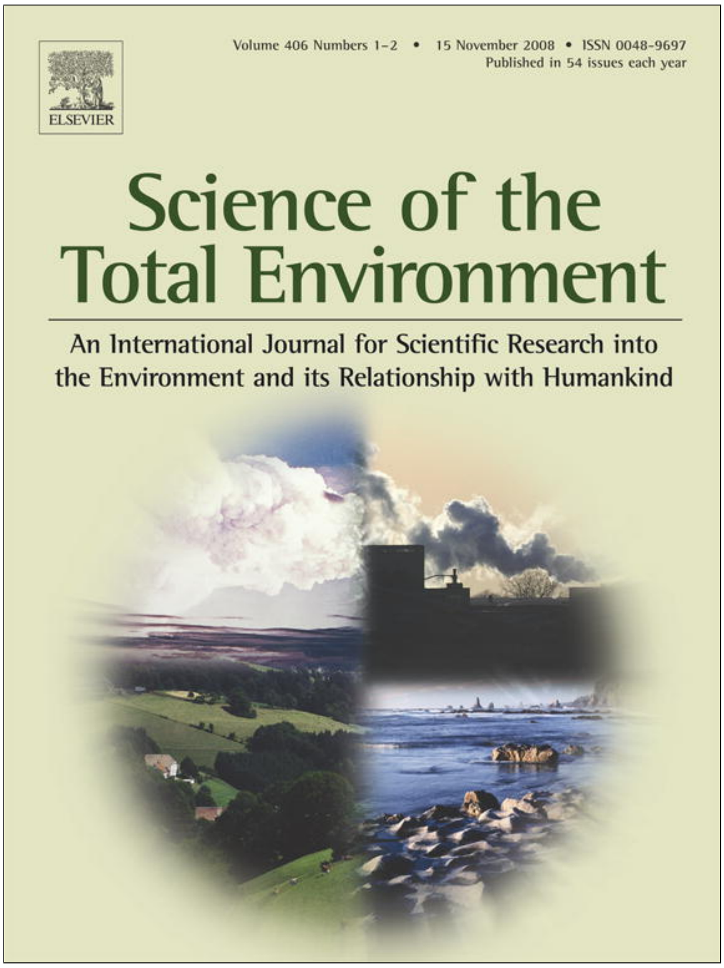
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Temporal and spatial patterns of contaminants in Lake Erie watersnakes (*Nerodia sipedon insularum*) before and after the round goby (*Apollonia melanostomus*) invasion

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Temporal and spatial trends in contaminant concentrations were assessed in Lake Erie watersnakes, a threatened (USA)/endangered (Canada) species restricted to western Lake Erie. Temporal changes in plasma contaminant levels were determined in 1990 and 2003, and spatial patterns in 2003 at 12 sites, throughout the species' range. During this period, the watersnakes' diet changed from fish (75%) and amphibians (25%) that avoid zebra mussels, to round gobies (95%) that feed extensively on zebra mussels. Temporal trends indicate that watersnakes on Pelee and North Bass Islands showed a marginal increase in hexachlorobenzene levels, and a significant decline in dieldrin, oxychlordane, and heptachlor epoxide, likely reflecting declines in aerial deposition and clearing of local vineyards. The contaminants with the greatest burdens, sum PCBs and *p,p′*-DDE, remained stable in the snakes, consistent with trends in other local biota, suggesting that although the dietary switch to round gobies meant consumption of a more contaminated diet, their diet remained at the same trophic position. We suggest that the watersnakes' PCB and *p,p′*-DDE temporal patterns reflect the lack of change in sediment concentrations with minimal influence from their dietary switch. Similar to top avian predators, PCBs, *p,p′*-DDE, and technical chlordane, are most prevalent in watersnakes; this ranking remains unchanged. In 2003, the watersnakes demonstrated significant spatial differences in concentrations of *p,p′*-DDE, dieldrin, technical chlordane and its metabolites. Their 2003 concentrations of *p,p′*-DDE, and to a lesser extent PCBs, exceed the recommended interim no-observable effects levels on watersnake embryonic survival. Further investigations are required to determine if these higher levels of PCBs, *p,p′*-DDE, and technical chlordane, affect reproductive and physiological parameters of the Lake Erie watersnake. Until concentrations of sediment contaminants decline in western Lake Erie, these endangered/threatened watersnakes will continue to be exposed to higher concentrations of persistent organic pollutants.

