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Release of persistent organic contaminants from carcasses of Lake Ontario Chinook salmon (*Oncorhynchus tshawytscha*)

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Carcasses of adult Chinook salmon from Lake Ontario contribute persistent contaminants to a river ecosystem.

Abstract

About 20,000 Chinook salmon (*Oncorhynchus tshawytscha)* from Lake Ontario enter the Credit River, Ontario, Canada every fall to spawn and die. In this study, samples of muscle and eggs collected from female Chinook salmon entering the Credit River contained total PCBs, DDT compounds and other organochlorine (OC) compounds at μg/kg concentrations. Semi-permeable membrane devices (SPMDs) were deployed at a reference site above the spawning grounds and at two downstream sites at intervals over a 14-month period that spanned two spawning runs. There was an increase in the concentrations of total PCBs, total DDT and other classes of OCs in the SPMDs deployed at the two downstream sites during and after both spawning runs; indicating that the decay of salmon releases contaminants into the river. Based upon the concentrations of contaminants in the salmon tissues, approximately 75 g of total PCBs and 35 g of total DDT compounds would be transported annually into the Credit River from this source.

Keywords: *Oncorhynchus tshawytscha*; Organic pollutants; Polychlorinated biphenyls; Organochlorines; Lake Ontario

1. Introduction

Persistent organic pollutants (POPs), including polychlorinated biphenyls (PCBs) and other organochlorines (OCs) accumulate to high concentrations in fish from contaminated aquatic ecosystems (Rasmussen and Rowan, 1990; Metcalfe and Metcalfe, 1997; Crimmins et al., 2002). The migration or movement of contaminated fish can redistribute POPs into uncontaminated areas (Merna, 1986; Lewis and Makarewicz, 1988; Scrudata and McDowell, 1989; Monte, 2002). The decomposition of spawning Pacific salmon has been shown to impact freshwater streams as a result of the release of elements such as carbon and nitrogen from salmon carcasses (Brickell and Goering, 1970; Bilby et al., 1996; Lyle and Elliott, 1998). The recycling of nutrients from carcasses is now recognized as an essential contribution to the productivity of salmon streams (Cederholm et al., 1999; Helfield and Naiman, 2001). For this reason, "planting" of salmon carcasses in streams is part of many salmon restoration projects in the Pacific Northwest region of the USA (Missildine, 2005). However, sockeye salmon (*Oncorhynchus nerka*) carcasses were recently identified as vectors for the movement of contaminants from the Pacific Ocean into remote freshwater lakes in Alaska; apparently through the remobilization of contaminants from carcasses after

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the adults spawn and die (Krummel et al., 2003). The concentration of ocean-derived contaminants in the lake sediments was correlated with the population density of the spawning fish.

Chinook salmon (*O. tshawytscha*) are the largest Pacific salmon that migrates into streams to spawn. After spawning, the females protect the nest as long as possible, but both males and females die within a few days to 2 weeks post-spawning (Scott and Crossman, 1973). Chinook salmon have been introduced as sport fish into the Great Lakes of North America. Introductions into Lake Ontario began in the 1960s through the release of smolt raised in government hatcheries in Ontario, Canada and in New York State, USA. These fish grow to reproductive age after three winters in the lake, and return in the fall to their site of release (Rand et al., 1992). Recently, juveniles that have not been produced by the hatcheries have been found in some rivers, suggesting that naturalized populations of Chinook salmon may be developing, in addition to the hatchery reared populations.

One of the major spawning runs of Chinook salmon is the population that enters the Credit River; an urbanized area near Toronto, ON, Canada. Approximately 20,000 Chinook salmon spawn in the Credit River annually (Jim Bowlby, Ontario Ministry of Natural Resources, personal communication). The majority of these salmon aggregate and die directly below the Streetsville Dam, that is located about 15 km upstream from Lake Ontario. The dam acts as a barrier to further upstream migration.

PCBs and OC pesticides are known to accumulate to mg/kg concentrations in the tissues of Lake Ontario salmon and trout (Rasmussen and Rowan, 1990; Smith et al., 1994; Heustis et al., 1996; Metcalfe and Metcalfe, 1997; Luc, 2000). Chinook salmon accumulate these organic contaminants in their tissues and may release them into river ecosystems in the eggs (Merna, 1986), and through post-spawning breakdown of lipid-rich tissues during carcass decay (Lewis and Makarewicz, 1988).

In this study, our goal was to definitively establish a relationship between spawning of Chinook salmon and the release of persistent contaminants into the water column of a tributary stream of Lake Ontario. In addition, concentrations of contaminants were measured in hatchery-raised and naturally produced juvenile Chinook salmon, in order to determine whether there is bioaccumulation of contaminants in juvenile salmon prior to their movement into Lake Ontario. We analyzed the feed used in the hatchery as a possible source of contaminants in hatchery smolt. We measured the release of contaminants into the Credit River by monitoring temporal changes in the concentrations of PCBs and OC pesticides in the river both above and below the Streetsville Dam. Monitoring was conducted with a 'passive' sampler, the semi-permeable membrane device (SPMD), which concentrates hydrophobic contaminants dissolved in the aqueous phase. The monitoring program began immediately after the spawning run (i.e. October) in the Fall of 2001 and continued for 14 months; concluding after the spawning run in the Fall of 2002 (i.e. December 2002).

2. Materials and methods

2.1. Study sites

The Credit River, which is 20 km west of Toronto, is located in the densely populated city of Mississauga; a suburb of Toronto located along the northwest shore of Lake Ontario (Fig. 1). The river runs northwest for 50 km through this urban zone. The majority of adult Chinook attempt to spawn and then decompose in an area below the Streetsville Dam (Fig. 1), which lies in the center of Mississauga. Chinook salmon spawning runs have been abundant in the Credit River since the early 1980s and salmon collected in the river are used as broodstock for the Ontario hatchery program. Large numbers of hatchery juveniles are released near the river mouth, as well as at the Streetsville Dam.

The hatchery that produces smolt for release into the Credit River is located at the Ringwood Fish Culture Station in Stouffville, Ontario, about 20 km north-east of Toronto. The water source is groundwater of high purity and is unconnected to the Credit River system.

