

# STATE OF THE STRAIT MONITORING FOR SOUND MANAGEMENT



## A BINATIONAL CONFERENCE ON THE DETROIT RIVER ECOSYSTEM

Convened December 2004 by Great Lakes Institute for Environmental Research, University of Windsor, The Greater Detroit American Heritage River Initiative of Metropolitan Affairs Coalition, The Detroit River Canadian Cleanup, The Detroit River International Wildlife Refuge, The Detroit Water and Sewerage Department, and other organizations.

**Cover photos:** photos left and center (upper and lower): Recreational fishing in the Huron-Erie Corridor (lower center photo by Kurt Byers, Michigan Sea Grant Extension, courtesy of United States Environmental Protection Agency, Great Lakes National Program Office; other photos courtesy of OMNR); upper right: Scientist sampling water, benthic invertebrates and sediment in Lake Erie (photo courtesy of Environment Canada and University of Windsor); lower right: Longear sunfish (*Lepomis megalotis*) (photo courtesy of Nicolas Lapointe)

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MONITORING FOR SOUND MANAGEMENT

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### 6.13. NEW CONTAMINANTS IN SNAPPING TURTLES (*CHELYDRA SERPENTINA*) FROM AREAS OF CONCERN IN THE DETROIT RIVER SYSTEM: HYDROXYLATED FORMS OF POLYCHLORINATED BIPHENYLS AND POLYBROMINATED DIPHENYL ETHER FLAME RETARDANTS

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#### Introduction

The occurrence of persistent organic pollutants in wildlife in the Great Lakes is an important concern. Polybrominated diphenyl ether (PBDE) flame retardants continue to increase in terms of environmental occurrence and persistence in the tissues of wildlife and humans (Law et al. 2003). Temporal studies over the last ten or more years have shown biomagnification and exponentially increasing levels of PBDEs in wildlife such as fish and herring gull eggs from the Great Lakes basin (Luross et al. 2002). Polychlorinated biphenyl (PCB) and PBDE metabolic products, hydroxylated-PCBs (HO-PCBs), and to a lesser extent HO-PBDEs, are also being found with increasing frequency in the blood of aquatic and marine wildlife (Soechitram et al. 2004).

The Detroit River is part of a channel connecting Lake Huron and Lake Erie via Lake St. Clair, and its sediments and vertebrate biota are highly contaminated with PCBs and PBDEs (Russell et al. 1999, Rice et al. 2002). For example, PBDEs and PCBs have been reported in muscle and some organics, and HO-PBDEs and HO-PCBs in blood, of benthic- and pelagic-feeding fish from the Detroit River (Russell et al. 1999, Rice et al. 2002, Li. et al. 2003, Valters et al. 2004). HO-PCBs and HO-PBDEs have been shown to form metabolically in fish (Hakk and Letcher 2003). However, uptake via the gills or food may also be a source, since an anthropogenic analogue (the HO-trichlorinated diphenyl ether triclosan®) has been reported in Detroit River fish and surface waters (Li. et al. 2003, Hua et al. 2004, Valters et al. 2004). Both HO-PCB and HO-PBDE persist in blood due to competitive binding with thyroid hormone transport proteins, and have demonstrated other endocrine-related activities (Hakk and Letcher 2003). To our knowledge, there are no published reports on HO-PCBs or HO-PBDEs in reptiles, such as the snapping turtle (*Chelydra serpentina*), from any aquatic or marine environment, including the Detroit River system.

The present study is part of a larger, Environment Canada-based initiative to assess the health of wildlife in selected Areas of Concern (AOC) on the Canadian side of the Great Lakes and to document improvements over time. Additional background information about this initiative is provided in the accompanying abstract by Fernie et al., which describes contaminant concentrations in snapping turtle eggs. The snapping turtle has been chosen as a biomonitoring species to determine the concentrations of historical and emerging contaminants in tissues, and to correlate these contaminants with the reproductive and physiological health of this species. Snapping turtle contaminant burdens provide a good indication of contaminant levels in the local environment because these turtles are non-migratory. They are highly susceptible to environmental

changes brought about by human activity due to their behavior and reproductive and feeding habits. In this study, the emerging halogenated phenolic contaminants (HPCs, HO-PCBs, HO-PBDEs and others) were identified in the plasma of snapping turtles from two contaminated AOCs, the Detroit River and Wheatley Harbour, and compared to a less contaminated reference site, Tiny Marsh in southern Ontario (Georgian Bay).

