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Estimating the Spatial Distribution of sediment Contamination in the lower great lakes.

BY:

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Estimating the Spatial Distribution of Sediment Contamination in the Lower Great Lakes

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Abstract

Lake Erie and Lake Ontario are located at the lower end of the Great Lakes system. Both have experienced considerable water and sediment contamination of over the last 150 years due to pollutants that enter via airborne and upstream pathways in addition to those that enter through each lake's drainage basin. Improvements in some key contaminant concentrations have recently been observed however large areas within both lakes still exceed Canadian sediment quality guidelines. Mercury, Lead, Polychlorinated Biphenyls, and Hexachlorobenzene are contaminants that can cause significant ecosystem damage. Estimates of the spatial distribution of these contaminants were derived using a GIS-based kriging technique. Initially, statistically valid results were obtained for three of four contaminants in Lake Erie and two of four in Lake Ontario. Suitable concentration estimates were subsequently achieved for all contaminants following log-normal transformation kriging analyses. In general, lower levels of sediment contamination were found in Lake Erie. Substantial portions of the lake are under both the Probable Effect Level (PEL) and the Threshold Effect Level (TEL), which relate to the severity of adverse biological effects that may be expected. Higher contamination levels were observed in Lake Ontario which can in part be explained by the bathymetry and current circulation patterns within the lake.

Key Words

Spatial distribution, interpolation, kriging, log-normal, sediment contamination

Introduction

The Great Lakes of North America extend 1200 kilometres from west to east and their surrounding area is home to approximately one quarter of Canada's population and more than one tenth of the United State's population (U.S. EPA 1995). The lakes together with their connecting rivers/canals provide water for industrial production and a wide range of other

consumptive uses including drinking water. They also function as transportation routes for natural resources and manufactured goods and additionally provide a source for hydropower generation. Furthermore, the lakes are utilized for recreational activities including swimming, fishing, and boating.

Some of the world's largest concentrations of industrial activity take place in the Great Lakes basin. Production is particularly concentrated in shoreline areas and amounts to 7% of the total U.S. production. The area is equally important for farming, supporting approximately 25% of the Canadian agricultural output (U.S. EPA 1995). The Canadian and American governments have recognized the need to respond to pollution concerns within the Great Lakes basin. In 1987, they signed the amended Great Lakes Water Quality Agreement. Among the recommendations in the agreement was the creation of a Lakewide Management Plan for each lake, adopting an ecosystem approach to address environmental issues (Lake Erie Lakewide Management Plan 2000; Forsythe 2004).

Industrialization and urbanization in the Great Lakes Basin have brought a wide range of problems (Forsythe 2004). Many industries located on water bodies to ease the transportation of goods. Untreated effluent was often discharged directly into waterways and leachate from disposal sites remains another source of contamination. Urban areas also discharged unprocessed municipal wastes into the lakes (U.S. EPA 1995). New chemicals were developed for agricultural purposes in part to increase production so that rapidly growing urban areas could be supplied. These chemicals were developed to control pests and provide fertilizer for the land. Epstein (2002) states that with the increase of industry and the boom in the production of synthetic organic chemicals and metals since the 1940's, a slow contamination throughout the basin has begun and indications of dangerous and substantial

levels of toxicity have surfaced. Runoff containing these substances as well as many other toxic pollutants such as trace metals has had many negative effects on the ecosystem (Forsythe 2004). Small particles in the water are very efficient at picking up certain types of these pollutants and holding them on their surface. As these chemicals are bound to the particles, they make their way to the bottom of the lakes and rivers and settle there. The combination of many of these polluted particles makes up what is known as contaminated sediment (Ashworth 1986). In addition, this toxic sediment can be re-suspended through the processes of harbour dredging, shipping and navigating, wind and wave action caused by storms, and biotic disturbances which can make it more noxious (U.S. EPA 1995). The consequences of utilizing some of these chemicals has led to the banning of their further use, while others have been phased out.

Ouyang et al. (2003a) state that sediment contamination may pose a significant hazard to aquatic life. As a result of sediment contamination, water quality is reduced and subsequently, the population of fish and wildlife is jeopardized. Additionally, human health and development opportunities suffer (Currie 1994). For example, it has been shown that the build-up of contaminants in top predators is magnified due to biological accumulation, the increase in concentrations of certain dangerous contaminants stored in the body of the animal. This contamination has been linked to genetic deformities in cormorants such as crossbill, thinning of osprey and herring gull eggshells causing a decline in birth rates, and tumours in top predatory fish such as the sauger (U.S. EPA 1995). An additional form of pollution enters the water system from the atmosphere directly through precipitation. This is especially important to take into account due to the large area of the Great Lakes basin and the prevailing annual wind patterns which act to bring industrial/manufacturing and coal-fired power generation emissions into the area. Unfortunately, due to a very small outflow of

approximately 1% per year, the increasing levels of pollutants being input to the Great Lakes far exceed the level of pollutants which are naturally escaping from them (U.S. EPA 1995).

Pollutants can remain in the environment for very long periods of time and their presence, even in minute concentrations, has the ability to have negative consequences on ecosystem health (Jakubek and Forsythe 2003). An example of chemical persistence in sediments can be found in the work of Ouyang et al. (2003a) in Florida. High DDT concentrations were found at the north end of the Ortega River and near the junction of the Cedar and Ortega Rivers in the upper 0.5 m of the sediments, indicating that the top layer of sediment was enriched with DDT although use of this chlorinated compound was banned in 1972. The study of contaminated sediments is one method to obtain an indication of water quality. The results can lead to assessment, management, remediation, and restoration efforts in areas of concern. More specifically, the measurability of sediment chemistry makes it possible to create guidelines and threshold levels within ecosystems and can lead to proper regulation of the waterways to ensure the health of the ecosystem (Crane and MacDonald 2003). Guidelines have been developed with respect to contaminant concentrations by the Canadian federal government which specifies the Threshold Effect Level (TEL) and Probable Effect Level (PEL) for sediment contamination. The TEL refers to the concentration below which adverse biological effects are expected to occur rarely, while the PEL defines the level above which adverse effects are expected to occur frequently (CCME 1999). These are outlined for the contaminants examined in this research in Table 1.

Table 1: Selected Contaminants and Federal Guidelines (Source: after CCME 1999)

Contaminant	TEL	PEL

Mercury	0.17 µg/g	0.486 µg/g
Lead	35 µg/g	91.3 µg/g
Polychlorinated Biphenyls (PCBs)	34.1 ng/g	277 ng/g
Hexachlorobenzene (HCB)	20 ng/g	480 ng/g

Kriging

The methods for interpolating spatial data can be divided into deterministic and probabilistic classes. Deterministic methods have a mathematical development based on assumptions about the functional form of the interpolator (e.g., inverse distance weighting). Probabilistic methods have a foundation in statistical theory and assume a statistical model for the data. When probabilistic methods are used for interpolation, they are referred to as methods for spatial prediction. These predictors have standard errors that quantify the uncertainty associated with the predicted or interpolated values (Krivoruchko and Gotway 2004).

If the data are Gaussian, the best predictor, one that minimizes the prediction mean-squared error, is a linear predictor (i.e., a linear combination of data values). For other distributions, the best predictor is not linear in the data. Thus, ordinary kriging is optimal for Gaussian data only (Krivoruchko and Gotway 2004). Cross validation is a general procedure that checks the compatibility between a set of data and its structural model (ASTM 1996 as found in Ouyang et al. 2003b). It is a simple way to compare various assumptions either about the model (e.g., the type of variogram and its parameters, the size of the kriging neighbourhood) or about the data (e.g., values that do not fit their neighbourhood like outliers or point wise anomalies). In the cross validation procedure, each sample value C at a location x is removed in turn from the data set and a value C^* at that location is estimated using the $n - 1$ samples (Wackernagel 1995 as found in Ouyang et al. 2003b). The difference between the measured value (C) and the cross validation estimated value (C^*) is the estimation error ($C -$

C^*), which gives an indication on how well the data value fits into the neighbourhood of the surrounding data values. If the average of the cross validation errors is not far from zero, one can say that there is no apparent bias, while a significant negative or positive average error can represent, respectively, systematic overestimation or underestimation (Osburn 2000 as found in Ouyang et al. 2003b).

The ordinary kriging predictor is a linear predictor, meaning that prediction at any location is obtained as a weighted average of the neighbouring data. Ordinary kriging assumes a constant, but unknown mean and estimates the mean value as a constant in the searching neighbourhood. Thus, this approach models a spatial surface in deviations from a constant mean, where the deviations are spatially correlated. Even though the assumption of a constant mean is rather simple, the modeled surfaces can be quite complex (Krivoruchko and Gotway 2004); and if the pattern of spatial continuity of the data can be described visually using a variogram model, it is difficult to improve on the estimates that can be derived in the kriging process (Isaaks and Srivastava 1989).

Kriging analysis has been used for analysis by numerous scientists and engineers in mining and petroleum explorations, environmental studies, and even agricultural practices (Ouyang et al. 2003b). Few however have applied this tool to the estimation large lake sediment contamination distribution. In this research, the Geostatistical Analyst extension of the ArcGIS software was used to interpolate the prediction surfaces.

Study Area

Lake Erie is the smallest of the Great Lakes (by volume) at 484 km^3, which can be attributed to a shallow average depth of 19 m, and a relatively small surface area of

approximately 25700 km^2. The main source of inflow to Lake Erie is from Lake Huron and Lake St. Clair via the St. Clair and Detroit Rivers, respectively. The drainage basin encompasses parts of the American States of Michigan, Ohio, Pennsylvania, New York, and Indiana, and the Canadian Province of Ontario (Forsythe 2004). The main outflow is to Lake Ontario via the Niagara River and the Welland Canal. The average water retention time is 2.6 years, shortest of all the Great Lakes (U.S. EPA 1995). Lake Erie is exposed to the greatest effects of agriculture and industrial processes due to the fertile soils which encompass it. In total, seventeen metropolitan areas exist along the shoreline and/or within its basin with populations of at least 50000 (U.S. EPA 1995). Lake Erie is a major sink for contaminants. The most heavily contaminated areas of the lake are found in the highly industrialized south western portion. There outflow from main tributaries such as the Detroit River enters the lake and this accounts for much of the pollution in the sediment throughout this region (Painter et al. 1994).

