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Historical Inputs of PCDDs, PCDFs, and PCBs to a British Columbia Interior Lake: The Effect of Environmental Controls on Pulp Mill Emissions

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A sediment core collected from Kamloops Lake, British Columbia, was used to assess historical inputs of polychlorinated dioxin and furans (PCDD/Fs) from a pulp mill and the effects of recent environmental controls. Principal components analysis reveals that four groups of compounds can be found in the sediments: moderately chlorinated PCDD/Fs produced during the bleaching of pulp with chlorine (e.g., TCDF); PCDD/Fs that have been produced by condensation of polychlorinated phenoxyphenol contaminants during pulping (e.g., HxCDDs); highly chlorinated PCDD/Fs that are derived from mixed sources (e.g., OCDD); and a series of PCBs that are probably derived from mixed sources. Strong correlations of CB13, CB15, and CB37 with the moderately chlorinated PCDD/Fs suggest that these PCBs have been produced in-situ by the pulp mill. In particular, CB15 is found in quantities rivaling those of total TCDF. In the 1930s−1950s, sediments exhibit minor contamination by the PCBs and higher chlorinated dioxins and furans. With the construction of the mill in 1965, large quantities of HxCDD and the tetra-chlorinated PCDD/Fs were released. Technological changes at the pulp mill have effected a drastic reduction in pulp mill PCDD/Fs in the 1990s.

Introduction

During the 1980s, pulp mills were discovered to be an important source of polychlorinated dioxins and furans (PCDD/Fs) to the environment (*1*−*3*). Concerns about toxicity led to a rapid response by the Canadian industry to reduce or eliminate PCDD/F emission, and recent monitoring shows dramatic downturns in many of the congeners (e.g., refs 4 and 5). However, the sequence of production and elimination of these compounds from pulp mills is still not well known (*6*).

Here, we use data from a sediment core collected from Kamloops Lake to establish the emission history for PCDD/Fs and PCBs. This lake was chosen because it is part of the Fraser River system (Figure 1), the most important salmon-bearing river in the world; a single bleached kraft pulp mill (Weyerhaeuser) was constructed in 1965 about 8 km above Kamloops Lake (*5*); surveys have shown high levels of dioxins and furans in sediments downstream of the pulp mill; and Kamloops Lake contains laminated sediments (*7*) that have excellent potential to record faithfully the contaminant chronology. The establishment of trends from the lake sediments is useful in the assignment of sources, the estimation of budgets, and the validation (final audit) of control strategies.

Kamloops Lake (Figure 1) is a short residence-time, intermontane lake (*7*). The Thompson River, with an annual mean flow of 700 m^3/s and drainage area about 55 000 km^2, passes through the lake. The bulk residence time is about 1 year in winter and less than 20 days at peak flow in spring. Due to the strong seasonal variability in water flow and sediment supply, the basin sediments exhibit laminae (annual seasonal couplets), which have been used to estimate sedimentation rate (*7*). Kamloops, a city of population 70 000, is situated upstream of the pulp mill about 10 km above the lake. In addition to the pulp mill, other potential local sources of PCDD/Fs include the Kamloops Sewage Treatment Plant, municipal and domestic burning, a saw mill at Savona (chlorophenates), and railway/hydro lines along the side of the lake (chlorophenates).

Methods

Sampling. Sediment cores were collected from a small boat using a KB gravity corer with an acrylic tube (10 cm i.d.) positioned with GPS. The coring site was chosen to provide an optimum sedimentation rate incorporating pre-industrial sediments up to the date of collection (June 1994). The sediments were penetrated slowly (<0.3 m/s) with a clear-vented tube without a core cutter or catcher. Upon retrieval of the core, laminae (varves) were easily seen through the clear plastic tube. The core was maintained upright and subsectioned on site within several hours by placing the corer onto a piston and extruding the core upwards incrementally. The sediment was subsampled into plastic bags for ^{210}Pb and metals analyses and into glass jars for organochlorine determination. Stainless steel subsectioning tools were cleaned between samples (tap water, distilled water, acetone), and sediment from the outer 1 cm of the core was discarded. The glass jars were stringently precleaned (detergent rinse, 4-h soak in 2% RBS, rinse, distilled water, rinse, and baked overnight at 350 °C). No attempt was made to section along laminae horizons; rather, subsamples were collected at 1-cm intervals for the first 10 cm, at 2-cm intervals from 10 to 20 cm, and at 5-cm intervals from deeper in the core.

Sediment Dating. ^{210}Pb was determined by measuring ^{210}Po (*8*) using a 300-mm silicon surface barrier detector with a Canberra 8180 MCA. Counting errors, maintained at less than 10%, were verified by replicate analyses on sediment samples (pooled CV was 8.8% ($\nu = 6$)). Because the sediments were varved, mixing was assumed not to be a problem for dating. Varve counts, used here to assign dates to the sediment horizons, were checked with the ^{210}Pb data. For the region of interest (1940−1990), the average sedimentation rate according to the varve counts was 0.55 ± 0.06 cm yr^{-1} (± 1 SE). From the ^{210}Pb data for the same region, the sedimentation rate was determined to be 0.32 ± 0.04 g cm^{-2} yr^{-1}, which is equivalent to 0.49 ± 0.06 cm yr^{-1}.

