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Geospatial Analysis of Zinc Contamination in Lake Ontario Sediments

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ABSTRACT. This study analyzed zinc contamination concentrations in Lake Ontario sediments. While trace amounts of zinc are important for overall biotic health, large quantities can lead to toxic ecosystem contamination. The data that were utilized in this research were collected as part of the Environment Canada Great Lakes Sediment Assessment Program. Geospatial analysis has become increasingly important when examining spatial trends. A GIS-based kriging technique was utilized to interpolate contamination estimates between sampling locations. The Canadian federal government 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 biological effects are expected to occur frequently. The historical and contemporary results indicate that areas of the lake have zinc concentrations that are above the PEL and represent a degree of enrichment of roughly twice the historical background levels. These are mostly associated with the major depositional basins in Lake Ontario with the southern parts of lake having higher concentrations than those in the north. This is related to the eastward flowing current along the southern shore which acts to transport contaminants from Canadian and American industrial estates towards the depositional basins, and bathymetry as the three primary deep-water depositional basins extend much closer to the southern shoreline, compared to the northern shoreline. The kriging analysis has provided an additional communication tool and means of influencing management options and decisions.

Keywords: GIS, lake Ontario, log-normalization, ordinary kriging, sediment contamination, zinc

1. Introduction

The moderately-reactive, bluish-white, metal zinc (Zn) is an important element in the health of biota. However, aquatic organisms have been affected by the heavy metal as a result of anthropogenic causes (Jones et al., 2000). Zinc is one of the essential trace elements and a significant component in protein functions. It is a member of one of the subgroups of micronutrients and has a dominant relative significance in human nutrition (Vallee and Falchuck, 1993; Hambidge, 2000). Zinc is very important in metabolism where it is a part of catalytic sites of at least one enzyme on every classified enzyme (McCall et al., 2000). In addition to its significance in human health, it also has prominent role in the animal and plant kingdoms where several hundred zinc metalloenzymes have been identified (Hambidge, 2000; Petrisor et al., 2004). However, when inorganic elements like Zn and Copper (Cu) have elevated concentrations in soil beyond the threshold; they might become toxic inhibiting plant growth. If taken from the roots, they might enter the food chain and become toxic to whole ecosystems constituting humans, animals and plants (Petrisor et al., 2004; Komnitas and Modis, 2006). Because of its vital role in terrestrial and aquatic ecosystems, there is a growing concern about the zinc contamination.

Zinc contamination in the aquatic ecosystem is one of the problems caused by the urban runoff, sewage, traffic emissions, industrial production and pollution, mining and other anthropogenic causes (Jones et al., 2000). Fish from the Great Lakes are prone to contamination as they are at the top of the aquatic food-chain and are affected most by pollution (U.S. EPA, 2006). Lake Ontario is prone to anthropogenic contamination due to its "location to the bottom end of the Great Lakes system" (Forsythe et al., 2004; Jakubek and Forsythe, 2004). There have been significant reductions in toxic contamination over the past 20 years, but high pollutant concentrations in the bottom sediments of estuaries and lakes can still affect humans, wildlife and aquatic organisms in the Great Lakes.

The Canadian Council of Ministers of the Environment (CCME) has defined limits with respect to contaminant concentrations. These are the Threshold Effect Level (TEL) which refers to the concentration below which adverse biological effects occur rarely and the Probable Effect Level (PEL) which refers to the level above which adverse biological effects may

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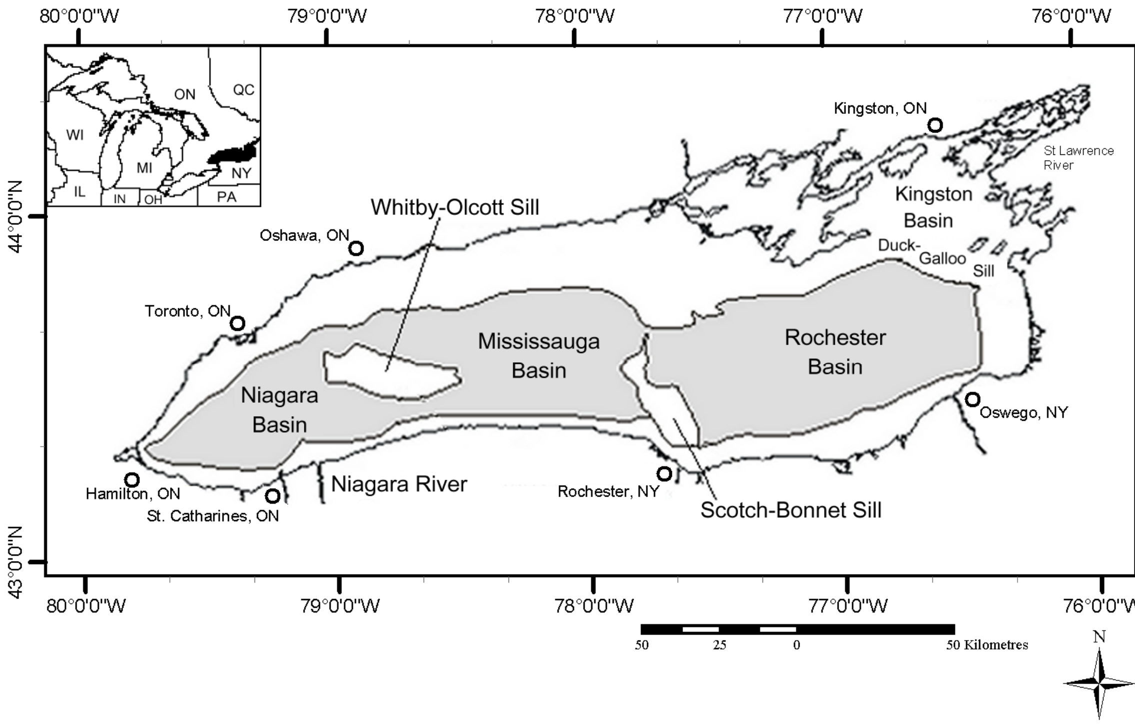

Figure 1. Lake Ontario including major cities and depositional basins (Source: modified after Marvin et al., 2003 and Forsythe et al., 2004).

occur frequently (CCME, 1999; Forsythe et al., 2004). For zinc, the TEL is 123 µg/g, while the PEL is 314.8 µg/g.

