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Snapping Turtles (*Chelydra serpentina*) as Bioindicators in Canadian Areas of Concern in the Great Lakes Basin. 1. Polybrominated Diphenyl Ethers, Polychlorinated Biphenyls, and Organochlorine Pesticides in Eggs

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We examined the concentrations and spatial patterns of congeners of PBDEs, PCBs, and organochlorine pesticides in snapping turtle (*Chelydra serpentina*) eggs from Areas of Concern (AOCs) on the Canadian shores of Lake Ontario, St. Lawrence River, and connecting channels. Eggs from Lyons Creek (Niagara River AOC) reflected a local PCB source over a range of 7.5 km (3.2 − 10.8) from the Welland Canal. PCB contamination in eggs declined with increasing distance from the Welland Canal, whereas the relative contribution of congeners associated with Aroclor 1248/1254 increased with ΣPCB concentrations. Compared to turtle eggs from other sites in Lake Erie and Lake Ontario, eggs from Lyons Creek and Snye Marsh had PCB congener patterns that reflected a strong contribution from Aroclor 1254. PCBs in the eggs were associated with industrial sources and reflected the composition of different Aroclor technical mixtures. Organochlorine pesticides in eggs tended to be highest at Hamilton Harbour and Bay of Quinte AOCs, and were dominated by DDE, Σchlordane, and mirex. In contrast, PBDE congener patterns in turtle eggs resembled PentaBDE technical formulations regardless of absolute concentrations or location, and were largely associated with urban environments.

Introduction

Canada and the United States are committed to the virtual elimination of persistent toxic substances and the restoration of ecosystems within the Great Lakes Basin Ecosystem by the Great Lakes Water Quality Agreement. Some of the contaminants designated as Level 1 and targeted for virtual elimination are DDT, polychlorinated biphenyls (PCBs), dibenzo-*p*-dioxins, and dibenzofurans. Polybrominated diphenyl ethers (PBDEs) are additive flame retardants that were produced commercially in North America as the product PentaBDE until the end of 2004, but their use continues. PBDEs have been increasing at near exponential rates (at least up to 2000) in North American biota and in particular Great Lakes herring gull eggs and fish (*1*, *2*).

PCBs and PBDEs are separate classes of environmental contaminants that possess physiochemical properties that lead to persistence and bioaccumulation in the environment and in biota. PCBs and PBDEs have been shown to have common mechanisms of toxicity, though not necessarily potency, which can alter thyroid function, aryl hydrocarbon receptor agonism, and neurotoxicity (*3*−*5*). Bicknell (*6*) used a scheme based upon toxicity, fate, and persistence to rank toxic contaminants in the Great Lakes, and concluded that PCBs were the second highest ranking compounds. PBDEs are not currently listed as Level II compounds, "as having the potential to significantly impact the Great Lakes ecosystem through [its] use and/or release" (*7*), but their similarity to PCBs (Level I) in fate and toxicity, as well as their recent rapid increase in abiotic and biotic environmental compartments, suggest they might be suitable candidates for such consideration.

The International Joint Commission designated 42 geographical regions as Areas of Concern (AOCs) within the Great Lakes basin, based upon impairment of the chemical, physical, or biological integrity of the Great Lakes System. Persistent organic pollutants (POPs) contribute to some beneficial use impairments, such as degradation of fish and wildlife populations, reproduction and deformities, and restrictions on fish and wildlife.

Snapping turtles (*Chelydra serpentina*) have long been used as indicators of local PCB and OC pesticide contamination in the Great Lakes basin (*8*, *9*). However, to our knowledge, PBDEs have yet to be reported in turtle tissues or eggs, and in particular in individuals from the Great Lakes basin. We presently report on the comparative spatial distributions of OC pesticides, PCBs, and PBDEs in snapping turtle eggs collected from most of the Canadian AOCs on the lower Great Lakes and connecting channels. We examined (i) whether concentrations of these compounds were elevated in AOCs relative to reference sites, and (ii) whether the concentrations in turtle eggs are predictable from the proximity to urban/industrial centers.

Materials and Methods

Sampling Locations. Eggs were collected from 15 locations from Lakes Erie and Ontario, and the Detroit and St. Lawrence Rivers (Figure 1; Table 1). Algonquin Provincial Park and Tiny Marsh were included as two inland reference sites. See Supporting Information for detailed site descriptions (Figure S1, Table S1).

Sample Collection. Snapping turtle eggs were collected for contaminant analysis in June, 2001 to 2004. Five eggs were selected from each clutch, although occasionally fewer eggs were selected from smaller clutches. Eggs were selected in a pseudorandom but stratified manner, such that eggs were selected throughout the entire clutch (*10*). Egg contents from each clutch were pooled, and frozen in hexane-cleaned amber glass jars.

