A GIS-based Kriging Approach for Assessing Lake Ontario Sediment Contamination

Daniel J. Jakubek and K. Wayne Forsythe
Department of Geography Ryerson University, 350 Victoria Street Toronto, Ontario, Canada M5B 2K3

This research utilized data from the 1998 Environment Canada Great Lakes Sediment Assessment Program. Contaminants were measured at 70 sediment core-sampling locations in Lake Ontario. The Sediment Quality Index (SQI) was calculated and assessed as being a satisfactory measure for areas where sediment quality is frequently threatened or impaired. Polychlorinated Biphenyls (PCBs), Mercury, Lead, and Hexachlorobenzene (HCB) were also examined, as they are contaminants that have major environmental significance. The 'ordinary kriging' spatial interpolation technique was employed to create individual prediction maps for the contaminants and the SQI. The advantage of the kriging technique is that the accuracy can be assessed through cross-validation procedures. In addition, the results provide prediction surfaces for lake-wide sediment contamination that more accurately represent overall pollution levels when compared to point measurements.

Keywords: Contamination, GIS, Interpolation, Lake Ontario, Kriging, Sediment

Over the past century, Lake Ontario has experienced contamination of sediment, water, and biota as a result of anthropogenic activities, including mass development along the Canadian portion of its western shoreline known as the Golden Horseshoe. Half of the population (approximately 5.5 million) of the Province of Ontario lives in this region (Statistics Canada, 2002). Canadian and American government institutions have combined resources in the development of a Lakewide Management Plan with the general objective of "restoring the overall health of the Great Lakes ecosystem" (LOLMP, 1998). As a result of these actions, toxic contamination in the Lake Ontario basin has decreased, however, contaminants remain in the ecosystem with the capacity to bioaccumulate (accumulate in aquatic organisms to levels that are harmful to human health) (LOLMP, 1998). It is due to the persistence of these toxic contaminants that research regarding the sediment and water quality in the Great Lakes continues.

Presently, research regarding the distribution of contaminated sediment in Lake Ontario is limited to a series of sampling locations that represent the aquatic system as a whole. The aim of this study is to produce interpolated surfaces on the basis of existing sediment sampling location data. The map surfaces derived using the kriging procedure can help to explain how stream loading and land use practices including urban development and agriculture, result in the distribution of contaminated sediment throughout Lake Ontario. The advantage of the kriging technique is that the accuracy can be assessed through cross-validation procedures. In addition, the results provide prediction surfaces for lake-wide sediment contamination that more accurately represent overall pollution levels when compared to point measurements.

Pollution in the Great Lakes

After the turn of the 20th century, growing urbanization and industrial development in the Great Lakes Basin caused widespread bacterial contamination and added to the floating debris produced by activities such as logging and agriculture. Continued industrialization and intensified agricultural practices were the causes for the development of new chemical substances. Polychlorinated Biphenyls (PCBs) and Dichloro-Diphenyl-Trichloroethane (DDT) were developed for use as pesticides in agricultural activity in the 1920s and 1940s respectively (Hodgson and Levi, 1997). Toxic runoff produced by these pesticides, the use of synthetic fertilizers developed to further enhance crop yield, existing sources of nutrient rich pollutants (untreated human waste from urban areas), and phosphate detergents accelerated the rate of biological production in the system (GLA, 1995). By 1980, the International Joint Commission (IJC) estimated that approximately 2500 chemicals were in common use in the Great Lakes Basin. The major industries located in the Great Lakes region include steel production, pulp and paper, chemicals, automobiles, and manufactured goods. The most significant urban areas were developed at the mouths of Great Lakes tributary rivers due to transportation needs and freshwater resources for domestic and industrial use (GLA, 1995).

Lake Ontario is vulnerable to human activities that have occurred throughout the Lake Superior, Michigan, Huron, and Erie basins, given its location at the bottom end of the Great Lakes system. The Lake Ontario ecosystem has experienced negative changes as a result of toxic pollution originating from widespread development in the Great Lakes region. Major industrial centres including Hamilton, Toronto, Oshawa, and Kingston are situated on its Canadian shoreline to the north. The cities of Rochester and Oswego are located on its American shore in the State of New York to the south. These point sources of pollution, combined with dredging practices in the upstream Great Lakes tributaries such as the Niagara River, have been major contributors to poor sediment and water quality in Lake Ontario (GLA, 1995). In 1972, the Canadian and United States governments agreed that water quality was to be improved in the Great Lakes, and future pollution input levels were to be decreased (Zarull *et al.*, 1999). The Great Lakes Water Quality Agreement was renewed in 1987 in order to ban and control contaminants entering the Great Lakes and restore the health of the Great Lakes ecosystem (LOLMP, 1998). In addition, a Lakewide Management Plan (LMP) was developed for each of the Great Lakes.

Kriging

Kriging techniques were initially developed by the South African mining geologist D.G. Krige (Bailey and Gatrell, 1995). Kriging methods utilize statistical models that incorporate autocorrelation among a group of measured points to create prediction surfaces (Johnston *et al.*, 2001). Specifically, weights are assigned to measurement points on the basis of distance in which spatial autocorrelation is quantified in order to weight the spatial arrangement of measured sampling locations (Johnston *et al.*, 2001). By accounting for statistical distance with a variogram model, as opposed to Euclidean distance utilized in deterministic interpolation, customization of the estimation method to a specific analysis is possible. Isaaks and Srivastava (1989) state that 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. Furthermore, kriging accounts for both the clustering of nearby samples and for their distance to the point to be estimated (Isaaks and Srivastava, 1989). Given the statistical properties of this method, measures of certainty or accuracy of the predictions can be produced using a cross-validation process.

Study Area and Data

Lake Ontario is located in the southeastern portion of the Great Lakes Basin (Figure 1). It has an area of approximately of 19010 square kilometres, and is the smallest of the Great Lakes (GLFS, 2002). Its drainage basin covers portions of the Canadian Province of Ontario and the American State of New York. It is fed primarily by the waters of Lake Erie through the Niagara River. The average inflow discharge is approximately 7000 m^3/s (Atkinson *et al.*, 1994), and this flow accounts for nearly 80 percent of the total inflow into Lake Ontario (Blair and Atkinson, 1993). Additional inflow (14 percent) stems from other Lake Ontario basin tributaries, while precipitation accounts for approximately six percent of the water body's total volume (LOLMP, 1998). Approximately 93 percent of the water in Lake Ontario is drained to the northeast by the St. Lawrence River, with the remaining seven percent lost through evaporation (LOLMP, 1998). The outflow discharge rate into the St. Lawrence River averages 7400 m^3/second (Rukavina *et al.*, 1990).

