

## Assessing Trends in Organochlorine Concentrations in Lake Winnipeg Fish Following the 1997 Red River Flood

A. Robin Stewart<sup>1§</sup>, Gary A. Stern<sup>1,\*</sup>, W. Lyle Lockhart<sup>1</sup>, Karen A. Kidd<sup>1</sup>, Alex G. Salki<sup>1</sup>, Michael P. Stainton<sup>1</sup>, Krystyna Koczanski<sup>1</sup>, G. Bruno Rosenberg<sup>1</sup>, Dan A. Savoie<sup>1</sup>, Brian N. Billeck<sup>1</sup>, Paul Wilkinson<sup>1</sup>, and Derek C. G. Muir<sup>2</sup>

<sup>1</sup>Freshwater Institute, Department of Fisheries and Oceans  
501 University Crescent  
Winnipeg, Manitoba R3T 2N6

<sup>2</sup>Environment Canada  
Burlington, Ontario L7R 4A6

**ABSTRACT.** As we move toward the virtual elimination of persistent organic pollutants (POPs) in the environment our understanding of how short-term variability affects long-term trends of POPs in natural populations will become increasingly more important. In this study we report short-term trends in organochlorine (OC) levels in fish from Lake Winnipeg in the months and years following the 1997 100-year flood of the Red River ecosystem. Our goal was to understand the effects of an episodic event on OC levels in benthic and pelagic invertebrates and in fish. Despite elevated loading of OCs into the south basin of Lake Winnipeg during the flood there were no differences in OC levels of surface sediments or emergent mayflies. After adjusting for differences in lipid content and length among sample times, we did find significant increases in total DDT ( $\Sigma$ DDT) and total polychlorinated biphenyl ( $\Sigma$ PCB) post-flood (March 1999) in top predators including walleye and burbot. Significant increases were also observed in OC concentrations of zooplankton and yellow perch ( $> 2$  fold in  $\Sigma$ PCB,  $\Sigma$ DDT, total chlordane ( $\Sigma$ CHL), total chlorobenzenes ( $\Sigma$ CBZ)) and walleye (1.4 fold  $\Sigma$ PCB) over a 2-month period in the summer following the flood. Analysis of specific congener patterns over time suggest that the major changes in fish OC levels pre- and post-flood did not appear to be linked to transport of new compounds into the Lake during the flood, but to species shifts within the plankton community. Our results indicate that short-term variation (~2 months) in OC distributions within biota may be equal to or greater than those resulting from episodic events such as spring floods.

**INDEX WORDS:** Bioaccumulation, PCB, DDT, floods, food webs.

### INTRODUCTION

Variability of contaminant levels in natural aquatic food webs over short time periods ( $< 3$  yr) has received relatively little attention. Contaminant levels are usually predicted at steady state using an equilibrium approach that assumes a constant contaminant load and stable food source. Often this is not the case for natural systems (Thomann and Connolly 1984). There has been evidence of a decline in the concentrations of organochlorines (OC) in surficial lake sediments and tissue burdens

of top predators in the Great Lakes over the past several decades following restrictions in OC use in North America (Schneider *et al.* 2001, DeVault *et al.* 1996, Hebert *et al.* 1997). Recently, declines in some top predators have been less apparent due to fluctuations in tissue burdens over time caused by factors other than abiotic inputs. For example, Hebert *et al.* (1997) explained sporadic variations in polychlorinated biphenyl (PCB) concentrations in herring gull eggs from Lake Ontario to be a result of annual variability in the population characteristics of alewife, their main food source. If we are to move toward the goal of virtual elimination of persistent contaminants, a better understanding is needed of factors that mediate changes in OC con-

\*Corresponding author. E-mail: sterng@dfo-mpo.gc.ca

§Current address: USGS, Water Resources Division, 345 Middlefield Rd., MS 465, Menlo Park, CA 94025

centrations of biota at moderate to low contamination levels.

In the absence of changes to point source inputs, remobilization of OCs from non-point sources, industrial sites, or agricultural land during extreme hydrologic events such as flash and spring floods could periodically increase the loading of OCs into receiving waters and change the magnitude of contaminant accumulation in aquatic food webs. Widespread flooding has been associated with the remobilization of agricultural and industrial sediments resulting in increased transport of nutrients such as nitrogen and phosphorus (Bergqvist *et al.* 1998), short-term increases in riverine dissolved and particulate-adsorbed organic contaminant concentrations (Bergqvist *et al.* 1998, Petty *et al.* 1998, Rostad 1997) and elevated OC concentrations in downstream sediments (Barber and Writer 1998). The potential for short-term episodic events such as floods to modify organic contaminant concentrations in aquatic biota in receiving waters is unknown. Flooding events resulting in higher dissolved OC concentrations and increased particulate contaminant load available to the base of the food web could lead to an increase in OC levels and toxicity in top predators (Ludwig *et al.* 1993). Furthermore, a flood could result in unexpected changes in nutrient status of receiving waters and food web structure that could influence contaminant accumulation in the food web.

Bioaccumulation of OCs in aquatic food webs is determined largely by compound hydrophobicity and structural characteristics (e.g., PCB chlorine substitution) (Carey *et al.* 1998), individual species attributes (size, age, sex, lipid, exposure history) (Stow *et al.* 1997), and ecology of the system (nutrient status, food web structure) (Larsson *et al.* 1998, Kidd *et al.* 1999). Relationships between species attributes and OC levels in natural fish populations are not understood and appear to be relatively complex (Stow *et al.* 1997, Rasmussen *et al.* 1990, Borgmann and Whittle 1992). Lipid content is often a good predictor of OC concentrations among fish species and within food webs (Kucklick and Baker 1998, Stapleton *et al.* 2001), but has been found to be less effective in predicting OC levels within individual species (Stow *et al.* 1997). Additional attributes such as size, spawning status, and age as well as data conditioning variables such as season and collection site may be as important as lipid in interpreting changes in OC levels in fish populations. Short-term seasonal fluctuations in the partitioning of OCs at the base of the food web have been shown in lakes (Epplert *et al.*

2000, Larsson *et al.* 1998) and may have consequences for top predators. The effect of nutrient status on the uptake of OCs in aquatic biota has been investigated for both lakes and streams. Larsson *et al.* (1992) found that levels of PCBs and *p, p'*-DDE in fish decreased as lake productivity increased, which they attributed to growth dilution in faster growing fish and sedimentation of particles with sorbed contaminant. In lotic environments, Berglund *et al.* (1997) found elevated levels of PCBs and DDT in young of year brown trout (*Salmo trutta*) in streams with the highest trophic status (total phosphorus). The authors suggested that the shift of the base of the food chain from heterotrophic detritus toward autotrophic periphyton, caused by eutrophication, resulted in higher levels of contaminants that could be transferred to fish. These studies emphasize the importance of pathways of carbon flow on pollutant bioaccumulation in fish. Lastly, Kidd *et al.* (1995) found that the same species of fish from remote lakes with longer underlying food chains had higher concentrations of OCs than those in lakes with shorter food chains. Their study used ratios of stable nitrogen isotopes to characterize the length of the food chain. Perturbations that affect the structure of an aquatic ecosystem may in turn affect the concentrations of persistent contaminants found in the biota.

In this paper we examine short-term variability in OC levels in natural fish populations in relation to ecosystem processes and natural perturbations. The Red River flood of 1997 was its largest in over 100 years. The flood provided a unique opportunity to examine variability in OC levels of Lake Winnipeg fish populations following a perturbation of the system. OC levels in fish collected up to 3 years following the flood were compared to fish collected prior to the flood in 1995 and among seasons and years following the flood. In addition to OC levels in fish, we examined several factors that could contribute to short-term variability including: 1) Environmental factors such as increased transport of OCs during the flood; 2) Biological factors such as fish size and lipid content, and 3) Ecological factors such as lake nutrient status and food web structure.

## MATERIALS AND METHODS

### Lake Winnipeg

The Red River originates near the junctions of Minnesota, North Dakota, and South Dakota and flows northward 800 km into the south basin of Lake Winnipeg. A detailed description of the physi-

cal characteristics of Lake Winnipeg can be found in Brunskill *et al.* (1980). Lake Winnipeg is the 10<sup>th</sup> largest lake in the world by surface area (23,750 km<sup>2</sup>) with the south basin contributing approximately 12% of the surface area. The south basin has an average depth of 9.7 m and a maximum depth of 14 m. Lake Winnipeg is unusually shallow with large seiches equal to 1–2 m at downwind shore locations. The south basin typically has a water renewal time of 0.4 to 0.8 yr, whereas the whole lake has a residence time of 2.9 to 4.3 yr. The Winnipeg and Red rivers are the two main rivers flowing into the south basin. The Winnipeg River has an inflow of  $39 \text{ m}^3/\text{y} \times 10^9$  and drains a watershed composed of Precambrian Shield deposits overlain by glacial Lake Agassiz sediments. The Red River has an inflow of  $8.1 \text{ m}^3/\text{y} \times 10^9$  and drains the prairie watershed to the south that is composed of sedimentary rock (Paleozoic) overlain by glacial Lake Agassiz sediments. Despite its relatively low concentrations of major ions and nutrient elements, the Winnipeg River contributes as much or more N, Ca, K,  $\text{HCO}_3^-$ , and Si to the south basin of Lake Winnipeg as the Red River, due to the large contribution of the Winnipeg River (75%) to the annual water budget of the south basin (Brunskill *et al.* 1980). The Red River contributes a considerably higher proportion of P and  $\text{SO}_4^{2-}$  to the south basin than the Winnipeg River in spite of its much lower contribution to the water budget. The south basin of Lake Winnipeg is usually turbid with limited light penetration (0.1 to 1.0 m) (Brunskill *et al.* 1979). It is mesotrophic with summer chlorophyll *a* ranging from 5 to 19  $\mu\text{g}/\text{L}$  and suspended nitrogen and phosphorus ranging from 446 to 902  $\mu\text{g}/\text{L}$  and 60 to 117  $\mu\text{g}/\text{L}$ , respectively ( $n = 4$  different years 1969, 1994, 1996, 1998, Brunskill *et al.* 1980, Salki 1996, Stainton unpublished data, Stewart *et al.* 2000). The relative contributions of OCs to the south basin of Lake Winnipeg from the Winnipeg and Red Rivers are not known. However, OC fluxes from non-atmospheric sources of  $\Sigma\text{PCB}$ ,  $\Sigma\text{DDT}$ ,  $\Sigma\text{HCH}$ ,  $\Sigma\text{CHL}$ , and hexachlorobenzene (HCB) exceed atmospheric fluxes to the south basin (Rawn *et al.* 2000).

## SAMPLE COLLECTION

### Flood Event Sampling

Water samples ( $n = 15$ ) were collected approximately every second day during the spring of 1997 from 28 April to 18 June from the Red River at Selkirk (Fig. 1), approximately 30 km upstream of Lake Winnipeg. Collections of river water were

made from the center of a bridge by pumping water from 1 m below the surface into an 18-L stainless steel container. Suspended sediments were allowed to settle to the bottom of the 18-L can and surface water was siphoned off the top, filtered, and extracted as described below. Remaining water was centrifuged to isolate suspended sediment that was then stored at 4°C until analysed for OCs.

### Sediment and Water

Sediment samples ( $n = 1$ ) were collected at 33 sites extending north along a depositional gradient from the mouth of the Red River in the south basin of Lake Winnipeg in the spring of 1998 from 23 February to 6 March (Fig. 1). The top 0.5 cm of sediment of a single grab sample (using an Eckman dredge sampler) was placed in a polyethylene bag and kept at 4°C until analyzed for organic contaminants. Duplicate sediment cores were collected at sites 4B, 9A, 9B, and 9C in March 1998 using a gravity corer with an internal diameter of 10 cm. Cores were sliced into 0.5 cm sections on site and placed in plastic Whirl pak bags and stored with grab samples. Large volume (~100 L) water samples ( $n = 1$ ) were collected at core sites 4B, 9A, 9B, and 9C in March 1998 for OC analysis. Sampling sites near Winnipeg Beach (4B), Gimli (7B), and Riverton (11B) were revisited during the summer of 1998 on 16 July and 15 September. In March, single water samples for OCs were collected by pumping water from 1 m below the water surface using an Infiltex 200 sampler (Axys Analytical, Sidney, BC) situated on the ice surface. Summer and fall collections were made by dropping weighted 18-L stainless steel containers off the side of a boat.

### Biota

Lower trophic level organisms were collected to examine changes in OC concentrations and fish dietary exposure at the base of the food web. Emergent mayflies (*Hexagenia rigida*) were collected on land at several locations prior to (Sandy Hook, Husavik, Grand Beach) and after the flood (Gimli) in the south basin (Fig. 1). Mayflies were collected after the flood only at the Gimli site due to the lack of emergence of adults during the summer of 1998. Mayflies were grouped into composites ( $n > 3$ ) based on sex and molt stage and frozen until analyzed for stable isotopes and OCs. Plankton samples were collected on 16 July, 12 August, and

15 September 1998 in vertical tows using a 160  $\mu\text{m}$  mesh net at 3 sites along transect 4 across from Winnipeg Beach, transect 7 across from Gimli and transect 11 below Riverton (Fig. 1). Excess water was drained and samples were scooped into hexane rinsed jars and frozen until analyzed. At that same time additional samples for zooplankton community analysis were collected using a 72  $\mu\text{m}$  net and preserved in formalin.

Fish were netted by commercial fishermen near Riverton prior to and after the flood (October 1995 and July 1998) and near Winnipeg Beach in October 1997, September 1998, March 1999, and March 2000) (Fig. 1). The fish were caught using a commercial 3 inch mesh gillnet and frozen whole in polyethylene bags ( $-30^{\circ}\text{C}$ ). Species collected represented a variety of feeding behaviors (Scott and Crossman 1973), including adult walleye (*Stizostedion vitreum* (Mitchill)), sauger (*Stizostedion canadense* (Smith)), burbot (*Lota lota* (Linnaeus)), yellow perch (*Perca flavescens* (Mitchill)), and freshwater drum (*Aplodinotus grunniens* Rafinesque). Pre-flood walleye and burbot were collected as part of another study in 1995/1996 (Kidd, unpublished data) and provided an opportunity to follow contaminant levels in the fish over time before and after the flood event. Pre-flood and post-flood fish were processed and analyzed in the same laboratory using the same methodologies.