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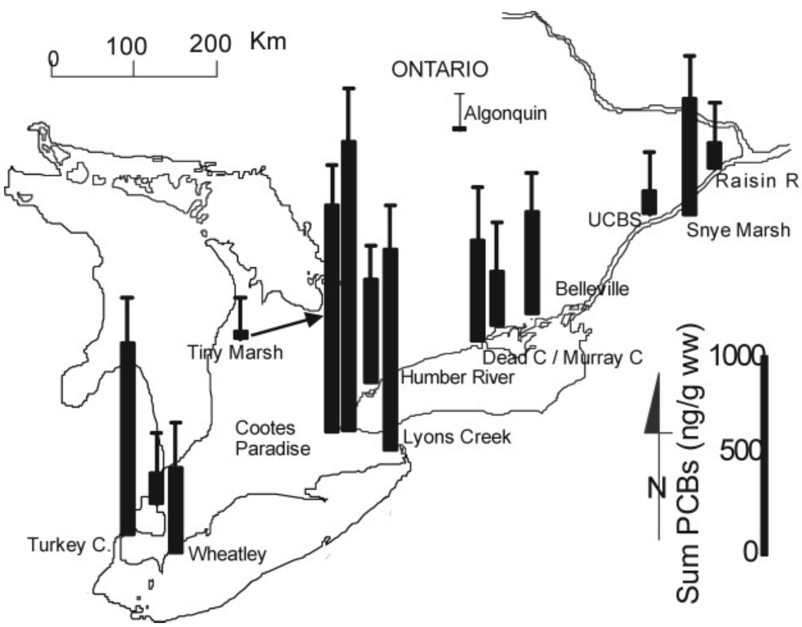

FIGURE 1. Mean sum-PCB (34 congeners) concentrations (ng/g wet weight) in snapping turtle eggs in the lower Canadian Great Lakes collected in 2001−2004. The error bars show the ±SD of the mean concentrations. All sites differed from the pooled reference sites (Algonquin Park and Tiny Marsh).

TABLE 1. Mean (±SD) Concentrations (ng/g ww) of Organochlorine Pesticides in Snapping Turtle Eggs from Lake Ontario, St. Lawrence River, and Connecting Channels (2001−2004)[a]

AOC	site	*n*	*n* HE[b]	HCB	OCS	sum chlordane	*p,p′*-DDE	*p,p′*-DDD	*p,p′*-DDT	mirex	dieldrin	HE
reference	Algonquin	15	12	0.16 (0.11)	0.04 (0.12)	1.34 (3.57)	3.75 (7.89)	0.12 (0.17)	0.17 (0.13)	0.31 (3.91)	0.21 (0.43)	0.20 (0.18)
reference	Tiny	14	10	0.19 (0.11)	0.04 (0.12)	1.90 (3.70)	3.83 (8.16)	0.03 (0.18)	0.36 (0.13)	1.79 (4.05)	0.42 (0.44)	0.21 (0.19)
Cornwall (US side)	Snye	9	9	0.48 (0.14)**A**	0.16 (0.16)	7.06 (4.61)**A**	11.6 (10.1)	0.15 (0.23)	0.09 (0.17)	6.86 (5.05)**A**	0.73 (0.56)	0.32 (0.20)
Cornwall (within)	RR	10	10	0.62 (0.13)**A**	0.07 (0.15)	6.42 (4.37)**A**	7.93 (9.66)	0.17 (0.21)	0.06 (0.16)**A**	5.29 (4.79)**A**	1.70 (0.53)	0.64 (0.19)
Cornwall (upstream)	UCBS	11	11	0.35 (0.12)**A**	0.41 (0.14)**A**	4.64 (4.17)**A**	16.7 (9.21)	0.14 (0.20)**A**	0.10 (0.15)	11.6 (4.57)**A**	0.48 (0.50)	0.24 (0.18)
Bay of Quinte	Belleville	10	10	0.60 (0.13)**A**	0.56 (0.15)**A**	25.4 (4.37)**A**	72.5 (9.66)**A**	0.32 (0.21)**A**	0.31 (0.16)**A**	48.8 (4.79)**A**	0.80 (0.53)**A**	0.58 (0.19)**A**
Bay of Quinte	Dead	7	7	0.43 (0.16)**A**	0.51 (0.18)**A**	14.2 (5.23)**A**	36.0 (11.5)**A**	0.20 (0.26)**A**	0.21 (0.19)	19.8 (5.73)**A**	0.96 (0.63)**A**	0.60 (0.23)**A**
Bay of Quinte	Murray	6	6	0.52 (0.17)**A**	1.58 (0.19)**A**	20.3 (5.65)**A**	131. (12.4)**A**	0.80 (0.28)**A**	0.27 (0.20)**A**	40.9 (6.19)**A**	1.03 (0.68)**A**	0.51 (0.25)**A**
Toronto	Humber	15	15	0.73 (0.11)**A**	0.40 (0.12)**A**	37.4 (3.57)**A**	28.0 (7.89)**A**	0.73 (0.17)**A**	0.33 (0.13)**A**	25.6 (3.91)**A**	3.16 (0.43)**A**	1.42 (0.16)**A**
Hamilton	Cootes	10	10	1.28 (0.13)**A**	0.55 (0.15)**A**	81.9 (4.37)**A**	89.2 (9.66)**A**	2.69 (0.21)**A**	0.50 (0.16)**A**	33.3 (4.79)**A**	4.05 (0.53)**A**	0.92 (0.19)**A**
Hamilton	Grindstone	6	6	2.92 (0.17)**A**	2.84 (0.19)**A**	55.6 (5.65)**A**	152. (12.4)**A**	3.57 (0.28)**A**	0.79 (0.20)**A**	41.5 (6.19)**A**	7.27 (0.68)**A**	1.79 (0.25)**A**
Niagara River	Lyons	9	9	0.23 (0.14)	0.10 (0.16)	2.31 (4.61)	6.73 (10.1)	0.05 (0.23)	0.14 (0.17)	0.67 (5.05)	0.68 (0.56)	0.25 (0.20)
Wheatley Harbour	WPP	8	5	0.84 (0.15)**A**	0.75 (0.16)**A**	29.8 (4.89)**A**	48.1 (10.8)**A**	1.10 (0.24)**A**	1.19 (0.18)**A**	1.79 (5.36)**A**	5.86 (0.59)**A**	2.42 (0.28)**A**
Detroit River	Turkey	8	4	2.33 (0.15)**A**	1.37 (0.16)**A**	24.2 (4.89)**A**	24.0 (10.8)**A**	0.59 (0.24)**A**	0.87 (0.18)**A**	8.82 (5.36)**A**	4.51 (0.59)**A**	2.31 (0.31)**A**
St Clair River	NWA	10	0	0.49 (0.13)**A**	0.28 (0.15)**A**	3.55 (4.37)**A**	5.23 (9.66)	0.12 (0.21)**A**	0.83 (0.16)**A**	0.29 (4.79)	0.93 (0.53)	n/a

