A GIS-KRIGING APPROACH AND ANALYSIS OF

HISTORICAL SEDIMENT CONTAMINATION IN LAKE SUPERIOR

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this Research Paper.

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ABSTRACT

The problem of estimating sediment contamination values at locations where no measurements are available is addressed in this research. Historical data from a 1973 survey conducted by Environment Canada were used to produce prediction maps, which display, for the first time, the spatial distribution of 34 major elements and trace elements in the surficial sediments of Lake Superior. Cross-validation statistics were used to assess the accuracy of the resulting surfaces produced with the ordinary kriging geostatistical method. Canadian sediment quality guidelines were utilized to identify areas where sediment quality was frequently threatened or impaired. In general, the concentration of contaminants was lower in sediment collected along the southern shore of Lake Superior and higher in depositional basins. Thunder Bay, Silver Bay, and Duluth were found to be influential point sources of contamination and nickel and chromium were found to be at concentrations above which adverse biological effects frequently occur. Reasons are brought forth to explain the distributions and patterns observed by incorporating: the location of known point pollution sources that existed in the basin in 1973, current locations of designated areas of concern, and knowledge of lake circulation patterns and bathymetry. The lake-wide prediction surfaces more comprehensively represent overall pollution levels when compared with point measurements. In addition, they provide a better understanding of sediment contamination and supply benchmark data concerning Lake Superior as it was over thirty years ago.

ACKNOWLEDGEMENTS

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LIST OF ACRONYMS

Ag	Silver
Al_2O_3	Aluminum oxide, Alumina
AOC	Area of Concern
As	Arsenic
ASE	Average Standard Error
ATSDR	Agency for Toxic Substances and Disease Registry
Be	Beryllium
Ca	Calcium
CaO	Calcium oxide, Calcia
CCME	Canadian Council of Ministers of the Environment
Cd	Cadmium
Co	Cobalt
CoSTTep	Contaminated Sediment Treatment Technology Program
Cr	Chromium
CSQG	Canadian Sediment Quality Guidelines
Cu	Copper
DDT	Dichloro-diphenyl-trichloroethane
ESRI	Environmental Systems Research Institute
Fe	Iron
GPI	Global polynomial interpolation
HCB	Hexachlorobenzene
HEOD	Dieldrin
Hg	Mercury
IADN	Integrated Atmospheric Deposition Network
IDW	Inverse distance weighting
K	Potassium
K_2O	Potassium oxide
LaMP	Lake Superior Lake Wide Management Plan
ME	Mean Error
MSE	Mean Standardized Error
MSDS	Materials Safety Data Sheets
Mg	Magnesium
MgO	Magnesium oxide, Magnesia
Mn	Manganese
MnO	Manganous oxide
Mo	Molybdenum
Na_2O	Sodium oxide, Soda
NJADN	New Jersey Atmopheric Deposition Network
Ni	Nickel
P_2O_5	Phosphorus pentoxide
Pb	Lead
PCB	Polychlorinated biphenyl
P,P-DDE	p,p'-Dichlorodiphenyldichloroethylene
PEL	Probable effect level
RBF	Radial basis function
RMSE	Root Mean Square Error
RMSSE	Root Mean Square Standardized Error
Se	Selenium
SiO_2	Silicon dioxide, Silica
Sn	Tin
Sr	Strontium
S	Sulfur
TEL	Threshold effect level

TiO$_2$	Titanium dioxide, Titania
U	Uranium
UNESCO	United Nations Educational, Scientific and Cultural Organisation
U.S. EPA	United States Environmental Protection Agency
V	Vanadium
WWII	World War II
Zn	Zinc

CHAPTER 1: INTRODUCTION

1.1 INTRODUCTION

Approximately 18% of the world's fresh water supply is contained within the Laurentian Great Lakes, collectively the largest freshwater body in North America (U.S. EPA, 1995). Lake Superior, Lake Michigan, Lake Huron, Lake Erie, and Lake Ontario are linked by four connecting channels and are drained by the St. Lawrence River (Figure 1.1). They hold 23000 km^3 of water in a total area of 244000 km^2, an impressive amount of freshwater second only to Lake Baikal in Siberia (exclusive of the polar ice caps) (UNESCO, 1996). Physical characteristics such as climate, soils, and topography vary across the basin (Parker, 1979; Gov.Can.1991).

The Great Lakes, despite their magnitude, are sensitive to the effects of a wide range of pollutants. Contaminated sediments, in particular, are a significant problem. This is due to the relatively small outflow (< 1% per year) in comparison to the total volume of water as well as the resuspension of sediment and cycling through biological food chains, which allows pollutants to remain in the system and concentrate over time (U.S. EPA, 1995). These contaminated sediments have been created by decades of waste from cities, combined sewer overflows, discharges from industrial areas and leachate from disposal sites, the runoff of soils and farm chemicals from agricultural lands and urban and agricultural non-point source runoff (U.S. EPA, 1995).
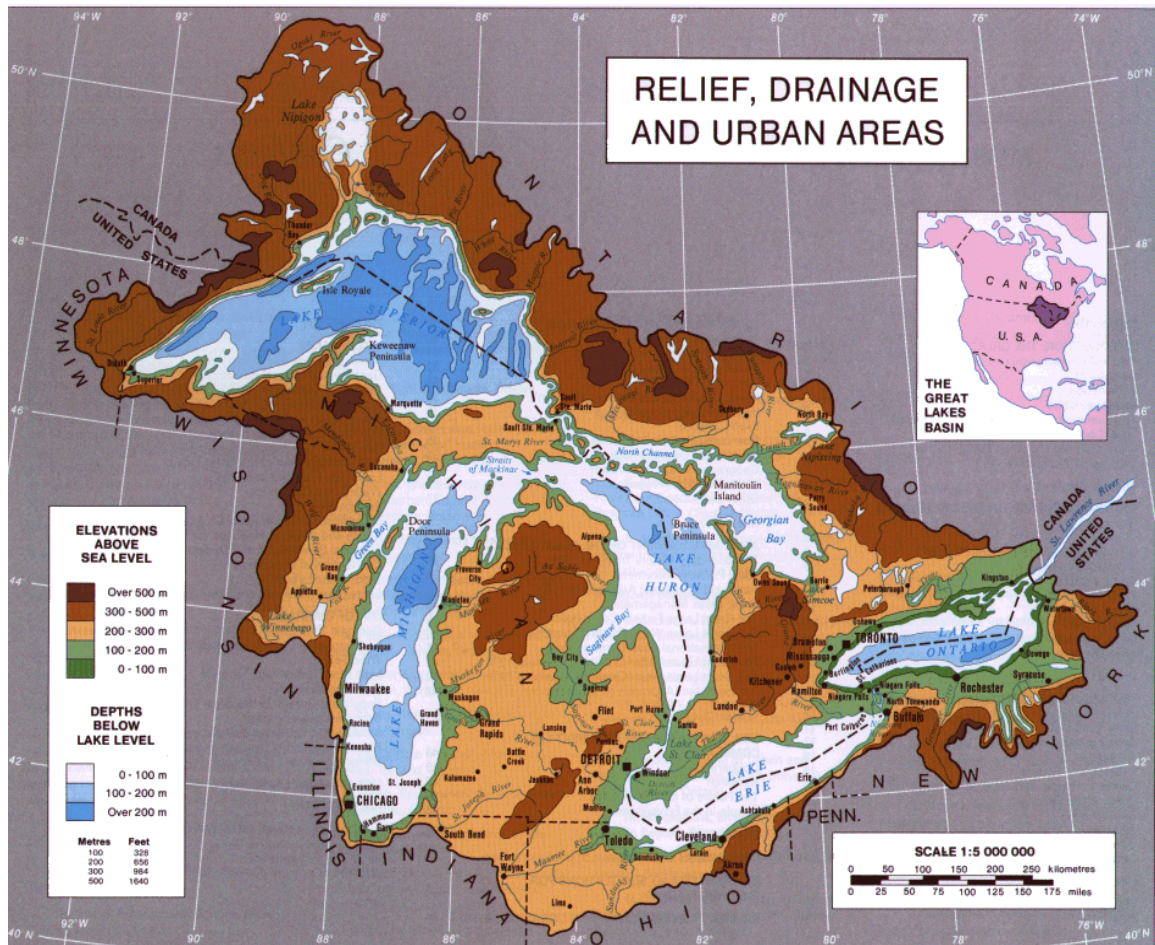
Figure 1.1: Relief, drainage and urban areas of the Great Lakes Basin. (Source: U.S. EPA, 1995)

1.2 LAKE SUPERIOR

Lake Superior, the 'greatest' of the Great lakes and focus of this study, is situated at the

top of the Great Lakes basin distinguishing itself from the rest of the lakes by having the

largest surface area, volume, drainage area, depth, and perimeter (Table 1.1). It is also the

coldest, a result of its size and its northerly geographic location. The geology, bedrock

and related soil affect both the lake water quality and the principal land uses in its

catchments. The Lake Superior watershed lies on igneous rock of the Canadian

Precambrian Shield. These rocks weather slowly, adding few nutrients to nurture either

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TABLE 1.1: HYDROLOGICAL FEATURES OF THE GREAT LAKES

	SUPERIOR	MICHIGAN	HURON	ERIE	ONTARIO
MAXIMUM DEPTH (m)	406	282	229	64	244
LAKE SURFACE AREA (km^2)	82,100	57,800	59,600	25,700	18,960
LAND DRAINAGE AREA (km^2)	127,700	118,000	134,100	78,000	64,030
TOTAL AREA (km^2)	209,800	175,800	193,700	103,700	82,990
VOLUME (km^3)	12,100	4,920	3,540	484	1,640
RESIDENCE TIME (YEARS)	191	99	22	2.6	6
OUTLET	St. Marys River	Straits of Mackinac	St. Clair River	Niagara River Welland Canal	St. Lawrence River

Source: Coordinating Committee on Great Lakes Basic Hydraulic and Hydrologic Data, 1992.

land or aquatic plant life. This results in thin, infertile soils that are difficult to farm. Agriculture is thus minimal and the majority of the Lake Superior basin is forested (Lake Superior Binational Program, 2002). Although Lake Superior is the most pristine of the Great Lakes, the Lake Superior Basin has a history of resource extraction and heavy industry, population growth beyond urban areas, as well as development of rural and waterfront vacation properties without proper planning and regulation (Lake Superior Binational Program, 2002). The legacy of this region's industrial history remains in areas of contaminated soils and sediments. Despite the fact that the extent and magnitude of sediment contamination in Lake Superior is much less than in the other Great Lakes (Lake Superior Binational Program, 2002), eight Areas of Concern (AOC) have been identified (Figure 1.2). These are areas that require high-priority attention because they

exhibit severe environmental degradation (Lake Superior Binational Program, 2002). Since it is the least developed basin with the sparsest population, the main entrance point for pollutants is through airborne transport. This influence has long-term implications because Lake Superior has the highest retention time of all the Great Lakes. Water that enters Lake Superior stays in the lake for an average of 191 years before it exits through the St. Mary's River. Lake Superior is also known to have a low production rate and is quite possibly the most fragile system (Parker, 1979).
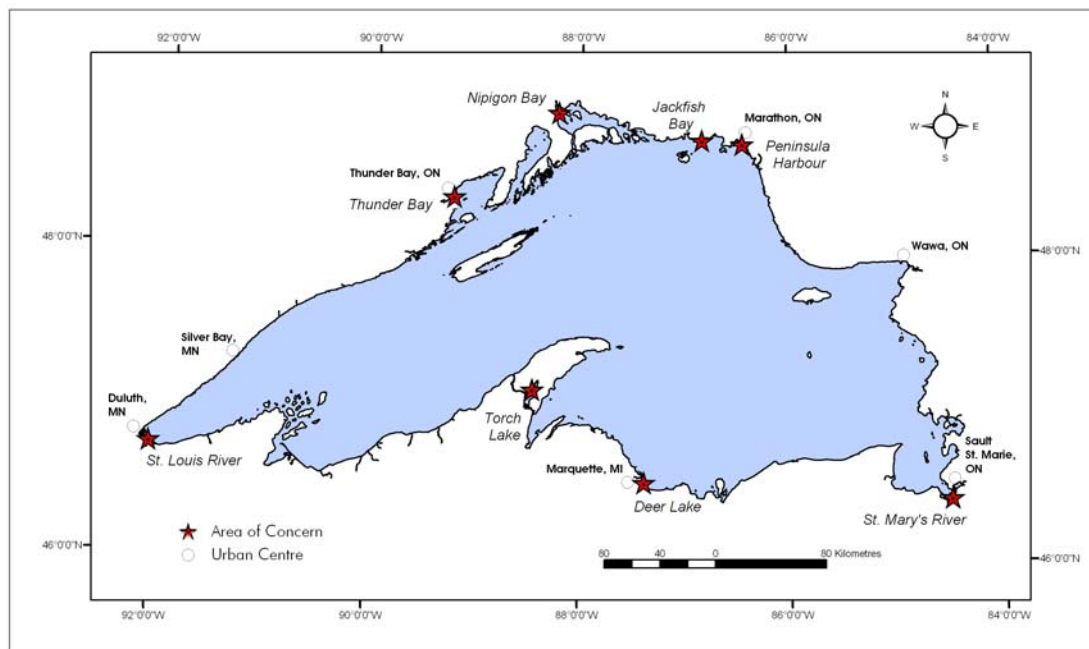
FIGURE 1.2: Areas of Concern.

1.3 STUDY AREA AND DATA SET

Historical data from a sediment survey carried out by Environment Canada in 1973 were used in this analysis. The survey, conducted across Lake Superior between April 29 and June 6, 1973, collected 402 surficial sediment samples, the distribution of which can be seen in Figure 1.3. This survey produced the first large scale, detailed data set available

for Lake Superior. The top 3 centimetres were sub-sampled for a variety of compounds in addition to particle size characterization, and nutrient analysis. Limnological characteristics such as depth, pH, and temperature were provided along with spatial coordinates for each sampled location.
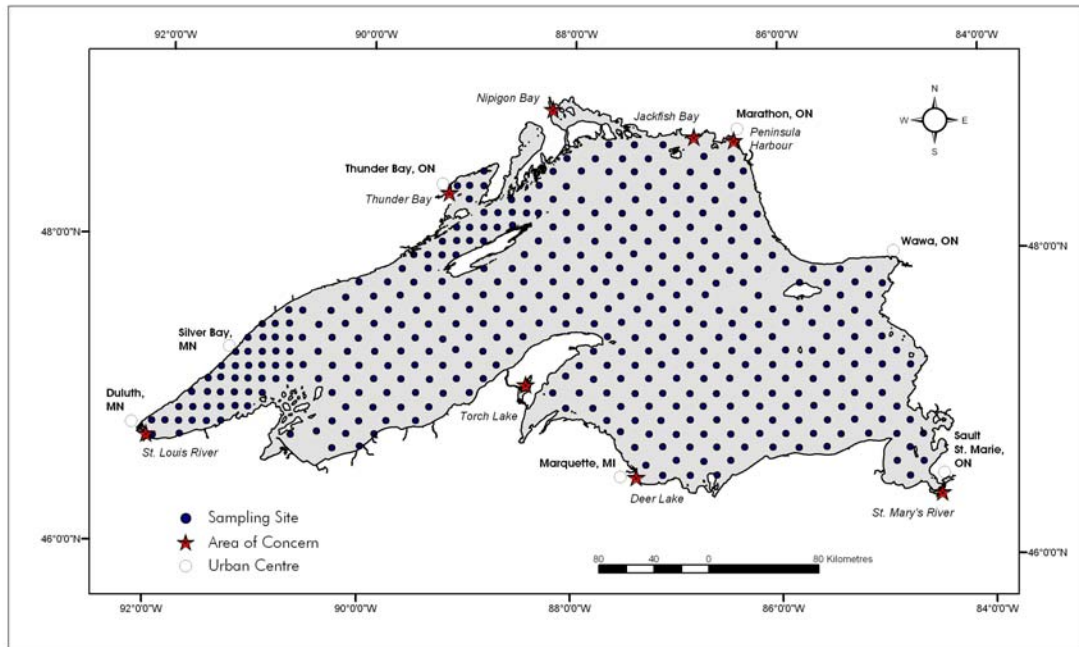
FIGURE 1.3: Lake Superior Sampling Locations.

1.4 SOURCES OF POLLUTANTS AND CONTAMINATED SEDIMENTS

Physical, chemical and biological laws govern the pathways and fate of toxic chemicals in lakes. A molecule of a chemical present in water may be taken up by the biota, be deposited in the sediments at the bottom of the lake, or be vapourized into the atmosphere, and can enter into chemical reactions that change its structure and increase or decrease its toxicity (Environment Canada, 2004; Gov. Can., 1991). The adsorptive capacity of sediment for hydrophobic compounds and elements of low solubility is well known (Surveillance Work Group, 1985). Adsorption can occur when direct interaction

takes place between particulate material, water and biota during transport to depositional zones (Surveillance Work Group, 1985). Moreover, many toxic substances such as metals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls (PCBs), chlorophenols, and organochlorine, which are found in only trace amounts in water, accumulate in sediments at much higher concentrations (Surveillance Work Group, 1985; MacDonald and Ingersoll, 2003).

Sediment contamination represents a significant problem in the AOCs, particularly as a residual source of contamination after all active sources of toxic substances have been eliminated. Polluted sediments that have settled out of the water can be stirred up and resuspended by dredging, by the passage of ships in navigation channels, and by wind and wave action. Sediments can also be disturbed by fish and other organisms that feed on bottom sediments (U.S. EPA, 2003). As a result, sediments act as long-term reservoirs and serve as potential sources of pollutants to the water column and to organisms living in or having direct contact with sediments (Environment Canada, 2004).

Direct discharges to waterways are known as point sources. In this way, toxic substances enter the lakes via direct industrial discharge pipes, effluent flow from municipal sewage treatment plants and storm sewers. Point source pollution tends to be easier to manage and control and is thus subject to varying degrees of government regulation (Gov. Can., 1991). Non-point sources of pollution, which include urban and agricultural run-off, airborne deposition of pollutants from automobiles and commercial activities, as well as contaminated sediments and contaminated groundwater are much more difficult to control (U.S. EPA, 1995).