Data Samples and Sampling Locations

Field research conducted in 1998 under the Environment Canada Great Lakes Sediment Assessment Program provided sediment contamination data for 70 specific sampled sites (Figure 2). Some deviations from the grid formation were made in order to assess certain Lake Ontario Areas of Concern (AOCs) including Hamilton Harbour and the mouth of the Niagara River. The U.S-Canada Great Lakes Water Quality Agreement defines AOCs as "geographic areas that fail to meet the general or specific objectives of the agreement where such failure has caused or is likely to cause impairment of beneficial use of the area's ability to support aquatic life".

Surficial sediment samples were collected using a mini-box core sampling procedure. The samples collected during the survey consisted of fine-grained sediments classified as clay, sand, silt, or mud. The initial 3 centimetres of the sediment was sub-sampled in order for analyses of persistent organic pollutants (POPs), metals, particle size characterization, and nutrients to be performed (Marvin *et al.*, 2002). Table 1 documents the specific contaminants (examined in this study) that were measured at each of the locations within Lake Ontario and their corresponding federal guideline levels.

Figure 1: Lake Ontario and the Great Lakes Region

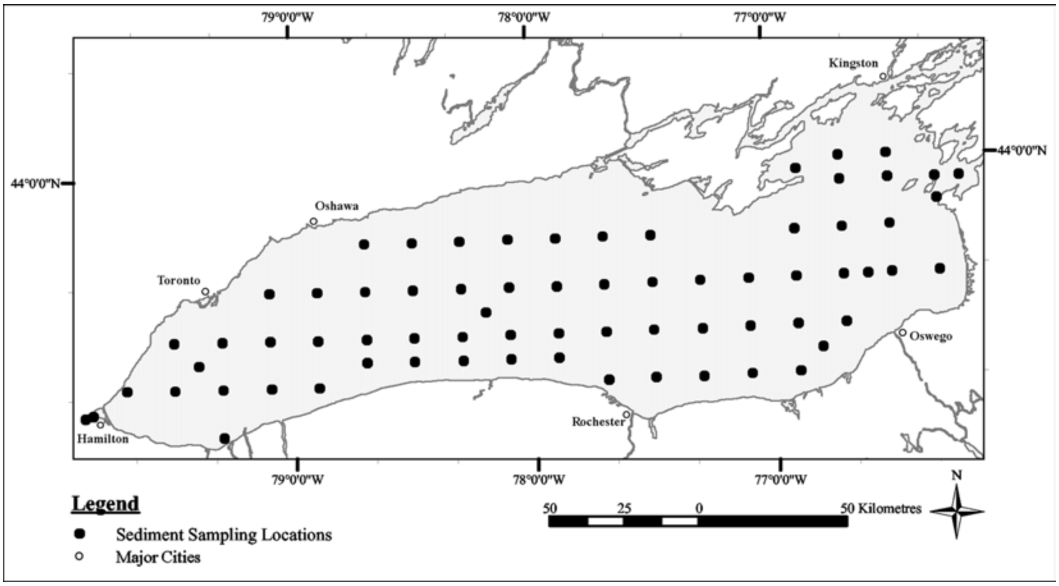

Figure 2: Sediment Sampling Locations in Lake Ontario

Methodology

Ordinary kriging is the most flexible kriging model because it functions under the assumption that the mean **u** is an unknown constant, and thus, the random errors at the data locations are unknown (Johnston *et al.*, 2001). Ordinary kriging is most appropriate for data that have a spatial trend and, furthermore, this system can easily be applied to block (average) estimation from point estimation. Thus, the average of a specific number of point estimates can be represented as a direct block estimate if one wishes to group the data values (Isaaks and Srivastava, 1989).

The estimation of contaminant loading into Lake Ontario and identification of the sources for this loading are difficult tasks. In order to identify the potential 'hotspots' (areas creating ecosystem risk) for sediment contamination in Lake Ontario, the Sediment Quality Index (SQI) was used. The SQI performs risk assessment by providing a general description of sediment quality on the basis of whether existing federal contamination guidelines are exceeded. Sediment quality can be assessed by utilizing the SQI, which is derived from the Canadian Water Quality Index (CWQI). The SQI formula was developed by the British Columbia Ministry of Environment, Lands and Parks, and modified by the Ministry of Environment in Alberta (CCME, 1999). A sediment quality index is a means of summarizing complex sediment contamination data mathematically, by

Table1: Contaminants and Federal Guidelines

Contaminant	Threshold Effect Level TEL	Probable Effect Level PEL
Lead	35 ug/g	91.3 ug/g
Mercury	0.17 u/g	0.486 ug/g
Hexachlorobenzene	20 ng/g	480 ng/g
Polychlorinated biphenyls (PCBs)	34.1 ng/g	277 ng/g

(Source: Canadian Council of Ministers of the Environment, 1999) combining all existing measures of contamination to provide a general description of sediment quality within a body of water. The index is useful in assessing sediment quality relative to its desired state, defined by specific objectives. Additionally, this index addresses the degree to which water quality is affected by human activity.

Marvin *et al.* (2002) applied the SQI to an assessment of sediment quality in Lake Ontario on the basis of the federal Threshold Effect Level (TEL) and Probable Effect Level (PEL) guidelines. They did not, however, use interpolation procedures to estimate sediment quality throughout the lakes; SQI scores were calculated on the basis of point data values in order to examine the spatial pattern of sediment quality.

Calculation of the Sediment Quality Index (SQI)

In order to calculate the SQI, the body of water for which the index applies and the specific variables and objectives (contaminant concentrations exceeding their PELs) applying to the study must be defined. The SQI computes an index score on a per site basis, with no grouping of sites (Marvin *et al.*, 2002). It is based on a two-component equation including 'scope' and 'amplitude'. These are defined as:

F_1 – The '**scope**' is a representation of the percentage of contaminants that do not meet their objectives even once during the time period for which they are being considered (Marvin *et al.*, 2002). In essence, these are failed tests, measured relative to the total number of variables considered.

F_2 – The **'amplitude'** is a representation of the amount by which failed test values do not meet their objectives (exceed the PEL for contaminant concentration in sediment) (Marvin *et al.*, 2002). Once these two factors have been obtained, The SQI can be calculated as:

SQI = $100 - \sqrt{(F_1)2 + (F_2)2 / 1.414}$

The value 1.414 is used to normalize the resulting values to a range between 0 and 100. This value is generated because $[100^2 + 100^2]^{0.5} = 141.4$ (Marvin *et al.*, 2002). According to this scale, a water quality of 100 is the 'best' and a water quality of 0 is the 'worst' (CCME, 2001).