Dioxin/Furan/PCB Extraction and Analysis. Sediment samples were homogenized unfrozen, and 2-g aliquots were removed for moisture determinations. Analytical samples, approximately 10 g wet weight (ww), were dried with 125 g of Na_2SO_4 in a mortar and transferred into the glass thimble of the Soxhlet where they were spiked with a mixture of $^{13}C_{12}$-labeled PCDDs/Fs and CBs internal standards as supplied

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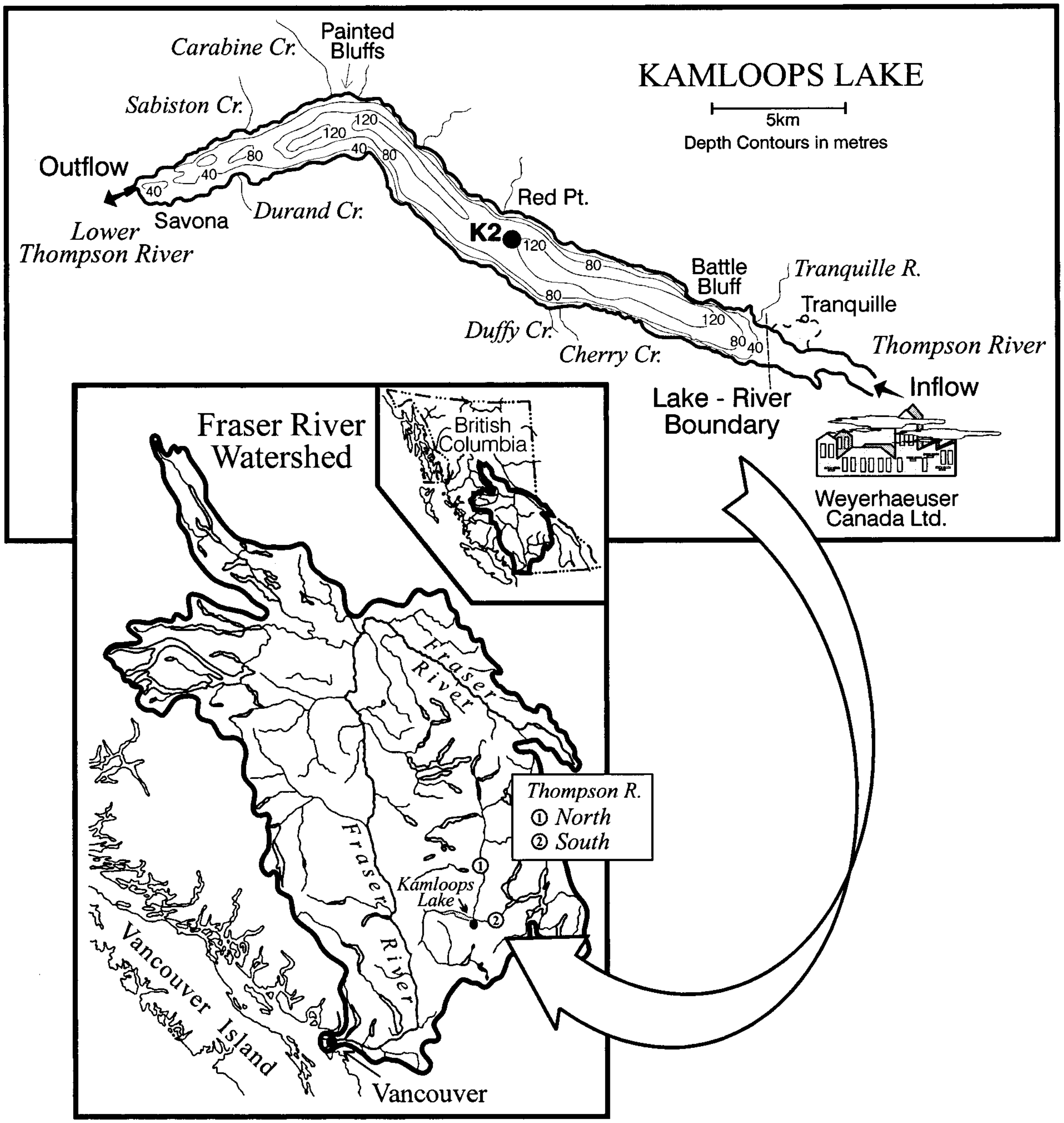

FIGURE 1. Kamloops Lake, British Columbia.

by Cambridge Isotope Laboratories (Andover, MA). The spiked samples were Soxhlet extracted for 16 h with 350 mL of toluene/acetone (80:20); washed with 40 mL of KOH, 80 mL of HPLC-grade water, and subsequently with 10 mL of H_2SO_4; rotary evaporated; and reconstituted in 10 mL of DCM/hexane (1:1). Sediment samples were analyzed in batches of six each, consisting of a procedural blank and four real samples out of which one was processed and analyzed in duplicate.

