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Sediment Contamination in Lake Erie: A 25-Year Retrospective Analysis

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ABSTRACT. *Lake Erie sediment surveys were conducted in 1997 and 1998 to characterize spatial and temporal trends in contamination and for comparison with historical levels to assess the degree of improvement in environmental quality since the advent of measures to reduce impacts from sources. These surveys were also designed to assist in identification of possible sources of contamination and areas where contamination exceeded Canadian sediment quality guidelines for protection of aquatic biota. Encouragingly, lakewide contaminant concentrations were found to have significantly decreased from levels observed in samples collected in 1971 in previous Environment Canada surveys. The lakewide average polychlorinated biphenyl (PCB) sediment concentrations decreased from 136 ng/g in 1971 to 43 ng/g in 1997. This decreasing temporal trend was also evidenced by contaminant profiles of core samples from all three major basins. There was a lakewide spatial trend in increasing sediment contamination from the eastern basin to the western basin, and from the north-central basin to the south-central basin. Sediments in many areas of Lake Erie still exceeded Canadian Federal and Provincial sediment quality guidelines. However, exceedences of sediment guidelines describing contaminated environments in 1997/98 were largely restricted to the western basin and the southern portion of the central basin. Exceedences of Canadian Sediment Quality probable effects guidelines were most numerous for dioxins and furans (40%) followed by mercury (6%). The Canadian threshold effects guideline for PCBs (34.1 ng/g) and the Provincial lowest effect guideline (70 ng/g) were exceeded at 52% and 22% of the sites, respectively. Mercury, PCBs and polychlorinated dibenzo-*p*-dioxins and dibenzofurans are responsible for fish consumption advisories in Lake Erie.*

INDEX WORDS: *Lake Erie, polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins, mercury, metals, sediment.*

INTRODUCTION

The presence of persistent pollutants can adversely impact Great Lakes wildlife, biodiversity, and aquatic ecosystems. Environment Canada together with collaborating agencies routinely conduct Great Lakes surveys to measure the occurrence and spatial distribution of toxic substances, to further understanding of the role human activities play in releasing these compounds to the environment, and to provide information for devising effective strategies to mitigate potentially deleterious health effects.

In 1971, Environment Canada conducted a survey in Lake Erie to characterize the spatial extent of sediment contamination by metals and organochlorine contaminants using surficial sediment samples (Frank *et al.* 1977, Thomas and Jaquet 1976, Thomas *et al.* 1976). In addition, the cultural impact of human activities over time was assessed using sediment cores (Kemp and Thomas 1976, Kemp *et al.* 1976). Sediment concentrations of metals including total mercury, lead, zinc, cadmium, and copper were compared to pre-colonial concentrations; the highest total mercury concentrations occurred in the western basin adjacent to the De-

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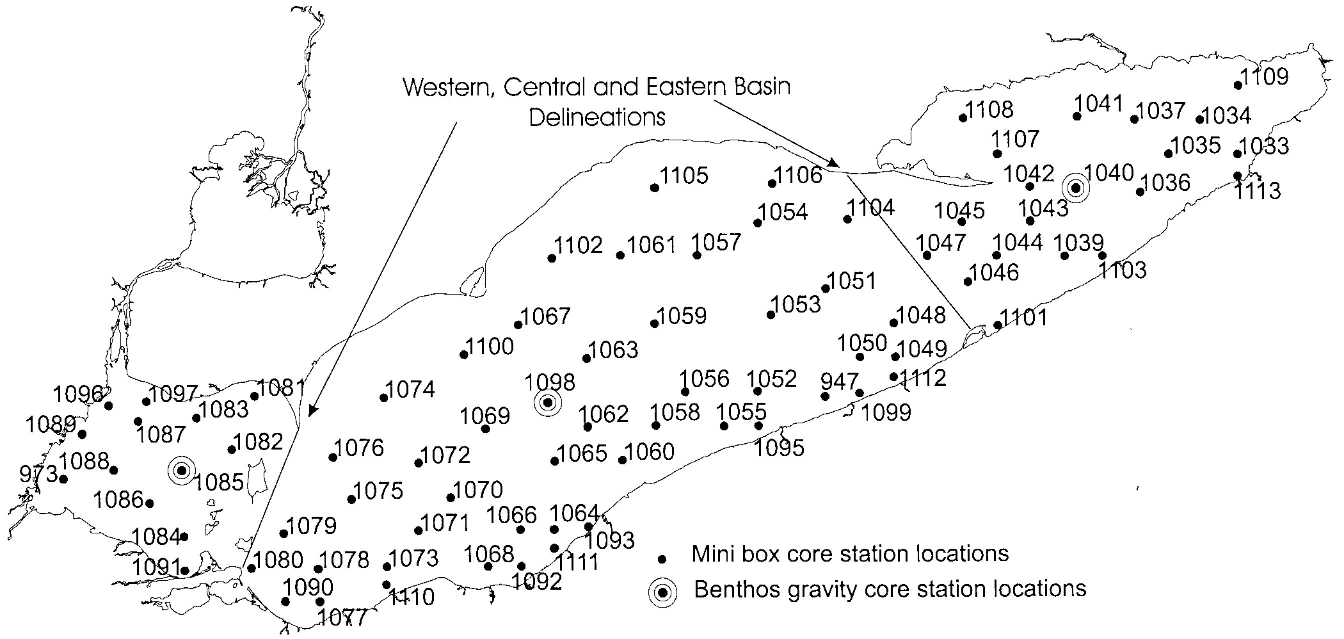

FIG. 1. Map of Lake Erie showing stations for sampling conducted in 1997 and 1998.

troit River; DDT was similarly distributed. Inputs of PCBs were apparent along the southern shore while dieldrin appeared to have sources along both the south and north shores. A western basin core sample indicated that PCBs and other organochlorines began to accumulate in the sediments during the period 1953 to 1958. In general, sediments in the western basin of Lake Erie exhibited high levels of contamination. Sediments in the central and eastern basins exhibited levels intermediate between those in the western basin and lower levels in sediments in Lake St. Clair, which discharges into the Detroit River.

In 1995, Environment Canada revisited 50 of the original 259 sites from the 1971 survey. The 1995 sediment samples, as well as archived 1971 samples, were analyzed for PCBs and other organochlorines. Encouragingly, the PCB and organochlorine pesticide concentrations had decreased considerably from those reported in 1971. Therefore, Environment Canada in collaboration with the Ohio Environmental Protection Agency conducted additional Lake Erie surveys in 1997 and 1998, to enable a broader range of analyses for the assessment of current sediment contamination relative to sediment quality guidelines, as well as further documentation of the improvement in sediment contaminant concentrations from the original 1971 survey. This paper presents an overview of the spatial and temporal characterization of sediment contamination in Lake Erie using results from the 1971 and 1997/98 surveys. Trace metals, especially total mercury and lead, nutrients, PCBs, and dioxins/furans are described in this paper. More detailed discussions of trends and spatial distributions of specific compound classes, such as toxaphene, can be found in other reports such as Marvin *et al.* 2000. The results are presented within the context of Canadian Sediment Quality Guidelines (CCME 1999). These guidelines are routinely applied as screening tools in the assessment of potential risk and determination of the relative priority of sediment quality concerns. Two benchmarks have been determined for a number of contaminants. "The lower value, referred to as the threshold effect level (TEL), represents the concentration below which adverse biological effects are expected to occur rarely. The upper value, referred to as the probable effect level (PEL), defines the level above which adverse effects are expected to occur frequently" (CCME 1999).

