Assessing historical versus contemporary mercury and lead contamination in Lake Huron sediments

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This research utilized surficial sediment core sample data that were collected in 1969/1973 and 2002 from Lake Huron as part of the Environment Canada Great Lakes Sediment Assessment Program. Concentrations for mercury and lead were analyzed due their persistence in the lake ecosystem and their detrimental environmental effects. The analysis area included the main basin of Lake Huron, Georgian Bay, and the North Channel. Comprehending overall pollution levels strictly on the basis of point data is a difficult task, however spatial analysis techniques combined with Geographic Information Systems can be used to gain a better understanding of lake-wide trends. The Geostatistical Analyst extension of the ESRI ArcGIS software was used to carry out ordinary kriging analyses on the datasets. They produced statistically valid concentration estimates with log-normal data transformation procedures occasionally being performed to obtain suitable prediction estimates. Geospatial analysis (including kriging) allows for samples that vary in number and location to be analyzed and compared with each other based on areal estimates. Overall decreases in contamination levels were observed between the historical and contemporary surveys. Mercury has seen a dramatic reduction in concentrations from 1969/1973 to 2002, while the lead results indicate that high levels of contamination (compared to background concentrations) still persist in the contemporary dataset, although they have subsided from historic values. Higher contaminant concentrations were generally found in depositional basins. The interpolated kriging surfaces are more informative than i.e. conventional dot and/or proportional circle maps in the amount of information they present. They also provide an increased understanding of both the spatial distribution and temporal trends in sediment contamination in Lake Huron.

Keywords: Kriging, sediment contamination, metals, estimation, geospatial analysis

Introduction

Five major lakes (Superior, Michigan, Huron, Erie, and Ontario) make up the Laurentian Great Lakes of North America. Lake Huron is located downstream from Lake Superior, is hydrologically inseparable from Lake Michigan (connected through the Straits of Mackinac), and upstream of Lake Erie. It is the 3rd largest lake by volume in the Great Lakes Basin (GLIN, 2004). The lake consists of three major sections; the main basin, Georgian Bay, and the North Channel.

Toxic pollutants and their distribution in the environment are increasingly under scrutiny (Bosworth and Thibodeaux, 2006; Gewurtz et al., 2007; Gewurtz et al., 2008; Hillery et al., 1998; Kolak et al., 1998; Makarewicz et al., 2003; Marvin et al., 2004a; Marvin et al., 2004b; Song et al., 2005a;

Aquatic Ecosystem Health & Management, 12(1):101–109, 2009. ISSN: 1463-4988 print / 1539-4077 online
DOI: 10.1080/14634980802690873

Sun et al., 2006). There seems to be much debate as to whether enough is being done by various levels of government to help regulate outflows into Great Lakes waters. The persistence of some contaminants also requires that remediation programs be ongoing to help alleviate pollution issues that stem from years of uncontrolled and in some cases continuing releases of toxic substances. The Canadian and American governments recognized the need to respond to pollution concerns in the Great Lakes Basin when they signed the amended Great Lakes Water Quality Agreement in 1987. Among the recommendations in the agreement was the creation of a Lakewide Management Plan for each lake (Great Lakes Commission, 2004). The cost of cleanup and the effectiveness of the agreement are some of the issues that have recently been considered (Benevides and De Leon, 2006; Shear et al., 2003).

Geospatial analysis (including kriging) allows for diverse samples that vary in number and location to be analyzed and compared with each other. Interpolation and mapping of sediment contamination data greatly improves the interpretation of spatial trends. Dot and/or proportional circle maps have been used to analyze distribution patterns however the use of geospatial analysis has the advantage of enabling a full investigation of areal trends that is not possible with either of these mapping methods. The kriging technique has been used in many application areas including: mining and petroleum exploration, environmental studies, and even agricultural practices. Few however have applied this tool for the estimation of sediment contamination distribution. Some recent examples for river environments include Ouyang et al. (2003a), and Ouyang et al. (2003b). In the Great Lakes Basin, Jakubek and Forsythe (2004), Forsythe et al. (2004), and Forsythe and Marvin (2005) utilized kriging to estimate sediment contamination levels. Panahi et al. (2003) also used kriging for modelling lake sediment geochemical distribution. The objective of this paper is to further develop sediment contamination distribution analyses utilizing the ordinary kriging technique. The advantages of this method over traditional dot and/or proportional circle mapping representations (including the ability to directly compare disparate data sets and the generation of statistically valid concentration estimates) are emphasized.