Sample cleanup took place in four stages: (a) silica gel column (with layers of basic, neutral, acidic, neutral silica); (b) column filled with copper filings and Na_2SO_4 and (to remove sulfur and residual water); (c) activated neutral alumina column capped with anhydrous Na_2SO_4; and (d) fractionation with a carbon fiber column connected to an automated high-performance liquid chromatography (HPLC) system. From this system, three fractions were collected: fraction II contained the MO-CBs, fraction III contained the NO-CBs, and fraction IV contained the PCDDs and the PCDFs. All three fractions were concentrated to less than 10 mL and spiked with corresponding ^{13}C-labeled method performance standards prior to GC/HRMS analysis. Details on method surrogate internal standard solution composition and on the solvents and conditions used in all the clean up and fractionation steps are reported elsewhere (*9*). The CBs analyzed from the MO fraction were tetrachlorinated: 72, 68, 57, 67, 58*, 63, 61*/74*, 70*/76, 66*, 55, 56/60*; pentachlorinated: 111, 120, 124*, 108*/107, 123*, 118*, 114*, 122*, 105*; hexachlorinated: 159*, 162*, 167*, 156*, 157*; and heptachlorinated: CB 189*. The CB congeners analyzed from the non-ortho fraction were dichlorinated: 14, 11*, 12, 13*, 15*; trichlorinated: 36, 39*, 38*, 35*, 37*; tetrachlorinated: 80*, 79*, 78*, 81*, 77*; pentachlorinated: 127, 126*; and hexachlorinated: 169*. The remaining di-ortho and tri-ortho CBs were collected in fraction I from the carbon fiber system but those were not examined in this work. CBs identified with the asterisk * are those present in the GC/HRMS calibration standards. The CBs presented as couples (i.e.,

TABLE 1. Concentrations (pg/g) of Selected Dioxin and Furan Compounds or Compound Classes

sample no.	sample interval (cm)	year interval	1 2,3,7,8-TCDD	2 total TCDD	3 1,2,3,7,8-PeCDD	4 total PeCDD	5 1,2,3,6,7,8-HxCDD	6 1,2,3,7,8,9-HxCDD	7 total HxCDD	8 1,2,3,4,6,7,8-HpCDD	9 1,2,3,5,6,7,8-HpCDD	10 OCDD	11 2,3,7,9-TCDF	12 total TCDF	13 1,2,3,7,8-PeCDF	14 2,3,4,7,8-PeCDF	15 total PeCDF
1	0−1	1993.7−1994.5	0.9	1.6	0.2	1.1	2.1	1.5	14.8	11.3	13.4	85.0	24.6	49.0	0.4	0.6	3.3
2	1−2	1993.4−1993.7	0.7	1.2	0.1	0.3	1.6	1.0	11.6	8.3	10.2	57.5	17.5	34.3	0.4	0.4	2.1
3	2−3	1993.1−1993.4	0.8	1.3	0.1	0.3	1.4	1.0	9.8	7.0	8.9	46.8	15.2	31.1	0.3	0.4	2.3
4	3−4	1990.6−1993.1	2.2	2.9	0.3	1.6	2.2	1.4	14.2	11.0	11.8	79.3	33.3	66.6	0.6	0.8	4.6
5	4−5	1988.6−1990.6	8.3	10.3	0.9	3.5	4.6	2.8	32.3	14.2	15.6	102.4	171.2	329.4	2.3	2.9	15.2
6	6−7	1983.3−1985.4	58.6	65.4	3.1	10.9	18.5	10.3	143.9	21.1	23.0	103.8	1784.5	3271.7	18.0	29.5	88.7
7	7−8	1981.6−1983.3	25.2	28.8	3.2	15.7	35.4	18.8	273.4	24.1	27.7	109.9	906.4	1677.9	9.6	15.3	50.7
8	8−9	1978.3−1981.6	9.7	13.2	4.7	24.4	76.6	38.8	553.1	30.2	30.7	100.5	306.3	581.0	5.0	6.0	25.1
9	10−12	1970.0−1975.4	7.4	13.8	9.2	52.6	155.4	85.2	1100.0	75.0	63.2	144.8	100.4	194.3	2.0	2.0	16.5
10	12−14	1964.4−1970.0	6.1	10.2	2.2	14.3	27.2	17.9	197.4	74.8	61.1	220.1	52.6	106.9	1.3	1.3	13.7
11	14−16	1958.4−1964.4	3.1	4.7	0.7	3.3	4.3	3.5	33.5	22.2	23.0	87.3	24.8	54.1	0.9	0.7	7.6
12	16−18	1954.9−1958.4	1.7	2.8	0.3	1.1	1.3	1.0	9.9	11.2	14.1	73.4	9.1	23.5	0.4	0.3	5.0
13	18−20	1950.2−1954.9	0.4	0.6	0.1	0.4	1.0	0.8	7.1	9.8	10.2	62.9	6.5	14.4	0.2	0.3	3.3
14	20−25	1941.6−1950.2	0.2	0.6	0.2	0.7	1.4	1.5	11.0	21.2	20.9	169.7	1.0	5.2	0.1	0.2	2.9
15	25−30	1932.4−1941.6	0.1	0.2	0.1	0.3	0.6	0.6	4.9	6.1	6.8	43.0	0.2	2.5	0.1	0.1	2.5
16	30−35	1924.2−1932.4	0.1	0.4	0.1	0.3	0.3	0.4	4.4	3.5	4.4	28.5	0.2	2.5	0.1	0.1	4.5
17	35−40	1915.2−1924.2	0.1	0.4	0.1	0.2	0.6	0.3	3.4	1.7	2.1	14.0	0.2	1.4	0.1	0.1	2.8
18	60−65	1878.9−1886.5	0.1	0.2	0.1	0.1	0.3	0.2	1.0	1.0	1.3	14.8	0.1	0.2	0.1	0.1	0.1
max blank			0.06	0.06	0.08	0.08	0.1	0.1	0.1	0.12	0.12	0.14	0.05	0.05	0.06	0.06	0.06

