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HISTORICAL DECLINE AND ALTERED CONGENER PATTERNS OF POLYCHLORINATED DIBENZO-*P*-DIOXINS AND DIBENZOFURANS IN FISH AND SEDIMENT IN RESPONSE TO PROCESS CHANGES AT A PULP MILL DISCHARGING INTO JACKFISH BAY, LAKE SUPERIOR

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Abstract: Improved regulations for pulp and paper mill effluents and an industry shift away from elemental chlorine bleaching in the 1990s greatly reduced the release of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) into the environment. However, the high potential of these contaminants to persist in sediment and bioaccumulate in biota means that they have remained a concern. To document current contamination from bleached kraft pulp mill effluent, PCDD/Fs were measured in white sucker (*Catostomus commersoni*) collected from Jackfish Bay, Lake Superior. These values were contrasted to historically reported fish data as well as PCDD/F patterns from dated sediment cores. Patterns of PCDD/Fs in sediment cores from Jackfish Bay and reference sites demonstrated a relationship between contamination and mill process changes. During the peak PCDD/F contamination period (1991), when the mill was still using elemental chlorine, the contamination patterns in fish and sediment were distinct and dominated by 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and 2,3,7,8-tetrachlorodibenzofuran. Following the reduction in the use of elemental chlorine during the early 1990s, a rapid decline was observed in PCDD/F contamination of fish tissue, and levels are now approaching background conditions with congener patterns more reflective of atmospheric sources. Although surface sediments from Jackfish Bay continue to have elevated PCDD/Fs, with some locations exceeding sediment quality guidelines, they do not appear to be highly bioavailable to benthic fish. *Environ Toxicol Chem* 2015;34:2489–2502. © 2015 SETAC

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INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are persistent organic pollutants that were historically formed as by-products of elemental chlorine bleaching during pulp and paper production. They have received international attention because of their high toxicity and long half-life in fish and sediment [1–4]. The presence of PCDD/Fs has been linked to the bleaching process in pulp and paper production, particularly the historical use of molecular chlorine (Cl_2) as a bleaching agent [5–8]. The implementation of new effluent regulations under the Canadian Environmental Protection Act and development of new Fisheries Act regulations in 1992, which included mandatory environmental effects monitoring, contributed to an industry shift toward the use of elemental chlorine-free bleaching practices [9,10]. The result of these process changes was a rapid decline of PCDD/Fs in effluent at bleached kraft pulp mills across Canada [11,12]. However, the persistence of highly chlorinated PCDD/F congeners may allow them to remain in sediment for long periods of time, providing a potential source of contamination to the receiving environment [4]. Because they are highly lipophilic and have a tendency to bioaccumulate in aquatic biota, PCDD/Fs may continue to pose a concern for aquatic ecosystem health and human consumption of resident fish species [13].

Jackfish Bay, Lake Superior, was listed as a Great Lakes Area of Concern in 1987 because of the quality of effluent discharged from the bleached kraft pulp mill located in Terrace Bay, Ontario, Canada. The Jackfish Bay Area of Concern included its embayments, Moberley Bay and Tunnel Bay, as well as a 14-km stretch of Blackbird Creek that receives effluent from the mill [14] (Figure 1). The benthic environment in Jackfish Bay, especially within Moberley Bay, has previously been identified as severely impacted with impaired benthic invertebrate community structure [15–17]. Studies conducted in the late 1980s and early 1990s identified a number of responses in fish collected from Jackfish Bay including delayed sexual maturity, depressed secondary sex characteristics in males, reduced circulating steroid hormone levels, metabolic disruption characterized by increased condition and liver size and decreased gonad size, and induction of liver detoxification enzymes [18–20]. At the same time, elevated PCDD/F concentrations were measured in the crustacean *Mysis relicta* and in white sucker (*Catostomus commersoni*) collected from Jackfish Bay, with PCDD/F contamination patterns consistent with the distinct congener pattern found in bleached kraft mill effluent [21,22]. A sediment core profile collected from Moberley Bay by Sherman et al. [22] demonstrated an abrupt appearance of tetrachlorodibenzofuran (TCDF) approximately in 1973, which remained elevated at the time of sampling in 1988. The sudden rise of TCDF concentrations corresponds to process upgrades at the mill involving chlorine gas bleaching

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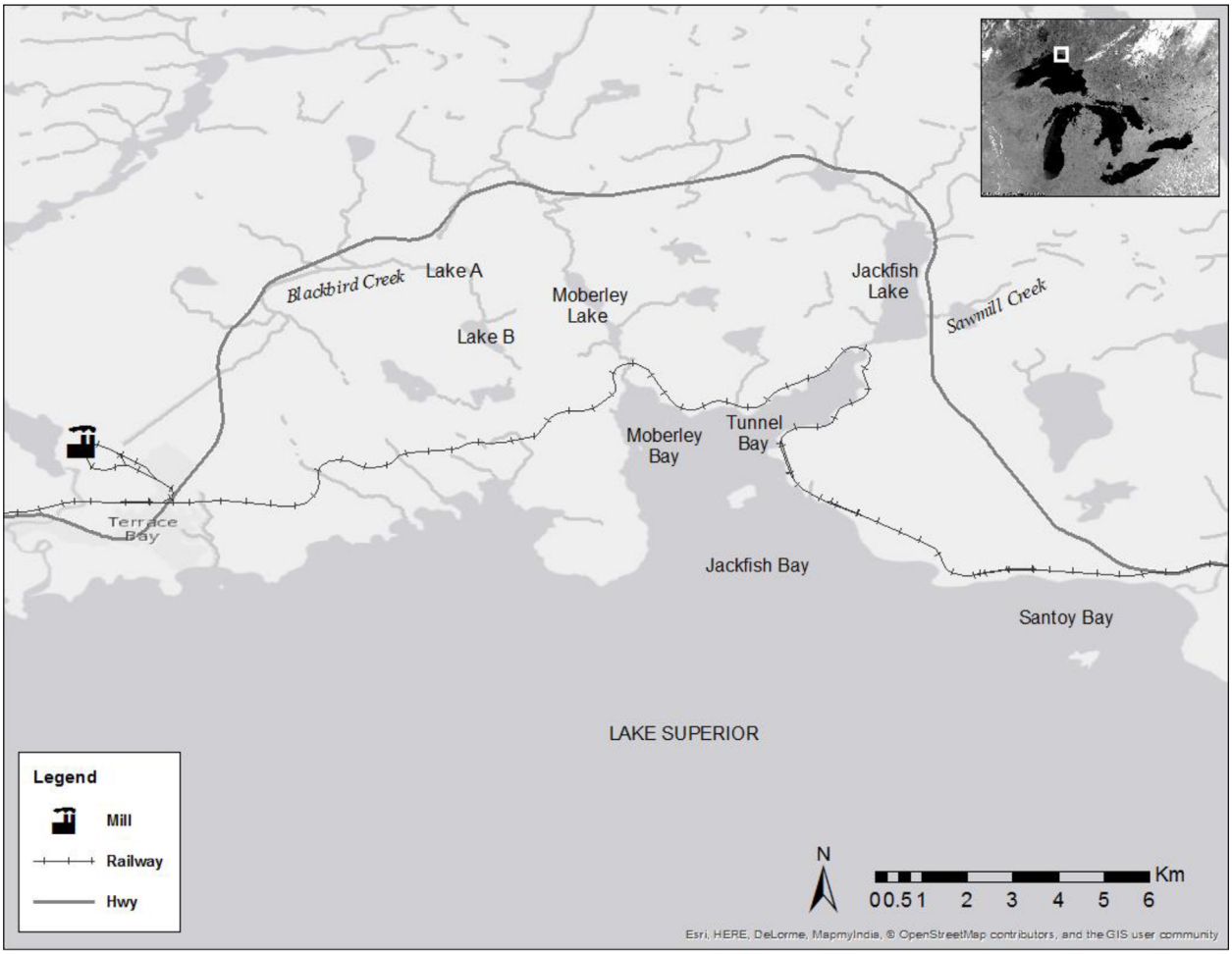

Figure 1. Map of study site at Jackfish Bay on the north shore of Lake Superior, Canada (inset). The Jackfish Bay area of concern in recovery includes Blackbird Creek, Moberley Bay, Tunnel Bay, and Jackfish Bay proper. The sediment reference site, Santoy Bay, is located to the east, just outside of the area of concern. A second reference site, Mountain Bay, is located approximately 60 km west on Lake Superior.

and the use of oil-based defoamers in brown stock washers containing furan precursors [22,23]. Increases in temperature during the chlorine bleaching process likely contributed to the formation of highly chlorinated polychlorinated dibenzofuran congeners [16,24].

Long-term studies have continued at Jackfish Bay over the last 27 yr [25] as the mill has undergone a number of process and treatment changes and temporary shutdowns (Table 1). Upgrades to mill processes have included installation of secondary treatment and removal of PCDD/Fs through increased chlorine dioxide (ClO_2) substitution. These upgrades resulted in reduced effluent toxicity, improved liver and gonad size, and partial recovery of reproductive function in white sucker [26]. However, complete recovery of fish populations has not been observed while the mill has remained in operation [25], and the responsible chemicals remain unidentified [27,28]. In early 2005, the mill went through the first of many temporary closures. The hardwood line was shut down in April 2005, followed in February 2006 by the softwood line. By fall 2006, a change in mill ownership had occurred, and the softwood line was reopened. In early 2009, the mill went through another period of reduced operations and closures. As of May 2011, Jackfish Bay has been designated an Area of Concern in Recovery under the Canada–US Great Lakes Water Quality Agreement [14]. Despite the observed signs of ecosystem recovery, benthic and fish community structures remain impaired throughout Jackfish Bay [29]. After reopening in 2010, the mill underwent a 12-mo shutdown, starting in October 2011, along with a change in ownership. The facility is expected to be converted to a dissolving pulp process (for the production of viscose staple fiber) over the next few years, with final completion expected in 2016 [30].