METHODS

Sample Collection

Surficial sediment samples were collected aboard the CCGS *Limnos* in 1997 from sixty-three locations (Fig. 1) using a mini box core sampling procedure. The top 3 cm of the sediment were sub-sampled for the analyses of chlorinated organic contaminants, total metals, grain size, and nutrients. At three index stations, one in each of the western, central, and eastern basins, both mini box core and benthos gravity core samples were obtained for surficial sediment sampling and sediment depth profiles. Mini box cores were sub-sampled in 1 cm increments from 0 to 15 cm, in 2 cm increments from 16 to 30 cm, and in 5 cm increments to a depth of 40 cm. Benthos gravity cores were sub-sampled in 1 cm intervals from 0–1 cm, 9–10 cm, 14–15 cm, 19–20 cm, 29–30 cm, and every 10 cm thereafter (i.e., 39–40 cm, 49–50 cm) to the bottom of the core. Samples for organic contaminant analyses were collected in pre-washed glass jars. Samples for other characterizations were collected in either high density polypropylene or Teflon jars. All samples were frozen immediately for transport to the laboratory. In April 1998, additional sediment samples were obtained for polychlorinated dibenzo-*p*-dioxin and dibenzofuran analyses, in addition to the previously identified parameters, using the mini box core method described above. The 1998 survey added six new sites resulting in a total of 69 sites; not all sites were analyzed for all parameters.

Analyses

Frozen sediment samples were thawed followed by air-drying of 5-gram subsamples. Dry sediment samples were extracted in dichloromethane at 100°C and 2,000 psi using an Accelerated Solvent Extractor (ASE, Dionex Inc.). Solvent extracts were gently reduced in volume under nitrogen to a final volume of 1 mL in iso-octane. Extracts were then subjected to an open-column deactivated Florosil [2g] cleanup procedure (National Laboratory for Environmental Testing 1997). Elution of the column with 10 mL 50% pentane in dichloromethane [fraction A] followed by 10 mL dichloromethane [fraction B] resulted in two fractions for analysis. Fraction A was treated with mercury to remove sulfur. Analyses were carried out on a Hewlett-Packard Model 5890 gas chromatograph equipped with dual columns (0.25 mm i.d. 0.25 µm stationary phase DB-5 and 0.25 mm i.d. 0.25 µm stationary phase HP-50) and dual electron capture detectors. Procedural method blanks and standard reference materials (SRMs) were processed with each set of 10 samples. The SRM used was Analytical Reference Material EC-5 (National Water Research Institute, Environment Canada). Surrogate standards applied to sediment prior to extraction included PCB #30, PCB #204, 1,3,5-tribromobenzene, 1,2,4,5-tetrabromobenzene and δ-BHC. Recovery criteria for surrogates were 70%; measurements of SRMs were required to be within 30% of certified values. Procedural blanks and surrogate recoveries were also evaluated against criteria established by the National Laboratory for Environmental Testing (Environment Canada) resulting from replicate analyses of SRMs over a 2-year period. Field replicates were typically within 30%. An external calibration method was employed for quantitation using individual organochlorine standards and a 132-congener PCB standard from the National Laboratory for Environmental Testing. Total PCB values are expressed as the sum of the following congeners, numbered according to the method of Ballschmiter and Zell (B/Z #): B/Z# 16, 24, 28, 31, 32, 44, 52, 74, 87, 99, 101, 110, 118, 138, 149, 163, 174, 180, 182, 187, 194, 195, 201, and 206.

Trace element, mercury, loss on ignition, and nutrient analyses were performed by Seprotech Laboratories. Trace metal concentrations were determined by a hot aqua-regia extraction with measurement by ICP-AES (McLaren 1981). Total mercury was determined by digestion with hot nitric acid and hydrochloric acid followed with measurement by cold vapor atomic absorption spectrometer (USEPA 1981). Loss on ignition was determined by igniting a sample at 1,000°C in a porcelain crucible. Total nitrogen and phosphorus were determined using United States Environmental Protection Agency standard methods (USEPA 1981).

Analysis of polychlorinated dibenzo-p-dioxins and furans was carried out in accordance with the USEPA Method 1613B protocol for dioxins and furans (USEPA 1994) by Axys Analytical Services Ltd (Sidney, British Columbia). Samples were spiked with ^{13}C-labelled surrogate standards. Toluene sediment extracts were subjected to a sequential cleanup including an acid/base wash, alumina column, carbon/celite column and a second alumina column procedure. Analysis by high-resolution gas chromatography—high resolution mass spectrometry was carried out in selected ion monitoring (SIM) mode using a VG Ultima mass spectrometer equipped with a Hewlett-Packard 5890 gas chromatograph. Chromatographic separation was carried out using split/splitless injection on a 0.25 mm i.d. 60 m DB-5 column with a 0.25 µm stationary phase thickness. All congeners were reported according to ion abundance ratio criteria, absolute and relative retention times, and signal to noise ratios as outlined in EPA Method 1613B. Procedural blanks and precision and recovery samples were processed with each sample batch and all data for individual samples were checked against surrogate recoveries. Toxic equivalents (TEQ) were calculated using the International Toxicity Equivalency Factor (ITEF) method (Van den Berg *et al.* 1998); congeners present at levels lower than the method detection limits were given zero values for TEQ calculations.

RESULTS AND DISCUSSION

The metals data from the central (Table 1) and eastern and western basins (Table 2) of Lake Erie

TABLE 1. Total trace metal, nitrogen, phosphorus, iron, manganese, and aluminum data from surficial sediment samples in Central Lake Erie in 1997/98.