1. Introduction

The North American Great Lakes have been subjected to invasions by more than 150 aquatic species (Ricciardi and MacIsaac, 2000; Ricciardi, 2001). Invasions by zebra (*Drussena polymopha*) and quagga mussels (*D. bugensis*) have had especially far-reaching effects, resulting in a shift from a predominately pelagic food web to a food web more strongly influenced by benthic

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organisms (Stewart et al., 1998). In addition to changing patterns of energy flow and nutrient cycles, it is likely that invasive species have also changed patterns of contaminant transfer (Kwon et al., 2006). Recently, Great Lakes food webs have been further modified by another invasive, the round goby (*Apollonia melanostomus*) (Stepien and Tumeo, 2006). Round gobies feed extensively on zebra and quagga mussels but also feed on and compete with native fishes (Ray and Corkum, 1997; French and Jude, 2001; Steinhart et al., 2004; Janssen and Jude 2001). Round gobies were first documented in the Great Lakes in the early 1990s (Marsden and Jude, 1995; Jude, 1997). They now reach remarkably high densities with populations in the western basin of Lake Erie estimated to exceed 9 billion (Johnson et al., 2005). Although the negative impacts of round gobies on native species are well known, they also represent an abundant food source for piscivorous predators. Small mouth bass (*Micropterus dolomieu*) exhibit accelerated growth and an earlier transition to piscivory (Steinhart et al., 2004). Similarly, Lake Erie watersnakes, whose diet has changed to one consisting of more than 90% round gobies, exhibit accelerated growth, larger body size, and increased fecundity since the invasion of round gobies (King et al., 2006a).

Because zebra and quagga mussels have higher fat content than do native mussels, consumption of mussel-eating round gobies by small mouth bass and watersnakes may result in greater bioaccumulation of lipophilic environmental contaminants in these and other top predators (Bruner et al., 1994; Renaud et al., 2004). Fortuitously, blood samples from Lake Erie watersnakes were collected before the round goby invasion by King and Lawson (1995), and again from the same study sites in 2003, providing the opportunity to test directly for temporal changes in watersnake contaminant concentrations.

Contaminant concentrations in Lake Erie watersnakes are of further interest from a conservation perspective. The Lake Erie watersnake is listed as endangered on Canadian islands and as threatened on U.S. islands in Lake Erie (Fazio and Szymanski, 1999), and its range as a subspecies is restricted to the islands in western Lake Erie. Western Lake Erie has been subjected to dramatic eutrophication, contaminant influxes, species invasions, and recovery during the last century. In addition to its restricted geographic distribution, justification for the protected status of this watersnake further included habitat loss, and incidental and intentional human-caused mortality (Fazio and Szymanski, 1999). Environmental contaminants may also be a contributing factor (Bishop and Rouse, 2006), and questions regarding a possible role of contaminants are often posed by members of the public and management. Finally, questions regarding differences in contaminant concentrations between male and female watersnakes, and among sampling localities, are of interest with respect to the health at the individual and population level.

This study extends work by Bishop and Rouse (2000, 2006), who analyzed contaminant concentrations in watersnakes from three sites on Pelee Island and two other sites in the Great Lakes basin. In this study, we examine spatial patterns of contaminant concentrations among multiple Lake Erie islands and formally compare recent contaminant concentrations in males and females. Contaminant concentrations were measured nondestructively, an important consideration for threatened and endangered species. In addition, given the dietary switch of these snakes from one dominated by native fish and amphibians in 1990, to one consisting nearly exclusively of round goby in 2003, we also determine the potential impact of this dietary change on the contaminant burdens of the watersnakes by assessing the temporal trends of their contaminant burdens in part of their range in the archipelago of western Lake Erie.

2. Methods

Adult Lake Erie watersnakes were captured by hand at 12 sites on Kelleys Island (three sites), South Bass Island (three sites), Middle Bass Island (two sites), North Bass Island (one site), and Pelee Island (three sites) (Fig. 1); Pelee Island is the Canadian study site while the other sites are American. Sampling locations on a given island were separated by straight-line distances of 2.0–10.5 km; sampling locations on different islands were separated by straight-line distances of 2.5–26.5 km. The home range of Lake Erie watersnakes typically encompasses 200–400 m of shoreline during their active summer season, although the movements of some individuals span as much as 1200 m (R. B. King and K. M. Stanford, unpublished data). Movements of these watersnakes among study sites and among islands are rare (R. B. King and K. M. Stanford, unpublished data). Sampling locations included here have been the focus of long-term population monitoring