The objective of the present study was to re-examine how PCDD/F concentrations and contamination patterns have changed in fish and sediment in response to mill process changes and temporary closures and to extend the assessment to current conditions in the Jackfish Bay Area of Concern in Recovery. The concentration of PCDD/Fs in male white sucker collected from Jackfish Bay and a remote reference site (Mountain Bay) in Lake Superior during 2011 and 2012 were compared with historical data collected in the early 1990s, as previously reported by Servos et al. [12,21]. Concentrations of PCDD/Fs were measured in dated sediment cores from Jackfish Bay and a reference site (Santoy Bay, Lake Superior) to compare with historical contamination of white sucker and to examine the relationship between PCDD/F contamination and process changes at the pulp mill. Surface sediment was collected throughout Jackfish Bay and reference sites (Santoy Bay and Mountain Bay) in 2012 to assess the present level and distribution of PCDD/F contamination. The present study further extends previous efforts by evaluating long-term changes in PCDD/F contamination patterns in fish and sediment

Table 1. Summary of process changes that have occurred at the bleached kraft pulp mill in Terrace Bay, Ontario, Canada, including changes to the hardwood (no. 1 mill) line, the softwood (no. 2 mill) line, and the bleaching sequence[a]

Year	Process change
1948	Mill began operations as an unbleached kraft mill with capacity of 270 ADMT/d (hardwood only). No effluent treatment.
1958	Cl added to bleaching circuit.
1959	Cold bleaching introduced.
1972	Mill expansion to fully bleached 2-line "hot" kraft mill with increased capacity of 400 ADMT/d. From 1972 to 1978, the mill used a mercury anode to produce chlorine gas for the bleaching process.
1975	Blackbird Creek diverted to bypass Lake A. Production capacity of 435 ADMT/d.
1978	New bleaching and finishing plant brought online, increasing capacity to 1135 ADMT/d; primary treatment facility installed incorporating 2 reactor clarifiers; no. 2 mill and dry debarking added.
1979	Clarifier installed for alkaline sewer.
1981	Major reconstruction after a fire, including installation of condensate stripper, turpentine decanter, NCG collection and destruction system, bypass domestic sewage treatment plant, and clarifier screening system.
1984	Spill control system completed in no. 2 mill; improved soap recovery; increased ClO_2 substitution; no.1 mill dedicated to hardwood; polymer feed system added to alkaline clarifier; additional clarifier added and improvements to no. 2 brownstock washing.
1985	No. 2 brownstock closure; spill control system completed in no. 1 mill; extraction oxidation (E_0) stage added to no. 2 bleachery; new instrumentation for bleachery to decrease chemical use.
1986	Completed modification of no. 1 brownstock washers: improved soap recovery, foam control and vacuum improvements.
1989	Secondary treatment installed: ASB; papricycle stage (wash cycle) added.
1990	Increased ClO_2 substitution to approximately 50%; hypochlorite replaced with papricycle; new control system.
1991	Chlorine strength analyzers and recirculation piping installed; new chip thickness screening plant and & hot water stave replaced; increased softwood production by 45 ADMT/d.
1993	Improvements to concentrator for no. 2 mill recovery boiler (black liquor) leading to formation of TRS compounds resulting in improved air quality; increased ClO_2 substitution from 50% to 70%.
1994	Replaced 250-m section of creosote-treated wooden stave piping.
1995	Updated ClO_2 generator from the R3 process to R8, allowing the mill to continually produce ECF pulp in both no. 1 and no. 2 mills and lowering the discharge of chlorinated organics; no untreated effluent has bypassed the ASB and no reported spills.
1996	More mature wood purchased (less lignin), resulting in less sulfur lignin by-products.
1997	Hydrogen peroxide use started in no. 2 mill bleaching sequence E2 stages; average production 1260 ADMT/d.
1998	Hydrogen peroxide use started in no. 2 mill bleaching sequence E0 stage; no. 1 mill switched production to batch softwood for periodic short campaigns and to 100% ECF bleaching (October).
1999	No. 2 mill switched over to 100% ECF bleaching in April 1999.
2000	New brownstock washing showers in September; mill producing bleached sulfate pulp at an average rate of 1260 ADMT/d.
2003	Acid-activated oxygen bleaching stage with 2 reactors installed in third 3rd stage of no. 2 bleach plant process; modification made to third stage of bleaching process reduced AOX by 47%.
2005	No. 1 mill shutdown 1 April 2005.
2006	No. 2 mill shutdown February 2006. Buchanan Forest Products Ltd. announced takeover of the Terrace Bay pulp mill and woodland operations. Formal transfer between Neenah and Buchanan was finalized in fall 2006, and mill reopened (softwood only) as Terrace Bay Pulp Inc. on 20 September 2006.
2007	OMOE issued an order to Terrace Bay Pulp Inc. requiring them to submit either an application to approve their bark resources pile as a waste transfer/processing site (including a schedule to remove the material from the site within 5 years) or alternatively provide supplemental information to allow for the designation/closure of the area as a waste disposal site, by 31 July 2007. The order also required the company to install a new groundwater monitoring well and conduct groundwater and surface water monitoring in the vicinity of the BRP, with a monitoring report to the ministry by March 2008.
2008	New steam turbine in operation; 1 mo "downtime" in November to December 2008.
2009	Mill reduced operations in no. 2 mill and shut down no. 1 mill indefinitely in January, followed by complete mill closure in February 2009; company filed for creditor protection in March 2009.
2010	Mill reopened October 2010.
2011	Mill announced temporary shutdown in October 2011.
2012	Mill purchased by Aditya Birla Group in July 2012. The mill will be operated under the Canadian subsidiary AV Terrace Bay. Operation of the NBSK process commenced in October 2012 with plans to convert the facility to a dissolving pulp mill over a 2-yr to 3-yr period.

[a]Adapted from Bowron et al. [25] with modification [13,17,32–33,41,72,73].
ADMT = air-dried metric tonne; AOX = adsorbable organic halides; ASB = aerated stabilization basin; ECF = elemental chlorine-free; NCG = noncondensable gas; OMOE = Ontario Ministry of the Environment; TRS = total reduced sulfur; BRP = bark resource pile; NBSK = Northern bleached softwood kraft.

collected from Jackfish Bay, in comparison with local reference sites. The results of the present study provide a comprehensive examination of changes in PCDD/F contamination in fish and sediment (dated sediment cores) and an evaluation of the time frame of recovery for Jackfish Bay, in response to process changes at the pulp mill over several decades.

MATERIALS AND METHODS

Study site

The bleached kraft pulp mill in Terrace Bay discharges effluent into Blackbird Creek, where it travels 14 km to reach Moberley Bay, the west arm of Jackfish Bay on Lake Superior (Figure 1). The pulp mill is the only known source of contamination to Jackfish Bay, which does not receive any additional industrial or municipal effluent [16]. Since the mill began operations in 1948, it has experienced a number of process changes, including multiple periods between 2005 and 2012 during which the facility was shut down for extended periods of time (Table 1). Production ceased over the period of the present study from October 2011 until October 2012, when the mill reopened under new ownership [30].

White sucker residing in Moberley Bay migrate during the spring through Tunnel Bay (part of Jackfish Bay) to Sawmill Creek, a small stream connected to Jackfish Lake (Figure 1). Tunnel Bay historically has received <1% effluent pollution and has been used as an additional reference site for invertebrate community assessment in environmental effects monitoring [31]. Neither Jackfish Lake nor Sawmill Creek receives industrial or municipal effluent.

Mountain Bay was used in the present study as the reference site for PCDD/F analysis of white sucker because of its location (~60 km west of Jackfish Bay) and similarity in fish community structure, as well as its historical use as a reference site for fish studies conducted at Jackfish Bay [19–21]. Santoy Bay, located immediately adjacent to Jackfish Bay (Figure 1), was used in the present study as an additional reference site for PCDD/F analysis of sediment. Neither Mountain Bay nor Santoy Bay receives industrial or municipal effluent. The Canadian Pacific rail line runs along the north shore of Lake Superior, but this is not believed to contribute to contaminant levels measured at any of the sites.

Fish collection and sampling procedures

Detailed sampling methods for fish collected between 1989 and 1995 have been reported by Servos et al. [12,21]. For the present study, fish were collected using the same sampling procedures and locations. White sucker were collected from Jackfish Bay and Mountain Bay prior to the mill closure in fall 2011 as well as twice during the closure period (spring and fall 2012). Fish collected during the gonadal recrudescent period (fall) were captured using overnight gill net sets (3.5- to 4-inch mesh). Prespawning white sucker were collected in the spring from spawning streams, Sawmill Creek (Jackfish Bay) and Little Gravel River (Mountain Bay), using overnight hoop net sets. For each site, 20 males and 20 females were sampled as part of a long-term monitoring program. A subsample of liver tissue (~5–10 g) was removed from each fish, wrapped in fired (400 °C, 2 h) foil, and frozen at –20 °C. For the present study, liver samples of male white sucker were randomly selected from Jackfish Bay ($n = 6$) and Mountain Bay ($n = 3$) during each sampling period for PCDD/F analysis. Fish collected in 2011 and 2012 were similar in size (length and weight) and age to those collected historically, although fish in fall 2011 tended to be younger (Tables 2 and 3).

Sediment collection

Sediment samples (surface and core) were collected from Jackfish Bay and 2 reference locations on the north shore of Lake Superior in summer 2012, during the time that the mill was shut down and undergoing a change in ownership. Surface sediment was collected at various distances from the mouth of Blackbird Creek to represent 4 areas within Jackfish Bay—Blackbird Creek (BBC; $n = 4$), Moberley Bay ($n = 2$), Jackfish Bay (JFB; $n = 2$), and Tunnel Bay ($n = 2$)—as well as 2 reference locations—Santoy Bay ($n = 2$) and Mountain Bay (MTB; $n = 2$). In the nearshore areas, surface sediment (i.e., top 2 cm) samples were collected using an Ekman grab. Ensuring that the sample was not mixed, a 5-cm (depth) core was obtained from the middle of each grab and sectioned at 1-cm intervals. In areas nearest to the shore, where sandy sediment was collected (sites BBC 104 and BBC 105), a mixed grab was used instead. In addition to surface sediment samples, a sediment core was collected from the depositional areas of Moberley Bay, Jackfish Bay, and Santoy Bay using a gravity corer with an internal diameter of 6.35 cm. Each core was sectioned into 1-cm intervals up to the depth at which a change in sediment composition to the original silt-clay sediment was visible (~20–30 cm). All sediment samples were stored in certified clean wide-mouth amber glass jars and frozen (–20 °C) immediately after collection.