Mercury and lead contamination in Lake Huron

The Michigan Department of Environmental Quality (2002) has identified mercury (Hg) and lead (Pb) as critical pollutants in the Lake Huron Ecosystem. There is however some reason for optimism with respect to contamination levels. The State of the Lake Huron 2005 report states that contamination levels in the ecosystem are mixed and improving (Binational.net, 2005). Mercury in Lake Huron has caused fish consumption advisories and has been detected in water, sediment and wildlife. Mercury is a naturally occurring metal that can be introduced to the environment through the weathering of rock and soil (Rheaume et al., 2000) and the processing of coal, wood and metal (Michigan Department of Environmental Quality, 2002). Although the mining of mercury has been in decline over the last two decades, and there are no mines currently operational in Canada (Environment Canada, 2002), mercury is still commonly used in batteries, medical and dental products, the electrical industry, and thermometers (Jakubek and Forsythe, 2004). Marvin et al. (2004a) found that the spatial distribution of mercury in sediments of Lakes Huron and Superior suggest that natural geochemical factors are an influence. Surficial sediment mercury contamination was found to have decreased markedly from the late 1960s and 1970s to 2002 in Lake Huron. Decreases in lakewide average sediment concentrations of mercury over this time period were in the order of 80%. The mean background sediment mercury concentration, estimated from the deepest sections of benthos cores that predated modern industrial activity (including gold and silver processing) was 0.026 $\mu g\ g^{-1}$ which is roughly equivalent to background concentrations. The current degree of mercury contamination in Lake Huron sediments does not represent a significant degree of anthropogenic enrichment (Marvin et al., 2004a).

Lead is a heavy metal common in hazardous waste and can damage organisms at low concentrations. It tends to accumulate in the food chain (Michigan Department of Environmental Quality, 2002). Lead can be found in rocks, soil, water, air, and biota (Rickard and Nriagu, 1978), and is well known to be readily absorbed in sediments. Lead is found in Lake Huron sediment and is associated with degradation of benthos and planktonic communities. In most cases, existing concentrations are due to historical discharges (Michigan Department of Environmental Quality, 2002), and the use of lead as an additive in gasoline (Li, 2003). Lead emissions to the atmosphere for 1993 in the Great Lakes Basin were attributed to non-ferrous metal production (34%), followed by steel manufacturing and waste disposal (27% and 25%, respectively), and coal combustion (10%) — (Pirrone and Keeler, 1996).

Methodology

Field research was conducted in 1969 and 1973 to acquire surficial sediment core samples. More recently (in 2002), Lake Huron was resampled, in part to assess whether sediment quality had improved. Bedrock control or glacial features separate the main basin of Lake Huron into six individual depositional basins (Thomas et al., 1973), while Georgian Bay has two depositional zones (Frank et al., 1979). The 2002 survey was designed to focus on depositional zones in Lake Huron while the 1969/1973 surveys were more comprehensive. The samples were collected as part of the Environment Canada Great Lakes Sediment Assessment Program. For the 2002 survey, the samples were collected aboard the Canadian Coast Guard Ship Limnos using a mini-box core sampling procedure (Marvin et al., 2003; Marvin et al., 2004b; Gewurtz et al., 2008). 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 lower Great Lakes (Marvin et al., 2003; Marvin et al., 2004b). This approach is consistent with the Canadian Sediment Quality Guidelines, which relate to total contaminant concentrations in the upper few centimetres of surficial sediment samples (Canadian Council of Ministers of the Environment, 1999). After collection, the sediment samples were sub-sampled from the mini-box core for the analyses of organic contaminants, metals, and grain size. Samples for organic contaminant analyses were collected in solvent washed glass jars and samples for metals were collected in high-density polypropylene or Teflon jars. All samples were immediately frozen for transport to the laboratory (Marvin et al., 2003; Marvin et al., 2004b; Gewurtz et al., 2007).