sample no.	sample interval (cm)	year interval	16 total HxCDF	17 total HpCDF	18 OCDF	19 CB13	20 CB15	21 CB37	22 60/56	23 61/74	24 CB66	25 70/76	26 CB77	27 CB105	28 107/108	29 CB118	30 CB156	31 CB167
1	0−1	1993.7−1994.5	2.3	5.6	4.5	2.4	68.2	9.2	8.2	6.9	11.7	12.2	2.4	17.9	2.7	40.1	8.7	4.0
2	1−2	1993.4−1993.7	1.3	3.9	3.0	2.1	50.8	7.0	7.7	6.5	10.8	14.5	1.8	13.5	2.3	28.2	6.2	2.9
3	2−3	1993.1−1993.4	1.4	3.3	2.7	1.1	33.9	5.1	5.8	5.0	9.0	11.4	1.4	11.6	1.7	25.5	4.9	2.2
4	3−4	1990.6−1993.1	2.5	6.5	5.6	0.6	14.1	5.7	12.3	9.9	31.0	19.3	11.5	44.1	5.4	73.2	17.1	8.1
5	4−5	1988.6−1990.6	3.6	8.1	7.4	1.7	181.0	19.5	8.7	7.5	15.1	13.2	3.4	34.7	2.9	62.7	18.3	9.4
6	6−7	1983.3−1985.4	6.2	8.9	6.9	6.7	2011.7	75.0	11.2	13.5	16.7	16.5	4.3	27.8	3.5	60.2	14.9	5.7
7	7−8	1981.6−1983.3	5.7	9.7	8.0	8.7	2025.8	55.3	9.5	11.3	16.0	15.0	3.8	23.7	2.6	51.6	13.7	5.5
8	8−9	1978.3−1981.6	5.1	10.9	9.2	1.7	307.3	19.2	8.4	7.2	12.7	13.2	3.3	17.5	2.8	52.2	11.7	5.9
9	10−12	1970.0−1975.4	6.2	10.6	8.7	2.9	303.1	18.4	21.5	20.4	43.0	51.8	5.2	39.5	8.9	102.1	28.7	12.4
10	12−14	1964.4−1970.0	5.9	15.3	13.9	3.2	175.4	19.6	24.2	24.2	50.7	53.2	8.3	71.1	11.5	173.2	64.1	25.1
11	14−16	1958.4−1964.4	3.8	6.4	4.8	1.3	49.6	14.6	21.0	20.9	52.7	58.4	7.8	70.8	13.0	188.9	34.7	14.1
12	16−18	1954.9−1958.4	2.8	5.5	4.7	1.6	31.0	12.4	23.6	24.4	57.5	78.8	8.9	95.8	18.8	216.7	36.6	14.8
13	18−20	1950.2−1954.9	2.2	5.2	5.0	2.2	18.7	13.6	30.9	30.0	63.3	98.8	8.8	70.3	20.0	314.9	122.0	56.3
14	20−25	1941.6−1950.2	2.8	7.0	8.8	0.9	7.4	6.8	20.4	20.3	44.1	71.2	5.6	43.9	10.8	117.3	21.8	10.0
15	25−30	1932.4−1941.6	1.6	2.4	2.2	0.5	3.2	2.8	5.8	5.5	12.4	19.1	1.7	19.2	4.1	52.9	13.7	9.1
16	30−35	1924.2−1932.4	2.4	1.4	0.8	0.3	3.0	1.5	3.2	3.5	9.0	13.2	0.9	20.9	3.9	54.0	11.5	5.1
17	35−40	1915.2−1924.2	1.4	0.9	0.4	0.4	4.3	1.8	1.4	1.1	2.9	4.3	0.5	8.3	1.3	23.6	6.9	2.6
18	60−65	1878.9−1886.5	0.1	0.1	0.1	0.1	4.7	2.0	0.9	0.5	1.0	1.1	0.3	2.1	0.2	8.3	4.5	1.9
max blank			0.08	0.1	0.12	0.12	0.12	0.06	0.1	0.1	0.1	0.1	0.04	0.4	0.4	0.4	0.4	0.4

33/29) were those found to co-elute on the 60-m DB5. Co-eluting isomers on the 60-m DB5 were confirmed by using authentic standard solutions of individual isomers (those identified with the *) and from algorithms that identify all the CB congeners against literature retention times on columns with similar properties to DB5 (*10*).