^{210}Pb dating of sediment cores

Total wet weight of each sediment core sample (1-cm intervals) was determined prior to subsampling. A well-mixed subsample (0.5 ± 0.05 g wet wt) of sediment from each 1-cm core section was collected to determine water (90 °C, 24 h), organic matter (550 °C, 1 h), and carbonate (950 °C, 1 h) content using a standard sequential loss-on-ignition procedure [32]. Measurements of wet weight and water content were used to calculate cumulative dry mass, which was required to develop the sediment core chronology.

Each sediment core was dated by gamma-ray spectrometric determination of ^{210}Pb, ^{137}Cs, and ^{226}Ra (inferred from the mean of ^{214}Bi and ^{214}Pb) activity at continuous 1-cm intervals. Subsamples (3–4 g dry wt) of freeze-dried sediment were packed into preweighed tubes (product no. 55.524; Sarstedt) to a height of 35 mm. A trifluoroacetyl silicone septum (Supelco) was placed over the sediment, followed by 1 cm^3 of epoxy resin. A 3-wk equilibration period followed to allow ^{222}Rn and its decay products to reach equilibrium with the parent isotope, ^{226}Ra. Samples were analyzed in an Ortec coaxial HPGe Digital Gamma Ray Spectrometer (GWL-120-15) interfaced with Maestro 32 software (Ver 5.32). Sample count times (1–5 d) were varied to allow net ^{210}Pb counts to exceed 10 times the standard deviation of sample blanks [33]. Background counts based on sediment-free "blanks" were conducted at regular intervals (first and last samples of each core and every 6–8 samples).

The constant rate of supply model was used to develop the ^{210}Pb core chronologies as described by Appleby [34]. The constant rate of supply model requires an estimate of supported ^{210}Pb activity, as determined by the activity of ^{214}Bi and ^{214}Pb. It assumes a constant supply of ^{210}Pb while considering variations in the sedimentation rate [34]. The mean value of all ^{226}Ra determinations for a given core was considered representative of supported ^{210}Pb activity. Background depth (where total ^{210}Pb activity equals supported ^{210}Pb activity) was determined similar to that described by Binford [35]. For further details regarding analysis, see Hall et al. [36].

PCDD/F analysis

Analysis of PCDD/Fs was conducted by AXYS Analytical Services according to US Environmental Protection Agency (USEPA) method 1613B [37] with some modifications (AXYS method MLA-017). Briefly, liver (1–5 g wet wt) or freeze-dried sediment (4–10 g dry wt) samples were homogenized and mixed in sodium sulfate, allowed to dry for 12 h to 24 h, and spiked with an internal standard mixture of ^{13}C- labeled isotopes. Samples were extracted for 18 h to 24 h in a Soxhlet extractor with 1:1 v/v dichloromethane:hexane (tissue) or 80:20 v/v toluene:acetone (sediment). Lipid removal and sample cleanup were conducted manually by gel permeation chromatography. The first column was a multilayer acid-base silver nitrate ($AgNO_3$) silica column (20 g 44% tissue, 30 g 44% sediment), followed by a Florisil (tissue) or copper column (sediment). Finally, activated alumina/carbon/Celite combination columns were used to isolate planar compounds. Extracts were concentrated to near dryness using nitrogen following cleanup. Lipid content of liver tissue was determined gravimetrically from the Soxhlet extracts. Sample analysis was performed with isotope dilution using high-resolution gas chromatography/high-resolution mass spectrometry. Quantification of target analytes was determined according to USEPA methods 8290 and 8290A [38,39]. For each batch of 20 or fewer samples, 1 spiked reference matrix, 1 procedural blank, and 1 replicate were processed. Final concentrations were corrected for the recovery of the ^{13}C labeled standards.

Table 2. Fall PCDD/F concentrations and total TEQ calculated as wet weight and lipid normalized values in liver tissue of male white sucker collected from Jackfish Bay and Mountain Bay between 1989 and 2012, as well as average length, weight, and age of white sucker for each sampling site and year[a]

	Sample site and year									
	JFB 1989	JFB 1991	JFB 1993	JFB 1995	JFB 2011	JFB 2012	MTB 1989	MTB 1991	MTB 2011	MTB 2012
Fall PCDD/F concentrations (pg/g wet wt)										
2,3,7,8-TCDD	44.2 ± 19.6	52.4 ± 17.5	17.7 ± 4.83	2.70 ± 1.14	2.79 ± 1.72	1.37 ± 0.98	4.03	ND	0.73 ± 0.17	0.47 ± 0.41
1,2,3,7,8-PeCDD	ND	2.12 ± 0.64	6.38 ± 6.19	ND	0.56 ± 0.19	0.43 ± 0.11	ND	ND	0.62 ± 0.18	0.42 ± 0.19
1,2,3,4,7,8-HxCDD	ND	0.43	3.44 ± 3.30	ND	0.19 ± 0.09	0.20 ± 0.05	ND	ND	0.19	N.D
1,2,3,6,7,8-HxCDD	1.68	0.61 ± 0.11	3.05 ± 3.35	1.11	0.26 ± 0.12	0.20 ± 0.09	ND	16.5 ± 19.0	0.35 ± 0.07	0.27
1,2,3,7,8,9-HxCDD	ND	ND	3.03 ± 3.59	ND	0.18	0.15 ± 0.04	ND	ND	0.15	0.20
1,2,3,4,6,7,8-HpCDD	1.68	1.43 ± 0.21	4.56 ± 4.32	1.64 ± 0.16	0.26 ± 0.07	0.22 ± 0.07	ND	3.77	0.30 ± 0.02	0.23 ± 0.12
OCDD	120 ± 161	4.38 ± 1.02	4.67 ± 3.25	13.4 ± 10.2	0.32 ± 0.15	0.53 ± 0.53	35.54	18.9 ± 16.0	0.25 ± 0.07	0.44 ± 0.07
2,3,7,8-TCDF	285 ± 136	265 ± 111	101 ± 49.1	21.0 ± 9.32	33.6 ± 23.9	20.8 ± 17.2	20.1 ± 3.65	5.35 ± 3.16	2.53 ± 0.68	1.31 ± 0.67
1,2,3,7,8-PeCDF	ND	3.68 ± 1.20	5.34 ± 4.04	2.15 ± 1.83	0.39 ± 0.17	0.33 ± 0.15	ND	ND	0.35 ± 0.09	0.20 ± 0.10
2,3,4,7,8-PeCDF	10.4 ± 3.98	12.5 ± 2.84	5.09	ND	1.33 ± 0.69	0.75 ± 0.31	ND	1.55	0.59 ± 0.15	0.46 ± 0.26
1,2,3,4,7,8-HxCDF	ND	0.72 ± 0.16	2.75 ± 3.21	1.06	ND	0.15 ± 0.06	ND	ND	N.D	N.D
1,2,3,6,7,8-HxCDF	ND	0.29	2.53 ± 3.11	ND	ND	0.20	ND	ND	N.D	N.D
1,2,3,7,8,9-HxCDF	ND	ND	2.60 ± 3.11	ND	ND	0.16 ± 0.06	ND	ND	N.D	N.D
2,3,4,6,7,8-HxCDF	ND	0.32	2.49 ± 3.05	ND	ND	0.16 ± 0.05	ND	ND	N.D	N.D
1,2,3,4,6,7,8-HpCDF	ND	1.49 ± 0.19	4.07 ± 4.21	ND	ND	0.15 ± 0.03	ND	ND	N.D	0.22
OCDF	ND	4.63 ± 0.49	2.85 ± 3.11	ND	ND	0.21 ± 0.10	ND	ND	N.D	0.28
Tetra-dioxins	44.4 ± 19.5	52.4 ± 17.5	17.7 ± 4.83	2.76 ± 1.16	3.04 ± 2.04	1.49 ± 1.15	6.59 ± 3.61	ND	1.73 ± 1.03	0.33
Penta-dioxins	ND	2.12 ± 0.64	6.38 ± 6.19	ND	0.57 ± 0.19	0.41 ± 0.13	ND	ND	0.62 ± 0.18	0.29
Hexa-dioxins	1.68	0.91 ± 0.37	8.37 ± 9.97	1.11	0.30 ± 0.20	0.29 ± 0.18	ND	12.0 ± 15.6	0.83	0.47
Hepta-dioxins	2.31	1.68 ± 0.52	4.90 ± 4.02	1.64 ± 0.16	0.28 ± 0.06	0.19 ± 0.04	ND	3.77	0.30 ± 0.02	0.14
Tetra-furans	285 ± 136	270 ± 108	101 ± 49.1	21.1 ± 9.32	34.2 ± 24.2	22.6 ± 18.3	20.1 ± 3.65	6.32 ± 3.57	4.84 ± 1.66	3.41 ± 3.74
Penta-furans	10.8 ± 4.22	16.8 ± 4.09	8.33 ± 4.15	2.15 ± 1.83	2.10 ± 1.32	1.33 ± 0.73	ND	1.55	2.58 ± 1.70	1.89 ± 1.80
Hexa-furans	ND	1.17 ± 0.28	10.4 ± 12.5	1.06	ND	0.47 ± 0.50	ND	ND	0.32	N.D
Hepta-furans	ND	1.49 ± 0.19	4.07 ± 4.21	0.64	ND	0.28 ± 0.12	ND	ND	N.D	0.22
n	4	5[c]	4	8	6	6	3	3	3	3
% Lipid	17.8 ± 8.80	14.8 ± 4.38	67.1 ± 12.4	7.21 ± 2.63	18.9 ± 5.17	11.5 ± 5.49	17.9 ± 10.6	17.7 ± 4.15	22.4 ± 12.2	8.59 ± 2.96
TEQ (pg TEQ /g wet wt)[b]	65.6 ± 28.0	74.29 ± 20.9	29.1 ± 11.6	4.82 ± 1.78	5.82 ± 3.42	3.34 ± 2.05	5.44 ± 1.89	1.93 ± 0.85	1.88 ± 0.45	1.06 ± 0.69
$TEQ_{(lipid)}$ (pg TEQ /g lipid)[b]	416 ± 225	563 ± 199	42.4 ± 9.42	70.8 ± 27.1	30.2 ± 13.2	27.8 ± 6.24	33.3 ± 8.14	11.9 ± 6.84	9.44 ± 3.06	11.8 ± 3.85
Average length (cm)	38.7 ± 1.3	38.5 ± 2.3	39.5 ± 1.6	38.3 ± 2.3	39.3 ± 1.1	42.6 ± 1.7	42.7 ± 1.48	42.8 ± 2.29	46.8 ± 10.1	41.5 ± 0.70
Average weight (g)	1055 ± 158	865 ± 160	972 ± 106	852 ± 170	963 ± 35.8	1195 ± 184	1210 ± 110	1087 ± 46.0	902 ± 94.1	943 ± 64.8
Average age (yr)	12.5 ± 4.4	10.8 ± 3.8	n/a	n/a	6.5 ± 1.4	10.7 ± 3.2	13.3 ± 4.5	10.3 ± 2.1	6.0 ± 2.8	11.0 ± 1.7