Lat dec.deg.	Lon dec.deg.	Site	Basin	Depth cm	Year	As µg/g	Cd µg/g	Cr µg/g	Cu µg/g	Pb µg/g	Ni µg/g	Zn µg/g	Hg µg/g	N µg/g	P µg/g	Fe %	Mn µg/g	Al %
41.9892	–80.6414	947	Central	0–3	1997	ND	2.4	44.2	46.4	51.5	38.0	283.8	0.218	1750	713	3.2	586.8	1.2
42.1811	–80.3933	1048	Central	0–3	1997	2.3	ND	9.3	3.1	10.7	9.1	26.7	0.006	146	465	0.9	233.1	0.3
42.0917	–80.3894	1049	Central	0–3	1997	ND	2.7	46.3	41.3	58.9	39.8	302.7	0.204	1300	616	2.9	465.0	1.1
42.0919	–80.5169	1050	Central	0–3	1997	5.8	ND	12.8	10.3	14.2	20.0	51.1	0.020	367	583	2.0	263.8	0.6
42.2725	–80.6367	1051	Central	0–3	1997	1.2	ND	9.8	4.7	7.7	7.9	24.0	0.012	416	826	1.3	329.7	0.3
42.0022	–80.8781	1052	Central	0–3	1997	5.6	1.8	36.4	38.9	44.0	38.5	176.6	0.202	2160	855	3.0	790.9	1.4
41.9108	–80.9975	1055	Central	0–3	1997	4.3	2.8	57.5	56.6	76.0	50.4	317.9	0.284	2180	780	3.4	483.7	1.5
42.0033	–81.1197	1056	Central	0–3	1998	15.0	3.0	36.0	45.0	48.0	43.0	187.0	0.155	2770	593	3.5	975.0	1.4
42.3631	–81.1236	1057	Central	0–3	1998	ND	1.0	17.0	22.0	17.0	22.0	80.0	0.055	1440	698	2.7	368.0	0.8
41.9125	–81.2397	1058	Central	0–3	1997	ND	0.7	25.3	27.8	21.8	39.6	105.0	0.070	1620	610	3.0	422.1	1.4
42.1808	–81.2428	1059	Central	0–3	1997	ND	1.1	40.6	45.6	47.1	48.5	183.9	0.144	2540	980	3.5	849.6	1.9
41.8222	–81.3600	1060	Central	0–3	1997	5.2	1.6	52.8	52.9	59.3	55.5	239.6	0.274	3730	1040	4.0	1160.0	2.1
42.3614	–81.3639	1061	Central	0–3	1997	ND	1.6	38.0	44.2	50.4	49.2	166.8	0.122	3010	939	3.4	904.4	1.9
41.9106	–81.4833	1062	Central	0–3	1997	11.4	2.5	56.9	55.4	78.1	59.4	266.5	0.284	3860	945	3.8	844.9	2.1
42.0908	–81.4856	1063	Central	0–3	1997	8.9	1.1	46.2	45.6	54.6	51.5	208.3	0.170	2690	998	3.7	863.8	2.0
41.6400	–81.6042	1064	Central	0–3	1997	5.8	2.2	48.0	50.3	61.1	52.5	221.1	0.280	2760	953	3.9	725.5	1.7
41.8197	–81.6000	1065	Central	0–3	1997	18.6	1.7	56.3	56.3	81.1	58.2	263.0	0.326	3630	928	3.5	690.7	1.9
41.6400	–81.7222	1066	Central	0–3	1997	7.5	ND	44.5	68.2	104.3	41.7	243.8	0.184	2180	780	5.0	968.7	1.2
42.1803	–81.7244	1067	Central	0–3	1997	11.1	1.0	43.9	48.2	63.7	53.0	206.6	0.160	3510	1160	3.5	1070.0	1.7
41.5428	–81.8389	1068	Central	0–3	1997	9.6	1.1	46.7	47.0	49.7	51.7	195.1	0.252	3200	953	4.3	817.4	1.8
41.9069	–81.8442	1069	Central	0–3	1997	2.3	1.2	53.0	49.2	68.6	55.8	238.8	0.198	3620	1110	3.8	668.8	2.1
41.6381	–82.0847	1071	Central	0–3	1997	ND	1.8	53.4	55.5	65.5	56.4	223.3	0.340	3980	1030	3.6	872.5	1.9
41.8164	–82.0833	1072	Central	0–3	1997	4.7	2.1	56.5	56.7	73.6	60.4	249.0	0.270	4090	1180	3.9	1050.0	2.0
41.5433	–82.1992	1073	Central	0–3	1997	13.7	4.4	23.0	32.2	44.2	29.0	232.9	0.130	1630	438	2.8	402.9	0.8
41.9894	–82.2064	1074	Central	0–3	1997	1.5	2.0	55.7	59.8	87.5	61.9	262.5	0.236	4160	878	3.7	779.8	2.0
41.7214	–82.3239	1075	Central	0–3	1997	16.8	0.8	33.5	34.2	41.9	38.9	142.6	0.266	2590	700	2.2	498.1	1.1
41.4514	–82.4372	1077	Central	0–3	1997	4.0	1.5	43.8	47.3	45.1	49.5	173.4	0.306	3230	883	3.2	1030.0	1.8
41.6311	–82.5628	1079	Central	0–3	1997	ND	1.3	30.5	30.6	29.8	34.0	122.6	0.237	1950	598	2.1	443.5	1.0
41.5397	–82.6786	1080	Central	0–3	1997	ND	0.5	41.8	41.7	43.0	47.1	169.7	0.208	2640	828	2.9	640.5	1.7
41.4519	–82.5583	1090	Central	0–3	1997	8.0	1.9	44.3	49.2	46.2	49.9	176.0	0.183	3000	781	3.1	818.2	1.7
41.5433	–81.7206	1092	Central	0–3	1997	10.9	ND	10.0	8.1	13.1	16.3	52.3	0.023	271	343	2.2	307.0	0.4
41.6472	–81.4833	1093	Central	0–3	1997	15.6	ND	10.9	11.7	12.9	13.9	91.1	0.023	381	462	1.6	323.9	0.5
41.9108	–80.8750	1095	Central	0–3	1997	8.4	2.2	36.5	44.5	50.8	40.9	196.0	0.181	1360	578	3.0	507.2	1.1
42.9986	–81.6008	1098	Central	0–3	1997	14.5	0.7	45.8	44.1	59.9	51.7	204.2	0.164	3200	889	3.6	871.5	1.9
41.9981	–80.5178	1099	Central	0–3	1997	5.7	ND	17.7	25.7	22.4	25.7	117.4	0.072	1200	522	2.5	422.8	0.8
42.0856	–81.9664	1100	Central	0–3	1998	NA	1.0	17.0	21.0	39.0	42.0	118.0	0.025	345	771	6.5	1551.0	0.7
42.3547	–81.6053	1102	Central	0–3	1997	1.5	1.0	40.8	46.0	57.6	51.6	188.2	0.159	3190	870	3.4	1020.0	1.7
42.5372	–81.2394	1105	Central	0–3	1997	ND	2.0	20.1	20.9	12.1	29.8	88.7	0.052	2350	532	2.0	915.0	1.2
42.5394	–80.7558	1106	Central	0–3	1998	12.0	1.0	8.0	6.0	10.0	10.0	29.0	0.015	323	266	1.5	547.0	0.4
41.4958	–82.2006	1110	Central	0–3	1997	6.6	ND	11.7	13.0	10.7	17.9	83.3	0.031	642	680	3.8	439.1	0.5
41.5903	–81.6042	1111	Central	0–3	1997	ND	3.3	47.3	52.4	59.5	43.4	305.8	0.301	1420	630	3.5	512.3	1.2
42.0394	–80.3964	1112	Central	0–3	1997	14.8	ND	12.4	8.2	15.8	14.2	73.4	NA	388	450	1.8	315.3	0.7

TABLE 2. Total trace metal, nitrogen, phosphorus, iron, manganese, and aluminum in surficial sediment samples from Eastern and Western Lake Erie.

Lat dec.deg.	Lon dec.deg.	Station	Basin	Depth cm	Year	As µg/g	Cd µg/g	Cr µg/g	Cu µg/g	Pb µg/g	Ni µg/g	Zn µg/g	Hg µg/g	N µg/g	P µg/g	Fe %	Mn µg/g	Al %
42.6192	–79.1700	1033	East	0–3	1997	ND	0.9	21.7	16.2	23.6	20.7	121.2	0.062	744	527	2.1	234.8	0.7
42.6214	–79.4139	1035	East	0–3	1997	5.7	1.0	35.9	40.4	33.9	43.1	168.9	0.126	2000	787	3.3	771.4	1.6
42.7114	–79.5350	1037	East	0–3	1997	ND	ND	26.0	24.7	25.3	31.5	109.5	0.072	1510	817	2.2	517.3	1.2
42.3564	–79.7867	1039	East	0–3	1997	0.7	1.2	43.1	37.7	49.2	54.7	198.4	0.136	2710	1040	3.7	1009.9	2.1
42.5333	–79.7833	1040	East	0–3	1997	12.0	0.7	37.3	38.2	36.5	45.2	165.5	0.097	2320	843	3.4	1206.6	1.8
42.5378	–79.9075	1042	East	0–3	1997	2.4	ND	32.0	32.6	25.5	39.0	130.9	0.072	1840	893	3.2	1120.0	1.8
42.4478	–79.9056	1043	East	0–3	1997	14.4	ND	34.0	33.3	25.8	40.5	137.3	0.086	1940	945	3.3	1140.0	1.9
42.3581	–80.0272	1044	East	0–3	1997	ND	0.8	22.4	26.2	7.7	29.4	76.1	0.016	679	705	2.7	792.2	1.5
42.4472	–80.1483	1045	East	0–3	1997	ND	1.1	25.9	32.6	32.1	35.5	112.2	0.084	2190	978	2.5	868.6	1.3
42.3589	–80.2744	1047	East	0–3	1997	12.0	ND	16.4	14.5	4.4	19.7	47.3	0.016	408	661	2.0	521.0	0.9
42.1742	–80.0239	1101	East	0–3	1997	15.6	ND	13.6	16.9	11.5	21.5	74.6	0.052	1470	405	1.8	432.5	0.7
42.3561	–79.6514	1103	East	0–3	1997	15.2	1.0	29.6	35.6	32.8	35.5	155.7	0.130	2020	673	2.8	505.7	1.2
42.6233	–80.0206	1107	East	0–3	1997	3.9	ND	24.7	24.9	12.0	28.5	90.3	0.045	1350	707	2.6	913.7	1.5
42.7167	–80.1414	1108	East	0–3	1997	1.7	ND	14.0	17.0	5.0	17.6	48.9	0.016	637	588	1.8	533.7	0.9
42.7986	–79.1650	1109	East	0–3	1997	8.6	ND	9.8	5.8	10.3	15.5	38.1	0.014	424	761	1.3	263.4	0.4
41.7967	–83.3175	973	West	0–3	1998	ND	4.0	53.0	58.0	51.0	49.0	210.0	0.296	2480	711	3.4	649.0	1.6
41.9889	–82.6906	1081	West	0–3	1998	10.0	2.0	41.0	44.0	42.0	40.0	158.0	0.458	2550	519	2.7	494.0	1.2
41.8531	–82.7472	1082	West	0–3	1997	ND	1.0	61.4	48.0	66.4	54.7	226.6	0.365	2670	679	3.2	655.4	1.7
41.9381	–82.8706	1083	West	0–3	1997	ND	1.1	44.0	44.6	45.7	40.9	179.1	0.690	2240	639	2.6	488.0	1.3
41.6239	–82.9178	1084	West	0–3	1997	ND	0.9	55.1	45.6	47.9	53.5	209.5	0.225	2670	833	3.4	588.7	1.9
41.8061	–82.9247	1085	West	0–3	1997	13.4	1.0	56.5	45.5	57.1	49.0	204.9	0.638	2403	841	3.0	663.6	1.6
41.7122	–83.0414	1086	West	0–3	1997	ND	2.4	72.8	58.3	73.4	63.5	264.7	0.692	3020	863	3.6	702.7	1.9
41.8011	–83.1678	1088	West	0–3	1997	4.5	ND	16.2	10.4	15.3	15.1	61.5	0.076	449	319	0.8	130.7	0.3
41.8964	–83.2783	1089	West	0–3	1997	8.4	1.5	40.1	39.9	34.9	36.4	171.5	0.179	2330	761	2.2	471.6	1.2
41.5347	–82.9158	1091	West	0–3	1997	7.5	0.9	26.6	30.6	24.3	32.5	109.4	0.113	2210	700	2.2	481.4	1.2
41.9711	–83.1850	1096	West	0–3	1997	10.9	0.7	23.8	18.3	18.1	16.1	105.9	0.220	504	755	1.0	181.9	0.3
41.9817	–83.0500	1097	West	0–3	1997	ND	1.4	47.8	46.4	57.1	43.6	180.9	0.940	1860	623	2.5	450.5	1.2