## Methods

Adult male snapping turtles (approximately 5 to 15 kg in weight) were collected in the areas indicated in Figure 1 from May to July 2002. The method for contaminant determination in plasma has been previously described (Li. et al. 2003, Valters et al. 2004, Sandala et al. 2004). Briefly, plasma samples (about one gram) were spiked with internal standards for contaminant quantification and also as a measure of recovery efficiency. Plasma was liquid-liquid extracted and separated in two fractions with basic and acid aqueous solution: 1) a HPC fraction containing HO-PCBs and HO-PBDEs (subsequently methylated to MeO-analogues), and 2) a neutral fraction containing PCBs and PBDEs.

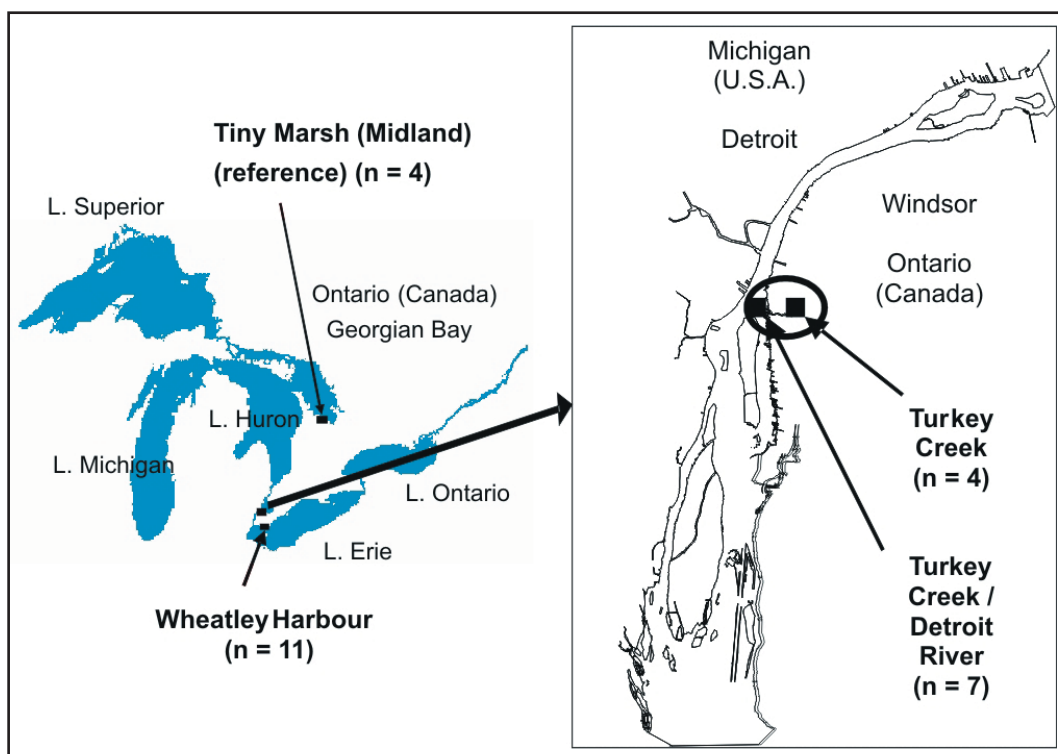


Figure 1. Maps showing snapping turtle sampling locations (black squares).