In the laboratory, fish were partially thawed, standard length, weight and sex (if mature) were recorded, and opercula (walleye, yellow perch, and sauger) and otoliths (burbot and freshwater drum) were removed for age determinations (Babaluk and Campbell 1987, Barber and McFarlane 1987). Dorsal muscle (skin on) and liver (burbot only) samples for organochlorine analysis were placed in polyethylene bags and stored at  $-40^{\circ}\text{C}$  until analyses were conducted. Portions of dorsal muscle (including burbot muscle) were placed in glass scintillation vials for stable isotope analysis. Changes in relative trophic position of organisms within and across systems can be assessed by nitrogen isotopes, whereby the heavier isotope of nitrogen,  $^{15}\text{N}$ , is enriched from prey to predator by 3 to 5 per mil (Peterson and Fry 1987). For this approach to be valid, lower trophic organisms were also analyzed for stable nitrogen isotope ratios to determine whether changes in nutrient inputs as a result of the flood had shifted the basal signature in the lake (Cabana and Rasmussen 1996).

### Core Dating and Sedimentation Rate Calculations

Cores were dated and sedimentation rates calculated using in the same laboratory and radionuclide techniques as those described in Rawn *et al.* (2000) and Lockhart *et al.* (1998). Sedimentation rates were calculated with  $^{210}\text{Pb}$ , using the linear and constant rate of supply (CRS) models. The models assumed a constant input flux of  $^{210}\text{Pb}$  over time.

### Extraction and Organochlorine Analysis

March 1998 surface water samples (100-L) were filtered and extracted in the field using a High Volume, Infiltrax 200 sampler (Axys Analytical, Sidney, BC). Water, pumped at 0.8 L/min for approximately 3 hour, passed through 4-inch LMO glass fiber filter cartridge (1  $\mu\text{m}$ ) and a XAD-2 resin column (3.7 cm i.d.  $\times$  10 cm, 75 g resin). All columns were pre-cleaned with 200 mL each of dichloromethane (DCM) and methanol before use. Field blanks were collected and processed in the same manner as the actual samples, but the pump was only turned on for  $\sim$  30 seconds. Columns were capped, sealed with Teflon tape, and shipped to the Freshwater Institute where they were stored at  $4^{\circ}\text{C}$  until analysis. Water samples collected in stainless steel containers were brought back to the Freshwater Institute and extracted using the Infiltrax 200 sampler as described above. All water samples (XAD-2 columns) were initially eluted with 200 mL of HPLC grade methanol followed by 200 mL of DCM at a flow rate of 1–2 drops per second. The elution solvents were reduced in volume using a rotary evaporator and 10 mL of saturated solution of sodium chloride added to increase ion strength and thus extraction efficiency. The resulting fractions were then extracted three times with 100 mL hexane, dried with sodium sulfate, and reduced to 10 mL using a rotary evaporator. Surrogate recovery standards of PCB 30 and octachloronaphthalene (OCN) were added prior to extraction.

Methodology for sediments has been described previously (Rawn *et al.* 2000, Muir *et al.* 1996). In brief, sediments were freeze-dried and extracted with DCM using accelerated solvent extraction (ASE, Dionex Canada Ltd. Oakville, ON, Canada). Sulfur was removed using activated Cu. All water and sediment sample extracts were separated into three fractions of increasing polarity on Florisil (8 g; 1.2% v/w water deactivated). The first fraction was eluted with hexane and contained PCBs, *p,p'*-DDE, *trans*-nonachlor, and mirex and a small por-

tion of toxaphene (chlorinated bornanes (CHB)), most notably T2/B8-1413 (Stern *et al.* 1992). Fraction two was eluted with hexane:DCM (85:15) and contained hexachlorocyclohexane (HCH), most CHBs and chlordanes (CHL). The third fraction, containing dieldrin and heptachlor epoxide, was eluted with a 1:1 mixture of hexane:DCM. The volume of each Florisil fraction was reduced to 1 mL and aldrin was then added as a volume corrector.

Methods for OC tissue analysis have been described previously in Muir *et al.* (1988, 1990), but are briefly described here. Fish muscle tissue samples were homogenized with dry ice in a blender. The homogenized tissue was then mixed with anhydrous Na<sub>2</sub>SO<sub>4</sub> (heated at 600°C for 16 hours prior to use) and mixed until a free-flowing mixture was obtained. Muscle samples were Soxhlet extracted with DCM:hexane (1:1) for 4 hr. Zooplankton and mayfly samples were freeze-dried, combined with sodium sulfate, and extracted using ASE. Extractable lipids were determined gravimetrically on a fraction (1/10) of each extract. Lipids were removed by gel permeation chromatography (GPC) using 200- to 400-mesh Bio-Beads® S-X3 beads (Bio-Rad Laboratories, Hercules, CA USA). The lipid-free eluate, containing the OCs, was evaporated to 1 mL. Burbot liver samples were partially thawed and 2 g were combined with anhydrous Na<sub>2</sub>SO<sub>4</sub>. Liver tissues were extracted twice with hexane in a small (50 mL) ball mill, centrifuging and decanting the hexane between extractions. Surrogate recovery standards of PCB 30 and octachloronaphthalene (OCN) were added prior to extraction for all samples. With every five samples a blank (250 g Na<sub>2</sub>SO<sub>4</sub>) also was extracted. Each lipid free tissue extract and a portion of each of the ball milled liver extracts equivalent to approximately 100 mg lipid were separated into three fractions of increasing polarity on Florisil as described above.

All samples were analyzed by high-resolution gas chromatography (GC) with <sup>63</sup>Ni electron capture detection (ECD) using a Varian 3400 GC (Varian Instruments, Palo Alto, CA). Samples were injected on a 60 m × 0.25 mm i.d. DB-5 column (film thickness = 0.25 μm). H<sub>2</sub> was used as the carrier gas (1 mL/min) and N<sub>2</sub> as the make-up gas (40 mL/min). A total of 103 PCB congeners (including co-eluting congeners) and 40 OC pesticides were quantified using external standard mixtures (Ultra Scientific, North Kingstown, RI), which were run after every six samples. Recoveries of the surrogates (for water, sediment and biota), PCB-30 and OCN were

consistently greater than 90% and no corrections were made for recoveries. Results for replicate water samples (XAD-2, n = 2) ranged from 7 to 22% for all major OC groups. Other quality assurance measures included the analysis of standard reference materials (National Institutes of Standard and Technology (NIST), Gaithersburg MD, cod liver oil 1588) and duplicated analysis of every 12<sup>th</sup> sample.

### Stable Isotope Analysis

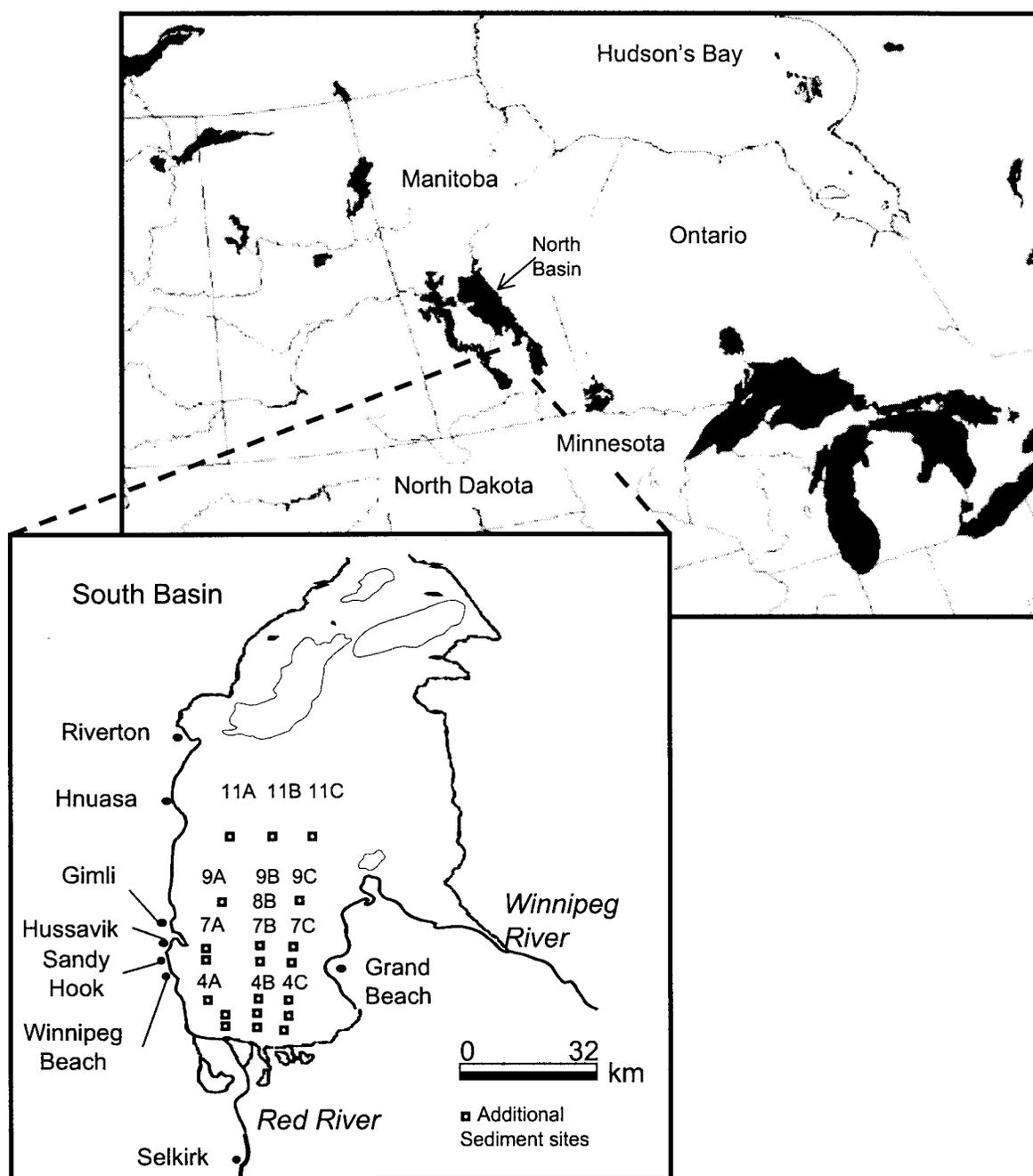
Methods described in Kidd *et al.* (1998) were used for stable isotope analysis. Individual fish, zooplankton, and mayflies were dried in an oven for several days at 60°C and then ground into a fine powder using a mortar and pestle. Dried samples of 1–2 mg were weighed into tin capsules and then combusted in a Carlo Erba NA1500 elemental analyzer. Sample gases were introduced into a VG Optima automated mass spectrometer with helium carrier gas, and water and CO<sub>2</sub> were cryogenically removed using magnesium perchlorate and an Ascarite® column respectively. All samples were standardized against Pee Dee Belemnite (C) or N<sub>2</sub> in air as follows:

$$\delta^{15}\text{N}\text{‰} = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$$

where R = <sup>15</sup>N/<sup>14</sup>N. A laboratory-working standard of Pharmamedium was run with every 10 samples. Precision of the instrument for nitrogen and carbon isotope analysis, based on several years of use, has been 0.4 ‰ and 0.3 ‰ (2 SD), respectively.

### Nutrient Analyses

Water samples for nutrient analyses were collected in March 1998 (sites 4B, 9A, 9B, 9C) and over the summer of 1998 at stations near Winnipeg Beach (4A, 4B, 4C), Gimli (7A, 7B, 7C) and Hnaua (11A, 11B, 11C) on 16 July (station 4B only), 21 August and 15 September (Fig. 1). Water samples were drawn from 1 m below the surface into a 1L Nalgene® bottle. Samples for nutrient analysis were filtered and analyzed on the day of collection for perishable constituents including particulate carbon, nitrogen, and phosphorous, suspended solids, chlorophyll *a*, dissolved nitrogen, and phosphorous (soluble reactive P, NO<sub>3</sub>, NH<sub>4</sub>). All methods for nutrient analysis are described in Stainton *et al.* (1977).



**FIG. 1.** Map of Lake Winnipeg and location of water, sediment, zooplankton, mayflies, and fish sampling sites.

#### Data Analysis

Statistical differences in fish morphometrics and contaminant concentrations among sample groups were determined using the MANOVA and ANCOVA models in Statistica 1999 (StatSoft 1999).

Multiple linear regression models in Statistica 1999 were used to test for relationships between OC concentrations and fish morphometrics (length, condition, lipid content, and growth rate). ANCOVA was used after significant differences were found in fish

**TABLE 1.** Contaminant concentrations (ng/g) in Red River suspended sediment, Lake Winnipeg pre-flood surface core slices dated 1991 and Lake Winnipeg post-flood surface bed sediment. Numbers of samples analyzed are in parentheses.

Contaminant <sup>1</sup>	Red River Suspended Sediment <sup>2</sup>		Pre-flood Core Sediment <sup>3</sup>		Post-flood Bed Sediment	
	Median (15)	Range (15)	Slice 1991 (1)	Slices 1940–1990 Range (10)	Site 8B (1)	South Basin Range (33)
Carbonate %	21	10–37	13	9–13	15	10–41
Organic carbon %	79	63–90	87	88–91	85	59–90
$\Sigma$ CBZ <sup>4</sup>	0.91	0.29–1.7	0.71		0.71	< 0.15–1.39
$\Sigma$ HCH <sup>5</sup>	0.74	0.60–1.3	0.36		0.35	< 0.22–0.85
$\Sigma$ CHL <sup>6</sup>	0.96	0.37–2.0	0.32		0.29	< 0.01–1.19
$\Sigma$ DDT <sup>7</sup>	5.9	2.1–16	3.4		3.2	1.3–6.6
<i>p,p'</i> -DDE/ <i>p,p'</i> -DDT	0.56	0.33–1.0	4.7	1.4–6.1	5.4	1.7–5.4
<i>p,p'</i> -DDD/ <i>p,p'</i> -DDT	0.22	0.076–0.89	7.2	1–12	3.7	2.5–11
$\Sigma$ PCB <sup>8</sup>	8.8	3.4–25	21		13	5.5–38
% di-, tri-, tetra-	51	14–58	46	34–52	37	28–83
% penta-	20	11–25	28	19–28	34	11–34
% hexa-	14	10–36	18	18–27	16	3.7–24

<sup>1</sup> A few congeners, for which standards were not available, were quantified with the response factors (RFs) estimated from other congeners of the same chlorine number and similar retention time.