A total of 189 samples were obtained in the main basin in 1969 with 118 and 54 samples being collected in Georgian Bay and the North Channel respectively in 1973. In 2002, 32 samples were collected in the main basin, 22 in Georgian Bay, and 13 in the North Channel. Table 1 provides a summary of the data used in this research. The surficial sediment samples differ in age since they do not accumulate evenly across the bottom of the Great Lakes (Thomas et al., 1973; Kemp et al., 1978; Song et al., 2004; Song et al., 2005a; Song et al., 2005b). Sedimentation rates were measured in at four locations throughout Lake Huron in 1999 and 2002 and ranged from 0.023 to 0.1 g $cm^{-2}yr^{-1}$ (median = 0.038 g $cm^{-2}yr^{-1}$) (Song et al., 2005a). It is important to note that most bioturbation generally occurs

Table 1. Data characteristics for Lake Huron, Georgian Bay, and the North Channel (minimum, maximum, average, and standard deviation in μg g^{-1}; some contaminants had missing data values).

Contaminant	No. of Sites	No. < TEL	No. ≥ TEL and < PEL	No. ≥ PEL	Minimum	Maximum	Average	Standard Deviation
Hg Main Basin 1969	175	109	51	15	0.03	0.81	0.22	0.16
Hg Georgian Bay 1973	116	100	8	8	0.00	9.50	0.26	1.02
Hg North Channel 1973	54	45	4	5	0.01	1.12	0.15	0.23
Hg Main Basin 2002	32	32	0	0	0.01	0.12	0.03	0.03
Hg Georgian Bay 2002	22	21	1	0	0.01	0.37	0.05	0.08
Hg North Channel 2002	13	13	0	0	0.01	0.13	0.06	0.04
Pb Main Basin 1969	158	60	79	19	0.00	139.68	48.06	33.83
Pb Georgian Bay 1973	111	51	51	9	0.00	123.90	45.34	28.74
Pb North Channel 1973	54	30	21	3	0.00	108.48	38.59	29.92
Pb Main Basin 2002	32	23	9	0	0.95	85.70	22.17	21.23
Pb Georgian Bay 2002	22	11	8	3	3.32	103.13	47.49	35.34
Pb North Channel 2002	13	7	5	1	11.59	117.49	41.90	29.17

in the top 2-5 cm of the sediment column (Bosworth and Thibodeaux, 2006).

The Geostatistical Analyst extension of the ArcGIS software was used to generate ordinary kriging prediction surfaces (and to produce dot maps). Ordinary kriging is the most widely used kriging method Ouyang et al. (2003a). 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 methods utilize statistical models which incorporate autocorrelation among a group of measured points to create prediction surfaces (Johnston et al., 2001). Kriging accounts for both the clustering of nearby samples and for their distance to the point to be estimated (Isaaks and Srivastava, 1989). Measures of certainty or accuracy of the predictions can be produced using a cross-validation process due to the statistical properties of this method. It is arguable that kriging is the optimal interpolation method on the basis of its functionality and its ability to assess error statistically, when forming prediction surfaces (Forsythe and Watt, 2006). For a kriging spatial interpolation model to provide accurate predictions, the Mean Prediction Error (MPE) should be close, to 0, the Average Standard Error (ASE) should be as small as possible (below 20), and the Standardized Root-Mean-Squared Prediction Error (SRMSPE) should be close to 1 (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). 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. (2003a).

Results and discussion

The Threshold Effect Level (TEL) and Probable Effect Level (PEL) are Canadian federal government guidelines 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 (Canadian Council of Ministers of the Environment, 1999). The values for mercury are 0.17 $\mu g\ g^{-1}$ (TEL) and 0.486 $\mu g\ g^{-1}$ (PEL), while lead is 35 $\mu g\ g^{-1}$ (TEL) and 91.3 $\mu g\ g^{-1}$ (PEL).