were analyzed for spatial patterns to assist in identification of source areas, to identify areas of noncompliance with Canadian Sediment Quality Guidelines (Table 3), and, in conjunction with the core data, to assess surficial sediment enrichment compared to historical norms. Core profiles of trace metals from all basins generally exhibited increasing analyte concentration gradients from the surface to depths of approximately 10 cm to 20 cm, decreasing gradients from 20 cm to 40 cm, and relatively constant concentrations from approximately 40 cm to 50 cm to the bottom of the core. Sedimentation rates from a number of studies were available to assist in the interpretation of temporal trends (Gottgens *et al.* 1999, Ritson *et al.* 1994, Kemp *et al.* 1976, and Nriagu *et al.* 1979). Using information from these studies, depths of 20 cm were estimated to represent the period 1960 to 1965 in the western basin core, 1965 to 1970 in the eastern basin core, and 1955 to 1960 in the central basin core. Gottgens *et al.* (1999) found the peak concentration of mercury in a sediment core from the western basin occurred at a depth of 15 cm that was estimated to represent 1970.

Concentrations of total mercury were highest in the western basin core and lowest in the eastern basin core (Fig. 2). Total chromium exhibited a pattern similar to mercury. Concentrations of total lead were highest in the central basin core at depths ranging from 10 cm to 30 cm, but decreased to values similar to the western basin core in more recent sediments at the surface (Fig. 3). Surface total lead concentrations were the lowest in the eastern core; total zinc core profiles were similar to lead. Total cadmium, copper, and nickel core profiles were similar in that the lowest values were in the surficial sediments from the eastern basin core, and the central and western basin cores had higher yet similar values in recent surficial sediments. Unlike the metals, total nitrogen and phosphorus concentra-

TABLE 3. Lake Erie basin-specific background concentrations and percentages of stations exceeding background, surficial basin-specific 75th percentiles, Canadian Sediment Quality Guidelines, and the number of sites exceeding the guidelines. Values for dioxin represent sum totals for both polychlorinated dibenzo-p-dioxins and dibenzofurans.

	Background Concentrations			Surficial vs Background			Surficial 75th Percentile			Canadian Sediment Quality Guidelines (CCME, 1999)			
	µg/g ex. Iron and Aluminum (%)			% Exceeding			µg/g			(µg/g)		% of sites Exceeding	
	West	Center	East	West	Center	East	West	Center	East	TEL	PEL	TEL	PEL
Arsenic	5.8	7.1	6.8	42	39	40	8.8	11.1	12.0	5.9	17	42	3
Cadmium	< 1	< 1	< 1	67	63	13	1.6	2.0	1.0	0.596	3.53	72	3
Chromium	22.2	31	27	92	73	47	55.4	46.6	33.0	37.3	90	49	0
Copper	15.1	35.1	28.4	92	63	47	46.8	49.2	34.5	35.7	196.6	55	0
Iron	2.34	3.53	3.17	67	34	33	3.2	3.6	3.2				
Lead	13.2	22.7	18.6	100	73	60	57.1	59.8	32.4	35	91.3	57	1
Manganese	519	573	780	42	59	47	650	872	962				
Mercury	0.034	0.049	0.042	100	80	73	0.65	0.25	0.09	0.174	0.486	46	6
Nickel	27.6	45.9	35.5	83	46	40	50.1	51.7	39.8	18*	35.9*		
Nitrogen	1,308	1,782	1,471	83	61	53	2,580	3,198	2,010				
Phosphorus	466	523	717	92	85	53	779	936	868				
Zinc	63.5	105.8	95.6	92	76	60	209	237	146	123.1	314.8	62	1
Aluminum	1.66	1.81	1.71	33	29	27	1.66	1.85	1.69				
PCBs (ng/g)							102	51	26	34.1	277	52	0
Dioxin (pg/gTEQs)							33	23	2	0.85	21.5	93	40
Total Dioxin (pg/g)							8,240	4,690	342				

* There is no recommended Canadian Sediment Quality Guideline (CSQG) for nickel; interim sediment assessment values (freshwater TEL of 18 µg/g and PEL of 35.9 µg/g) have been published by Smith *et al*. (1996). Values for nickel are not recommended CSQGs.

tions increased towards the surface of the core (Figs. 4 and 5). Surficial sediment concentrations were highest in the central basin core.

The western, central, and eastern basin background contaminant concentrations were determined from the average of the concentrations from the 40 to 50 cm interval to bottom of each core (Table 3). The percentages of stations exceeding basin-specific background concentrations for each chemical are also summarized in Table 3. The western basin had the highest percentage of exceedences, suggesting the greatest anthropogenic impact has occurred in the western basin. More than 40% of the stations in each of the basins have elevated surficial concentrations for total mercury, zinc, lead, phosphorus, nitrogen, manganese, copper, chromium, and nickel. Total mercury had the highest number of stations exceeding background concentrations. Average background concentrations were used to express the surficial concentrations as a ratio above the background concentration to further illustrate the impact of anthropogenic enrichment. The average background concentrations for total arsenic, cadmium, chromium, copper, lead, nickel, zinc, and mercury were determined for each basin. The surficial concentrations were compared to their respective background concentrations and an enrichment ratio for each metal was calculated. The average enrichment ratio for the eight metals at each site was computed and is illustrated in Figure 6. The spatial pattern of the average enrichment ratio was enhanced to illustrate west to east trends by analyzing the minimum and maximum ratios in each of the basins and selecting breakpoints that would provide a simple pattern for clarity. The eastern basin and the northeast portion of the central basin were the least contaminated above background with average ratios less than 1.725. The western basin was most contaminated above background with 6 of the 10 sites having average ratios above 2.715. The central basin ratios were intermediate between the western and eastern basins. The