[a] Pesticides with "**A**" different from combined reference sites Algonquin Park and Tiny Marsh. Data were log transformed prior to statistical analyses. [b] Sample size for heptachlor epoxide (HE) only.

Chemical Analysis. The frozen eggs were shipped to GLIER (University of Windsor). A complete description of sample extraction, partitioning, and cleanup procedures for determination of PCBs, OC pesticides and byproducts, and PBDEs in egg samples is outlined elsewhere (*11*, *12*). Briefly, turtle egg homogenate (~3 g) was dehydrated with anhydrous sodium sulfate. Dichloromethane/*n*-hexane (100 mL, 1:1 v/v) was added to the recipient extraction column. PCBs and OC pesticides analyzed by gas chromatography−electron capture detection (GC−ECD) were spiked with 1,3,5-tribromobenzene (Accu-Standard Inc., New Haven, CT) internal standards (*11*). If analyzed by GC−mass spectrometry (electron ionization) (GC−MSD(EI)), the internal standards were $^{13}C_{12}$-labeled CB-37, CB-52, and CB153 (*12*). For PBDE determination by

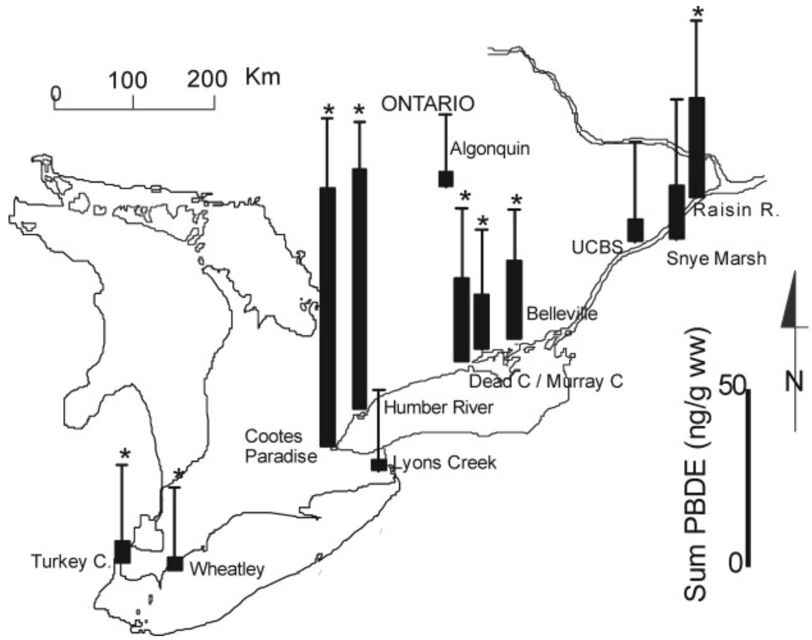

FIGURE 2. Mean sum-PBDE (eight congeners) concentrations (ng/g wet weight) in snapping turtle eggs in the lower Canadian Great Lakes collected in 2001−2004. The error bars show the ±SD of the mean concentrations. Sites significantly different from the reference site (Algonquin Park) are marked with asterisks.

GC−mass spectrometry−electron capture negative ionization (GC−MS(ECNI)), the internal standard was BDE71 (*12*). After ~1 h the extraction column was eluted to dryness and an additional 200 mL of dichloromethane/*n*-hexane (1:1 v/v) was used to complete the extraction. Lipid content was determined gravimetrically from a 10% portion of the extract. Lipids were removed from the remaining extract by gel permeation chromatography, followed by Florisil chromatography for final cleanup of the PCBs/OC pesticides and PBDEs.