Lake Ontario is more than three times larger than Lake Erie (by volume) at 1640 km^3, although by surface area it is the smallest of the Great Lakes at 19010 km^2 (Lake Ontario Lakewide Management Plan 1998). It is fed primarily by the waters of Lake Erie through the Niagara River and Welland Canal. Its drainage basin covers portions of the Canadian Province of Ontario and the American State of New York. Approximately 93 percent of the water in Lake Ontario is drained to the northeast by the St. Lawrence River (Lake Ontario Lakewide Management Plan 1998). Lake Ontario has a water retention time of 6 years due to its higher volume of water when compared to Lake Erie. The northern Canadian shores are intensely developed with major urban industrial centres such as Hamilton and Toronto. Alternatively, the southern U.S. shores are much less urbanized (U.S. EPA 1995). The intensely populated and developed shores of Lake Ontario result in a much more

contaminated region. Many different toxins can be found in dangerous levels throughout the lake. Marvin et al. (2004) suggest that maps produced for mercury levels in the lake sediment give a good indication of generally where the rest of the pollutants reside.

Data

Field research was conducted in 1997-98 under the Environment Canada Great Lakes Sediment Assessment Program that provided sediment contamination data for 80 sites in Lake Erie (Fig. 1) and 71 sites in Lake Ontario (Fig. 2) using a mini-box core sampling procedure. Some specific sites were sampled in order to assess certain Lake Ontario Areas of Concern (AOCs) including Hamilton Harbour and the mouth of the Niagara River (Jakubek and Forsythe 2003). The top 3 cm of the sediment were sub-sampled from the mini-box core for the analyses of organic contaminants, metals, grain size, and nutrients. Samples for organic contaminant analyses were collected in solvent-washed glass jars. Samples for other characterizations were collected in either high-density polypropylene or Teflon jars. All samples were frozen for transport to the laboratory where contamination analyses were performed (Marvin et al. 2002). The data used in this research were sampled in order to undertake a comprehensive suite of analyses for assessment of contemporary sediment contamination relative to sediment quality guidelines (Marvin et al. 2002).
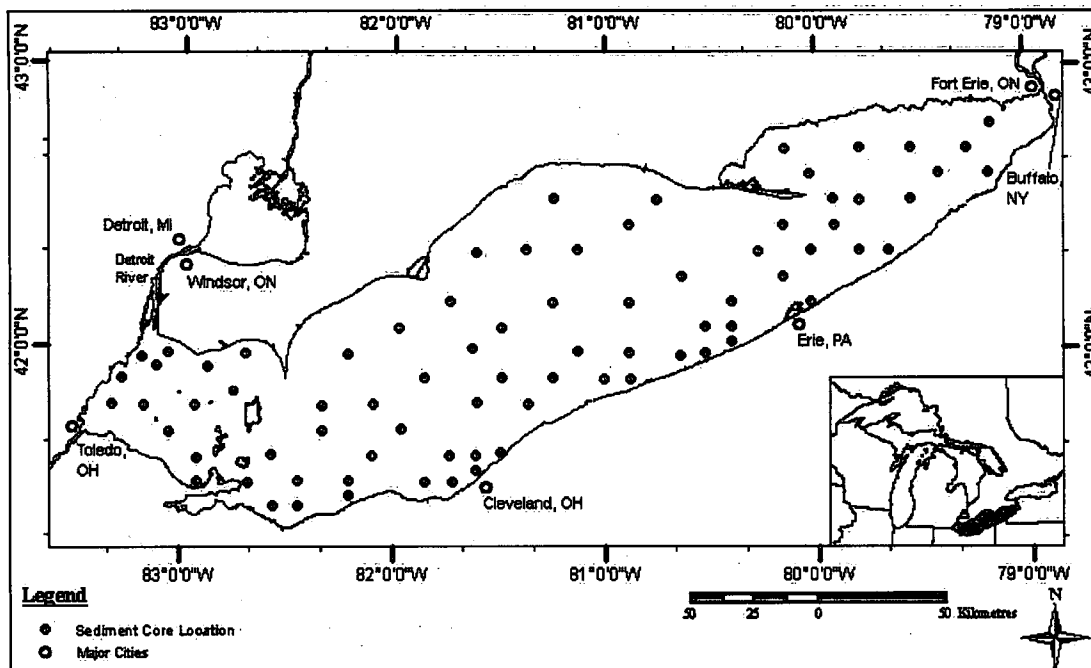
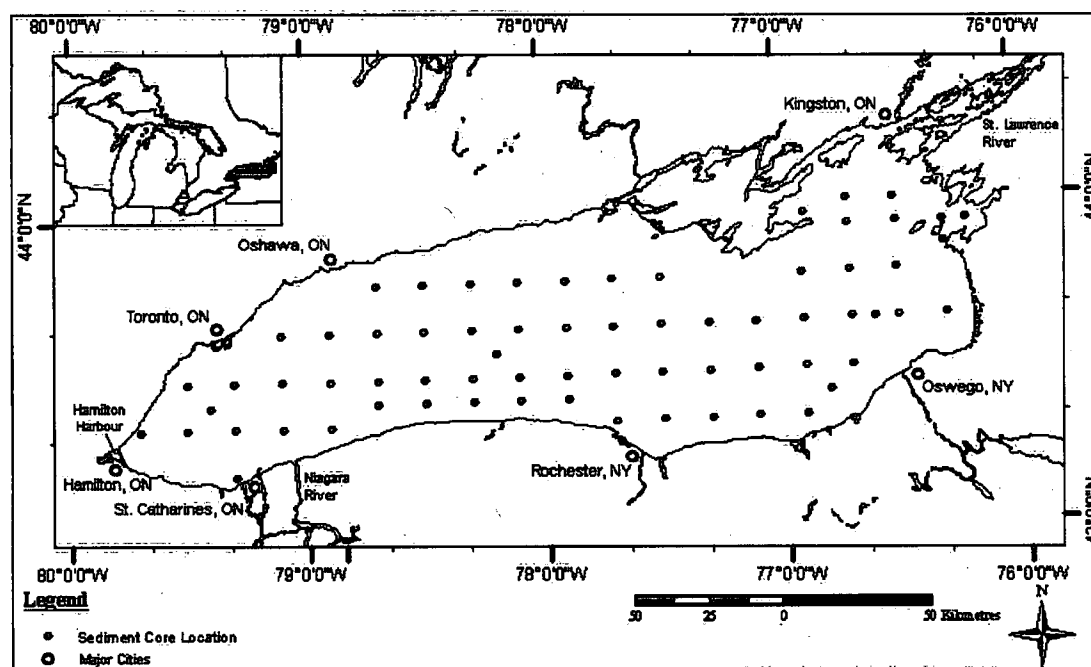**Fig. 1:** Sediment Core Locations and Major Cities for Lake Erie