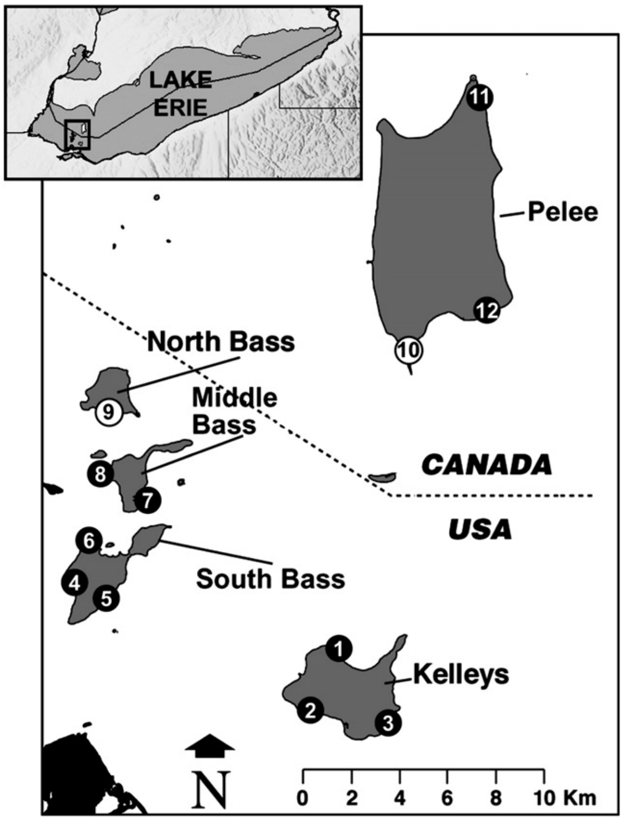

Fig. 1 – The island region of western Lake Erie showing sampling locations included in this study. Sites denoted with filled circles were sampled in 2003. Sites denoted with open circles (9 and 10) were sampled in 1990 and 2003.

since the early 1980s (King et al., 2006b). Watersnakes are locally abundant at all sampling locations but densities vary markedly (by more than an order of magnitude) among sites (King et al., 2006b). All work was conducted according to animal care guidelines approval (Northern Illinois University Institutional Animal Care and Use Committee) and necessary permits from the U.S. Fish and Wildlife Service, Ohio Department of Natural Resources, Ontario Ministry of Natural Resources, and Canadian Wildlife Service.

Watersnakes were hand-captured, and each individual was weighed, and blood samples (up to 1.5 mL) drawn from the caudal vessel using a heparinized sterile syringe and needle. Samples were placed on ice within 15 min, separated into plasma and red cell fractions by centrifugation, stored in standard cryovials, and frozen for later analysis. To obtain enough material for contaminant analysis, plasma from three to five watersnakes of a given sex and site were pooled. Plasma from individual watersnakes averaged 0.52 g (range = 0.10–0.99 g), and pooled samples averaged 2.03 g (range = 0.81–3.32 g). A total of 26 pooled samples were analyzed, including separate pools for males and females at two sites collected in both 1990 and 2003 ($n = 8$), males and females at eight sites collected in 2003 ($n = 16$), and females only from two sites (Sites 6 and 12 in Fig. 1 and Table 1) collected in 2003 ($n = 2$) (Fig. 1).

Watersnake plasma samples from 1990 and 2003 were analyzed concurrently for contaminants at the Great Lakes Institute of Environmental Research (University of Windsor, Windsor, ON). Plasma samples were thawed to room temperature, spiked with 1,3,5-tribromobenzene as a recovery standard, added to a 15 mL glass centrifuge tube and deproteinated by addition of an equivalent volume of methanol by vortexing for 1 min. The deproteinated plasma was then extracted with dichloromethane (DCM):hexane (1:1 v/v) by vortex for 1 min, followed by centrifugation and removal of the solvent layer. The process was repeated three times and the extracts dried over anhydrous Na_2SO_4. Lipids and biogenic material were removed using gel permeation chromatography and cleaned by florisil column chromatography (Lazar et al., 1992). Samples were analysed using capillary gas chromatography, coupled with an electron capture detector (GC/ECD; Lazar et al., 1992). Of the polychlorinated biphenyl (PCBs) congeners, 45 individual or co-eluting congeners common to all analyses were included (IUPAC numbers 31/28, 42, 44, 49, 52, 60, 64, 66/95, 70, 74, 87, 97, 99, 101, 105, 110, 118, 128, 138, 141, 146, 149, 151, 153, 158, 170/190, 171, 172, 174, 177, 178, 179, 180, 182/187, 183, 194, 195, 200, 201, 203, 206). Sum PCBs were the sum of all 45 congeners. Organochlorine pesticides analysed included *p,p′*-dichloro-diphenyl-trichloroethane (*p,p′*-DDT), *p,p′*-dichloro-diphenyl-dichloroethane (*p,p′*-DDD), and *p,p′*-dichloro-diphenyl-dichloroethylene (*p,p′*-DDE), hexachlorobenzene (HCB), octachlorostyrene (OCS), mirex, dieldrin, *trans*-, *cis*- and *oxy*-chlordane, *cis*- and *trans*-nonachlor, heptachlor epoxide (HE), and α- and γ-hexachlorocyclohexane. The technical chlordane mixture consisted of the sum of *trans*- and *cis*-nonachlors (sum nonachlor metabolites), *oxy*-, *trans*- and *cis*-chlordanes and HE. All samples were quantified against external standards consisting of Aroclor 1242:1254:1260 or certified organochlorine pesticide standard (AccuStandard, Brockville, ON). The method quantification limits for PCBs and

Table 1 – Contaminant concentrations (±standard error of mean) in the plasma of Lake Erie watersnakes from various sites on five islands in western Lake Erie, 2003