1.5 ATMOSPHERIC DEPOSITION

The large surface area of Lake Superior makes it particularly vulnerable to direct atmospheric pollutants that fall with rain or snow and as dust on the lake surface. This source of pollution, commonly referred to as atmospheric deposition or fallout, is among the most important and least understood (Parker, 1979; U.S. EPA, 1995). What is known is that wind-raised soil dust, automobile exhaust, and emissions from cement and steel manufacturing all contribute trace elements to the atmosphere. Direct deposition on the surface of lakes provides the major input mechanism for trace elements such as mercury, cadmium, copper, zinc, and lead (Parker, 1979; Kemp et al., 1978). The combustion of fossil fuels, particularly coal, is the major anthropogenic source of atmospheric trace elements to the lakes. Atmospheric deposition is directly linked to air turbulence. Unfortunately, this mechanism is most intense when the temperature of water is higher than the overlying air, a situation that occurs over the Great Lakes throughout most of the year, particularly during the fall, winter, and early spring. Parker (1979) explains that this was aggravated by society when a greater demand for electricity was observed during the cooler periods of the year. Historically, stack emissions consequently increased during cooler months when atmospheric conditions were conducive to trace element deposition. The origins of contaminants released into the atmosphere may be from sources outside the basin. Konasewich (1979) described the discovery of man-made radionuclites in the Great Lakes that originated not along the lakeshores but at atomic testing sites in the Pacific and in China. Distance of source is thus not necessarily a limiting factor. Similarly, toxic pollutants, such as PCBs, can enter the Great Lakes from the atmosphere as a result of rain or other atmospheric processes. PCBs are a man-made mixture of

chemicals most commonly used as coolants and lubricants, and in electrical equipment. A New Jersey Study (NJADN, 2005) found PCB concentrations at sites surrounding the Great Lakes to be problematic due to atmospheric deposition. The study proposed that local transport modelling be supported to identify the major emission sources to the atmosphere with a focus on fresh sources of PCBs from ongoing industrial processes and not just from legacy PCB emissions (NJADN, 2005). Evidence in the growing concern of toxic chemicals via atmospheric deposition can also be seen with the existence of the Integrated Atmospheric Deposition Network (IADN). This group sees the United States and Canada working together to measure the levels of toxic chemicals in the air and precipitation in the Great Lakes basin (U.S. EPA, 2003).

1.6 RESEARCH OBJECTIVES

The first objective of this research is methods based. This research aims to provide prediction surfaces for lake-wide sediment contamination that more accurately represent overall pollution levels when compared to point measurements. This is the first time that lake-wide distribution of contaminants is being mapped for the entire area of Lake Superior. The created surfaces will not be more accurate than the point data rather they will provide an estimate of the contamination between the sampled points and provide a better visual picture of lake-wide pollution trends. The second objective, and one that is a by-product of the first, is that the created contamination surfaces will lead to a better understanding of historical sediment contamination in Lake Superior as it was over thirty years ago. Canadian Sediment Quality Guidelines are used to better interpret the results and this paper brings forth reasons to explain the distributions and pattern observed with

the historical data set and does not make predictions or assumptions concerning the contemporary situation.

CHAPTER 2: LITERATURE REVIEW

2.1 SEDIMENT CONTAMINATION MANAGEMENT

As early as 1960, severe environmental problems could be seen in the Great Lakes as a result of increased population growth and industrialization. Contaminated sediments were recognized as significant contributors to impaired water quality in the Great Lakes by the governments of Canada and the United States (Santiago et al., 2003). It was determined that without corrective action it would take hundreds or thousands of years for the pollutants in bottom sediments to degrade or disperse (Environment Canada, 2000). In response to concerns raised regarding contaminated sediments, responsible authorities throughout North America launched programs to support the assessment, management, and remediation of contaminated sediments (MacDonald and Ingersoll, 2003). In 1972, Canada and the United States signed the Great Lakes Water Quality Agreement (GLWQ), which established common water quality objectives. Until that time no broad controls existed on industrial and municipal sources of pollution. A more decisive step was taken in 1987 with an amendment to the GLWQ that identified 43 Areas of Concern (AOC) where impaired water quality prevented full beneficial use of rivers, bays, harbours, and ports. These areas were known to have experienced serious local damage through historic pollution. The amendment committed both Canada and the United States to concentrate remediation efforts in the AOC. Consequently, a Remedial Action Plan (RAP) team was formed to be responsible for cleanup planning in these areas. In 1989, the Canadian government created the five-year $125-million Great Lakes Action Plan in support of the Great Lakes Water Quality Agreement. In 1991, a binational program to restore and protect Lake Superior was established. Nine critical pollutants affecting Lake

Superior were identified in the 1995 Stage 1 Lake Superior Lake Wide Management Plan (LaMP). Commonly referred to as the 'Nasty Nine', the zero discharge of mercury, polychlorinated biphenyls (PCBs), dioxin, foxaphene, dieldrin, DDT, chlordane, hexachlorobenzene, and octachlorostyrene were specifically targeted by the 2000 LaMP. Similarly, the Great Lakes 2000 Cleanup Fund (funded by the Great Lakes Action Plan) allocated $55 million for the 17 Canadian Areas of Concern. A portion of the Cleanup Fund was designated for the development and demonstration of technologies for assessment, removal and treatment of contaminated sediment (Environment Canada, 2000). Two of the five AOCs found in the Lake Superior Basin: Thunder Bay Harbour and the St. Mary's River, are both known to have serious sediment contamination problems (Environment Canada, 2000).

2.2 CANADIAN SEDIMENT QUALITY GUIDELINES

Nationally endorsed, science-based benchmarks termed Canadian Sediment Quality Guidelines were developed to evaluate the potential of adverse biological effects in aquatic systems (CCME, 1999). These benchmarks are defined as numerical concentrations that are recommended as levels that should result in negligible risk to biota, their functions, or any interactions that are integral to sustaining the health of ecosystems and the designated resource uses they support (Environment Canada, 2004). The guidelines are derived from the available toxicological information in order to calculate two assessment values. The lower value is referred to as the Threshold Effect Level (TEL) and the upper value is referred to as the Probable Effect Level (PEL). Consequently, TEL's and PEL's allow for three ranges of chemical concentrations

defined as 1. the minimal effect range within which adverse effects rarely occur (fewer than 25% adverse effects occur); 2. the possible effect range within which adverse effects occasionally occur (the range between TEL and PEL); and 3. the probable effect range within which adverse biological effects frequently occur (more than 50% adverse effects occur). Canadian Sediment Quality Guidelines have a few limitations: they are limited to chemical stressors, and there are many chemicals for which guidelines have not yet been developed. Another limitation is the potential for confounding effects of the physicochemical attributes of the sediment, such as grain size, total organic carbon content, sulphides, chemical species and complexes. These attributes may increase or decrease the potential for toxic effects at a specific site, particularly by influencing the bioavailability of contaminants. These factors can be taken into account through the development of site-specific guidelines (Environment Canada, 2004).

2.3 POLLUTANTS AND AREAS OF CONCERN

Toxic pollutants include human-made organic chemicals and heavy metals that can be acutely toxic in relatively small amounts and harmful through chronic exposure in minute concentrations. Predicting the route of transport and eventual fate of a metal ion or an organic molecule once it is in a lake body is extremely difficult (Konasewich, 1979). The complexity of the behaviour of metals is so great, that it is beyond comprehension, even to chemists. Thus scientists assigned by the International Joint Commission to derive water-quality objectives for the Great Lakes decided that all forms of heavy metals are or could be potentially toxic. The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic, highly toxic or poisonous at low

concentrations (MSDS, 2006). Moreover, metals collectively known as priority heavy metals include arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc (Konasewich, 1979). In fact, a heavy metal concentration within 1.5 m of sediment depth is a threat (Ouyang et al., 2003). The organic compounds that cause the most concern are generally those that do not readily biodegrade or photodegrade into harmless forms and thus persist in the environment. Some compounds may actually biodegrade into more persistent and toxic forms such as the pesticide aldrin, which can be metabolized by several organisms into dieldrin (Konasewich, 1979). Once such persistent compounds enter the Great Lakes, considerable time is required to significantly reduce the levels of contamination as a result of the large volumes and long water-retention times of the bodies of water. Mathematical model calculations show that even after all pollution sources have been eliminated, it would take Lake Superior about five hundred years for 90% of the pollutants to be carried out of the lake (Konasewich, 1979). The complexity of the system demands the consideration of lake stratification, water circulation, and the dynamics of distribution of the pollutant among the atmosphere, the water, the biota, and the sediment for precise assessments (Konasewich, 1979).

Four of the nine critical pollutants designated for Lake Superior are considered in this study; mercury is a contaminant of concern in the St. Louis River (Duluth-Superior Harbour) AOC; Thunder Bay, Jackfish Bay, and Peninsula Harbour in Canada; St. Mary's River (Michigan-Ontario), and Deer Lake in Michigan (Lake Superior Binational Program, 1999). Mercury sediment contamination in these areas is due in part to historical discharges. Peninsula Harbour, located on the northeastern shore of Lake Superior was designated an AOC due to its residual mercury contamination. From 1952-

1977, a chlor-alkali plant used mercury in its production of caustic soda and chlorine that resulted in discharge of mercury into the harbour (Milani et al., 2003). Mercury in natural ore deposits is also a widespread source to Lake Superior sediments (Gov. Can., 1991). Dieldrin is a persistent toxic chemical that was developed after WWII along with the related pesticide aldrin. They were used in Canada for more than 25 years to control insects in crops and in domestic, forestry, and industrial situations. Chronic exposure resulted in eggshell thinning, reproductive failure and population declines in birds. Periodic re-evaluation of aldrin and dieldrin by Agriculture Canada resulted in their decreased use and was limited to termite control until its complete ban by both Canada and the United States between 1989 and 1991 (Environment Canada, 2005). DDT (1,1,1-triochoro-2,2-bis(p-chlorophenyl)ethane) was introduced in North America in 1946 as an insecticide to control insects on crops and vector-borne diseases. In the environment, degradation and metabolism in mammals, fish, birds and microorganisms results in the persistent degradation products, DDD and DDE (Minnesota Pollution Control Agency, 1999). All forms have been linked to decreases in the reproductive abilities of fish and birds (Environment Canada, 2005). It was banned in the U.S. in 1972, restricted in Canada in 1974 and suspended in 1985. Polychlorinated biphenyls (PCBs) are mixtures of up to 209 individual chlorinated compounds with no known natural sources (ATSDR, 2000). Many commercial PCB mixtures are known by the trade name Aroclor. PCBs have been used as coolants and lubricants in transformers, capacitors, and other electrical equipment, but evidence of persistence and build up in the environment along with harmful associated health effects banned their manufacture in the U.S. in 1977 (ATSDR, 2000). PCBs do not readily break down in the environment and thus remain there for very

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long periods of time. They can travel long distances in the air and be deposited in areas far away from where they were released. In water, a small amount may remain dissolved, but most PCBs stick to organic particles and bottom sediments (ATSDR, 2000).

2.4 SEDIMENT DISTRIBUTION: BATHYMETRY AND CIRCULATION PATTERNS

An analysis of contaminant distribution and fate would not be logical without an understanding of the sedimentology of the Great Lakes. Modern surficial sediment distribution in Lake Superior is related to bathymetry (the underwater equivalent of topography), circulation patterns and the proximity to terrestrial sediment sources (Lake Superior Binational Program, 2000). The Keweenaw Peninsula (Figure 2.1), which extends 95 km into the lake from the southern shore, strongly influences Lake Superior's bathymetry as can be seen in the arrangement of the depositional basins (Figure 2.2). The lake, which averages 147m in depth with a maximum depth of 406m is divided into three main basins. The eastern basin is characterized by a series of long, parallel, steep-sided troughs 100 to 300m in depth with a north-south orientation. The central

FIGURE 2.1: The Keweenaw Peninsula.
(Source: http://www.geo.mtu.edu/rs/keweenaw/)

basin is comprised of very deep (up to 400m) steep-sided sub-basins bounded on the north by extensive underwater cliffs, which fringe a complex series of islands. The western basin encompasses relatively shallower offshore waters and a very deep channel, the Thunder Bay Trough, which separates Isle Royale from the adjacent mainland. Water

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depths of less than 100m are found in a narrow band paralleling the shore, with a rapid fall-off to deeper waters (Lake Superior Binational Program, 2000). In addition, water depths of less than 100m are also found around islands and offshore shoals, especially in eastern Lake Superior. Shoals are numerous along the eastern shore and northern shore; the Superior Shoal, for example, is prominent mid-lake as an extension of the Keweenaw Sill. A distance variation of only 5km means the difference between a depth of 300m and a potentially deadly one (for ships) of only 6m beneath the surface. Along the north shore, the Sibley and Black Bay Peninsulas, and associated islands, delineate three large, sheltered bays; Thunder Bay, Black, and Nipigon Bay (Lake Superior Binational Program, 2000).
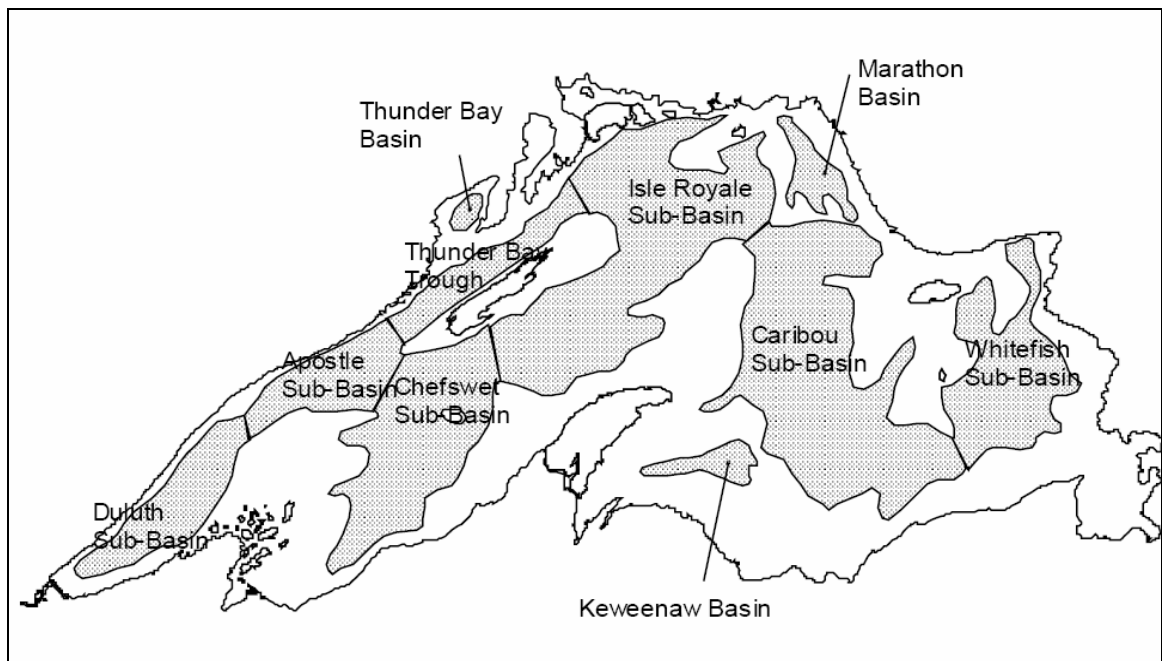

FIGURE 2.2: Depositional basins of Lake Superior (Source: Lake Superior Binational Program, 2000).

Circulation patterns are the second factor towards understanding sediment distribution in a lake. Knowledge of the mean circulation provides an indication of transport pathways of nutrients and contaminants on longer time scales (Beletsky et al., 1999).

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Circulation is defined to mean a long-term pattern of motion, or residual motion remaining after the irregular water movements involved in wind drift, sieches, and other short-term phenomena are averaged (Emery and Csanady, 1973). Due to limitations in data, only summer circulation patterns are available for Lake Superior and many properties of seasonal circulation remain unknown due to the variable nature of lake currents. In Lake Superior, currents generally flow parallel to the shore in a counter-clockwise (cyclonic) direction (Figure 2.3). The pattern of surface circulation has been mapped for more than 40 lakes, all within the northern hemisphere and all except one are known to have a counterclockwise pattern. Cyclonic patterns are thus commonly found in the larger lakes (Beletsky et al., 1999; Csanady, 1977; Emery and Csanady, 1973). This consistent pattern is attributed to the drag of wind blowing across the bodies of water, particularly on the fact that wind blowing over warm water exerts a drag force greater than over cold water (Emery and Csanady, 1973). There are also smaller gyres
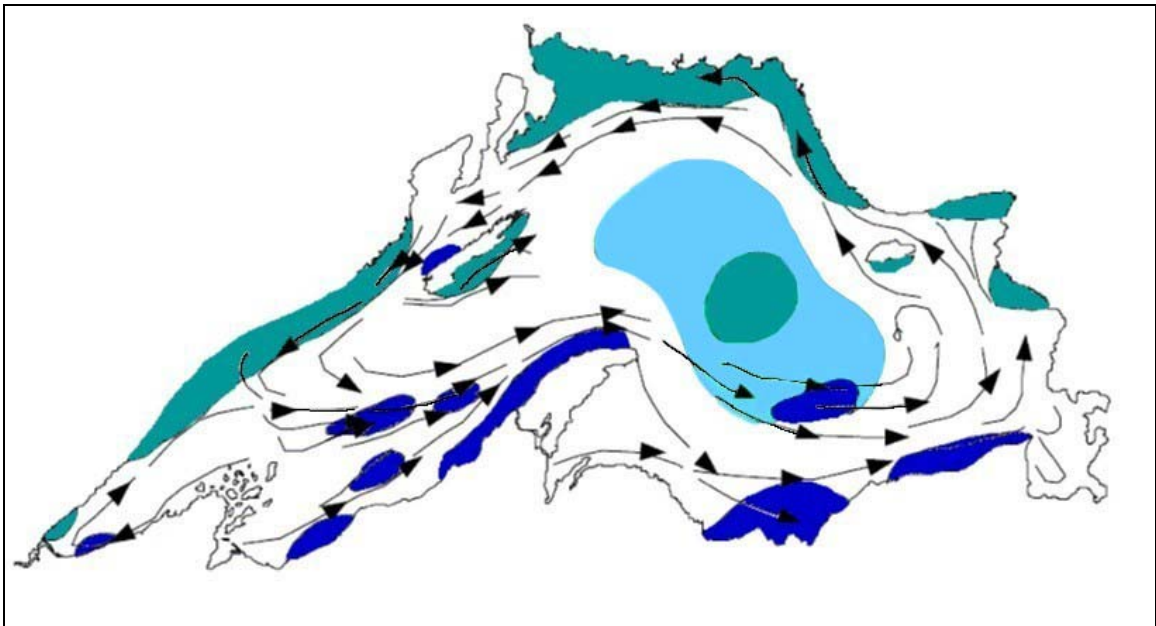

FIGURE 2.3: Major surface currents and upwellings. Downward water movement (blue), significant areas of upwelling (teal), and extent of central upwelling (aqua). (Source: Modified from Lake Superior Binational Program, 2000).