(i) PCBs and OCs. For PCBs and OCs, all of the 2003 and 2004 eggs were analyzed using GC−MSD(EI), and eggs from 2001 to 2002 were analyzed using GC−ECD. The different GC detectors identified a different number of PCB congeners, so only 34 individual congeners common to all analyses were included, which comprised sum (Σ)PCBs.

For GC−ECD, an Agilent 6890, Agilent 7673 splitless injector, and a ^{63}Ni μ-ECD detector were used. Compound separation was completed using a fused silica DB-5 column [(5% phenyl)methylpolysiloxane, 30 m, 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific]. Helium was used as carrier gas. The MS was set in electron impact (EI) ionization, using selected ion monitoring (SIM) mode. PCBs and OCs were determined using 36 PCB congener and 13 OC external standards.

(ii) PBDEs. Nine PBDE congeners were monitored by GC−MS(ECNI), i.e., BDE-28, -47, -99, -100, -138, -153, -154 (coelutes with possible BB-153), -183, and -209, and comprised the ΣPBDE concentration. PBDEs were determined on an Agilent 6890N series GC, fused silica DB-5 column, and Agilent 5973N series quadrupole MS in the ECNI and selected SIM modes. Helium and methane were used as the carrier and reagent gases, respectively. The GC ramping programs for PBDEs have been detailed elsewhere (*12*). PBDE congeners were monitored using the isotopic bromine anions of m/z 79 and 81. BDE congeners were identified by comparison of retention times and ECNI mass spectra to those of the standards, and were quantified based on the relative response of the internal standard. See Supporting Information for description of quality control, and method for calculating replacement values for observations below detection limits.

Data Analysis. See Supporting Information for the estimation of the relative contribution of each Aroclor (1242, 1248, 1254, and 1260) to the PCB egg burden.

PCB congener patterns in eggs were examined using ANOVA and Factor Analysis (FA) using varimax normalized rotation on untransformed contaminant concentrations. FA is frequently used for examining sources of complex mixtures of contaminants, including PCBs. Factors were selected using maximum likelihood. The 31 most prevalent PCB congeners were included, and were expressed as a proportion of the ΣPCBs. Tukey's HSD test was used for all multiple comparisons ($\alpha = 0.05$). Kolmogorov−Smirnov and Levene's tests were used to test for normality and homogeneity of variances; data were ln transformed unless otherwise stated. We used regressions to compare contaminant burdens with population sizes of the adjacent municipalities. Statistical analyses were performed using Statistica 7.1 and Mathcad 11.

Results

Spatial Contaminant Trends. ΣPCB concentrations in the turtle eggs were similar between Algonquin Park and Tiny Marsh reference sites ($p = 0.1844$), and between UCBS and Raisin River ($p = 0.3985$; (Figure 1). Algonquin Park and Tiny Marsh were pooled together as the reference site, and UCBS and Raisin River were pooled together as the Cornwall site. ΣPCB concentrations were higher at all sites compared to the reference sites ($p < 0.0001$; Figure 1). Eggs from Snye Marsh had significantly higher concentrations of ΣPCBs compared to the pooled Cornwall sites ($p = 0.0006$; Figure 1). Sum PCBs in turtle eggs increased with the ln-transformed population size of adjacent municipalities ($r^2 = 0.611$, $p = 0.0016$).

Generally, OC pesticides were highest in eggs from Hamilton (Cootes Paradise and Grindstone), followed by the Bay of Quinte sites $p < 0.0001$; Table 1. There were no differences in OCs between Algonquin Park and Tiny Marsh (all $p \geq 0.1555$). OC residues in eggs from Lyons Creek did not differ significantly from those in eggs from Algonquin Park and Tiny Marsh (Reference A; all $p \geq 0.0623$). Pesticide concentrations were generally similar in eggs from UCBS and Raisin River ($p > 0.0514$), and between Snye Marsh and