Island	Site	N	Lipids (%)	Σ_{45} PCBs (µg/kg)	*p,p′*-DDE (µg/kg)	Σ Technical chlordane (incl. HCE) (µg/kg)	Σ Nonachlor metabolites (µg/kg)	Oxychlordane (µg/kg)	Dieldrin (µg/kg)
Kelleys Island	1. State Park	2	0.34±0.05	178.09±42.18	9.82±2.91	2.59±0.14	2.32±0.06	0.16±0.01	0.44±0.01[a]
	2. South Shore	2	0.34±0.05	115.75±16.04	5.00±1.57	3.12±0.51	2.58±0.51	0.19±0.02	0.86±0.12[a,b]
	3. Southeast Shore	2	0.30±0.13	40.07±0.08	2.15±0.26	0.80±0.14	0.60±0.16	0.06±0.01	0.47±0.02[a]
South Bass Island	4. State Park	2	0.27±0.06	150.94±52.35	5.62±1.78	3.41±0.04	2.41±0.22	0.18±0.02	0.74±0.16[a,b]
	5. East Shore	2	0.27±0.04	94.09±14.13	3.35±1.14	1.62±0.45	1.36±0.39	0.08±0.03	0.49±0.05[a]
	6. Research Dock	1	0.32	48.4	2.19	1.28	1.02	0.09	0.52
Middle Bass Island	7. State Park	2	0.26±0.10	108.84±18.65	10.72±2.27	2.06±0.13	1.75±0.21	0.11±0.03	0.42±0.02[a]
	8. West Shore	2	0.43±0.18	150.41±58.70	6.49±1.77	2.31±1.03	1.75±0.73	0.13±0.05	1.07±0.15[b]
North Bass Island	9. South Shore	2	0.29±0.07	101.08±19.67	9.48±0.13	1.24±0.21	0.92±0.29	0.07±0.02	0.48±0.07[a]
Pelee Island	10. Fish Point	2	0.31±0.04	83.79±45.74	2.39±0.97	1.13±0.41	0.76±0.35	0.07±0.02	0.52±0.19[a]
	11. Lighthouse Point	2	0.34±0.07	66.01±25.39	2.26±0.55	0.79±0.24	0.62±0.22	0.08±0.01	0.62±0.23[a]
	12. Mill Point	1	0.28	83.92	3.24	1.11	0.92	0.08	0.65

Site numbers correspond to locations shown in Fig. 1. N refers to the number of pooled samples (3–5 snakes each). For dieldrin, superscripts identify homogeneous groups of means based on Student–Newman–Keuls multiple comparisons. For *p,p′*-DDE and oxychlordane, Student–Newman–Keuls multiple comparisons placed all sites in a single homogeneous group despite significant differences among sites (Results). Inclusion of lipid concentration as a covariate precluded multiple comparisons among sites for Σ technical chlordane and Σ nonachlor metabolites.

organochlorine pesticides in the samples ranged between 0.01 and 0.09 ng/g. Recoveries for internal standard during processing were 103.5±5.4% (mean±standard deviation). Contaminants were measured as μg/kg ww. Values for samples having non-detectable concentrations were substituted by using half of the detection limit for that individual chemical. Contaminants for which more than 40% of samples fell below detection limits were excluded from analysis (DDD, DDT, mirex, α- and γ-hexachlorocyclohexane).

Statistical tests for temporal changes in contaminant concentrations made use of contaminant concentrations observed in males and females at two sites (Sites 9 and 10) in 1990 and 2003. A three-way analysis of variance (ANOVA) was used to detect changes in contaminant concentrations over time. Time, site, and sex were included as main effects but due to lack of replication, two- and three-way interactions were not tested. Analyses were conducted both with and without plasma lipid concentration included as a covariate (Hebert and Keenleyside, 1995). When not significant, site and sex were deleted as factors to increase statistical power to detect time effects. Temporal changes in the ranking of the mean concentrations of individual contaminants across both sites were assessed using regression analysis, and testing if the slope of the two equations was significantly different from 1.0.

Statistical tests for differences between males and females, and for spatial variation among sampling locations, made use of contaminant concentrations observed in 20 samples from both males and females from each of ten sites collected in 2003. ANOVA was used with sex and site included as main effects. Due to lack of replication, the sex-by-site interaction was not tested. Analyses were repeated with plasma lipid concentration included as a covariate. When not significant, sex was deleted as a factor to increase statistical power to detect site effects. For those contaminants that varied significantly among sites and for which lipid concentration was not a significant covariate, post-hoc Student–Newman–Keuls tests were used to identify homogeneous sets of sites.

