

## SPATIAL DISTRIBUTION OF TOXAPHENE IN LAKE ERIE SEDIMENTS

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### Introduction

Toxaphene is a complex mixture of chlorinated bornanes and bornenes comprised of several hundred congeners having from four to ten chlorines. Prior to its restriction of use, toxaphene was applied as a broad spectrum pesticide and next to DDT and PCBs is considered the most predominant organic contaminant in the Great Lakes basin<sup>1</sup>. Toxaphene has been designated as a critical pollutant of concern by the International Joint Commission.

The determination of concentrations, accumulations and inventories of persistent organic pollutants such as toxaphene in the Great Lakes provides important information for the implementation of remedial activities and lake area management plans. However, the analysis of toxaphene is difficult due to the complexity of the technical toxaphene mixture. Advances in analytical methods in the last decade and the commercial availability of analytical standards have resulted in the reporting of total, homologue and individual congener toxaphene data for a variety of matrices in the Great Lakes. Pearson et al.<sup>2</sup> have reported toxaphene data for Great Lakes sediments, including accumulations and inventories based on core samples. Swackhamer et al.<sup>3</sup> have reported data for toxaphene in water, sediments and biota in the Great Lakes while Whittle et al.<sup>1</sup> and Scheider et al.<sup>4</sup> have reported toxaphene levels in Great Lakes predator and forage fish species.

The vast majority of current data on toxaphene levels in the Great Lakes is related to Lakes Superior, Michigan and Ontario. We are unaware of sediment data for Lake Erie, yet use patterns, particularly those related to the growing of crops such as corn and soybeans, lead us to surmise that the watershed may be a source of toxaphene to Lake Erie. In addition, atmospheric inputs be a source of toxaphene to Lake Erie as is the case for the other Great Lakes<sup>2,5</sup>. In 1997, Environment Canada conducted a sediment survey in Lake Erie to characterize the spatial extent of sediment contamination using surficial sediment samples. In this report, we present the spatial distribution of toxaphene determined in Lake Erie surficial sediments.

### Materials and Methods

Sediments were collected in July 1997 using a mini box corer. The top three cm of sediment was removed, frozen, returned to the lab and air dried. Dry sediment was extracted with dichloromethane using a Dionex ASE 200 Accelerated Solvent Extractor (ASE). Solvent extracts were cleaned up on Florosil columns; subsequent elution with hexane and then hexane/dichloromethane (50:50 v/v) resulted in collection of chlorinated organics including PCBs and toxaphene in two separate fractions.

Toxaphene was analyzed by GC-ECNIMS using a Hewlett-Packard 6890 GC containing a 30 m 0.25 mm i.d. DB5-MS column with a 0.25  $\mu$ m stationary phase and equipped with a Hewlett-Packard 5973 mass selective detector. The carrier gas was helium at a flow rate of 1.2 mL/min. A splitless injection volume of 2  $\mu$ L was used with the following temperature program: initial temp. 80°C for 2 min; 80°C to 200°C at 10°C/min; 200°C to 240°C at 1.5°C/min; 240°C

to 285°C at 10°C/min; 5 min final time at 285°C. The injector, transfer line, mass spectrometer source and quadrupole temperatures were 250°C, 300°C, 150°C and 106°C, respectively. The emission current was 200 µA and the electron energy was 200 eV.

**Results and Discussion**

Figure 1 and Table 1 show the spatial distribution of toxaphene in Lake Erie surficial sediments. In general, there is trend towards decreasing concentrations from the western basin to the eastern basin which is similar in nature to those trends exhibited by other chlorinated contaminants such as DDT and PCBs. Historically, the western basin of Lake Erie exhibits a greater degree of sediment contamination by chlorinated organic pollutants, primarily as a result of discharges from the Detroit River.

The ranges and mean toxaphene concentrations for sediments from each of the four Lake Erie basins are shown in Table 1. The whole lake mean concentration was  $8 \pm 6$  ng/g (N=23 stations) which is roughly half the combined average concentration of  $15 \pm 4$  ng/g in surficial sediments in Lakes Michigan, Ontario and Superior<sup>3</sup>. The highest mean toxaphene concentration among the four lake basins was observed in the south-central basin (11 ng/g); this was due in large part to two sites along the Ohio shoreline exhibiting levels of 20 ng/g and 28 ng/g, respectively. Sediment concentrations at the three sites in the eastern basin were relatively low; these levels approached the method detection limit.