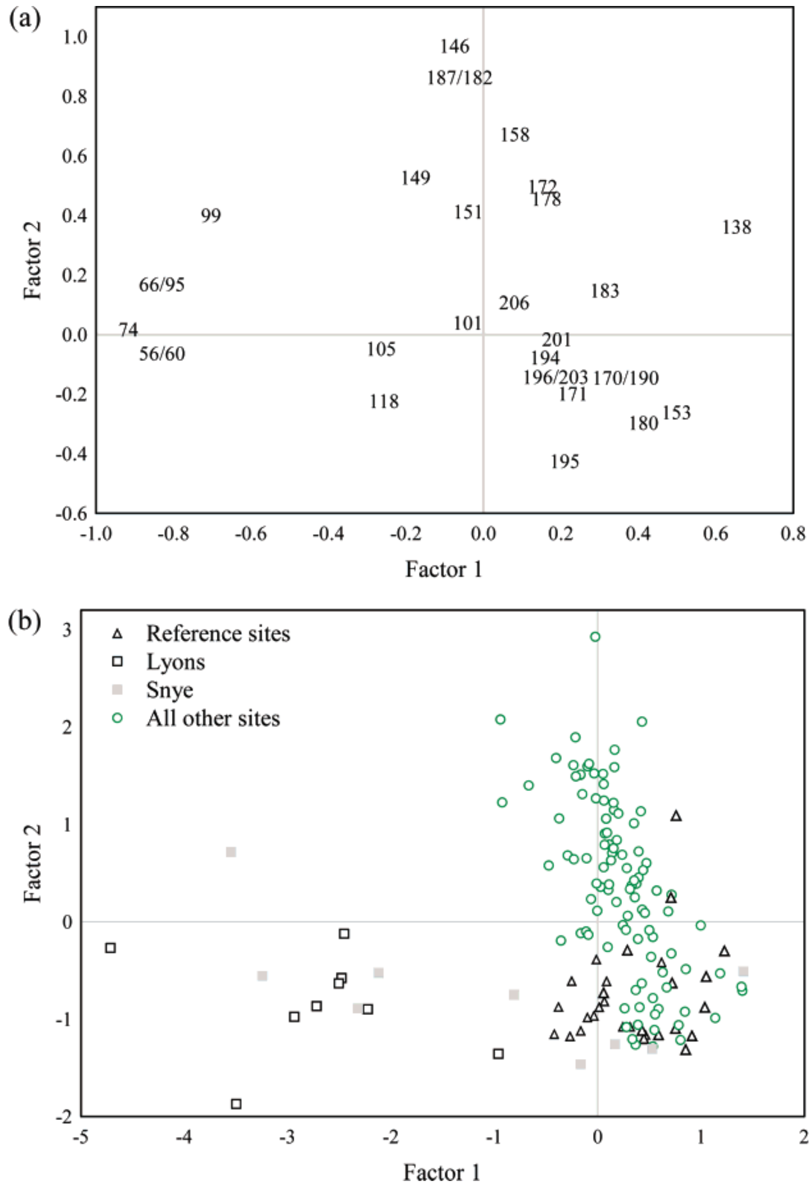

FIGURE 3. (a) Factor loadings of PCB congener patterns in snapping turtle eggs from the lower Canadian Great Lakes. High loadings of factor 1 are indicative of Aroclor 1260 and low loadings of factor 1 are indicative of Aroclors 1254/1248. (b) Factor scores of PCB congeners in turtle eggs from the lower Canadian Great Lakes collected in 2001−2004.

the Cornwall sites ($p \geq 0.2241$). Although pesticide concentrations differed among sites, the relative contribution of each pesticide to the total egg burden was similar for all sites; the correlations among pesticides were ≥0.63. There was a greater difference between the most contaminated site (Grindstone Creek, Hamilton) and the reference sites with respect to ΣPCBs (ratio 84.0:1) relative to OC pesticides (e.g., *p,p′*-DDE, ratio 40.5:1). Concentrations of DDE in turtle eggs increased with the ln-transformed population size of adjacent municipalities ($r^2 = 0.413$, $p = 0.0132$).

Mean ΣPBDEs concentrations in turtle eggs ranged from 3.8 ng/g ww (Algonquin Park) to 73.3 ng/g (Hamilton Harbour AOC; Figure 2). ΣPBDE concentrations were higher in eggs from every site ($p < 0.0001$) compared to Algonquin Park except for Lyons Creek, Snye Marsh, and the UCBS ($p > 0.05$). Eggs from Raisin River had significantly higher concentrations of ΣPBDEs compared to UCBS eggs ($p = 0.0008$), whereas eggs from Syne Marsh had concentrations very similar to those of UCBS eggs ($p = 0.8385$).

ΣPBDE concentrations were lowest in eggs from Algonquin Park, where airborne deposition is assumed to be the main contaminant source. Consistent with reports that large urban areas have the highest PBDE exposures, turtle eggs from the Hamilton Harbour and Toronto AOCs were the most contaminated among all sites (Figure 2). However, concentrations of ΣPBDE in turtle eggs did not increase with the ln-transformed population size of adjacent municipalities ($r^2 = 0.014$, $p = 0.6970$) among all sites. Mean concentrations of ΣPBDEs in eggs from Lyons Creek, Niagara River, were relatively low (4.39 ng/g) compared to most other AOCs. There was a greater difference between the most contaminated site (Grindstone Creek, Hamilton) and the pooled reference sites with respect to ΣPCB concentrations (ratio 84.0:1) relative to the ΣPBDE concentrations (ratio 19.1:1); suggesting that background deposition contributes less to overall PCB vs PBDE or OC pesticide contamination.