<sup>2</sup> Red River floodwater samples were collected from the Red River from 28 April to 18 June 1997.

<sup>3</sup> Pre-flood data is from Rawn *et al.* (2000). Their core site 7A (50°40'N 96°48'W) corresponds to our site 8B (50°41'N 96°47'W).

<sup>4</sup> Total chlorinated benzene was the sum of 1245TCB, 1234TCB, P5CBz, and HCBz.

<sup>5</sup> Total hexachlorocyclohexane was the sum of all HCHs including, alpha, delta, beta, and gamma.

<sup>6</sup> Chlordane related compounds were quantified with individual standards except for Cl<sub>9</sub> components, nonachlor III and C5, which were quantified using the RF of *trans*-nonachlor, and the Cl<sub>7,8</sub> containing components (Dearth and Hites 1991), 'C', C1, C2 and C4 which were quantified using *trans*-nonachlor. Total chlordane was the sum of all chlordane related compounds, including heptachlor epoxide.

<sup>7</sup> Total DDT was the sum of *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT, *o,p'*-DDE and *o,p'*-DDD.

<sup>8</sup> Total PCB corresponds to the sum of all congeners CB1, 3, 4/107, 6, 8/5, 19, 18, 17, 24/27, 16/32, 26, 25, 31, 28, 33, 22, 45, 46, 52, 49, 47, 48, 44, 42, 41/71, 64, 40, 74, 70/76, 66, 95, 56/60, 91, 84/89, 101, 99, 83, 97, 87, 85, 136, 110, 82, 151, 144/135, 149, 118, 134, 114, 131, 146, 153, 132, 105, 141, 130/176, 179, 137, 138, 158, 178/129, 175, 187, 183, 128, 185, 174, 177, 171, 156, 201/157, 172/197, 180, 193, 191, 200, 170, 190, 198, 199, 196/203, 189, 208, 195, 207, 194, 205, 206, 209.

morphometrics within a species among sample dates and significant relationships between morphometrics and OCs were observed. Slopes were tested, non-significant interaction terms were removed, and data were adjusted for the effects of significant variables. In the few cases where significant interaction terms were found (lipid by sample date in walleye for  $\Sigma$ chlorinated benzenes (CBZ),  $\Sigma$ HCH, and  $\Sigma$ CHL) a separate slopes model was used. All data were natural log transformed prior to analysis.

## RESULTS

### Trends in OC Exposures: Sediment, Water, and Biota

#### Among-year Trends—Sediment

Despite elevated loadings of OCs dissolved in flood water and associated suspended sediments (Stewart *et al.* 2000) surficial sediment OC concentrations in the south basin of Lake Winnipeg did not change appreciably after the 1997 Red River flood when compared with pre-flood concentrations (Rawn *et al.* 2000) (Table 1). From 28 April

through 18 June 1997 approximately  $2.5 \times 10^8$  kilograms of suspended solids along with 2.4 kg  $\Sigma$ PCBs, 1.7 kg  $\Sigma$ DDT, 0.23 kg  $\Sigma$ CHL, 0.21  $\Sigma$ HCH, and 0.21 kg  $\Sigma$ CBZ were transported in the Red River into Lake Winnipeg (Stewart *et al.* 2000). Dissolved floodwater contributions over the same time period were considerably less for  $\Sigma$ PCBs (0.67 kg) and  $\Sigma$ DDT (0.22 kg), similar for  $\Sigma$ CHL (0.24 kg), and higher for  $\Sigma$ HCH (2.5 kg) and  $\Sigma$ CBZ (0.67 kg). Sedimentation rates in the slice dated 1997/1998 were 3,896 g/m<sup>2</sup>/y at site 4B, 1,548 g/m<sup>2</sup>/y at site 9B, and 1,800 g/m<sup>2</sup>/y at site 11B (Fig. 1). These rates were 87%, 68%, and 24% higher, respectively, than in 1991 slices, using the same cores and <sup>210</sup>Pb/<sup>137</sup>Cs dating techniques. Median concentrations of OCs on suspended sediments in Red River floodwater were higher than pre-flood core sediment concentrations and maximum OC concentrations were up to 10% higher, except for  $\Sigma$ PCBs, which were lower (Table 1). Concentrations of  $\Sigma$ CBZ,  $\Sigma$ HCH,  $\Sigma$ CHL and  $\Sigma$ DDT in surface core slices dated 1991 from Rawn *et al.* (2000) and in surface grab sediments collected at a similar location in March 1998 were virtually identical at 0.71 and 0.71 ng/g, 0.36 and 0.35 ng/g, 0.32 and 0.29, and 4.7 and 5.4 ng/g, respectively.  $\Sigma$ PCB concentrations were only slightly lower in post-flood sediments (13 ng/g) than pre-flood cores (21 ng/g). The proportion of carbonate and organic carbon in Red River suspended sediments, pre-flood cores, and post-flood bed sediments were similar (ANOVA,  $p > 0.05$ ) suggesting there were no significant differences in the characteristics of the particles among the sediments.

There were some differences in the contribution of PCB and DDT compounds associated with floodwater suspended sediments entering the lake relative to the bed sediments pre- and post-flood. Homologue contributions to  $\Sigma$ PCBs in Red River floodwater suspended sediments were similar to pre-flood core sediments, but had slightly higher contributions of the di-, tri-, tetra-, and hexa-chlorinated congeners and a slightly lower contribution of the penta-chlorinated congeners relative to post-flood sediments. Ratios of degradation products *p,p'*-DDE or *p,p'*-DDD relative to the parent molecule *p,p'*-DDT in Red River floodwater suspended sediments were considerably lower than in pre- and post-flood sediments. This shift in DDT compounds has been associated with other flood events and is thought to reflect the transport of newer sources of DDT; however Lake Winnipeg sediments did not

reflect a shift in compounds whereby ratios were marginally higher after the flood suggesting sediments deposited during the flood were mixed with pre-flood sediments containing older DDT sources.

#### Within-year Trends—Water

Water samples were not collected from Lake Winnipeg prior to the flood in 1997, which precludes among year comparisons. Water samples collected from the Red River at Selkirk during the flood and in the spring, summer, and fall in Lake Winnipeg surface water after the flood showed some temporal and location-dependent changes in OC concentrations (Table 2). Maximum concentrations in floodwater were no more than 10 times higher than post-flood summer concentrations, except for  $\Sigma$ DDT, which were higher in the summer. Concentrations in Lake Winnipeg surface water across all sites and sample dates ranged from 0.23 to 2.8 ng/L for  $\Sigma$ PCBs, 0.036 to 1.5 ng/L for  $\Sigma$ DDT, 0.045 to 0.13 ng/L for  $\Sigma$ CHL, 0.13 to 2.9 ng/L for  $\Sigma$ HCH, and 0.037 to 1.1 ng/L for  $\Sigma$ CBZ. Water-borne OC concentrations were generally higher in under-ice samples collected in March 1998 than in summer samples, except  $\Sigma$ HCH (Table 2). OC levels in under-ice water samples were higher at site 4B, near the mouth of the Red River, than at site 9B located towards the northern end of the south basin (Fig. 1). From July to September,  $\Sigma$ DDT increased significantly (all sites, paired *t*-test,  $p = 0.03$ ) and  $\Sigma$ CBZ decreased significantly (all sites, paired *t*-test,  $p = 0.02$ ) in the south basin. Results for  $\Sigma$ CHL,  $\Sigma$ HCH, and  $\Sigma$ PCB did not show basin-wide trends. Southern stations (4B and 7B) showed significant increases in  $\Sigma$ PCB (paired *t*-test,  $p = 0.04$ ) and non-significant decreases in  $\Sigma$ CHL and  $\Sigma$ HCH water concentrations between July and September, while the opposite was true for station 11B.

#### Among-year Trends—Mayflies

There were no statistically significant differences in any of the major OC groups (mean  $\pm$  standard error (SE), dry wt.) in *H. rigida* collected pre-flood in July 1995 and post-flood in July 1998. In July 1998 *H. rigida* were slightly lower in concentrations of  $\Sigma$ HCH ( $0.67 \pm 0.11$  ng/g) and  $\Sigma$ CHLOR ( $1.6 \pm 0.34$  ng/g) compared to pre-flood values of  $0.97 \pm 0.19$  ng/g and  $2.0 \pm 0.45$  ng/g, respectively. Post-flood  $\Sigma$ CBZ ( $1.2 \pm 0.52$  ng/g),  $\Sigma$ DDT ( $10 \pm 2.6$  ng/g), and  $\Sigma$ PCB ( $54 \pm 5.8$  ng/g) concentrations

**TABLE 2.** OC concentrations (ng/L) in filtered Red River floodwater at Selkirk ( $n = 15$ ) and filtered lake water collected at sites ( $n = 1$ ) in the south basin of Lake Winnipeg during the spring and summer of 1998.

	Red River Floodwater		Lake Winnipeg Surface Water									
	April 28– June 18, 1997		March 1998				July 1998			August 1998		
	Median	Range	4B	9A	9B	9C	4B	7B	11B	4B	7B	11B
$\Sigma$ CBZ	0.18	0.53–5.9	2.8	1.2	1.1	1.0	0.34	0.39	0.66	0.53	0.62	0.34
$\Sigma$ HCH	2.6	0.009–5.3	0.19	0.14	0.13	0.096	0.077	0.039	0.036	0.11	0.084	0.061
$\Sigma$ CHL	0.20	0.12–0.54	0.13	0.11	0.11	0.10	0.071	0.061	0.045	0.067	0.051	0.081
$\Sigma$ DDT	0.12	0.015–1.1	2.9	1.9	1.5	1.9	2.9	2.2	1.2	1.4	1.8	1.8
<i>p,p'</i> -DDE/ <i>p,p'</i> -DDT	1.6	0.60–11	1.7	8.3	7.0	—	—	6.7	2.1	—	18	20
<i>p,p'</i> -DDD/ <i>p,p'</i> -DDT	1.4	0.33–8.0	3.4	16	12	—	—	14	—	—	39	70
$\Sigma$ PCB	0.52	0.14–2.0	0.26	0.83	0.23	0.18	0.058	0.037	0.065	0.033	ND	0.047
% di-, tri-, tetra-	39	4.3–53	54	40	48	35	43	47	36	54		54
% penta-	23	5.3–46	22	27	24	29	24	19	23	21		23
% hexa-	25	19–43	17	25	21	27	20	17	23	13		15

were slightly higher than pre-flood levels ( $\Sigma$ CBZ  $0.76 \pm 0.17$  ng/g,  $\Sigma$ DDT  $8.1 \pm 1.8$  ng/g,  $\Sigma$ PCB  $39 \pm 8.4$  ng/g). Lipid content in mayflies was also similar before ( $16 \pm 1.3$  %) and after the flood ( $15 \pm 1.8$  %).

#### Within-year Trends—Zooplankton

Bulk zooplankton OC concentrations varied among sample times and location (Table 3). Similar to water, concentrations tended to be higher near the mouth of the Red River (Transect 4) and lower at the northern sites.  $\Sigma$ PCB concentrations increased over 3 fold between July and September 1998 (ANOVA  $F = 14.78$ ,  $p = 0.0002$ ). Smaller non-significant increases occurred in  $\Sigma$ DDT, although significant increases were found for *p,p'*-DDE (MANOVA, Rao  $R = 3.42$ ,  $p = 0.01$ ) over the same time period.  $\Sigma$ CHL concentrations showed non-significant increases, however, oxychlorane, *trans*- and *cis*-chlordane, and *trans*-nonachlor congeners all increased significantly between July and September 1998 (MANOVA, Rao  $R = 12.83$ ,  $p = 0.001$ ). Lipid content of the zooplankton decreased marginally between July and September 1998 and was not significantly related to changes in OC concentrations between sample times (Table 3), although it was a significant predictor of  $\Sigma$ PCB

concentrations for all sample sites in September 1998 ( $R^2 = 0.85$ ,  $p = 0.009$ ).

#### Among-year Trends in Lake Winnipeg Nutrient Status

Despite the highest nutrient loadings (N and P) in recent history into the south basin during the flood (Stewart *et al.* 2000), algal biomass, as inferred from chlorophyll *a* concentrations, was among the lowest recorded values during the summer of 1998 (chl *a* =  $5.0$   $\mu$ g/L) (Table 4). The south basin of Lake Winnipeg is typically light and nitrogen limited (N:P molar ratios  $< 22$  in particles or seston), which can favor the growth of nitrogen fixing blue-green algae. Post-flood summer mean molar ratios of N:P were low (9.4) and relatively constant (CV = 6.4), but these values are typical of Lake Winnipeg in mid to late summer. However, saturated surface water  $p\text{CO}_2$  levels (500–1,100 ppm,  $n = 6$ ) indicated the water column was strongly dominated by respiration in August 1998. Furthermore, preliminary analyses of seston samples found resuspended algal cell remains and large numbers of bacteria (personal communication, H. Kling, Freshwater Institute). High respiration rates and an increase from previous years in the abundance of cyclopoid zooplankton that feed on detritus and bacteria suggest that bacterial-based production may have been im-

TABLE 3. Zooplankton community, isotopic composition, lipid (% wet. wt.) and OC concentrations (ng/g wet wt.) for samples collected at sites in the south basin of Lake Winnipeg during the summer of 1998. Values are means  $\pm$  SE.