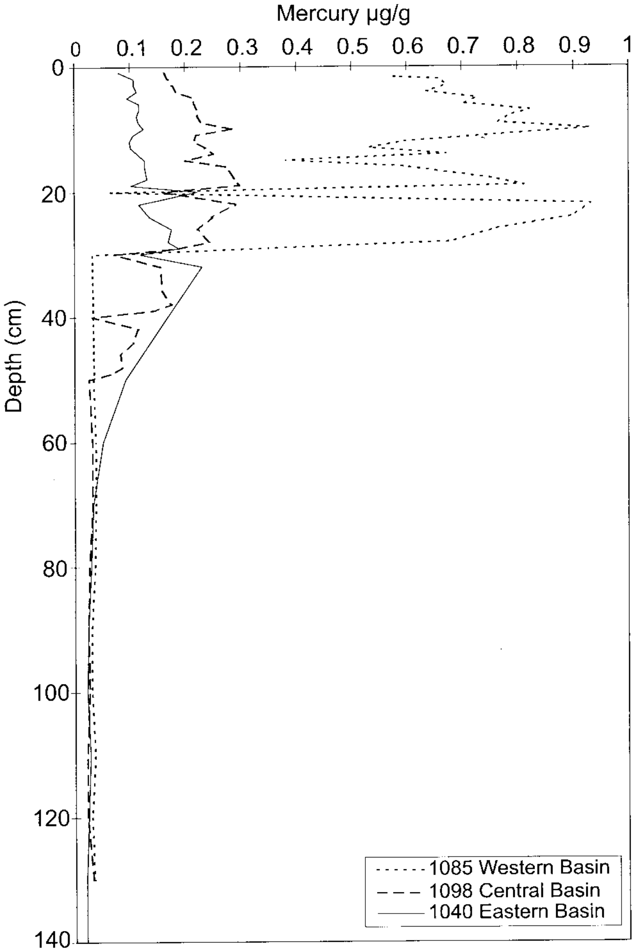

FIG. 2. Profiles of total mercury concentrations (µg/g) in core samples from each of the three major Lake Erie basins.

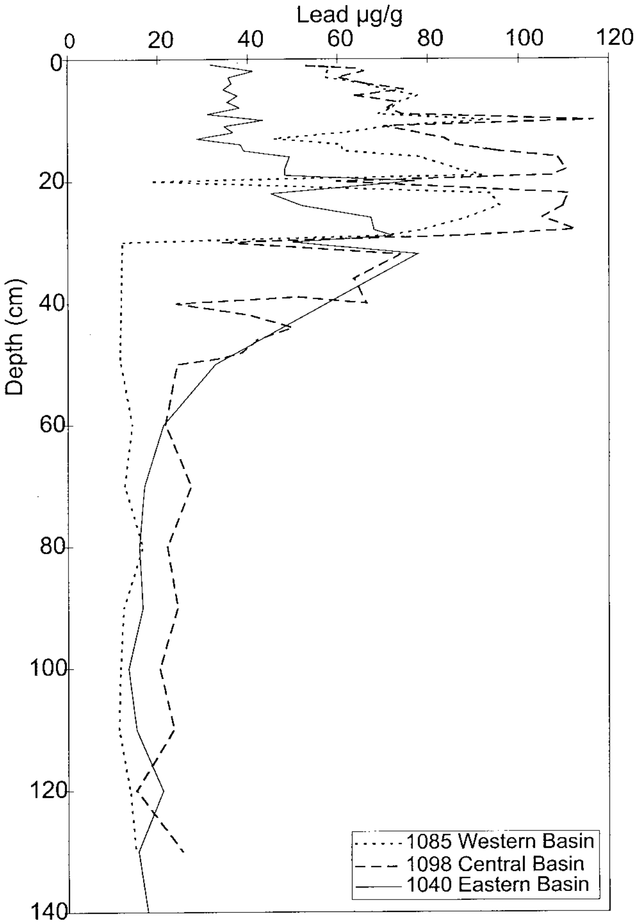

FIG. 3. Profiles of total lead concentrations (µg/g) in core samples from each of the three major Lake Erie basins.

spatial pattern in the anthropogenic enrichment is an indication of the influence of historical and present day human activity. However, it is also an indication of substrate type. The spatial chemical concentration patterns were comparable to the spatial bottom sediment type distribution as described by Thomas *et al.* (1976). Sediments dominated by fine-grain silts and clays absorb contaminants more effectively compared to sediments dominated by sands, hence the spatial patterns of contaminants are not only a function of proximity to source but also substrate type.

The spatial pattern evident in the surficial enrichment map was also evident in the individual chemical distribution maps. The highest total mercury concentrations and greatest number of exceedences of the Canadian Sediment Quality probable effects level (PEL) were located in the western basin (Fig. 7). The 75th percentile for the western basin was more than 20 times the background concentration, meanwhile, it was only twice the background concentration in the eastern basin (Table 3). Stations exhibiting the lowest concentrations and concentrations less than the Canadian Sediment Quality threshold effects level (TEL) were located in the eastern basin and the northeast area of the central basin. Figure 8 illustrates the 1971 surficial sediment total mercury concentrations reported by Thomas and Jaquet (1976). Consistent with the temporal trends apparent in the core profile, sediment concentrations have decreased with time throughout the entire lake. In 1971, the 75th percentiles for mercury in the western, central, and eastern basins were 1.72, 0.58 and 0.65 µg/g, re-

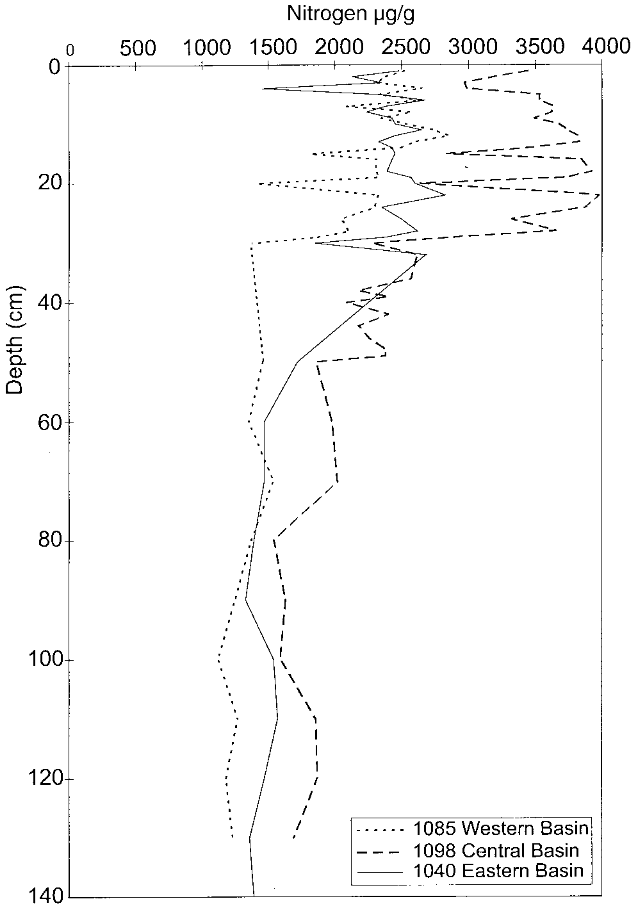

FIG. 4. Profiles of total nitrogen concentrations (µg/g) in core samples from each of the three major Lake Erie basins.

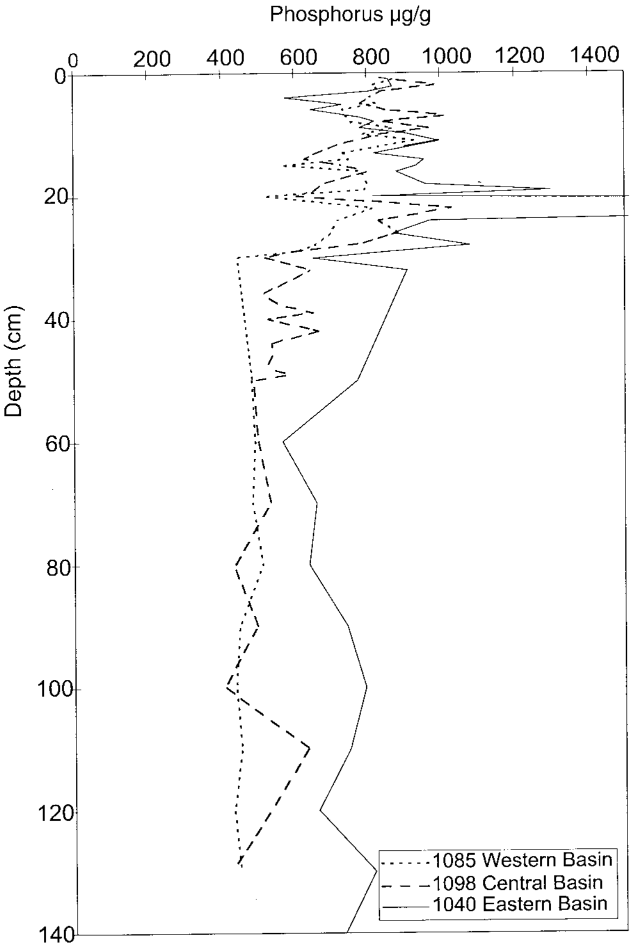

FIG. 5. Profiles of total phosphorus concentrations (µg/g) in core samples from each of the three major Lake Erie basins.

spectively. Meanwhile the 75th percentiles were 0.65, 0.25, and 0.09 µg/g in 1997.