Moffett et al. (2003) undertook a study that compared the soil biodiversity using zinc-contaminated soil with that of a control soil from a long-term sewage sludge experiment. Using 190 operational taxonomic units in the control soil and 90 in the "treated soil" (zinc-contaminated soil), restriction fragments length polymorphisms (RFLP) of 236 clones from each soil were compared. The results indicate that stress caused by zinc toxicity plays a critical role in lowering bacterial diversity (Moffett et al., 2003). An et al. (2006) found that Pteris vittata L. could take up zinc "into its fronds, with a maximum of 737 mg/kg under field conditions". Watzin and Roscigno (1997) conducted an experiment with benthos (invertebrate organisms that live in or near the sea beds) that showed higher zinc concentrations adversely affect survival. The total number of organisms in the zinc-treatment boxes were compared with those in the control boxes. There were significantly different results showing that fewer individuals in the zinc-treated boxes survived than those of the control boxes (Watzin and Roscigno, 1997). Studies such as these suggest that the zinc contamination is an issue to our overall ecosystem.

2. Site Location and Data

Lake Ontario (Figure 1) is located at the bottom end of the Great Lakes system along the Canada-USA border. It is the smallest of the Great Lakes with an area of 18,960 km^2. The main part of the lake is divided into three major depositional sub-basins (Niagara, Mississauga, Rochester). The lake has the highest ratio of watershed area to lake surface of any of the Great Lakes and its average depth is 86 m. Approximately 80% of the in-flow water comes from Lake Erie through Niagara River (Forsythe et al., 2004; U.S. EPA, 2007). Inflow averages of 7,000 m^3/s over the year (Atkinson et al., 1994; 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). The Lake Ontario ecosystem is adversely affected by industrial pollution from the surrounding major cities and the widespread development of Toronto, St. Catharines, Hamilton, Oshawa and Kingston on the Canadian shoreline and Rochester and Oswego on the U.S. side (Forsythe et al., 2004).

The Lake Ontario Lakewide Management Plan aims to recognize human capabilities and responsibilities in preserving the Lake Ontario basin in order to preserve the aquatic organisms and waters of the lake (U.S. EPA, 2007). With an objective of aquatic habitat conservation, more recent stewardship shows a positive trend in Lake Ontario water contamination. A recent comparison of mercury (Hg) and lead (Pb) contamination between 1968 and 1997/98 using the kriging method shows that contamination levels have decreased in Lake Ontario in recent years. However, challenges still exist, particularly in the central regions of both the Mississauga and Rochester sub-basins (elevated Hg concentrations), and in terms of Pb concentrations which are higher near Hamilton in the Niagara sub-basin (For-