Wilmot Creek, which has a natural population of juvenile Chinook salmon, is a groundwater fed river located near Bowmanville, Ontario, to the east of Toronto. The creek flows for about 20 km through a region of relatively pristine, mixed deciduous forest, with scattered agriculture, and finally discharges into Lake Ontario. Wilmot Creek has never been stocked with Chinook salmon. There are no reported point sources of contaminants, and a wide riparian zone limits impacts from agricultural runoff.

2.2. Adult and juvenile Chinook salmon

Seven adult female Chinook salmon were collected directly below the Streetsville Dam in the Credit River by the Ontario Ministry of Natural Resources (OMNR) on 1 October, 2001, during their collection of broodstock. Samples of dorsal muscle and eggs were collected on-site from these salmon, and wrapped in aluminum foil that had been pre-washed with acetone and hexane. The samples were shipped on ice to Trent University and kept frozen until preparation for analysis.

A total of five hatchery-raised juvenile Chinook salmon at the smolt stage of development were collected in August 2003 from the Ringwood Fish Culture

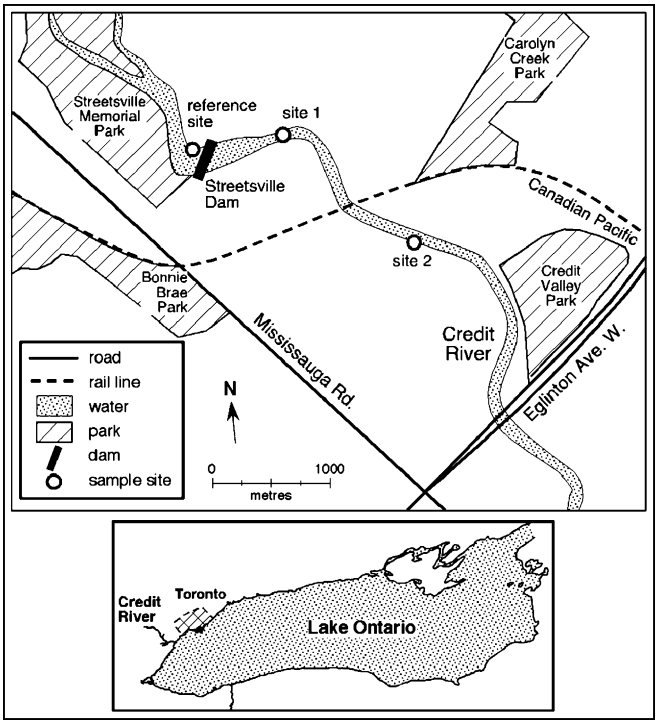

Fig. 1. Locations of the three sites for deployment of SPMDs in the Credit River near the Streetsville Dam, Ontario, Canada. The reference site is above the dam, from where salmon are excluded, while Sites 1 and 2 are located in areas of salmon congregation and spawning.

Station. In addition, five wild juvenile salmon at the parr stage of development were collected on 17 June, 2003 from Wilmot Creek. The fish were wrapped whole in solvent-washed aluminum foil, shipped on ice to Trent University and frozen until preparation for analysis.

2.3. Food for hatchery-raised juveniles

Samples were provided by the Ringwood hatchery of the pellet food used to raise Chinook salmon from fry through to juvenile stages Although the food formulation is the same for all pellet sizes, we analyzed three different batches of food, from each of three size categories. The 1CR pellet is used to feed juvenile Chinook salmon between 0.8 and 1.5 g, the 2CR pellet is used for 1.5–3.0 g fish and the 1.2-mm pellet is used to feed 3.0–5.0 g fish. The formulation is advertised by the manufacturer (EWOS Manufacturing, British Columbia, Canada) to consist of $>68\%$ crude protein and $<10\%$ lipid. The formulation is made up from fish meal (30%), Brewer's dried yeast (5%), wheat (12%), corn gluten meal (19%), animal blood meal (7%), poultry by-product meal (10%), plant oil (5%) and fish oils (10%), with additions of lysine, vitamin mix, and mineral mix.

2.4. SPMDs

The SPMD is a passive sampling device for monitoring the distribution of hydrophobic organic contaminants that are present in water at parts per trillion (i.e. ng/L) concentrations; levels that would be difficult to detect using conventional extraction techniques. The SPMD is a tube of polyethylene that contains a thin film of triolein; a synthetic lipid compound. Once the SPMD is deployed in the aquatic environment, organic contaminants with octanol-water partition coefficients (i.e. log Kow) greater than approximately 3.0 pass from the aqueous phase through the polyethylene and are concentrated in the triolein (Huckins et al., 1996). The SPMDs concentrate only the contaminants that are in the truly dissolved phase of the surrounding aqueous medium. Any compounds adsorbed to suspended particulates or dissolved organic material (e.g. colloids, humic acids) will not pass through the polymer membrane into the triolein. The device is retrieved, usually 1 month after deployment and contaminants are extracted from the triolein. These devices have given good results in previous monitoring studies for PCBs and OC insecticides (Huckins et al., 1993; Ellis et al., 1995; Bennett et al., 1996; Metcalfe et al., 2000; Wang et al., 2002).

SPMDs were assembled at Trent University according to methods described previously by Metcalfe et al. (2000). Briefly, 1 mL of triolein lipid was pipetted into a 40-cm section of polyethylene layflat tubing. The bag was heat sealed, with loops at both ends and the SPMDs were stored at $-10\ ^{\circ}C$ until deployment. At each site, four SPMDs were assembled into a cylindrical shroud (77×10 cm diameter) constructed of galvanized metal

stovepipe. The metal shrouds had holes punched throughout to allow for water flow through the SPMDs. As illustrated in Fig. 1, the locations for deployment of SPMDs in the Credit River included a reference site located directly above the Streetsville Dam, Site 1 approximately 150 m below the dam, and Site 2 approximately 1 km downstream from the dam. The SPMDs were first deployed on 1 October, 2001 and the sampling program continued over the next 14 months until retrieval of the last SPMDs on 11 December, 2002. The SPMDs were retrieved every 28 days after deployment, with the exception of the first sampling month in October 2001, which was sampled in two 15-day intervals (i.e. Oct. 1–16, Oct. 16–Nov. 1) in order to obtain a more focused view of post-spawning contaminant levels.