[a]Data are presented as mean ± standard deviation.
[b]TEQ calculated using fish toxic equivalency factors [48].
[c]Lipid-normalized TEQ values calculated using $n = 4$.
PCDD/F = polychlorinated dibenzo-*p*-dioxins and dibenzofurans; TEQ = toxic equivalency; JFB = Jackfish Bay; MTB = Mountain Bay; HpCDD = heptachlorodibenzo-*p*-dioxin; HpCDF = heptachlorodibenzofuran; HxCDD = hexachlorodibenzo-*p*-dioxin; HxCDF = hexachlorodibenzofuran; OCDD = octachlorodibenzodioxin; OCDF = octachlorodibenzofuran; PeCDD = pentachlorodibenzo-*p*-dioxin; PeCDF = pentachlorodibenzofuran; TCDD = tetrachlorodibenzo-*p*-dioxin; TCDF = tetrachlorodibenzofuran; ND = not detected.

Table 3. Spring PCDD/F concentrations and total TEQ calculated as wet weight and lipid normalized values in liver tissue of male white sucker collected from Jackfish Bay and Mountain Bay between 1989 and 2012, as well as average length, weight, and age of white sucker for each sampling site and year[a]

	Sample site and year						
	JFB 1989	JFB 1991	JFB 1993	JFB 1995	JFB 2012	MTB 1989	MTB 1991
Spring PCDD/F concentrations (pg/g wet wt)							
2,3,7,8-TCDD	26.6 ± 19.1	70.8 ± 23.5	23.5 ± 16.2	3.36 ± 1.91	2.40 ± 2.88	1.20 ± 0.38	1.70 ± 0.53
1,2,3,7,8-PeCDD	1.93 ± 0.46	2.87 ± 0.46	ND	ND	0.86 ± 0.30	0.87	ND
1,2,3,4,7,8-HxCDD	0.43	ND	1.51	ND	0.22 ± 0.09	0.32 ± 0.08	ND
1,2,3,6,7,8-HxCDD	1.69 ± 0.46	2.80 ± 0.73	1.53	2.30 ± 0.15	0.35 ± 0.18	1.45 ± 0.01	1.35 ± 0.18
1,2,3,7,8,9-HxCDD	ND	ND	1.19	ND	0.170	0.63 ± 0.06	ND
1,2,3,4,6,7,8-HpCDD	1.37 ± 0.74	2.31 ± 1.00	5.58 ± 3.14	3.98 ± 2.41	0.38 ± 0.15	1.18 ± 0.40	3.07 ± 2.13
OCDD	3.62 ± 1.55	6.85 ± 3.87	14.8 ± 2.87	24.5 ± 30.0	0.40 ± 0.29	3.72 ± 0.68	4.13 ± 2.32
2,3,7,8-TCDF	202 ± 169	280 ± 111	140 ± 162	9.28 ± 4.48	32.8 ± 43.4	4.59 ± 2.67	5.34 ± 1.19
1,2,3,7,8-PeCDF	3.63 ± 1.06	5.92 ± 0.80	4.69	ND	0.51 ± 0.39	ND	ND
2,3,4,7,8-PeCDF	15.0 ± 9.31	20.2 ± 2.34	ND	4.44 ± 1.58	1.55 ± 1.25	ND	ND
1,2,3,4,7,8-HxCDF	0.96 ± 0.57	ND	0.9	1.53 ± 0.75	0.18 ± 0.05	ND	ND
1,2,3,6,7,8-HxCDF	ND	0.95	ND	ND	0.13	ND	ND
1,2,3,7,8,9-HxCDF	ND	0.95	0.58	ND	ND	ND	ND
2,3,4,6,7,8-HxCDF	ND	0.7	ND	ND	0.13	ND	ND
1,2,3,4,6,7,8-HpCDF	0.43 ± 0.31	0.80 ± 0.45	ND	4.21 ± 3.83	ND	0.27 ± 0.04	0.20 ± 0.18
OCDF	0.48 ± 0.37	1.41 ± 0.37	2.60 ± 3.87	9.38 ± 10.86	ND	0.44 ± 0.10	0.51 ± 0.12
Tetra-dioxins	26.7 ± 19.0	71.7 ± 23.8	23.9 ± 15.9	3.36 ± 1.91	2.44 ± 2.98	1.69 ± 0.17	1.70 ± 0.53
Penta-dioxins	1.50 ± 0.77	2.87 ± 0.46	ND	ND	0.86 ± 0.30	0.87	ND
Hexa-dioxins	1.71 ± 0.69	2.80 ± 0.73	ND	1.83 ± 0.95	0.56 ± 0.49	1.45 ± 0.01	1.47 ± 0.04
Hepta-dioxins	1.28 ± 1.05	3.14 ± 1.78	6.84 ± 3.03	4.39 ± 4.10	0.54 ± 0.31	1.47 ± 0.17	3.26 ± 1.88
Tetra-furans	208 ± 168	281 ± 111	140 ± 162	9.41 ± 4.54	34.1 ± 44.2	5.41 ± 3.11	3.47 ± 3.23
Penta-furans	23.4 ± 20.1	27.6 ± 2.66	15.4 ± 11.4	3.90 ± 1.93	3.43 ± 2.47	2.94 ± 2.51	ND
Hexa-furans	1.71 ± 1.84	2.60	0.83	2.17 ± 1.09	0.39 ± 0.38	ND	ND
Hepta-furans	0.43 ± 0.31	0.89 ± 0.51	ND	4.21 ± 3.83	ND	0.27 ± 0.04	0.33
n	6	4	6	16	5	3	3
% Lipid	30.6 ± 9.61	40.7 ± 6.47	19.7 ± 7.90	11.3 ± 12.6	13.0 ± 7.07	32.5 ± 4.35	28.8 ± 6.58
TEQ (pg TEQ /g wet wt)[b]	44.8 ± 31.7	97.8 ± 28.3	30.0 ± 26.7	6.22 ± 2.82	5.82 ± 6.04	2.36 ± 0.59	2.46 ± 0.97
$TEQ_{(lipid)}$ (pg TEQ /g lipid)[b]	149 ± 115	238 ± 38.1	147 ± 91.7	97.6 ± 73.0	38.7 ± 19.4	7.19 ± 0.86	8.38 ± 1.64
Average length (cm)	37.4 ± 3.00	36.8 ± 2.85	37.7 ± 1.8	40.8 ± 3.8	40.1 ± 1.7	39.9 ± 1.64	39.0 ± 1.03
Average weight (g)	860 ± 155	682 ± 171	760 ± 95.2	849 ± 230	872 ± 108	889 ± 87.9	740 ± 20.4
Average age (yr)	9.0 ± 3.3	n/a	n/a	n/a	10.0 ± 2.2	8.0 ± 1.0	8.0 ± 0.0

[a]Data are presented as mean ± standard deviation.
[b]TEQ calculated using fish toxic equivalency factors [48].
PCDD/F = polychlorinated dibenzo-*p*-dioxins and dibenzofurans; TEQ = toxic equivalency; JFB = Jackfish Bay; MTB = Mountain Bay; HpCDD = heptachlorodibenzo-*p*-dioxin; HpCDF = heptachlorodibenzofuran; HxCDD = hexachlorodibenzodioxin; HxCDF = hexachlorodibenzofuran; OCDD = octachlorodibenzodioxin; OCDF = octachlorodibenzofuran; PeCDD = pentachlorodibenzo-*p*-dioxin; PeCDF = pentachlorodibenzofuran; TCDD = tetrachlorodibenzo-*p*-dioxin; TCDF = tetrachlorodibenzofuran; ND = not detected.

Statistical analysis

Toxic equivalency (TEQ) was calculated using congener-specific fish toxic equivalency factors (TEFs) reported by the World Health Organization [40]. The TEQ values for tissue samples are reported as wet weight (pg/g wet wt) and lipid-normalized (pg/g lipid) values, whereas sediment TEQs are reported on a dry weight (pg/g dry wt) and organic matter–normalized (pg/g organic matter) basis. For the purposes of comparison, raw PCDD/F congener concentrations were used to calculate TEQs using World Health Organization TEF values [40] on all fish, including those previously reported [12,21].