Fig. 2: Sediment Core Locations and Major Cities for Lake Ontario

Basin Characteristics

Knowledge of lake bathymetry and circulation processes is important for understanding the patterns of sediment distribution within the Great Lakes. Studies relating to sediment characterization have been performed by Thomas et al. (1976) for Lake Erie and Thomas et al. (1972) for Lake Ontario. Sediments in both lakes are classified either as non-depositional, consisting of bedrock, glacial tills, and glacio-lacustrine clays, or depositional, which are comprised of fine-grained material including silts and clays that accumulate in deep water areas (Forsythe et al. 2004). The bathymetry of both lakes (Fig.3) is characterized by depositional areas that are interrupted by sills. Lake Erie is divided into three basins; the Pelee-Lorraine Sill separates the western basin from the central basin, and the central basin is separated from the eastern basin by the Long Point-Erie Sill. Lake Ontario is also divided into three major depositional areas; the Niagara Basin is separated from the Mississauga Basin by the Whitby-Olcott Sill, and the Scotch-Bonnet Sill separates the Mississauga Basin from the Rochester Basin (Forsythe et al. 2004). Outflow from the lake into the St. Lawrence River is characterized by minimal sediment transport from the main body of the lake due to the presence of a major topographical barrier, the Duck-Galloo Sill, which separates the Rochester and Kingston Basins (Thomas et al. 1972; Forsythe et al. 2004). Lake current circulation patterns (Fig. 4) were identified by Beletsky et al. (1999). The annual circulation pattern in Lake Erie is characterized by eastward flowing currents along the northern and southern shorelines with a westward flowing current in the middle of the lake. The majority of water circulation in Lake Ontario occurs in a counter-clockwise direction with a small clockwise gyre in the northwestern part of the lake (Beletsky et al. 1999).
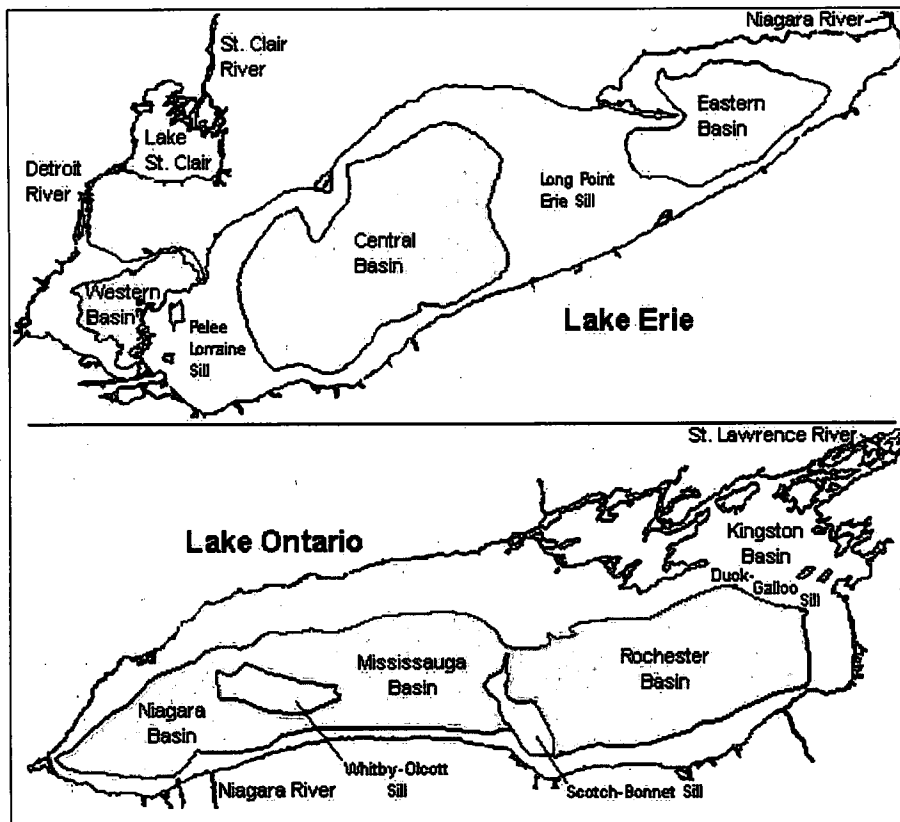
Fig. 3. Lakes Erie and Ontario Bathymetry including major depositional basins (Source: modified after Painter et al. 2001 and Marvin et al. 2003a respectively)
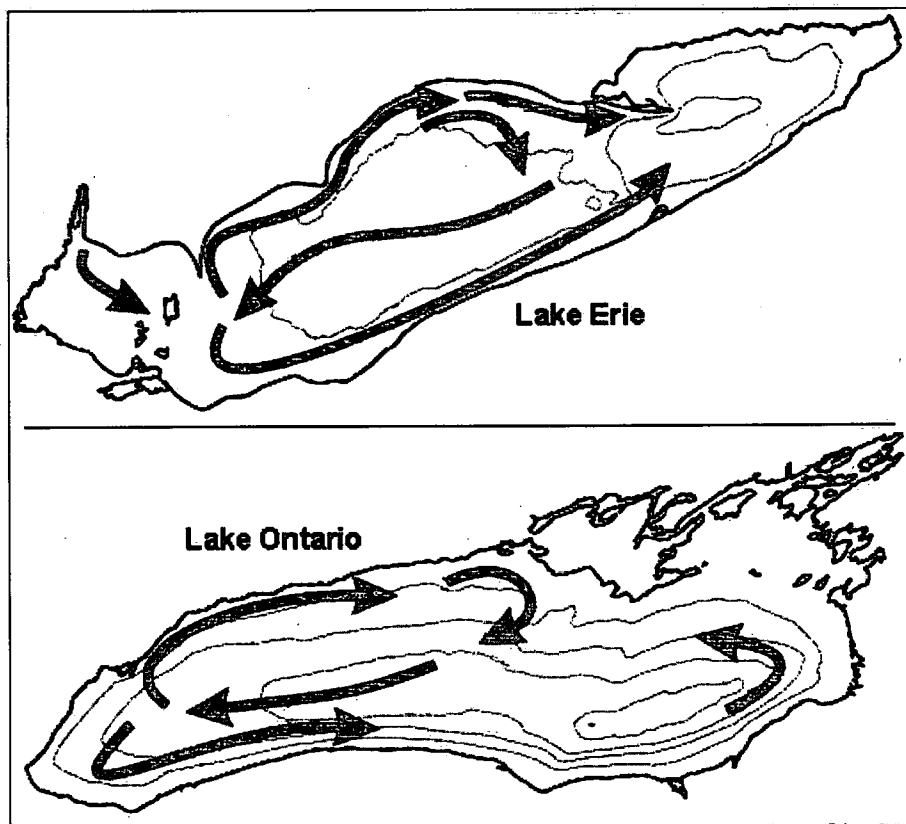
Fig. 4. Annual Circulation in Lake Erie (Isobaths at 20m and 50m) and Lake Ontario (Isobaths every 50m) - (Source: modified after Beletsky et al. 1999)

Analysis and Results

Data characteristics are important when trying to analyze spatial patterns. Tables 2 and 3 display the important characteristics of the datasets used in this research. Information is provided that relates to the data distributions and the levels of contamination in the sampling location data. The range of values in the datasets can also be compared to the standard deviation which is indicative of the variability among the sampling locations. It is interesting to note that no sediment core sampling sites exceeded the PEL for PCBs or HCB in either of the lakes.

Table 2. Data Characteristics for Lake Erie (Minimum, Maximum, Average, and Standard Deviation in μg/g for Mercury and Lead; ng/g for PCBs and HCB)

Contaminant	No. of Sites	No. <TEL	No. ≥TEL and <PEL	No. ≥PEL	Minimum	Maximum	Average	Standard Deviation
Mercury	55	28	23	4	0.006	0.940	0.202	0.185
Lead	55	22	32	1	4.979	104.273	43.084	23.425
PCBs	67	10	57	0	1.850	244.476	95.304	61.015
HCB	57	57	0	0	0.00	11.826	1.594	2.237

Table 3. Data Characteristics for Lake Ontario (Minimum, Maximum, Average, and Standard Deviation in μg/g for Mercury and Lead; ng/g for PCBs and HCB)

Contaminant	No. of Sites	No. <TEL	No. ≥TEL and <PEL	No. ≥PEL	Minimum	Maximum	Average	Standard Deviation
Mercury	71	12	17	42	0.015	1.138	0.586	0.353
Lead	68	16	26	26	5.169	196.617	71.812	41.908
PCBs	71	17	54	0	2.601	254.763	100.226	71.123
HCB	71	32	39	0	0.312	57.969	23.161	18.717

The cross validation procedure provides measures of accuracy for the predictions made using the ordinary kriging method (Johnston et al. 2001; Krivoruchko and Gotway 2004). The measures produced include the Mean Prediction Error (MPE), Average Standard Error (ASE), and Standardized Root-Mean-Squared Prediction Error (SRMSPE). Values calculated for these measures are documented for Lake Erie in Table 4 and Lake Ontario in Table 5. Statistically valid results should have MPE results near 0, ASE values that are <20 (otherwise predictions are straying quite far from the measured locations), and SRMSPE values approaching 1 (Jakubek and Forsythe 2003; Forsythe et al. 2004). If the SRMSPE is greater than 1, there is an underestimation of the variability of the predictions and if the SRMSPE is less than 1, overestimation of the variability is the result (Johnston et al. 2001; Forsythe et al. 2004).

Table 4: Kriging Cross Validation Results for Lake Erie

Contaminant	MPE	ASE	SRMSPE
Mercury	0.0006	0.144	1.102
Lead	0.4266	18.26	1.165
Polychlorinated biphenyls (PCBs)	0.1522	42.30	1.056
Hexachlorobenzene (HCB)	0.0122	2.115	0.917

Table 5: Kriging Cross Validation Results for Lake Ontario

Contaminant	MPE	ASE	SRMSPE
Mercury	0.0107	0.36	0.9474
Lead	1.3490	39.77	0.9331
Polychlorinated biphenyls (PCBs)	2.5720	72.86	0.9336
Hexachlorobenzene (HCB)	0.4687	14.64	0.9748

Mercury

The Lake Erie and Lake Ontario Lakewide Management Plans identify mercury as a critical pollutant (Lake Erie Lakewide Management Plan 2000; Lake Ontario Lakewide Management Plan 1998). Mercury is present in the environment but its concentrations are now well in excess of those expected from natural sources. The industries responsible for the majority mercury emissions are base metal smelting, coal power generation, hazardous and biomedical wastes, municipal solid waste and sewage sludge incineration (Canadian Council of Ministers of the Environment 2003). Pirrone et al. (1998) estimate that increasing mercury emissions from waste incineration account for up to 40% of current anthropogenic emissions to the atmosphere in North America. Mercury is still commonly used in batteries, medical and dental products, the electrical industry and thermometers (Jakubek and Forsythe 2003). Mercury continues to be a prevalent contaminant across the entire Great Lakes Basin, with the highest levels in the western basin of Lake Erie and the three major basins of Lake Ontario (Marvin et al. 2004). Mercury contamination in sediments of Lakes Erie and Ontario is primarily related to historical sources, including chlor-alkali production in the Detroit, St. Clair, and Niagara Rivers (Marvin et al. 2004). However, atmospheric deposition is now the predominant source of mercury (Pirrone et al. 1998) and, as a result, further declines in sediment contamination are expected (Forsythe et al. 2004).