south of Isle Royale and around the Superior Shoal that reflect the bottom topography, temperature and wind conditions of those areas (Lake Superior Binational Program, 2000). Lake currents lack persistence and depend more on short-term atmospheric forcing due to the relatively small size of lake basins (even for Lake Superior) (Beletsky et al., 1999). Storm-induced currents can be strong (up to several tens of cm/s) while average currents are rather weak through most seasons (in the order of only a few cm/s) (Beletsky et al., 1999). Harrington (1894, as found in Beletsky et al., 1999) reported the earliest whole-basin studies of lake currents. He released drift bottles from ships during the summer months of 1892, 1893, and 1894 and charted the summer currents around the deeper lake basins as dominantly counter-clockwise, with the suggestion of a clear cellular structure within each distinct basin in the largest lakes. Harrington inferred that his drift bottles mainly followed lake bathymetry. The study described surface circulation and was thus more sensitive to direct wind drift. New observations are consistent with Harrington's data only in the larger lakes (Beletsky et al., 1999). In addition to wind stress, long-term circulation is also affected by surface heat flux and thus internal pressure caused by density variations and the slope of the thermocline; an area of water within the water column in which the warmer upper waters are prevented from mixing with those at a deeper level (Lake Superior Binational Program, 2000). This causes density-driven currents. The interplay of these two factors plus the influence of lake bathymetry makes circulation patterns in large lakes complex (Beletsky et al., 1999). In addition to influencing patterns of currents and density structure, water temperature also affects vertical and horizontal mixing. Lake Superior has a unique thermal regime due to its size with the lowest summer surface temperature (13 $^{\circ}$C) and mean annual

temperature (3.6 °C) of the Great Lakes (Lake Superior Binational Program, 2000). Stronger currents can be found along the southern shore where there is less dense warmer water and the thermocline is deeper. The strongest current is near the north side of the Keweenaw Penninsula, appropriately named the Keweenaw Current where current speeds reach 7.1cm/s. It is a wind-driven coastal current, running northeastward along the shore and appears mainly to be responsible for the longshore transport of fine sediments (Jeong and McDowell, 2003). Superior's minimum current speed is observed at 0.2 cm/s with the average mean at 2.2 cm/s (Beletsky et al., 1999). Currents typically change their direction with depth, and their speed decreases, which reflects the importance of baroclinic effects (when surfaces of constant pressure do not coincide with those of equal density) in the presence of the seasonal thermocline (Beletsky et al., 1999). This indicates the significance of lake-induced mesoscale vorticity, which refers to the local component of rotation in the flow of the wind field. Two factors could contribute to this in the case of larger lakes: larger surface area, and stronger lake-atmosphere temperature gradients. In wind-driven circulation models where density-driven currents are ignored, currents are generated by the interplay between horizontal pressure gradient and wind stress. In the nearshore region, the wind stress is the dominant factor and transport is in the downwind direction (Beletsky et al., 1999; Emery and Csanady, 1973). In the deeper offshore regions, the pressure gradient (caused by the surface water level gradient) generates transport opposite to the wind direction (Beletsky et al., 1999). Even early on, charts of circulation patterns were assembled with the expectation that they may be useful to other researchers, particularly in connection with prediction of pollution down-current from

points of sewage and industrial discharge into large bodies of water (Emery and Csanady, 1973).

2.5 KRIGING ANALYSIS OF LARGE LAKES

Geostatistical methods of ordinary kriging are used in this study to address the problem of estimating values of sediment contamination at locations from which measurements have not been taken. In the last 30 years, numerous scientists and engineers in mining and petroleum exploration, environmental studies, and even agricultural practices have used kriging analysis, but few have employed kriging as a tool to estimate the distribution of pollution in large lakes (Forsythe and Marvin, 2005). However, in recent years, this tool has been applied to estimate lake-wide distributions of contaminants such as Hexachlorobenzene (HCB), PCBs, lead (Pb), and mercury (Hg) in the lower Great Lakes (Forsythe and Marvin, 2005; Forsythe et al., 2004; Jakubek and Forsythe, 2004). It has become clear that discrete point measurements obtained from sediment sampling are limiting and have been unsatisfactory in the analysis of spatial trends. Though kriging began in the field of geology, it's ability to interpolate point data and generate a continuous surface allows more accurate representation of overall pollution levels when compared to point measurements (Forsythe et al., 2004; Jakubek and Forsythe, 2004).

This kriging technique has also garnered preference over other methods such as Inverse Distance Weighting (IDW) since the interpolated prediction surfaces can be statistically validated (Forsythe et al., 2004; Jakubek and Forsythe, 2004).

Forsythe et al. (2004) used kriging to assess historical sediment data (1968 and 1971, for Lakes Ontario and Erie respectively). The kriged historical dataset results suggest that

statistical validity may be improved with data normality. This is due to the fact historical point sources of pollution are likely to affect the analysis by having some individual stations with very high contaminant concentrations. Forsythe and Marvin (2005) found success when using a log-normal distribution on initially non-valid statistical results.

Previous studies (Forsythe and Marvin, 2005; Forsythe et al., 2004; Jakubek and Forsythe, 2004) have been able to exploit point sediment sampling data with the aid of kriging and have drawn similar conclusions that explain the distributions of the contaminants observed. Greater concentrations of HCB, PCBs, PB and Hg in the lower lakes can be related to the location of urban/industrial areas, lake currents and lake bathymetry.

This research paper will apply similar methods (Forsythe and Marvin, 2005; Forsythe et al., 2004; Jakubek and Forsythe, 2004) but will extend the work thus far completed (on the Lower Great Lakes) by concentrating on the much larger Lake Superior.

CHAPTER 3: METHODOLOGY

Ordinary kriging was carried out using the ArcGIS software with the Geostatistical Analyst extension. The statistical methods are simplified by the geostatistical analyst that prompts for the required information, outlined in sections 3.41-3.42, with an easy to follow sequence of steps. The options that are ultimately used are tailored to the data set and are thus unique. This is a good starting step with which to further customize the kriging process to the data set being analyzed. In order to fully appreciate the complexity of kriging, the following methods section is as much about the relevant theoretical background as it is about the practical methodology followed in the GIS environment. The spatial distributions of 34 elements and compounds are analyzed in this paper. A list of these can be found in Table 3.1. Concentrations were not available for each of the 34 contaminants in all 402 sampling sites. The corresponding sample size for each chemical is also listed in Table 3.1. The tabular data were brought into the GIS environment with a UTM Zone 16N (NAD83) projection.

3.1 GEOSTATISTICS AND ORDINARY KRIGING

Continuous phenomena, such as sediment contamination, can be measured at any location in space but practically, data are only available in a limited number of sampled points. In order to effectively analyze the available data, there is a need to predict or interpolate values where no samples have been collected. There are two main families of interpolation methods. Deterministic interpolation techniques (i.e. Inverse Distance Weighing, Radial Basis Functions, Global Polynomial Interpolation) that use mathematical functions such as Euclidean distance while the family of geostatistics relies on both mathematical and statistical models that take positive autocorrelation into

TABLE 3.1: CONTAMINANT LIST

Contaminant	Sample Size	Contaminant	Sample Size
Sodium Oxide, Soda (Na_2O)	402	Iron (Fe)	402
Magnesium (Mg)	402	Cobalt (Co)	402
Magnesium Oxide, Magnesia (MgO)	397	Nickel (Ni)	402
Aluminum Oxide, Alumina (Al_2O_3)	401	Copper (Cu)	402
Phosphorus pentoxide (P_2O_5)	400	Zinc (Zn)	402
Sulfur (S)	401	Selenium (Se)	392
P,P-DDE	402	Strontium (Sr)	402
Dieldrin	402	Molybdenum (Mo)	393
Aroclor	402	Beryllium (Be)	401
Potassium (K)	402	Silver (Ag)	393
Potassium Oxide (K_2O)	401	Cadmium (Cd)	402
Calcium (Ca)	402	Tin (Sn)	393
Calcium oxide, Calcia (CaO)	402	Mercury (Hg)	402
Titanium dioxide, Titania (TiO_2)	401	Lead (Pb)	402
Chromium (Cr)	402	Uranium (U)	389
Manganese (Mn)	402	Arsenic (As)	393
Manganous oxide (MnO)	401	Vanadium (V)	402

account (Johnston et al., 2001). The field of geostatistics can be generally subdivided into

1. modeling the semivariogram or covariance and 2. kriging (Johnston et al., 2001).

Positive autocorrelation is a statistical relationship among measured points that assumes

that things that are close to one another are more alike than those farther away. By

creating and modeling a semivariogram, the positive autocorrelation of the dataset can be

examined and quantified (Johnston et al., 2001). Kriging is a linear predictor, meaning

that a prediction at any location is obtained as a weighted average of the neighbouring

data. The weights used in the kriging estimation are computed so that the variance

between the estimated value and the unknown value is minimized (Ouyang et al., 2003).

Not only are the weights based on the distance between the measured points and the

prediction location but also on the spatial arrangement among the measured points. The

data set is essentially used to define what the weights should be. This is the purpose of

quantifying the spatial positive autocorrelation through the semivariogram, which is accomplished by using the concept of spatial stationarity (Section 3.2) (Johnston et al., 2001).

Once the modelling is complete, a kriging interpolator is used to generate a surface of predicted values. As with most modeling processes, the true model (in this case the empirical semivariogram) is almost never known and consequently there is no method to determine it exactly. Before modern computers and software became available, semivariograms were often fitted visually (Gribov et al., 2001). A great advantage of geostatistical methods and modern technology is that it can provide some measure of the accuracy of the predictions (Section 3.5). The type of interpolator is specified first in the Geostatistical Analyst. Among the interpolation methods described in the literature, ordinary kriging has been found attractive by reason of its simplicity and ease of use (Schanbel et al. 2002; Prudhomme and Reed, 1999; Atkinson and Lloyd, 1998). Ordinary kriging assumes a constant, but unknown mean, and estimates the mean value as a constant in the searching neighbourhood. Ordinary kriging is mathematically defined as:

$$Z(s) = \mu + \varepsilon(s) \ (1)$$

where $Z(s)$ is the value at that location; s is a sampled location; μ is the constant mean and $\varepsilon(s)$ are random errors with spatial dependence (Johnston et al., 2001). The predictor is generated as a weighted sum of the data mathematically defined by equation (2):

$$\hat{Z}(s_O) = \sum_{i=1}^{N} \lambda_i Z(s_i) \ (2)$$

where s_o is the prediction location; N is equal to the number of measured values that will be used to predict the value at the unknown location; λ_i is an unknown weight for the

measured value at the *i*th location, and $Z(s_i)$ is the measured value at the *i*th location (Johnston et al., 2001).

3.2 SPATIAL DEPENDENCY, SECOND-ORDER STATIONARITY, AND DISTRIBUTION

Geostatistical analysis functions on several assumptions. The concept that it is impossible to predict values between data values that are spatially independent is implied by spatial dependency. In the case of spatially dependent data, if the dependency is ignored, the result of the analysis will be inadequate as will any decisions based on that analysis (Krivoruchko, 2005). In order to estimate the dependency rules, replication is required (Johnston et al., 2001). The concept of stationarity in a spatial setting is what is used to obtain the necessary replication. Statistical replication is what statistics generally relies on since it is believed that estimates can be derived and the variation and uncertainty of the estimate understood from repeated observations (Johnston et al., 2001). Second-order stationarity implies that the mean of a variable at one location is equal to the mean at another location and the correlation between any two locations depends only on the vector that separates them, not their exact locations. Thus similar distances between different pairs of data points provide the statistical replication (Krivoruchko, 2005). Stationarity is an assumption that is often reasonable for spatial data and it is what the semivariogram analysis assumes and is dependant on (Ouyang et al., 2003). If data are not stationary, they should be modified to approximate a Gaussian distribution (normally distributed), usually by data detrending and data transformation. Geostatistics, in general, works best when input data are Gaussian (Krivoruchko, 2005; Ouyang et al., 2003). Kriging can take place once the dependency rules are known.

3.3 TRANSFORMING VARIABLES AND LOG-NORMALITY

The kriging estimator is a weighted average and as a result sensitive to few very large values. Consequently, if the distribution of the data is skewed, modelling the semivariogram becomes a harder task. The logarithmic transformation is particularly useful for positively skewed distributions. The transformation will help to make the variances more constant and normalize the data resulting in a more symmetric Gaussian distribution (Krivoruchko, 2005; Tolosana-Delgado and Pawlowsky-Glahn, 2003). Ordinary kriging is quite robust and so there is some potential for applying it without modification even when the data do not have a normal distribution. However, the most commonly employed alternative is to transform the data to a normal distribution, undertake ordinary kriging, and then apply a back transformation. Lognormal kriging applied on logarithmic data is easily implemented and yields the best results compared to other kriging methods (Saito and Goovaerts, 2000; Papritz and Moyeed, 1999). The lognormal estimator provides an approximately unbiased estimate, but only works well when the transformed data are Gaussian, although error estimations are often exaggerated (Juang et al., 2001). Thus, the kriging estimation in the logarithmic space should be performed with caution because the lognormal kriging estimation is nonrobust against departures from the lognormal distribution (Juang et al., 2001; Chiles and Delfiner, 1990). In fact the problem lies in the back-transform. When the back-transform is applied to the results uncertainty is introduced to some values and through exponentiation tends to exaggerate any error associated with the kriging estimation. Simply explained, the best unbiased predictor for the kriged equation of the transformed variable cannot be the best unbiased estimator of the transformed variable (Tolosana-Delgado and Pawlowsky-

Glahn, 2003; Juang et al., 2001; Atkinson and Lloyd, 1998; Cressie, 1993). However, although many authors use a logarithmic transformation when interpolating environmental variables, very few apply a correction to the final estimate to take account of the bias (Cressie, 1993). Prior to using the Geostatistical Analyst, summary statistics for each data set were examined. Histograms were created and the normality of each data set was investigated by studying skewness and kurtosis statistics.

Figure 3.1A shows the original Calcium data set positively skewed (skewness = 5.509; kurtosis = 32.647) and normalized with a logarithmic transform in Figure 3.1B. After the transformation, the skewness value was much closer to zero (-.871) thus indicating higher symmetry. The resulting kurtosis value was also much closer to the desired value of three (8.292). All transformed data sets are identified in Table 3.1 as having a log model. Consequently, the logarithmic transform was used to improve the normality of 15 data sets but a back-transform was not used on the resulting predictions in order to avoid introducing more bias. The log kriged surfaces were created with the log values. The legend, however, indicates actual concentration values. A back-transform was not applied, simply the anti-log of the legend values is shown since these values are easier to comprehend. The log transformation was generated for each data set without a normal distribution in SPSS 10.0.
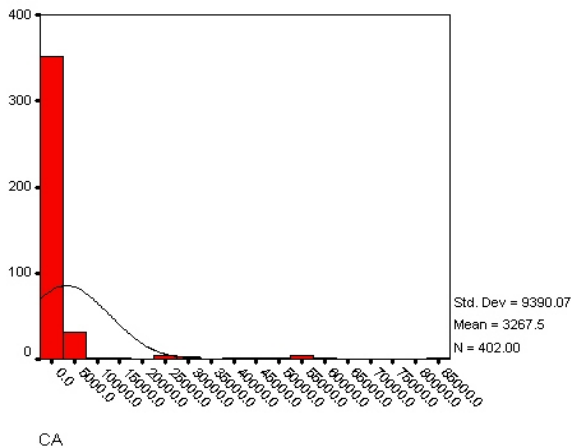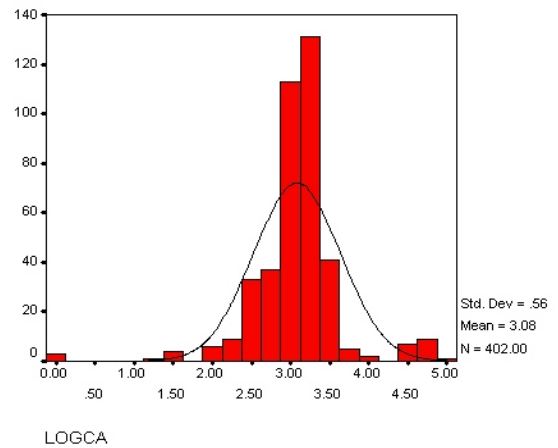
FIGURE 3.1A: Distribution of Ca values.

FIGURE 3.1B: Distribution of log Ca values.

3.4 SEMIVARIOGRAM ANALYSIS

The purpose of the semivariogram analyses are to: (1) identify the spatial structure of a stochastic (random) process by computing an empirical semivariogram; and (2) fit the empirical semivariogram using a selected semivariogram model (Ouyang et al., 2003).

3.41 THE EMPIRICAL SEMIVARIOGRAM

Creating an empirical semivariogram involves a) finding all pairs of measurements (any two locations), b) calculating for all pairs the squared difference between values, c) grouping vectors (or lags) into similar distance and direction classes, termed binning, and d) averaging the squared differences for each bin (Krivoruchko, 2005). After choosing ordinary kriging as the type of interpolation method to be employed and selecting the data set to be interpolated (one sediment pollutant at a time), the geostatistical wizard creates the semivariogram cloud and map which is mathematically defined as the average of one half of the squared differences between data values as a function of the separation distance and the direction;

28

$$\gamma(h) = \frac{1}{2n}\sum_{n}(C(x) - C(x+h))^2 \quad (3)$$

where h is the separation distance; C is the value of the data point, x is the location of the data point; n is the number of pairs of data points separated by a distance more or less equal to h (Ouyang et al., 2003).

The semivariogram cloud is used to create a semivariogram graph, which describes the spatial variability between samples and the distance between samples. If a semivariogram cloud is randomly distributed or does not show a pattern of increasing semivariogram (y-axis) with separation distance (x-axis) it indicates no positive spatial autocorrelation among data points and therefore kriging analysis is invalid. Conversely as pairs of locations become farther apart their squared difference will also be greater (Johnston et al., 2001). To plot all pairs becomes unmanageable. Instead of plotting each pair, the pairs are grouped into lag bins of similar distances and direction, a process termed binning. As a result the empirical semivariogram is a graph of the averaged semivariogram values on the y-axis and distance (or lag) on the x-axis. The intrinsic stationarity assumption that allows replication is what allows the use of binning (Johnston et al., 2001).