The values can be grouped into the following categories:

Excellent: (SQI Value of 95 – 100) – sediment is devoid of any contaminant-related impairment and is indicative of ambient environmental background conditions. Index values within this range are achieved when practically all measurements fall within the guideline values.

Good: (SQI Value 80 – 94) – only a minor degree of sediment impairment is indicated. Most measurements fall within guideline values and rarely deviate from ambient environmental background levels.

Fair: (SQI Value 60 – 79) - sediment quality is usually protected but occasionally threatened or impaired. Some measurements deviate from ambient environmental background levels.

Marginal: (SQI Value 45 – 59) - sediment quality is frequently threatened or impaired. Some measurements deviate from ambient environmental background levels.

Poor: (SQI Value 0 – 44) - sediment quality is almost always threatened or impaired. Most measurements deviate substantially from ambient environmental background levels (Marvin *et al.*, 2002).

'Categorization' is the term for the assignment of the SQI values to the four categories for any particular contaminant and is based on three factors including the most reliable information available for each specific application, leading expert opinions, and the expectation of sediment quality by the general public (CCME, 2001).

Spatial Interpolation: Geostatistical Kriging Methods

Geostatistical interpolation methods utilize statistical models incorporating autocorrelation or statistical relationships among a group of measured points to create prediction surfaces (Johnston *et al.*, 2001). Kriging is based on Regionalized Variable Theory (RVT), which assumes that the spatial variation of a variable represented at specific measurement locations is statistically homogeneous throughout the defined surface

(Buttner *et al.*, 1998). The equation used to perform ordinary kriging is:

$$Z(s) = u + e(s)$$

where **Z(s)** represents the value for the unknown variable at a spatial location **s**, **u** represents an unknown constant mean for the data (thus no trend), and **e(s)** represents the random errors (Johnston *et al.*, 2001). It is important here to consider intrinsic stationarity, which is defined as "an assumption that the data come from a random process with a constant mean, and a semivariogram that only depends on the distance and direction separating any two locations" (Johnston *et al.*, 2001). It is necessary to ensure that the prediction is unbiased. When predictions are made at numerous locations, some will be greater than the actual values, and some will be below the values. On average, the difference between the actual and predicted values should be zero.

A semivariogram is a graph that plots half the difference squared between pairs of locations (the averaged semivariogram values) on the y-axis, relative to the distance that separates them on the x-axis (Johnston *et al.*, 2001). Averaged values can be used due to the assumption of intrinsic stationarity. The ability to plot all pairs in a manageable time frame is a difficult task. ArcGIS utilizes a technique in which pairs of locations are grouped based on specified ranges of distances and directions. This process is referred to as 'binning,' by which the average empirical semivariance for all pairs of points is recorded. A model can then be fit to the empirical semivariogram, however, first it is necessary to determine whether the data are normally distributed. If the distribution were skewed, it would be necessary to perform the appropriate transformations. A normal distribution is not necessary to obtain prediction maps in the ordinary kriging process. However, kriging is the best predictor among unbiased predictors when data are normally distributed (Johnston *et al.*, 2001).

Determining the Search Neighbourhood

As measured data points become located at greater distances from the prediction locations, they become less spatially autocorrelated with one another. The ability to set the size of the search neighbourhood, and assign the number of measured locations to be used in making a prediction, allows for the elimination of locations that have minimal influence on the overall prediction. Furthermore, a search neighbourhood customized to fit the spatial arrangement of a dataset increases the speed at which predictions can be made because sampling locations that are not spatially autocorrelated are excluded from the prediction process.

An elliptical search neighbourhood was chosen to account for the eastward sedimentation patterns stemming from the Niagara River. The major and minor axes were assigned values of 1 and 0.5 degrees respectively, and the ellipse was divided into four sectors in which the maximum number of neighbours was limited to 5 and the minimum was limited to 1. This is similar to Buttner *et al.* (1998) who utilized ordinary kriging to predict the spatial distributions of 12 elements in an acidic mining lake using an isotropic search neighbourhood including the ten nearest neighbours from each prediction location. The ratio of sampled sites with respect to the surface area of the lake was the reason for a search neighbourhood featuring 10 neighbours. The shorter distances between sampling locations increased the probability of autocorrelation between their contamination concentrations. The ratio between the surface area of Lake Ontario and the grid of 70 sampling locations is the reason the maximum number of neighbours was limited to 5 in this analysis. Additional neighbours would surpass the range of the semivariogram, and thus, they would lack spatial autocorrelation.

Cross-Validation: Identification of the Best Model

In order to identify the degree of accuracy that the semivariogram parameters and the search neighbourhood possess in predicting the unknown locations, the ArcGIS Geostatistical Analyst can be used to perform cross-validation. Cross-validation is a method that removes each measured location one at a time in order to predict their values on the basis of the measured values in the entire dataset. On the basis of cross-validation results, accuracy can be determined regarding the chosen model and search neighbourhood for each prediction. Cross-validation also provides values including Mean Prediction Error (MPE), Standardized Mean Prediction Error (SMPE), Root-Mean Squared Prediction Error (RMSPE), Average Standard Error (ASE) and Standardized Root-Mean-Squared Prediction Errors

(SRMSPE), which assess the accuracy of the chosen model. A good model will calculate MPE and SMPE values near a value of zero to show that predictions are unbiased or are centred on the measured locations. Additionally, low RMSPE values identify that predictions are close to their true values. The ASE values are used to assess the variability in the predictions from the measurement values. Therefore, the average standard error must be similar to the root-mean square prediction error in order to correctly assess the variability in the prediction. For instance, if the ASE value is greater than the RMSPE value, the variability of the prediction is being overestimated. The SRMSPE value also provides another method to assess variability. If the prediction standard errors are valid, the SRMSPE values should be close to 1 (Johnston *et al.*, 2001). However, SRMSPE values greater than 1 translate to an underestimation in the variability of the predictions.

Results and Discussion

Previous analyses performed on suspended sediment concentrations demonstrated that the Niagara River supplies approximately 1.8 million tons of sediment to Lake Ontario annually (Joshi *et al.*, 1992). The Niagara Bar is a physical feature located at the mouth of the Niagara River that is an example of a shallow inshore zone created by the inflow of sediment. Sediment is deposited at this junction because the velocity of the current in Lake Ontario is lower than that of the Niagara River. As a result, shear stress on the river bottom is increased and buoyant discharge conditions result in a defined surface plume. Due to inertia and buoyancy, and after a moderate distance, Coriolis acceleration, the plume is deflected in an easterly direction (Atkinson *et al.*, 1994). 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).