Sediments in the central and western basins generally exhibited total organic carbon (TOC) levels in the range of 1.5% to 3.4% (mean value 2.0%). The mean TOC value for the sample sites in the eastern basin was lower (0.9%). Normalization of toxaphene burden to TOC did not alter the relative spatial distribution and trends shown in Figure 1. However, sediments from two stations in the western basin with relatively low TOC levels (0.4%) also exhibited the two lowest concentrations of toxaphene in this basin (2.4 ng/g and 2.7 ng/g). Normalization of toxaphene levels in the western basin sediments to TOC (mean value of 550 ng/g organic carbon) resulted in a more consistent areal distribution of toxaphene as was evidenced by a reduction in the percent relative standard deviation to 27%, compared to a value of 53% for the data prior to normalization.

Table 1. Toxaphene levels in surficial sediments from the four basin areas of Lake Erie.

Basin	Concentration Range (ng/g)	Mean Concentration (ng/g)
West	2.4 - 16	8.2 (N=9)
North Central	5.8 - 12	8.7 (N=4)
South Central	0.4 - 28	11 (N=7)
East	1.7 - 3.0	2.4 (N=3)

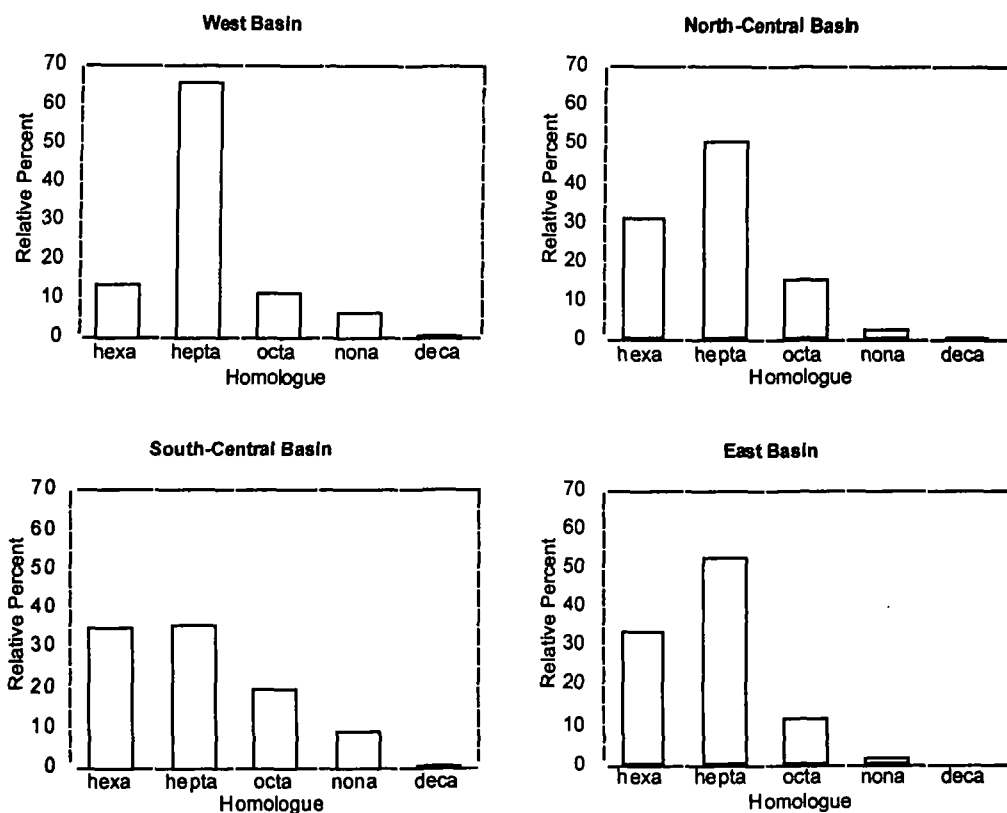


Figure 2. Mean homologue distributions of toxaphene in sediments from the Lake Erie basins.

Figure 2 shows the mean homologue compositions for the Lake Erie basins and are dominated by hexa- and heptachlorinated compounds. The relative percent contributions of these homologues ranged from 71% for the south-central basin to 87% for the east basin. Pearson et al.<sup>2</sup> showed these two homologues accounted for 45% to 70% of the toxaphene in Great Lakes sediment cores. The west basin profile is very similar to that exhibited by a core sample from Siskiwit Lake; this site is exposed to toxaphene exclusively from atmospheric deposition<sup>5</sup>. Toxaphene in sediments of the west basin of Lake Erie may be present as a result of atmospheric deposition or may have originated in the upstream Great Lakes and connecting channels.