The dot maps for mercury and lead are presented in Figures 1 and 2 respectively. The concentrations have been grouped based on the TEL and PEL guidelines. The use of geospatial analysis and mapping to assess sediment contamination helps in the identification of contamination patterns and provides a basis for decisions concerning remediation measures that may be implemented (Forsythe and Watt, 2006). Some information on the spatial distribution of contamination is discernable using the dot and/or proportional circle mapping techniques. Gewurtz et al. (2007) found however that it was difficult to identify spatial trends when contamination levels are low using proportional circles. Marvin et al. (2004a) used dot maps to analyze mercury contamination in the Great Lakes but a complete spatial analysis of mercury distributions was not possible. Kriging provides areal estimates of contamination which greatly assist pattern identification.

Figures 3 and 4 illustrate the concentration estimates for mercury and lead respectively while Table 2 presents the cross-validation kriging results. Due to the unique structure of the lake and especially the location of Manitoulin Island, three separate kriging procedures were necessary for each part of the lake (main basin, Georgian Bay, and North Channel) and for each contaminant. The intervals used are three equal divisions below the TEL, three between the TEL and PEL, and (where necessary) similar divisions above the PEL.

Mercury

The mercury results clearly indicate a dramatic reduction in contamination from 1969/1973 to 2002. All of the kriging estimates were statistically valid. The 1969/1973 SRMSPE values 0.881 and 0.975 indicate that the predictions for the main basin and Georgian Bay (respectively) are slightly overestimated, while the value of 1.115 indicates that the North Channel is slightly underestimated. The MPE and ASE values are very close to optimal. It is possible to see very detailed areal estimates for the 1969/1973 data due to the higher density sampling program on which the predictions were based. Areas of high contamination exist and these are mostly found in the deeper depositional zone parts of the

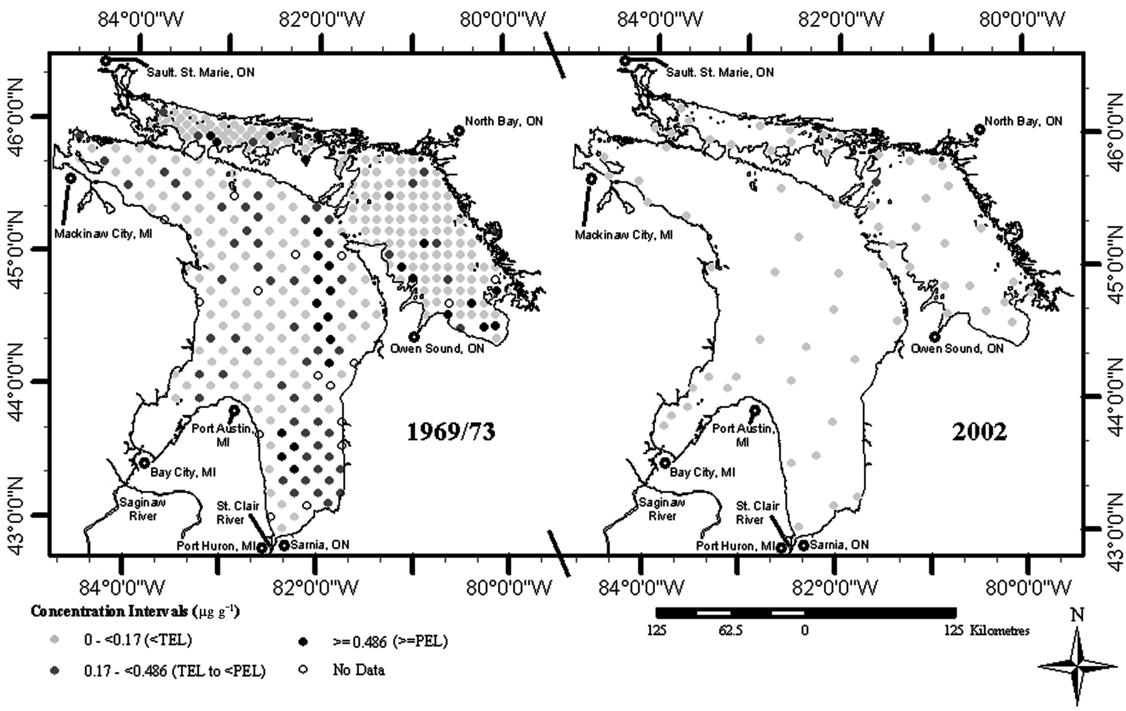

Figure 1. Mercury Dot Map Results for Lake Huron 1969/1973 and 2002.