Contaminants have a tendency to bind to sediments on lake bottoms. Thus, they have the ability to remain in lake ecosystems for periods of time extending beyond Lake Ontario's seven-year water retention span (Sly, 1991). While toxic substances have the capacity to remain in lake-bottom sediment indefinitely, the processes of bioturbation and re-suspension may result in their reintroduction. Bioturbation results from the activity of benthic invertebrates in which sediment can be recycled from as deep as 40 cm from the active surface layer (Zarull *et al.*, 1999). Re-suspension of sediment may occur due to major storm events, internal waves, currents, and vessel traffic (Zarull *et al.*, 1999). Such external forces are causes for high flow events, which have been observed to cause significant mass loadings of contaminants from a river into a lake (Cardenas and Lick, 1996 in Zarull *et al.*, 1999). The sediment plume developed at the mouth of the Niagara River leads directly to areas with high estimated sediment contamination levels.

Application of the Sediment Quality Index in Lake Ontario

The availability of data depicting sediment contamination in Lake Ontario presents the opportunity for the evaluation of sediment quality by using the Canadian Sediment Quality Guidelines (CCME, 1999). The specific guidelines were designed as aids in the identification of potential ecosystem risk, and in order to assist in the prioritization of sediment quality concerns (Marvin *et al.*, 2002). The TEL represents "the concentration below which adverse biological effects are expected to occur rarely," whereas, the PEL defines the level above which adverse effects are expected to occur frequently (CCME, 1999). These assessment values are developed using a weight of evidence approach in which biological and chemical data from modelling, laboratory, and field studies performed on fresh water sediments are analyzed (Smith *et al.*, 1996). The calculation of two such assessment values defines three ranges of chemical concentration: those that are rarely, occasionally, and frequently associated with adverse biological effects. Using sediment contamination levels and spatial interpolation among the 70 stations in Lake Ontario provides a means for assessing the relative risk of contamination between sites. The basis for risk assessment is the individual site's departure from the TEL or PEL (whichever are being used in the specific analysis). Fundamentally, the SQI is an index of sediment quality over space (Marvin *et al.*, 2002). The SQI is effective because it is sensitive to the degree of contamination above or below a set guideline. Given this sensitivity, poorer scores should result at sites with sediment contamination exceeding the TELs and PELs.

Knowledge of the sedimentation and current circulation patterns in Lake Ontario was useful in estimating the sediment dispersal within the system. As displayed in Figure 2, the sampling locations are not evenly dispersed throughout the lake. The region for highest concern of inaccurate predictions is the entire northern shoreline of Lake Ontario. Unlike the southern shoreline, no data were generated from sampling locations in close proximity to the northern shoreline. Additionally, with the exception of the Niagara River and Hamilton Harbour, sediment samples were not analyzed at other Areas of Concern (AOC) such as the Toronto Harbourfront or major contaminating rivers flowing into Lake Ontario along the northern shoreline.

Excluding Hamilton Harbour, the sampling locations where sediment quality is frequently threatened or impaired are mostly located within the deep lake basins (Figure 3). The explanation for the location of high sediment contamination levels in these areas is described in the following process. First, the major factor contributing to the loading of pollutants into Lake Ontario is surface runoff. The clearing of original forested areas for agricultural purposes and logging, results in less soil stability and erosion/runoff into Lake Ontario and its tributaries (GLA, 1995). These processes increase the transport of soil particles and pollutants as suspended soil particulates in water, and the sediment is deposited to near and offshore areas. Variations in the distribution of these particles exist due to their physical properties such as particle size and atomic weights. The distribution of these elements can be explained due to the specific sedimentation and circulation patterns in Lake Ontario.

Cross-Validation Results for Ordinary Kriging

The cross-validation procedure provides measures of accuracy for the predictions made using the ordinary kriging method. The measures produced include MPE, SMPE, RMSPE, ASE and SRMSPE. Values calculated for these measures are documented in Table 2. Given each specific contaminant, the results are most variable when considering RMSPE values and when comparing RMSPE values with ASEs. Before the interpolated surfaces can be assessed, it is necessary to document possible explanations for inaccuracies that occurred in the kriging process. Using ordinary kriging produces prediction surfaces where portions of Lake Ontario's area are featured as no data. The rectangular prediction surfaces almost cover the entire area of Lake OntarioAreas located along the southwest and northeast edges of sampling site locations.

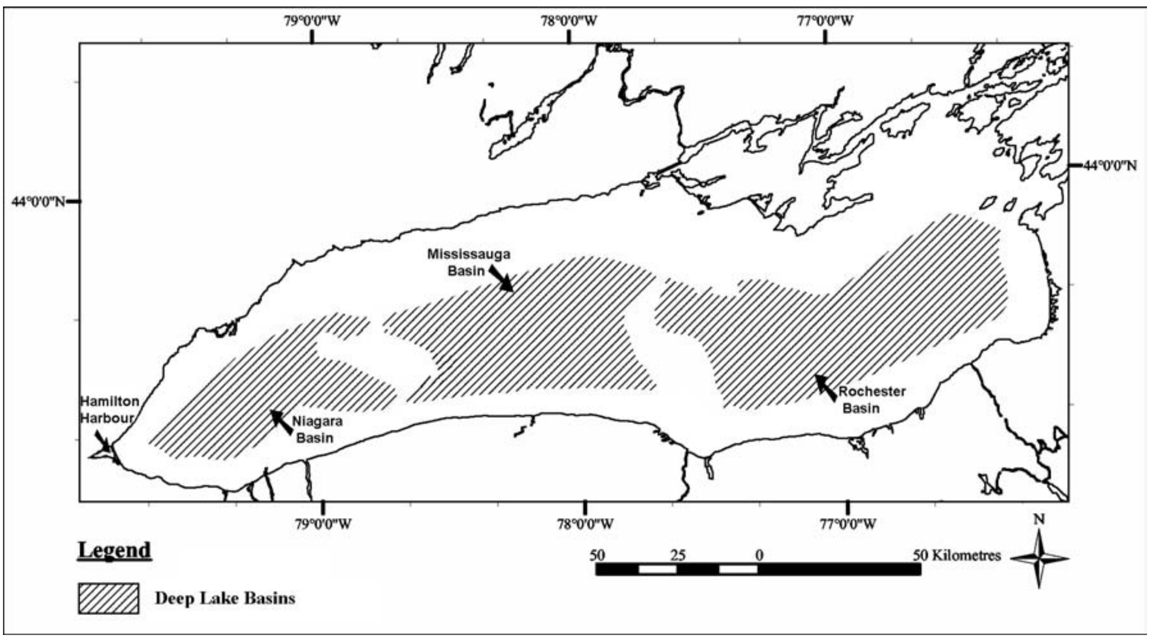

Figure 3: Deep Lake Basins within Lake Ontario

Table 2: Cross-Validation Results for Ordinary Kriging

SQI and Major Contaminants	Mean Prediction Error (MPE)	Root-Mean Squared Prediction Error (RMSPE)	Average Standard Error (ASE)	Standardized Mean Prediction Error (SMPE)	Standardized Root-Mean Squared Prediction Errors (SRMSPE)
SQI	-0.5935	13.31	13.56	-0.03925	0.9789
Lead	3.091	42.72	42.26	0.07361	1.011
Mercury	0.01983	0.3452	0.3584	0.05032	0.9693
Hexachlorobenzene (HCB)	0.4908	14.46	14.65	0.02495	0.9689
Polychlorinated biphenyls (PCDs)	3.813	65.52	68.1	0.04724	0.9617