2.5. Sample preparation

2.5.1. Salmon tissues and fish food

Samples (2–5 g) were prepared from dorsal muscle from both adult salmon and hatchery-raised juvenile salmon, eggs from adult female salmon, the whole body minus the viscera, head and tail of wild juvenile salmon, and hatchery fish food. The samples were prepared for analysis using methods previously described by Metcalfe et al. (2000). Briefly, the samples were ground with sodium sulfate and extracted by 'cold column' extraction techniques for 2 h into 1:1 hexane/dichloromethane (DCM). The extracts were rotary-evaporated to a volume of 1 mL and lipids in the extracts were separated from analytes by gel permeation chromatography (GPC) in a 3 × 30-cm glass column packed with 50 g of SX-3 Biobeads® (Bio-Rad, Toronto, ON, Canada).

The samples were then rotary evaporated to 1 mL and subfractionated by silica gel chromatography with 5 g of activated 60–200 mesh silica gel (Aldrich, Toronto, ON, Canada), topped with a small amount of sodium sulfate. The samples were eluted in two separate fractions; Fraction 1, eluted with 40 mL hexane, contained all PCB congeners and some DDE, and Fraction 2, eluted with 75 mL 1:1 hexane/DCM, contained the rest of the DDE and the majority of other OC compounds. These fractions were rotary-evaporated to 1 mL and further concentrated to the volume for analysis (0.1–0.5 mL) using a centrifuge evaporator.

2.5.2. SPMDs

Three SPMDs were prepared for analysis from each deployment. The SPMDs were extracted according to methods described by Metcalfe et al. (2000). Briefly, the SPMDs were thawed and scrubbed with a clean brush in distilled water to remove any fouling that had collected on the bag. Each SPMD bag was blotted with a paper towel and placed in a glass beaker containing 350 mL of hexane. The beaker was covered with solvent-washed foil and placed in a dark, vented area for 18 h at ambient temperature for dialysis. The dialysis was repeated in a new beaker with fresh hexane for another 6 h. The combined dialysate was passed through anhydrous sodium sulfate to remove excess water and was then rotary evaporated to approximately 1 ml. The SPMD extracts were cleaned up using GPC and silica gel chromatography, as described above. After silica gel cleanup, approximately 0.2 g of powdered copper was added to each silica gel fraction to remove any residual elemental sulfur in the extract.

2.6. Contaminant analysis

Samples prepared from fish tissue, fish food and SPMDs were analysed using a Varian 3500 high resolution gas chromatograph coupled to an electron capture (^{63}Ni) detector (GC-ECD) and equipped with a 60 m × 0.25-mm DB-5, 0.25 micron column. The carrier gas was UHP hydrogen and the make-up gas for the detector was UHP nitrogen. Instrument conditions for the PCB fraction consisted of an injector temperature of 250 °C and detector temperature of 275 °C. The column oven program was: 80 °C hold for 1 min, to 160 °C at 4 °C/min, to 220 °C at 1.5 °C/min, and to 250 °C at 7 °C/min hold for 35 min. The conditions for the OC pesticide fraction consisted of an injector temperature of 250 °C and a detector temperature of 275 °C. The column oven program was 70 °C hold 0 min, to 210 °C at 15 °C/min hold for 9 min, to 270 °C at 2 °C/min hold for 5 min.

Samples were analyzed for 33 PCB congeners with IUPAC numbers 28, 18/31, 33, 44, 52, 70, 74, 87, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 151/82, 153, 156, 170, 180, 187, 191, 194, 195, 201, 205, 206 and 209. The samples were also analyzed for a range of organochlorine compounds, including *p,p′* and *o,p′*-isomers of DDT, DDE and DDD, HCB, α-HCH, β-HCH, δ-HCH and γ-HCH, *trans*- and *cis*-chlordane, *trans*- and *cis*-nonachlor, heptachlor and heptachlor epoxide, aldrin, dieldrin, endrin, endrin ketone and endrin aldehyde, endosulfan, endosulfan II and endosulfan sulfate, methoxychlor, mirex and octachlorostyrene.

The Limits of Detection calculated according to Keith et al. (1983) were between 0.3 and 1.0 ng/mL for PCB congeners, between 0.6 and 1.0 ng/mL for DDT and metabolites and between 0.3 and 0.6 ng/mL for all other organochlorine analytes. Procedural blanks and a National Institute for Standards and Testing (NIST) cod liver oil reference material (SRM 1588) were analyzed for quality control/quality assurance purposes. Trip blanks were prepared for all SPMD sampling sites to account for any uptake of organic contaminants from the air, or other sources during the deployment and retrieval of the SPMD bags. All contaminant data for SPMDs were corrected for this background contamination.

All analyte concentrations were calculated on a wet-weight basis. The total PCB concentration was calculated as the sum of all PCB congeners and the total DDT concentration was calculated as the sum of *p,p′*- and *o,p′*-isomers of DDT, DDE and DDD. Total cyclodienes A was calculated as the sum of aldrin, dieldrin, endrin and metabolites, and heptachlor and metabolites. Total cyclodienes-b was calculated as the sum of *trans*- and *cis*-chlordane and *trans*- and *cis*-nonachlor. Total endosulfans was calculated as the sum of endosulfan, endosulfan II and endosulfan sulfate. The total of all other OC compounds was calculated as the sum of mirex, the four HCH isomers, methoxychlor, HCB, and octachlorostyrene.

3. Results

The mean fork length and mean weight of female Chinook salmon collected from the Credit River during spawning in 2001 were 88.9 cm (range 84.3–95.9 cm) and 9.4 kg (range 7.7–11.5 kg), respectively. PCBs and OCs were detected in the muscle tissue and eggs from the females (Table 1). Total PCBs and total DDT were present at the highest concentrations among contaminants in muscle tissue, with mean concentrations of 370.7 and 169.9 μg/kg wet weight, respectively. The *p,p′*-isomer of DDE was the major DDT compound, and among other OC compounds, mirex was the major contaminant (Table 1). Total PCB concentrations in the salmon eggs were on average almost 2.5 times greater than in muscle tissues; reflecting the higher lipid content of eggs. The mean concentration of total PCBs in eggs was 905.4 μg/kg, and total DDT in eggs was 674.9 μg/kg, wet weight. The major PCB congeners detected in both muscle tissue and eggs were (in order) 153, 138, 101, 118, 180, 187, 110, 99, 170, 151, 128, 149, 105 and 87 (Table 1), which accounted for 86–89% of the total PCBs in muscle and eggs.