PCDD/Fs, NO-PCBs, and MO-PCBs were analyzed by gas chromatography/high-resolution mass spectrometry (GC/HRMS). The instrument was a VG-Autospec high-resolution mass spectrometer (Micromass, Manchester, UK) equipped with a Hewlett-Packard Model 5890 Series II gas chromatograph and a CTC A200S autosampler (CTC Analytics, Zurich, Switzerland). Details on the GC conditions and programs are reported elsewhere (*9*). For all analyses, the MS was operated at 10 000 resolution under positive EI conditions (35 eV electron energy), and data were acquired in the single ion resolving (SIR) mode. Two or more ions, M^+ and $(M + 2)^+$ in most cases, of known relative abundances were monitored for each molecular ion cluster representing a group of isomers and two for each of the ^{13}C-labeled surrogate standards. Compounds were identified only when the GC/HRMS data satisfied all of the following criteria: (1) two isotopes of the specific congeners were detected by their exact masses with the mass spectrometer operating at 10 000 resolving power or higher during the entire chromatographic run; (2) the retention time of the specific peaks was within 3 s to the predicted time obtained from analysis of authentic compounds in the calibration standards; (3) the peak maxima for both characteristic isotopic ions of a specific congener coincided within 2 s; (4) the observed isotope ratio of the two ions monitored per congener were within 15% of the theoretical isotope ratio; (5) the signal-to-noise ratio resulting from the peak response of two corresponding ions was ≥ 3 for proper quantification of the congener. The presence of certain compounds (e.g., CB-15, 37, and 77) was further confirmed from library spectra as compared against those obtained from GC/HRMS full-scan experiments, +ve EI (70 eV electron energy), with the MS operating at 5000 resolution. All the characteristic fragments were detected and matched those of library spectra and also those obtained from authentic standards. The identity and concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF were confirmed by re-analyzing all the extracts on a 30-m DB-225 fused silica capillary column (0.25 mm i.d. with 0.15 μm film thickness) from J&W Scientific (Folsom, CA). The criteria for identification and quantification and the quality assurance and quality control measures undertaken for the sample work up and the GC/HRMS analysis of all the analytes of interest were based on Environment Canada protocols (*11, 12*).

Principal Components Analysis. Unsupervised Principal Components Analysis (PCA) was performed using the non-linear iterative partial least squares (NIPALS) algorithm (software provided by Chemometics Clinic, Seattle, WA). The data were reduced to 31 compounds or compound classes (Table 1) and autoscaled. The detection limit was used for the few cases (4.7% of the total data points) where concentrations were less than the detection limit. Hierarchical Cluster Analysis (HCA) was performed using Einsight.

Results and Discussion

The vertical profiles (Table 1) generally have low background values near the bottom of the core, rise to a maximum within the central or upper portion of the core, and then decrease in the top 5 cm of the core. It is clear that the depth (date) of maximum concentration in the core differs among compounds, suggesting that more than one source has been operating. Patterns in the congener distributions for PCDDs, PCDFs, and PCBs have been shown to provide insight into relationships between congeners and potential sources (e.g., refs 13−15). PCA is a powerful way to organize and display multivariate data in terms of both the samples (scores) and the variables (loadings) (16, 17).