Sediment Quality Index (SQI)

The lowest SQI scores (Figure 4) are found in the region of Hamilton Harbour and the central regions of the Niagara, Mississauga, and Rochester basins. The highest SQI values are estimated along the northern shoreline of Lake Ontario. However, they may be inaccurate in this area given the lack of measured sampling locations. Furthermore, in Lake Ontario, sediment from near shore areas eventually accumulates in the deep lake basins or moves through the St. Lawrence River to the

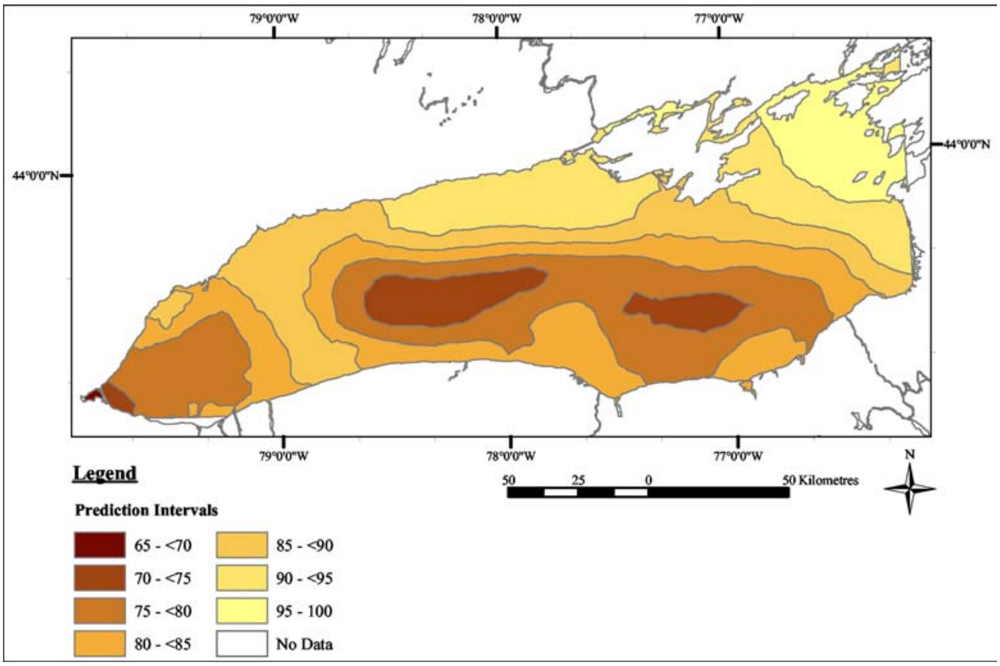

Figure 4: Sediment Quality Index (SQI) Kriging Results

Atlantic Ocean (Allan, 1984; Sorokin, 1966; Karickhoff and Morris, 1995 in Zarull *et al.*, 1999).

The cross-validation results derived from the SQI score interpolation predictions are unbiased and reasonably close to the measured locations. The variability assessed by the deviations of the ASE from the RMSPE and the SRMSPE from the value 1, is slightly overestimated. The SQI kriging results show higher contamination levels in the deep lake basins. Kriging accounted for the sedimentation process where low SQI scores are situated within the deepest extent of each basin, and in close proximity to Lake Ontario AOCs. Given the general water circulation patterns and inflows from rivers and tributaries, sediment has the capacity to be re-suspended, and deposited in deeper extents of the Lake Ontario basin.

Mercury

Mercury is a naturally occurring element that can be found in most rocks and soils. Unlike heavy metals such as copper and zinc, which are essential biological micronutrients required for the growth of organisms, Mercury is considered to be extremely toxic with respect to human health and aquatic life (Ouyang *et al.*, 2002). Mercury was initially used as an additive to paints in order to control the creation of mildew. Presently, its most common uses include medical and dental products and thermometers, and it is a major constituent of batteries (LOLMP,1998). Figure 5 estimates the locations for the highest Mercury concentrations in the deep central regions of both the Mississauga and Rochester sub-basins. The predicted surface for Mercury produced very reliable cross-validation results, which were relatively unbiased and rendered a low RMSPE value.

Lead

The prediction surface representing Lead (Figure 6) near perfectly estimated the variability and featured a standardized RMSPE value of 1.011, however, Lead features a RMSPE value of 42.72. With RMSPE values greater than 20, predictions are straying quite far from the measured locations. Therefore, when analyzing the prediction surface, these errors must be considered. The prediction map representing Lead is possibly inaccurate given that the highest predicted concentration interval indicates Lead values ranging from 80 to100 ug/g, while measured concentrations of Lead were documented at amounts well over