	Transect 4			Transect 7			Transect 11		
	July 1998 n = 3 <sup>a</sup>	August 1998 n = 2	September 1998 n = 3	July 1998 n = 3	August 1998 n = 3	September 1998 n = 2	July 1998 n = 3	August 1998 n = 3	September 1998 n = 1
<b>72 <math>\mu</math>m hauls</b>									
Individuals/L	223	307	136	201	188	125	170	100	127
% cyclopoids	40 $\pm$ 13	31 $\pm$ 13	40 $\pm$ 3.4	50 $\pm$ 17	31 $\pm$ 5	27 $\pm$ 1.8	30 $\pm$ 4.8	23 $\pm$ 3	49.2
% calanoids	29 $\pm$ 7.4	47 $\pm$ 26	52 $\pm$ 6.3	40 $\pm$ 16	52 $\pm$ 11	63 $\pm$ 5.7	57 $\pm$ 3.5	71 $\pm$ 4	47.0
% cladocera	31 $\pm$ 9.5	22 $\pm$ 13	7.9 $\pm$ 3.6	11 $\pm$ 1.8	18 $\pm$ 6	10 $\pm$ 3.8	13 $\pm$ 4.2	4 $\pm$ 0.8	3.8
<b>160 <math>\mu</math>m hauls</b>									
Zooplankton biomass (%)			89			97			60
$\delta^{13}\text{C}$	-29.6 $\pm$ 0.2	-31.9 $\pm$ 0.4	-29.9 $\pm$ 0.4	-30.2 $\pm$ 0.7	-30.8 $\pm$ 0.7	-30.8 $\pm$ 0.2	-30.1 $\pm$ 0.4	-31.8 $\pm$ 0.4	-29.9
$\delta^{15}\text{N}$	11.6 $\pm$ 0.5	11.4 $\pm$ 1.5	15.3 $\pm$ 2.1	12.3 $\pm$ 0.8	12.6 $\pm$ 1.0	15.6 $\pm$ 1.7	11.1 $\pm$ 0.1	17.0 $\pm$ 0.4	14.4
Lipid	1.1 $\pm$ 0.11	0.60 $\pm$ 0.090	0.87 $\pm$ 0.22	1.2 $\pm$ 0.085	0.37 $\pm$ 0.029	0.84 $\pm$ 0.075	0.99 $\pm$ 0.101	0.43 $\pm$ 0.037	0.54
$\Sigma\text{CBZ}$	0.051 $\pm$ 0.017	0.085 $\pm$ 0.034	0.056 $\pm$ 0.012	0.048 $\pm$ 0.019	0.109 $\pm$ 0.048	0.052 $\pm$ 0.006	0.027 $\pm$ 0.005	0.064 $\pm$ 0.006	0.033
$\Sigma\text{HCH}$	0.030 $\pm$ 0.005	0.01 $\pm$ 0.004	0.058 $\pm$ 0.028	0.043 $\pm$ 0.020	0.01 $\pm$ 0.004	0.011 $\pm$ 0.005	0.12 $\pm$ 0.053	0.021 $\pm$ 0.009	0.034
$\Sigma\text{CHL}$	0.050 $\pm$ 0.006	0.03 $\pm$ 0.002	0.10 $\pm$ 0.072	0.057 $\pm$ 0.018	0.035 $\pm$ 0.013	0.023 $\pm$ 0.007	0.042 $\pm$ 0.001	0.051 $\pm$ 0.018	0.037
$\Sigma\text{DDT}$	0.48 $\pm$ 0.084	0.45 $\pm$ 0.067	0.84 $\pm$ 0.59	0.35 $\pm$ 0.14	0.188 $\pm$ 0.025	0.24 $\pm$ 0.13	0.13 $\pm$ 0.03	0.16 $\pm$ 0.015	0.26
$\Sigma\text{PCB}$	1.8 $\pm$ 0.043	2.04 $\pm$ 0.302	6.3 $\pm$ 2.2	1.4 $\pm$ 0.32	1.3 $\pm$ 0.122	5.8 $\pm$ 0.71	1.0 $\pm$ 0.27	2.1 $\pm$ 0.38	2.4

<sup>a</sup> Values are means for 3 sites (A, B & C) along each transect.

**TABLE 4.** Comparison of nutrients and zooplankton abundance/species composition in the south basin of Lake Winnipeg before and after the Red River flood. Values are ice-free summer means  $\pm$  SD.

	1969 <sup>a</sup>	1994 <sup>b</sup>	1996 <sup>c</sup>	1998
Suspended N $\mu\text{g/L}$	100 $\pm$ 54 n = 56	349 $\pm$ 624 n = 21	262 $\pm$ 298 n = 21	133 $\pm$ 36 n = 18
Suspended P $\mu\text{g/L}$	23 $\pm$ 20 n = 56	35 $\pm$ 39 n = 21	26 $\pm$ 18 n = 21	32 $\pm$ 11 n = 18
Molar N:P	11 $\pm$ 5.5	18 $\pm$ 7.7	20 $\pm$ 9.3	9.4 $\pm$ 1.8
Chlorophyll <i>a</i>	7.3 $\pm$ 9.6 n = 24	19 $\pm$ 33 n = 21	15 $\pm$ 18 n = 21	5.0 $\pm$ 2.1 n = 18
Zooplankton abundance <sup>d</sup> individuals/L				
% cyclopoids	82	103		175
% calanoids	17	29		38
% cladocera	71	57		47
	11	14		16

<sup>a</sup>Patalas and Salki 1992.

<sup>b</sup>Salki 1996.

<sup>c</sup>Stainton, unpublished data

<sup>d</sup>summer means

portant in the summer of 1998 (Table 4). Despite the apparent decrease in algal biomass, zooplankton abundances were among the highest recorded for the south basin, suggesting that zooplankton were not food limited.

#### Trends in Nitrogen and Carbon Isotope Signatures of Biota

Post-flood  $\delta^{15}\text{N}$  values for mayflies collected at Gimli (mean value =  $11.87 \pm 1.34$  SD) in July 1998 were not different from mayflies collected at several sites in the south basin prior to the flood ( $11.90 \pm 0.53$  SD) (Table 5, Fig. 2). This result suggests that basal nitrogen  $\delta^{15}\text{N}$  did not change and that comparisons of  $\delta^{15}\text{N}$  values among top predators collected in 1995 and 1998 are valid for the purpose of determining changes in food chain length (Cabana and Rasmussen 1996). However, within-year differences in the  $\delta^{15}\text{N}$  value of the zooplankton indicates that there may have been seasonal changes in basal nitrogen or changes in zooplankton feeding habits. All sites showed an increase in zooplankton  $\delta^{15}\text{N}$  values ( $\sim 3.3$  ‰) between July and September (all sites, paired *t*-test,  $p = 0.014$ ), which was accompanied by changes in zooplankton community composition. Zooplankton community composition determined for 72  $\mu\text{m}$  net hauls showed an increase

in the proportion of calanoid copepods at transects 4 and 7 and a decrease in the proportion of cladocera at transect 4 near the mouth of the Red River between July and September (Table 3). The zooplankton community at northern transect 11 was dominated by calanoids in July and then shifted to an equal proportion of cyclopoids and calanoids by September. Despite changes in zooplankton isotope composition there were no significant differences in the isotopic signatures of fish among sample times, except for March 1999 and March 2000 walleye. These walleye had statistically lower  $\delta^{15}\text{N}$  values ( $F_{5,53} = 4.41$ ,  $p = 0.002$ ) and significantly enriched  $\delta^{13}\text{C}$  values ( $F_{5,53} = 15.31$ ,  $p < 0.0001$ ) than other post-flood walleye.

Feeding relationships among biota in southern Lake Winnipeg were not readily apparent from isotope analysis. The fish and their potential invertebrate food did not share similar  $\delta^{13}\text{C}$  signatures, suggesting different sources of carbon and thus, a food source different from those measured (Fig. 2). Invertebrates clustered together and had carbon isotopic signatures that were roughly 2.5‰ and 4‰ more depleted than freshwater drum and the other fish species, respectively. There were some slight differences in trophic position among the fish species. Freshwater drum and yellow perch were

**TABLE 5.** Mean  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  values (‰) of mayfly composites (>3 individuals) or individual fish caught in the north and south basin of Lake Winnipeg pre- and post-flood. Values are means  $\pm$ SD. W. Beach—Winnipeg Beach

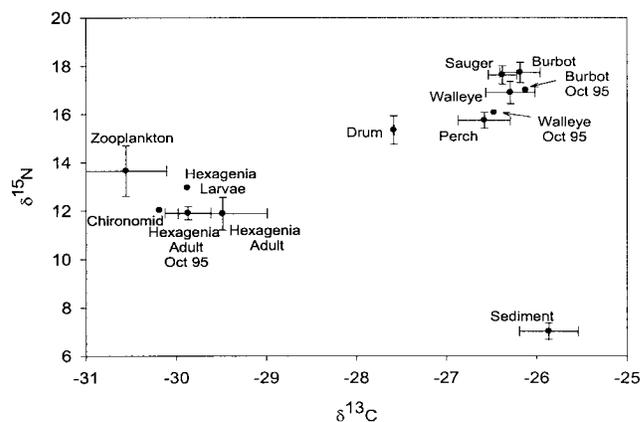
Species	Site	Basin	Date	n	$\delta^{13}\text{C}$	$\delta^{15}\text{N}$
<i>H. rigida</i>	Several sites	North	Jul 95	2	$-29.01 \pm 0.23$	$8.62 \pm 1.56$
	Sandy Hook, Hussavik, Grand Beach	South	Jul 95	4	$-29.87 \pm 0.51$	$11.90 \pm 0.53$
	Gimli	South	Jul 98	4	$-29.49 \pm 0.99$	$11.87 \pm 1.34$
Walleye	Several sites	North	Oct 95	3	$-25.84 \pm 0.71$	$12.59 \pm 0.54$
	Riverton	South	Oct 95	5	$-26.47 \pm 0.15$	$16.06 \pm 0.54$
	W. Beach	South	Oct 97	9	$-26.91 \pm 0.45$	$17.80 \pm 0.79$
	Riverton	South	Jul 98	10	$-26.44 \pm 0.23$	$17.12 \pm 0.61$
	W. Beach	South	Sep 98	10	$-26.77 \pm 0.38$	$17.89 \pm 0.89$
	W. Beach	South	Mar 99	10	$-25.50 \pm 0.52$	$15.76 \pm 1.44$
	W. Beach	South	Mar 00	15	$-25.82 \pm 1.52$	$15.86 \pm 0.61$
Burbot	Riverton	South	Oct 95	6	$-26.12 \pm 0.21$	$16.99 \pm 0.35$
	W. Beach	South	Oct 97	7	$-25.75 \pm 1.02$	$16.47 \pm 2.25$
	W. Beach	South	Sep 98	10	$-26.11 \pm 1.20$	$17.93 \pm 1.47$
	W. Beach	South	Mar 99	10	$-26.07 \pm 0.53$	$18.31 \pm 0.98$
	W. Beach	South	Mar 00	15	$-26.80 \pm 0.16$	$18.18 \pm 0.28$
Sauger	W. Beach	South	Oct 97	10	$-26.69 \pm 0.44$	$17.85 \pm 0.60$
	Riverton	South	Jul 98	5	$-26.21 \pm 0.52$	$16.87 \pm 1.44$
	W. Beach	South	Mar 99	10	$-26.23 \pm 0.52$	$18.13 \pm 0.81$
Freshwater drum	Riverton	South	Jul 98	10	$-27.59 \pm 1.19$	$14.74 \pm 1.21$
	W. Beach	South	Sep 98	10	$-27.58 \pm 0.56$	$15.93 \pm 0.71$
Yellow perch	Riverton	South	Jul 98	10	$-26.28 \pm 0.53$	$15.41 \pm 1.26$
	W. Beach	South	Sep 98	10	$-26.87 \pm 0.54$	$16.08 \pm 2.50$

roughly 2‰ lower in  $\delta^{15}\text{N}$  than sauger and burbot, suggesting a slightly shorter food chain for these fish, and walleye appeared to be feeding at a trophic level between the two groups.

#### Relationship between Morphometrics and OC Concentrations in Fish

There were statistically significant differences in the size, age, lipid content, condition, and growth rates of fish among sample times, except for yellow perch (Table 6). Since these differences could confound variation in OC levels in fish associated with the flood, relationships between morphometrics and OCs levels in fish tissues were investigated. Multiple linear regression analysis (MLRA) using natural log transformed length, lipid, condition, and growth rate as variables found lipid to be an excellent intraspecific predictor of OC concentrations within individual sample groups. For example, lipid content could explain between 87 to 93% of the variability in  $\Sigma\text{PCB}$  concentrations in the five different fish species (Fig. 3). In the case of walleye, where significant differences in lipid content were found

among sample times, wet weight OC concentrations were adjusted for the effects of lipid using ANCOVA. In addition to lipid, length was found to be a significant predictor (MLRA,  $p < 0.05$ ) of walleye  $\Sigma\text{DDT}$  and  $\Sigma\text{PCB}$  and burbot liver  $\Sigma\text{HCH}$ ,  $\Sigma\text{CHL}$ ,