Contribution of Commercial Mixtures of PCBs and PBDEs in Turtle Eggs. Six factor scores explained 71.4% of the total variance in PCB congeners among sites, although the first two factors contributed 28.3% and 13.7%, respectively. The first factor had weak but positive loadings with congeners associated with Aroclor 1260, particularly recal-

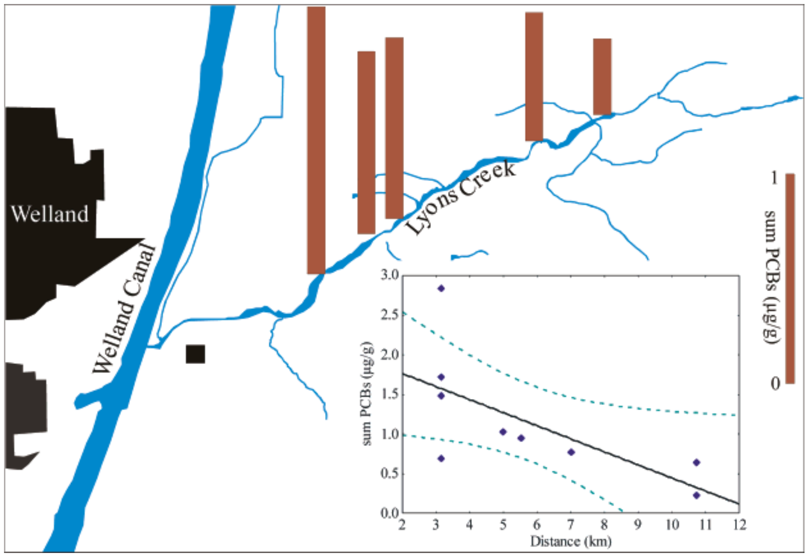

FIGURE 4. Sampling location and the mean sum-PCB (34 congeners) concentrations (ng/g wet weight) in snapping turtle eggs along Lyons Creek, ON, downstream from the Welland Canal.

citrant congeners (Figure 3a; *13*), and strong negative loadings with congeners associated with Aroclor 1254. Factor 1 scores were lowest ($p < 0.0001$) at Lyons Creek ($x = -2.72$) and Snye Marsh ($x = -1.12$) relative to all other sites (Figure 3b). Tiny Marsh ($x = 0.70$) had a higher mean score compared to Murray Canal ($x = -0.30$). Factor 3 had negative loadings with CB-201, -206, -196/203, and -194; eggs from both Algonquin Park and Wheatley Provincial Park had low mean scores for this factor ($x = -1.61$, $x = -1.46$, respectively). Wheatley appears to have a relatively high contribution of Aroclor 1260, whereas most of these congeners were below the MLOQ in eggs from Algonquin Park; the relatively high contribution of these congeners may reflect an artifact of generating replacement data below detection limits.

The Factor Analysis was duplicated using only observations from Lyons Creek (Figure 4) in order to identify anticipated spatial patterns within this AOC including potential local PCB sources. Factor 2 contributed the most to the total variance after rotation (29.5%). Factor 2 had high positive loadings for CB-118 and -110 and weak loadings for CB-105, -87, and -74, all from Aroclor 1248 and 1254 (*12*), and had negative loadings with CB-153/132, -170/190, -180, -183, -194, -195, -196/203, and -206 (Aroclor 1260; *12*). The ΣPCB concentrations declined with the distance from the Welland Canal ($r^2 = 0.45$, $p = 0.0486$; Figure 4). There was also a positive relationship between ΣPCBs and Factor 2 scores at Lyons Creek ($r^2 = 0.58$, $p = 0.0175$), thus the higher the PCB burden, the greater the association with Aroclor 1254/1248. Finally, there was a positive relationship between the distance from the Welland Canal and Factor 2 scores ($r^2 = 0.64$, $p = 0.0099$).

Aroclor 1254 contributed from 14.3% to 36.0% of the PCB burden in turtle eggs, except at Lyons Creek and Snye Marsh in the St. Lawrence, in which Aroclor 1254 contributed 55.7% and 56.7%, respectively, of the total egg burden (Table 2). Aroclor 1248 did not appear to contribute to egg burdens at any site, except minor contributions in eggs from Lyons Creek and Snye Marsh. Aroclor 1242 and 1016 did not contribute to PCB burdens at any site. The contribution of the lower chlorinated Aroclors is likely underestimated, particularly due to the lower bioaccumulation and metabolic susceptibility (increased rate) of many lower chlorinated congeners. Thus, most of the lower chlorinated PCB congeners of these Aroclors would not be present at high concentrations in biota, leaving primarily the higher chlorinated congeners, some of which are also present in higher chlorinated Aroclors. The higher chlorinated, and thus more recalcitrant, PCB congeners make up a larger proportion of the higher chlorinated Aroclor mixtures. The % contribution of BDE congeners to ΣPBDE concentrations was more similar among sites compared to PCBs (Table 3). The PBDE profile in turtle eggs is consistent with Penta-PBDE exposure, and there is little evidence to suggest bioaccumulation of congeners originating from Octa- or Deca-BDE commercial mixtures (Table 3).