The kriging results for Lake Erie (Fig. 5) are very good with ASE and SRMSPE values that are very close to the optimum. Areas of high contamination still exist and these are

mostly found directly downstream from the Detroit-Windsor area in the direction of prevailing lake currents. The eastward extension of the higher mercury concentrations along the southern shoreline is certainly related to lake currents and urban sources from the Cleveland, Ohio area.
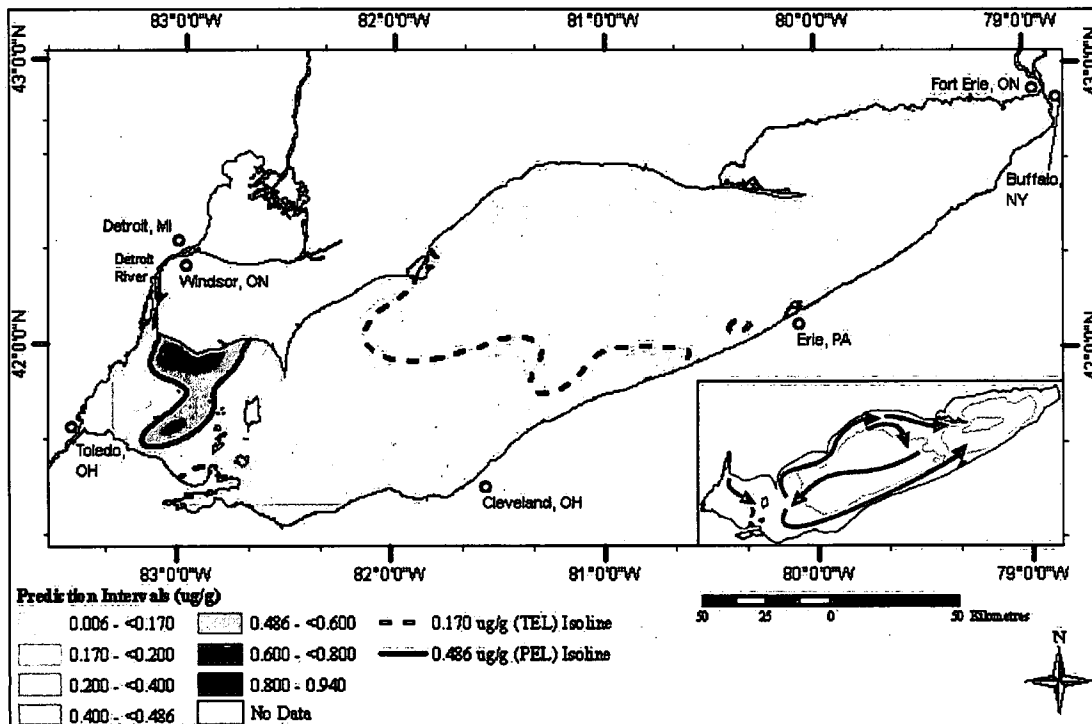

Fig. 5: Mercury Kriging Results for Lake Erie (Inset: Annual Circulation in Lake Erie - Isobaths at 20 m and 50 m - Source: modified after Beletsky et al. 1999)

Fig. 6 estimates the locations for the highest mercury concentrations in the central deep lake regions of Lake Ontario. The predicted surface produced very reliable cross validation results, which were relatively unbiased and rendered a low ASE value (0.36). Upstream sources certainly have a role in the estimated contaminant concentrations. The prevailing lake currents along the southern shoreline act to move sediment eastward in the direction of the Mississauga and Rochester basins. The PEL isoline corresponds very well with the Duck-Galloo Sill which has been identified in reducing sediment outflows from the lake (Thomas

et al. 1972). The higher concentration values in the western portion of the Niagara Basin may be influenced by the presence of two highly contaminated sampling locations in Hamilton Harbour, Ontario (Forsythe et al. 2004).
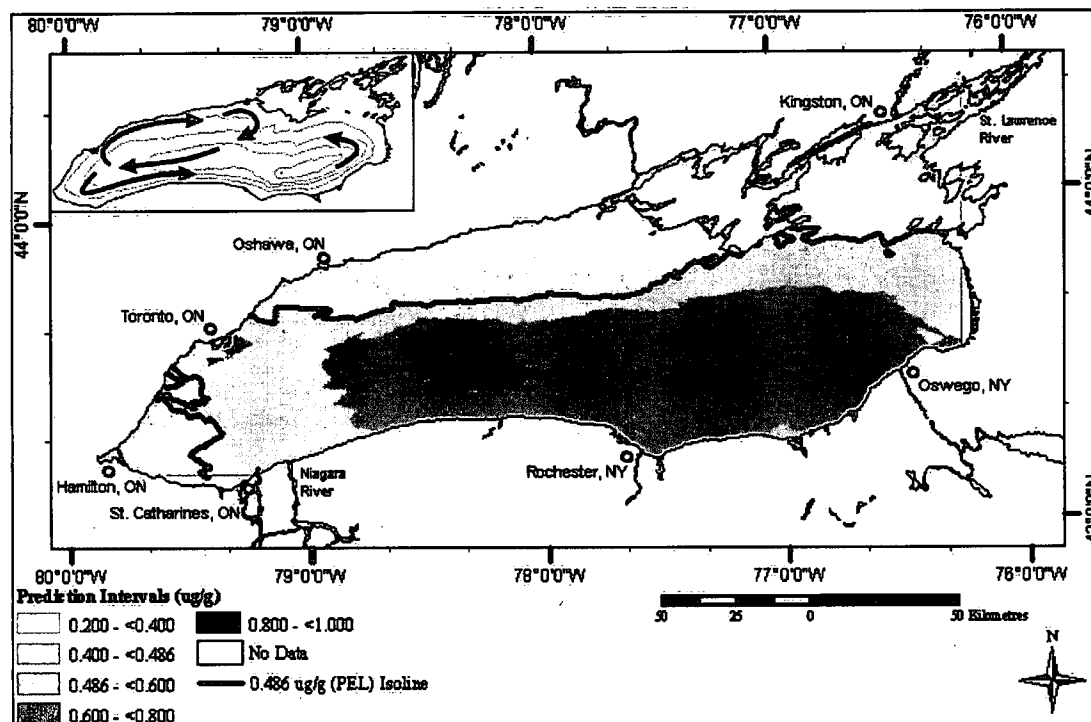

Fig. 6: Mercury Kriging Results for Lake Ontario (Inset: Annual Circulation in Lake Ontario - Isobaths every 50 m - Source: modified after Beletsky et al. 1999)

Lead

Lead is routinely detected in sediments of the Great Lakes as a result of its historically heavy use, primarily as an additive in gasoline. The move from leaded to unleaded gasoline in the 1980's has led to decreasing levels of lead in the environment. Presently, the main sources are non-ferrous metal production (34%), followed by steel manufacturing and waste disposal (27 and 25%, respectively), and coal combustion (10%) - (Pirrone and Keeler, 1996). The proximity of Lake Erie and Lake Ontario to industrial and agricultural areas makes it likely that point sources and runoff are also significant sources (Forsythe et al.

2004). Painter et al. (2001) indicate that the spatial distribution of lead in Lake Erie shows the highest concentrations in the western basin and in the southern area of the central basin, while Marvin et al. (2003a) state that the distribution in Lake Ontario is more consistent across the depositional basins.

The lead prediction surface for Lake Erie (Fig. 7) had acceptable cross validation results although the ASE value of 18.26 is slightly higher than desirable. Areas of higher concentrations were found in the south-central part of the lake near Cleveland. The high concentration pocket (>PEL) corresponds well to the single sampling location with a value greater than the PEL value of 0.486 µg/g.
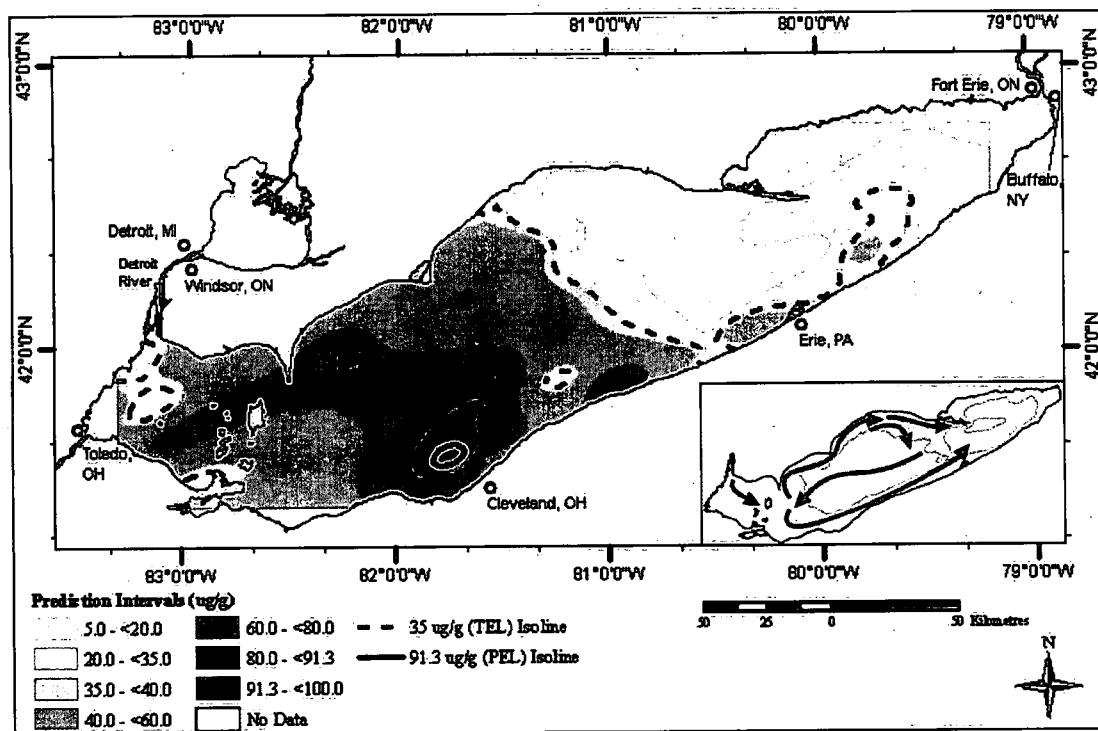

Fig. 7: Lead Kriging Results for Lake Erie (Inset: Annual Circulation in Lake Erie - Isobaths at 20 m and 50 m - Source: modified after Beletsky et al. 1999)

The prediction surface representing lead for Lake Ontario (Fig. 8) estimated the variability well with a SRMSPE value of 0.9331; however, it features an ASE value of 39.77.