Figure 9 illustrates the pattern for surficial sediment total lead concentrations. Only a single site in the southern portion of the central basin exceeded the PEL. Total lead exceedences of the TEL were more spatially extensive in the central basin and the eastern basin, compared to total mercury. The 75th percentiles were less than 4 times the background concentrations (Table 3). Figure 10 illustrates the 1971 pattern for total lead reported by Thomas and Jaquet (1976); lakewide concentrations have decreased over time which was consistent with the observed trend in the core profile. Control measures restricting the use of leaded gasoline have undoubtedly contributed to the observed decreases. Spatial distributions of other metals exhibited patterns similar to total lead. Total arsenic exceeded the PEL at two locations and total zinc had one site with a concentration greater than the PEL, all in the southern area of the central basin. Total cadmium concentrations exceeded the PEL at two locations, one in the western basin and one in the southern portion of the central basin. However, each of these exceedences was unique in location. In total, 10 stations exhibited sediment levels that exceeded the Canadian Sediment Quality PELs; 5 in western Lake Erie for total mercury (4) and cadmium (1), and 5 in the southern portion of the central basin for total arsenic (2), cadmium (1), lead (1), and zinc (1).

Total nitrogen (Fig. 11) and phosphorus (Fig. 12) concentrations compared to Ontario Provincial Sediment Quality Guideline lowest effect (LEL) and severe effect (SEL) sediment concentrations (Persaud *et al.* 1993) depict a more widespread spatial contamination compared to the trace metals. How-

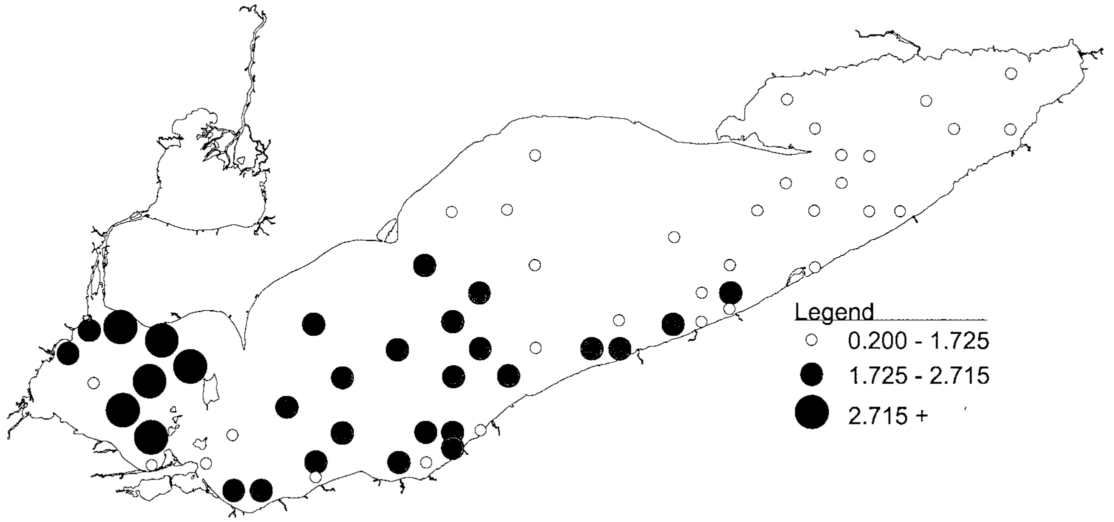

FIG. 6. Map of Lake Erie showing surficial sediment enrichment by metals. Ratios were calculated using surficial sediment concentrations and background concentrations determined from the bottom of cores. Values represent the average of the ratios calculated for arsenic, cadmium, chromium, copper, nickel, lead, zinc, and mercury.

ever, none of the locations exceeded the provincial SEL. The highest concentrations of both nutrients were observed in the central basin, which was also consistent with the core profiles.

The spatial pattern of polychlorinated dibenzo-*p*-dioxins and dibenzofurans is presented using toxic equivalents for a subset of the survey stations (Fig. 13). Toxic equivalents (TEQs) were calculated using the International Toxicity Equivalency Factor (ITEF) method (Van den Berg *et al.* 1998). The pattern was similar to the metal spatial patterns. Table 3 shows the 75th percentile values of dioxins and furans, expressed as both totals and TEQs, for each of the three basins. The 75th percentiles for dioxin

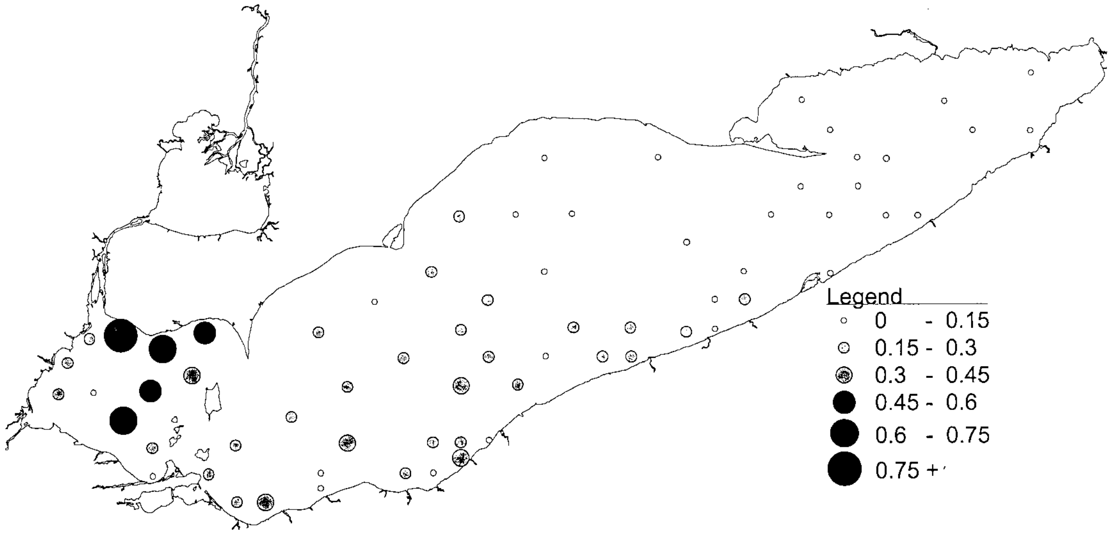

FIG. 7. Lake Erie surficial sediment total mercury concentrations (µg/g) in samples collected in 1997/98. The Canadian Sediment Quality threshold effect level (TEL) is 0.174 µg/g and the probable effect level (PEL) is 0.486 µg/g.

FIG. 8. Lake Erie surficial sediment total mercury concentrations (µg/g) in samples collected in 1971. The Canadian Sediment Quality threshold effect level (TEL) is 0.174 µg/g and the probable effect level (PEL) is 0.486 µg/g.

and furan TEQs were 33, 23, and 2 pg/g TEQ for the western, central, and eastern basins, respectively. Only two locations were lower than the Canadian Sediment Quality proposed TEL (0.85 pg/g) while 12 sites, or 40% of the stations, exceeded the proposed PEL (21.5 pg/g). The highest levels of dioxins and furans were found at stations in the western basin and the southern portion of the central basin. Ongoing monitoring of suspended sediments in Lake Erie has shown that the western basin continues to be subjected to active loadings of these contaminants, with the Detroit River implicated as a primary vector. Fish consumption advisories for dioxins and furans have been implemented for some species in United States waters.