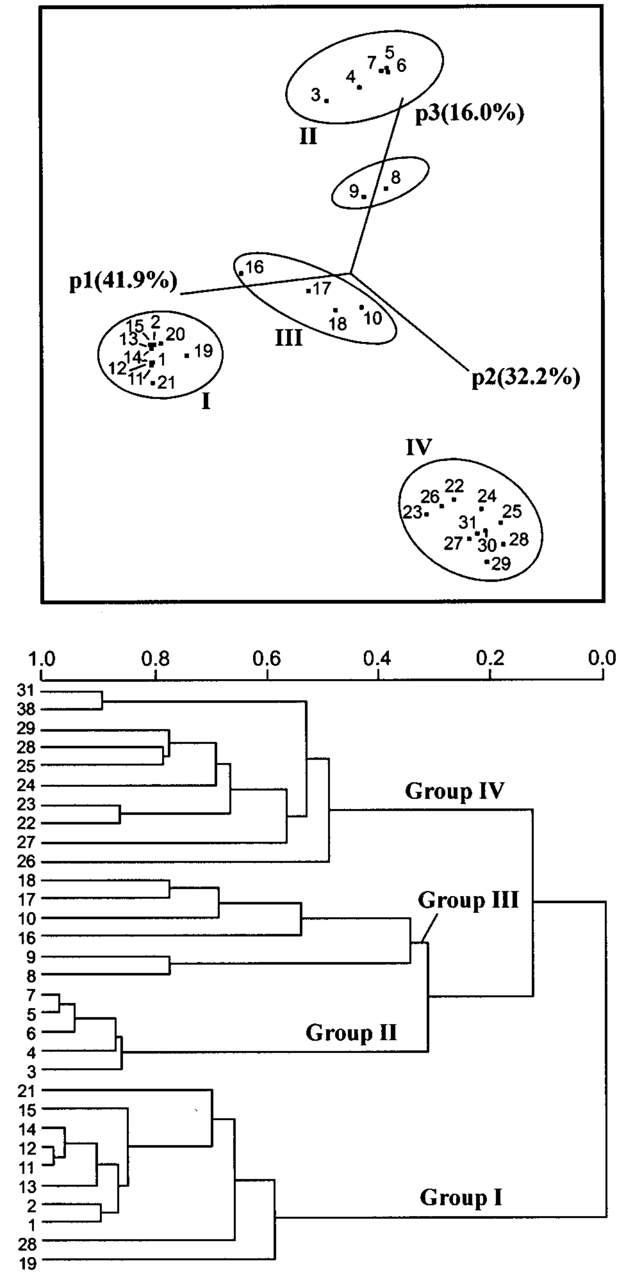

FIGURE 2. PCA variable loadings plot for the first three PCs (top) and the HCA results (bottom). The numbers refer to compounds or compound classes as listed in the top row of Table 1. Group assignments are based on the separation of variables in three-dimensional PC space. Note that PCA places variables 8 and 9 between groups II and III whereas HCA suggests that these two variables belong more closely to group III.

The first three PCs (Figure 2, top) show four main groups of compounds. Group I is a compact cluster including as the most important member total TCDF; group II includes the HxCDDs as the most important members; group III contains OCDD as the most important member; and, finally, group IV contains most, but not all, of the PCBs. The two hepta CDDs (8 and 9 on Figure 2) fall between groups II and III (note that the separation of 8 and 9 from group III is shown only in the third PC). The HCA (Figure 2, bottom) also clearly separates the compounds into the same groupings, suggesting that the two hepta CDDs (8 and 9) are more closely associated with group III.