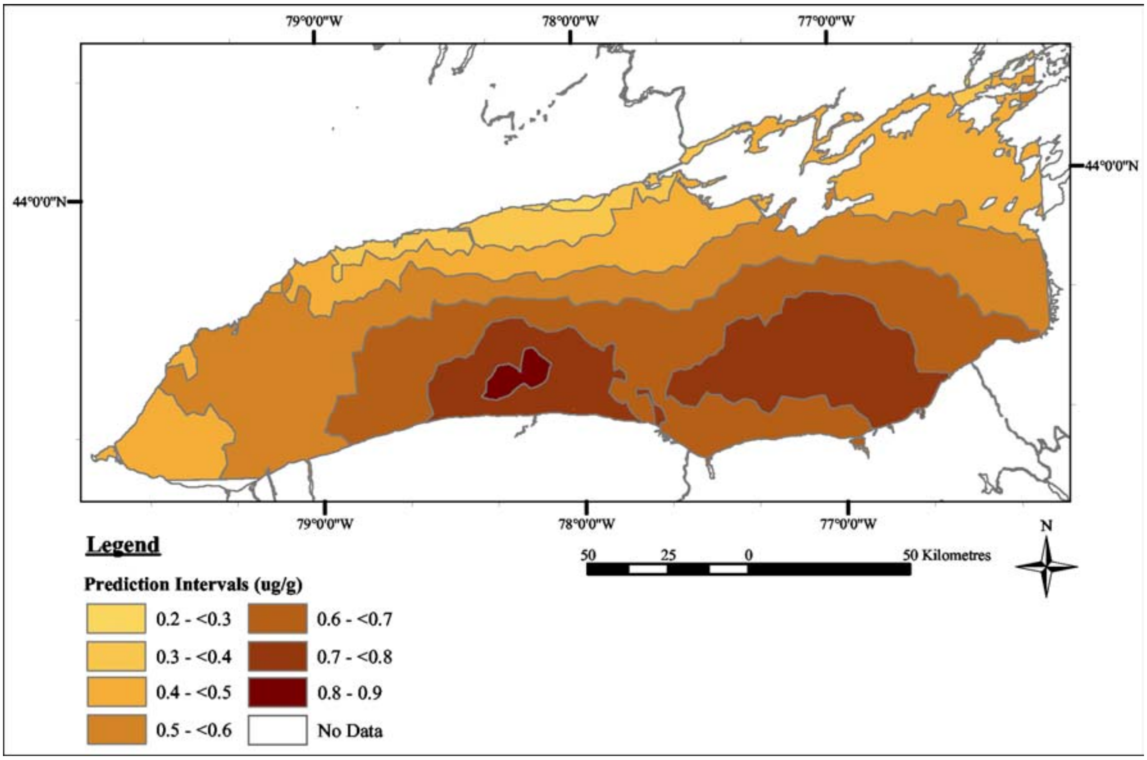

Figure 5: Mercury Kriging Results

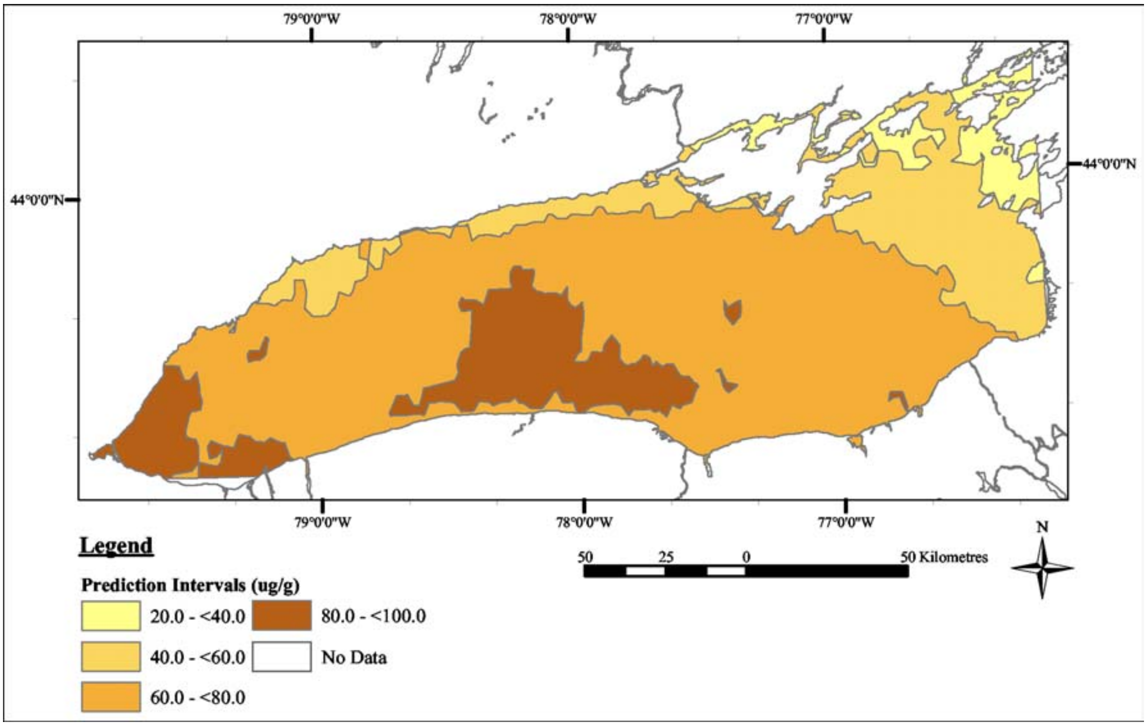

Figure 6: Lead Kriging Results

100 ug/g in the central regions of Lake Ontario, and approximately 200 ug/g near Hamilton Harbour. The high Lead concentrations stem largely from steel mills and associated practices along the shoreline of Hamilton Harbour (Ecowise, 2002). Hamilton Harbour is a reservoir for industrial and municipal wastes, including Lead-laden effluents, and acts as a port that receives 400 to 1000 vessels per year (Ecowise, 2002). As a result, these contaminants infiltrate the sediment and are deposited in the deep central basin over time. However, the prediction results may not be reliable due to the cross-validation values and a simple comparison of measured and predicted values.

PCBs

The manufacturing of PCBs occurred between the years 1929 and 1977. PCBs were utilized as an industrial safety product in processes that required high heat inputs, and/or were fire hazards. After 1977, the production of PCBs no longer continued due to the discovery that their release into the environment caused bioaccumulation warranting high levels of concern for a wide range of organisms (GLA, 1995). This contaminant is still considered a critical pollutant even though PCB production has been banned. As seen in Table 3, it continues to find its way into Lake Ontario where it may cause health and reproduction problems in aquatic and terrestrial wildlife (LOLMP, 1998). The majority of PCB loadings into Lake Ontario originate from the upstream Great Lakes basins through the Niagara River totalling 440 kg/yr (LOLMP, 1998). In addition, point and non-point sources, combined with atmospheric deposition, contribute approximately 165 kg/yr of PCBs to the lake (LOLMP, 1998). The highest concentrations of PCBs in sediment are located in the deep central basins of Lake Ontario due to sediment originating from the mouth of the Niagara River. PCB's were measured at high concentrations in the deep regions of the Mississauga and Rochester basins (Figure 7). Comparing the measured values to the filled contours throughout the basin, the predictions seem reasonable, but high RMSPE results and large deviations from the ASE are the reason to suspect inconsistent outcomes from the kriging analysis. A possible explanation for

Table 3: Origin of PCB Loadings for Lake Ontario

Origin of Loading	Loading (kg/yr)
Upstream Great Lakes Basins	302 kg/yr
Niagara River Basin	138 kg/yr
Lake Ontario Basin (Point and Non-Point Source)	100 kg/yr
Atmospheric Loading	64 kg/yr

Source: LOLMP, 1988

these cross-validation results is a biased prediction supported by a MPE value of 3.813. It is due to the severe impacts that PCBs continue to make on aquatic ecosystems that the prediction map was included in this analysis despite its possible errors.