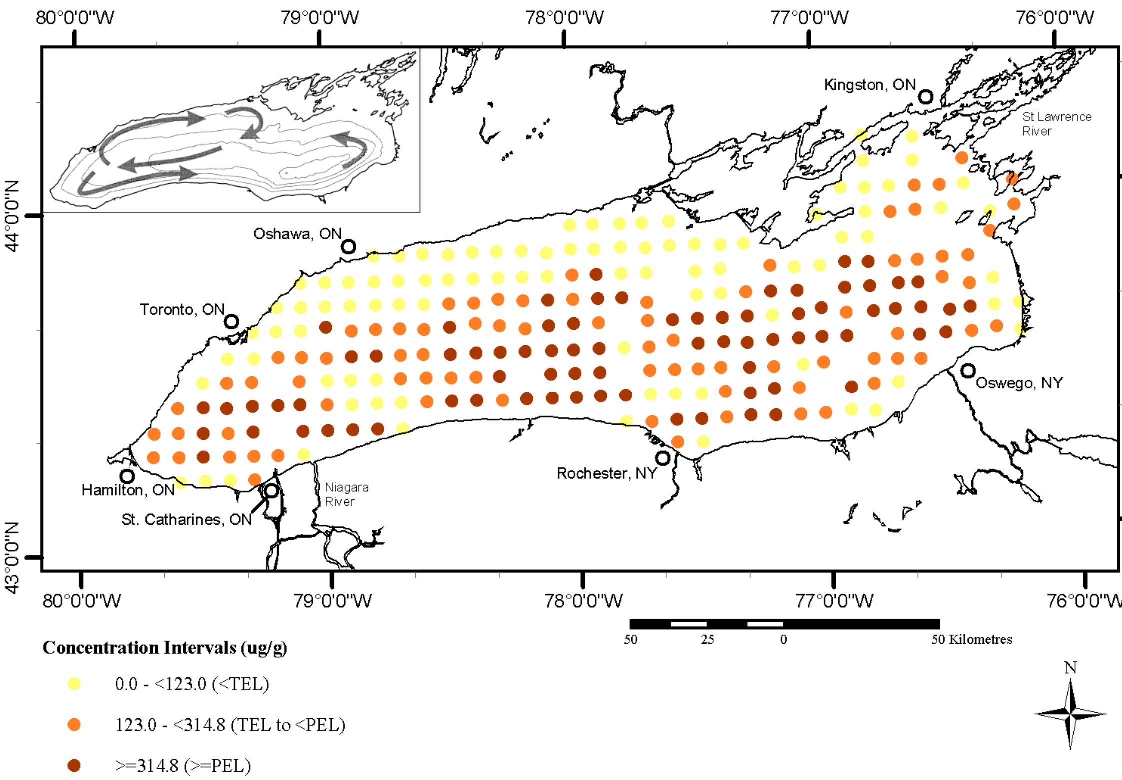

Figure 2. 1968 Sediment Sampling with zinc concentrations divided by the TEL and PEL (inset: time-averaged circulation in Lake Ontario - isobaths every 50 m - Source: modified after Beletsky et al., 1999).

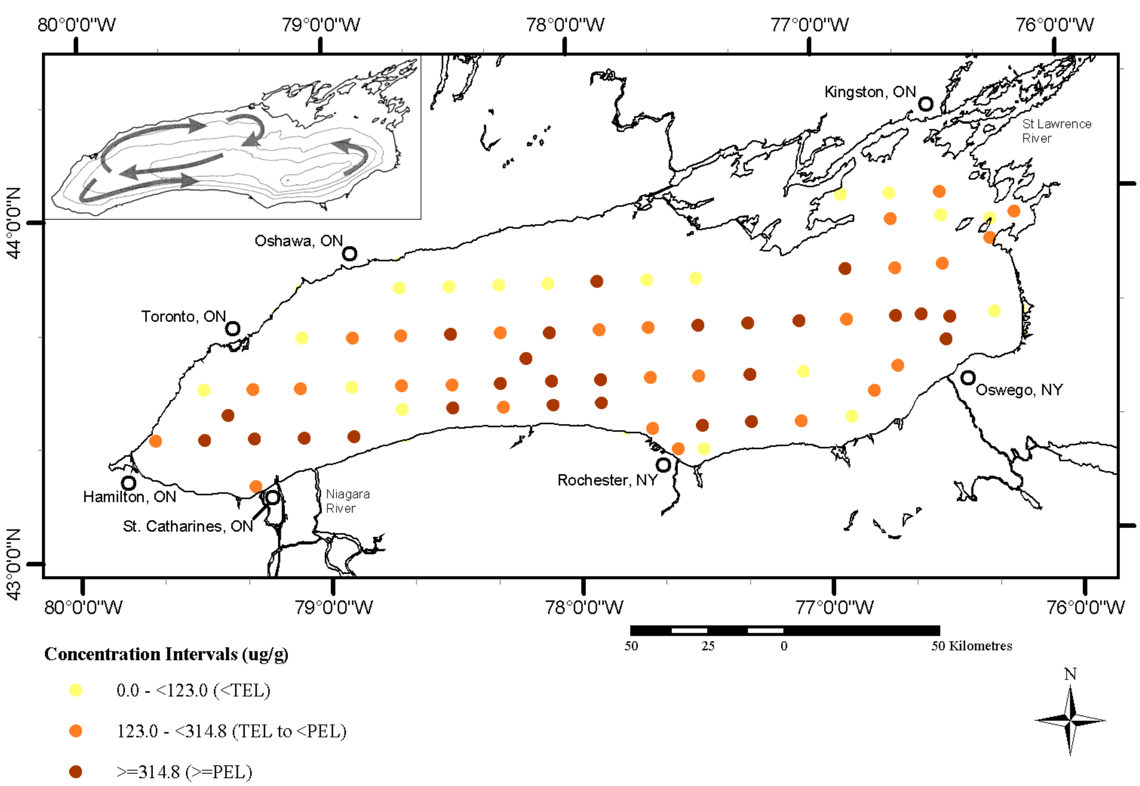

Figure 3. 1968R Sediment Sampling with zinc concentrations divided by the TEL and PEL (inset: time-averaged circulation in Lake Ontario - isobaths every 50 m - Source: modified after Beletsky et al., 1999).