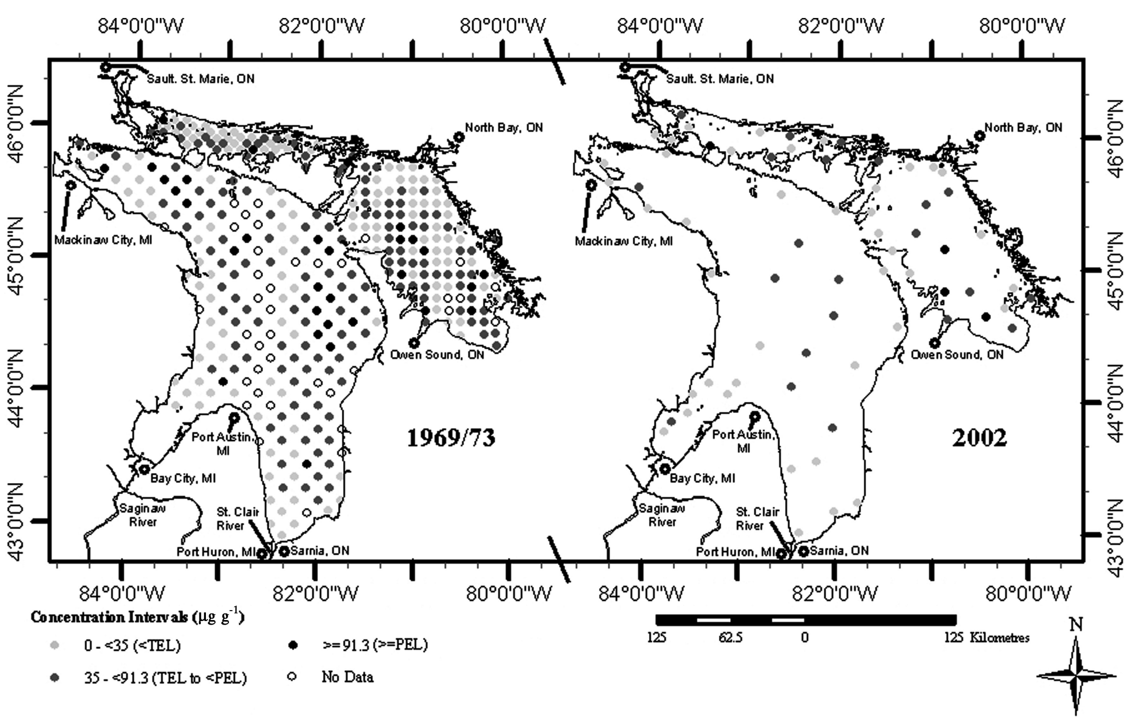

Figure 2. Lead Dot Map Results for Lake Huron 1969/1973 and 2002.