Where PCDD/F concentrations were below detection limits (reported as *not detected*), a value of one-half of the sample detection limit was used to calculate TEQ. Detection limits were not available for white sucker tissue samples collected during spring and fall 1995; TEQ values for samples reported as not detected during this time were calculated using 1993 mean detection limits for each congener. Normality was examined using normal-quantile plots for each site and season. Data were $\log_{10}$-transformed and analyzed for differences ($\alpha = 0.05$) in mean TEQ values between sampling sites among years using 1-way analysis of variance, followed by Tukey's honestly significant difference test performed using the software IBM SPSS Statistics 21. All statistical tests were performed between samples collected during the same season, unless otherwise noted. White sucker were collected from the reference site at Mountain Bay during spring (site MTB 89/91) and fall (sites MTB 89/91, MTB 11/12). Unless otherwise noted, white sucker collected from Jackfish Bay during 1989–1995 collections were compared with site MTB 89/91 samples and white sucker collected in 2011 and 2012 were compared with site MTB 11/12 samples. Principal component analysis and ordination plots were developed using SYSTAT 12 (Systat Software) incorporating mean PCDD/F congener concentrations in liver tissue of male white sucker, dated sediment cores, or surface sediment by site and year (all data were standardized).

RESULTS

PCDD/F contamination of white sucker

Contamination with PCDD/Fs observed in male white sucker collected from Jackfish Bay declined over the period 1991 to 2012 (Figure 2), with the highest mean liver TEQ concentrations observed in fish collected during 1991. There was no difference between mean liver TEQ measured in 1989 compared with 1991 ($p = 1.00$, Tukey's honestly significant difference) or 1993 ($p = 0.444$, Tukey's honestly significant difference) for fish collected during the fall (Figure 2A). However, the mean TEQ of

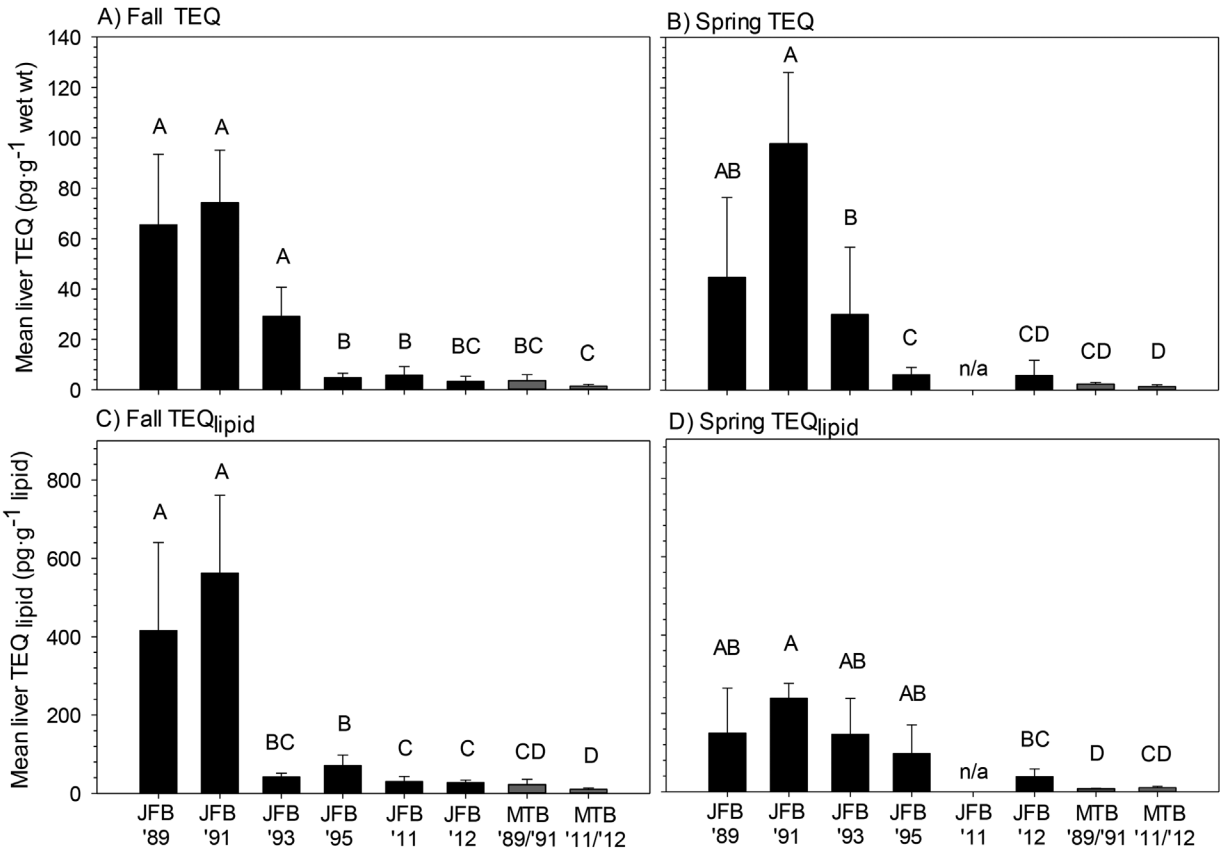

Figure 2. Mean liver toxic equivalency (TEQ; pg/g wet wt) and lipid-normalized TEQ (pg/g lipid), calculated using fish toxic equivalency factor values, for liver tissue of male white sucker collected from Jackfish Bay (black) and Mountain Bay (gray) during fall (**A**,**C**) and spring (**B**,**D**). Bars represent mean TEQ ± standard deviation, and letters indicate significant difference ($p < 0.05$, Tukey's honestly significant difference). MTB 11/12 represent fish collected during fall sampling only for all plots. JFB = Jackfish Bay; MTB = Mountain Bay.

white sucker collected during the spring of 1993 was significantly ($p = 0.012$, Tukey's honestly significant difference) lower compared with that from fish collected in spring 1991 (Figure 2B). Furthermore, a significant reduction in mean TEQ was measured in white sucker liver tissue of fish collected in 1995 compared with 1993 during both spring ($p = 0.005$, Tukey's honestly significant difference) and fall ($p < 0.001$, Tukey's honestly significant difference). This decline in liver TEQ corresponds to an increase, from 50% to 70%, in the amount of ClO_2 substitution used in mill processes (Table 1). The lipid-normalized mean TEQ values of male white sucker collected from Jackfish Bay during spring and fall showed a similar pattern to nonnormalized values, reaching the highest observed level of PCDD/F contamination in 1991, followed by a decline in recent years (Figure 2C and D). Mean TEQ measured in the liver tissue of white sucker collected from Jackfish Bay (during spring and fall) between 1989 and 2012 ranged from 3.35 pg/g to 97.8 pg/g (wet wt). White sucker collected from the reference site at Mountain Bay had notably lower PCDD/F contamination, with mean TEQ ranging from 1.06 pg/g to 2.46 pg/g (wet wt), with the exception of an elevated level (5.44 ± 1.89 pg TEQ/g) during fall 1989. Mean TEQs measured in white sucker collected from Mountain Bay were significantly ($p < 0.05$) lower compared with fish collected at Jackfish Bay during both fall and spring (Figure 2) between 1989 and 2011. White sucker PCDD/F contamination in Jackfish Bay appears to be approaching background (reference) levels in recent years. In 2012, during the period when the mill was closed, mean TEQ values illustrated little (lipid-normalized) or no (wet wt) statistically significant difference ($p < 0.05$) compared with reference fish.

A distinct contaminant profile was evident in fish and sediment from Jackfish Bay, compared with Mountain Bay. The contaminant profile observed in white sucker from Jackfish Bay was consistently dominated by 5 congeners: 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD); 2,3,7,8-TCDF; 2,3,4,7,8-pentachlorodibenzofuran (PeCDF); 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin (PeCDD); and 1,2,3,7,8-PeCDF (Tables 2 and 3). No difference in relative contribution to total calculated TEQ values was observed in individual congeners between 1989 and 2012. In fall 1989 and 1995, elevated concentrations of octachlorodibenzodioxin (OCDD) were observed in white sucker from both Jackfish Bay and Mountain Bay. Regardless of this, the contribution to total TEQ remained small and was not significant. In general, 2,3,7,8-TCDD and 2,3,7,8-TCDF had the greatest influence on total calculated TEQ values in fish collected at Jackfish Bay between 1989 and 2012. At Mountain Bay, total TEQ calculations for white sucker liver tissue were influenced by a broader range of PCDD/F congeners, compared with Jackfish Bay. The contaminant profile of reference fish from Mountain Bay was consistently dominated by 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD (Tables 2 and 3) during the period from 1989 to 2012. An exception to that pattern was during fall 1991, when 2,3,7,8-TCDD accounted for only a small portion of mean TEQ calculations.

In the principal component analysis, the first principal component (PC1) explained 38.6% of the total variance and had many different PCDD/F congeners, including 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD, loading highly (Figure 3A; Supplemental Data, Table S1). The second principal component (PC2) explained 16.5% with several congeners, including 2,3,7,8-