The range of weights and fork lengths of the 5 juvenile salmon collected from the Ringwood hatchery were 6.6–8.3 g and 9.0–10.0 cm, respectively. PCBs and OC compounds were detected at low μg/kg concentrations in the muscle of these juvenile fish (Table 1). The mean concentrations of persistent contaminants were much lower than the concentrations detected in the muscle of adult Chinook salmon collected in the Credit River. The range of weights and fork lengths of the five juvenile salmon collected from Wilmot Creek were 1.0–1.4 g and 4.5–5.3 cm, respectively. Concentrations of PCBs and OCs in wild juvenile salmon were generally slightly lower than the concentrations in hatchery raised salmon; perhaps reflecting the lower lipid content of the wild juveniles (Table 1).

Our analysis of the food used at the Ringwood hatchery indicates that the diets of Chinook salmon were contaminated with POPs. Contaminants detected included total PCBs at a mean concentration of 7.6 μg/kg (range of 5.9–12.1 μg/kg), total DDT at a mean concentration of 26.3 μg/kg (range of 16.9–40.6 μg/kg), total cyclodienes-b at a mean concentration of 2.9 μg/kg (range of 1.7–4.1 μg/kg), total endosulfan at a mean concentration of 3.7 μg/kg (range of 1.7–7.1 μg/kg), and mirex at a mean concentration of 0.1 μg/kg (range of <0.1–0.2 μg/kg).

Fig. 2 shows the mean amounts of total PCBs, total DDT, total cyclodienes-b, total endosulfan and mirex in the SPMDs (μg per SPMD) deployed during the 2002 spawning period, from 17 September to 17 October. At the reference site, there was accumulation in the SPMDs of PCBs, DDT, cyclodienes and mirex in amounts <1 μg per SPMD. The mean amounts of PCBs, DDT and cyclodienes-b in the SPMDs were elevated at Sites 1 and 2 below the Streetsville Dam, relative to the reference site above the dam. Site 2 showed elevated levels of these contaminants relative to Site 1. Accumulation of mirex in SPMDs was very low relative to the other OCs (Fig. 2). The amounts of total endosulfan in SPMDs, although relatively high, were not significantly different between the reference site and the sites below the dam (Fig. 2).

To examine temporal trends in aqueous concentrations of contaminants over the sampling period, we adopted an approach of calculating a ratio between the amounts of contaminants in SPMDs at Sites 1 and 2 below the dam relative to the amounts in SPMDs at the reference site above the dam, for each deployment interval. In a few cases, the SPMDs were lost due to high flows in the Credit River. In the two cases where SPMDs were lost from the reference site (i.e. 28 May, 2002; 12 November, 2002), the concentrations in the SPMDs at the reference site were estimated as the mean of the concentrations at the sampling intervals before and after the missing data set.

Plots of these temporal trends for total PCBs and total DDT (Fig. 3) showed that the relative amounts of these contaminants that accumulated in SPMDs were high at Site 1 and Site 2 from late September through late November in 2001, and the same pattern appeared again in the fall of 2002. In addition, there was a minor increase in the amounts of these contaminants that accumulated in SPMDs deployed at Site 2 during the summer months of June and July of 2002. Overall, the accumulation of total DDT and total PCBs was greater in SPMDs deployed at Site 2, in comparison to the SPMDs at Site 1 (Fig. 3). The trends seen with total PCBs and total DDT in SPMDs were replicated for most other classes of OC compounds, as illustrated in the plots for total cyclodienes-b and mirex (Fig. 4). The relative amounts of total endosulfan in SPMDs deployed in the Credit River did not show a distinct pattern that could be related to the spawning runs of Chinook salmon in 2001 or 2002 (Fig. 5).

Table 1
Mean ± S.D. of concentrations (μg/kg wet weight) in fish tissues of: (A) individual OC compounds, total DDTs, total cyclodienes-a, total cyclodienes-b, total endosulfans, and total other OCs, and (B) PCB congeners and total PCB. Tissues analyzed were muscle and eggs of adult female Chinook salmon ($n = 7$) collected in the Credit River in October 2001, muscle of juvenile Chinook salmon collected from the Ringwood Fish Culture Station ($n = 5$) in August 2003, and muscle of wild juveniles collected from Wilmot Creek, Ontario ($n = 5$) on 17 June, 2003. The lipid content (%) of the samples is provided. ND, not detected