Figure 3.2 shows what a semivariogram should look like if positive autocorrelation is present. The components of a
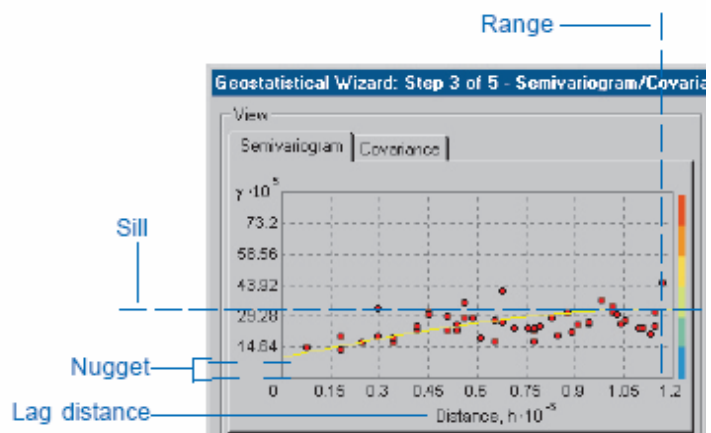

FIGURE 3.2: The semivariogram graph. (Source: Johnston *et al.*, 2001).

semivariogram include the nugget, an apparent discontinuity near the origin caused by measurement errors or microscale variations (Ouyang et al., 2003). Theoretically the value of the semivariogram (y-axis) must be zero at the origin. However, in the presence of a nugget, the semivariogram does not seem to approach zero but rather some positive value (in the y-axis). A sill is the upper limit of any semivariogram model in which the semivariogram tends to level off at a large distance and where the variable becomes spatially uncorrelated. A final characteristic, the range, is the lag distance beyond which there is little or no positive autocorrelation among variables (Ouyang et al., 2003).

3.42 MODELING THE SEMIVARIOGRAM

The next step after calculating the empirical semivariogram is estimating the model that best fits it. Modeling the spatial dependency (semivariogram modeling) is the most important step in kriging (Krivoruchko, 2005). The line of fit through the points forming the empirical semivariogram is the model. At this point the Geostatistical Analyst prompts for several model parameters, beginning with a function selection that will serve the model. There are several to choose from such as; Spherical, Circular, Exponential, Gaussian which are among the more common models to use as well as some not so common models like Tetraspherical, Pentaspherical, Rational Quadratic, Hole Effect, K-Bessel, J-Bessel and Stable. The selected model will affect the prediction of the unknown values, particularly near the origin of the curve where the closest neighbours will have more influence on the prediction (Johnston et al., 2001). The model best suited to each particular data set was gauged by visually inspecting the shape of the empirical semivariogram and from the cross-validation results. Table 4.1 shows that most of the

semivariograms were best fitted by circular and spherical models. Anisotropy is a characteristic of a random process that shows higher positive autocorrelation in one direction than in another (Johnston et al., 2001) and can also be taken into account in the modelling. If a semivariogram cloud map from a data set shows high values along a direction, it implies the spatial correlation of the data set is dependent on direction, and therefore an anisotropic model should be used to fit the experimental semivariogram. (Ouyang et al., 2003). The anisotropy function in ArcGIS was selected for all data sets. Wind and water currents are likely to have a directional influence on the distribution of the pollutants. Consequently, predictions near the existence of point pollution sources near shorelines and AOC's may not be as accurate since anisotropy will be more acute in these areas yet anisotropy is modelled in the same way across the lake. These are areas where concentrations may be underestimated. Loadings of contaminant from a point-source will be more influenced by the direction in which it is being emitted until it is able to mix and becomes affected by general current and wind circulation in that area.

Default model parameters accepted for all data sets include those for the partial sill, nugget, lag size and number of lags. Though default values were accepted for these parameters, the geostatistical analyst customizes these parameters for each data set. These were thus, not necessarily the same numbers from one surface to the next. The final parameter to specify is the searching neighbourhood, which is the area that determines how many sample points are to influence the prediction. Kriging can use all input data, however there are several reasons for not using this option. 1. Kriging with all 402 observations leads to the computational problem of solving a large system of linear equations. 2. At some distance, the points will have no correlation with the prediction

location. Consequently, it is possible that interpolation with a large number of neighbours will produce a larger mean-squared prediction error than interpolation with a relatively small number of neighbours (Johnston et al., 2001). 3. Using a local neighbourhood allows for the requirement that the mean value should be the same only in the moving neighbourhood, not for the entire data domain (Krivoruchko, 2005). The Geostatistical Analyst also allows one to define the shape of the searching neighbourhood ellipse, the number of angular sectors, and the minimum and maximum number of points in each sector. The shape is dictated by the input data. Since anisotropy is present, an elliptical shape angled 70º with four sectors was chosen by considering directional influence, optimal cross-validation results, and in attempts to minimize the probability that the five nearest neighbours are located along one sampling transect. Given the total number of sampled sites and their dispersion throughout the lake, five and two observations were chosen as the maximum and minimum number of neighbours.

3.5 CROSS-VALIDATION

Since input data are contaminated by errors and models are only approximations of the reality, the Geostatistical Wizard automatically accompanies the predictions with cross-validation results of the fitted semivariogram model in the final step. This allows the user to examine the kriging results and go back to previous steps if necessary in order to change parameters and improve the results. The cross-validation procedure involves deleting a sample value from the dataset one at a time and kriging the remaining sample values to estimate the value at the location of the deleted sample (Johnston et al., 2001). The difference between the measured value and the cross validation estimated value is the mean error which gives an indication of how well the data value fits into the

neighbourhood of the surrounding values. If the average of the cross validation errors is not far from zero there is no apparent bias. A positive bias indicates an overestimation of the model, whereas a negative bias shows an underestimation (Osburn, 2000 in Ouyang, et al., 2003). However, the mean error value depends on the scale of the data, so the mean error divided by the standard deviation is the mean standardized error (MSE). This value should also be as close to zero as possible. Moreover, standardized errors between –2.5 and 2.5 represent robust data and indicate that the semivariogram model can be used to predict the estimated values (ASTM, 1996 in Ouyang, et al., 2003). The optimum is for the predictions to be as close to the measured values as possible. The root-mean-squared error (RMSE) indicates how closely the model predicts the measured values and is therefore a measure of accuracy and consistency of the method. The estimates are considered accurate if RMSE is close to zero. The average bias or average standard error (ASE) is also calculated; a value close to zero indicates the smallest deviation from the observation (Prudhomme and Reed, 1999). Moreover, statistically valid results should have ASE values that are less than 20, otherwise predictions are straying quite far from the measured locations (Jakubek and Forsythe, 2004; Forsythe et al., 2004). Besides making predictions, the variability of the predictions from the measured values is estimated. If the average standard error is close to the root-mean-squared prediction error, then the variability in prediction is being correctly assessed. If the average standard error is greater than the root-mean-squared prediction error, the variability of the predictions is overestimated and vice versa. Consequently, if each prediction error is divided by its estimated prediction standard error, they should be similar. Thus the root-mean-square standardized error (RMSSE) should be close to one if the prediction standard errors are

valid. Greater than one RMSSE values indicate an underestimation and less than one RMSSE values indicate that the prediction errors are being over estimated (Krivoruchko, 2005).

CHAPTER 4: RESULTS AND DISCUSSION

The first part of this results section discusses the cross-validation results of the predicted surfaces. The second part discusses the resulting patterns of the generated surfaces.

4.1 CROSS-VALIDATION RESULTS

According to the cross-validation results presented in Table 4.1 all models proved robust and can thus be used to predict values and create surfaces. However, some models proved to be less trustworthy than others. A closer look at the cross-validation results is warranted prior to examining the interpolated surfaces.

TABLE 4.1: CROSS-VALIDATION RESULTS FOR ORDINARY KRIGING

Contaminant	Mean Error	Root-Mean-Square Error	Average Standard Error	Mean Standardized Error	Root-Mean-Square Standardized Error	Semivariogram Model
Sodium Oxide, Soda (Na_2O)	-0.003084	0.3396	0.3343	-0.006544	0.9947	Spherical
Magnesium (Mg)	0.003846	0.267	0.246	0.008116	1.064	Log Circular
Magnesium Oxide, Magnesia (MgO)	0.0009745	1.076	0.9131	-0.00131	1.207	Circular
Aluminum Oxide, Alumina (Al_2O_3)	0.02849	1.696	1.814	0.008711	0.9516	Circular
Silicon dioxide, Silica (SiO_2)	-0.1348	10.61	10.43	-0.009646	0.9772	Spherical
Phosphorus pentoxide (P_2O_5)	0.0009289	0.09839	0.1106	0.006899	0.893	Spherical
Sulfur (S)	0.00106	0.05724	0.05683	0.01723	1.008	Circular
P,P-DDE	0.01369	1.004	1.057	0.01219	0.9509	Spherical
Dieldrin (HEOD)	-7.458	0.0001848	0.0001878	-0.003843	0.9866	Spherical
Aroclor	0.000041	0.00503	0.00518	0.007708	0.9692	Spherical

Contaminant	Mean Error	Root-Mean-Square Error	Average Standard Error	Mean Standardized Error	Root-Mean-Square Standardized Error	Semivariogram Model
Potassium (K)	0.006771	0.2309	0.2424	0.01622	0.9444	Log Circular
Potassium Oxide (K_2O)	0.007994	0.4603	0.532	0.01142	0.8559	Spherical
Calcium (Ca)	0.0009139	0.4648	0.474	0.0003237	0.9567	Log Spherical
Calcium oxide, Calcia (CaO)	-0.02585	1.496	1.37	-0.01538	1.059	Spherical
Titanium dioxide, Titania (TiO_2)	0.002719	0.1477	0.1709	0.01338	0.8606	Spherical
Chromium (Cr)	0.01015	0.3803	0.3852	0.0177	0.9574	Log Spherical
Manganese (Mn)	0.0085	0.4314	0.4569	0.01396	0.9398	Log Spherical
Manganous oxide (MnO)	0.001228	1.812	1.862	0.0006433	0.9766	Spherical
Iron (Fe)	0.004783	0.1991	0.2008	0.01543	0.9744	Log Spherical
Cobalt (Co)	0.1393	10.69	10.61	0.01012	1.017	Circular
Nickel (Ni)	0.00846	0.309	0.2909	0.01905	1.028	Log Spherical
Copper (Cu)	0.008426	0.2789	0.3262	0.02044	0.8516	Log Spherical
Zinc (Zn)	0.007709	0.2885	0.3205	0.01815	0.9025	Log Spherical
Selenium (Se)	0.000631	0.1141	0.1149	0.005	1.002	Log Spherical
Strontium (Sr)	0.005418	0.2439	0.2657	0.01283	0.9056	Log Spherical
Molybdenum (Mo)	0.0001945	0.1096	0.0964	0.002095	1.13	Spherical
Beryllium (Be)	0.007945	0.388	0.3728	0.01435	1.052	Circular
Silver (Ag)	0.001285	0.1046	0.1109	0.009637	0.9455	Tetraspherical
Cadmium (Cd)	0.005301	0.3054	0.319	0.01262	0.9435	Log Spherical
Tin (Sn)	0.004364	21.46	21.4	0.0004051	1.01	Spherical
Mercury (Hg)	0.005822	0.2378	0.2735	0.01629	0.8602	Log Spherical
Lead (Pb)	0.009188	0.3113	0.359	0.01946	0.8619	Log Spherical
Uranium (U)	0.003888	0.371	0.3798	0.008715	0.9805	Circular
Arsenic (As)	0.00408	2.338	2.466	0.001565	0.9497	Circular
Vanadium (V)	0.00772	0.310	0.346	0.01825	0.8836	Log Spherical

In summary, both measures of bias (ME and MSE) showed that the predictions are centered on the measured values. The MSE results with a minimum of –0.015 and a maximum of 0.020 were well within the accepted –2.5 to +2.5 range, with the majority (86%) of the datasets being underestimated. The models of calcium and tin displayed the least bias along with magnesium oxide, calcium oxide, manganous oxide, molybdenum, and arsenic. While the metals nickel, copper, and lead were the most underestimated (Figure 4.1). In fact, with the exception of arsenic, all priority heavy metals were among the greatest underestimated models. Non-priority heavy metals such as iron and vanadium are also on the upper range of underestimated models. Interestingly, arsenic is also the only heavy metal that was not interpolated with logarithmic values since the log transform did not improve the normality of the data nor the cross-validation results. This is perhaps a result of the arsenic concentrations being fairly evenly distributed across the lake sediments, another explanation is also proposed in Section 4.3. Four of the five overestimated models are of datasets provided in terms of true percentages. Unlike the bias estimation, there is no clear general over or under estimation of variability assessment (Figure 4.2). Models to be weary of include arsenic, as the lone metal with a larger difference between ASE and RMSE and the models of magnesium oxide, aluminum oxide, silicon dioxide, and calcium oxide. Tin also has an ASE slightly higher then the threshold value of 20 discussed in Section 3.5.
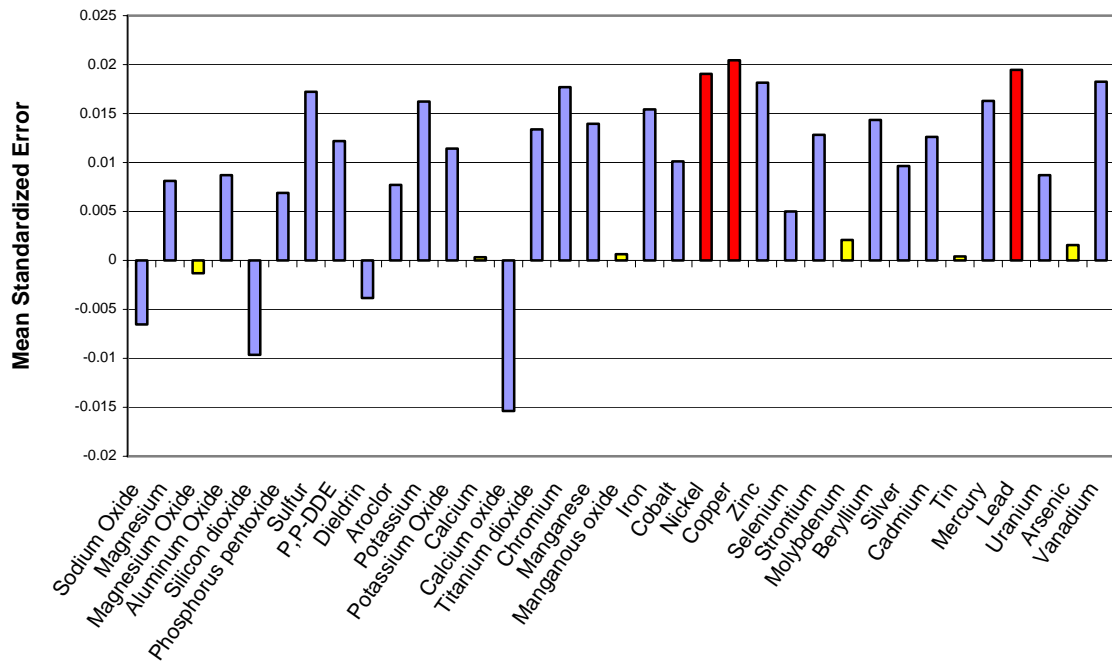
FIGURE 4.1: Measure of Bias (most biased results are highlighted in red, least biased results are highlighted in yellow, the remainder of the results are shown in blue).
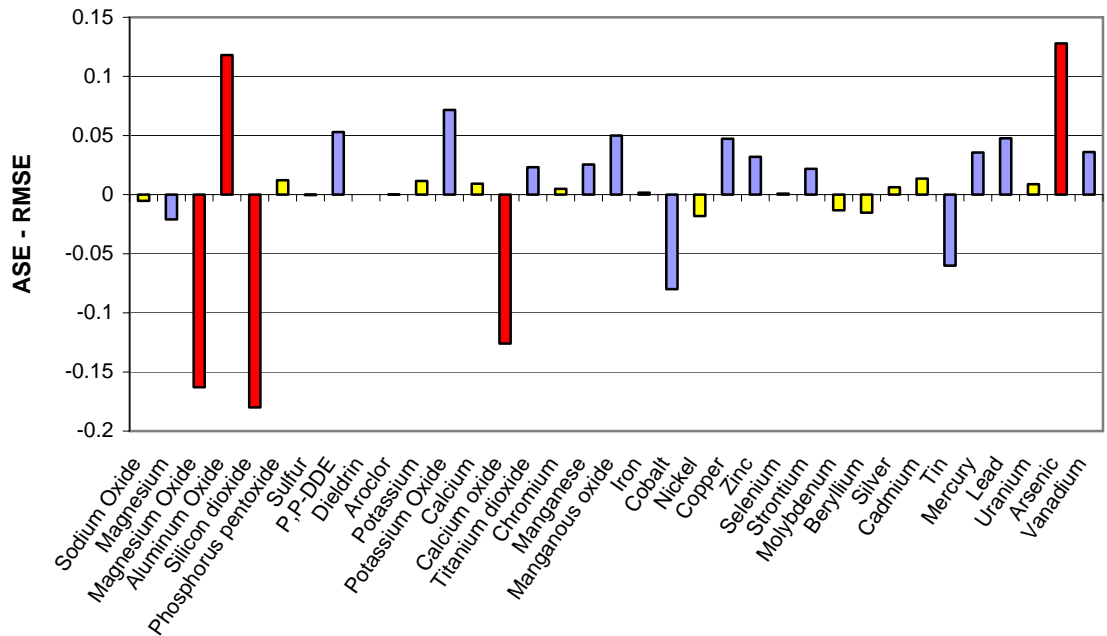
FIGURE 4.2: Measure of Variability (most variable results highlighted in red, least variable results are highlighted in yellow, the remainder of the results are shown in blue).

Higher prediction errors were expected to be associated with log-transformed datasets, particularly those with transformations that deviate from a lognormal distribution. But among the datasets showing the worst and best prediction errors, there were an equal number of transformed and non-transformed examples (Figure 4.3).
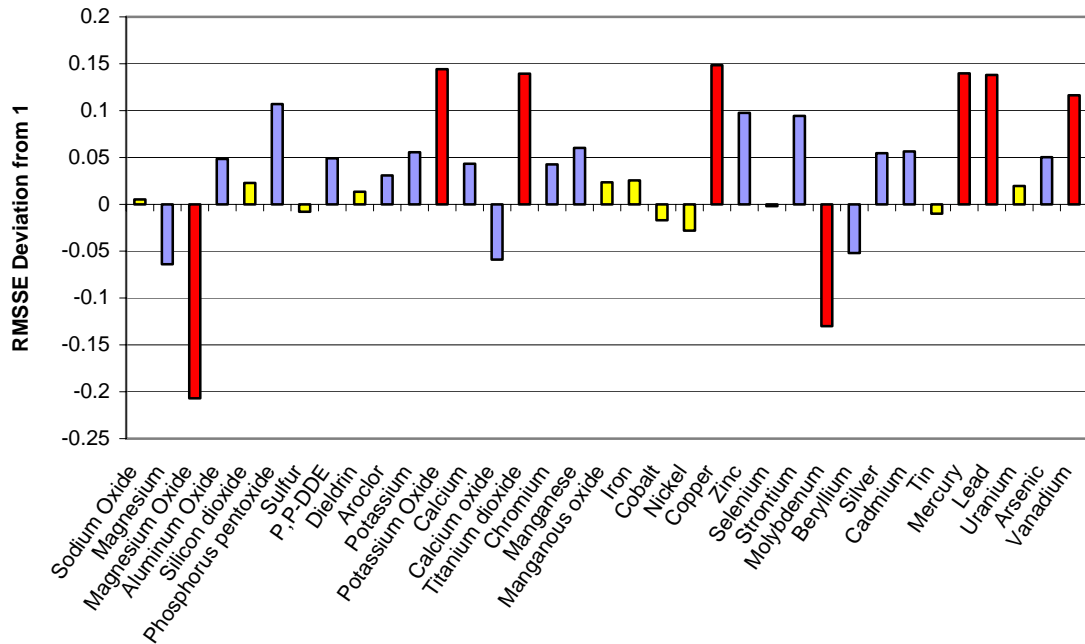
FIGURE 4.3: Accuracy of Prediction Errors (results with the least accurate prediction errors are highlighted in red, results with the most accurate prediction errors are highlighted in yellow, the remainder of the results are shown in blue).