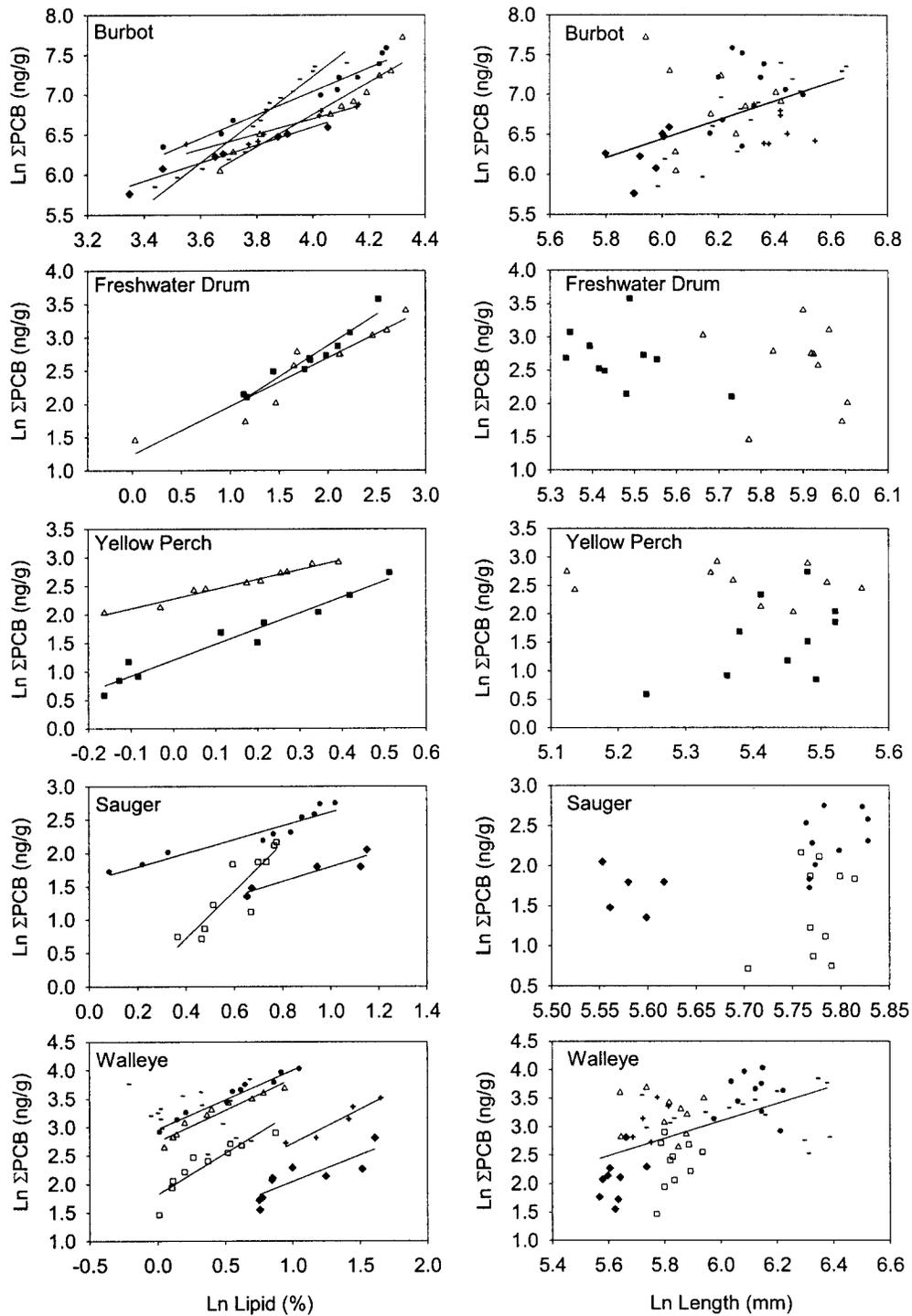
**FIG. 2.** Stable isotope plot of Lake Winnipeg food web. Pre-flood samples from Kidd et al. (2002) are plotted separately. Values are means  $\pm$ SE.

**TABLE 6.** Sample collection, morphological characteristics, and OC (ng/g wet weight) data for fish collected from Lake Winnipeg. Lipid and contaminant data are for muscle tissue, except for burbot. Values are means ± SE. ANOVA/ANCOVA results (F and p-values) for differences across dates for each fish species are shown with significant values in bold. ANCOVA adjusted results are shown in Figure 4. W. Beach—Winnipeg Beach.

Location	Date	N	Age y	Length mm	Weight g	Lipid %	Condition <sup>1</sup>	Growth rate g/yr	ΣCBZ	ΣHCH	ΣCHL	ΣDDT	ΣPCB
<b>Burbot Liver</b>													
F-value			1.33	<b>8.9</b>	<b>16</b>	<b>3.7</b>	—	<b>11.2</b>	<b>18.5</b>	3.08	5.02	5.61	3.37
p-value			0.28	< <b>0.0001</b>	< <b>0.0001</b>	<b>0.017</b>	—	< <b>0.0001</b>	< <b>0.0001</b>	0.03	0.002	0.001	0.018
Riverton	Oct 95 <sup>2</sup>	6	9.0 ± 1.1	612 ± 20	1829 ± 161	48 ± 4.2	7.9 ± 0.22	223 ± 38	5.5 ± 1.2	4.7 ± 0.44	44 ± 5.9	302 ± 39	708 ± 61
W. Beach	Oct 97	7	5.6 ± 0.3	384 ± 11	388 ± 31	42 ± 3.9	6.8 ± 0.15	70 ± 5	2.9 ± 0.29	3.5 ± 0.38	26 ± 2.8	216 ± 18	547 ± 55
W. Beach	Sep 98	10	6.5 ± 1.4	491 ± 26	768 ± 107	59 ± 4.1	6.2 ± 0.17	134 ± 20	17 ± 2.2	6.8 ± 0.95	69 ± 9.9	489 ± 77	1064 ± 170
W. Beach	Mar 99	10	6.6 ± 0.7	553 ± 19	1366 ± 137	56 ± 5.6	8.0 ± 0.36	183 ± 18	16 ± 2.3	7.5 ± 0.94	95 ± 16	618 ± 73	1232 ± 150
W. Beach	Mar 00	15	8.3 ± 1.0	549 ± 31	1633 ± 231	46 ± 2.1	9.2 ± 0.31	197 ± 17	13 ± 1.5	7.6 ± 0.9	76 ± 9.3	437 ± 51	922 ± 113
<b>Freshwater Drum</b>													
F-value			<b>24</b>	<b>70</b>	4.5	0.43	—	0.23	0.002	0.86	0.002	0.03	0.29
p-value			<b>0.0001</b>	< <b>0.0001</b>	0.05	0.52	—	0.64	0.97	0.36	0.96	0.87	0.60
Riverton	Jul 98	10	12.7 ± 2.0	363 ± 11	722 ± 66	7.7 ± 1.5	15 ± 0.4	62 ± 5	0.75 ± 0.12	0.60 ± 0.10	1.4 ± 0.22	9.8 ± 1.6	15 ± 2.5
W. Beach	Sept 98	10	3.0 ± 0.3	239 ± 9	191 ± 24	6.6 ± 0.9	14 ± 0.4	64 ± 3	0.89 ± 0.29	0.54 ± 0.17	1.5 ± 0.51	11 ± 3.6	18 ± 6.0
<b>Yellow Perch</b>													
F-value			0.49	1.1	0.61	0.01	—	0.04	<b>30.4</b>	5.58	<b>22.0</b>	<b>18.0</b>	<b>16.6</b>
p-value			0.49	0.3	0.44	0.92	—	0.85	< <b>0.0001</b>	0.03	<b>0.0002</b>	<b>0.0004</b>	<b>0.0007</b>
Riverton	Jul 98	10	5.7 ± 0.4	230 ± 6	176 ± 12	1.2 ± 0.1	14 ± 0.4	32 ± 3	0.11 ± 0.03	0.13 ± 0.03	0.30 ± 0.07	2.5 ± 0.53	6.0 ± 1.4
W. Beach	Sep 98	10	5.3 ± 0.7	223 ± 9	157 ± 16	1.2 ± 0.1	14 ± 0.7	31 ± 5	0.41 ± 0.04	0.21 ± 0.03	0.89 ± 0.11	6.0 ± 0.56	13 ± 1.2
<b>Sauger</b>													
F-value			<b>76</b>	<b>93</b>	0.98	3.3	—	0.92	<b>8.84</b>	<b>11.8</b>	<b>3.96</b>	<b>5.35</b>	<b>8.81</b>
p-value			< <b>0.0001</b>	< <b>0.0001</b>	0.39	0.056	—	0.41	<b>0.002</b>	<b>0.0003</b>	<b>0.03</b>	<b>0.013</b>	<b>0.002</b>
W. Beach	Oct 97	5	2.0 ± 0.0	266 ± 3	210 ± 51	2.5 ± 0.3	11 ± 3.2	105 ± 26	0.27 ± 0.04	0.16 ± 0.03	0.79 ± 0.16	2.8 ± 0.68	5.6 ± 0.69
Riverton	Jul 98	10	3.0 ± 0.0	322 ± 3	306 ± 6	1.8 ± 0.1	9.2 ± 0.21	102 ± 2	0.43 ± 0.07	0.26 ± 0.04	0.81 ± 0.14	2.8 ± 0.55	4.9 ± 0.82
W. Beach	Mar 99	10	3.8 ± 0.1	328 ± 3	334 ± 9	2.06 ± 0.2	9.5 ± 0.13	89 ± 4	0.69 ± 0.07	0.47 ± 0.05	1.3 ± 0.13	5.1 ± 0.53	10 ± 1.1
<b>Walleye</b>													
F-value			<b>12</b>	<b>21</b>	<b>22</b>	<b>15</b>	—	<b>22</b>	<b>12.8</b>	<b>7.74</b>	<b>15.2</b>	<b>13.6</b>	<b>26.1</b>
p-value			< <b>0.0001</b>	< <b>0.0001</b>	< <b>0.0001</b>	< <b>0.0001</b>	—	< <b>0.0001</b>	< <b>0.0001</b>	< <b>0.0001</b>	< <b>0.0001</b>	< <b>0.0001</b>	< <b>0.0001</b>
Riverton	Oct 95 <sup>2</sup>	5	2.8 ± 0.2	314 ± 7	358 ± 28	3.9 ± 0.5	11 ± 0.22	129 ± 9	0.43 ± 0.09	0.5 ± 0.08	1.09 ± 0.11	7.9 ± 1.2	24 ± 3.5
W. Beach	Oct 97	9	4.4 ± 0.5	278 ± 5	200 ± 11	3.6 ± 0.5	9.2 ± 0.21	48 ± 3	0.23 ± 0.03	0.13 ± 0.02	0.58 ± 0.11	5.5 ± 0.77	8.6 ± 1.2
Riverton	Jul 98	10	3.0 ± 0.0	343 ± 6	372 ± 17	1.5 ± 0.1	9.3 ± 0.36	124 ± 6	0.33 ± 0.04	0.24 ± 0.03	0.81 ± 0.11	8.2 ± 0.95	11 ± 1.3
W. Beach	Sep 98	10	3.3 ± 0.2	333 ± 10	316 ± 20	1.6 ± 0.2	8.5 ± 0.36	99 ± 9	0.40 ± 0.05	0.31 ± 0.04	1.30 ± 0.14	11 ± 1.0	26 ± 2.8
W. Beach	Mar 99	10	5.5 ± 0.4	455 ± 11	1036 ± 101	1.8 ± 0.2	11 ± 0.37	191 ± 17	0.65 ± 0.07	0.43 ± 0.05	1.9 ± 0.21	14 ± 1.5	37 ± 3.9
W. Beach	Mar 00	15	5.6 ± 0.4	450 ± 26	1485 ± 286	1.3 ± 0.1	13 ± 0.56	240 ± 33	0.66 ± 0.08	0.34 ± 0.04	1.91 ± 0.25	8.4 ± 0.6	27 ± 2.6

<sup>1</sup>Condition = 10<sup>3</sup> x (wet weight, g)/(standard length, cm)<sup>3</sup> after Anderson and Gutreuter (1983)d).

<sup>2</sup>Data are from Kidd (unpublished data).



**FIG. 3.** Relationship between  $\Sigma\text{PCB}$  concentrations, percent lipid, and length in individual fish collected near Winnipeg Beach (diamonds Oct 97, triangles Sep 98, circles Mar 99, dashes Mar 00) and Riverton (crosses Oct 95, squares Jul 98) in the south basin of Lake Winnipeg. Organochlorine concentrations are for muscle tissue (except burbot liver) on a wet weight basis. Pre-flood data (Oct 95) are from Kidd (unpublished data). Significant intraspecific (lipid) and interspecific (length) regressions are identified with a solid line. Relationships for other OC compounds are not shown, but have patterns similar to  $\Sigma\text{PCBs}$ .

$\Sigma$ DDT and  $\Sigma$ PCBs concentrations across all sample dates (Fig. 3). In these cases, length was also used to adjust wet weight tissue OC concentrations using ANCOVA.

### Temporal Trends in Fish Tissue OCs

Wet weight tissue organochlorine concentrations varied significantly among sample times and species (Table 6). Specific differences in OC concentrations (adjusted for lipid or length using ANCOVA as described above) between pre- and post-flood fish as well as differences among sample dates in the months and years after the flood are shown in Figure 4.

#### *Among-year Trends—Walleye and Burbot*

Maximum OC concentrations in walleye and burbot were typically found in March 1999 and were significantly higher than pre-flood fish collected in October 1995, except for  $\Sigma$ HCH in walleye. October 1995 and October 1997 fish tended to have similar OC concentrations that were significantly lower than OC levels in fish collected at later sample dates (Fig. 4).

#### *Among- and Within-year Trends—Each Fish Species, Post-flood*

OC concentrations for each species were generally similar among and within years following the flood, except in a few cases. Fish collected in fall of 1997, immediately after the flood, had lower OC concentrations than at any other sample time, including another fall sampling in 1998 (Table 6).  $\Sigma$ CBZ concentrations were significantly lower in burbot, walleye, yellow perch and sauger collected in October 1997 compared to all other sample times (Fig. 4).  $\Sigma$ HCH concentrations did not vary in burbot, but were significantly lower in October 1997 in walleye and sauger compared to all subsequent sample times.  $\Sigma$ CHL concentrations were also significantly lower in October 1997 compared to all subsequent sample times in burbot, and compared to March 1999 in sauger.  $\Sigma$ DDT in burbot and  $\Sigma$ DDT and  $\Sigma$ PCB in walleye were significantly lower in October 1997 than in March 1999. Overall,  $\Sigma$ CBZ,  $\Sigma$ HCH,  $\Sigma$ DDT and  $\Sigma$ PCB concentrations nearly doubled between October 1997 and March 1999 in walleye (1.9–2.6 fold) and in sauger (1.8–2.9 fold).

There was significant within year variation in yellow perch over the summer of 1998 with  $\Sigma$ CBZ,

$\Sigma$ CHL,  $\Sigma$ DDT, and  $\Sigma$ PCB concentrations more than doubling and  $\Sigma$ HCH concentrations significantly increasing between July and September 1998. Walleye OCs did not vary significantly over the same time period, except for  $\Sigma$ PCB, which increased 1.4 fold. Freshwater drum OC concentrations did not vary between July and September 1998. Comparisons between fall (September 1998) and spring (March 1999) OC concentrations also showed no significant change over the winter months in both burbot and walleye.