HCB

HCB produced comparable results (Figure 8) to the SQI kriging analysis. Similar to Mercury and Lead, reports documenting the origin of pollutant loadings for this contaminant are minimal. Due to low concentration levels of this contaminant in LakeOntario sediment, it is difficult to hypothesize its origin. The predicted surface for HCB produced reasonable cross-validation results, which were relatively unbiased and rendered a moderately low RMSPE value. The prediction surface near perfectly estimated the variability and featured a standardized RMSPE value of 0.9689.

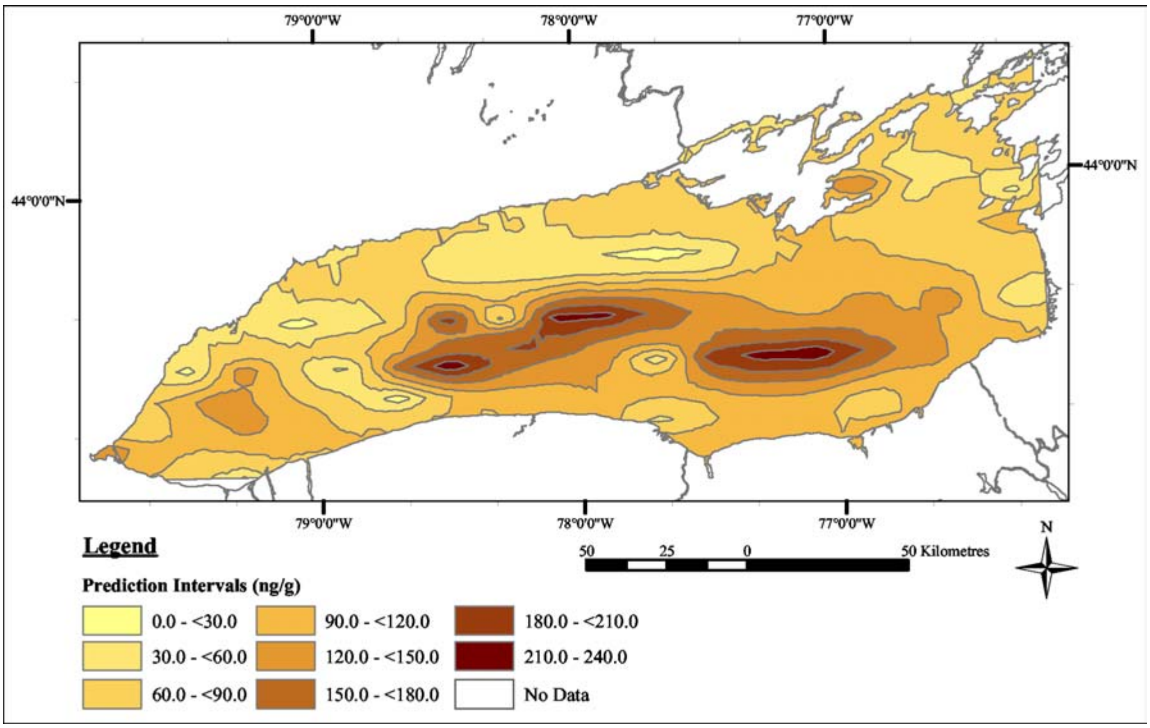

Figure 7: PCB Kriging Results

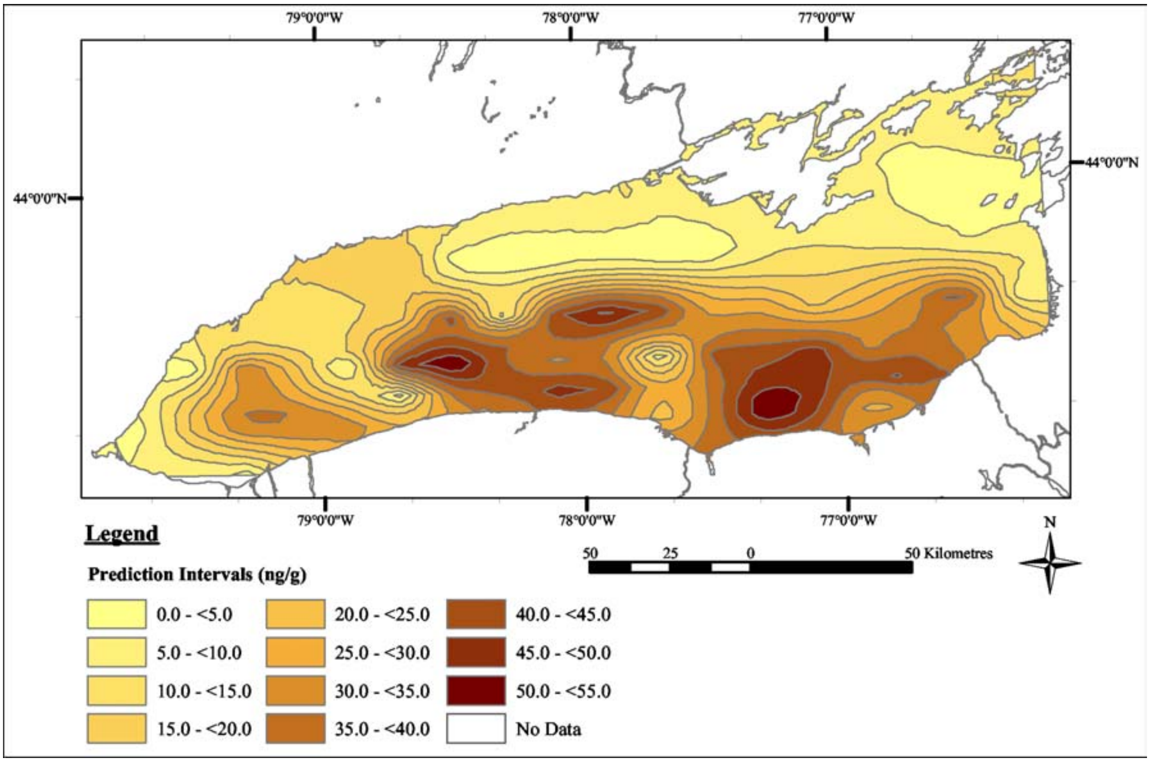

Figure 8: HCB Kriging Results

Summary and Conclusions

The measurement of sediment contamination throughout Lake Ontario is an immense task if one is to make thorough observations about the aquatic ecosystem as a whole. The total number of major contaminants at each measurement location exceeding the TEL and the PEL was determined together with the amount by which each threshold was exceeded. The SQI was found to be a good general measure for frequently threatened or impaired sediment after applying it to each of the 70 measurement locations and reviewing the results.