3. Results

3.1. Temporal patterns in Lake Erie watersnakes, 1990 to 2003

Male and female watersnakes were sampled at Fish Point on Pelee Island (Site 10) and the South Shore of North Bass Island (Site 9) in both 1990 and 2003. Analysis of covariance indicated that lipid concentration was uncorrelated with the concentrations of all the measured contaminants (all $P \geq 0.073$), that sex effects were non-significant for all contaminants (all $P \geq 0.433$) and that site effects were non-significant for all contaminants (all $P \geq 0.306$) except *p,p′*-DDE ($F_{1,5}=10.54$, $P=0.023$). In contrast, there were significant declines in the concentrations of heptachlor epoxide (from 0.38 to 0.12 μg/kg; $F_{1,6}=11.22$ $P=0.015$), oxychlordane (from 0.33 to 0.19 μg/kg; $F_{1,6}=10.10$, $P=0.019$) and dieldrin (from 1.06 to 0.50 μg/kg; $F_{1,6}=6.47$ $P=0.044$), and a marginally significant increase in the concentration of HCB (from 0.14 to 0.18 μg/kg; $F_{1,6}=5.81$, $P=0.053$) in the plasma of watersnakes from 1990 to 2003 (Fig. 2). Changes in the concentrations of sum PCBs, OCS,

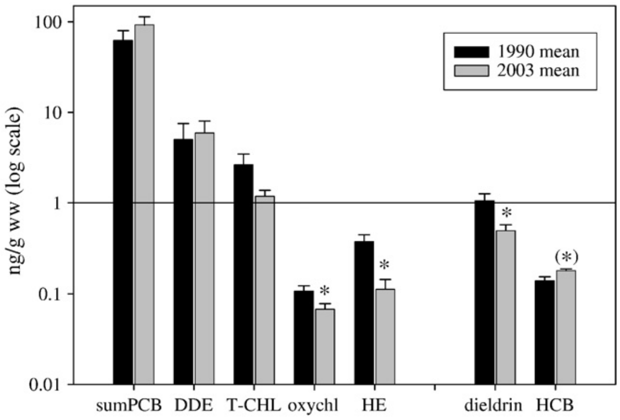

Fig. 2 – Temporal trends in contaminant concentrations measured in the plasma of Lake Erie watersnakes, 1990 to 2003.

p,p′-DDE, technical chlordane and its sum nonachlors metabolite, were not significant during this 13-year period (all $P \geq 0.143$; Fig. 2).

Despite the significant changes in contaminant concentrations in the watersnakes, there was no significant change in the ranking of the contaminants across both sites between 1990 and 2003. After 13 years, sum PCB concentrations remained the dominant contaminant in watersnakes, having considerably greater concentrations than any of the other chemicals measured, with *p,p′*-DDE and technical chlordane following in descending order (Table 1, Fig. 2). In 1990 and 2003, PCB 153 accounted for 13.7% and 13.3% of the sum PCBs respectively, PCB 138 accounted for 12.7% and 11.6% respectively, and PCB 180 accounted for 10.6% and 12.0% respectively.

3.2. Differences between the sexes and among study sites, 2003 only

Plasma lipid content differed significantly between the sexes (paired *t*-test, $t_{10}=3.52$ $P=0.007$), averaging 0.25% (range=0.16–0.40) in males and 0.38% (range=0.29–0.43) in females. Analysis of covariance indicated that lipid concentration was correlated with contaminant concentrations only for technical chlordane ($F_{1,9}=5.55$, $P=0.043$) and nonachlor metabolites ($F_{1,9}=5.81$, $P=0.039$). Sex was a significant source of variation only for dieldrin, with concentrations in females exceeding those in males (0.69 vs. 0.52 μg/kg; $F_{1,9}=8.56$ $P=0.017$).

Among the ten sites sampled in 2003, there were significant differences in the concentrations of *p,p′*-DDE ($F_{9,10}=4.379$, $P=0.015$), dieldrin ($F_{9,9}=3.98$, $P=0.026$), technical chlordane ($F_{9,9}=7.00$ $P=0.004$), and its oxychlordane ($F_{9,9}=5.92$, $P=0.007$) and nonachlor ($F_{9,9}=6.57$, $P=0.005$) metabolites (Fig. 2). Differences among the study sites in the plasma concentrations of sum PCBs, HCB, OCS, and heptachlor epoxide were not significant (all $P \geq 0.149$) (Fig. 2).

Watersnakes from the southeast shore of Kelleys Island (Site 3) had consistently low concentrations of all contaminants except dieldrin (Table 1), while snakes from the south shore of North Bass Island (Site 9) had consistently high concentrations of all contaminants, particularly *p,p′*-DDE (Table 1). Snakes at Middle Bass Island State Park (Site 7) had the highest concentrations of *p*,*p*′-DDE of all the study sites, and snakes at South Bass Island State Park (Site 4) had the highest concentrations of technical chlordane and high concentrations of dieldrin and PCBs. Snakes at the three sites on Pelee Island, particularly at Lighthouse Point (Site 11), tended to have lower contaminant concentrations (Table 1). However, snakes at South Bass Island State Park (Site 4) and Lighthouse Point (Site 11) showed greater variation in rankings among the measured contaminants.