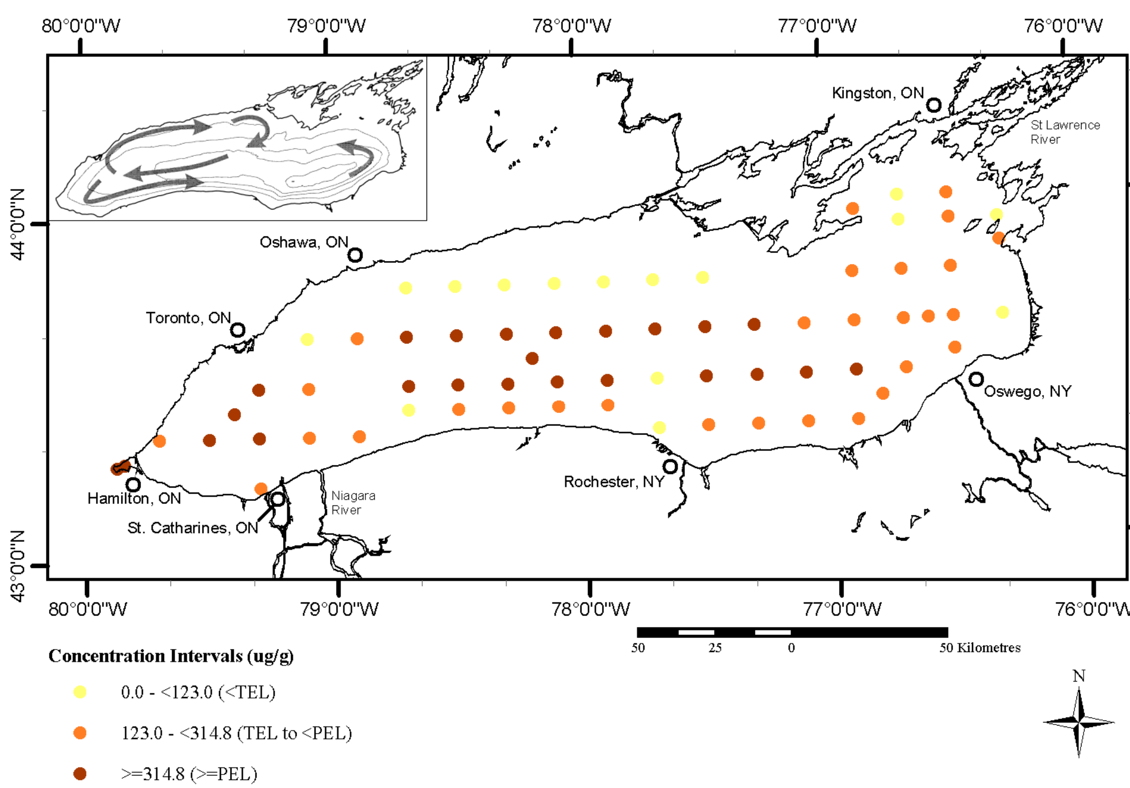

Figure 4. 1998 Sediment Sampling with zinc concentrations divided by the TEL and PEL (inset: time-averaged circulation in Lake Ontario - obaths every 50 m - Source: modified after Beletsky et al., 1999).

sythe et.al, 2004; Jakubek and Forsythe, 2004).

The data for this study were obtained by Environment Canada under the Great Lakes Sediment Assessment Program. The samples were analyzed in the laboratory using standard procedures described in Marvin et al. (2002). The historical (1968) dataset contains 249 sample sites (Figure 2). In order to more readily compare the datasets, the original 1968 dataset was also reduced (Figure 3, denoted hereafter as 1968R) to match (as closely as possible) the 68 locations in the contemporary (1998) dataset (Figure 4). The question is whether the same types of contamination patterns can be seen in the reduced data set (1968R) as compared to the full 1968 dataset. The characteristics of each dataset are presented in Table 1. The percentages and numbers for each dataset in relation to the TEL and PEL are presented in Table 2. Although the range of minimum to maximum values has decreased in the contemporary (1998) data, the overall percentage of zinc ≥PEL has increased when compared with the full historical dataset. The 1968R and 1998 datasets are however very similar when looking at the numbers of points in each category in Table 2, however the maximum value in the 1968R dataset is much lower than the 1998 dataset and it is 7 times lower than the maximum in the full dataset. The contemporary dataset contains a smaller number of sample sites due to the prohibitive cost of resampling all of the original locations. Besides, the 1998 survey specifically targeted fine-grained offshore sediments in primarily depositional areas, as opposed to the 1968 survey, which was based on lake-wide grids (Forsythe et al., 2004). A mini-box core sampling procedure (Marvin et al., 2003; Marvin et al., 2004b; Gewurtz et al., 2008) was utilized where the top 3 cm of the sediment were sampled at each station in order to be consistent with the previous sediment surveys conducted by Environment Canada and collaborators in these lakes (Frank et al., 1979) as well as with the more recent surveys conducted in the Great Lakes (Marvin et al., 2003; Forsythe et al., 2004; Marvin et al., 2004a; Marvin et al., 2004b; Forsythe and Marvin, 2009). The sediments were analyzed in order to measure organic and metallic contamination (Marvin et al., 2004c; Forsythe et al., 2004).

Table 1. Zinc Sediment Sampling Location Statistics for Lake Ontario (1968, 1968R, and 1998)

Year	Site No.	Min*	Max	Median	Average	SD**
1968	249	6	3507	201	214	246.45
1968R	68	18.3	499.5	273.9	231.3	125.91
1998	68	11	1343	239	261	200.26

*Unit: µg/g; ** SD: Standard Deviation.

Table 2. Percent and Number of Zinc Sediment Sampling Locations in Relation to TEL and PEL Categories (1968, 1968R, and 1998)

Year	Site No.	< TEL	≥ TEL and < PEL	≥ PEL
1968	249	36.6% (91)	32.9% (82)	30.5% (76)
1968R	68	25.0% (17)	36.8% (25)	38.2% (26)
1998	68	22.1% (15)	42.6% (29)	35.3% (24)

3. Methodology

Many phenomena can be measured and interpolated using spatial analysis tools. Examples such as temperature, precipitation and other similar phenomena cannot be measured over an entire study area. Therefore, interpolation techniques can be applied to obtain the estimates for non-sampled locations. A "goodness of fit" for the interpolation can be determined by different measures including a ground-truth measure where the results are compared with the true points on the earth surface (Carfora, 2007). There are different types of formulations for triangular interpolation methods. The linear interpolations with different methods are identical and can be compared using their interpolation weights (Carfora, 2007).

