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# A River-wide Survey of Polychlorinated Biphenyls (PCBs), Polycylic Aromatic Hydrocarbons (PAHs), and Selected Organochlorine Pesticide Residues in Sediments of the Detroit River—1999

**Ken G. Drouillard[1,*], Maciek Tomczak[1,†], Stan Reitsma[2,‡], and G. Douglas Haffner[1]**

[1]*Great Lakes Institute for Environmental Research*
*University of Windsor*
*Department of Biological Sciences*
*401 Sunset Ave.*
*Windsor, Ontario N9B 3P4*

[2]*Department of Civil & Environmental Engineering*
*University of Windsor*

***ABSTRACT.*** *The spatial distribution of hydrophobic organic contaminants, including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and octachlorostyrene (OCS) in sediments of the Detroit River was established using data from a 1999 river-wide survey. The survey employed a stratified random sampling design that divided the river into six geostatistical zones consisting of upper, middle, and lower U.S. and equivalent Canadian river reaches. Organic carbon normalized OCS sediment concentrations demonstrated no significant differences between U.S. or Canadian sediments or upstream/downstream gradients suggesting that OCS is derived primarily from sources upstream of the Detroit River. In contrast, sum PCBs and sum PAHs were significantly elevated at U.S. as compared to Canadian stations and demonstrated significant increasing upstream/downstream gradients in organic carbon normalized sediment contamination. The upper and middle U.S. river reaches contained a number of near-shore stations with high localized PCB and PAH sediment concentrations suggesting multiple inputs along the upper U.S. portion of the river. Consistent with past surveys, wide-spread sediment contamination of PCBs and PAHs continues to be observed in the highly industrialized Trenton Channel and downstream of Grosse Isle. Threshold effect level (TEL) sediment quality guidelines for PAHs and PCBs were exceeded in 92.6 and 77.8%, respectively, of stations in Trenton Channel and downstream of Grosse Isle. This large reservoir of degraded sediments in the lower U.S. river reach has the potential to enter Lake Erie during sediment disturbance events and likely contributes to gentoxic stress and increased bioaccumulation of PCBs in resident benthos, fish, and wildlife.*

***INDEX WORDS.*** *Persistent organic pollutants, contaminated sediments, Areas of Concern, Remedial Action Plans.*

## INTRODUCTION

The Detroit River has been designated as a Great Lakes Area of Concern (AOC) due to recognized impairments of at least nine beneficial uses (UGLCCS 1988). The river forms the lower 50 km of the Huron-Erie corridor and has been recognized as the single most important source of heavy metals and organic contaminants to Lake Erie (Oliver and Bourbonniere 1985, Kelly *et al*. 1991, Carter and Hites 1992). The history of contamination of the Detroit River is complex as it receives inputs from upstream waters (Lake St Clair and the St. Clair River) as well as point and non-point source inputs from two major urban centers (Detroit, MI and Windsor, ON) that include effluents from multiple industries, hazardous waste sites, sewage treatment plants, combined sewer overflows, and urban runoff.

*Corresponding author. E-mail: kgd@uwindsor.ca
†Current address: Sweetwater Engineering, P.O. Box 609, Gibsons, B.C., Canada, V0N 1VO
‡Current address: GeoSource Energy Inc., 6 Santa Fe Crt., Hamilton, ON, Canada, L9C 5Z7

Many contaminants from the above sources are released in association with or become partitioned into particles that are hydraulically sorted and focused along depositional zones of the river. A number of studies have demonstrated linkages between Detroit River contaminated sediments and ecosystem effects as observed through sediment bioassays (Rosiu *et al*. 1989, Maccubbin *et al.* 1991, Ali *et al*. 1993, Besser *et al*. 1996), spatial surveys to assess frequencies of deformities, tumors or lesions in fish and invertebrates (Hudson and Ciborowski 1996, Leadley *et al*. 1998), benthic invertebrate community composition (Reynoldson and Zarull 1989), and spatial trends of chemical bioaccumulation in biomontors and within food webs (Suns *et al*. 1985, Pugsley *et al*. 1985, Russell *et al.* 1999, Gewurtz *et al*. 2003).

While several studies have reported concentrations of priority pollutants such as PCBs, PAHs, pesticides, mercury, and heavy metals in Detroit River sediments (Fallon and Horvath 1985, Kaiser *et al*. 1985, Mudrock 1985, Hamdy and Post 1985, Pugsley *et al*. 1985, Furlong *et al*. 1988, Kannan *et al*. 2001), most surveys have focused on portions of the river or were designed to sample only soft sediment areas. An exception included the Upper Great Lakes Connecting Channel Study (UGLCCS 1988) which integrated datasets collected in the early to mid-1980s by the U.S. EPA, U.S. Fish and Wildlife Service, Environment Canada, and Ontario Ministry of Environment. Taken together, the combined datasets provided a description of contaminant trends throughout the river and, when combined with water monitoring programs, enabled a mass balance to assess the Detroit River as a source of contaminants to Lake Erie (UGLCCS 1988).

Contaminated sediments have since become a major concern for the Detroit River Remedial Action Plan. Hedtkie *et al*. (2002) reported that between 1993 and 2001, a total of $130 million was spent on sediment remediation activities within the Detroit River and western Lake Erie. Despite these efforts, there have been few attempts to link cleanup activities with ecosystem recovery (Besser *et al*. 1996) or to establish if remediation efforts changed the system mass balance of in-place pollutants (Heidtke *et al*. 2002). The present study provides an update of spatial trends of hydrophobic organic contaminants in Detroit River sediments as determined from 147 sampling locations collected during 1999. A unique aspect of the current study was the implementation of a stratified random sampling design that encompassed the entire river. This design permitted a statistical comparison of contaminant concentrations within the U.S. and Canadian portions of the river and an assessment of concentration trends along the river length.

## METHODS

### Survey Design

The sediment survey was performed during May–June, 1999 and encompassed the entire Detroit River. All sample locations were selected prior to the survey implementation using a stratified random design. Stratification of sampling areas was implemented to ensure 1) dispersion of samples across the river length, 2) equal sampling intensity within Canadian and U.S. waters, and 3) limited sampling of sediments associated with dredged navigation channels. To ensure dispersion of samples, sampling stations were assigned to six geostatistical zones comprising of U.S. upper, U.S. middle, U.S. lower, and equivalent Canadian river reaches. These divisions were based on large-scale features that included international boundary divisions, hydraulic considerations, sediment transport, and point source locations suspected as being different in each reach. The upper river reach contained 30 sampling stations (15 in U.S. waters and 15 in Canadian waters) that encompassed 15.7% of the river surface area. The upper reach included the river headwaters (mixing zone with Lake St. Clair) and downstream waters up to a transect established at the Ambassador Bridge. The middle reach consisted of 30 sample stations (15 U.S. and 15 Canadian stations) encompassing 6.3% of the river surface area and included sediments downstream of the Ambassador Bridge up to a transect located 500 m north of Fighting Island. The lower reach included 90 sampling stations (45 U.S. and 45 Canadian stations) that encompassed the remaining river surface area (78% of the river surface area) up to the Detroit River/western Lake Erie mixing zone. Geostatisical zone boundaries and sampling locations are presented in Figure 1. The sampling strategy also de-emphasized dredged shipping channels since these areas are less susceptible to sediment accumulation. To ensure this condition, two-thirds of the stations within a given geostatistical zone appeared in waters shallower than or equal to the median depth of the reach.

### Sample Collection and Chemical Analysis

Sampling stations were located by differential global positioning system (GPS) to ensure consis-