### Congener Profiles in Sediment, Water, and Biota

OC pesticide and PCB congener profiles were examined in pre- and post-flood sediment, water, zooplankton, and fish in order to identify changes in potential sources of exposure that may have mediated the increases in total OCs in biota over the summer in 1998, and before and after the flood. The percent contribution of several dominant PCB, DDT and CHL congeners to total OCs were determined for suspended sediments in Red River floodwater, Lake Winnipeg pre-flood cores and post-flood bed sediment, and for water, zooplankton, perch, and walleye in March 1998, July 1998, and September 1998, and walleye and burbot in October 1995 and March 1999 (Fig. 5). Congener profiles for Red River floodwater and suspended sediments were generally similar to post-flood water and sediments, with some notable exceptions. There were no characteristic patterns in any of the OC groups that distinguished “within” from “among year” variation in OC concentrations in fish.

#### *PCB Congeners*

Red River floodwater and suspended sediments were characterized by a slightly larger contribution of higher chlorinated PCBs relative to pre-flood and post-flood water and sediment. Red River suspended sediments had 2-times the contributions from hepta-chlorinated PCBs (16%) compared to pre-flood core sediments (8%) and post-flood Lake Winnipeg bed sediments (9%). Red River floodwater shared similar contributions of tetra- through hepta-chlorinated PCBs compared to that in the spring and summer post-flood, but had half the contributions from the mono/di/tri-chlorinated congeners. A slightly larger contribution of hepta-chlorinated congeners to  $\Sigma$ PCBs was also observed in post-flood surface water from Lake Winnipeg in

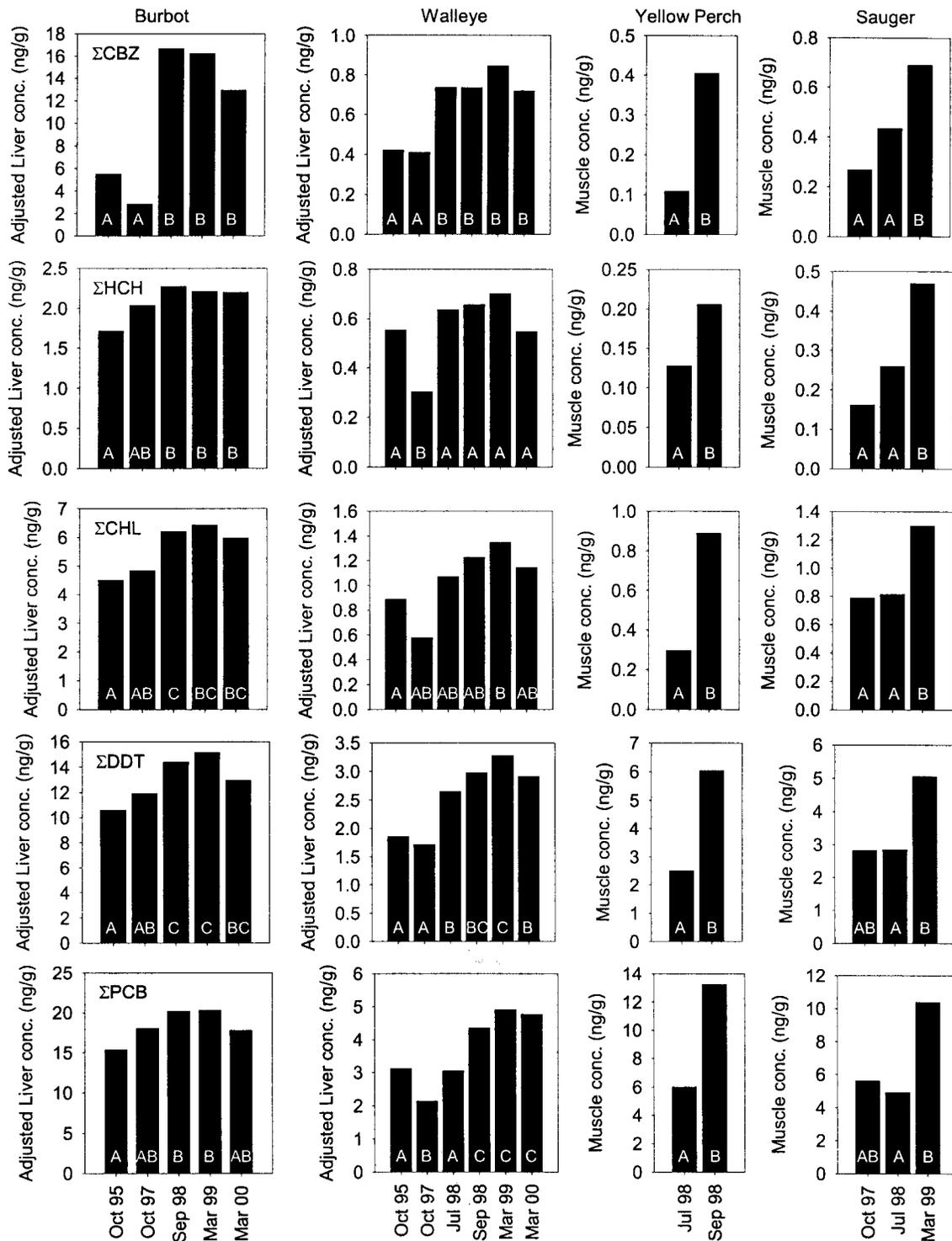
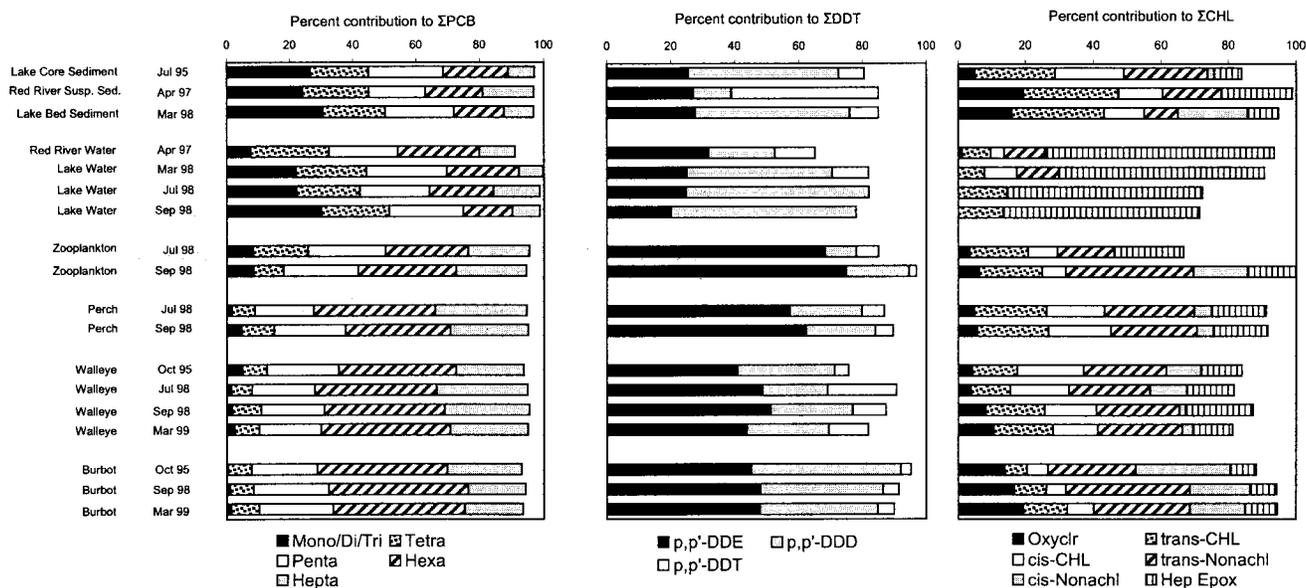


FIG. 4. Mean OC concentrations in burbot liver and walleye, yellow perch, and sauger muscle. Burbot liver  $\Sigma$ HCH,  $\Sigma$ CHL,  $\Sigma$ DDT, and  $\Sigma$ PCB data are adjusted for length using ANCOVA. Walleye  $\Sigma$ CBZ,  $\Sigma$ HCH, and  $\Sigma$ CHL are adjusted for lipid and  $\Sigma$ DDT and  $\Sigma$ PCB are adjusted for lipid and length using ANCOVA. For each species and OC, bars with different letters are significantly different ( $p < 0.05$ ).



**FIG. 5.** Percent contribution of individual congeners to total PCB, DDT, and CHL concentrations in sediment, water, zooplankton, perch, walleye, and burbot liver over time. Values are based on means of samples for each individual group and time period. Red River floodwater suspended sediments and water correspond to samples collected during the flood period at Selkirk ( $n = 15$ ). PCB Congeners included in the analysis were mono/di/tri-, tetra-, penta-, hexa- and hepta-chlorinated PCBs,  $p,p'$ -DDT,  $p,p'$ -DDE and  $p,p'$ -DDD, and oxychlordane (oxyclr), *cis*- and *trans*-chlordanes, *cis*- and *trans*-nonachlor, and heptachlor epoxide (hep epox).

July 1998 relative to spring or fall values. Water and sediment were characterized by different PCB congener profiles than biota. Higher chlorinated PCBs (penta-, hexa-, hepta-) accounted for > 75% of the total PCBs in zooplankton, perch, walleye, and burbot and showed little change over time. September zooplankton had a slightly greater contribution of hexa- and hepta-chlorinated PCBs than in July, very similar to September yellow perch (Pearson's  $r = 0.990$ ) and walleye (Pearson's  $r = 0.983$ ). Perch and walleye were more similar to each other than to burbot with slightly higher contributions from the hepta- versus hexa-chlorinated PCBs. Patterns in PCB congeners for each of the perch, walleye and burbot changed less than 10% between sample dates, suggesting that chemical exposure conditions leading to increased bioaccumulation within and among years may have been similar.

#### DDT Congeners

Congener patterns for DDT were substantially different in floodwater and suspended sediments relative to pre- or post-flood core and bed sediments and lake water. Contributions of  $p,p'$ -DDT were 5-

fold higher in Red River suspended sediments (46%) than pre-flood cores and post-flood bed sediments (~9%), while contributions of  $p,p'$ -DDE were essentially the same among sample types and times. The high percent contribution of  $p,p'$ -DDT to  $\Sigma$ DDT in the Red River suspended sediments suggests that "fresh" unweathered DDT made its way into the lake. Red River floodwater had contributions of  $p,p'$ -DDT and contributions from  $o,p'$ -DDT (20%—data not shown) that were not observed in any other samples. But, most notably was a lack of contributions from  $p,p'$ -DDD to  $\Sigma$ DDT in floodwater compared to other water samples.

As for PCBs, percent contributions in sediment and water of individual DDT congeners to  $\Sigma$ DDT were distinct from biota. Contributions of  $p,p'$ -DDE were higher in biota ranging from 57–75% in zooplankton and perch to 41–51% in walleye and burbot. A small percentage (~10%) of  $\Sigma$ DDT in sediment and water from March 1998, and zooplankton from July 1998 was  $p,p'$ -DDT. In fish,  $p,p'$ -DDT contributed to < 10% of the  $\Sigma$ DDT in all perch and burbot, and pre-flood walleye, but contributed somewhat more (11–22%) in post-flood walleye.

*Chlordane congeners*

Patterns in CHL congeners were more variable among sample types and over time compared to the other OCs, but showed some similarities among biota. Red River floodwater and suspended sediments had greater contributions of *trans*-nonachlor and heptachlor epoxide relative to other water and sediment samples. The composition of  $\Sigma$ CHL in sediment and water were very different, whereby water  $\Sigma$ CHL on all sample dates was primarily heptachlor epoxide (~60%), with smaller contributions from *trans*-CHL. Red River floodwater concentrations of heptachlor epoxide, the oxidation product of heptachlor, peaked with maximum flow reaching a maximum value of 0.336 ng/L. Sediment was composed of similar amounts of *trans*-chlordane > *cis*-nonachlor > oxychlordane. Contributions of the different CHL congeners in zooplankton, perch, and walleye were roughly in the order of *trans*-nonachlor (~26%) > *trans*-chlordane > heptachlor epoxide > *cis*-chlordane > *cis*-nonachlor ~ oxychlordane. Relative contributions in burbot were somewhat different from other species with greater contributions from the nonachlors, where *trans*-nonachlor (~30%) > *cis*-nonachlor > oxychlordane > *trans*-chlordane ~ heptachlor epoxide ~ *cis*-chlordane. The most notable change over time in congener patterns was a progressive increase in oxychlordane, a toxic metabolite of chlordane, and a decline in *cis*-nonachlor from pre-flood to March 1999 in both walleye and burbot.

**DISCUSSION**

Significant among- and within-year differences in OC concentrations were found in fish from the south basin of Lake Winnipeg. Short-term (< 3 yr) variability in OC concentrations in natural fish populations such as these has not been widely examined or understood due to the difficulty in assessing real variability (stochastic verses trends) and identifying the underlying processes (Hebert *et al.* 1997). To do this, one must systematically account for sources of variability that extend from biological attributes to ecosystem processes. For example, burbot and walleye were most different in size and lipid content among sample dates; however, even after adjustment for lipid and length (where required) OC concentrations were still significantly different among and within years. Relationships between contaminants and fish size may be important in determining broad geographical trends in PCBs (Amrhein *et al.* 1999, Stow *et al.* 1997), but were

not the only factor contributing to differences in fish tissue OC concentrations among sample dates. Beyond individual characteristics of sample populations other sources of variability include environmental and ecological factors that have been proposed to explain spatial differences in OCs such as: 1) Contaminant loadings (Jeremaison *et al.* 1999), 2) Differences in food chain length and diet (Kidd *et al.* 1995, Hebert *et al.* 1997), and 3) Contaminant partitioning at the base of the food web (Larsson *et al.* 1998, Kidd *et al.* 1999). In the discussion that follows we examine the extent to which these factors may explain the temporal variability in OC concentrations observed in fish from Lake Winnipeg in the years and months following the 1997 Red River flood.