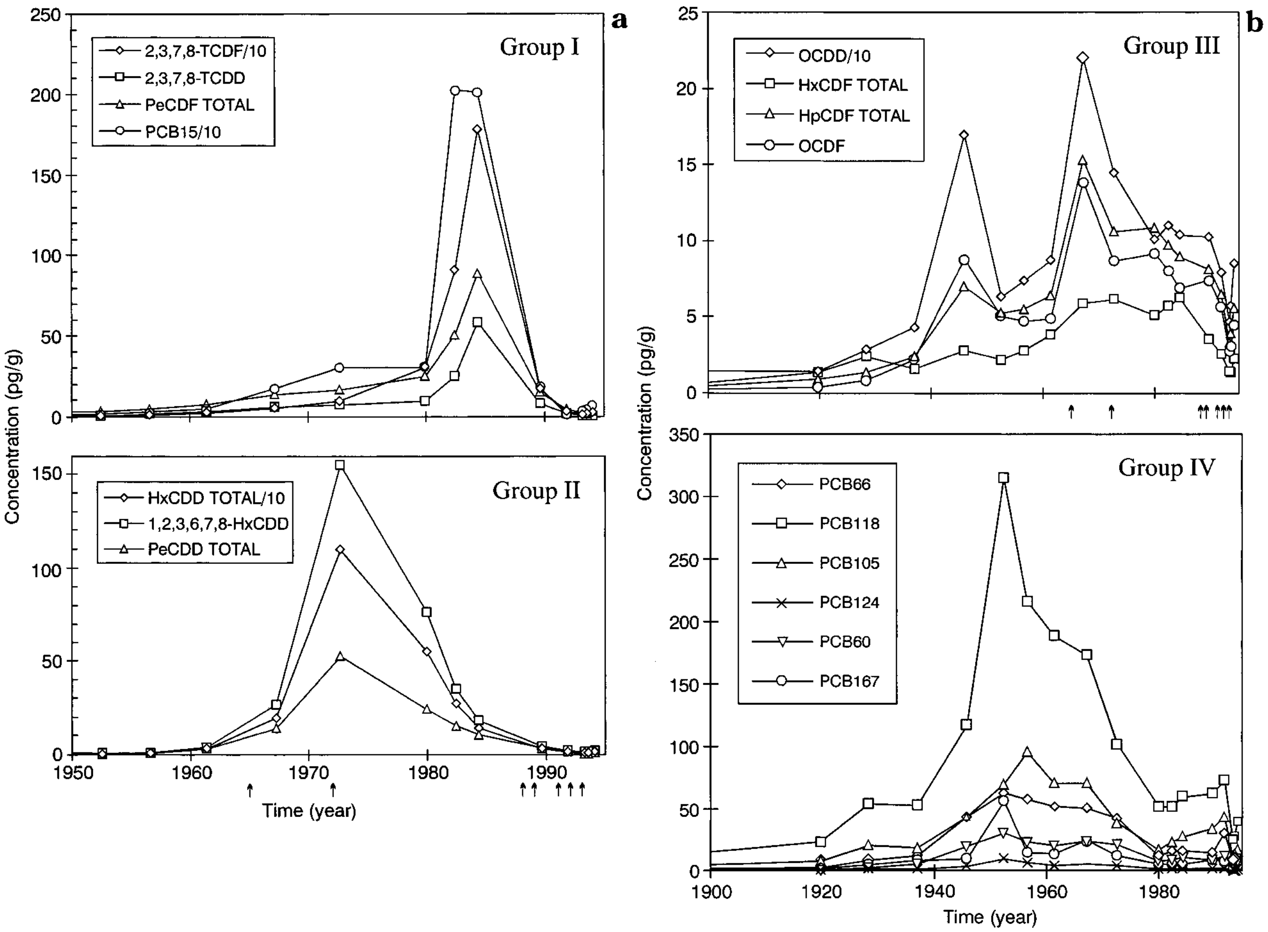

FIGURE 3. Reconstructed historical trends are given for (a) groups I and II and (b) groups III and IV. Note that the concentrations of the leading components 2,3,7,8-TCDF, total HxCDD, and OCDD have been divided by 10. Arrows along the time scale refer to the following abbreviated mill history: 1965, mill opens; 1972, major expansion, electrostatic precipitator installed, hog fuel boilers replace beehive burners, high stack built to push gases above inversion layers, mill A goes to 10% ClO_2; 1988, mill B goes to 30% ClO_2; 1989, mill A goes to 30% ClO_2; 1991, mills A and B go to 60% ClO_2; 1992, mill A goes to 100% ClO_2; 1993, mill B goes to 100% ClO_2.

Sources for PCDD/Fs include pulp mills using chlorine bleach or wood chips contaminated with polychlorinated phenol (*18*–*21*), combustion of wood (*22*), exhaust from cars using leaded gasoline (*23*, *24*), and a number of other combustion or chemical contamination sources (e.g., refs 13, 23, and 25–27). Considering the patterns of dioxins in these various sources, the groupings in the loadings plot (Figure 3) can be explained as follows.

Group I: 2,3,7,8-TCDD, Total TCDD, 2,3,7,8-TCDF, Total TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, Total PeCDF, CB13, CB15, and CB37. All of the members of group I are highly correlated with one another as is evident from the tight clustering in the loadings plot (Figure 2). The leading component of this group, total TCDF, is a characteristic marker for chlorine bleaching (*4*, *6*), and we conclude that the source for all of these compounds was pulp mill effluent when chlorine was used as the predominant bleaching agent.

A surprising result in the loadings plot is the association of three di- and trichloro PCBs with group I. The strong correlation between these PCBs and 2,3,7,8-TCDF ($0.81 < r < 0.97$) suggests that these compounds have also been produced *in-situ* during the bleaching of pulp with chlorine. Although measurable quantities of PCBs have been found in pulp mill effluent (*28*), the PCBs have been inferred to enter pulp mills as contaminants rather than being produced *in-situ* (cf. refs 29 and 30). It appears unlikely that these three congeners derive from a PCB spill of, for example, Arochlor 1254 coincident with the TCDD/F maximum because one would expect concentrations of CBs 70, 66, and 118 to exceed CB15 concentrations in our data (*31*). That we are aware, the production of some PCB congeners during the chlorination of pulp is a new finding. Identification of the PCB congeners reported here relies on retention time (checked against authentic standard) and molecular mass. For CB15, we validated this identification using the fragmentation pattern. The simplest mechanism to produce CB15 (4,4') would be the direct chlorination of biphenyl in aqueous media (*32*), which favors the ortho (2) or para (4) positions (*33*). Substituting chlorine with chlorine dioxide (ClO_2) as a bleaching agent seems to have eliminated the production of these PCBs along with the TCDD/Fs.

Group II: 1,2,3,7,8-PeCDD, Total PeCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, Total HxCDD (Probably Also Some 1,2,3,4,6,7,8-HpCDD and 1,2,3,5,6,7,8-HpCDD). The leading component of this group, HxCDD, is a marker of polychlorinated phenol (polyCP) contaminated wood chips used in pulping (*4*, *20*). The hexachlorinated dioxins, which are produced by digester-mediated condensation of polychlorinated phenoxyphenol contaminants in polyCPs, have been found in pulps, effluents, and sludges. The strong correlations in our data suggest that pentas and heptas are produced along with HxCDDs, but in far smaller amounts (cf. ref 20). There is potentially another source for the hexas—the burning of wood (*22*) or salt-laden wood (*19*)—the latter source being improbable at BC interior mills. The hepta CDDs, which lie between group II and group III, show patterns characteristic of both groups, and we infer therefore that these compounds come from mixed sources.