**References**

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2. Pearson R.F., Swackhamer D.L., Eisenreich S.J. and Long D.T. (1997) *Environ. Sci. Technol.* 31, 3523.
3. Swackhamer D.L., Pearson R.F. and Schottler S.P. (1998) *Chemosphere*. 37, 2545.
4. Scheider W.A., Cox C., Hayton A., Hitchin G. and Vaillancourt A. (1998) *Environmental Monitoring and Assessment*. 53, 57.
5. Swackhamer D.L., Schottler S. and Pearson R.F. (1999) *Environ. Sci. Technol.* 33, 3864.

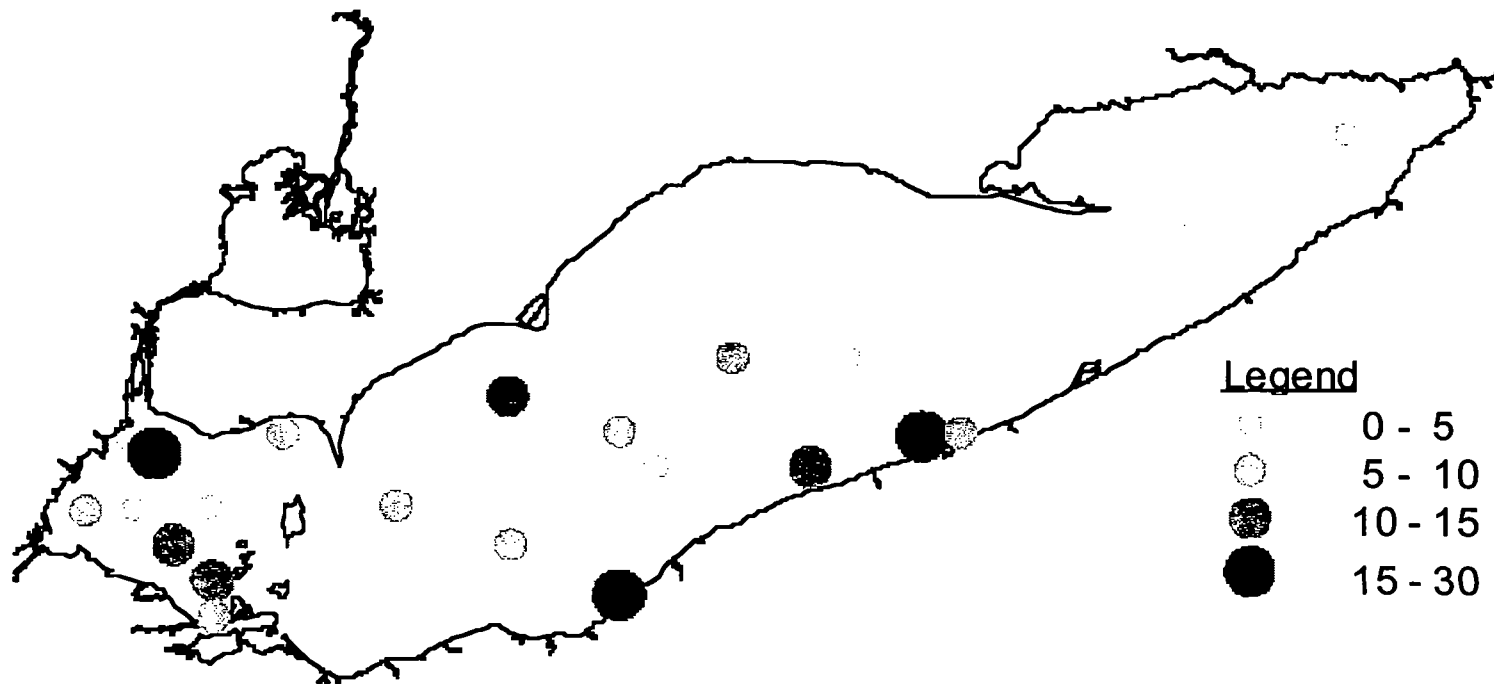


Figure 1. Spatial distribution of toxaphene in Lake Erie surficial sediments. All concentrations in ng/g (dry wt.)