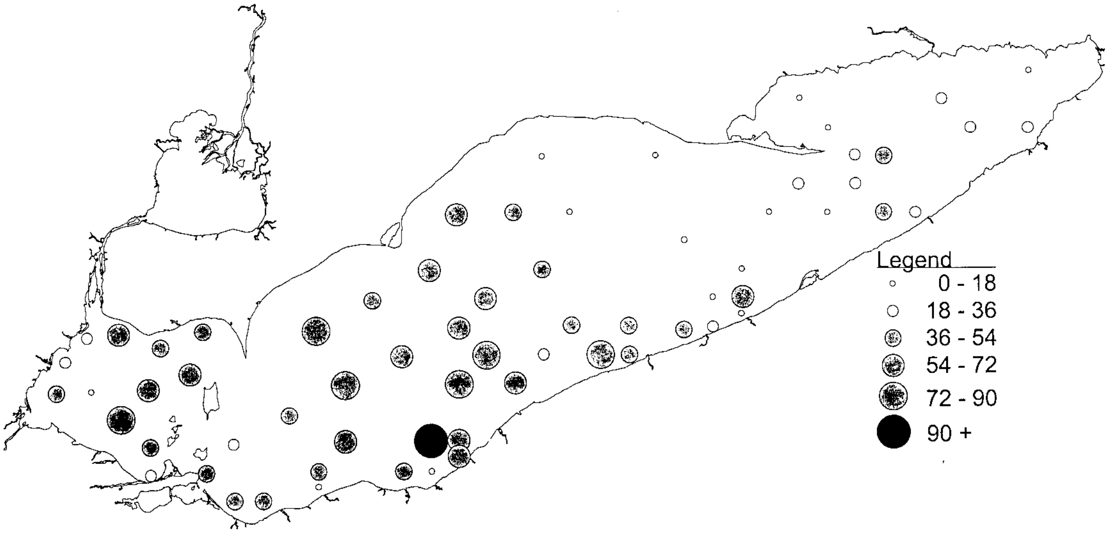

FIG. 9. Lake Erie surficial sediment total lead concentrations (µg/g) in samples collected in 1997/98. The Canadian Sediment Quality threshold effect level (TEL) is 35 µg/g and the probable effect level (PEL) is 91.3 µg/g.

FIG. 10. Lake Erie surficial sediment total lead concentrations (μg/g) in samples collected in 1971. The Canadian Sediment Quality threshold effect level (TEL) is 35 μg/g and the probable effect level (PEL) is 91.3 μg/g.

Total polychlorinated biphenyl (PCB) concentrations in 1997 (Fig. 14) showed a lake-wide decrease since 1971 (Fig. 15). Total PCB values are based on the sum total concentrations of the 24 most predominant congeners. Levels reported for the 1971 survey were generated from analysis of frozen sediment archives. Therefore, the data for both 1997 and 1971 were generated using the same methodology enabling a direct and valid comparison. Further analysis of a subset of samples (N = 6) showed that the total PCB values based on the sum of 24 individual congeners reported in this study represented 54 ± 2.7% of a total PCB value based on the sum of 131 individual congeners, quantitated using a dual-column method and a mixed congener analytical standard from the National

FIG. 11. Lake Erie surficial sediment total nitrogen concentrations (μg/g) in samples collected in 1997/98. The Province of Ontario Sediment Quality lowest effect level (LEL) is 550 μg/g and the severe effect level (SEL) is 4,800 μg/g.

FIG. 12. Lake Erie surficial sediment total phosphorus concentrations (µg/g) in samples collected in 1997/98. The Province of Ontario Sediment Quality lowest effect level (LEL) is 600 µg/g and the severe effect level (SEL) is 2,000 µg/g.

Laboratory for Environmental Testing (Environment Canada).

The PCB totals from eight stations in the western basin were on average within 30% of the values reported by Frank *et al.* (1977) using a packed-column method, indicating that there were no appreciable losses of analytes during the prolonged frozen archive storage period. Levels of PCB contamination were observed to have decreased from a lakewide average value of 136 ng/g to 43 ng/g in 1997. The 1997 75th percentiles were 102, 51, and 26 ng/g in the western, central, and eastern basins,

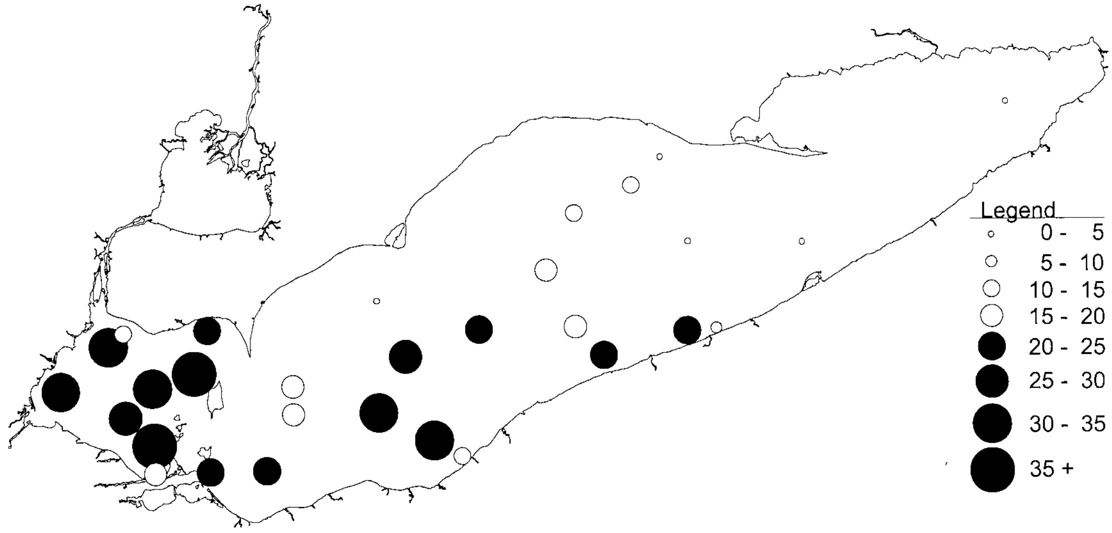

FIG. 13. Lake Erie surficial sediment dibenzo-*p*-dioxin and dibenzofuran concentrations (pg/g TEQ) in samples collected in 1997/98. The proposed Canadian Sediment Quality threshold effect level (TEL) is 0.85 pg/g and the probable effect level (PEL) is 21.5 pg/g.

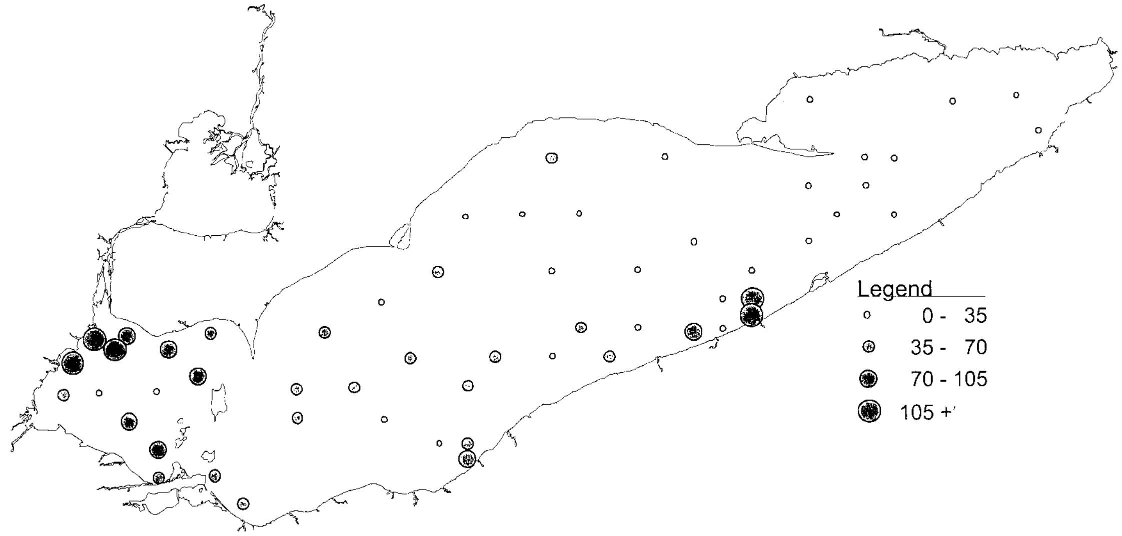

FIG. 14. Lake Erie surficial sediment polychlorinated biphenyl concentrations (ng/g) in samples collected in 1997/98. The Canadian Sediment Quality threshold effect level (TEL) is 34.1 ng/g and the probable effect level (PEL) is 277 ng/g. The Province of Ontario lowest effect level (LEL) is 70 ng/g.

respectively. Meanwhile, the 1971 75th percentiles were 343, 128, and 99 ng/g, respectively. None of the stations surveyed in 1997 exceeded the Canadian PEL for total PCBs, compared to three areas off the mouth of the Detroit River in 1971. In 1997, 30 sites, or 52% of the stations, exceeded the Canadian TEL and 13 sites (22%) exceeded the Ontario provincial LEL. Those sites exceeding the Ontario provincial LEL were in the western basin and southern portion of the central basin.