Therefore the results should be interpreted with some caution as they are not statistically valid. Again a possible reason for these results is the location of two sediment sampling sites in Hamilton Harbour which may skew the results in the western part of the lake. The higher concentrations in the middle of the Mississauga Basin are related to lake currents and bathymetry which combine for increased deposition of sediments in this area.
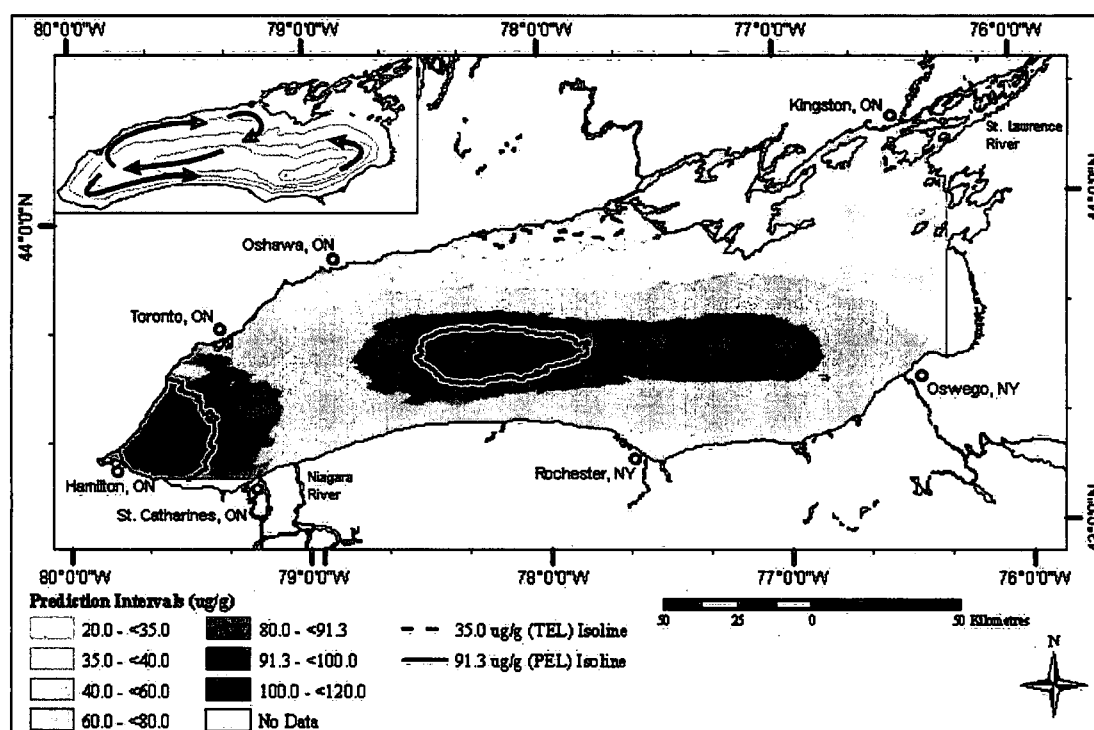

Fig. 8: Lead Kriging Results for Lake Ontario (Inset: Annual Circulation in Lake Ontario - Isobaths every 50 m - Source: modified after Beletsky et al. 1999)

Polychlorinated Biphenyls (PCBs)

The manufacturing of PCBs was banned in Canada and the U.S. in 1977 after scientific evidence revealed that they were the cause of environmental and human health problems (U.S. EPA 1995). In the 1960s, PCBs were found to be the cause of the death of thousands of birds in the Irish Sea and in Sweden, and 1200 people in Japan were poisoned by rice oil containing PCBs (Canadian Council of Resource and Environment Ministers 1986; Hodgson and Levi 1997). In 1929, the Monsanto Company began to produce PCBs commercially for

use as a cooling and insulating fluid for electrical equipment. They have also been used for a variety of other industrial purposes, including heat exchangers, plasticizers, hydraulic fluids and flame retardants. PCBs are still used in closed electrical systems, and can be found in landfills. Oliver and Bourbonniere (1985) found PCB concentrations in the western basin of Lake Erie to be much higher than in Lake St. Clair and Lake Huron, indicating major sources along the Huron-Erie corridor. Drouillard et al. (2003) revealed that an area downstream of the Trenton Channel contains 62% of the total PCB mass balance for the Detroit River system. This area is highly industrialized, with coal power generation, and steel and chemical production predominating (Marvin et al. 2003b). The sediments in this area consist of silts, which are vulnerable to resuspension and loadings to the western basin of Lake Erie during major storm events (Reitsma et al. 2003). Nettesheim (2003) states that PCBs exhibit a "strong urban effect," with atmospheric PCB concentrations higher in urban areas. The highest concentrations of PCBs in the air over the Great Lakes were found by McConnell et al. (1998) at the eastern and western extremes of Lake Erie, near Detroit and Buffalo, respectively. This indicates that local point source emissions to the air from industrial and urban areas are a significant source of PCBs through atmospheric deposition. PCBs are highly persistent; degrading very slowly by weathering and microbial processes, and have the ability to bioaccumulate in the food chain (Canadian Council of Resource and Environment Ministers 1986; Ontario Ministry of the Environment 1999).

The results for Lake Erie (Fig. 9) have a higher than desired ASE result (42.30), the MPE value of 0.1522 is also high; however the SRMSPE result of 1.056 is very close to normal. The observed patterns can be related to lake bathymetry, currents, and the proximity to urban areas. The plume along the southern shoreline eastward from Cleveland is in sharp contrast to the sparsely populated Canadian shoreline to the north although current and past

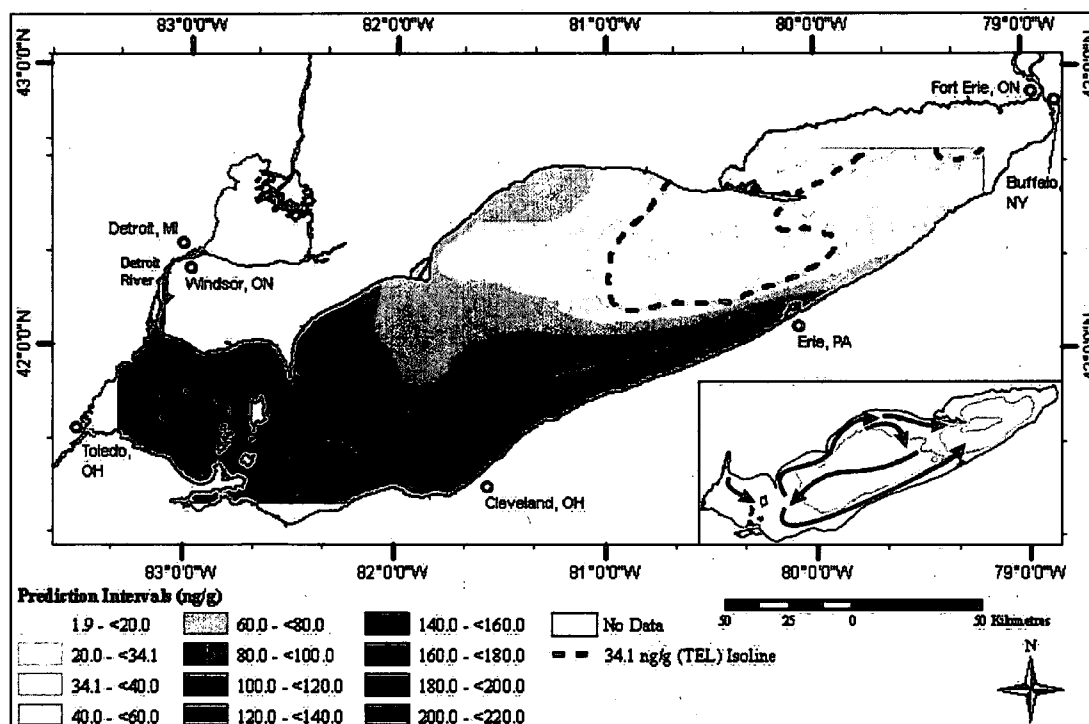runoff from agricultural land certainly does have a role in the higher than TEL concentrations found there.

Fig. 9: PCB Kriging Results for Lake Erie (Inset: Annual Circulation in Lake Erie - Isobaths at 20 m and 50 m - Source: modified after Beletsky et al. 1999)

PCBs were estimated to have high concentrations in the deep lake regions of Lake Ontario (Fig. 10). When the actual measured values are compared to the isobaths throughout the lake, the predictions seem reasonable, but high ASE results are the reason to suspect inconsistent outcomes from the kriging analysis. A possible explanation for these cross-validation results is a biased prediction supported by a MPE value of 2.572. The majority of the lake is estimated as having values higher than the TEL but lower than the PEL which corresponds well with the original data points. The large standard deviation of 71.123 does however adversely influence the results as it is indicative of a high amount of variation in the dataset (Forsythe et al. 2004).
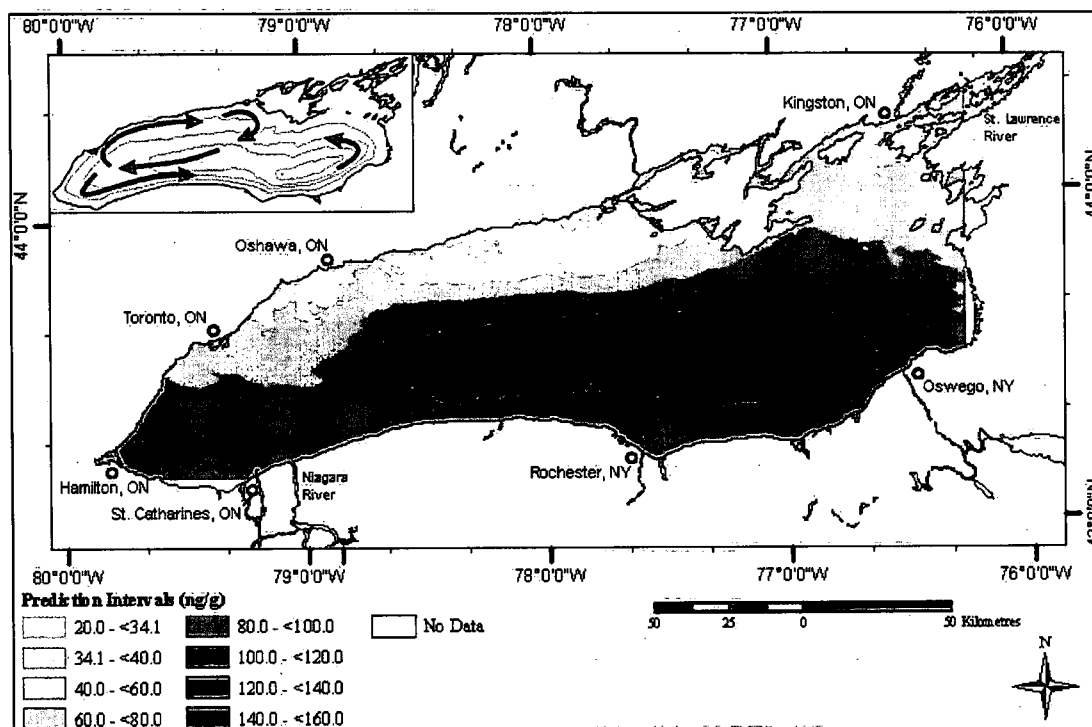
Prediction Intervals (ng/g)