	Adult females (μg/kg)	Eggs (μg/kg)	Hatchery juveniles (μg/kg)	Wild juveniles (μg/kg)
(A) OC Compounds				
Lipid content (%)	4.2 ± 1.4%	11.8 ± 3.2%	3.4 ± 0.9%	1.9 ± 0.6%
o,p′-DDT	1.14 ± 0.48	6.02 ± 2.28	0.11 ± 0.08	0.14 ± 0.08
p,p′-DDT	8.31 ± 3.02	28.21 ± 18.14	1.41 ± 0.12	1.31 ± 0.19
o,p′-DDE	ND	0.49 ± 0.60	ND	ND
p,p′-DDE	149.85 ± 29.72	597.3 ± 114.48	4.65 ± 2.72	3.15 ± 1.17
o,p′-DDD	0.44 ± 0.22	2.10 ± 1.11	ND	ND
p,p′-DDD	10.13 ± 3.29	40.84 ± 11.09	0.94 ± 0.16	0.88 ± 0.17
α-HCH	ND	0.27 ± 0.37	ND	0.06 ± 0.06
β-HCH	ND	ND	ND	ND
δ-HCH	ND	ND	ND	ND
γ-HCH	ND	0.07 ± 0.17	ND	0.29 ± 0.22
Aldrin	ND	0.17 ± 0.46	ND	ND
Dieldrin	2.17 ± 0.76	30.76 ± 10.25	0.13 ± 0.09	0.11 ± 0.08
Endrin ketone	0.35 ± 0.14	1.39 ± 0.75	ND	0.06 ± 0.03
Endrin	ND	0.17 ± 0.44	ND	ND
Endrin aldehyde	ND	ND	ND	ND
Heptachlor	ND	ND	ND	ND
Heptachlor epoxide	0.17 ± 0.06	9.95 ± 3.23	ND	0.02 ± 0.01
cis-Chlordane	3.97 ± 1.06	17.09 ± 4.41	0.34 ± 0.11	0.39 ± 0.27
trans-Chlordane	0.99 ± 0.28	4.03 ± 1.22	ND	ND
cis-Nonochlor	6.28 ± 2.20	20.93 ± 5.41	0.59 ± 0.32	0.43 ± 0.17
trans-Nonachlor	12.62 ± 3.97	37.99 ± 8.27	1.13 ± 0.75	0.98 ± 0.43
Methoxychlor	ND	ND	ND	ND
Endosulfan II	0.36 ± 0.18	1.07 ± 1.40	ND	0.04 ± 0.03
Endosulfan	ND	ND	ND	0.04 ± 0.02
Endosulfan sulfate	0.13 ± 0.02	0.17 ± 0.45	ND	0.06 ± 0.04
HCB	ND	ND	0.14 ± 0.02	1.14 ± 0.99
Mirex	64.97 ± 25.17	86.25 ± 21.27	1.11 ± 0.45	0.56 ± 0.22
Octachlorostyrene	3.82 ± 0.86	10.21 ± 2.34	ND	ND
Total DDT	169.87 ± 35.27	674.98 ± 118.12	7.12 ± 4.33	5.49 ± 2.23
Total endosulfan	0.49 ± 0.31	1.23 ± 1.73	ND	0.14 ± 0.09
Total cyclodienes-b	24.05 ± 7.30	90.00 ± 21.63	2.12 ± 0.98	1.78 ± 0.76
Total cyclodienes-a	2.52 ± 0.83	32.49 ± 10.49	0.13 ± 0.52	0.13 ± 0.07
Total other OCs	68.78 ± 25.97	96.79 ± 23.52	1.18 ± 0.52	2.01 ± 0.15
(B) PCBs				
Lipid content (%)	4.2 ± 1.4%	11.8 ± 3.2%	3.4 ± 0.9%	1.9 ± 0.6%
28	0.80 ± 0.37	4.16 ± 2.12	0.31 ± 0.22	ND
18/31	ND	1.86 ± 1.75	ND	ND
33	ND	ND	ND	ND
44	1.81 ± 0.44	9.87 ± 2.67	0.65 ± 0.33	0.44 ± 0.37
52	5.00 ± 1.01	18.78 ± 4.48	1.23 ± 0.89	0.76 ± 0.55
70	6.66 ± 1.37	21.99 ± 4.27	1.41 ± 1.02	ND
74	3.71 ± 0.83	11.94 ± 2.89	ND	ND
87	7.78 ± 1.91	17.30 ± 8.87	0.99 ± 0.65	0.21 ± 0.05
95	1.85 ± 1.17	ND	ND	ND
99	17.76 ± 4.56	51.75 ± 11.36	2.54 ± 2.55	1.97 ± 0.55
101	24.51 ± 6.61	73.17 ± 16.72	4.33 ± 2.21	1.66 ± 0.98
105	8.10 ± 2.42	25.75 ± 6.14	ND	ND
110	17.33 ± 4.47	57.13 ± 13.69	4.79 ± 2.11	3.88 ± 2.65
118	24.51 ± 6.61	65.70 ± 15.81	3.30 ± 2.21	3.02 ± 1.15
128	8.10 ± 2.43	19.67 ± 4.23	2.89 ± 2.34	1.82 ± 1.44
132	3.98 ± 1.06	12.63 ± 2.86	ND	ND
138	62.55 ± 24.90	135.52 ± 39.59	6.86 ± 3.84	3.41 ± 2.26
149	18.42 ± 4.88	49.68 ± 10.86	2.42 ± 1.33	0.99 ± 0.32
151/82	10.59 ± 2.62	20.54 ± 4.25	1.22 ± 11	0.12 ± 0.05
153	62.63 ± 20.80	139.84 ± 35.52	4.82 ± 3.51	3.65 ± 1.65

Table 1 (*continued*)

	Adult females (μg/kg)	Eggs (μg/kg)	Hatchery juveniles (μg/kg)	Wild juveniles (μg/kg)
156	3.42 ± 1.29	8.23 ± 2.79	0.27 ± 0.14	ND
170	11.01 ± 3.94	22.91 ± 7.45	1.69 ± 1.23	0.98 ± 0.19
180	29.22 ± 9.11	54.34 ± 13.28	3.68 ± 2.47	1.11 ± 0.39
187	23.99 ± 6.30	53.19 ± 11.72	3.51 ± 2.23	0.98 ± 0.77
191	0.44 ± 0.28	0.95 ± 0.69	ND	ND
194	5.20 ± 1.26	9.27 ± 3.37	0.22 ± 0.16	ND
195	1.75 ± 0.49	3.29 ± 0.87	0.11 ± 0.09	ND
201	6.39 ± 1.55	12.74 ± 2.86	0.61 ± 0.54	0.55 ± 0.51
205	ND	ND	ND	ND
206	1.87 ± 0.52	2.96 ± 0.77	0.17 ± 0.11	ND
209	1.27 ± 0.63	0.22 ± 0.18	ND	ND
Total PCBs	370.70 ± 111.92	905.42 ± 219.89	45.37 ± 28.64	24.32 ± 14.63

4. Discussion

Our study has demonstrated that there are temporal and spatial patterns of POP contamination in the Credit River that are correlated with the spawning and decay of Chinook salmon carcasses. In addition, our study has shown that hatchery-raised and wild juvenile salmon are contaminated by POPs. Contaminated salmon have previously been reported to be sources of persistent contaminants in river sediments (Krummel et al., 2003). However, the temporal and spatial patterns of contamination throughout the year, and the presence of these contaminants in the aqueous phase have not been previously reported.