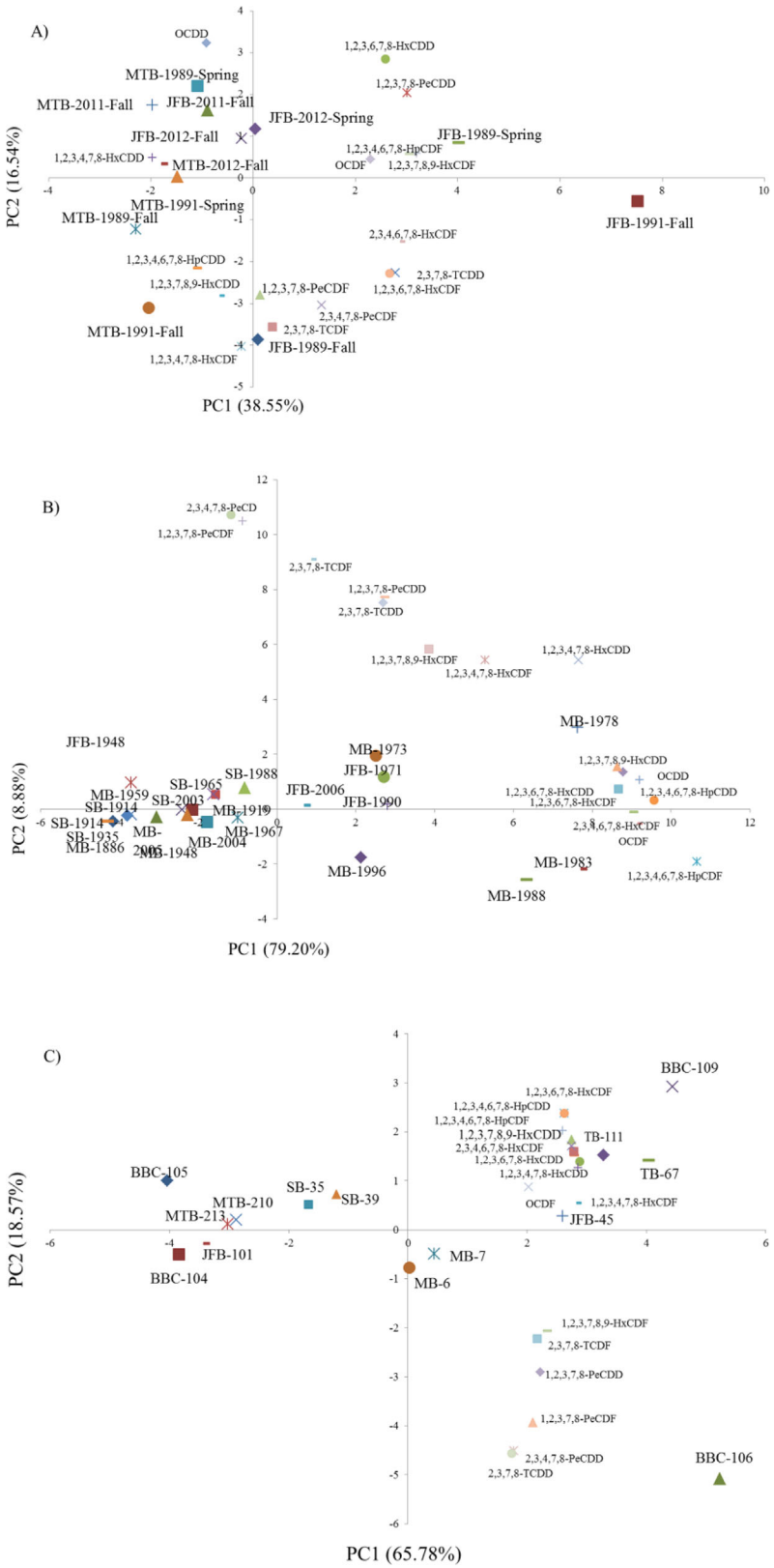

Figure 3. Ordination biplots of the principal component analysis of sites from exposed and reference locations and corresponding principal component analysis loading values of PCDD/F congener concentrations in (**A**) liver tissue of male white sucker collected intermittently in the spring and fall from 1989 to 2012 at Jackfish Bay (JFB) and Mountain Bay (MTB); (**B**) dated sediment cores collected from Jackfish Bay, Moberley Bay (MB), and Santoy Bay (SB); and (**C**) surface sediments collected at various distances from Blackbird Creek (BBC) in 2012. PC1/PC2 = principal components 1 and 2; HpCDD = heptachlorodibenzo-*p*-dioxin; HpCDF = heptachlorodibenzofuran; HxCDD = hexachlorodibenzo-*p*-dioxin; HxCDF = hexachlorodibenzofuran; OCDD = octachlorodibenzodioxin; OCDF = octachlorodibenzofuran; PeCDD = pentachlorodibenzo-*p*-dioxin; PeCDF = pentachlorodibenzofuran; TCDD = tetrachlorodibenzo-*p*-dioxin; TCDF = tetrachlorodibenzofuran.

TCDF and 2,3,4,7,8-PeCDF loading highly. Fish collected from Jackfish Bay during years in which the pulp mill was using chlorine bleaching (i.e., spring 1989 and fall 1991) correlated positively with PC1 (to the right of the plot). The Jackfish Bay fall 1989 fish did not separate on PC1 with these previous fish but were distinctly separated (negatively correlated) on PC2. Both the historical and recent samples collected from the Mountain Bay reference site orient close together to the left of ordination plot; and, interestingly, fish collected from Jackfish Bay during 2011 and 2012 also ordinated in a similar fashion to the fish collected at the reference site.

Historical PCDD/F contamination of sediment

A dated sediment core collected from the middle of Moberley Bay illustrated an increase in TEQ values from the early 1900s until the mid to late 1980s, followed by a sharp decline in recent years (Figure 4A). Once normalized to organic matter content (Figure 4B), the distribution becomes bimodal, with 2 distinct peaks. The first peak in organic matter–normalized TEQ was observed in approximately 1967, when elevated levels of 404 pg/g organic matter were measured. This was followed by a gradual decline until the early 1980s, when TEQ values increased again, reaching levels as high as 533 pg/g organic matter in approximately 1988. A similar pattern of increasing TEQ can be observed in the core collected from the deeper water of Jackfish Bay (Supplemental Data, Figure S1). The TEQ values from the reference core collected at Santoy Bay remained relatively constant, and low, with a slight peak in organic matter–normalized TEQ values occurring in the late 1960s (Supplemental Data, Figure S1). Organic matter–normalized sediment TEQ values from the reference core collected in Santoy Bay ranged from 9.34 pg/g to 23.0 pg/g organic matter. Overall, Moberley Bay and Jackfish Bay sediment TEQ values were consistently elevated compared with Santoy Bay. The TEQ values at Moberley Bay were higher than those in Jackfish Bay during most years, with the exception of the 1930s to 1940s and the early 2000s. The contaminant profiles from the 3 core samples were consistently dominated by the same congeners: 2,3,7,8-TCDD; 1,2,3,7,8-PeCDD; 1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin (HxCDD); 1,2,3,4,6,7,8-HxCDD; 2,3,7,8-TCDF; and 2,3,4,7,8-PeCDF. In the "exposed" sediment cores, from Moberley Bay and Jackfish Bay, the 2,3,7,8-TCDF and 2,3,7,8-TCDD congeners had the greatest influence on TEQ calculations The reference core collected from Santoy Bay was dominated by 1,2,3,7,8-PeCDD and 2,3,7,8-TCDD, with a broader range of individual congeners influencing total TEQ calculations.

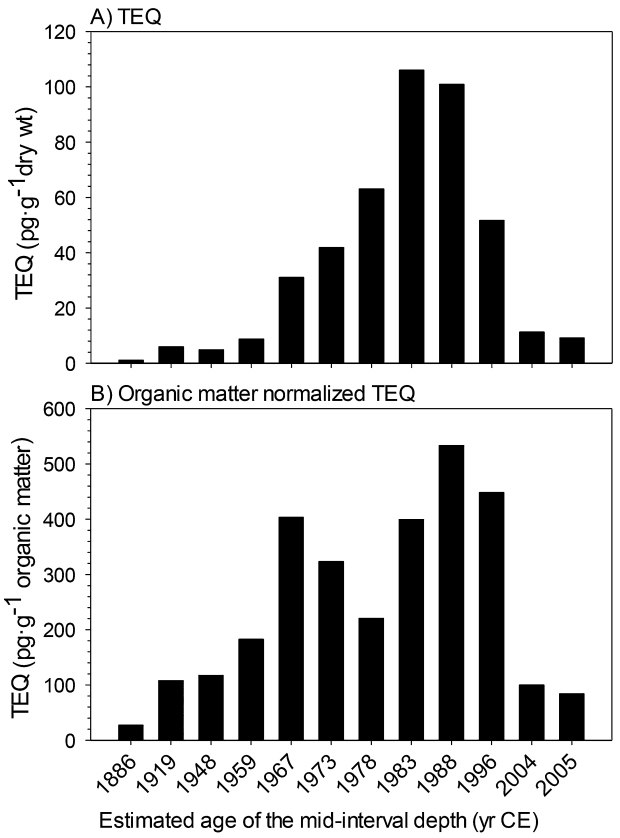

Figure 4. Toxic equivalency (TEQ; pg/g dry wt) and organic matter–normalized TEQ (pg/g organic matter), calculated using fish toxic equivalency factor values, for a dated sediment core collected from the depositional area of Moberley Bay.

In terms of the ordination of the data (principal component analysis) from the dated sediment core, 79.2% of the total variance was explained by PC1 and 8.9% by PC2 (Figure 3B; Supplemental Data, Table S1). Whereas PC1 loaded highly with most congeners, PC2 loaded negatively with 2,3,7,8-TCDD, 2,3,78-TCDF, and the PeCDF congeners and positively with HxCDD and OCDD/F congeners. Dated sections from the sediment core collected at the reference area, Santoy Bay, oriented to the left (negative) on the PC1 axis, along with sections from the Moberley Bay core that corresponded to years (approximate year at midpoint of each section) representative of pre–chlorine bleaching and post–chlorine bleaching at the pulp mill. Sediment core sections from Moberley Bay dated from 1973 through 1996, as well as all of the samples from the Jackfish Bay core, oriented to the right (positive) on the PC1 axis. Moberley Bay sediment samples further separated along PC2 (negative), with dated sediment from the period of 1989 to 1996 clustering together, likely reflecting the use of chlorine bleaching at the pulp mill.