☐ 20.0 - <34.1	▨ 80.0 - <100.0
☐ 34.1 - <40.0	■ 100.0 - <120.0
☐ 40.0 - <60.0	■ 120.0 - <140.0
▨ 60.0 - <80.0	■ 140.0 - <160.0

☐ No Data

Fig. 10: PCB Kriging Results for Lake Ontario (Inset: Annual Circulation in Lake Ontario - Isobaths every 50 m - Source: modified after Beletsky et al. 1999)

Hexachlorobenzene

Hexachlorobenzene (HCB) occurs as a by-product of several chlorination processes, in particular chlor-alkali plants, during the manufacturing of solvents, and in the production of pesticides (Jakubek and Forsythe 2003). It can also be produced in the combustion of chlorinated organic chemicals, chlorine manufacturing, metal manufacturing, and the incineration of municipal waste. Until 1984, HCB was used as a pesticide. Other uses include the manufacture of fireworks, ammunition, and synthetic rubber. HCB is resistant to degradation, and adsorbs strongly in soil and sediment (Agency for Toxic Substances and Disease Registry 2002).

The cross validation results for Lake Erie were very good and the predicted surface (Fig. 11) indicates that concentrations of HCB are low throughout the lake. Slightly higher

concentrations (although well below the TEL) were found in the western basin which can be related to transport from the Detroit River in the direction of prevailing lake currents.
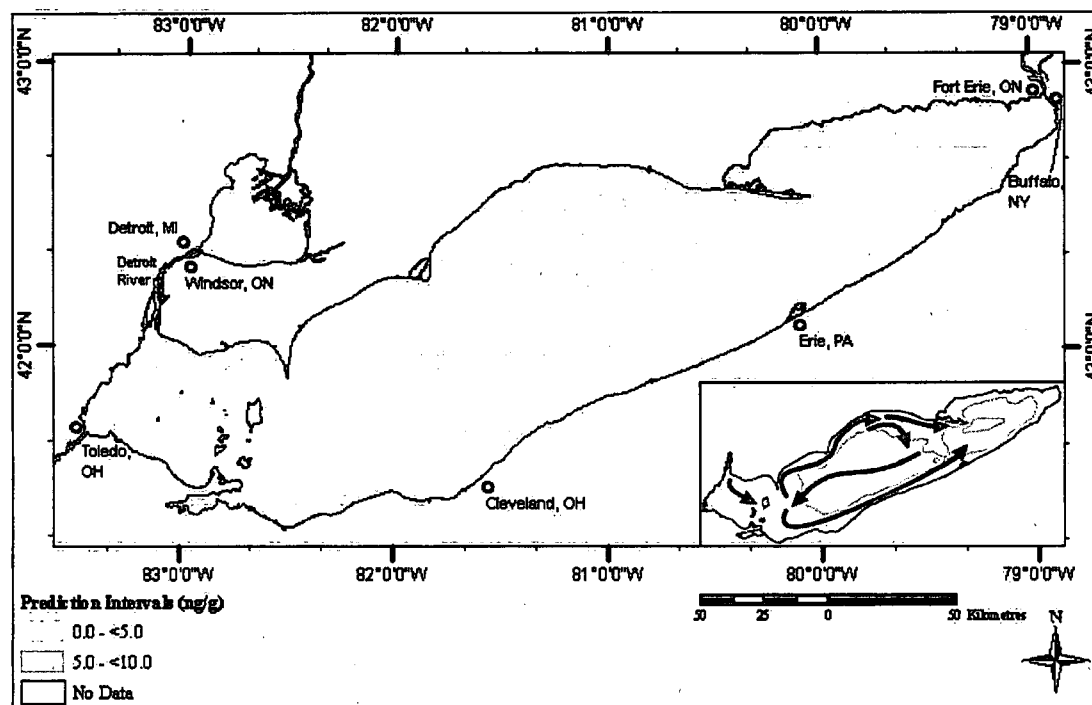

Fig. 11: HCB Kriging Results for Lake Erie (Inset: Annual Circulation in Lake Erie - Isobaths at 20 m and 50 m - Source: modified after Beletsky et al. 1999)

The predicted surface for Lake Ontario HCB (Fig. 12) contrasts sharply with that of Lake Erie. Higher concentrations are again found in the deep lake basins. The prediction surface near perfectly estimated the variability and featured a SRMSPE value of 0.9748. It would appear that large amounts of HCB have migrated from upstream sources such as Lake Erie and settled in Lake Ontario.
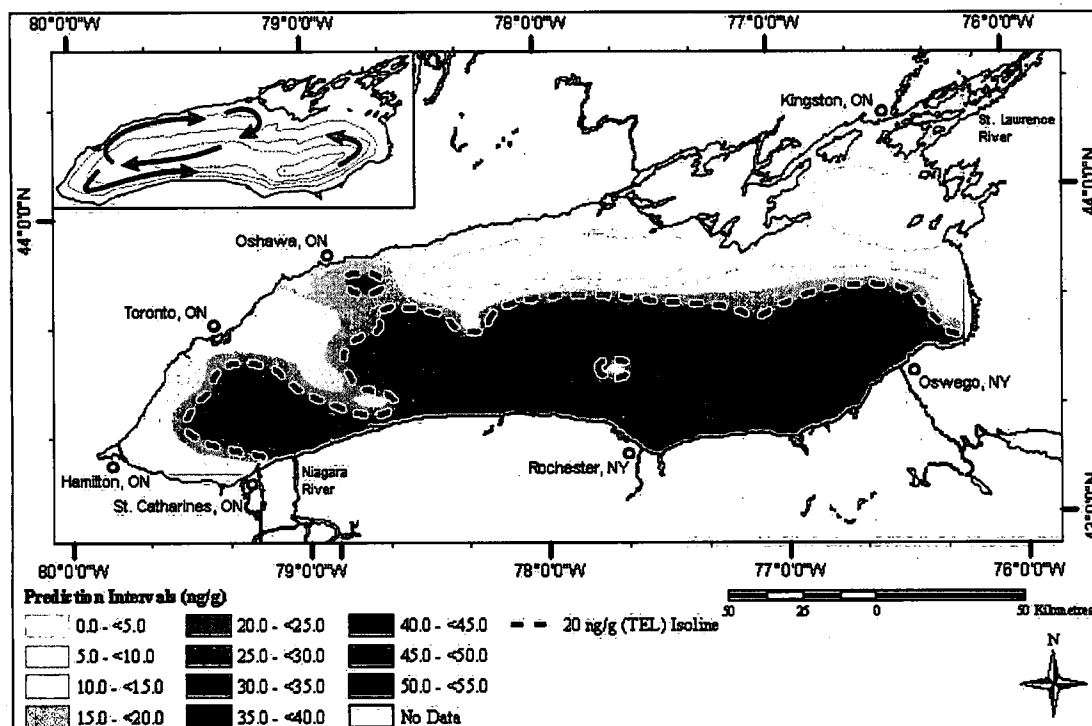
Fig. 12: HCB Kriging Results for Lake Ontario (Inset: Annual Circulation in Lake Ontario - Isobaths every 50 m - Source: modified after Beletsky et al. 1999)

Log-Normal Transformation

To improve upon the results of this research, log-normal procedures were performed on the non-statistically valid results for lead and PCBs. Ouyang et al. (2003b) state that in general, a normal distribution requirement in kriging analysis may not be so critical, but when the data set is too skewed or contains outliers, some kind of transformation is needed. If the data are not Gaussian, statistical transformations (e.g., log, Box-Cox) can be used to transform them so that they do follow a Gaussian distribution. However, with the exception of the log-transform, it is not possible to directly back transform the data to the original scale without bias (Krivoruchko and Gotway 2004).

The log-normalized cross validation statistics (Tables 6 and 7) for lead and PCB's for both lakes are excellent indicating that the parameters used for creating the models are satisfactory

and estimate the surfaces very well. The MPE, ASE, and SRMSPE statistics are all within acceptable limits.