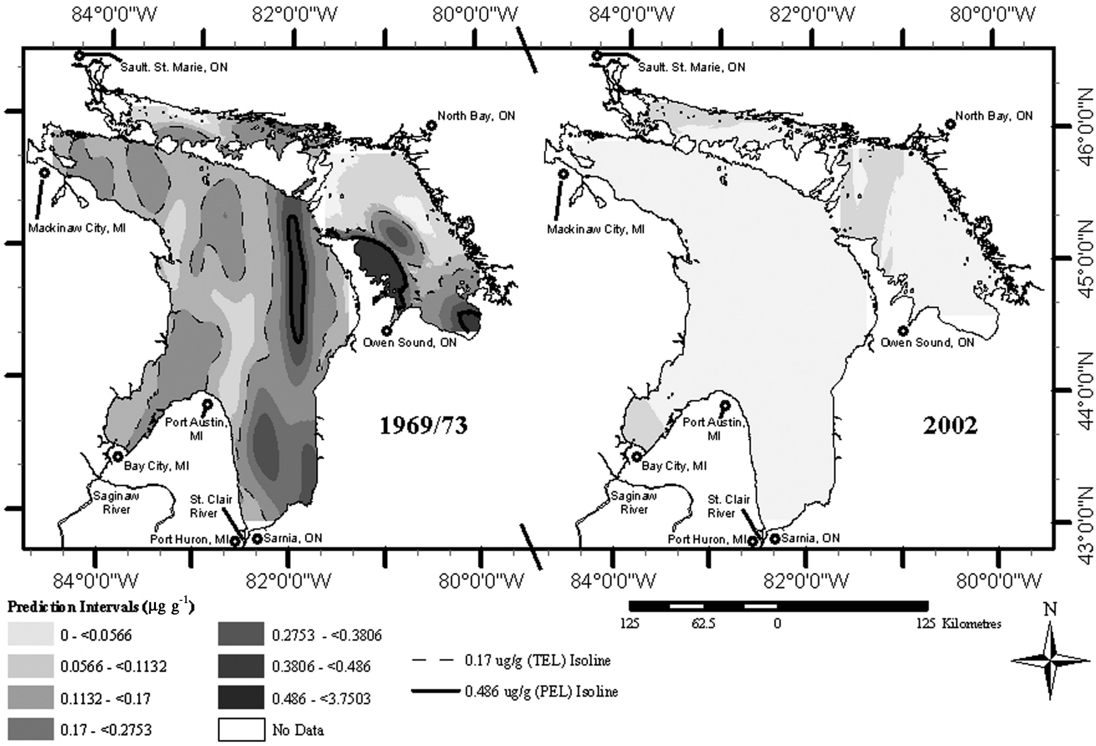

Figure 3. Mercury Kriging Results for Lake Huron 1969/1973 and 2002.

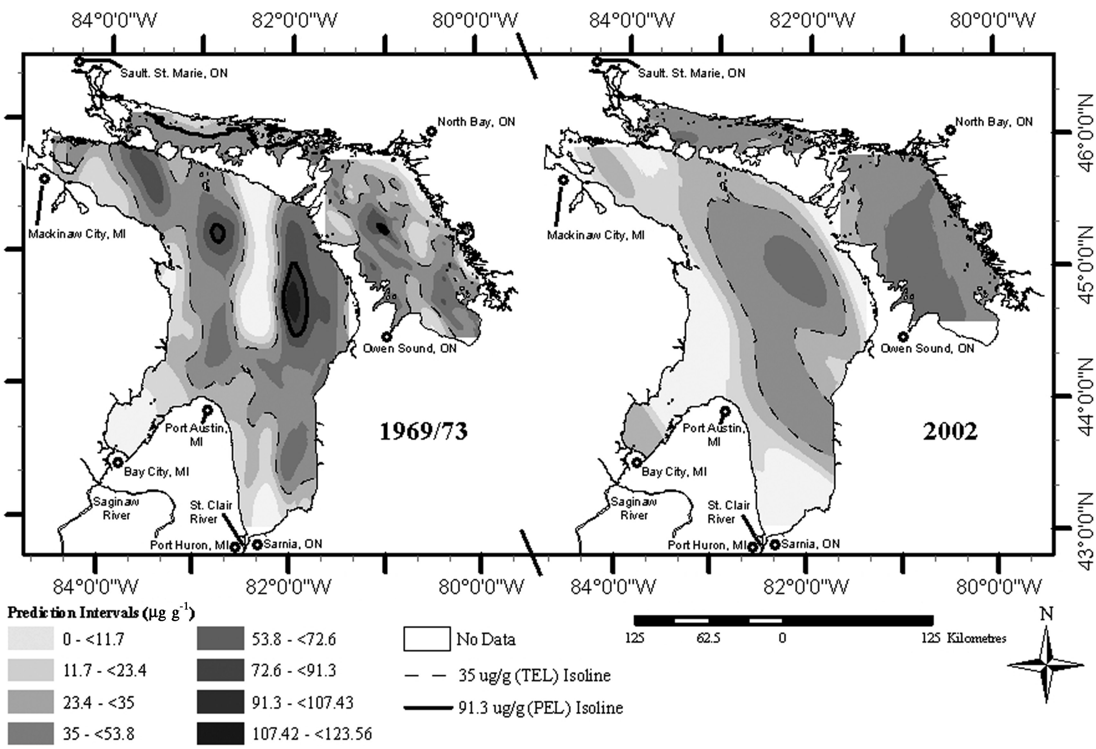

Figure 4. Lead Kriging Results for Lake Huron 1969/1973 and 2002.