Adult Chinook salmon are in the Credit River during September and October, where they gather in large numbers below the Streetsville Dam that restricts their spawning area to the lower reaches of the river. Carcasses accumulate in October and continue to decay through November, but by December the water temperature drops to 1–3 °C, which retards further decay. It is not until the early summer of the following year that water temperatures increase to above 10 °C, which renews rapid decomposition.

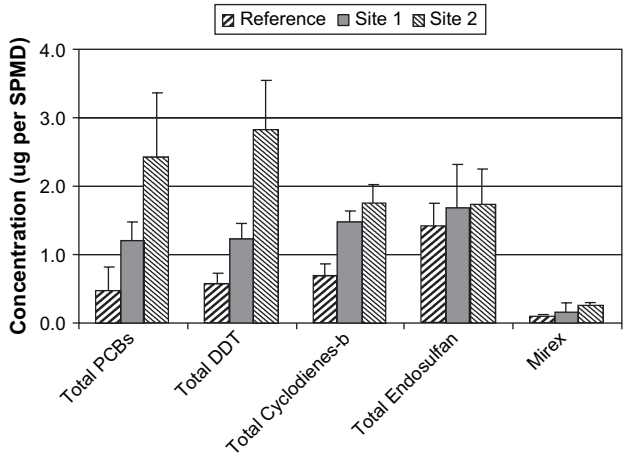

Fig. 2. Mean ± S.D. ($n = 3$) amounts of contaminants accumulated in SPMDs (μg per SPMD) deployed during the spawning period from 17 September to 17 October, 2002 at the reference site above the dam, and at Sites 1 and 2 below the dam.

In the Credit River, the amounts of contaminants that accumulated in SPMDs deployed below the dam increased by up to five times above the levels in SPMDs deployed at the reference site above the dam during late September to November of 2001 and 2002; the months following the peak period of spawning. It appears from these data that there was release of PCBs, DDT compounds and some other OCs from decaying salmon tissue and from eggs during and after the spawning run, with subsequent accumulation of contaminants from the aqueous phase into the SPMDs. The relatively minor increase in the concentrations of these compounds in SPMDs deployed during the summer of 2002 may reflect the release of contaminants from tissues that had not yet completely decayed over the previous winter months because of low water temperatures. The early summer rise in the levels of PCBs and DDT in SPMDs deployed at Site 2, but not at Site 1, likely reflects the downstream migration of residual tissues, and their continued decay and mobilization.

Accumulation of hydrophobic contaminants by SPMDs is affected by both the temperature and the flow of the surrounding aqueous medium (Huckins et al., 1996). Over the sampling period in the Credit River, temperature and flow rates varied widely. At each sampling site, the amounts of contaminants in SPMDs would be expected to decline as water temperatures and hydrological flows declined in the late fall and winter, and increase with temperature and flow in the spring, regardless of contaminant concentrations in the aqueous phase. However, the increases in POPs concentrations observed in the Credit River in the fall coincided with a period of decreasing water temperatures, indicating that hydrological conditions cannot explain the trends observed in the SPMDs. Moreover, the declines seen in December and January may reflect both a decrease in

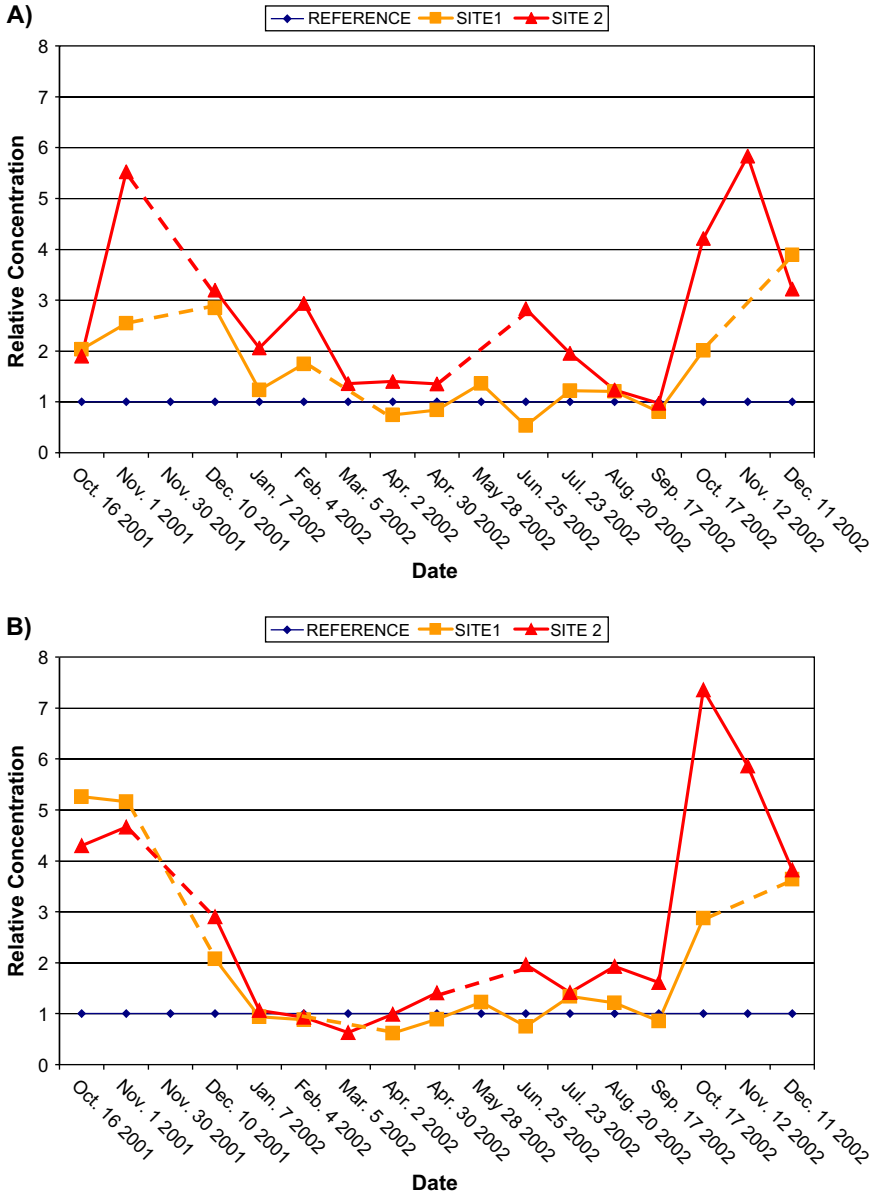

Fig. 3. Ratios relative to the reference site of mean amounts of: (A) total PCBs and (B) total DDT accumulated in SPMDs deployed in the Credit River at Sites 1 and 2 over the period of October 2001 through December 2002. The dates of SPMD collection are shown on the *x*-axis. Where sampling dates were excluded because of the loss of SPMDs, dashed lines join the adjacent data points.