4. Discussion

Lake Erie watersnakes on Pelee Island and North Bass Island in western Lake Erie showed a significant decline in some plasma contaminant burdens from 1990 to 2003. Declines occurred in the concentrations of dieldrin, heptachlor epoxide and the oxychlordane metabolite. However, there were no significant temporal changes in the concentrations of the top two ranked chemicals, sum PCBs and *p*,*p*′-DDE, and a marginal increase in HCB concentrations, in the plasma of the watersnakes. The temporal declines in dieldrin and oxychlordane concentrations, and the stability of sum PCBs and *p*,*p*′-DDE concentrations, in the watersnakes are similar for walleye fish (*Sander vitreus*) from Middle Bass Island (Whittle et al., 2003 reported in Heidtke et al., 2006), although Hickey reports declines in PCB and *p*,*p*′-DDT concentrations for walleye between 1991 and 1996 (Hickey et al., 2006). The ranking of the top 3 chemicals in the watersnakes, PCBs, DDE, and then technical chlordane, is the same as the ranking pattern in the plasma of avian predators, specifically bald eagles (*Haliaeetus leucocephalus*) (Donaldson et al., 1999) and peregrine falcons (*Falco peregrinus*; K. Fernie, Environment Canada, unpublished data).

The temporal declines in concentrations of dieldrin, and the two chlordane metabolites, heptachlor epoxide and oxychlordane, found in the Lake Erie watersnakes also occurred in other biota at Middle Bass Island, particularly walleye that showed a very rapid decline between 1992 and 1995 (Hickey et al., 2006). The declines in heptachlor epoxide, oxychlordane and dieldrin in the watersnakes are likely a reflection of changes in local land use practices and a decline in concentrations resulting from aerial deposition. Chlordane, one of the most heavily used pesticides until its restriction in the 1980s and world-wide ban in 1997, is one of the most predominant persistent organic pollutants, and many of its components bioaccumulate and biomagnify in aquatic food chains including those in the Arctic (Fisk et al., 2001). The production, importation, and use of dieldrin in the USA, a widely used insecticide from the 1950s to the early 1970s, was banned in 1971 by the U.S. Environmental Protection Agency, but dieldren continues to persist and bioaccumulate in fish, wildlife and humans. On the three Bass islands and Kelleys Island, there has been a sharp decline in acreage dedicated to vineyards and wine production in the last 40 years. Vineyards dominated North Bass Island for 100 years, including the period of major use of chlordane and dieldrin up to the 1980s. In comparison, vineyards on Pelee Island were introduced in the 1980s, after the ban of dieldrin and chlordane, and occupy only a small percentage (200 ha of 42 km^2) of the island, thereby also partially accounting for the spatial differences among the islands in 2003.

High PCB concentrations have been reported for *Nerodia* spp. using whole body tissues or livers, with some of the highest reported concentrations ranging from 0.46 to 56.64 ppm ($N = 12$) in northern watersnake livers at a PCB-contaminated site in South Carolina (Fontenot et al., 2000). In this study, sum PCBs had the highest concentrations of all of the measured chemicals, and some of the highest plasma concentrations ever reported for plasma samples in watersnakes. Moreover, sum PCB concentrations have not declined in this species since 1990, and instead show a marginal, albeit insignificant increase from 1990 to 2003 (Fig. 2). This trend is reflected in other biota in western Lake Erie during this time period (Whittle et al., 2003 reported in Heidtke et al., 2006), as well as the watersnakes caught at Lighthouse Point on Pelee Island (Site 11). Bishop and Rouse (2006) report a mean plasma Σ_{54}PCB concentration of 34.4 μg/kg in 1999 compared to the mean Σ_{45}PCB concentrations of 66.0 μg/kg in 2003 in this study. The highest mean PCB concentrations found in the watersnakes in 1999, 90.4 μg/kg on the west shore of Pelee Island (Bishop and Rouse, 2006), are comparable to the range of mean PCB concentrations found in this study (40.1 to 178.1 μg/kg). Furthermore, consistent with northern watersnakes in South Carolina (Fontenot et al., 2000), this study found that there were no differences between males and females in PCB concentrations.