**Contaminant Loading**

Sediment and mayfly OC concentrations were similar before and after the flood. The fact that we did not observe any marked changes may not be surprising given the size of the sediment sink and degree of sediment resuspension due to physical mixing of the shallow south basin during the ice-free season. Concentrations in pre-flood cores (Rawn *et al.* 2000) were at the lower range of those found throughout the basin post-flood, indicating there were more contaminated areas in the south basin that may have received greater suspended sediment loads during the flood. We did in fact observe strong concentration gradients starting from the mouth of the Red River for sediment  $\Sigma$ DDT, but not for PCBs (Stewart *et al.* 2000). Using sedimentation rates and mixing depths from post-flood cores, it is possible to obtain an estimate of projected sediment PCB concentrations in the south basin following the flood. The mass of surface sediment in the south basin (1,390 km<sup>2</sup>, surface area south of Elk Island, Fig. 1) following the flood is estimated, based on the median sediment deposition and mixing depths of cores 4B and 9B, to be  $1 \times 10^{10}$  kg. Mixing depths, estimated from <sup>210</sup>Pb and <sup>137</sup>Cs profiles in the cores, were 4.56 cm and 2.32 cm for sites 4B and 9B, respectively, and were in the range of those reported by Rawn *et al.* (2000). If we assume 100% retention of the Red River  $\Sigma$ PCB load during the flood (2.4 kg) in sediments south of Elk Island we would expect a surface sediment concentration of 0.23 ng/g, which is a negligible contribution relative to all other recorded values for the south basin. This rough estimate suggests that high-suspended sediment loads diluted the

mass of PCB transported into the lake during the flood event. Barber and Writer (1998) also reported decreases in *p,p'*-DDE and  $\Sigma$ PCBs and a single increase in *p,p'*-DDD concentrations in bed sediments along the upper Mississippi River after the 1993 flood. Sediments and associated organisms (mayflies) did not indicate a change in OC loading, suggesting that other factors contributed to post-flood increases in fish OC burdens.

### Food Web Dynamics and Chemical Partitioning

There are several lines of evidence that suggest changes in the partitioning of OCs at the base of the food web, as opposed to an increase in food chain length, may have contributed to concurrent seasonal increases in  $\Sigma$ DDT and  $\Sigma$ PCB of zooplankton, perch, and walleye and increases in the major OC groups in fish pre- and post-flood. Chemical partitioning of POPs in aquatic ecosystems is not only driven by the chemical's hydrophobicity, the capacity of a particle to sorb a chemical and chemical kinetic rates (Epplert *et al.* 2000, Morrison *et al.* 1996), but also ecosystem processes that vary the composition of particles in time and space (Epplert *et al.* 2000). Seasonal trends in nutrients and plankton in the year following the flood may provide some insight into processes mediating short-term variability in OC levels at the base of the food web that ultimately affect OC levels in fish. Further sampling of seasonal trends will be required to determine whether or not observations are specific to a flood event or are truly representative of the system.

#### *OC Partitioning at the Base of the Food Web*

Although basal  $\delta^{15}\text{N}$  values can vary spatially and temporally due to changing sources of inorganic nitrogen (dissolved inorganic nitrogen (DIN)) to the lake we found no effects of the flood on  $\delta^{15}\text{N}$  values of mayflies or fish. This suggests that dietary habits of fish did not change pre- and post-flood and there was no shift in trophic position of the fish ( $\delta^{15}\text{N}$ ), which would indicate a longer food chain. Alternatively, seasonal variation in the  $\delta^{15}\text{N}$  of zooplankton samples suggested that changes did occur in basal  $\delta^{15}\text{N}$  values, zooplankton community structure, and/or zooplankton feeding habits, with the latter two changes having potential consequences for the partitioning of OCs at the base of the food web. Leggett *et al.* (2000) showed that variability observed in the  $\delta^{15}\text{N}$  of the zooplankton in Lake

Ontario could be attributed to heterogeneity in the  $\delta^{15}\text{N}$  of basal nitrogen, seasonal fluctuations in the  $\delta^{15}\text{N}$  of the particulate organic matter (POM), and differences in trophic status. It is unlikely that enriched sources of dissolved inorganic nitrogen (DIN) caused the dramatic shift in the  $\delta^{15}\text{N}$  of the zooplankton since signatures did not vary with distance from the mouth of the Red River, which is the primary source of nutrient inputs to the south basin. Horizontal gradients in major ions originating from the Red River have been reported in earlier studies and thus, would have been observed for nitrogen if present (Brunskill *et al.* 1979). Enrichment of DIN signatures of zooplankton have been found to increase proportionally with increasing molar C:N ratios of seston (e.g. algae, range 7.3 to 24.8) leading to shifts in fractionation of up to 6‰ (Adams and Sterner 2000). These shifts are in the range of those observed in zooplankton from this study, however, molar C:N ratios remained constant over the time period in question (Jul = 9.7 vs. Sep = 9.4). This leaves features of the zooplankton community structure as the source of the variability in  $\delta^{15}\text{N}$ .

Concomitant changes in  $\delta^{15}\text{N}$  values of zooplankton, zooplankton community structure, and partitioning of OCs in zooplankton have been reported in other lakes. Kidd *et al.* (1998) report declining  $\delta^{15}\text{N}$  values for zooplankton from May through September corresponding to declining  $\Sigma$ DDT levels in two species of cyprinids in an oligotrophic and eutrophic lake, over the same time period, in northwestern Ontario Canada. In a comparison of PCB turnover in an oligotrophic and eutrophic lake, Larsson *et al.* (1998) found higher contaminant concentrations in the zooplankton fraction ( $> 150 \mu\text{m}$ ) in the fall compared to the summer, and peak OC concentrations also coincided with a proportional increase in the percentage of calanoid copepods in the zooplankton fraction. Increases in zooplankton OC concentrations in the present study coincided with a shift in zooplankton community structure towards calanoid copepods and not to changes in lipid fraction. Further, the higher  $\delta^{15}\text{N}$  of the September zooplankton dominated by calanoid copepods corresponds to Leggett *et al.* (2000) who found calanoid copepods to be consistently more enriched in  $^{15}\text{N}$  than cladocerans. The cause of the increase in zooplankton community OC concentrations in Lake Winnipeg may be a function of the life history of the calanoid herbivore, *Diaptomus ashlandi*. This species dominates the crustacean community of southern Lake Winnipeg (Patalas and Salki 1992) and during 1998 in-

creased 20 fold between March and August (Stewart *et al.* 2000). Calanoids are among the longest-lived zooplankton and the life cycle of *D. ashlandi* is known to last for almost one year (Comita and Anderson 1959). Nauplii and immature copepodid instars that were first observed in March, when water OC concentrations were at a maximum, would have grazed heavily on phytoplankton accumulating OCs as they grew from the spring through the summer.

Post-flood increases in cyclopoid and calanoid copepods and  $\delta^{15}\text{N}$  values of zooplankton could also reflect a change in food, possibly from a shift toward bacterial-based production in south basin water column in 1998. Adsorption of OCs onto particles increases with increasing organic carbon content and decreasing particle-size (Skoglund and Swackhamer 1999, Eisenreich 1987), which would be expected to characterize the bacterial portion of the seston. Leggett *et al.* (2000) found that the  $\delta^{15}\text{N}$  signatures of Lake Ontario copepods were too high to suggest a stepwise enrichment over that of phytoplankton and suggested that their elevated signatures may be due in part to consuming a portion of mixotrophic algae, ciliates, and rotifers. Repartitioning of OCs in zooplankton food could increase the bioavailability of the OCs, leading to greater bioaccumulation by zooplankton over time.

Identifying the source of the changes in zooplankton  $\delta^{15}\text{N}$  values and OC concentrations is beyond the scope of this paper; however, these changes may have played an important role in the rapid accumulation of OCs in yellow perch and walleye over a season. No statistically significant differences in isotope signatures of fish were found over time.  $\delta^{15}\text{N}$  values generally increased 0.5 to 1.5 ‰, which may reflect a change in zooplankton signatures. Although we do not have OC values for the smaller seston fractions containing the ciliates and rotifers (< 160  $\mu\text{m}$ ), we did observe a 3 to 5-fold increase for  $\Sigma\text{PCB}$  in the zooplankton between July and September. Increases were less than 2-fold for  $\Sigma\text{DDT}$  and  $\Sigma\text{CBZ}$  and only occurred at southern sites. Factor increases in  $\Sigma\text{PCB}$  were higher in yellow perch (2.4) than walleye (1.4), although absolute concentrations in yellow perch were roughly half that of walleye in September 1998. The larger factor increase and lower absolute concentrations in yellow perch may be due to their closer proximity to zooplankton in trophic level ( $\Delta\delta^{15}\text{N} = 3.41$ ) than walleye ( $\Delta\delta^{15}\text{N} = 5.12$ ) within the Lake Winnipeg food web. This trophic position may have resulted in a more rapid, marked response to changes in OC

partitioning in the zooplankton, but also an overall lower biomagnification of OCs than in walleye (Kidd *et al.* 1998). The smaller body size of yellow perch relative to the walleye may have also been a factor since it would have allowed them to reach new steady-state concentrations with their food within the two month summer period (Olsson *et al.* 2000).

#### Fish Migration

Lastly, it is worth mentioning the potential role of fish migration on contaminant exposure in these fish. Some fish species in Lake Winnipeg are known to migrate between the north and south basins as well as rivers such as the Red and this in turn impacts upon their contaminant burden (K. Kidd, unpublished data). Higher concentrations of OCs have been observed in fish that are known to have been feeding in the south basin based on their carbon isotopic values matching mayfly isotopic values collected in the south basin (Table 5). In this study,  $\delta^{15}\text{N}$  values of the fish suggest they were feeding predominantly within the south basin. The lower nitrogen isotopic signature of the spring 1999/2000 walleye suggests that these groups may have spent some time in the north basin feeding. Work by Hesslein *et al.* (1993) suggests that turnover of isotopes in slow-growing wild populations could take years and therefore, the “north basin” isotopic signal of the spring walleye may reflect feeding locations in previous years. This result is consistent with known migration patterns of walleye in Lake Winnipeg and morphological attributes of the sample group (Lysack 1995). The older, and larger fish that compose the March 1999 sample group might include at least some north basin fish. The fact that this group had OC concentrations (after adjusting for length and lipid using ANCOVA) as high or higher than other sample groups is surprising given the earlier findings of Kidd (unpublished data) who report lower OC concentrations in fish in the north basin relative to the south basin.

#### Sources of OC Exposure—Congener Profiles

Congener profiles of Red River floodwater and suspended sediments indicate that the chemical composition of the major OC groups entering Lake Winnipeg during the flood were not different from those in pre- and post-flood sediments, except in a few instances (e.g. *p,p'*-DDT). Given that the rela-

tive contribution of the flood sediments to total bed sediment concentrations were relatively small it is unclear if these congener profiles had any effect on the short-term variability in OC levels in biota.

OC congener patterns in the Lake Winnipeg food web remained relatively stable over the sampling periods, suggesting similar mechanisms of exposure and bioaccumulation pre- and post-flood and within subsequent years post-flood. Congener patterns in zooplankton were not similar to water or sediment suggesting an alternative source of exposure at the base of the food web that was not directly measured (i.e., microplankton < 160  $\mu\text{m}$ ). This is in contrast to PCB results for arctic marine zooplankton reported by Fisk *et al.* (2001), who report similar OC congener patterns for zooplankton and water in the Canadian Arctic. The fact that the metabolized DDT isomer *p,p'*-DDE was dominant in zooplankton compared to anaerobically produced *p,p'*-DDD also suggests that shifts in dietary exposures and not water or sediment were critical in mediating short-term changes in OCs in the system.

One of the objectives of this study was to determine if changes in OC exposures associated with the flood were unique to the event, such as the composition of source inputs, or if the flood influenced within-system processes leading to changes in OC exposures. Increases in  $\Sigma\text{PCB}$  levels in walleye were greater pre- and post-flood than within-year suggesting that the flood may have changed OC bioavailability. However, these changes do not appear to be the result of new source inputs to the lake as evidenced by similar sediment OC concentrations and consistent congener profiles before and after the flood. Only post-flood walleye showed an increase in proportion of the parent compound *p,p'*-DDT corresponding to recent inputs from Red River floodwater suspended sediments containing original compounds, contrary to the trends observed in the bed sediments. These combined results suggest that floods or other short-term episodic events in the Red River basin may not directly result in increases in OCs in natural fish populations, but instead may indirectly influence within-system processes leading to increases in OC accumulation in Lake Winnipeg biota. These results are contrary to those reported following a 100 year flood event in the Saginaw River/Bay ecosystem that was accompanied by rapid increases in OC exposures and significant depression of reproductive success in piscivorous birds (e.g., Caspian tern) (Ludwig *et al.* 1993).

## CONCLUSIONS

This study has shown that a major perturbation in OC loading to Lake Winnipeg had no effect on concentrations in sediment and mayflies pre- and post-flood. It did result in post-flood increases in more recalcitrant OC pesticides (e.g.,  $\Sigma\text{DDT}$ ) and  $\Sigma\text{PCBs}$  in top predators such as walleye. However, congener and OC pesticide proportions remained relatively constant within species over time. Perhaps a more important observation is that significant seasonal and annual changes in concentrations and profiles occurred in the south basin of Lake Winnipeg that are best attributed to food web factors, especially shifts in the zooplankton community. These shifts have rarely been observed in other studies of OC food web dynamics in large lakes due to the typical short sampling season. Our results also indicate that short-term variability is best observed in lower trophic level consumers such as forage fish (i.e., yellow perch or young-of-the-year fish) and supports the contention that the critical mechanisms leading to this variability lies in the partitioning of OCs in plankton.