TABLE 2. Percent Contribution of Each Aroclor Mixture to ΣPCB Concentrations in Snapping Turtle Eggs from Great Lake and Connecting Channels (2001−2004)

Site 2	AOC	1248	1254	1260
Algonquin Park	reference	0	16.9	83.1
Tiny Marsh	reference	0	29.7	70.3
NWA	St. Clair River	0	31.9	68.1
Turkey Creek	Detroit River	0	28.4	71.6
Wheatley P. Park	Wheatley Harbour	0	14.3	85.7
Cootes Paradise	Hamilton	0	24.2	75.8
Grindstone Creek	Hamilton	0	22.4	77.6
Humber River	Toronto	0	27.3	72.7
Dead Creek	Bay of Quinte	0	34.7	65.3
Murray Canal	Bay of Quinte	0	36.0	64.0
Belleville	Bay of Quinte	0	30.4	69.6
Raisin River	St. Lawrence	0	34.9	65.1
UCBS	St. Lawrence	0	29.3	70.7
Snye Marsh	St. Lawrence	1.4	56.7	41.9
Lyons Creek	Niagara River	1.7	55.7	42.6
Grand Total		0.2	30.5	69.3

Discussion

Consistent with earlier reports (*8*, *14−16*), PCB contamination in snapping turtle eggs was associated with local industrial sources, and was higher near large urban centers. The congener profiles in snapping turtles varied geographically, and were associated with different Aroclor sources. With a couple of exceptions, PCB concentrations were highest at large urban areas with substantial industry (i.e., Hamilton Harbour, Toronto, and Detroit River). Two exceptions were Lyons Creek, which appeared to have a local source of PCBs, and Snye Marsh, downstream of heavy industry (*14*). Lyons Creek appears to have a local source of primarily Aroclor 1254 and/or 1248 at the junction with the Welland canal. Various Aroclors, including 1248, have been used throughout Akwesasne (Snye Marsh), particularly the General Motors

TABLE 3. Proportion of Individual PBDE Congener to ΣBDE Concentrations in Snapping Turtle Eggs from Various Sites in Southern Ontario (Bromkal and Great Lakes Chemical Penta- and Octa-BDE Formulations Are Included for Comparison; Values Are Proportion of the Sum of the 10 PBDE Congeners Presented in the Table)

site	BDE 28	BDE 47	BDE 99	BDE 100	BDE 138	BDE 153	BDE 154[a]	BDE 183	BDE 209	ΣPBDE (ng/g)
Algonquin Park	0.3	29.4	30.1	14.9	0.1	7.2	16.3	1.6	0.0	3.85
Belleville	0.2	29.9	24.9	20.9	0.0	2.5	21.0	0.5	0.0	22.25
Cootes Paradise	0.2	52.4	22.5	15.7	0.1	3.3	5.7	0.2	0.0	73.29
Dead Creek	0.3	37.4	17.9	21.6	0.0	2.2	19.7	0.8	0.0	15.35
Humber River	0.2	46.9	17.3	20.6	0.1	3.4	11.3	0.3	0.0	68.17
Lyons Creek	0.1	36.2	33.1	17.4	0.0	6.8	6.3	0.1	0.0	3.05
Murray Canal	0.3	36.0	19.9	18.4	0.0	1.4	23.5	0.6	0.0	23.44
Raisin River	0.0	37.9	35.4	14.9	0.0	5.2	6.0	0.5	0.0	28.14
Snye Marsh	0.0	24.5	32.0	23.0	0.0	9.2	9.0	2.2	0.0	15.13
Turkey Creek	0.1	38.8	22.6	23.3	0.0	5.6	9.2	0.4	0.0	5.80
UCBS	0.0	20.8	27.6	21.3	0.0	13.6	12.5	4.2	0.0	6.37
Wheatley P. Park	0.1	46.3	21.7	18.1	0.0	3.7	9.7	0.4	0.0	3.36
grand total	0.2	37.1	24.5	19.2	0.0	4.8	13.4	0.9	0.0	n/a
GLC DE-71[b]	0.2	34.4	43.8	11.8	0.7	4.9	4.1	0.1	0	n/a
Bromkal 70-5DE[b]	0.1	41.0	42.9	7.5	0.5	5.1	2.6	0.3	0	n/a
GLC DE-79[b]	0	0	0	0	1.2	16.1	2.0	78.3	2.4	n/a
Bromkal 79-8DE[b]	0	0	0	0	0	0.2	0.1	20.2	79.5	n/a

[a] Includes any coeluting BB-153 if present. [b] Data from ref *34*.

Foundry, the former Reynolds Aluminum, and Aluminum Company of America (ALCOA) (*14*). Previous studies have demonstrated differences in Aroclor use throughout the lower Great Lakes region (*17*, *18*). OC pesticide concentrations were highest in eggs from Hamilton Harbour AOC, followed generally by eggs from the Bay of Quinte AOC sites, Wheatley and Detroit River AOCs, and the concentrations were relatively low at other AOCs. DDE, chlordane, and mirex were the dominant OC pesticides, and contributed 47.4%, 24.8%, and 17.9%, respectively, to the total pesticide burden. Otherwise, the relative contribution of each pesticide to the total egg burden was similar for all sites. Although PBDEs were highest at the two largest urban sites (Toronto and Hamilton), there was otherwise a poor relationship with the size of the local urban municipality and ΣPBDE in turtle eggs.