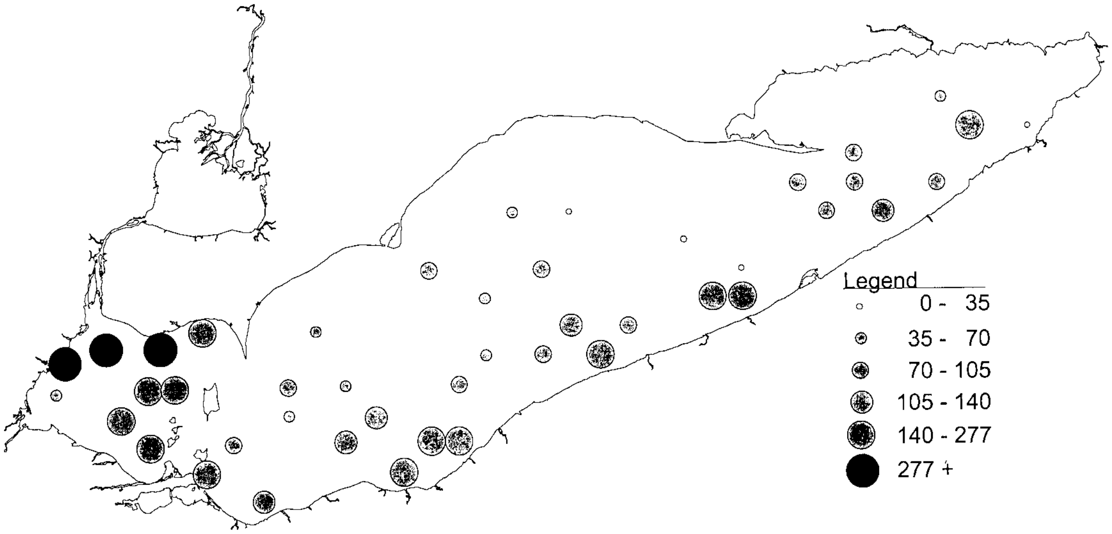

FIG. 15. Lake Erie surficial sediment polychlorinated biphenyl concentrations (ng/g) in samples collected in 1971. The Canadian Sediment Quality threshold effect level (TEL) is 34.1 ng/g and the probable effect level (PEL) is 277 ng/g. The Province of Ontario lowest effect level (LEL) is 70 ng/g.

Temporal trends in total PCB contamination were further defined through analyses of core samples (Fig. 16). The western basin (Station 1085) core profile was distinct; there was a marked increase in contamination from 30 cm to a depth of 20 cm representing the mid 1950s and 1960s. Consistent total PCB concentrations were detected to a depth of 6 cm where concentrations began a trend toward decreasing concentrations to the top of the core. The maximum total PCB contamination in the central basin (Station 1098) core occurred at the 17 to 18 cm interval. There was a bimodal distribution in the central basin core profile, and a trend toward decreasing total PCB contamination in the top 6 cm of the core similar to the western basin core. The eastern basin (Station 1040) core profile was more difficult to interpret; concentrations of total PCBs in this core were consistent with depth and representative of ambient background levels.

SUMMARY AND CONCLUSIONS

The observed spatial trends in sediment contamination in Lake Erie were similar for a number of compound classes including total PCBs, polychlorinated dibenzo-*p*-dioxin and dibenzofuran TEQs, total mercury, and metals. There was a trend toward increasing contamination from the eastern basin to the western basin, and from the northern portion of the central basin to the southern portion of the central basin. Presumably, these trends were influenced by industrial activities in the watersheds along major tributaries including the Detroit River, and areas along the southern shoreline. Other major influences in the observed trends may have included prevailing currents, sediment transport and deposition processes, open-lake disposal of dredged material, and remediation of contaminated areas. Frank *et al.* (1977) reported that trends in total PCB and total mercury contamination in the western basin were attributable to the outflow from the Detroit River in west bank, center bank, and east bank water masses. It was not possible to infer any such source information in this study because of the decreased sampling intensity compared to the 1971 study. However, Environment Canada monitoring of suspended sediment quality in Lake Erie has shown that the western basin continues to be subjected to active loadings of contaminants. The Detroit River has been identified as a primary vector for these contaminants, but potential loadings from other tributaries cannot be discounted. In addition, atmospheric deposition may have contributed to these loadings.

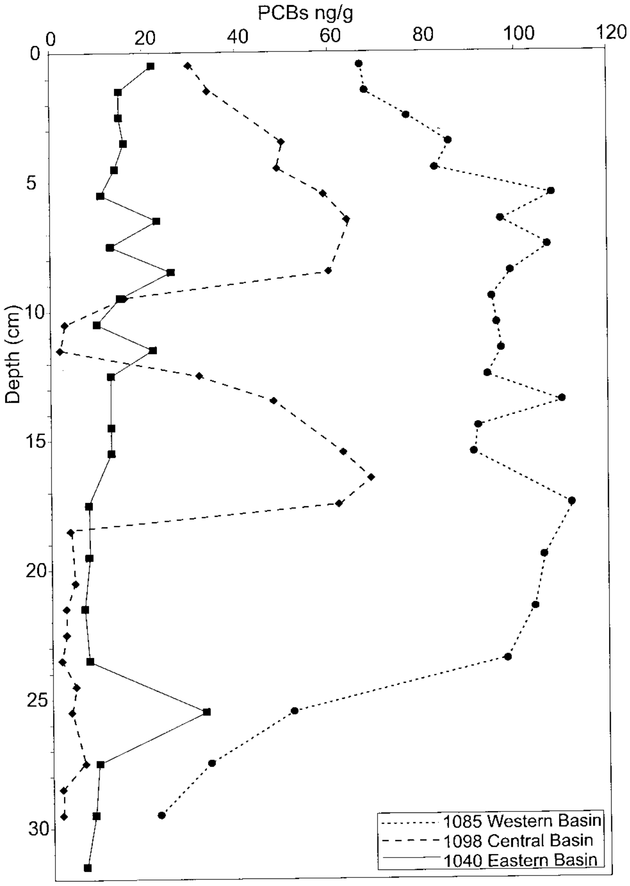

FIG. 16. Profiles of polychlorinated biphenyl levels (ng/g) in core samples from each of the three major Lake Erie basins.

Concentrations of contaminants in Lake Erie sediments have decreased significantly over the period 1971 to 1997/98. This trend is also evidenced by the profiles of core samples from the three major basins. Sediments in many areas of Lake Erie still exceeded the strictest Canadian and Province of Ontario Sediment Quality Guidelines as defined by the threshold effect level (TEL) or lowest effect level (LEL), respectively. However, exceedences of sediment guidelines describing contaminated environments (probable effect level [PEL] and severe effect level [SEL]) in 1997/98 were largely restricted to the western basin and the southern portion of the central basin. Exceedences of Canadian Sediment Quality probable effects guidelines (PEL) were most numerous for dioxins and furans (40%)

followed by mercury (6%). The Canadian threshold effects guideline (TEL) for PCBs and the Provincial lowest effect guideline (LEL) were exceeded at 52% and 22% of the sites, respectively. The pollutants identified as exceeding various guidelines, mercury, PCBs, and dioxins and furans, are responsible for the fish consumption advisories in Lake Erie.

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