In terms of accuracy and consistency in the models predicting results as close to the measurement value as possible, there are three models that stand out: Silicon dioxide, Cobalt, and Tin (Figure 4.4). Since the prediction errors for these three models also prove to be among the more accurate, the created surfaces should not be trusted. The exploratory analysis of Tin also supports these results. The data set was found to be non-normal, and the semivariogram revealed no positive autocorrelation (Figure 4.5).
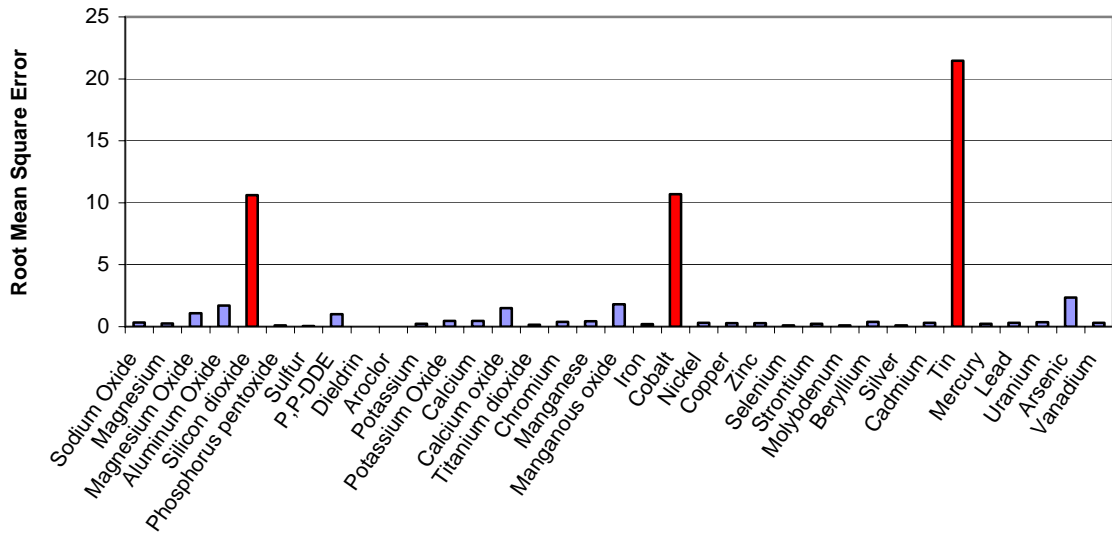
FIGURE 4.4: Accuracy and Consistency (results with the least accuracy and consistency are highlighted in red, the rest of the results are shown in blue).
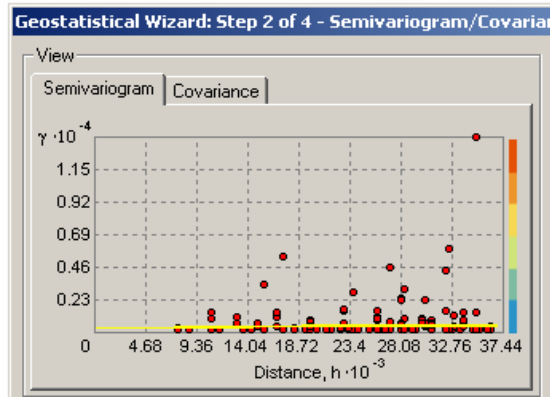
FIGURE 4.5: Semivariogram of Tin (Sn) dataset.

4.2 KRIGING RESULTS

A combination of smart quantile and manual classification scheme was used to generate data classes for the prediction results. For the pollutants with standard concentration

guidelines, areas that fall below or above the specific criterion need to be identified. In order to do this the upper and lower limits of the guidelines were specified manually. The rest of the classes were generated based on natural groupings of the data values (Smart Quantiles). The Smart Quantiles method divides the prediction intervals where there are relatively big jumps in the data values, so groups with similar values are placed in the same class. This method is a compromise between Equal Interval and Quantile (with unequal-sized intervals). This class scheme strikes a balance between highlighting changes in the middle values and the extreme values (ESRI, 2002).

4.21 PRIORITY HEAVY METALS

All priority heavy metals (Figures 4.6 - 4.15) had guidelines with which to compare the results. Arsenic was the only contaminant whose entire surface was below the threshold effect level (TEL) of 5.9 ug/g. Areas with concentrations nearing the TEL include the Thunder Bay Trough and the Duluth sub-basin. In fact, the point data show that at 24 of the sampling locations (mainly in the Thunder Bay Trough and Duluth sub-basin), the concentrations in fact exceed the TEL of 5.9 ug/g. The pattern does not seem to follow the general circulation and bathymetry of the Lake, unlike the rest of the priority heavy metals. Cadmium (Cd), Hg, Pb, and zinc (Zn) display areas that are above their respective TELs without ever reaching their respective PELs. Cadmium concentrations above the TEL cover most of the lake bottom including the Thunder Bay AOC and Trough, as well as the area near the St. Louis River AOC and the centre of Caribou Sub-basin reaching the highest concentrations up to the PEL. Areas at lower concentrations below the TEL are found along the southern shoreline of Lake Superior, a pattern also displayed in the rest of the priority heavy metals. Aside from arsenic, mercury is the least problematic of