Algonquin Park has no known local sources of PCBs (*9*), and consequently the PCB burdens likely reflect PCB contamination via airborne deposition. Although lower chlorinated PCBs have higher volatilization rates than higher chlorinated PCBs, dry deposition rates of PCBs may be dominated by hexachloro- and heptachlor-CBs (*19*), probably due to greater partitioning of heavier PCBs in the particulate rather than gaseous phase (*21*). Dry deposition of particulate-borne PCBs occurs at a faster rate than diffusion of gaseous PCBs (*19*). Aroclor 1260 is dominated by hexachloro- and heptachlor-CBs, which may partially explain the similarity of the congener profile in Algonquin Park to Aroclor 1260. Algonquin Park is distant from large bodies of water, and is dominated by terrestrial habitat interspersed with small wetlands. Unlike the atmosphere, terrestrial soils far away from local PCB sources tend to have higher relative abundance of the higher chlorinated congeners (*21*). Lower chlorinated biphenyls that are deposited through the atmosphere in which the turtles are subsequently exposed are also more readily metabolized and/or eliminated, which also would contribute to the observed congener profile.

PCBs typical of Aroclor 1260 are prevalent in snapping turtle eggs throughout the Great Lakes (*8*), which is consistent with other species monitored along the shorelines of the lower Great Lakes. Aroclor 1254 is generally a secondary mixture, except where there are local sources, such as at Sturgeon Lake (*18*) and Lyons Creek and Snye Marsh (this study). Although other, lower chlorinated PCB containing Aroclors can be important in biota in the lower Great Lakes (e.g., Aroclor 1248 in Akwesasne; *17*), generally they tend to contribute little to PCB burdens. Conversely, lower chlorinated Aroclors dominated PCB production; Aroclor 1242 comprised >50% of total PCB production in the United States (*22*), whereas Aroclor 1260 was the least produced of the major Aroclor mixtures. The relative contributions of Aroclor 1248 to body burdens in turtle eggs (particularly at Lyons Creek and Snye Marsh) are likely underestimated, as only the higher chlorinated congeners from that mixture are likely to be bioaccumulative. Lyons Creek and Snye Marsh eggs had relatively high concentrations of CB-74, -66/95, and -99, which are found in both Aroclor 1254 and 1248, thus confounding the estimate of the contribution of Aroclor 1248 and 1254. Regardless, the turtle eggs demonstrate a PCB source immediately upstream of Lyons Creek, likely by the juncture with the Welland Canal (Figure 4).

In contrast to PCBs, the relative contribution of different BDE congeners to ΣPBDEs is fairly consistent among sites, despite large site differences in absolute concentrations. PCBs were produced as Aroclors and vary considerably in congener composition among technical mixtures (*23*). Conversely, PBDE mixtures are much more consistent due to the thermodynamic control during industrial production (see Table 3), rather than the kinetic versus thermodynamic control typical of PCB formation. Although Penta-BDE formulations are not the only mixtures used in North America, bioaccumulation of congeners from Penta-BDE mixtures is dominant in turtles, based on the relatively high contribution of BDE congeners 47, 99, and 100 to ΣPBDE concentrations in eggs.

Unlike many other species used to monitor environmental contamination (herring gulls (*24*), ospreys (*18*)), snapping turtles are nonmigratory, have short dispersal distances, and have small home ranges. Consequently, the maternal burden reflects the environment throughout their home range. Although the ratio of contaminants between eggs and muscle in snapping turtles deviates from the equilibrium partitioning model (*25*), there is good agreement in relative concentrations between maternal and egg burdens (*26*). Snapping turtle eggs are sufficiently sensitive to monitor local contamination, and as few as eight clutches demonstrated a significant plume of PCB contamination in a fairly small area.

Concentrations of PCBs (16.2−1755.5) were on average 45.6 (range 4.6−254.6) times higher than PBDEs (4.3−73.3) ng/g ww in the snapping turtle eggs in Canadian AOCs, except for Algonquin Park (3.9× higher), where aerial deposition dominates. In urban landscapes, PDBEs were between 1.1 and 63× higher than PCBs in organic films lining glass windows (*27*), and are more prevalent in air samples from a rural site in Ontario (*28*), thus PBDEs may be more prevalent in transient environments. Conversely, ΣPBDEs exceeded DDE, mirex, and Σchlordane concentrations in turtle eggs from 4, 7, and 8 sites out of 12, respectively, in our study, while concentrations of all other pesticides were lower.

A number of studies have found or suggested biological effects of organohalogens in various taxa, often at environmentally relevant exposures (*29*, *30*), including snapping turtles (*31*−*33*). Many AOCs have substantial sources of sewage and industrial effluent, and some have substantial PAH sources. How important these stressors are to turtle development, or how they may interact with other stressors, is unknown. Thus, determining causal links between anthropogenic stressors and embryonic development of exposed turtles is difficult. Nevertheless, the burdens of organohalogens in developing turtle eggs at some areas may contribute to impacts upon turtle development (*10*).

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Supporting Information Available

Figure S1 and Table S1 give detailed site descriptions; a description of quality control, the method for calculating replacement values for observations below detection limits, and details on the estimation of the relative contribution of different Aroclors to the PCB egg burden. This material is available free of charge via the Internet at http://pubs.acs.org.

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