Present PCDD/F contamination of surface sediment

In the surface (0–2 cm) sediment samples, the highest TEQ values were observed in Moberley Bay, where levels as high as 81.4 pg TEQ/g (Figure 5) were reached. Once normalized for organic matter content, elevated TEQ values were observed in surface sediment throughout Jackfish Bay, including Moberley Bay, Jackfish Bay proper, and Tunnel Bay (Figure 5B). Organic matter–normalized TEQ of surface sediment collected at the reference locations outside of Jackfish Bay ranged from 30.4 pg/g to 50.3 pg/g organic matter, whereas sandy (i.e., low in organic matter) grab samples collected near the mouth of Blackbird Creek demonstrated the lowest values. Because the samples collected closest to Blackbird Creek represent an erosional zone, it is likely that the surface sediment represents only a few years, compared with surface sediment collected from depositional areas where the top 2 cm represent approximately 10 yr. The congener profile of surface sediment from all sampling locations was dominated by the same congeners as previously described for the sediment cores collected in similar areas. The 2,3,7,8-TCDF and 2,3,7,8-TCDD congeners strongly influenced TEQ calculations in surface sediment collected from all areas of Jackfish Bay, with a decline in their influence on TEQ with increasing distance from Moberley Bay. On the other hand, the influence of 1,2,3,7,8-PeCDD concentrations on total TEQ calculations

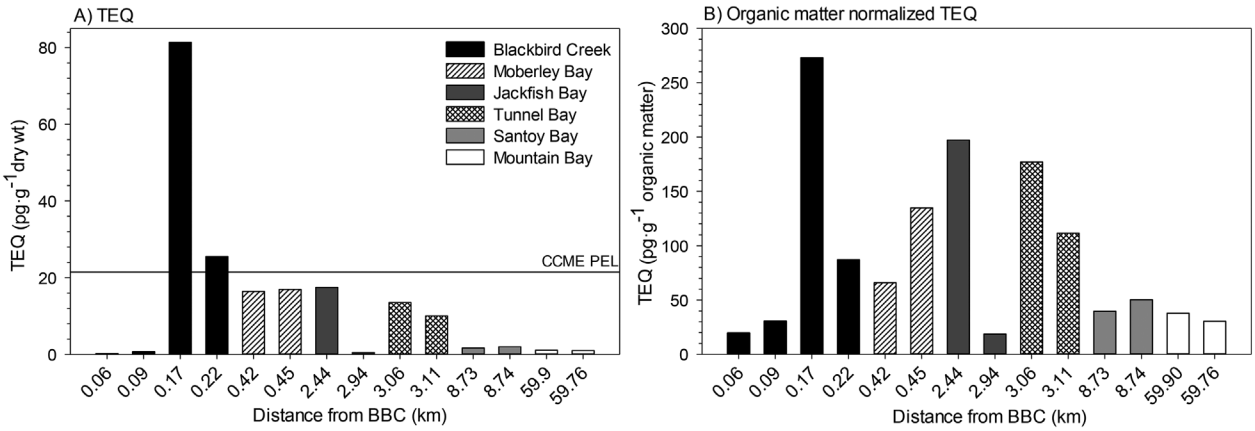

Figure 5. Toxic equivalency (TEQ; pg/g dry wt) and organic matter–normalized TEQ (pg/g organic matter), calculated using fish toxic equivalency factor values, for surface sediment (top 2 cm) collected at various distances from Blackbird Creek with the Canadian Council of Ministers of the Environment probable effects level shown at 21.5 pg TEQ/g. BBC = Blackbird Creek; CCME PEL = Canadian Council of Ministers of the Environment probable effects level.

increased with distance from Blackbird Creek and became the most influential congener for TEQ at the reference locations (Santoy Bay and Mountain Bay).

In the principal component analysis ordination plot of PCDD/F contamination measured in surface sediment, 65.8% of the total variance was explained by PC1 and 18.6% by PC2 (Figure 3C; Supplemental Data, Table S1). The loadings were similar (with some differences) to the pattern seen in sediment cores. Surface sediment collected from the reference areas, Santoy and Mountain Bays, tended to orient close together to the left on the PC1 axis, which suggests that these may be comparable sites in terms of PCDD/F contamination identified in surface sediment. Jackfish Bay (site JFB 101, 2.94 km from BBC), which also had very low TEQ values, loaded into this group as well. This may be because of the location of this sample, which was collected slightly outside of the main depositional area of the bay. The surface sediments collected near the mouth of Blackbird Creek (sites BBC 104 and BBC 105; 0.06 and 0.09 km, respectively) also fell into this group, likely because they were collected from a very shallow, highly erosional, nearshore area. Many of the surface sediment samples collected from deeper areas of Moberley Bay, Jackfish Bay, and Tunnel Bay but in closer proximity to mouth of Blackbird Creek (compared with reference areas) all oriented positively (right) on PC1, although distance from Blackbird Creek did not appear to be an important factor. Interestingly, the samples collected in the deeper water near the mouth of Blackbird Creek (sites BBC 105 and BBC 106; 0.17 and 0.22 km, respectively) also loaded positively on PC1 but differed (opposite) in their loadings on PC2.

DISCUSSION

Elimination of PCDD/Fs from effluent

Elevated PCDD/F concentrations measured in fish at Jackfish Bay in the late 1980s and early 1990s caused concern for human consumption of fish as well as ecosystem health. Analysis of a dated sediment core collected from the depositional area of Moberley Bay illustrated increasing concentrations of PCDD/Fs, particularly 2,3,7,8-TCDF, from approximately the late 1960s to the late 1980s or early 1990s. This corresponds to a period of mill expansion, which included the introduction of a fully bleached "hot" kraft process (Table 1). Because molecular chlorine is less soluble at higher temperatures, this had the potential to affect by-product formation [24]. In addition, the use of oil-based defoamers in brown stock washers may have provided precursors for 2,3,7,8-TCDF formation [22,23]. These results are consistent with the trends observed in a dated sediment core from Moberley Bay collected by Sherman et al. [22] in 1988 (prior to the mill changing from Cl_2 bleaching practices). The Canadian federal government responded to growing international concerns regarding the release of PCDD/Fs into aquatic environments by implementing new effluent regulations under the Canadian Environmental Protection Act, which came into effect in 1992. At the same time, existing Pulp and Paper Effluent Regulations under the Fisheries Act were updated to include stricter limits for biological oxygen demand, total suspended solids, and acute lethality, as well as the development of a regulated, cyclical, environmental effects monitoring program [41]. To meet new regulations, the mill underwent a number of process changes (Table 1), which virtually eliminated the formation of PCDD/Fs from mill effluent and resulted in a dramatic decline in PCDD/F concentrations in fish and sediment at Jackfish Bay.

Altered PCDD/F contamination in response to process changes

Fish collection in 1989 occurred prior to the installation of secondary treatment at the bleached kraft pulp mill in Terrace Bay, which was installed to meet new biological oxygen demand and total suspended solids limits. The mill also increased ClO_2 substitution to 50% in 1990, to improve effluent quality [16]. No immediate response was observed in PCDD/F contamination of fish following these process changes; in 1991, mean TEQ of white sucker liver tissue reached levels as high as 97.8 ± 28.2 pg/g and 74.3 ± 20.9 pg/g during spring and fall, respectively (Figure 2). These results are consistent with many studies worldwide, which reported elevated PCDD/Fs in aquatic biota and wildlife exposed to bleached kraft mill effluent prior to the early 1990s [42–47]. A decline in mean liver TEQ (wet wt) was observed between 1991 and 1993 in male white sucker collected during spring and fall. Despite the observed decline, mean liver TEQ values and PCDD/F contamination patterns for these years remained elevated compared with reference fish collected from Mountain Bay, Lake Superior, during the same time period (Figures 2 and 5). A similar decline in PCDD/F contamination was observed in a dated sediment core from Moberley Bay (Figure 4), with sediment TEQ values peaking in the mid to late 1980s, followed by a rapid decline. Between 1993

and 1995, a further decline in TEQ levels was measured in white sucker. This corresponded to an increase in ClO_2 substitution, from 50% to 70%, as well as upgraded ClO_2 generators, which allowed the mill to continually produce elemental chlorine-free pulp by eliminating the production of chlorine by-products. Process changes at the mill in 1998 (hardwood line) and 1999 (softwood line), resulting in 100% ClO_2 substitution, led to further reductions in sediment PCDD/F concentrations (Figure 4). It has been well documented that a dramatic reduction, to nonmeasurable levels, in the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF can occur following an increase to 70% or greater ClO_2 substitution in the first stage of the bleaching process [48]. From 1995 to the present, PCDD/F contamination of white sucker from Jackfish Bay has remained relatively stable, but low, despite the 12-mo mill closure from October 2011 until October 2012. The pattern of PCDD/F contamination of liver tissue for male white sucker collected from Jackfish Bay in 2011 and 2012 was more similar to that in fish collected at the reference site in Mountain Bay than to that in fish historically collected at Jackfish Bay (Figure 3A).

Implications of PCDD/F contamination

Reproductive responses have been measured in fish collected from Jackfish Bay for more than 2 decades [18,25,26]. In the early 1990s, investigations measured the response of fish exposed to a variety of mill effluents, with and without chlorine bleaching, and determined that PCDD/F exposure in the receiving environment was not directly correlated to the biological effects observed [21,49]. It has been reported that although PCDD/Fs can be responsible for part of the hepatic mixed-function oxygenase induction observed in fish exposed to bleached kraft pulp mill effluent, other chemicals are likely responsible and may not be associated with chlorine bleaching [21,27,28,50,51]. Bowron et al. [25] reported a gradual recovery of white sucker health over time at Jackfish Bay. Although improvements were observed in fish health, especially following conversion of the mill to elemental chlorine-free bleaching practices, a number of reproductive parameters remained impacted compared with the reference condition. The recent temporary closures of the Terrace Bay pulp mill have demonstrated the potential for further recovery of fish in Jackfish Bay. It is unlikely that the current low concentrations of PCDD/Fs measured in the present study play a role in the continued responses observed in fish at this location.

To address the potential concern posed by PCDD/Fs to aquatic ecosystems, tissue residue guidelines were developed using 1998 World Health Organization mammalian TEF values to protect wildlife consumers of aquatic biota [52]. The PCDD/F contamination of liver tissue from white sucker collected in Jackfish Bay exceeded the tissue residue guideline (4.75 pg TEQ/g) for avian consumers of aquatic biota during all sampling periods except fall 2012. It is important to note that these guidelines serve only as a framework for predicting ecosystem health. The present study evaluated PCDD/F contamination in liver tissue, which is high in lipid and tends to accumulate greater amounts of PCDD/F. When considering consumption guidelines for birds and mammals, PCDD/F TEQ measured in muscle tissue (the major mass of fish and primary food source to consumers) is most informative. Because lipid normalization allows for a direct comparison of PCDD/F contamination between different types of tissue [21], TEQ values for muscle tissue of male white sucker from Jackfish Bay would be expected to be below the tissue residue guideline. The interim tissue residue guideline developed for mammalian species (0.71 pg TEQ/g) is lower than the tissue residue guideline for avian species [52]; however, it is not likely that mammalian species would be feeding directly on white sucker.