Ordinary kriging was used for this study. It is one of the geostatistical tools that were developed for the estimation of ore reserves in mining (Bailey and Gatrell, 1995; Johnson et al., 2001). This method uses statistical models that are based on the assumption that spatial autocorrelation exists within a collection of sampled points. Kriging uses a semivariogram to model empirical data in order to predict unknown values for a variable using the known values (Johnston et al., 2001). Ordinary kriging is found to perform better than other interpolation methods such as Inverse Distance Weighting (IDW) because it uses cross-validation and generates standard error surfaces, therefore allowing prediction surfaces to be statistically validated (Zimmerman et al., 1999; Van Groenigen 2000; Johnston et al., 2001; Forsythe et al., 2004; Jakubek and Forsythe, 2004; Forsythe and Marvin, 2009). In order to create a prediction surface from the empirical point-sampled data, ordinary kriging uses the following equation:

$$Z(s) = U + e(s) \tag{1}$$

where Z(s) are the unknown values for a variable at location s, U is an unknown constant mean for the data (with an assumption of no apparent trend) and e(s) is the random error associated with the prediction (Isaaks and Srivastava, 1989; Oliver, 1990; Johnston et al., 2001; Jakubek and Forsythe, 2004). While computing the weights, this method minimizes the variance between the "estimated value and unknown values" (Quyang et al., 2003).

The inferences made by kriging are more efficient if the data are normally distributed. The size of the search neighborhood becomes crucial as increased distance can decrease the spatial autocorrelation among measured points (Johnston et al., 2001; Jakubek and Forsythe, 2004; Paudel, 2008). In order to avoid the influence of the measured points that have minimal impacts on the prediction, the maximum and minimum neighbourhood size was assigned as 5 and 1 respectively. These values produced the best overall statistics and represented what was actually present in the sediment. They were also found to function very well in previously published research using these sampling locations for mercury, lead, PCBs, and hexachlorobenzene (Forsythe et al., 2004; Forsythe and Marvin, 2005). They help to identify local "hotspots" without too much pattern generalization.

Cross-validation was conducted in order to determine the "best fit" of three models (spherical, Gaussian, and exponential) that were evaluated. Semivariogram analysis is used to identify and describe the spatial structure of a stochastic (random) process by mathematically computing an empirical semivariogram and then fitting it with a model (Ouyang et al., 2003). Modeling the spatial dependency (semivariogram modelling) is the most important step in kriging (Krivoruchko, 2005). The line of fit through the points forming the empirical semivariogram is the model.

In the prediction surfaces that were created, prior knowledge of lake currents (annualized current flow from west to east) and bathymetry was incorporated into our choices. We used 90 degrees for the direction after extensive experimentation with various options for this feature. In addition, the maximum/minimum ranges were set at 50,000/25,000 metres and 100,000/-50,000 metres for 1968 and 1968R/1998 data sets respectively. This takes into account the distance between sampling points in the respective sediment surveys that were conducted.

Ordinary kriging cross validation statistics should have a mean prediction error (MPE) close to 0, a root-mean square prediction error (RMSPE) and average standard error (ASE) as small as possible (less than 20), and a standardized root-mean squared prediction error (SRMSPE) close to one (Johnston et al., 2001; Forsythe et al., 2004). The average standard error should be less than 20 to ensure that the predicted kriging values do not stray too much from the original point data values. The common approach is that the average standard error should be as close as possible to the root mean squared prediction error (regardless of value) but when these values are above 20, the predicted values are not very close to the actual point values at each location (Jakubek and Forsythe, 2004; Forsythe and Marvin, 2005; Forsythe and Marvin 2009). 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 and Marvin, 2005).

When kriging models are not statistically valid, it is possible to improve estimation outcomes by putting the original data through a log normalization process. This has been shown to provide suitable estimation outcomes by Forsythe and Marvin (2005) and Ouyang et al. (2003).

Table 3. Kriging Log-Normalized Data Cross Validation Statistics for 1968, 1968R, and 1998

Year	Model	MPE	ASE	SRMSPE
1968	Gaussian	0.004	0.278	0.994
1968R	Exponential	0.011	0.303	1.029
1998	Exponential	0.018	0.305	0.945

4. Results

The data from all of the datasets were found to be skewed. They were therefore log transformed to obtain normalized distributions. Although "normal" data are not required for kriging,