the metals with most of the lake falling below the TEL except for the Thunder Bay AOC which appears to be an influential point-source for mercury exceeding the TEL of 0.17 ug/g. The other area that exceeds the TEL is near St. Louis River, a recognized AOC (Figure 1.2). Chromium (Cr), copper (Cu), and nickel (Ni) have concentrations above the PEL with chromium and nickel being problematic over most of the lake bottom. Similarly, the areas of lowest concentrations occur along the southern shoreline of the lake. Non-priority heavy metals, iron (Fe) and vanadium (V), generally follow the patterns observed with the rest of the metals with vanadium displaying more local variations in concentration which results in a more visually complex surface. In general, all of the surfaces displayed variable concentrations across the lake bottom, indicating the complexity of heavy metals.
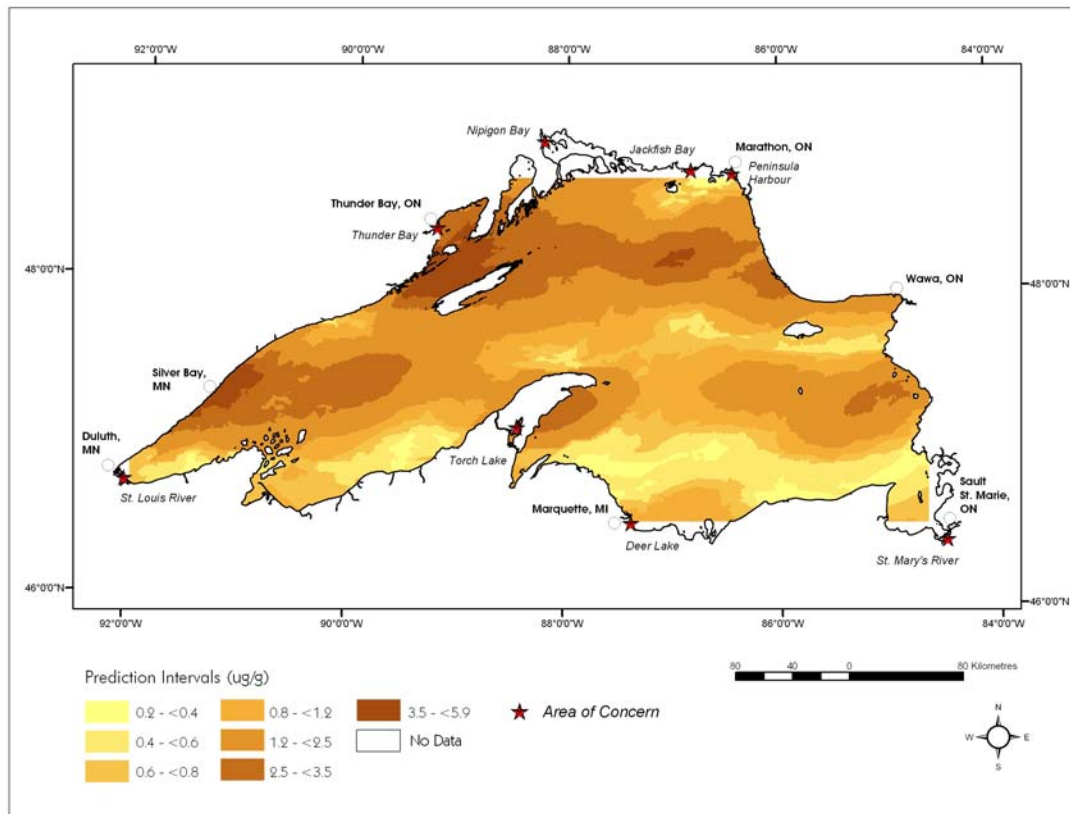
FIGURE 4.6: Arsenic (As)
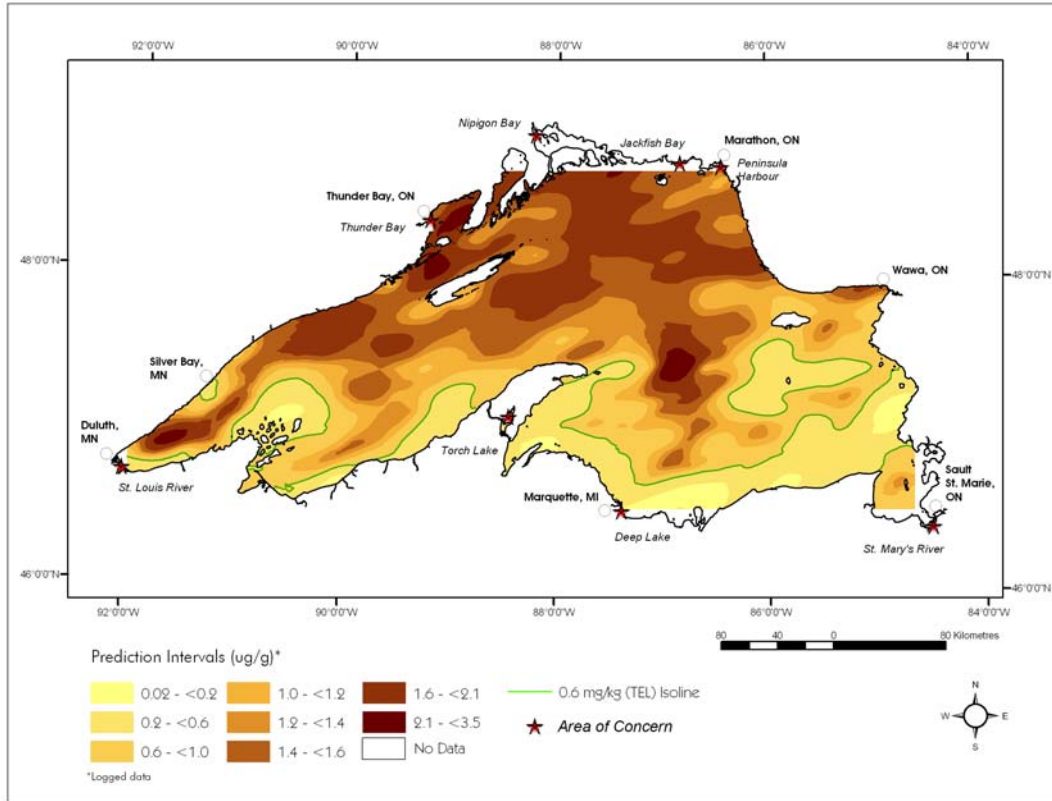
FIGURE 4.7: Cadmium (Cd)
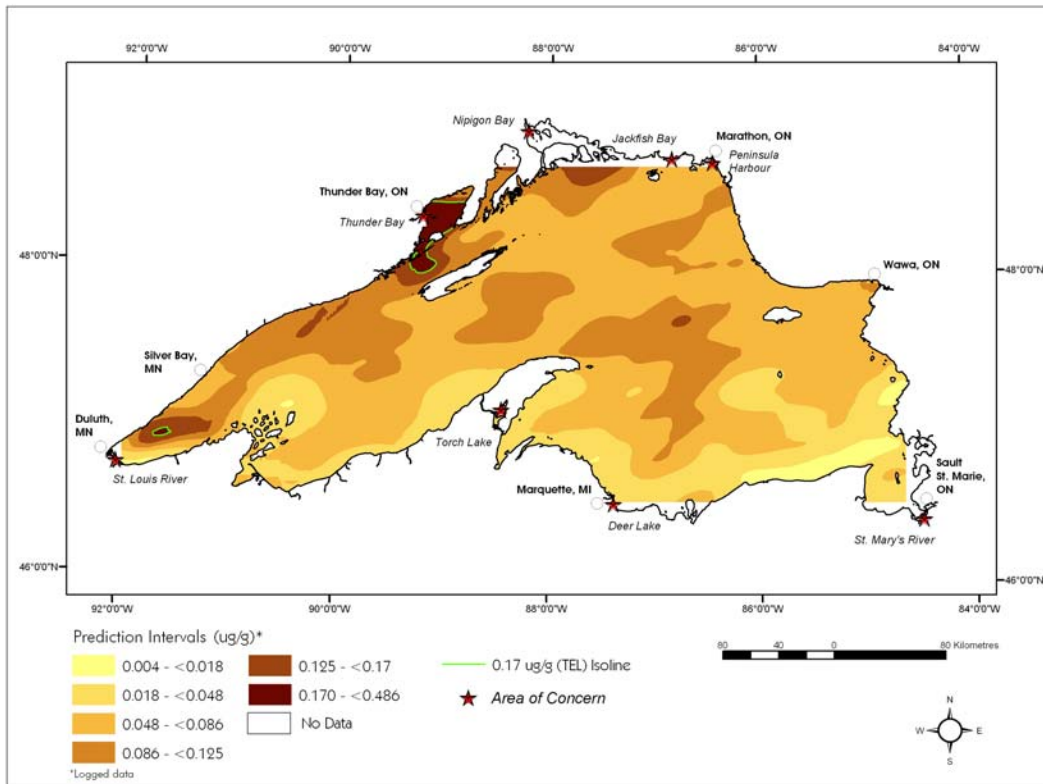
FIGURE 4.8: Mercury (Hg)
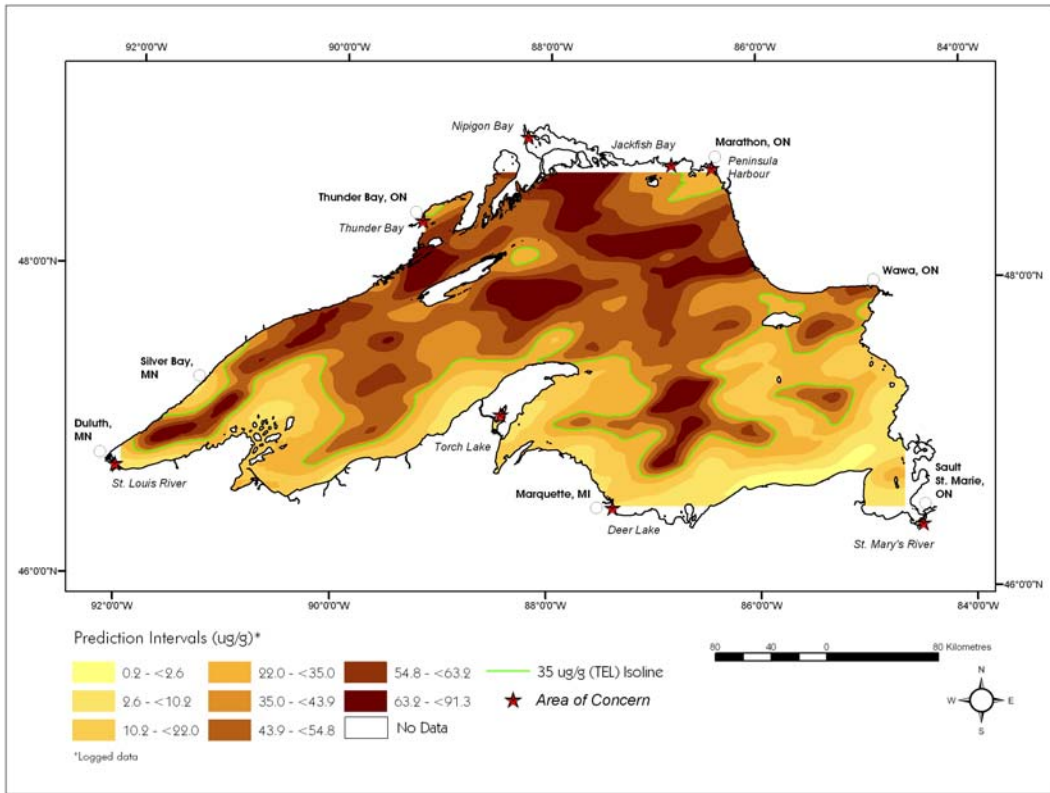
FIGURE 4.9: Lead (Pb)
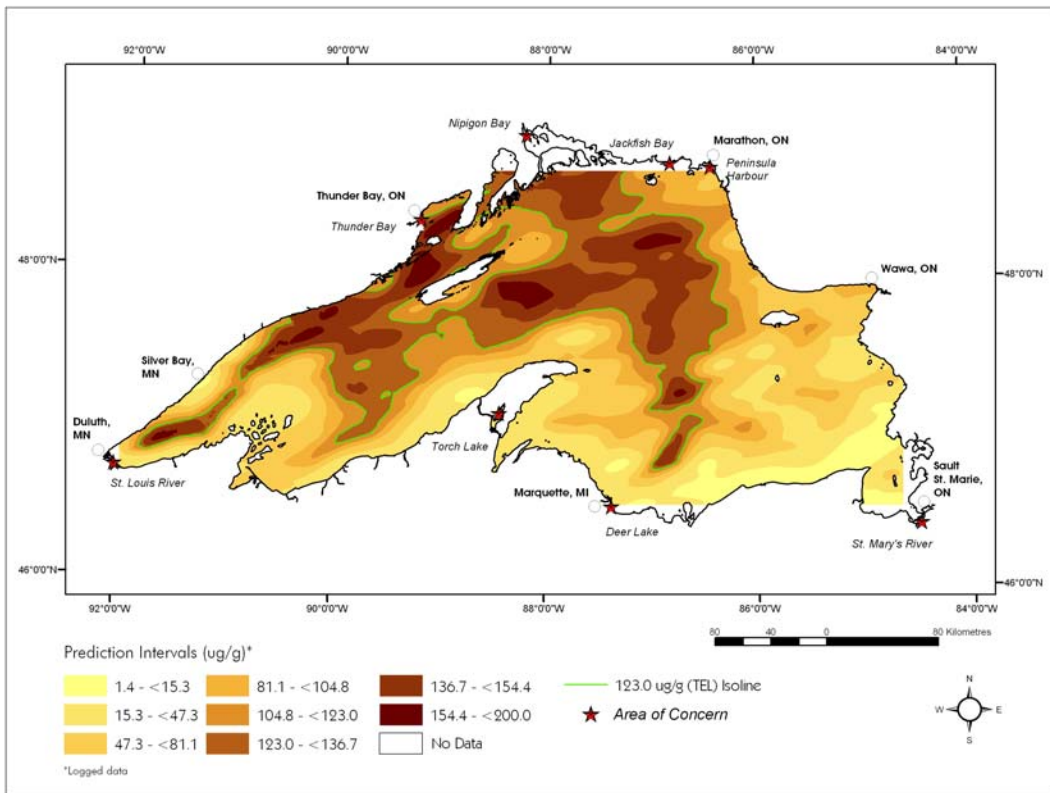
FIGURE 4.10: Zinc (Zn)
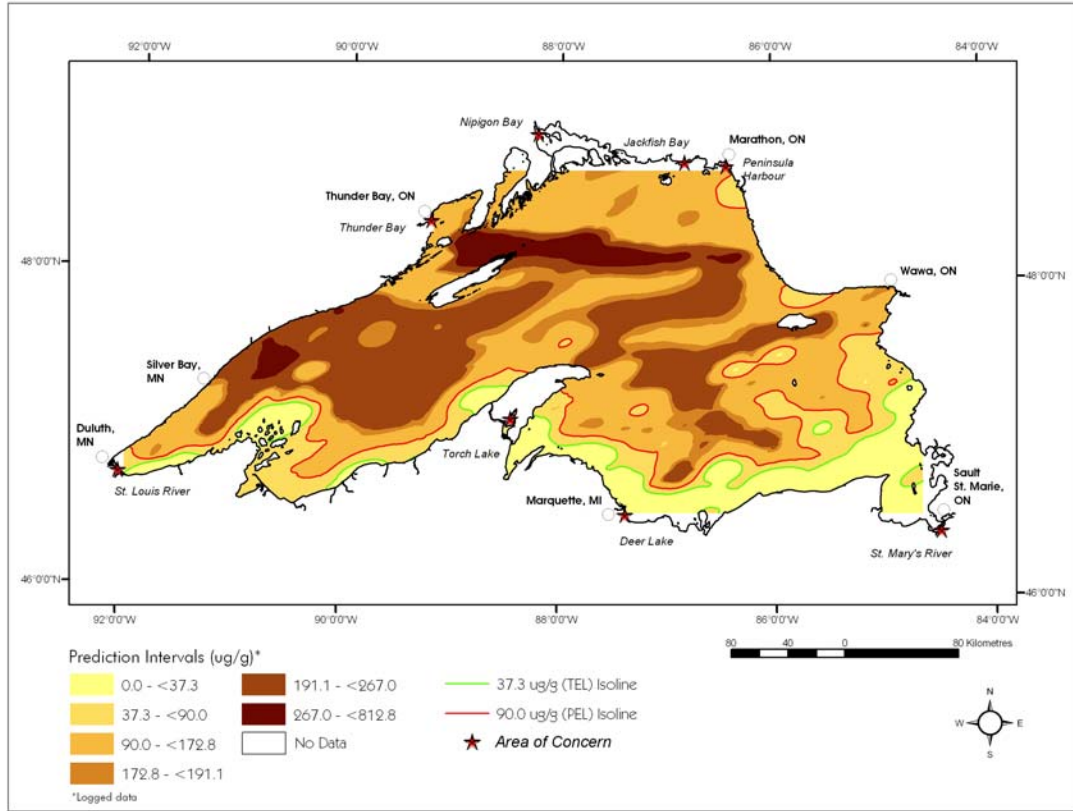
FIGURE 4.11: Chromium (Cr)
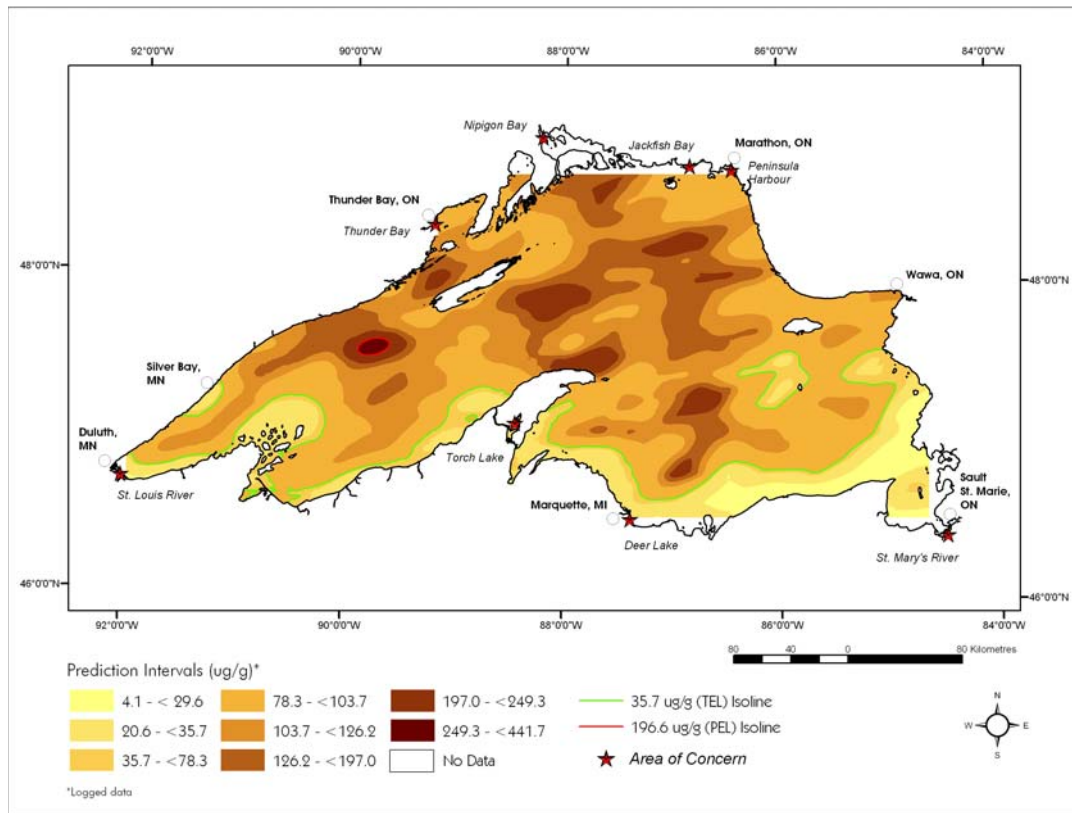
FIGURE 4.12: Copper (Cu)
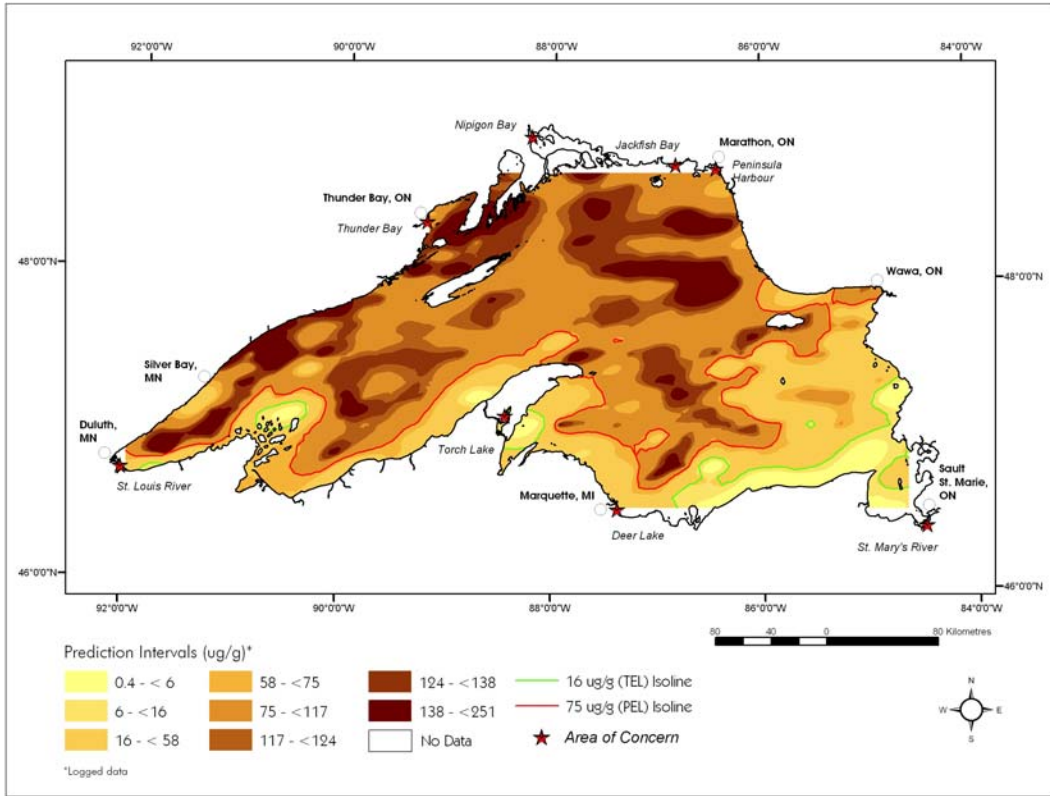
FIGURE 4.13: Nickel (Ni)
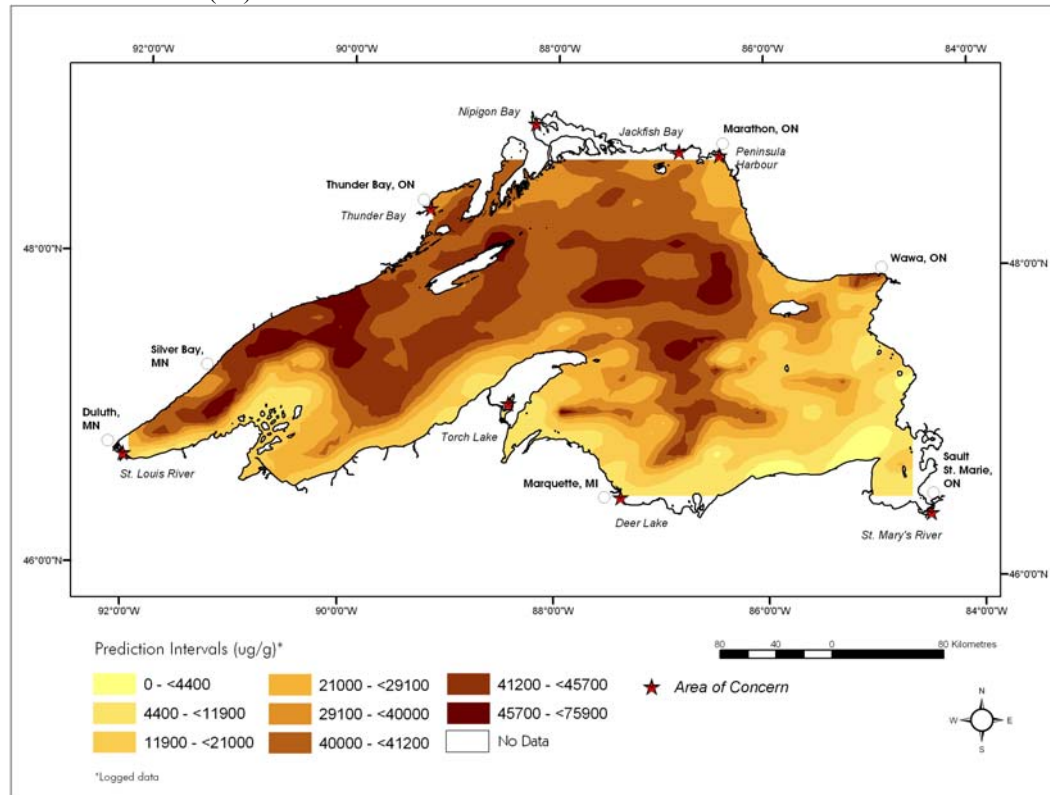
FIGURE 4.14: Iron (Fe)
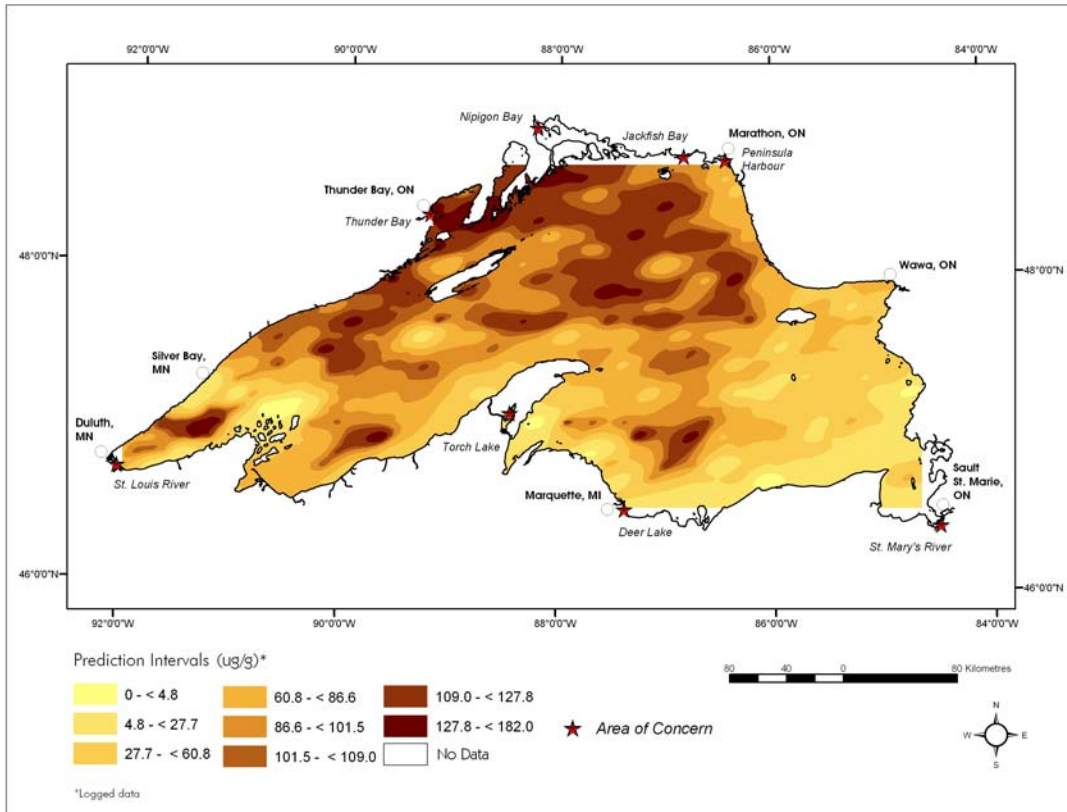
FIGURE 4.15: Vanadium (V)

4.22 CRITICAL POLLUTANTS

Guidelines were also available for the PCB aroclor, the pesticide DDE and the insecticide dieldrin, which are currently found along with the heavy metal mercury in Lake Superior's critical pollutants list (Figures 4.16 - 4.18).