the concentrations of POPs in the water, coupled with a decrease in the ability of the SPMDs to take up these contaminants.

The concentrations of PCBs and OC pesticides in the tissues of the adult salmon sampled in the Credit River in 2001 are very similar to the concentrations reported in the muscle of Chinook salmon collected from the Credit River in 1994 (Feely and Jordan, 1998). However, concentrations of total PCBs, total DDT and mirex in muscle tissue and eggs were lower than concentrations detected in Credit River Chinook salmon sampled in 1990 (Smith et al., 1994). No male Chinook salmon were sampled in this study, but a study by Jackson et al. (2001) found no significant differences in PCB levels between male and female Chinook salmon in Lake Michigan.

In the tissues of Credit River salmon, mirex concentrations were very high (Table 1), so significant accumulation of mirex in SPMDs would have been expected. However, while mirex is resistant to metabolic degradation in vivo, in the aqueous environment it quickly forms the photodegradation product, photomirex, with a half-life of only 0.83 h in river water (Mackay et al., 1992). Thus, mirex released from the salmon tissues may have quickly degraded to photomirex in the Credit River, explaining the relatively low concentrations of this OC compound in SPMDs.

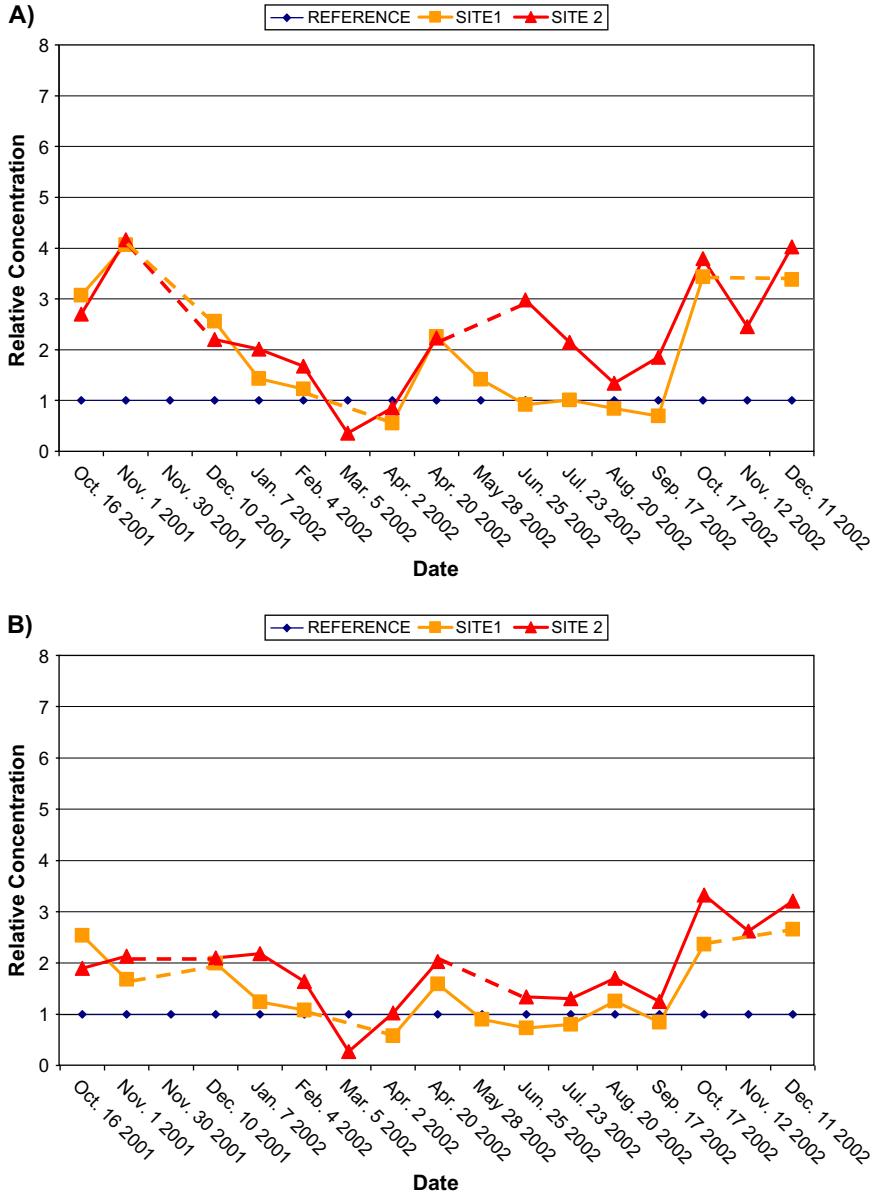

Fig. 4. Ratios relative to the reference site of mean amounts of: (A) total cyclodienes-b and (B) mirex accumulated in SPMDs deployed in the Credit River at Sites 1 and 2 in the Credit River over the period of October, 2001 to December, 2002. The dates of SPMD collection are shown on the *x*-axis. Where sampling dates were excluded because of the loss of SPMDs, dashed lines join the adjacent data points.