Group III: OCDD, Total HxCDF, Total HpCDF, OCDF (Probably Also 1,2,3,4,6,7,8-HpCDD and 1,2,3,5,6,7,8-HpCDD). These highly chlorinated PCDD/Fs likely have an important component of their source in a variety of combustion processes and are derived partly from long-range transport (cf. refs 13 and 26). Since the highly chlorinated PCDD/Fs dominate profiles for most background soil samples, their route of entry into the lake probably includes soil erosion in the drainage basin. PolyCPs contain highly chlorinated dioxin and furan impurities (*4, 20, 34, 35*) and therefore are potentially another important source of group III congeners that could enter the environment either directly through poorly-controlled use of polyCPs or indirectly through combustion or weathering of treated materials. The spread of the group III variables (Figure 2) implies a relatively large range in source characteristics or that more than one source contributes to group III. Other emissions, like beehive burners (where wood waste is burned) and hogfuel combustion, could contribute some of these compounds as could municipal and domestic incineration. Suspended river sediments from above the mill contain predominantly these more highly chlorinated PCDD/Fs (*36*), supporting the notion that they are derived from sources other than pulpmill effluent.

Group IV: PCBs (in Order of Concentration: 118, 105, 70, 66, 156, 60, 61, 167, 108, and 77). The PCB congeners (note: the analysis includes only a selected set of non-ortho and mono-ortho CBs) form a relatively broad group suggesting variation among them. Group IV is well separated from the other groups (Figure 2), implying different patterns and sources. These CBs, which almost certainly are derived from multiple sources, are not the focus of this paper and have been included here primarily to illustrate that the three group I CBs (13, 15, and 37) are exceptional.

Timing of Events. Group I compounds start to increase in the sediments in the early 1960s which, within the error of the dating, coincides with the opening of the mill (Figure 3a, top panel). The concentrations increase dramatically up to about 1988 −1990 at which point they decrease equally dramatically. Within the error of the dating, the decrease for this group coincides with the conversion from 10% to 30% ClO_2 in both mills A and B. Recent sediment concentrations for all of these compounds are very low.

Group II compounds start to increase in sediments at about the same time as the group I compounds, rise to a maximum in the early 1970s, and decrease thereafter (Figure 3a, bottom panel). A decrease in group II compounds occurs after the mill phased out its beehive burners, installed an electrostatic precipitator, and built a high stack to push furnace gases above inversion layers. Therefore, it is tempting to infer that burning of wood and stack emissions contributed the HxCDDs (*19, 22*) and these were either reduced or distributed more widely after 1972. However, the exceptional predominance of HxCDD accompanied by smaller amounts of heptas and pentas points overwhelmingly to digester-mediated condensation of polyCPP as the major source (*20*). It has not been possible to obtain a record of polyCP-contaminated wood used in this pulp mill, but the sediment record clearly shows that polyCP-contaminated wood chips were used in the 1960s and 1970s and then phased out in the late 1970s or early 1980s.

Group III compounds (Figure 3b, top panel) show trends with time that roughly follow those observed elsewhere for OCDD (*6, 26*). However, there are important local differences. Peak concentrations of OCDD are only about one-third those observed elsewhere, and there are two prominent spikes, one corresponding to 1940−1950 and the other to 1964−1970. As outlined earlier, the sources for the group III compounds are numerous and varied, and there is a great deal of difficulty in pinpointing the sources accurately. The trends and the observed concentrations suggest that the group III compounds have been supplied partly by general, broadly distributed, combustion or mixed industrial/municipal sources as outlined above and partly by local events (spikes). While the 1964−1970 spike could reflect environmental controls introduced at the mill in 1972, the earlier spike cannot relate to the mill. We compared the PCDD/F profile of the 20−25-cm (1940−1950) sediment sample to those of a variety of PCDD/F sources (*37*), finding an excellent match with the outer layers of PCP-treated power poles. It seems highly probable, therefore, that the earlier spike was caused by contamination from PCP treatment of either the railway ties or power poles that run along both sides of the lake.

PCB histories have been inferred from sediment core records at a number of sites in North America (*38−41*). With some regional variations, these compounds are first observed in sediment records after about 1920−1930, exhibit a maximum in the mid 1960s to early 1970s, and then decrease slowly to the present. The Kamloops Lake sediment record follows a similar trend to those observed in other temperate lake cores except that the peak concentrations for most of the congeners are observed earlier (in the 1950s). Whether this is due to a local input of the contaminant (i.e., a spill in the early 1950s), a different history than observed in eastern North America, or the particular CBs analyzed here remains an open question.

A Budget for 2,3,7,8-TCDF. The total sedimentation in Kamloops Lake ($\sim 3.4 \times 10^8$ kg yr^{-1}) together with recent 2,3,7,8-TCDF concentrations in sediments yields a present sediment flux of about 7.7 g yr^{-1}. Recent mill loadings are estimated at 7 ± 2 g yr^{-1} (*5*), which could supply most of the 2,3,7,8-TCDF estimated to be accumulating in the lake. Concentrations of 2,3,7,8-TCDF observed in the river below the lake (36) indicate that a further 0.8−2.5 g yr^{-1} passes the lake. Taken together, the various measurements suggest that present loadings from the pulp mill are probably augmented by resuspension of older river and shallow lake sediments containing half as much again of contaminant. Prorating these figures using the maximum observed in the sediment cores implies that in the mid to late 1980s the mill may have released as much as 600 g yr^{-1} of 2,3,7,8-TCDF. This figure is very large, but perhaps not unfeasible given the estimated discharge of 5000 g of TCDF for all mills in British Columbia in 1991 (*42*).

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