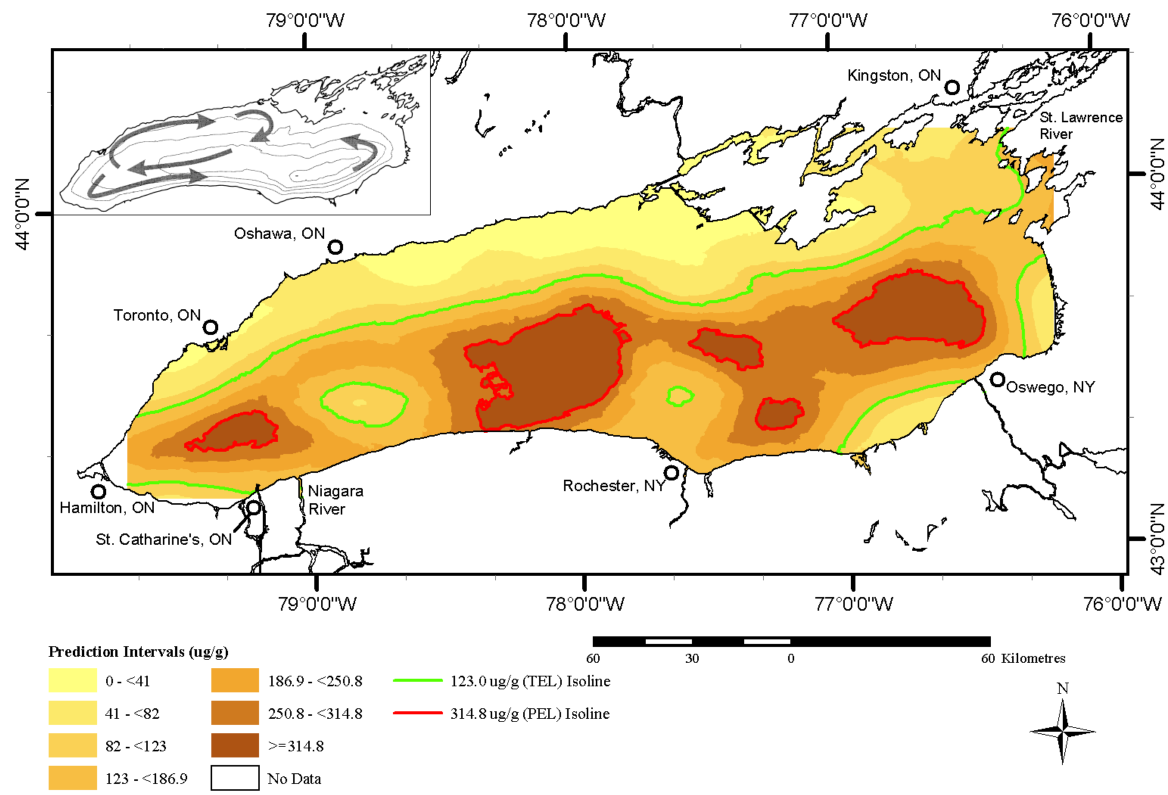

Figure 5. 1968 kriged zinc log-normal concentrations (inset: time-averaged circulation in Lake Ontario - isobaths every 50 m - Source: modified after Beletsky et al., 1999).

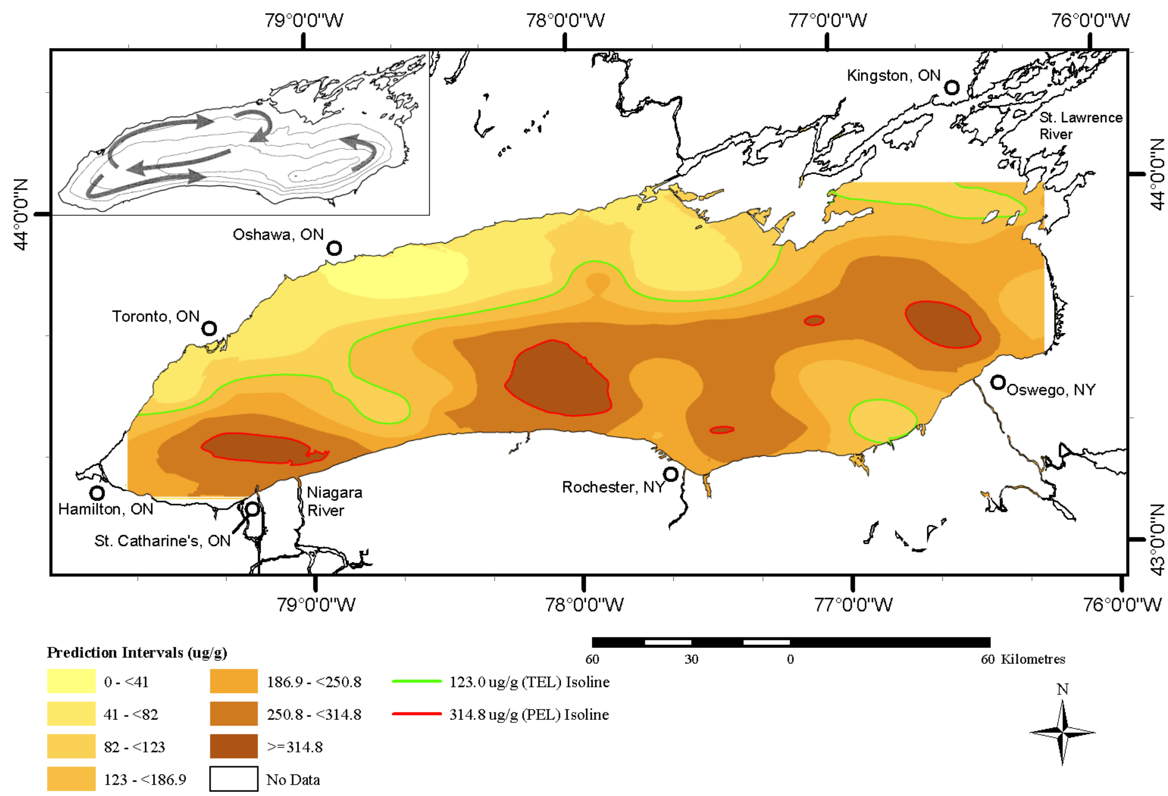

Figure 6. 1968R kriged zinc log-normal concentrations (inset: time-averaged circulation in Lake Ontario - isobaths every 50 m - Source: modified after Beletsky et al., 1999).

a normalized distribution generally provides for improved statistics in the kriging process (Forsythe and Marvin, 2005; Forsythe and Marvin, 2009). The historical log-normalized data functioned best using the Gaussian model for the predictions (Table 3), whereas the historical reduced and contemporary log-normalized data performed best using the exponential prediction model.

All of the log-normalized historical and the contemporary data match the criteria outlined for the best models (Johnston et al., 2001; Forsythe et al., 2004). The historical data has a MPE of 0.004, ASE of 0.278, and SRMSPE of 0.994. The result shows the model has very slightly overestimated the variability of the prediction (0.994 < 1), however this is one of the best results that can be achieved using ordinary kriging methods.