## ACKNOWLEDGMENTS

Funding for this work was provided by the International Joint Commission and the Canadian Department of Fisheries and Oceans. We would like to thank the Canadian Coast Guard crew of C.C.G.S. *Wabuno II* and Gord Jacobson who assisted with field collections and personnel of the Department of Fisheries and Oceans for their assistance with sample collections and processing including, D. Tenkula, R. Danell, A. Yarchewski, and others. Rick Wassel determined the ages of the fish and Don Cobb advised on the species determination of the mayflies. R. Hesslein, W. Franzin, and two anonymous reviewers are acknowledged for their constructive comments on the manuscript.

## REFERENCES

- Adams, T.S., and Sterner, R.W. 2000. The effect of dietary nitrogen content on trophic level  $^{15}\text{N}$  enrichment. *Limnol. Oceanogr.* 45:601–607.
- Amrhein, J.F., Stow, C.A., and Wible, C. 1999. Whole-fish versus file polychlorinated-biphenyl concentrations: an analysis using classification and regression tree models. *Environ. Toxicol. Chem.* 18:1817–1823.
- Anderson, R.O., and Gutreuter, S.J. 1983. Length, weight, and associated structural indices. In *Fisheries Techniques*, eds. L.A. Nielson and D.L. Johnson, pp. 283–300. Blacksburg, VA: American Fisheries Society.

- Babaluk, J.A., and Campbell, J.S. 1987. Preliminary results of tetracycline labeling for validating annual growth increments in opercula of walleyes. *N. Amer. J. Fish. Manag.* 7:138–141.
- Barber, L.B., and Writer, J.H. 1998. Impact of the 1993 flood on the distribution of organic contaminants in bed sediments of the upper Mississippi River. *Environ. Sci. Technol.* 32:2077–2083.
- Barber, W.A., and McFarlane, G.A. 1987. Evaluation of three techniques to age Arctic Char from Alaskan and Canadian waters. *Trans. Amer. Fish. Soc.* 116: 874–881.
- Berglund, O., Larsson, P., Brönmark, C., Greenberg, L., Eklöv, A., and Okla, L. 1997. Factors influencing organochlorine uptake in age-0 brown trout (*Salmo trutta*) in lotic environments. *Can. J. Fish. Aquat. Sci.* 54:2767–2774.
- Bergqvist, P., Strandberg, B.O., Ekelund, R., Rappe, C., and Granmo, A. 1998. Temporal monitoring of organochlorine compounds in seawater by semipermeable membranes following a flooding episode in Western Europe. *Environ. Sci. Technol.* 32:3887–3892.
- Borgmann, U., and Whittle, D.M. 1992. Bioenergetics and PCB, DDE, and mercury dynamics in lake Ontario lake trout (*Salvelinus namaycush*): a model based on surveillance data. *Can. J. Fish. Aquat. Sci.* 49:1086–1096.
- Brunskill, G.J., Campbell, P.G.C., and Elliot, S.E.M. 1979. *Temperature, oxygen, conductance and dissolved major elements in Lake Winnipeg*. Canadian Fisheries Marine Service Manuscript Report, Report No.1526.
- , Elliot, S.E.M., and Campbell, J.S. 1980. *Morphometry, hydrology, and watershed data pertinent to the limnology of Lake Winnipeg*. Canadian Manuscript Report of Fisheries & Aquatic Sciences, Report No.1556.
- Cabana, G., and Rasmussen, J.B. 1996. Comparison of aquatic food chains using nitrogen isotopes. *Proc. Natl. Acad. Sci.* 93:10844–10847.
- Carey, J.H., Cook, P.M., Giesy, J., Hodson, P., Muir, D.C.G., Owens, W., and Solomon, K. 1998. *Ecotoxicological risk assessment of the chlorinated organic chemicals*. Pensacola, FL: SETAC Press.
- Comita, G.W., and Anderson, G.C. 1959. The seasonal development of a population of *Diaptomus ashlandi* Marsh, and related phytoplankton cycles in Lake Washington. *Limnol. Oceanogr.* 4:37–52.
- Dearth, M.A., and Hites, R.A. 1991. Chlordane accumulation in people. *Environ. Sci. Technol.* 25:1279–1285.
- DeVault, D.S., Hesselberg, R., Rodgers, P.W., and Feist, T J. 1996. Contaminant trends in lake trout and wall-eye from the Laurentian Great Lakes. *J. Great Lakes Res.* 22:884–895.
- Eisenreich, S.J. 1987. The chemical limnology of nonpolar organic contaminants: PCBs in Lake Superior. In *Sources and fates of organic contaminants*, eds. R.A. Hites and S.J. Eisenreich, pp. 393–469. Washington, D.C.: American Chemical Society.
- Epplett, T.D., Gewurtz, S., Lazar, R., and Haffner, G.D. 2000. Seasonal dynamics of PCBs in the plankton of Lake Erie. *J. Great Lakes Res.* 26:65–73.
- Fisk, A.T., Hobson, K.A., and Norstrom, R.J. 2001. Influence of chemical and biological factors on trophic transfer of persistent organic pollutants in the northwater Polyna marine food web. *Environ. Sci. Technol.* 35:732–738.
- Hebert, C.E., Shutt, J.L., and Nordstrom, R.J. 1997. Dietary changes cause temporal fluctuations in polychlorinated biphenyl levels in herring gull eggs from Lake Ontario. *Environ. Sci. Technol.* 31:1012–1017.
- Hesslein, R.H., Hallard, K.A., and Ramlal, P. 1993. Replacement of sulfur, carbon and nitrogen in tissue of growing broad whitefish (*Coregonus nasus*) in response to a change in diet traced by  $\delta^{34}\text{S}$ ,  $\delta^{13}\text{C}$ , and  $\delta^{15}\text{N}$ . *Can. J. Fish. Aquat. Sci.* 50:2071–2076.
- Jeremaison, J.D., Eisenreich, S.J., Paterson, M.J., Beaty, K.G., Hecky, R.E., and Elserk, J.J. 1999. Biogeochemical cycling of atmospherically derived PCBs in lakes of variable trophic status: a paired-lake experiment. *Limnol. Oceanogr.* 44:889–902.
- Kidd, K.A., Schindler, D.W., Muir, D.C.G., Lockhart, W.L., and Hesslein, R.H. 1995. High concentrations of toxaphene in fishes from a subarctic lake. *Science* 269:240–242.
- , Schindler, D.W., Hesslein, R.H., and Muir, D.C.G. 1998. Effects of trophic position and lipid on organochlorine concentrations in fishes from subarctic lakes in Yukon Territory. *Can. J. Fish. Aquat. Sci.* 55:869–881.
- , Paterson, M.J., Hesslein, R.H., Muir, D.C.G., and Hecky, R.E. 1999. Effects of northern pike (*Esox lucius*) additions on pollutant accumulation and food web structure, as determined by  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ , in a eutrophic and an oligotrophic lake. *Can. J. Fish. Aquat. Sci.* 56:2193–2202.
- Kucklick, J.R., and Baker, J. 1998. Organochlorines in Lake Superior's food web. *Environ. Sci. Technol.* 32:1192–1198.
- Larsson, P., Okla, L., and Cronberg, G. 1998. Turnover of polychlorinated biphenyls in an oligotrophic and an eutrophic lake in relation to internal lake processes and atmospheric fallout. *Can. J. Fish. Aquat. Sci.* 55:1926–1937.
- , Collvin, L., Okla, L., and Meyer, G. 1992. Lake productivity and water chemistry as governors of the uptake of persistent pollutants in fish. *Environ. Sci. Technol.* 26:346–352.
- Leggett, M.F., Johannsson, O., Hesslein, R.H., Dixon, D. G., Taylor, W.D., and Servos, M.R. 2000. Influence of inorganic nitrogen cycling on the  $\delta^{15}\text{N}$  of Lake Ontario biota. *Can. J. Fish. Aquat. Sci.* 57:1489–1496.
- Lockhart, W.L., Wilkinson, P., Billeck, B.N., Danell, R.,

- Hunt, R.V., Brunskill, G.J., Delaronde, J., and St. Louis, V. 1998. Fluxes of mercury to lake sediments in central and northern Canada inferred from dated sediment cores. *Biogeochem.* 40:163–173.
- Ludwig, J.P., Auman, H.J., Kurita, H., Ludwig, M.E., Campbell, L.M., Giesy, J.P., Tillit, D.E., Jones, P., Yamashita, N., Tanabe, S., and Tatsukawa, R. 1993. Caspian tern reproduction in the Saginaw Bay ecosystem following a 100-year flood event. *J. Great Lakes Res.* 19:96–108.
- Lysack, W. 1995. *Mesh size effects in Lake Winnipeg's commercial fisheries*. Department of Natural Resources, Fisheries Branch MS Report No. 95-02.
- Morrison, H.A., Gobas, F.A.P.C., Lazar, R., and Haffner, G.D. 1996. Development and verification of a bioaccumulation model for organic contaminants in benthic invertebrates. *Environ. Sci. Technol.* 30:3377–3384.
- Muir, D.C.G., Nordstrom, R.J., and Simon, M. 1988. Organochlorine contaminants in arctic marine food chains: accumulation of specific polychlorinated biphenyls and chlordane-related compounds. *Environ. Sci. Technol.* 22:1071–1079.
- , Ford, C.A., Grift, N.P., Metner, D.A., and Lockhart, W.L. 1990. Geographic variation of chlorinated hydrocarbons in burbot (*Lota lota*) from remote lakes and rivers in Canada. *Arch. Environ. Contam. Toxicol.* 19:530–542.
- , Omelchenko, A., Grift, N.P., Savoie, D.A., Lockhart, W.L., and Brunskill, G.J. 1996. Spatial trends and historical deposition of polychlorinated biphenyls in Canadian midlatitude and Arctic lake sediments. *Environ. Sci. Technol.* 30:3609–3617.
- Olsson, A., Valters, K., and Burreau, S. 2000. Concentrations of organochlorine substances in relation to fish size and trophic position: a study on perch (*Perca fluviatilis* L.). *Environ. Sci. Technol.* 34:4878–4886.
- Patalas, K., and Salki, A. 1992. Crustacean plankton in Lake Winnipeg: variation in space and time as function of lake morphology, geology, and climate. *Can. J. Fish. Aquat. Sci.* 49:1035–1059.
- Peterson, B.J., and Fry, B. 1987. Stable isotopes in ecosystem studies. *Ann. Rev. Ecol. Syst.* 18:293–320.
- Petty, J.D., Poulton, B.C., Charbonneau, C.S., Huckins, J.N., Jones, S.B., Cameron, J.T., and Prest, H.F. 1998. Determination of bioavailable contaminants in the lower Missouri River following the flood of 1993. *Environ. Sci. Technol.* 32:837–842.
- Rasmussen, J.B., Rowan, D.J., Lean, D.R.S., and Carey, J.H. 1990. Food chain structure in Ontario lakes determines PCB levels in Lake Trout (*Salvelinus namaycush*) and other pelagic fish. *Can. J. Fish. Aquat. Sci.* 47:2030–2038.
- Rawn, D.F.K., Muir, D.C.G., Savoie, D.A., Rosenberg, G.B., Lockhart, W.L., and Wilkinson, P. 2000. Historical deposition of PCBs and organochlorine pesticides to Lake Winnipeg (Canada). *J. Great Lakes Res.* 26:3–17.
- Rostad, C. 1997. From the 1988 drought to the 1993 flood: transport of halogenated organic compounds with the Mississippi River suspended sediment at Thebes, Illinois. *Environ. Sci. Technol.* 31:1308–1312.
- Salki, A. 1996. The crustacean plankton community of Lake Winnipeg in 1929, 1969 and 1994. In *Lake Winnipeg Project: cruise report and scientific results*, pp. 319–344. Geological Survey of Canada.
- Schneider, A.R., Stapleton, H.M., Cornwall, J., and Baker, J.E. 2001. Recent declines in PAH, PCB and toxaphene levels in the northern Great Lakes as determined from high resolution sediment cores. *Environ. Sci. Technol.* 35:3809–3815.
- Scott, W.B., and Crossman, E.J. 1973. *Freshwater fishes of Canada*. Ottawa. Fisheries Research Board of Canada. Bulletin 184.
- Skoglund, R.S., and Swackhamer, D.L. 1999. Evidence for the use of organic carbon as the sorbing matrix in the modeling of PCB accumulation in phytoplankton. *Environ. Sci. Technol.* 33:1516–1519.
- Stainton, M.P., Capel, M.J., and Armstrong, F.A.J. 1977. *The chemical analysis of fresh water*. 2<sup>nd</sup> edition. Canadian Fisheries Marine Service, Misc. Spec. Publ. 25.
- Stapleton, H.M., Materson, C., Skubina, J., Ostrom, P., Ostrom, N.E., and Baker, J.E. 2001. Accumulation of atmospheric and sedimentary PCBs and toxaphene in the Lake Michigan food web. *Environ. Sci. Technol.* 35:3287–3293.
- StatSoft, I. 1999. *Statistica for Windows* (Computer program manual). Tulsa.
- Stern, G.A., Muir, D.C.G., Ford, C.A., Grift, N.P., Dewailly, E., Bidleman, T.F., and Walla, M.D. 1992. Isolation and identification of two major recalcitrant toxaphene congeners in aquatic biota. *Environ. Sci. Technol.* 26:1838–1840.
- Stewart, A.R., Stern, G.A., Salki, A., Stainton, M.P., Lockhart, W.L., Billeck, B.N., Danell, R., Delaronde, J., Grift, N.P., Halldorson, T., Koczanski, K., MacHutcheon, A., Rosenberg, G.B., Savoie, D.A., Tenkula, D., Tomy, G., and Yarchewski, A. 2000. *Influence of the 1997 Red River flood on contaminant transport and fate in southern Lake Winnipeg*. Report to the International Red River Basin Task Force. <http://www.ijc.org/pdf/winnipegwaterquality.pdf>
- Stow, C.A., Jackson, L.J., and Amrhein, J.F. 1997. An examination of the PCB:lipid relationship among individual fish. *Can. J. Fish. Aquat. Sci.* 54:1031–1038.
- Thomann, R.V., and Connolly, J.P. 1984. Model of PCBs in the Lake Michigan lake trout food chain. *Environ. Sci. Technol.* 18:65–71.

Submitted: 4 June 2002

Accepted: 24 March 2003

Editorial handling: Arthur J. Niimi