Table 6: Log Transformed Kriging Cross Validation Results for Lake Erie

Contaminant	MPE	ASE	SRMSPE
Lead	0.0115	0.236	1.059
Polychlorinated biphenyls (PCBs)	0.0048	0.269	1.005

Table 7: Log Transformed Kriging Cross Validation Results for Lake Ontario

Contaminant	MPE	ASE	SRMSPE
Lead	0.0153	0.311	0.9831
Polychlorinated biphenyls (PCBs)	0.0131	0.530	0.9920

Lead (Log-normal)

Although the initial kriging results for Lake Erie lead were with the statistical limits of the models, a log-normal analysis was performed. The results (Fig. 13) are similar in pattern to the original (Fig. 7) with the exception that the pocket of higher than PEL concentrations has disappeared. Additionally, larger portions of the lake also have <TEL concentrations than were determined in the non-logged kriging estimate. There was only one original data point with a value (0.586 μg/g) that was slightly above the PEL of 0.486 μg/g and the SRMSPE of 1.059 indicates that the estimation may be slightly underestimated.
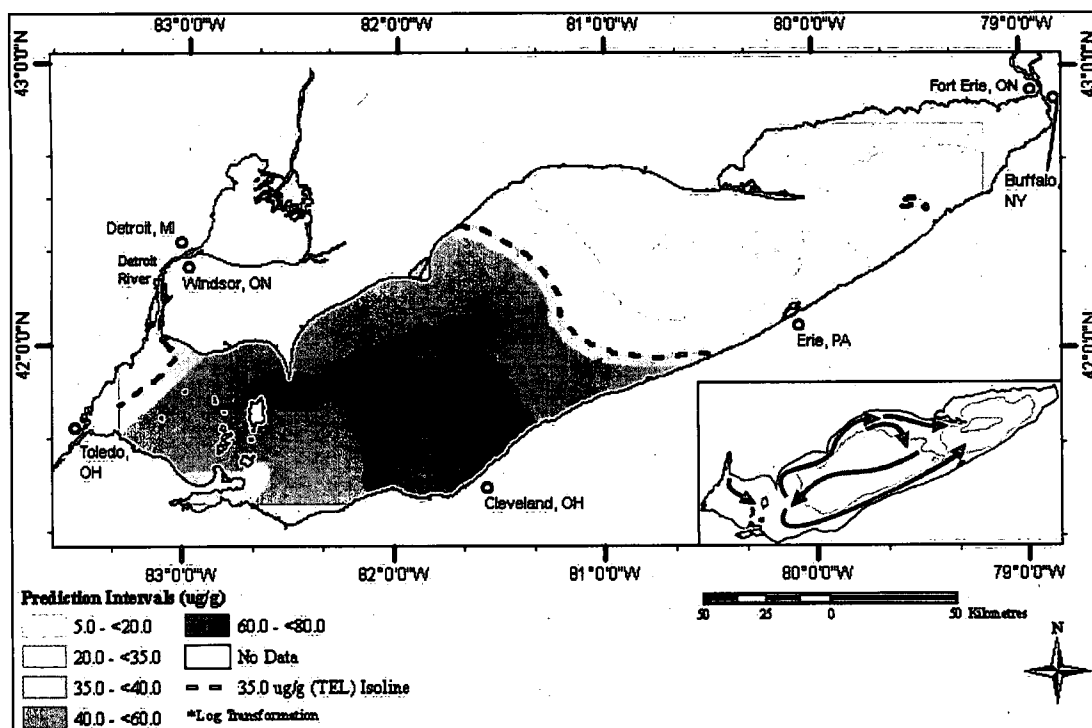
Fig. 13: Lead Kriging Results (log transformation) for Lake Erie (Inset: Annual Circulation in Lake Erie - Isobaths at 20 m and 50 m - Source: modified after Beletsky et al. 1999)

Statistically the log-normal lead estimates for Lake Ontario (Fig. 14) are a great improvement on the non-logged surface. The predictions are however slightly overestimating the values as indicated by the SRMSPE value of 0.9831. This however is a great improvement on the former value of 0.9331. The major differences occur in the areas found to be above the PEL (all three deep lake basins and in the vicinity of Hamilton Harbour) and in the expansion of areas that are below the TEL. The <TEL regions along the northern shoreline of the lake are much larger which can be related to the deposition of lead in the deep lake basins through lake circulation patterns and the low level of industrial production in this area. The location of sills on the lake bottom is also very evident in the overall results.
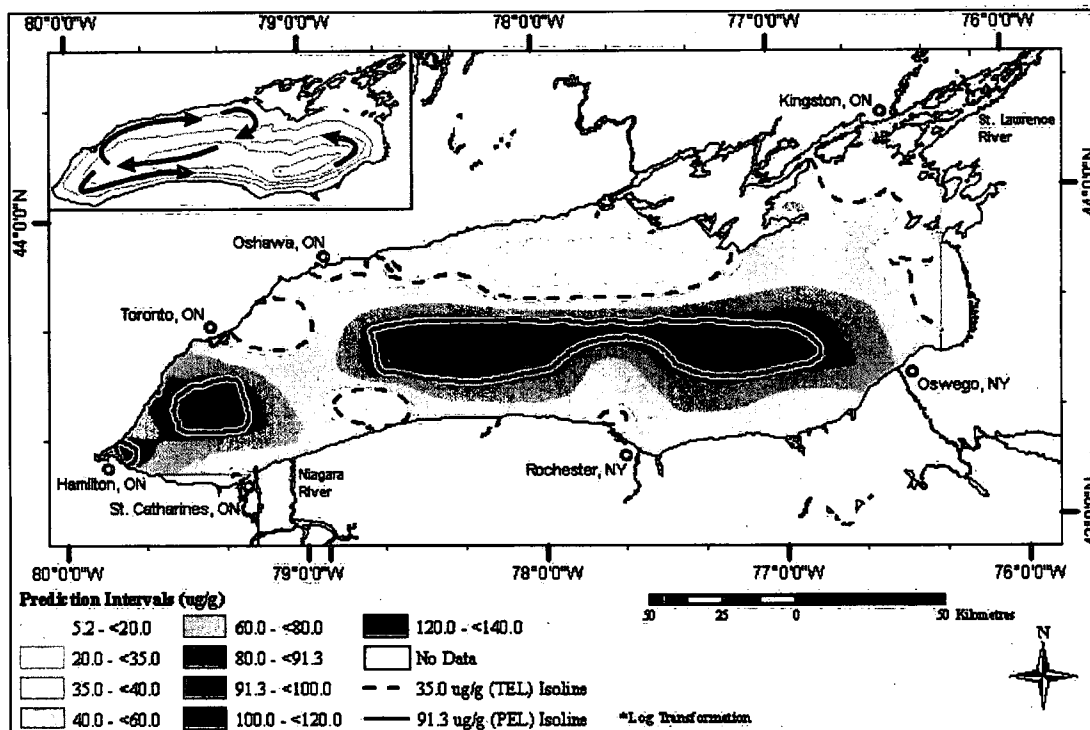
Fig. 14: Lead Kriging Results (log transformation) for Lake Ontario (Inset: Annual Circulation in Lake Ontario - Isobaths every 50 m - Source: modified after Beletsky et al. 1999)

PCBs (Log-normal)

The log-normal PCB results for Lake Erie (Fig. 15) are similar in pattern to the statistically non-valid results (Fig. 9) however overall concentration levels are lower. The SRMSPE value of 1.005 is very close to optimal. Higher concentrations are found in proximity to major urban centres and improved values (<TEL) are found in areas where currents and land use combine to produce lower concentrations.
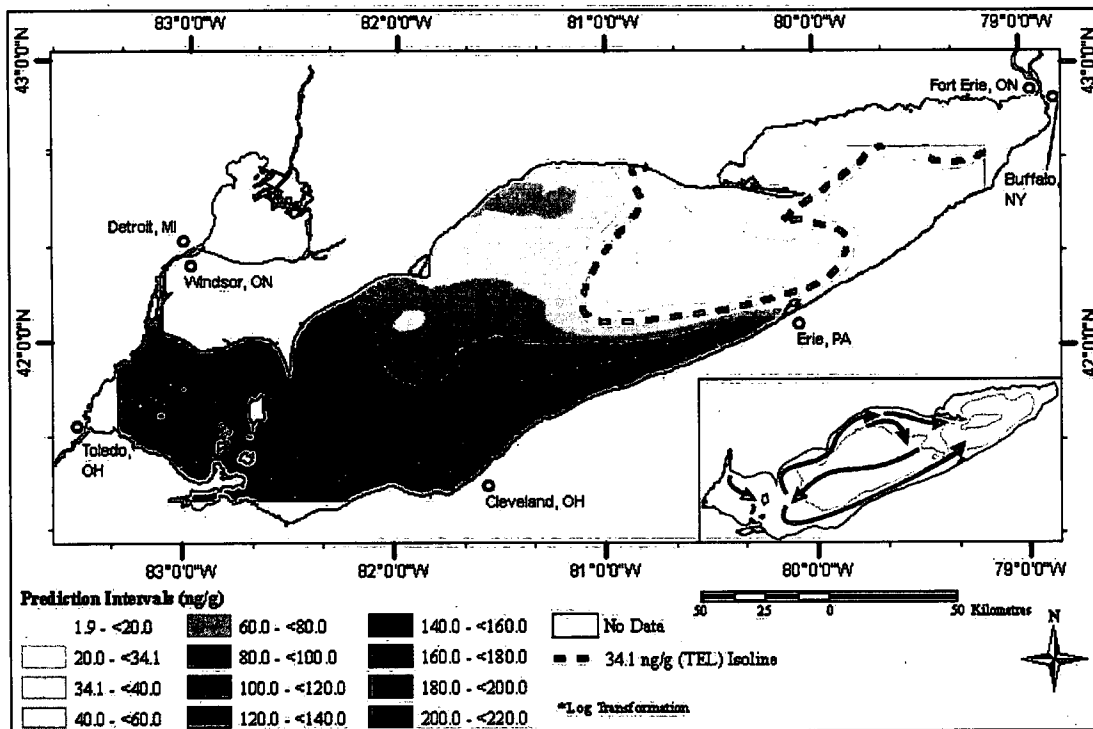
Fig. 15: PCB Kriging Results (log transformation) for Lake Erie (Inset: Annual Circulation in Lake Erie - Isobaths at 20 m and 50 m - Source: modified after Beletsky et al. 1999)