The pesticide metabolite, *p*,*p*′-DDE, had the second highest mean concentration of the measured contaminants in these snakes, and there were no temporal changes in the concentrations of this metabolite between 1990 and 2003. The mean concentrations of *p*,*p*′-DDT, including *p*,*p*′-DDD and *p*,*p*′-DDE (range of means: 1472–3254 ng/g lw), reported for Spanish viperine snakes (*Natrix maura*), a European species ecologically equivalent to that in this study, are comparable to the lipid *p*,*p*′-DDE concentrations (range of means: 670–4399 ppb) found in the watersnakes in this study (Santos et al., 1999). It would appear that adult *Neroidia* snakes can survive exposure to high concentrations of *p*,*p*′-DDE as evidenced by diamondback watersnakes (*Neroidia rhombifer*) in Texas (Clark et al., 2000) whose whole blood *p*,*p*′-DDE concentrations (3000 μg/kg) were an order of magnitude higher than the highest plasma concentrations reported here (10.7 μg/kg). Watersnakes at Middle Bass State Park (Site 5, 10.7 ppb) and Kelleys Island State Park (Site 1, 9.8 ppm) had the highest mean concentrations of *p*,*p*′-DDE in this study, and are the highest concentrations reported to date for Lake Erie watersnakes. These *p*,*p*′-DDE concentrations are twice the levels as those reported for these snakes on Pelee Island in 1998 (5 μg/kg ww; Bishop and Rouse, 2000), although the concentrations of *p*,*p*′-DDE found in the watersnakes on Pelee Island in 2003 (mean range: 2.3 to 3.2 μg/kg) were comparable to those found on the island in 1999 (mean range: 1.6 to 3.6 ppb ng/g ww; Bishop and Rouse, 2006). In fact, plasma *p*,*p*′-DDE concentrations reported for watersnakes at Lighthouse Point (Site 11) show a slight decline from 1999 (3.0 μg/kg; Bishop and Rouse, 2006) to 2003 (2.3 μg/kg).

The temporal stability and spatial homogeneity of the PCB and *p*,*p*′-DDE concentrations in the watersnakes among the sites are likely a function of dietary and environmental factors. The diet of the Lake Erie watersnakes dramatically changed from the early 1990s to 2003. Until 1995, these snakes had a broader diet comprised predominantly of native benthic feeding fishes (approximately 75%) such as logperch (*Percina* *caprodes*), madtom and stonecat (*Noturus*), and to a lesser extent, mudpuppies (*Necturus maculosus*) (20%), frogs and toads (5%) (King et al., 2006a). Shortly after their introduction into Lake Erie in 1995, round gobies constituted 24% of the watersnake diet, and by 2003, gobies comprised >90% of their diet (King et al., 2006a). Unlike native fish, round gobies feed extensively on zebra and quagga mussels (Jude and DeBoe, 1996; Ray and Corkum, 1997); these mussels occur in high densities, have relatively high lipid content, and have a prodigious filtering ability that redistributes contaminants previously adsorbed to settling particulate matter. Consequently, the mussels increase contaminant bioavailability and the likelihood of trophic transfer (see Kwon et al., 2006 and references therein). The initial objective of this study was to determine if the dietary switch of the Lake Erie watersnakes to round gobies, which biomagnify organochlorine residues accumulated by zebra mussels, has altered the contaminant burdens of this threatened/endangered species. For the major pollutants, PCBs and *p*,*p*′-DDE, there is no evidence that this diet shift has changed Lake Erie watersnake exposures to legacy pollutants. Given that the pre-goby diet of Lake Erie watersnakes incorporated several benthic fish species, it appears that the shift to a more exclusive diet of round gobies has not substantially changed the degree to which this species' exposure reflects sediment-associated contaminants.

Although, there has been a general temporal decline for PCBs in sediment and other biota in western Lake Erie between the mid-1970's and present, this decline in environmental residues has slowed considerably over the past decade and may have reached steady state (Heidtke et al., 2006). Approximately 75% of PCBs in Lake Erie originate from the Detroit River, and 70% of the sediment-bound pollutants from the river are retained in the shallow western basin of Lake Erie (Carter and Hites, 1992). The shallowness of the western basin subjects it to frequent episodes of sediment re-suspension from wind and heat flux (Mortimer, 1987), and flow interruptions in the Detroit River ensure constant mobilization of contaminated sediments from this major source (Drouillard et al., 2006). PCB concentrations measured in water, sediment and freshwater mussels within the Detroit River remained stable from 1996 to 2000 (Heidtke et al., 2006). Lake Erie watersnake residues of PCBs and *p*,*p*′-DDE appear to be strongly influenced by sediment contamination patterns, and thus residue concentrations in this species are expected to follow changes in sediment quality.

Spatial differences in contaminants of Lake Erie watersnakes among sites in the western Lake Erie basin in 2003 are suggestive of the potential usefulness of this species as an indictor of local sources of sediment-associated contaminants and benthic food web tropho-dynamics. Despite the general availability of PCBs in western Lake Erie, there were large, non-significant differences in PCB concentrations of the watersnakes among the sites on individual islands. On Kelleys Island, watersnakes in the state park (Site 1) on the north shore had the highest sum PCB concentrations in the study, while those on the southeast shore (Site 3) had the lowest sum PCB concentrations. Similarly, watersnakes at the latter site had the lowest technical chlordane concentrations while those on the south shore (Site 2) had the highest such concentrations. Radio-telemetry studies indicate that Lake Erie watersnakes utilize only 66 to 1244 m of shoreline during the active season (R. B. King and K. M. Stanford, unpublished data). This site specificity contributes to the utility of watersnakes as indicators of local sources of contaminants.