The 1968R data reveal a slight underestimation for the prediction with a SRMSPE of 1.029. The MPE of 0.011 and ASE of 0.303 are very close to the optimal values. Similarly, the contemporary results indicate the same pattern with the best model prediction errors (MPE = 0.018, ASE = 0.305 and SRMSPE = 0.0945). The SRMSPE value (0.945 < 1) shows an overestimation of the variability in the prediction (Johnston et al., 2001; Forsythe et al., 2004).

4.1. Zinc 1968

The mapped kriging results shown in Figure 5 indicate that more than 50% of Lake Ontario (in the analysis area) had a zinc concentration above the TEL but below the PEL whereas approximately 12% of Lake Ontario had a concentration of zinc ≥ PEL. Higher concentrations were found near the southern shorelines with five specific pockets within the three major depositional basins. The southern part of the Mississauga basin had the largest patch of zinc concentrations above PEL. In addition to the Mississauga basin, the Rochester basin had three distinct zones where the zinc concentrations were above the PEL. There is a clear indication that the three depositional basins (see Figure 1) have the highest concentrations of zinc when compared to the rest of Lake Ontario.

The contamination patterns show that the northern shoreline of Lake Ontario does not have any areas of high zinc concentrations. In fact, these areas have the lowest zinc pollution levels in the entire lake. Lake circulation and bathymetry seem to play a major role in the observed patterns. The eastward flowing current along the southern shore acts to transport contaminants from Canadian and American industrial estates which has resulted in high (above PEL) concentrations to the east in depositional basins. Figure 1 clearly shows the shallow water shelf running along the north shore of Lake Ontario, while the deep water depositional basins are much closer to the southern shoreline.

4.2. Zinc 1968R

The 1968R results shown in Figure 6 provide a more general overview of contamination patterns than the 1968 kriged predictions. This is similar to the results for Lake Huron as discussed by Forsythe and Marvin (2009) where more recent and less intensive sediment surveys revealed similar outcomes. The area that is between the TEL and PEL is now 64% which is more than the full 1968 dataset. In addition, the area ≥ PEL has decreased to 6% of the analysis area.

When comparing the 1968 and 1968R kriging results, the patterns are very similar when the classes on either side of the PEL are investigated. This is particularly noticeable when examining the contamination patterns in the Mississauga and Rochester Basins. The removal of some ≥ PEL data points in the reduced 1968R dataset can to a large extent explain the loss of some of the ≥ PEL areas and the lower area percentage in this category. Additionally, there is definitely an influence of points with values that are lower than the PEL affecting the results.

4.3. Zinc 1998

Figure 7 shows that more than 54% of the zinc concentration in Lake Ontario for 1998 (in the analysis area which varies slightly from the 1968 boundaries) is above the TEL but below the PEL, whereas approximately 18% has concentrations ≥ PEL. The ≥ PEL areas have therefore increased in comparison to both the 1968 and 1968R predictions. The highest concentration levels have been reduced (overall) but the areas ≥ PEL have become more widespread. The pattern of zinc concentrations has shifted towards the deeper, central parts of the lake, possibly due to redistribution via currents and ongoing contaminant inputs (Beletsky et al., 1999; Forsythe et al., 2004). The higher concentrations in the western part of the lake may have been influenced by the two higher concentration sediment sampling sites in Hamilton Harbour that may skew the results (Forsythe et al., 2004).

5. Discussion

In all of the kriging results, the influence of bathymetry is quite clear. When the location of the Whitby-Olcott and Scotch-Bonnet Sills (see Figure 1) is considered, the pattern of lower contaminant levels in the vicinity of these features is quite evident. The Niagara, Mississauga, and Rochester Basins all contain areas that are highly contaminated with zinc. The 1968 and 1968R results are quite similar although more general trends are revealed in the 1968R kriging results. The 1968R pattern is also partially explainable with one missing value point and another that is < TEL in the Rochester Basin when compared to the 1998 prediction result where both points are ≥ PEL. In addition, there is a persistent pattern of sample points that are ≥ PEL in the 1998 dataset that runs through the major depositional basins that is not present in either of the 1968 or 1968R datasets.

Ordinary kriging, as a predictor, preformed well with statistically valid results. Although kriging does not require data to be normalized, recommendations from Forsythe et al. (2004) and Quyang et al. (2003) were considered and the results were statistically valid after log-transformation. Zinc concentrations from 1968, 1968R, and 1998 showed that areas above the PEL are generally found in the southern and central portions of Lake