The bathymetry of Lake Ontario appears to have a great influence on the log-normalized PCB results (Fig. 16). Higher concentrations are found in the deep lake basins, with lower levels found in sill areas on the lake bottom. The SRMSPE value of 0.9920 is very close to optimum. Less than TEL values are found along the northern shoreline away from large population centres and where sediments from the Niagara River are not circulated to a great extent.
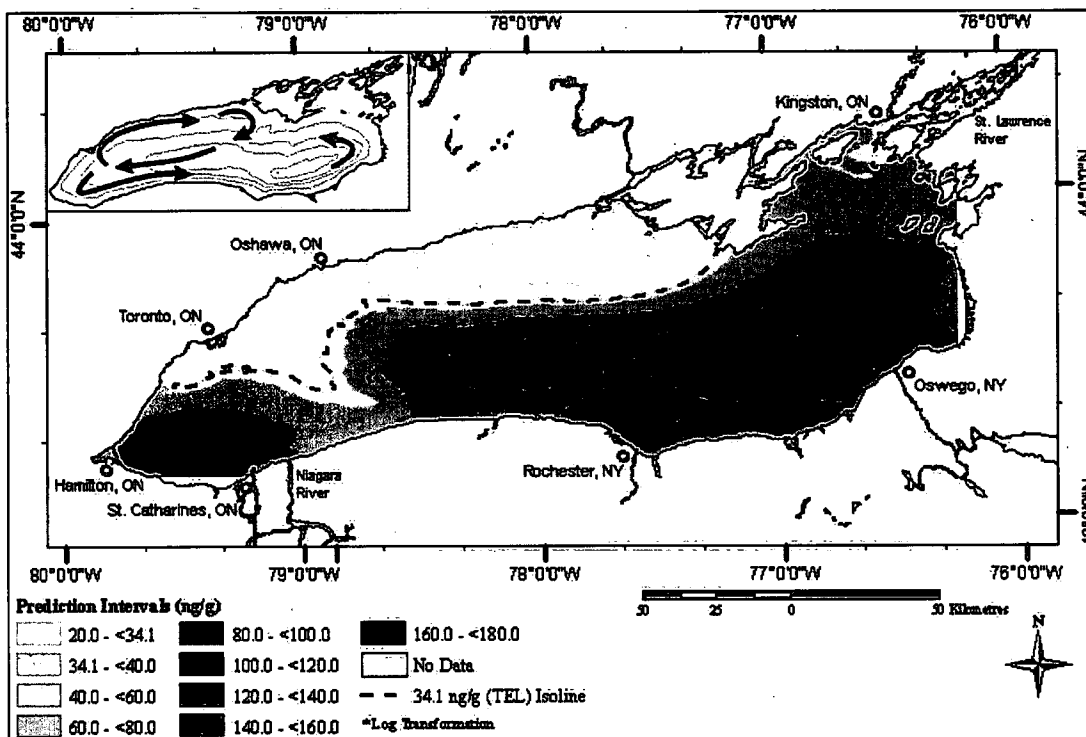
Prediction Intervals (ng/g)

☐ 20.0 - <34.1	■ 80.0 - <100.0	■ 160.0 - <180.0	
☐ 34.1 - <40.0	■ 100.0 - <120.0	☐ No Data	
☐ 40.0 - <60.0	■ 120.0 - <140.0	- - 34.1 ng/g (TEL) Isoline	
▨ 60.0 - <80.0	■ 140.0 - <160.0	*Log Transformation	

Fig. 16: PCB Kriging Results (log transformation) for Lake Ontario (Inset: Annual Circulation in Lake Ontario - Isobaths every 50 m - Source: modified after Beletsky et al. 1999)

Conclusion

Human activities have certainly had a great influence of the types and amounts of contaminants that have entered the Great Lakes system in both historical and present times. The estimated patterns of sediment contamination that were developed in this research can be related to the location of urban/industrial areas, lake currents, and lake bathymetry. Measures including the banning of some chemicals such as PCBs have had a positive effect on the amount contamination present in lake sediments. The longevity and persistence of these substances does however necessitate that monitoring and remediation measures be continued.

The kriging technique allows for improved estimates of the level of sediment contamination to be obtained in comparison with point measurements alone. The lakewide distributions allow for the derivation of areal estimates. Through the use of cross validation

techniques, a statistical validation of the surfaces can be produced. The implementation of log-normal data conversion enables (when necessary) the production of statistically valid contamination surfaces which can be back transformed to the original values after processing.

The kriging analyses have led to an improved understanding of the Lake Erie and Ontario contaminant data sets. The longer water retention time and greater depth of Lake Ontario together with lake bathymetry can be utilized in explaining the contamination estimates. In addition, the lake continues to receive contaminated sediments from upstream sources including Lake Erie. The location of urban and industrial areas is also important in providing reasons for the results in both lakes. Statistically valid results were obtained for all contaminants in both lakes either through normal ordinary kriging or after the implementation of log-normal data transformation procedures.

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Table 1: Selected Contaminants and Federal Guidelines (Source: after CCME 1999)

Contaminant	TEL	PEL
Mercury	0.17 µg/g	0.486 µg/g
Lead	35 µg/g	91.3 µg/g
Polychlorinated Biphenyls (PCBs)	34.1 ng/g	277 ng/g
Hexachlorobenzene (HCB)	20 ng/g	480 ng/g

Table 2. Data Characteristics for Lake Erie (Minimum, Maximum, Average, and Standard Deviation in µg/g for Mercury and Lead; ng/g for PCBs and HCB)

Contaminant	No. of Sites	No. <TEL	No. ≥TEL and <PEL	No. ≥PEL	Minimum	Maximum	Average	Standard Deviation
Mercury	55	28	23	4	0.006	0.940	0.202	0.185
Lead	55	22	32	1	4.979	104.273	43.084	23.425
PCBs	67	10	57	0	1.850	244.476	95.304	61.015
HCB	57	57	0	0	0.00	11.826	1.594	2.237

Table 3. Data Characteristics for Lake Ontario (Minimum, Maximum, Average, and Standard Deviation in µg/g for Mercury and Lead; ng/g for PCBs and HCB)

Contaminant	No. of Sites	No. <TEL	No. ≥TEL and <PEL	No. ≥PEL	Minimum	Maximum	Average	Standard Deviation
Mercury	71	12	17	42	0.015	1.138	0.586	0.353
Lead	68	16	26	26	5.169	196.617	71.812	41.908
PCBs	71	17	54	0	2.601	254.763	100.226	71.123
HCB	71	32	39	0	0.312	57.969	23.161	18.717

Table 4: Kriging Cross Validation Results for Lake Erie

Contaminant	MPE	ASE	SRMSPE
Mercury	0.0006	0.144	1.102
Lead	0.4266	18.26	1.165
Polychlorinated biphenyls (PCBs)	0.1522	42.30	1.056
Hexachlorobenzene (HCB)	0.0122	2.115	0.917

Table 5: Kriging Cross Validation Results for Lake Ontario

Contaminant	MPE	ASE	SRMSPE
Mercury	0.0107	0.36	0.9474
Lead	1.3490	39.77	0.9331
Polychlorinated biphenyls (PCBs)	2.5720	72.86	0.9336
Hexachlorobenzene (HCB)	0.4687	14.64	0.9748

Table 6: Log Transformed Kriging Cross Validation Results for Lake Erie

Contaminant	MPE	ASE	SRMSPE
Lead	0.0115	0.236	1.059
Polychlorinated biphenyls (PCBs)	0.0048	0.269	1.005

Table 7: Log Transformed Kriging Cross Validation Results for Lake Ontario

Contaminant	MPE	ASE	SRMSPE

Lead	0.0153	0.311	0.9831
Polychlorinated biphenyls (PCBs)	0.0131	0.530	0.9920

Abbreviated Title

Spatial Distribution of Sediment Contamination

Fig. 1: Sediment Core Locations and Major Cities for Lake Erie

Fig. 2: Sediment Core Locations and Major Cities for Lake Ontario

Fig. 3. Lakes Erie and Ontario Bathymetry including major depositional basins (Source: modified after Painter et al. 2001 and Marvin et al. 2003a respectively)

Fig. 4. Annual Circulation in Lake Erie (Isobaths at 20m and 50m) and Lake Ontario (Isobaths every 50m) - (Source: modified after Beletsky et al. 1999)

Fig. 5: Mercury Kriging Results for Lake Erie (Inset: Annual Circulation in Lake Erie - Isobaths at 20 m and 50 m - Source: modified after Beletsky et al. 1999)

Fig. 6: Mercury Kriging Results for Lake Ontario (Inset: Annual Circulation in Lake Ontario - Isobaths every 50 m - Source: modified after Beletsky et al. 1999)

Fig. 7: Lead Kriging Results for Lake Erie (Inset: Annual Circulation in Lake Erie - Isobaths at 20 m and 50 m - Source: modified after Beletsky et al. 1999)

Fig. 8: Lead Kriging Results for Lake Ontario (Inset: Annual Circulation in Lake Ontario - Isobaths every 50 m - Source: modified after Beletsky et al. 1999)

Fig. 9: PCB Kriging Results for Lake Erie (Inset: Annual Circulation in Lake Erie - Isobaths at 20 m and 50 m - Source: modified after Beletsky et al. 1999)

Fig. 10: PCB Kriging Results for Lake Ontario (Inset: Annual Circulation in Lake Ontario - Isobaths every 50 m - Source: modified after Beletsky et al. 1999)

Fig. 11: HCB Kriging Results for Lake Erie (Inset: Annual Circulation in Lake Erie - Isobaths at 20 m and 50 m - Source: modified after Beletsky et al. 1999)

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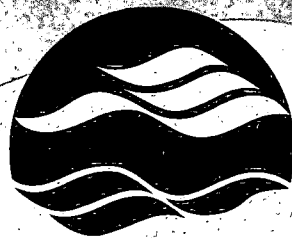
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