Limitations in the spatial distribution of the sediment contaminant data prevented the prediction of an accurate SQI score distribution without implementing a technique known as ordinary kriging. It is a geostatistical method that utilizes statistical models incorporating autocorrelation among the group of measured points to create a prediction surface. Also, cross-validation results including MPE, ASE, SMPE, and SRMSPE are produced exclusively in the kriging process. These results include measures relating to the level of bias in a prediction and estimations of variability in the production of interpolated surfaces. The most statistically optimal prediction surfaces were created for Mercury, and adequate results were rendered for Lead. The results calculated for the critical pollutants (PCBs and HCB) were variable. The most inaccurate results were calculated for PCBs while similar results to the SQI scores were obtained for HCB.

In the future, more resources should be expended to develop a sampling scheme that will account for the proper range in which autocorrelation exists between sampling sites. The development of a specific stratification scheme could be based on the calculated range in the semivariogram process. If sampling locations follow this defined stratification process, a more statistically accurate prediction surface can be created. It is vital to note that the semivariogram distribution will change for each contaminant. Thus, the ranges produced for each contaminant will not be identical. Before creating a sampling strategy, it is necessary to decide which contaminant distribution is most important to the organization in order to produce the best possible interpolation results. In this analysis, it is equally important to take samples at Lake Ontario AOCs and other rivers and tributaries that are sources of contaminant loading into Lake Ontario. Kriging allows for lake-wide measurement of contaminant concentrations and the results obtained are much more valuable than the point measurements from which they are derived. The integration of kriging within Geographic Information Systems such as ArcGIS provides an efficient means for visual display, data integration, and advanced data analysis.

References

Allan, R.J. 1984. The role of particulate matter in the fate of contaminants in aquatic ecosystems. Inland Waters Directorate Series No. 142, NWRI, Burlington, Ontario.

Atkinson, J.F., G. Lin, and M. Joshi. 1994. Physical Model of Niagara River Discharge. Journal of Great Lakes Research 20, 3: 583.589.

Bailey, T.C. and A.C. Gatrell. 1995. Interactive Spatial Data Analysis. Essex, UK: Longman Group Limited.

Beletsky, D., J.H. Saylor, and D.J. Schwab. 1999. Mean Circulation in the Great Lakes. Journal of Great Lakes Research 25(1): 78-93.

Blair, S.F., and J.F. Atkinson. 1993. Effect of Flow Diversions on Contaminant Modeling in the Niagara River. Journal of Great Lakes Research 19, 1: 83.95.

Buttner, O., A. Becker, S. Kellner, B. Kuehn, K. Wendt-Potthoff, D.W. Zachmann, and K. Friese. 1998. Geostatistical Analysis of Surface Sediments in an Acidic Mining Lake. Water, Air, and Soil Pollution 108: 297-316.

Canadian Council of Ministers of the Environment (CCME). 1999. Canadian environmental quality guidelines. Winnipeg, Manitoba, Canada.

Canadian Council of Ministers of the Environment (CCME). 2001. Canadian water quality guidelines for the protection of aquatic life: Canadian Water Quality Index 1.0, Technical Report.

Ecowise. 2002. http://www.mcmaster.ca/ecowise/contents.htm

Environmental Systems Research Institute, Inc. (ESRI). 2001. ArcGIS 8.1 software. Redlands, CA: Environmental Systems Research Institute, Inc.

The Great Lakes: An Environmental Atlas and Resource Book-Third Edition (GLA). 1995. http://www.epa.gov/glnpo/atlas/intro.html.

The Great Lakes Forecasting System, Lake Bathymetry (GLFS). 2002.http://superior.eng.ohio-state.edu/lakes/ontario/nf-index.html

Hodgson, E. and P.E. Levi. 1997. A Textbook of Modern Toxicology. Stamford, Connecticut: Appleton and Lange.

Isaaks, E.H. and M.R. Srivastava. 1989. An Introduction to Applied Geostatistics. New York, NY: Oxford University Press.

Johnston, K., J. Ver Hoef, K. Krivoruchko, and N. Lucas. 2001. Using ArcGIS Geostatistical Analyst. New York, NY: Environmental Systems Research Institute.

Joshi, R. S., B. Shukla, and A. Bobba. 1992. Lead-210 Sedimentation in Lake Ontario. Environmental Geology and Water Sciences 19, 2: 121.126.

Lake Ontario Lakewide Management Plan (LOLMP). 1998. http://www.epa.gov/glnpo/lakeont/

Marvin, C., L. Grapentine, and S. Painter. 2002. Application of a Sediment Quality Index to the Lower Great Lakes. National Water Research Institute and Ontario Region. Environment Canada, Burlington, Ontario.

Ouyang, Y., J. Higman, J. Thompson, T. O'Toole, and D. Campbell. 2002. Characterization and spatial distribution of heavy metals in sediment from Cedar and Ortega rivers subbasin. Journal of Contaminant Hydrology 54: 19-35.

Rukavina, A. N., A. Mudroch, and S.R. Joshi. 1990. The Geochemistry and Sedimentology of the surficial sediments of Lac St-Louis, St. Lawrence River. Science of the Total Environment. 97/98: 481.494.

Sly, P.G. 1991. The Effects of Land Use and Cultural Development on the Lake Ontario Ecosystem since 1750. Ottawa, Ontario: Rawson Academy of Aquatic Science.

Smith, S.L., D. Macdonald, K. Keenleyside, C. Ingersoll, and L.J. Field. 1996. A Preliminary Evaluation of Sediment Quality Assessment Values for Freshwater Ecosystems. Journal of Great Lakes Research 22(3): 624.638.

Sorokin, Y.I. 1966. Carbon-14 method in the study of the nutrition of aquatic animals. International Revue of Hydrobiology 51: 209-224.

Statistics Canada. 2002. http://www.statscan.ca.

Zarull, M.A., J.H. Hartig, G. Krantzberg, K. Burch, D. Cowgill, G. Hill, J. Miller, and I.G. Sherbin. 1999. Contaminated Sediment Management in the Great Lakes Basin Ecosystem. Journal of Great Lakes Research 25(2): 412.422.