With the highest concentration reaching 22.3 ng/g, aroclor falls a great deal below the current TEL guideline of 60 ng/g. The highest concentrations of aroclor are observed in the Duluth sub-basin increasing down to the St. Louis River AOC. Dieldrin with a

maximum concentration of 0.3 ng/g also falls below the set TEL guideline of 2.85 ng/g. The surface does not display much of a pattern with just four isolated areas displaying concentrations of dieldrin. Most of the lake surface falls below the TEL guideline of 1.42 ng/g currently set for the now banned pesticide of DDE. Like aroclor, the exception occurs in the Duluth sub-basin/St Louis River AOC. There DDE levels exceed the TEL but do not come close to the PEL of 6.75 ng/g. In general, these patterns do not follow the lake bathymetry as much as was observed with the metals, and the smallest contaminant concentrations are not necessarily observed along the southern shoreline of the lake.
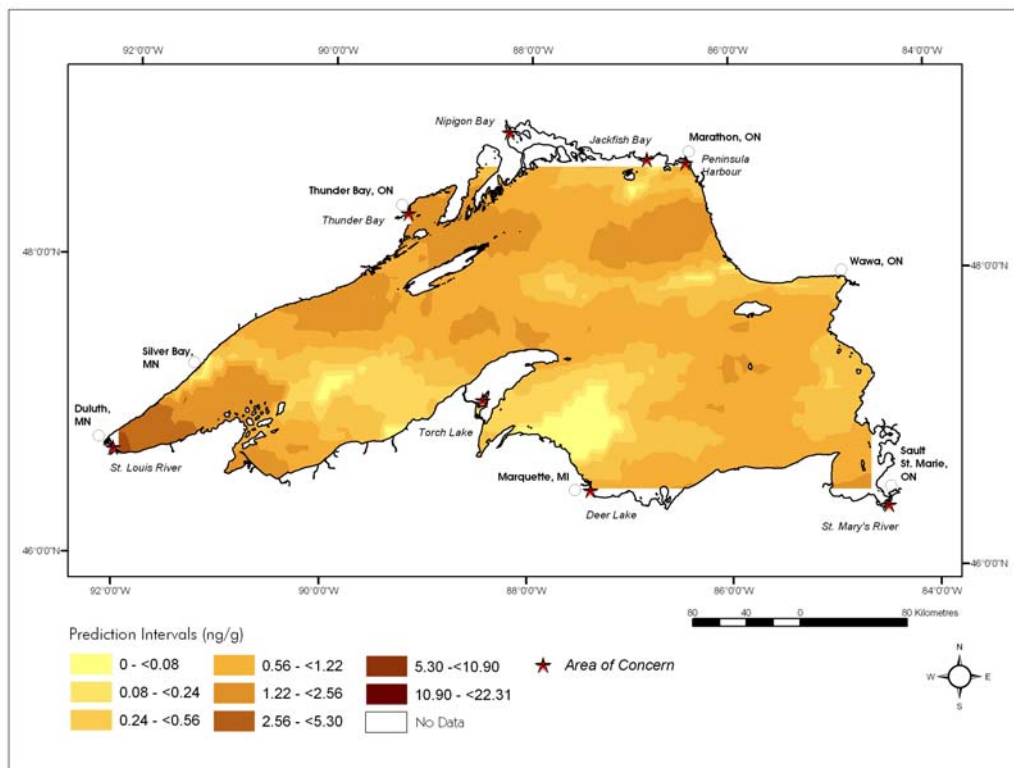
FIGURE 4.16: Aroclor
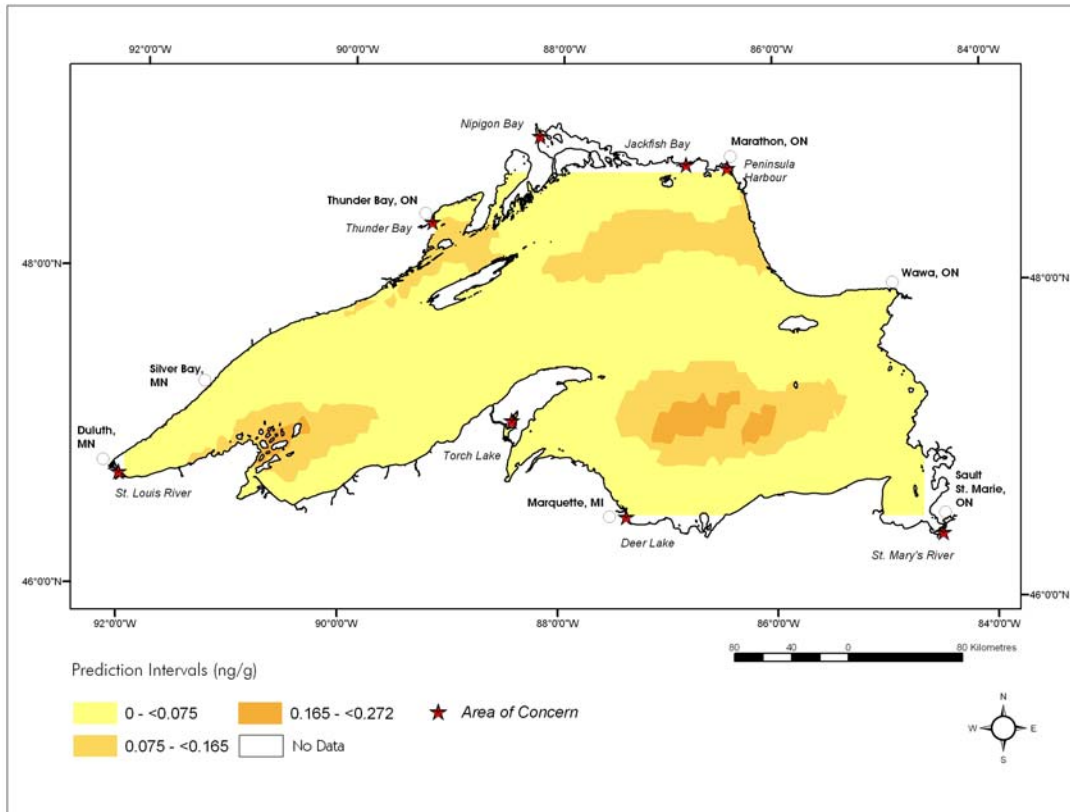
FIGURE 4.17: Dieldrin
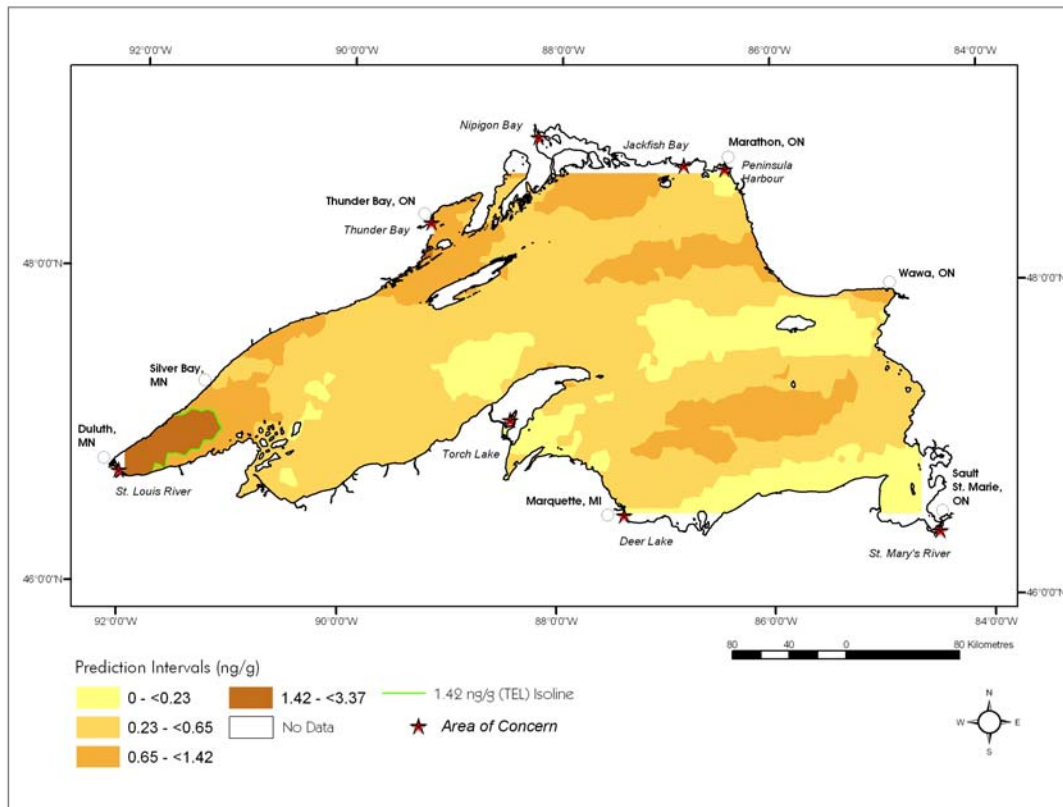
FIGURE 4.18: DDE

4.23 COMPOUNDS

Some organometallic compounds are commonly expressed as true percentages (parts per 100) because their levels tend to be high. Eight such compounds were present in the sediment survey and their surfaces are presented in Figures 4.19– 4.26.

The resulting surfaces from this group provided interesting patterns. Alumina (Al_2O_3), phosphorus pentoxide (P_2O_5), and potassium oxide (K_2O) display similar patterns seen with the priority heavy metals of higher contaminant concentration occurring in areas of high basin deposition. The pattern of lower concentrations along the southern shoreline is also present. Contrary to the heavy metals, these surfaces show less variation across the lake, resulting in less complex patterns. Magnesia (MgO), calcia (CaO), and soda (Na_2O) also had some similarities in terms of higher concentrations generally occurring in depositional basins and lower percentages along the southern shoreline but these surfaces show much more variation across the lake along with some distinct areas of higher percentages in areas not yet affected by the other contaminants.

Both calcia and soda have high percentages occurring in the Thunder Bay AOC, north of Isle Royale, along the shoreline half way down to Duluth (Silver Bay), Minnesota along with some distinct areas in the upper east Canadian shoreline from Marathon to Wawa, Ontario. Though the general trend, correlating with depositional basins is still there, these additional distinct areas (with the exception of the Thunder Bay basin) are not in depositional basins. Moreover, soda has an additional distinct, non-depositional area of high percentages found directly off the tip of the Keweenaw Peninsula. This leaves the two peculiar surfaces of titania (TiO_2) and manganous oxide (MnO) left to discuss in this group. Six of the seven areas with the highest percentages of titania (Figure 4.25) occur

in non-depositional areas with the highest of these occurring off the tip of the Keweenaw Peninsula but unlike soda, the affected area wraps around the tip and extends southward. The pattern of manganous oxide (Figure 4.26) is reminiscent of those seen with the critical pollutants. There is no visible pattern other than high percentages occurring in the upper Thunder Bay Trough and upper Isle Royale sub-basin, followed by noticeable areas in both the St. Louis River and Deer Lake AOC.
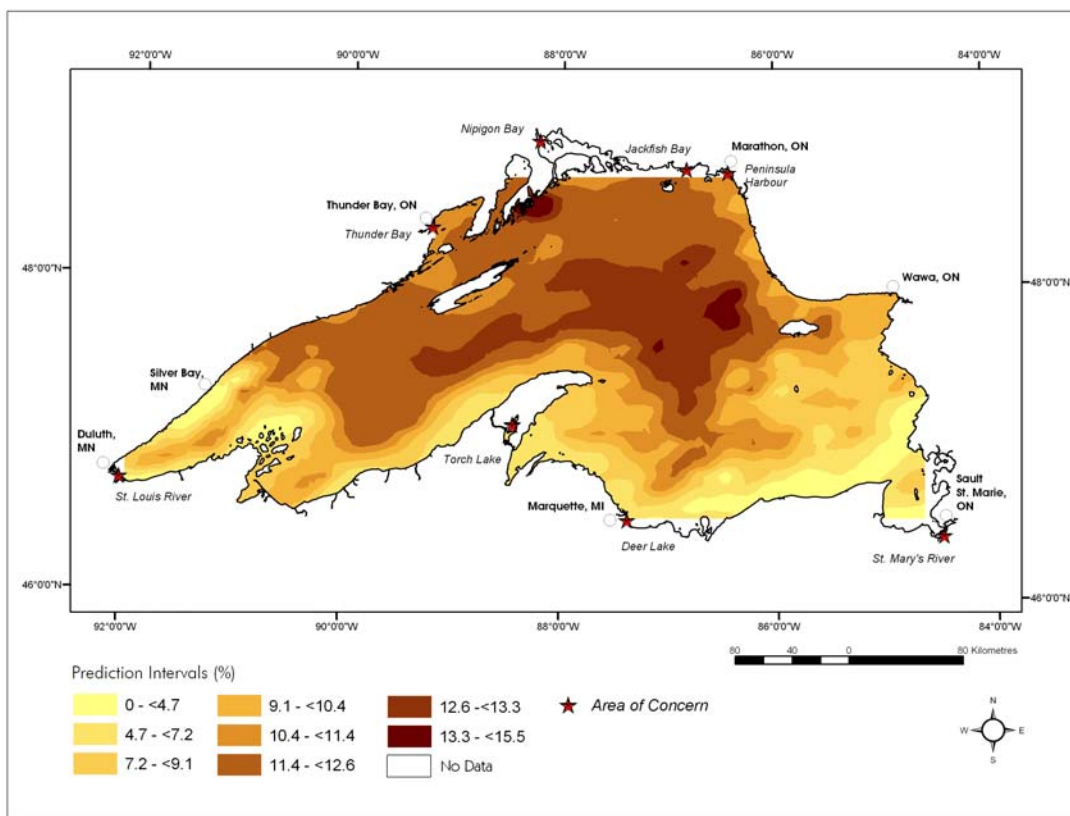

FIGURE 4.19: Alumina (Al$_2$O$_3$)
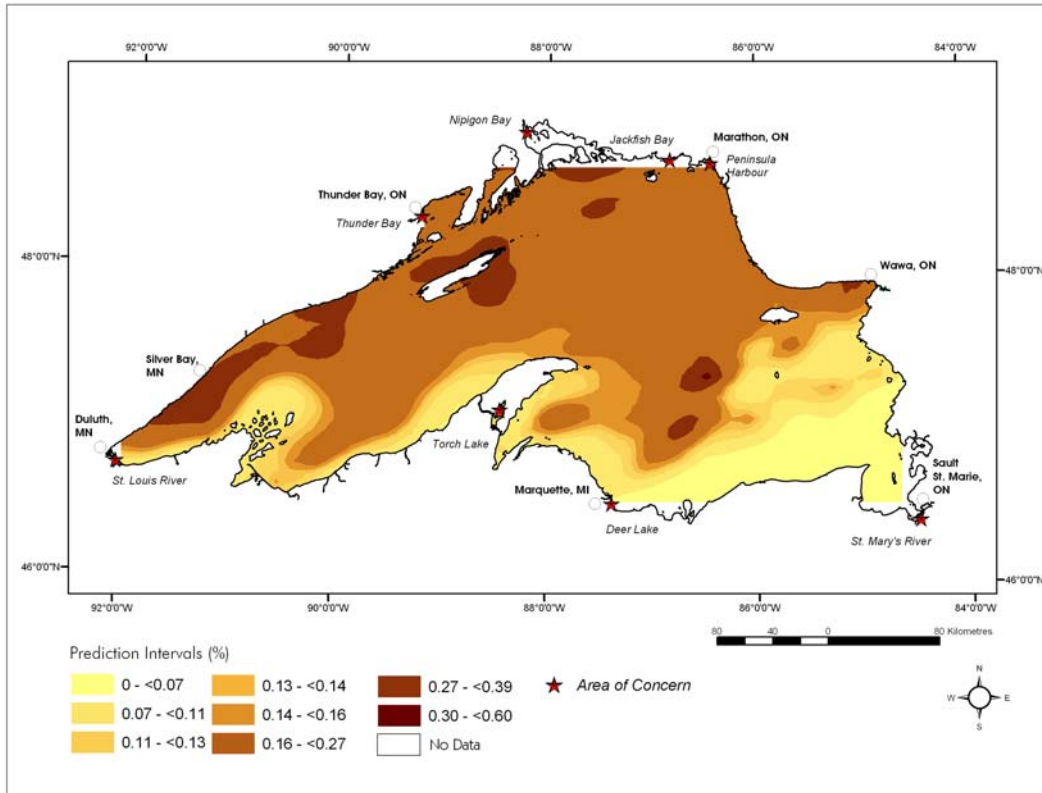
FIGURE 4.20: Phosphorous Pentoxide (P_2O_5)
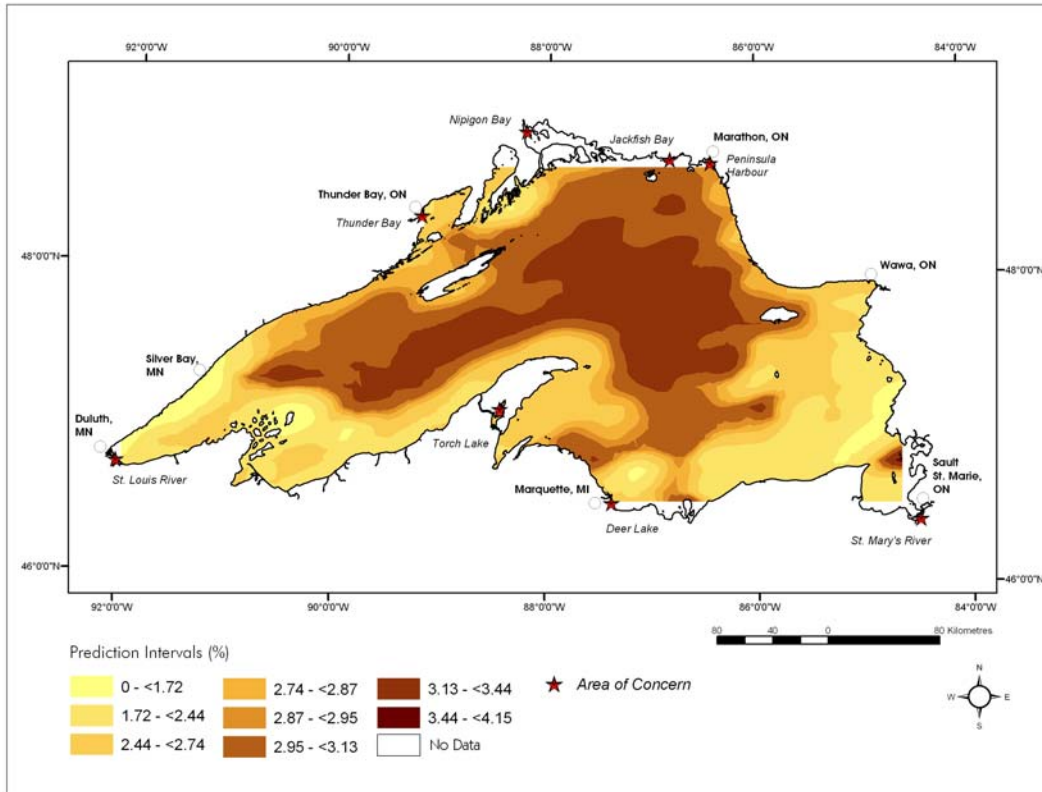
FIGURE 4.21: Potassium oxide (K_2O)
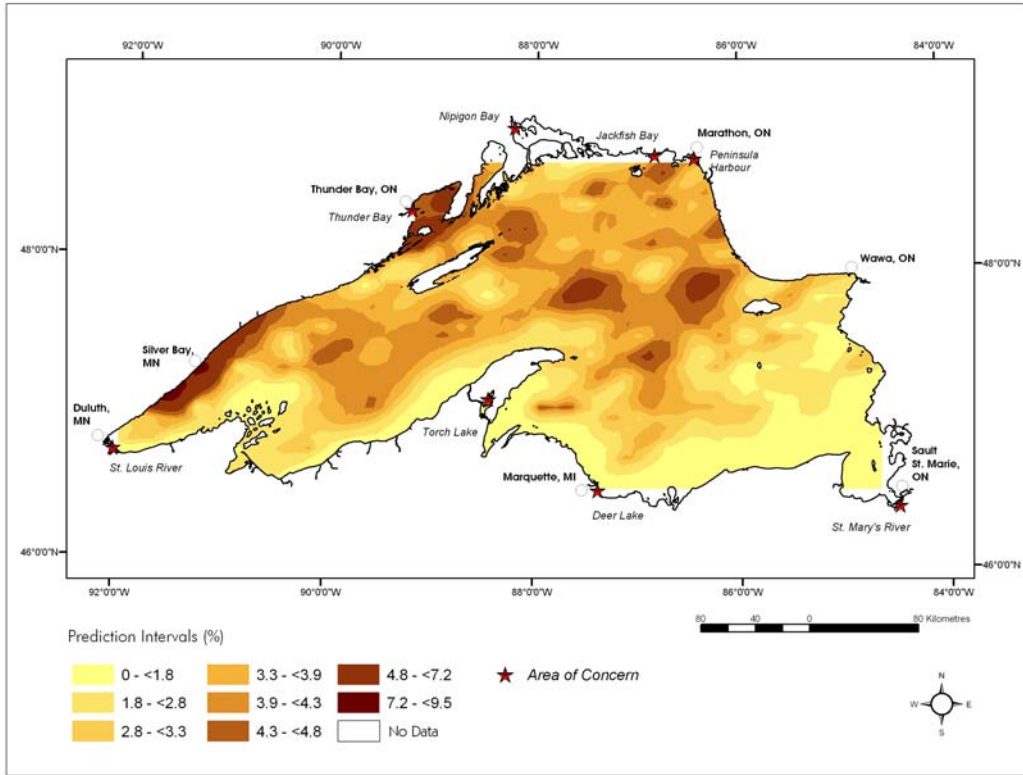
FIGURE 4.22: Magnesia (MgO)