The organochlorine pesticide, endosulfan, and its metabolites are relatively minor contaminants in Chinook salmon tissues (Table 1); reflecting the low persistence of this class of compounds in biota relative to many other OCs. However, there were relatively large amounts of endosulfan compounds that accumulated in SPMDs at the reference site above the Streetsville Dam. It is likely that these data reflect active inputs from point sources in the Credit River watershed, such as from agricultural areas, golf courses, residential areas or landfills. At the reference site, there was accumulation in the SPMDs of other OC contaminants, such as PCBs, DDT and cyclodienes in amounts >100 ng per SPMD. There are both point and non-point sources of these persistent contaminants in the Lake Ontario basin (Chan et al., 2003; Williams et al., 2003). For instance, a total PCB concentration of 4.1 ng/L was reported in water collected on 16 September, 1997 from the upstream part of the Credit River (Boyd and Biberhofer, 1999). If we assume a sampling rate of 5 L per day for PCBs in an SPMD (Huckins et al., 1996) over a 30-day sampling period, this level in water would concentrate to 615 ng per SPMD. This amount is consistent with the mean of 476 ng (i.e. 0.476 μg) of PCBs accumulated in the SPMDs deployed at the reference site in the early fall of 2002 (Fig. 2).

The sources of contamination in salmon muscle are varied. Some of the contamination in adult Chinook

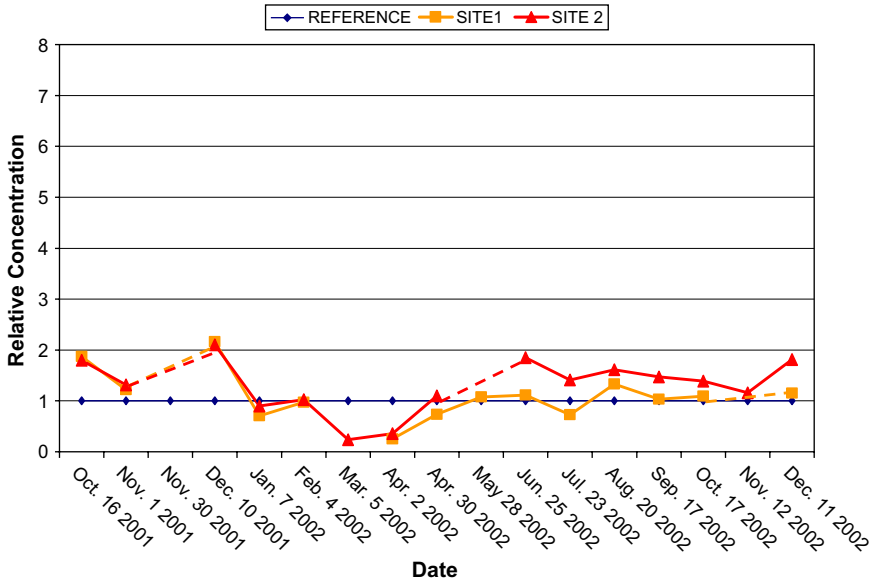

Fig. 5. Ratios relative to the reference site of mean amounts of total endosulfan accumulated in SPMDs deployed at Sites 1 and 2 in the Credit River over the period of October 2001 to December 2002. The dates of SPMD collection are shown on the *x*-axis. Where sampling dates were excluded because of the loss of SPMDs, dashed lines join the adjacent data points.

would have come from maternal transfer to the eggs, but the OC levels seen in the eggs in this study would only contribute a very small percentage of the total body burden seen in the adults. A second source of contamination comes during juvenile development. Both the wild juveniles from Wilmot Creek and the hatchery-produced juveniles from the Ringwood Hatchery showed similar levels of OCs. The wild fish could have acquired some of the contaminants that entered the creek from atmospheric sources (Macdonald and Metcalfe, 1991), but it is possible that the decaying tissues and the eggs of spawning adult salmon in Wilmot Creek also contributed to contamination of the ecosystem. The contamination in hatchery-produced Chinook salmon most likely came from their food. Samples of the hatchery feed used to rear juvenile salmon in the Ringwood hatchery showed contamination similar to that reported by Easton et al. (2002). We also found some variation in the concentrations among the three size classes of pellets in the diet. This probably reflects variations in the batches of the food (Mac, 1979).

The contaminants incorporated during juvenile development would contribute to POPs burdens in the adult fish. However, salmon increase in mass by at least 1000-fold from about 8 g when they enter Lake Ontario as smolt to approximately 10 kg when they return as spawning adults about 3 years later. The 'growth dilution' of contaminants over this period would make any contaminants accumulated as a juvenile insignificant relative to subsequent accumulation while the fish is feeding in Lake Ontario.

Overall, these data indicate that salmon spawning and subsequent mobilization of contaminants from decaying tissues are a source of persistent contaminants dissolved in the water of the Credit River. The spawning run of Chinook salmon in the Credit River is approximately 20,000 fish. Based upon the concentrations of contaminants observed in Chinook salmon tissues and assuming an average mass of 10 kg per salmon, the tissue burdens of contaminants transported annually into the Credit River would be approximately 75 g of total PCBs and 35 g of total DDT compounds.

Studies in rivers along the Pacific coast have shown that contaminants accumulated in juvenile salmon during out-migration can cause biological effects, including reduced immunocompetence (Collier et al., 2000) and induction of hepatic cytochrome P450-dependent enzymes (Stein et al., 1995). It is possible that juvenile salmon and other fish species in rivers receiving contaminants mobilized from Great Lakes salmon could experience toxicological impacts prior to out-migration. These potential impacts should be considered with regard to the advisability of planting salmon carcasses in streams as a component of salmon habitat restoration.

5. Conclusions

This study has shown that persistent contaminants accumulated in Chinook salmon from Lake Ontario are released into the water column of a tributary stream (i.e. Credit River) as a result of the post-spawning decay of the salmon carcasses. The peak in concentrations of contaminants in stream water in the fall months coincides with the period of post-spawning decay, but a more minor peak was observed during the following

spring, when water temperatures rose. Analysis of juvenile salmon from a tributary stream with a natural population of salmon (i.e. Wilmot Creek) indicated that the salmon accumulate low levels of persistent contaminants before entering Lake Ontario. Decaying carcasses of adult salmon may have contributed to the contamination of juveniles in Wilmot Creek, although atmospheric deposition of contaminants is another potential source.

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