each Aroclor in the sample. Regressions were performed with a constant term, allowing the intercept of the best fit line to vary from the origin. The size of the constant term (among other regression statistics) provided an indication of model fit, with a value approaching zero indicating improved agreement between observed and predicted congener proportions. The regression residuals (defined as the difference between observed and predicted congener proportions) were also evaluated to assess the quality of model fit and to identify whether differences could be attributed to alternative Aroclors, the effects of chemical or physical weathering, or other factors. Because a combination of Aroclors 1242 and 1254 can resemble the congener composition of Aroclor 1248, selected effluent samples were evaluated with Aroclor 1248 as a candidate mixture. In all but one location, a better model fit was generally obtained with the 1242/1254/1260 combination.

Chemical or physical weathering was assessed using a model of equilibrium partitioning based on published congener-specific octanol-water partition coefficients (K_{ow}) (Hawker and Connell 1988). The partitioning model was used to simulate the congener composition of Aroclor standards resulting from losses of specified quantities (up to 30%) of PCB mass during the desorption and volatilization of lower molecular weight PCB congeners that was assumed to originally be associated with particulate matter. The resulting altered Aroclor compositions were used as candidate independent variables in certain multiple regressions. A significant improvement in model fit compared to unaltered Aroclors, indicated in part by improved R^2 values, was considered to be evidence that the observed sample congener composition may have resulted from a weathered Aroclor mixture.

RESULTS

Because PCBs are very hydrophobic, it is reasonable to expect them to partition onto solids. Thus, one might expect that a high percentage of any PCBs in treated mill effluents would be associated with the suspended solids and, therefore, discharge levels might correlate with TSS. Where participating mills supplied TSS data, they were plotted vs. the total PCB concentrations. In no instances were significant relationships observed.

If the PCBs were associated with any raw materials (e.g., wood or chips, caustic, hydrogen peroxide) or if the PCBs were being produced in the process, it might be reasonable to expect a relationship between PCB discharge levels and mill pulp production. To explore this possibility, total PCBs released per day were compared to mill production if mills supplied the necessary information. In no instances were any significant relationships observed.

Total PCBs were compared to total mill flow, but there were no apparent relationships. Aroclor composition estimates (discussed below) were used to calculate individual Aroclor concentrations for selected mills, and these were compared to flow to see if any single Aroclor correlated. Again, no correlations were observed.

Total PCB concentrations for each mill were plotted against sampling dates. These plots were then compared to each other to see if there were any constant seasonal trends. Although some of the facilities seemed to show increased concentrations in the late Fall and again in the early Spring, this was not consistent across all facilities. Thus, this could be (and probably is) purely coincidental.

Some of the mills chose to have their raw water tested. In most cases, there were detectable PCBs in the raw water. To examine the hypothesis that the PCBs in the effluent might be due to raw water contamination, a comparison was made between the concentrations of individual congeners in the raw water vs. the mill effluent. For most of the mills, the PCBs in the raw water accounted for a small portion of the total PCBs in the effluent. However, for a short period of time in one mill, the levels in the raw water were as high as, or higher than, those observed in the effluent. Thus, although raw water can have PCB contamination, it does not appear to explain the PCBs in the effluents from the majority of the mills.

Statistical fingerprinting analyses indicated that the PCBs detected in the effluent samples could be described as mixtures of Aroclors. Both the UC and MLR methods provided similar results for evaluations involving combinations of either 1242/1254/1260 or 1016/1254/1260. Most often, the presence of Aroclors 1242, 1254, and 1260 in varying proportions was indicated, but in two cases congener composition most closely resembled Aroclors 1016 or 1248. At some mills the relative percentages were fairly consistent among effluent samples, while at others there was more variability.

The chemical or physical weathering assessment showed little evidence of substantial changes in the basic Aroclor fingerprints. If an unintentional release or spill of PCBs in the past had contaminated soils, some weathering of the fingerprint due to partial volatilization, photodegradation, and/or microbial degradation could be expected, especially for effluents dominated by Aroclors 1242 and 1016 which contain a higher percentage of lower molecular

weight, more soluble, and volatile PCB congeners. At one mill, where Aroclor 1242 predominates, the data suggest some depletion of trichlorobiphenyl congeners relative to the Aroclor 1242 standard. It should be noted, however, that the lack of mono- and dichlorobiphenyl congener data (not analyzed in the MENV laboratory method) limits the sensitivity of the weathering assessment.

In order to see if there was any particular pattern associated with mill type, the Aroclor distributions for all the mills (where total PCB concentrations exceeded 2000 pg/L) were analyzed using a discriminate function analysis. This analysis indicated three general groupings of the mills: bleached kraft mills; TMP mills (which all have some recycle pulp production capacity); and deink/paper mills. Upon further examination, it was observed that the same general groupings were shown when examining the ratio of Aroclor 1242 to 1254. Thus, both approaches lead to the same conclusions. Because the ratios are easier to describe and understand, the findings based on both techniques are summarized below using the ratio data.