Bioavailability of PCDD/Fs

White sucker collected at Jackfish Bay during fall 1993 exhibited unusually high (57–84%) lipid composition of liver tissue. This may be related to previously reported observations of metabolic disruption in white sucker exposed to pulp mill effluent at Jackfish Bay, which could lead to more energy being put into storage [18]. Several studies have observed disproportionate accumulation of chlorinated organic compounds in lean tissue, compared with fatty tissue, of a variety of marine and freshwater species [53–55]; others have reported no significant differences [56]. Jones et al. [2] observed that the greatest proportion, by mass, of 2,3,7,8-TCDD accumulation in rainbow trout (*Oncorhynchus mykiss*) occurred in muscle tissue during gonadal recrudescence and in gonads prior to spawning. Furthermore, accumulation of 2,3,7,8-TCDD in liver tissue appeared to reach steady state more quickly than muscle or ovaries [2]. Although lipid-normalized TEQ of white sucker liver tissue provides additional insight into the temporal distribution of PCDD/Fs within Jackfish Bay, it is important to consider potential additional factors controlling bioaccumulation in wild fish, such as food chain structure and feeding behavior [53,55,57,58].

In Jackfish Bay, changes in habitat, water quality (e.g., color, toxicity), and community structure may alter a fish's access to contaminated sediment and food within different areas of the lake. Many studies have determined that the bioaccumulation of PCDD/Fs, such as 2,3,7,8-TCDD, in fish is not linked to surface sediment contamination and that uptake of highly chlorinated PCDD/Fs occurs predominantly through particulate organic matter and dissolved organic matter via food chain transfer [58–64]. For example, Owens et al. [58] attributed an observed difference in bioaccumulation of 2,3,7,8-TCDD and 2,3,7,8-TCDF between fish species to differences in feeding behavior, with higher lipid-normalized concentrations found in mountain whitefish (*Prosopium williamsoni*), which feed on hydropsychid caddis flies that build webs to trap particles for feeding. Servos et al. [65] showed a shift in the 1,3,6,8-TCDD uptake route in mesocosms over time, transitioning from initial equilibrium partitioning in the water column to detrital food chain transfer. In Moberley Bay, Sherman et al. [22] speculated that suspended solids in mill effluent, not surficial sediment, were the primary source of 2,3,7,8-TCDF. Experimental determination of depuration rates in liver tissue of rainbow trout fed 2,3,7,8-TCDD suggests that following removal of the source of contamination the tissue concentration will decrease by approximately one-half every 40 d [2]. These results indicate that 2,3,7,8-TCDD would be virtually eliminated from white sucker in Jackfish Bay within 1 yr of complete removal of the source of PCDD/Fs. This is consistent with the decline in PCDD/F TEQ observed in white sucker following mill process changes to remove chlorine from the bleaching sequence, suggesting that uptake of PCDD/Fs by fish was minimal, despite the physical–chemical properties, which allow PCDD/Fs to persist in sediment with the potential for bioaccumulation. Despite removal of PCDD/F from effluents (through removal of precursors and Cl_2 from the bleaching sequence), their persistence may allow PCDD/Fs to remain in surface sediment for long periods of time.

Moderate contamination of surface sediments (0–2 cm) was found throughout Jackfish Bay (Figure 5). The PCDD/Fs of 2

surface sediment samples collected in the depositional area of Moberley Bay exceeded the Canadian Council of Ministers of the Environment probable effects level (21.5 pg TEQ/g), developed using fish TEFs [40] to evaluate the potential for PCDD/F exposure to cause adverse biological effects [66]. This is consistent with the pattern observed for total organic carbon, which was highest in the depositional area of Moberley Bay and decreased with distance from the mouth of Blackbird Creek. Surface sediment samples collected closest to the mouth of Blackbird Creek represent an erosional area with low organic matter. Surface sediment from this area likely represents only a few years, with sediment being removed quickly and transported to the depositional areas of Moberley Bay or exported to Lake Superior. The sediment core collected from the further depositional area of Jackfish Bay, near St. Patrick Island, Canada, illustrates TEQ levels below the probable effects level in the top 2 cm (representing ~10 yr). Below this level, the probable effects level was exceeded, with TEQ ranging from 31.0 pg/g to 106 pg/g between 1967 and 1996 (approximate year at midpoint of each section; Supplemental Data, Figure S1). During the same time, the core from Jackfish Bay also exceeded the probable effects level, reaching a maximum TEQ of 35.9 pg/g. Surface sediments collected from Tunnel Bay illustrated elevated TEQ values compared with reference sediments but remained below the probable effects level (Figure 5). These results are consistent with benthic invertebrate community collections within Jackfish Bay, indicating a polluted environment in Moberley Bay [29]. Milani [29] also found that the benthic communities outside of Moberley Bay were similar to those observed in reference locations, with some differences in the densities of tubificids and amphipods.

Shift in PCDD/F contamination patterns and sources

Mean TEQ values of fish collected at Jackfish Bay between 1995 and 2012 appear to be approaching levels observed in reference fish from Mountain Bay. The PCDD/F contamination of male white sucker collected at Jackfish Bay from 1989 to 2012 ranged from 3.34 pg TEQ/g to 97.8 pg TEQ/g, compared with 1.06 pg TEQ/g to 5.44 pg TEQ/g at Mountain Bay over the same period. A unique contamination pattern of highly chlorinated PCDD/F congeners has been identified that is distinct from the pattern produced by air emissions. The PCDD/F contamination pattern produced by incineration includes hepta- (HpDD) and octa- (OCDD) dioxin congeners, as well as 1,3,6,8-TCDF, 1,3,7,9-TCDF, and penta- (PeCDF) furans [6,67]. The congener pattern produced by bleached kraft pulp effluent is dominated by 2,3,7,8-TCDD and 2,3,7,8-TCDF [6]. Differences in the relative proportion of 2,3,7,8-TCDD and 2,3,7,8-TCDF have been identified in fish collected from contaminated sites in the upper and lower Great Lakes, indicating different sources of pollution [43,68,69]. In Lake Superior increased proportions of 2,3,7,8-TCDF compared with 2,3,7,8-TCDD have been measured in fish, suggesting that the source of contamination originates from the historical bleached kraft mill effluent discharge with significant localized sources in various areas of the lake, including Jackfish Bay [21,69]. Five congeners consistently dominated TEQ calculations at Jackfish Bay: 2,3,7,8-TCDD; 2,3,7,8-TCDF; 2,3,4,7,8-PeCDF; 1,2,3,7,8-PeCDD; and 1,2,3,7,8-PeCDF. Throughout the time period of the present study, the relative contribution of individual congeners to TEQ levels evolved to partially resemble the contaminant profile observed in white sucker collected from Mountain Bay. For example, the gradual increase in proportion of 2,3,7,8-TCDD observed at Jackfish Bay in recent years more closely reflects contamination seen in reference fish from Mountain Bay than that seen in historical fish collected at Jackfish Bay. However, white sucker from Jackfish Bay continue to show elevated levels of 2,3,7,8-TCDF relative to reference fish (Tables 2 and 3). Sediment contaminant profiles differed from that of white sucker, with a greater emphasis on penta- (PeCDD/F) and hexa- (HxCDD/F) congeners; however, 2,3,7,8-TCDF and 2,3,7,8-TCDD remained the most influential congeners toward TEQ for sediment collected from all areas of Jackfish Bay. High concentrations of OCDD observed in white sucker from Jackfish Bay (Tables 2 and 3) and sediment cores from Moberley Bay do not provide a meaningful contribution to total TEQ calculations and can likely be attributed to emission sources or the use of treated wood. Pentachlorophenol and creosote used to treat wood products have been shown to contain high levels of highly chlorinated PCDD/Fs, including OCDD [70]. The use of treated wood likely resulted in contamination of mill effluent at some period of time during the history of the mill operation. For example, a 250-m section of creosote-treated wooden stave pipe was replaced at the mill in 1994 (Table 1). According to Pearson et al. [71], the current PCDD/F load received by Lake Superior comes almost entirely from atmospheric sources.

Ecosystem recovery

The results observed in Jackfish Bay are consistent with analyses conducted on a variety of fish species across Lake Superior [42]. A similar rapid decline of 2,3,7,8-TCDD; 2,3,7,8-TCDF; and 1,2,3,7,8-PeCDD concentrations in lake trout (*Salvelinus namaycush*) were reported between 1989 and 1993. Recent data suggest that PCDD/F contamination of lake trout, a top predator in Lake Superior, may have reached a steady state [42]. Since the early 1990s, PCDD/F concentrations have been declining in fish and sediment from Jackfish Bay. The present study provides evidence that the decline in PCDD/F contamination in Jackfish Bay is associated with mill process changes that resulted in a reduction of the use of Cl_2 in the bleaching sequence. Current PCDD/F concentrations measured in white sucker from Jackfish Bay are below tissue residue guideline levels and therefore likely are not indicative of impaired ecosystem health. High PCDD/F concentrations buried in sediment or remaining in the surface layers (top 2 cm) throughout Jackfish Bay do not appear to be translated to the tissue of bottom-feeding white sucker. The pattern of PCDD/F contamination that remains in surface sediment appears to be moving toward a congener signature more indicative of background atmospheric sources. These results are in line with those reported in other areas [72,73] showing that, although local contamination patterns from historical sources are discernible, the atmosphere remains a major source of PCDD/F globally.

SUPPLEMENTAL DATA

Table S1.
Figure S1. (41 KB DOCX).

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Data availability—Data, associated metadata, and calculation tools are available on request (mservos@uwaterloo.ca).

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