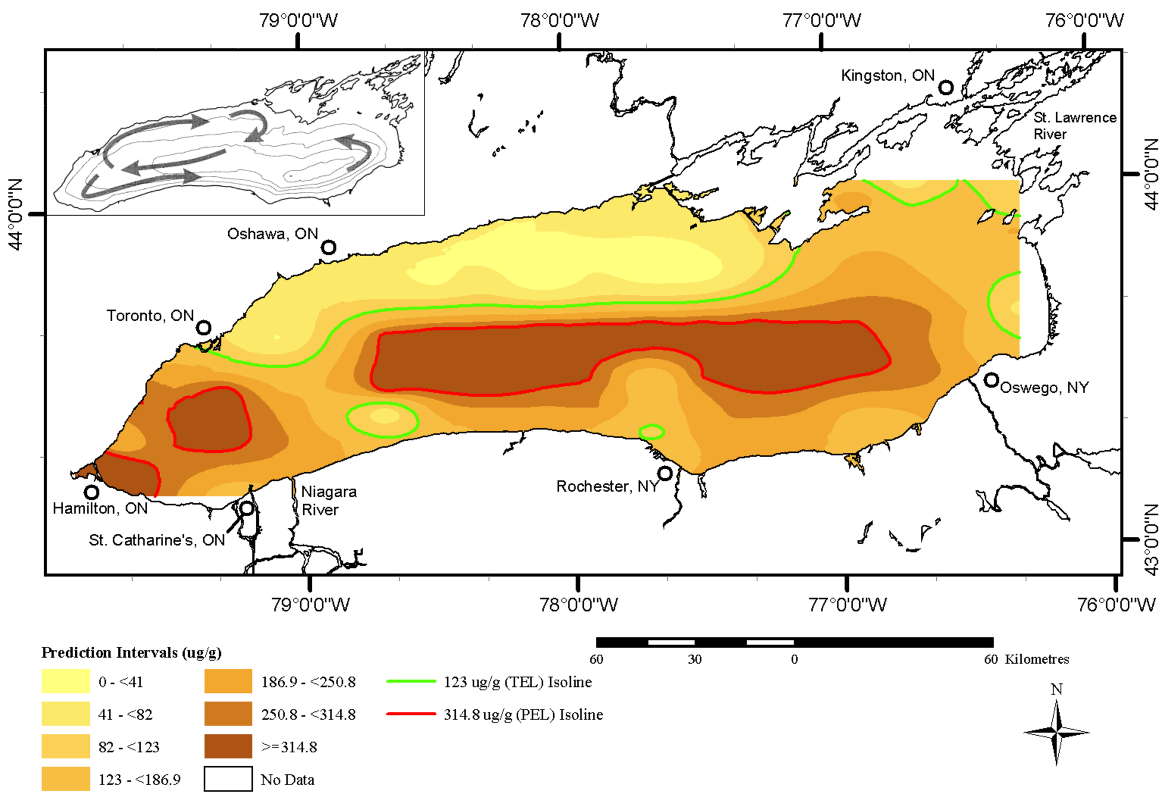

Figure 7. 1998 kriged zinc log-normal concentrations (inset: time-averaged circulation in Lake Ontario - isobaths every 50 m - Source: modified after Beletsky et al., 1999).

Ontario (Figures 5 to 7). This is in agreement with the study done to evaluate the historical (1968) and contemporary (1998) mercury sediment contamination in Lake Ontario (Forsythe et al., 2004). The results also support the fact that counterclockwise, eastward moving currents in Lake Ontario have acted to deposit sediments in deep-water basins further to the east (Beletsky et al., 1999; Forsythe et al., 2004). In addition, another contributing factor, industrial pollution, may have influenced the concentrations near the southern shorelines because major industrial areas, including Hamilton, Rochester and Buffalo are located in this region. Contrastingly, areas near the northern shoreline are shallower and the industrial regime is not as significant.

The northeastern part of the lake has lower zinc concentrations due to a lack of direct sediment deposition from a major river and the influence of the Duck-Galloo Sill which acts as a barrier to sediment transport. Zinc is a component of tires and is released as tires wear. The role of roads or transportation networks (Doss et al., 1995) which are much less concentrated near the northeastern part of the lake might also play a role in the lower concentrations in this area. This would agree with the findings of Nabulo et al. (2006) which verified that the distance from roads has inverse relationship with the zinc concentrations in soils. The southwestern part of Lake Ontario has one of the highest levels of zinc concentrations, which may be influenced by the negative effects of the factors discussed in this section.

6. Conclusions

A closer look at zinc pollution levels between 1968 and 1998 reveals that the concentrations have shifted towards the central part of Lake Ontario in recent years, instead of being closer to the mouth of the major river systems. The historic data shows that higher concentrations of zinc were closer to major industrial areas (in contrast to the recent data), therefore it might be appropriate to draw the conclusion that lower amounts of zinc were deposited in recent years as compared to 40 years ago. This suggests that zinc concentrations could have been a function of early-and mid-20th century industrial development, and there has been a gravitational shift towards the centre of the lake as urban and industrial pollution have gradually decreased in recent years. For future research it would be interesting to analyze zinc concentrations from past and present in order to determine if environmental awareness and conservation actions such as the Lake Ontario Lakewide Management Plan have significantly helped to reduce the zinc concentrations in more recent times.

Ordinary kriging, as a tool, has provided a clear insight on the status of the concentrations of zinc in Lake Ontario in historic and contemporary contexts, especially where compared to dot or point mapping. This visual representation of aquatic ecosystems should help decision makers better implement existing and future polices, targeting the most critical areas in order to support a sustainable lake ecosystem. However, the results should be used while also considering the prediction errors. Although ordinary kriging is the least biased interpolation method, it is important to understand that the edges of the prediction surfaces are more likely to have higher prediction errors than those of the central areas (Johnston et al., 2001; Forsythe et al., 2004; Jakubek and Forsythe, 2004; Paudel, 2008; Forsythe and Marvin, 2009). In addition, ordinary kriging shows potential as a tool for survey design over large geographic areas. A sediment survey of the scope and resolution of the 1968 Lake Ontario study would today be prohibitive in terms of infrastructure requirements, time and cost. The comparison of the kriging of the reduced 1968R, 1968 and 1998 data sets for zinc show the survey design for the contemporary 1998 survey of 68 stations was justified. Although there was some loss of detail in the western area of the Rochester Basin in comparing the 1968 and 1968R data sets, the spatial distributions among the two data sets, and correspondingly the conclusions regarding sources of chemical contamination, bathymetry and physical regime, remained the same.

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