With one exception, within the bleached kraft mill grouping the median ratio of Aroclor 1242 to Aroclor 1254 was 0.3, with a range of 0 to 1.4. Thus, Aroclor 1254 was most often the predominant formulation present. In most samples a small percentage of Aroclor 1260 was indicated (usually less than 10%). There was one exception, where a mill showed an Aroclor 1016 pattern instead of Aroclor 1242.

Within the TMP/recycle group the median Aroclor 1242 to Aroclor 1254 ratio was 1.0, indicating roughly equal proportions of these Aroclors. A range of 0.2 to 2.9 was observed. Again, low percentages of Aroclor 1260 were indicated in most samples. The one exception was a mill which showed better correlations after including Aroclor 1248 with Aroclors 1242, 1254, and 1260.

The final grouping of deink/paper mills showed the highest ratio for Aroclor 1242 to Aroclor 1254, with the range starting at 2.86 and going up to a high of 32.52. The pattern for this group of mills can best be described as showing predominantly Aroclor 1242 with comparably small portions of Aroclors 1254 and 1260.

DISCUSSION

Although laboratory blank levels were generally lower than sample levels, the analysis undertaken above demonstrates that these blanks need to be taken into account if total PCB concentrations are below 1000 to 1500 pg/L. Below this concentration range, consideration must be given to addressing the presence of PCB congeners in the laboratory blanks. Although somewhat controversial, blank correction is one approach. Generally, it would be preferable that the laboratory work to control laboratory contamination.

The lack of a correlation with bleached pulp production is consistent with the hypothesis that PCBs are not being formed in the process. It also suggests that PCBs are not being introduced into the process by furnish or by pulping or bleaching chemicals.

Aroclor 1242 was used in the earliest formulations of carbonless paper and has been reported to be a source of PCBs in the effluents of mills which recycle office waste paper. Although little is known about current PCB contamination levels in recycle pulp, it is somewhat surprising to see a

lack of correlation between recycle pulp production and Aroclor 1242 discharge. However, it is noteworthy that Aroclor 1242 dominates the fingerprint of the 100% recycle mills.

Aroclors 1016, 1242, 1248, and 1254 were historically most commonly used in electrical equipment. Aroclor 1016 was used only in capacitors, but the other Aroclors were used in both capacitors and transformers. The statistical analyses of Aroclor proportions indicated a relatively close match to mixtures of Aroclor formulations. If the PCB congener mixtures were dominated by other (non-Aroclor) sources, this match would not be likely. The close match would also not be consistent with atmospheric deposition of PCBs, as this would have a markedly different fingerprint (which would be non-Aroclor). Thus, from the point of view of similarity of patterns and the fact that the most common use of Aroclors was electrical equipment, it seems probable that past or ongoing use or maintenance of electrical equipment could be the source of the PCBs in the effluent. However, there are insufficient data available at this time to draw any strong conclusions, and other potential hypotheses should be considered.

Aroclor PCB formulations were also used in some hydraulic fluids, paints, insulation for underground cables, and ink formulations. Although these other potential sources were minor compared to transformer and capacitor uses, they should still be kept in mind.

SUMMARY AND CONCLUSIONS

Some of the main observations are summarized herein:

- Laboratory blank levels and appropriate techniques to account for and/or correct for laboratory contamination need to be addressed. This is of particular significance for samples with total PCB concentrations below 1000 pg/L. In the future, it is recommended that information pertaining to results for the concentrations of congener totals, along with the data for the individual congeners detected in blanks associated with all sample analyses, be requested. This additional information would enable a more robust evaluation of analytical results.

- It is recommended that information pertaining to the concentration that corresponds to the lowest calibration level be requested and that all data reported to MENV be flagged or qualified so that it may take this into account in its use of the data.

- No correlations were found with production, TSS, flow, or season.

- With one exception, levels of PCBs in raw water did not account for a large portion of the PCBs found in effluents.

- With one exception, bleached kraft mills showed a mixture of Aroclors 1254, 1242, and occasionally 1260 (in descending order of concentration). The exception was a mill that showed the presence of Aroclor 1016.

- The PCB congener fingerprints showed little evidence of substantial chemical or physical weathering. The lack of mono- and dichlorobiphenyl data limits the ability of this analysis to detect relatively small weathering effects that may have occurred.

- With one exception, the TMP/recycle mills showed Aroclors 1242, 1254, and 1260 (in descending order of concentration). The exception was a mill that also showed the presence Aroclor 1248.

- Recycle mills were dominated by Aroclor 1242, with significantly lesser amounts of Aroclor 1260.

- Although these data cannot conclusively prove that PCBs are not being formed in the process, the strong correlation with formulaic Aroclor mixtures (i.e., used in lubricating and electrical service) indicates consistency with that hypothesis.

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