Table 2. Kriging cross validation results.

Contaminant	MPE	ASE	SRMSPE
Hg Main Basin 1969	0.004	0.146	0.881
Hg Georgian Bay 1973	0.004	1.054	0.975
Hg North Channel 1973	-0.002	0.217	1.115
Hg Main Basin 2002	-0.001	0.030	0.934
Hg Georgian Bay 2002	-0.003	0.075	1.097
Hg North Channel 2002	-0.003	0.040	1.015
Pb Main Basin 1969 (log)	0.009	0.448	0.965
Pb Georgian Bay 1973 (log)	0.001	0.289	0.984
Pb North Channel 1973 (log)	-0.934	9.65	1.016
Pb Main Basin 2002	1.656	18.87	0.913
Pb Georgian Bay 2002 (log)	0.004	0.459	1.003
Pb North Channel 2002 (log)	-0.001	0.310	1.029

lake. Lower contamination values are located away from industrial, manufacturing, and mining areas and the main circulation patterns (where currents act to distribute or redistribute contaminants). The 2002 data provide a more general overview of contamination patterns. There is also not much variation in the estimates due to the reduction in contamination observed in the original sample values (only one point near the southern shore of Manitoulin Island was above the TEL). Some slightly higher contamination areas (although below the TEL) are located near the mouth of the St. Marys River in the North Channel, in the northern portion of Georgian Bay, and in Saginaw Bay in the main basin.

Lead

The lead results indicate that high levels of contamination still persist in the contemporary dataset (compared to background levels of 23 μg g^{-1}, Gewurtz et al., 2008), although they have subsided from historic values. Log normalization was necessary for all parts of the lake using the 1969/1973 data and was also performed for Georgian Bay and the North Channel with the2002 data to improve estimation outcomes. As with mercury, the 1969/1973 estimates provide more specific detail with respect to contaminant distribution. The SRMSPE values 0.965 and 0.984 for the main basin and Georgian Bay (respectively) indicate the predictions are slightly overestimated, while the value of 1.016 indicates that the North Channel is slightly underestimated. For 2002, the SRMSPE value of 0.913 for the main basin indicates a slight overestimation.

The ASE value of 18.87 is very close to the limit and it may have been advantageous to perform log normalization with these data. The SRMSPE values of 1.003 and 1.029 for Georgian Bay and the North Channel respectively are very close to optimal. In addition, the MPE and ASE values are very close to the desired results. Contamination predictions above the PEL exist in all areas of the lake for the 1969/1973 dataset. In 2002, all of these areas have disappeared with only one small area in the North Channel being close to the PEL value of 91.3 μg g^{-1}. Areas of above PEL values from 1969/1973 have seen contamination reduced to where they are now mostly between the TEL and PEL. Higher concentrations are mostly located in the deeper depositional zone parts of the lake.

Conclusions

This research utilized sediment core sample data from Lake Huron that were collected in 1969/1973 and 2002 as part of the Environment Canada Great Lakes Sediment Assessment Program. Although the number of samples collected in 1969/1973 was far greater than those collected in the 2002 survey, the use of the kriging spatial interpolation technique allowed for the areal comparison of contamination levels. It was possible to fully assess the level of contamination in the top three centimetres of sediment between the historical and contemporary surveys. This is important due to the possibility of bioturbation and other disturbances reintroducing contaminants into the water column. Dot maps were also produced to provide a tool to help assess the information generated with the kriged estimates. Mercury pollution levels have been dramatically reduced in all parts of the lake and reductions were also observed for lead. The Geographic Information System (GIS) based ordinary kriging technique allowed for the determination of lake-wide trends. Statistically valid concentration estimates were produced for all of the mercury datasets. For lead, it was necessary to perform log-normal data transformation procedures on five of the six datasets. The interpolated kriging surfaces are more informative than conventional dot or proportional circle maps in the amount of information they provide. They also supply an increased understanding of both the spatial distribution and temporal trends in sediment contamination in Lake Huron.

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