PCBs were determined by gas chromatography coupled with an electron capture detector (GC-ECD), and all other analytes by gas chromatography coupled with mass spectrometer detector (GC/MS) with electron capture negative impact ionization source (ECNI). Analysis of PCBs (41 congeners), PBDEs (eight congeners, Br<sub>3</sub> to Br<sub>7</sub>), MeO-PCBs (14 congeners, Cl<sub>5</sub> to Cl<sub>8</sub>), and MeO-PBDEs (17 congeners, Br<sub>3</sub> to Br<sub>6</sub>) was accomplished using the GC-ECD and GC-MS (ECNI) parameters described by Li et al. (2003), Valters et al. (2004) and Sandala et al. (2004) with some modifications. Mass chromatograms of the MeO-PCB- and MeO-PBDE-containing fractions were compared with authentic standard mixtures.

## Results

HO-PCB congeners greater than ten were quantified in most plasma samples, but 4-HO-CB187 was generally the dominant congener (Table 1). HO-PBDE congeners detected were predominantly comprised of 4'-HO-BDE49 and 4-HO-BDE42. The PBDE and PCB concentrations were similar to the concentrations of their hydroxylated metabolic byproducts;  $\Sigma$ HO-PBDE concentrations were similar to 4'PBDEs as were  $\Sigma$ HO-PCBs to PCBs at all sampling sites (Table 1). Turtles from the Detroit River and Wheatley Harbour AOCs were significantly more contaminated in terms of HO-PCB and HO-PBDE concentrations than those from the Tiny Marsh reference site (Table 1; see Figure 1 for site locations). Relative to other organohalogen classes, HO-PCBs are very important circulating contaminants in the blood of snapping turtles from southern Ontario.

## Conclusions and Recommendations

Snapping turtles from AOCs in southwestern Ontario, where halogenated pollutants contamination is relatively higher than that in non-AOC areas, appear to be at greater risk from halogenated phenolic compound (HPC) exposure, particularly to HO-PCBs.

**Table 1.** Organohalogen and phenolic contaminant concentrations in plasma of snapping turtles from southern Ontario (ng/g, wet weight) (mean concentration  $\pm$  SD)

	Tiny Marsh (Southern Georgian Bay) (n=4)	Turkey Creek / Detroit River (n=7)	Turkey Creek (n=4)	Wheatley Harbour (Western Lake Erie) (n=11)
$\Sigma$ -PCB <sup>1</sup>	10.4 $\pm$ 7.7	134.0 $\pm$ 72.0	330.2 $\pm$ 329.1	
$\Sigma$ -HO-PCB <sup>2</sup>	3.6 $\pm$ 4.8	113.9 $\pm$ 45.2	119.4 $\pm$ 9.7	116.6 $\pm$ 68.4
$\Sigma$ -PBDE <sup>3</sup>	0.8 $\pm$ 0.6	6.2 $\pm$ 5.1	5.4 $\pm$ 3.0	3.5 $\pm$ 6.2
$\Sigma$ -HO-PBDE <sup>4</sup>	0.4 $\pm$ 0.2	7.1 $\pm$ 2.7	2.6 $\pm$ 2.4	1.4 $\pm$ 0.8

<sup>1</sup>The  $\Sigma$ -PCB concentration was that of 41 congeners.

<sup>2</sup>Of the  $\Sigma$ -HO-PCB concentrations (12 congeners above quantification limit (> 0.001 ng/g)), >95% composed of 4-HO-CB112, 4-HO-CB163 and 4-HO-CB187.

<sup>3</sup> $\Sigma$ -BDE concentrations were the sum of BDE-28, -47, -99, -100, -153, -154, -138 and -183. The  $\Sigma$ -PBDE conc. were 70% or greater of BDE-47, -99 and -100.

<sup>4</sup>Of 14 HO-PBDE congeners analyzed,  $\Sigma$ -HO-PBDE conc. were 43–100 % comprised of 4'-HO-BDE49 and 4-HO-BDE42.

Increasing levels of PBDEs in Great Lakes aquatic biota such as fish (Luross et al. 2002, Li et al. 2003, Valters et al. 2004) and potential toxicities (e.g., endocrine) of exposure to circulating levels of HO-PCBs and HO-PBDEs are suggested, especially in the Detroit River watershed, and are thus a potential health concern to the snapping turtle and perhaps other reptilian species. Preliminary results indicate that these HO-PCBs and HO-PBDEs found in the plasma of these adult snapping turtles are associated with changes in the functioning of multiple organs.

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