The potential impact of the sum PCBs and *p*,*p*′-DDE concentrations on the reproduction and physiology of the watersnakes bears further investigation, especially as the highest mean concentrations of sum PCBs and *p*,*p*′-DDE found in the watersnakes at Kelleys Island and Middle Bass State Parks in this study exceed the interim estimates of a no-effect level on embryonic survival in *N. sipedon insularum* recommended by Bishop and Rouse (2006). Their recommended estimates for no-effect levels on embryonic survival were a maximum average of 90.4 μg/kg ww of PCBs and a maximum average of 3.6 μg/kg ww of *p*,*p*′-DDE in plasma, compared to mean plasma concentrations of 178.07 μg/kg ww of PCBs and 9.82 μg/kg ww of *p*,*p*′-DDE in snakes at Kelleys Island State Park, and 108.84 μg/kg ww PCBs and 10.72 μg/kg ww *p*,*p*′-DDE in snakes at Middle Bass State Park. Further studies are required in order to determine if the higher plasma PCB concentrations observed in 2003 samples would have a negative impact on the survival, physiology or growth of embryonic and juvenile watersnakes at Middle Bass, South Bass and Kelleys Islands where this species is listed as endangered. Annual census data from the U.S. islands indicate that adult population sizes have been increasing since 2001 (R. B. King and K. M. Stanford, unpublished data). It would also be useful to determine if these contaminant concentrations are associated with sub-lethal health and physiological effects in adult watersnakes.

The sum PCB and *p*,*p*′-DDE concentrations found in the Lake Erie watersnakes in this study were generally within the range of concentrations found in snapping turtles in the nearby Detroit River and Wheatley Harbour Areas of Concern (de Solla and Fernie, 2004; de Solla et al., 2007). Lake Erie watersnakes had chemical concentrations that were comparable or higher than those in snapping turtles in nearby Wheatley Harbour in the early 2000s (de Solla and Fernie, 2004; Fernie, de Solla, Letcher, unpublished data). In 2001 and 2002, the plasma from male snapping turtles had mean concentrations of 87.9±55.1 (SD) and 113.8±20.5 (SEM) sum PCBs respectively, and 4.63±1.98 (SD) ng/g *p*,*p*′-DDE in 2001, which are higher than those reported here for the watersnakes at nearby Lighthouse Point on Pelee Island (Site 11). However, watersnakes at the three sites on Pelee Island had some of the lowest mean concentrations reported for this study. While the watersnakes at Kelleys Island State Park (Site 1), and the two sites on Middle Bass Island (Sites 7 and 8), had twice the sum PCB and *p*,*p*′-DDE concentrations as the Wheatley Harbour turtles, their concentrations were lower than those found in male snapping turtles in the Detroit River Area of Concern. The mean Σ_{36} PCB concentration of these male snapping turtles was 227.15±61.9 (SEM). Although there were fewer PCB congeners measured in the snapping turtle plasma, the additional 9 PCB congeners measured in the watersnakes are of relatively minor concentrations. The data for these two species are consistent with the fact that the main source of PCB contamination in Wheatley Harbour is ultimately Lake Erie fish from the processing plant within the Harbour (Bedard, 1995), and that PCB concentrations from the Detroit River contribute approximately 75% of PCBs in Lake Erie (Carter and Hites, 1992).

In conclusion, the concentrations of some pesticides, particularly dieldrin and the chlordane metabolites, heptachlor epoxide and oxychlordane, in Lake Erie watersnakes have declined between 1990 and 2003. These declines are likely a function of changes in historical land use from vineyards to tourism on these islands, and suggest that these pesticides have not yet reached equilibrium in the biotic environment of western Lake Erie. The two contaminants with the greatest burdens, sum PCBs and p,p'-DDE, show no temporal changes in the watersnakes from 1990 to 2003. This temporal stability is likely due to environmental factors specific to western Lake Erie and the evidential lack of major changes in sediment contamination during this period of time. The switching by watersnakes to a diet consisting almost exclusively of round gobies (which in turn feed on lipid-rich zebra and quagga mussels), did not appear to influence exposures of these animals. Like top avian predators, PCBs, p,p'-DDE, and technical chlordane, were the most prevalent contaminants in the watersnakes, and this ranking remained unchanged from 1990 to 2003. In addition, the concentrations of p,p'-DDE, and to a lesser extent PCBs, reported in watersnakes in this study, are higher than those previously reported on Pelee Island by Bishop and Rouse (2006), and exceed their recommended interim no-observable effects levels on embryonic survival. Subsequently, we suggest that further studies be completed to investigate whether the higher concentrations of these two contaminants, PCBs and p,p'-DDE, as well as technical chlordane, affect reproductive parameters or have sub-lethal biological and physiological effects on the endangered/threatened Lake Erie watersnake as the concentrations of these contaminants are likely to remain stable until sediment concentrations decline in western Lake Erie and the Detroit River.

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