FIGURE 4.23: Calcia (CaO)

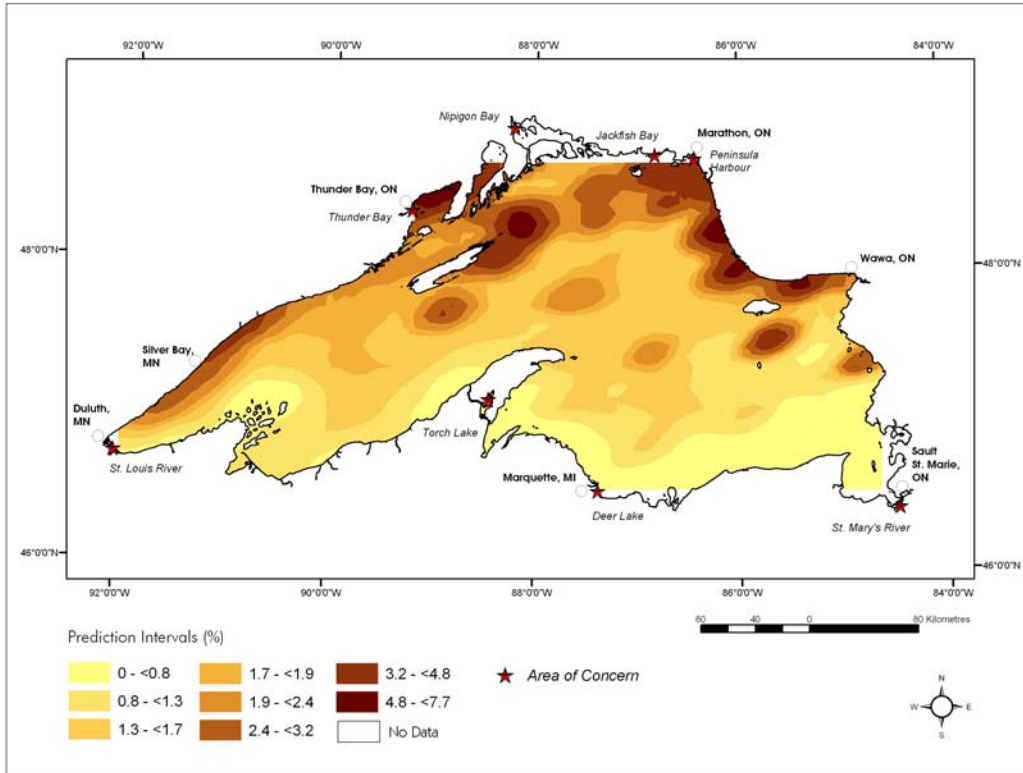53
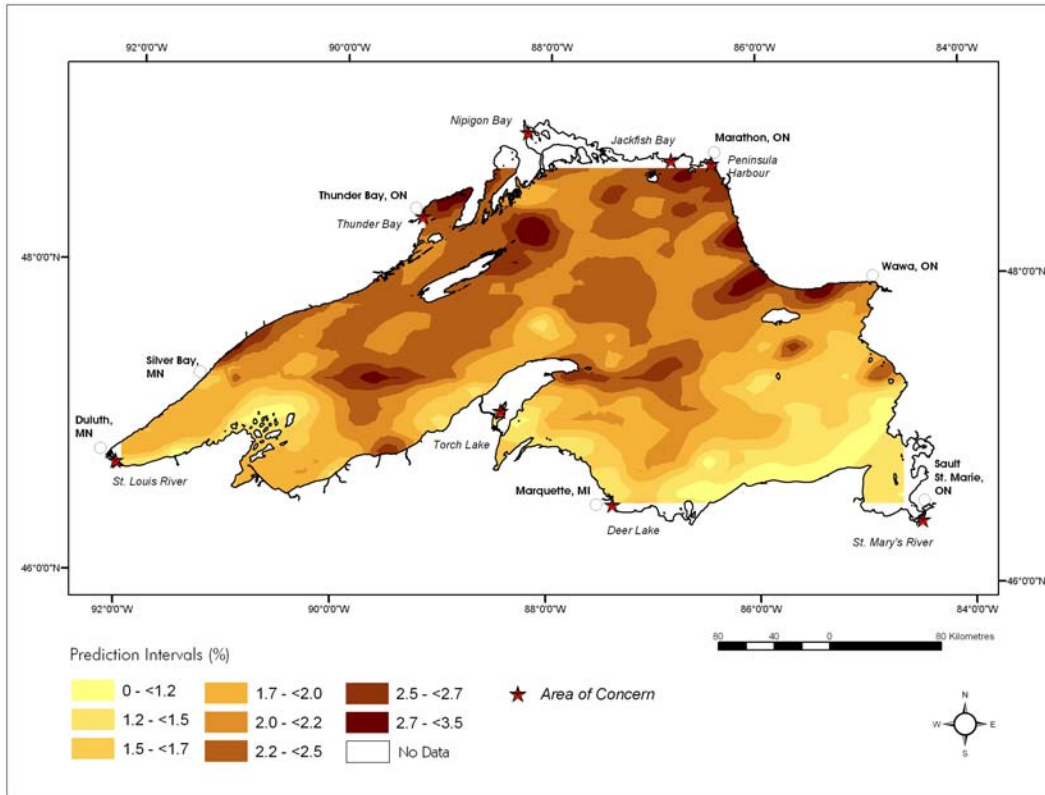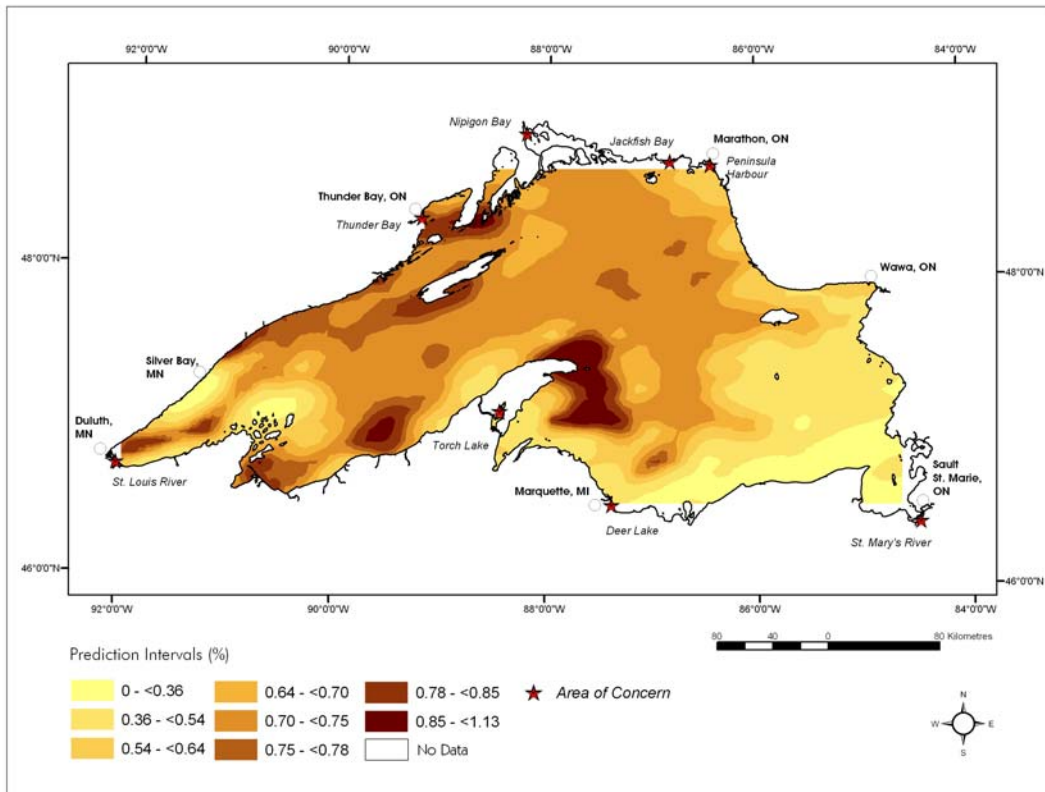
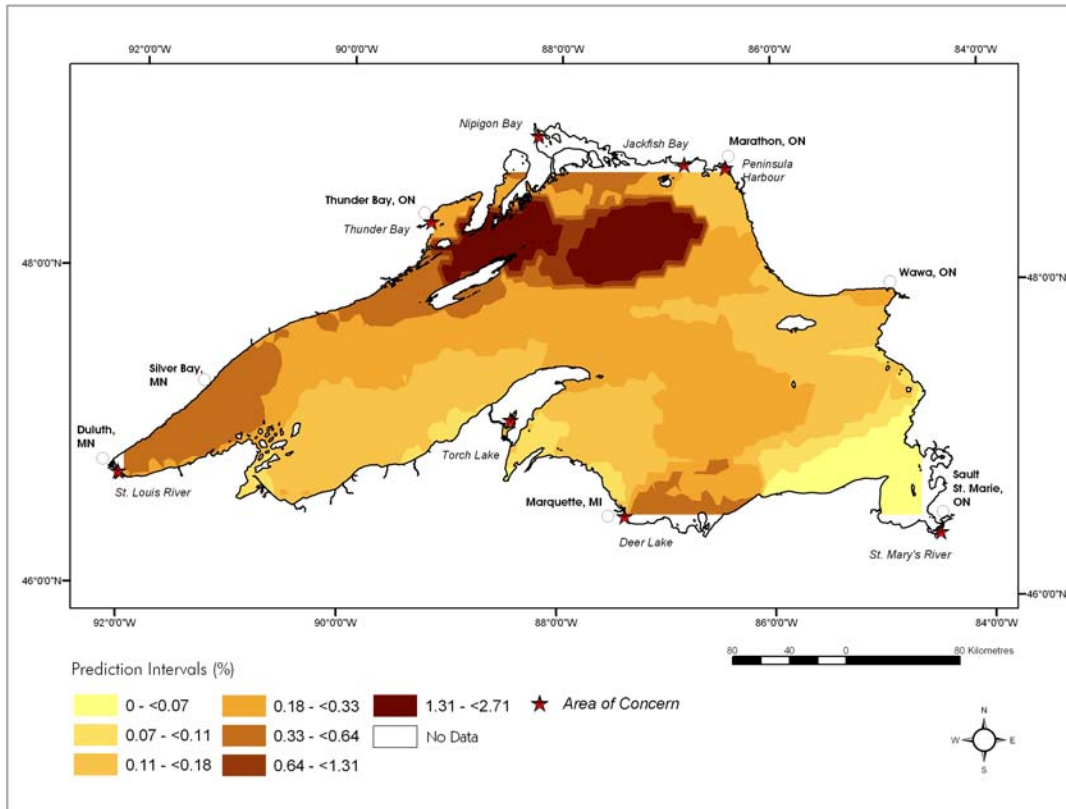FIGURE 4.24: Soda (Na$_2$O)

FIGURE 4.25: Titania (TiO$_2$)

FIGURE 4.26: Manganous oxide (MnO)

4.24 OTHER CONTAMINANTS

A lot of the same patterns as previously reported are also observed in the remainder of the contaminants (Figures 4.27 – 4.39) with a few noteworthy exceptions. Lower concentrations along the southern shoreline are once again observed in all but uranium (U), silver (Ag), and sulfur (S). Higher concentrations following the pattern of depositional basins do not occur in silver, sulfur, calcium (Ca) and uranium as well as selenium (Se), molybdenum (Mo), and tin (Sn). The latter three contaminants do not show any variation at all across the lake. There are only 3 or 4 isolated areas where selenium and molybdenum and tin are found in Lake Superior. Calcium follows the same pattern as calcia (CaO) (refer to Section 4.23) by having the same distinct areas of higher concentrations in the northern half of the lake (particularly Thunder Bay, above Isle

55

Royale and along the Canadian shoreline from Marathon to Wawa, Ontario). Silver produced one of the more peculiar surfaces with the north half of the lake being the most affected similarly to Ca and CaO but also displays a lot of contrast between the higher concentrations in the top third of the lake, the lowest concentrations along the middle, and higher concentrations albeit in more distinct areas along the southern shoreline. Silver and sulfur are also the only two surfaces with higher concentrations near the St. Mary's River, Lake Superior's outlet. One final observation concerns Thunder Bay. Strontium (Sr), potassium (K), and magnesium (Mg) were found in higher concentrations at the very northern tip of the bay.
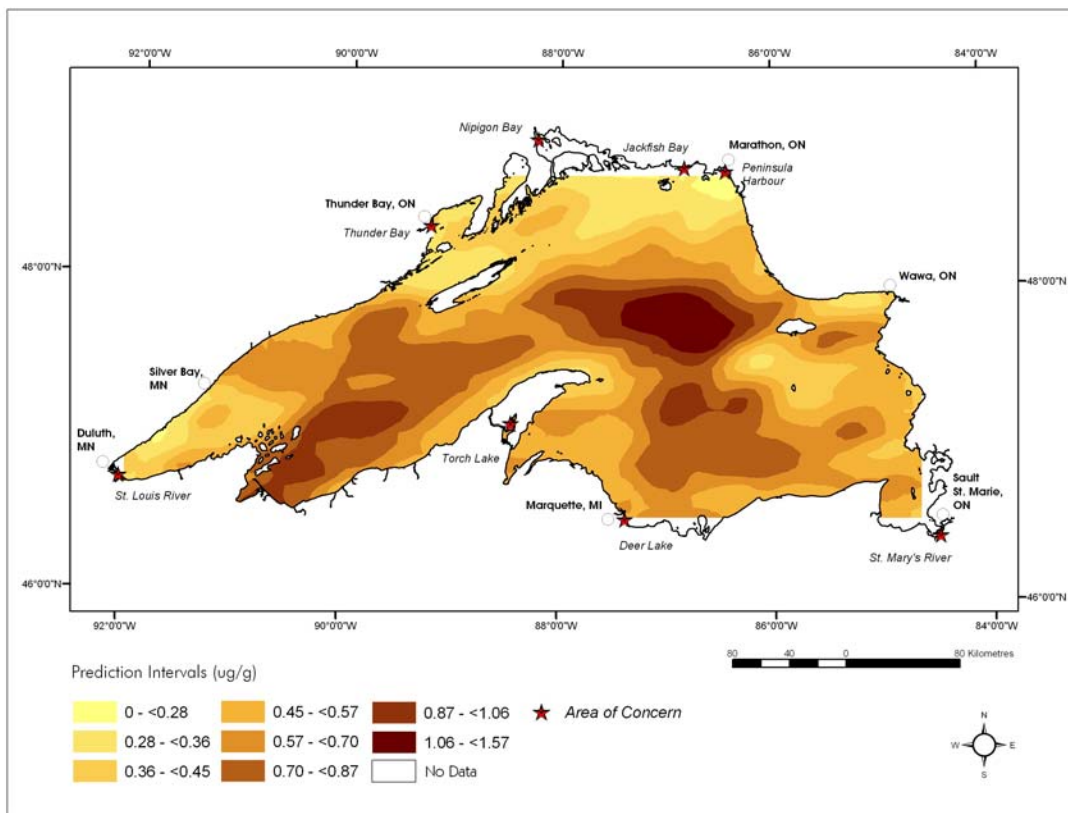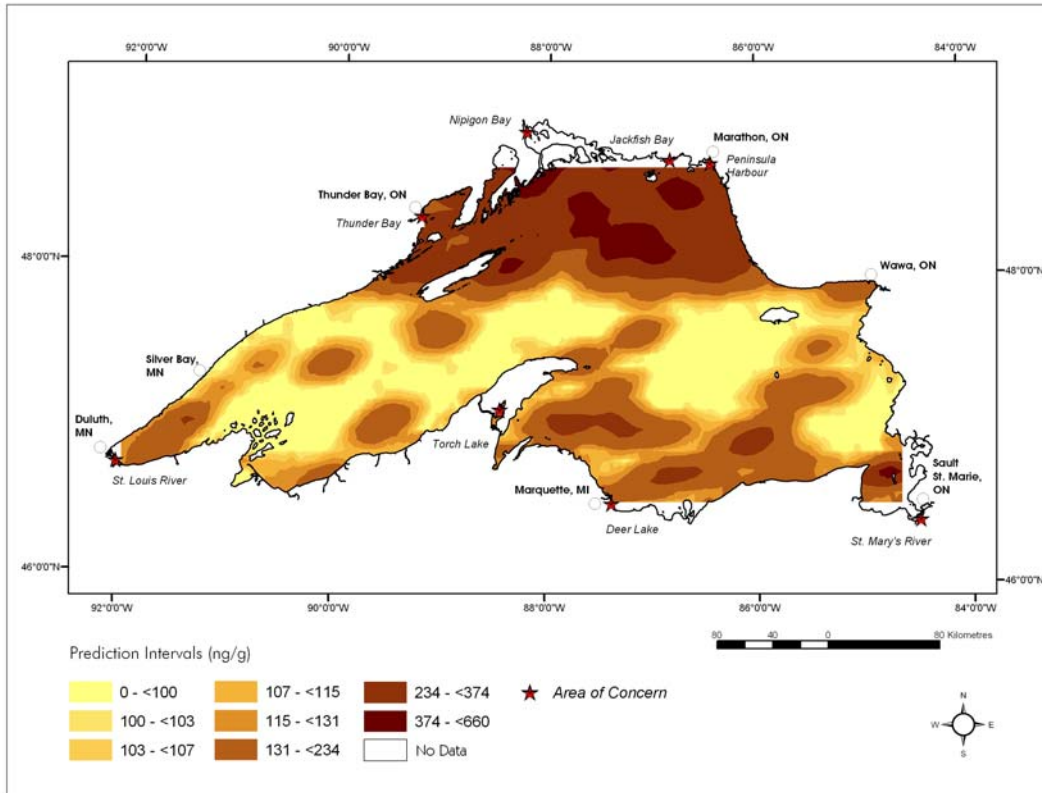

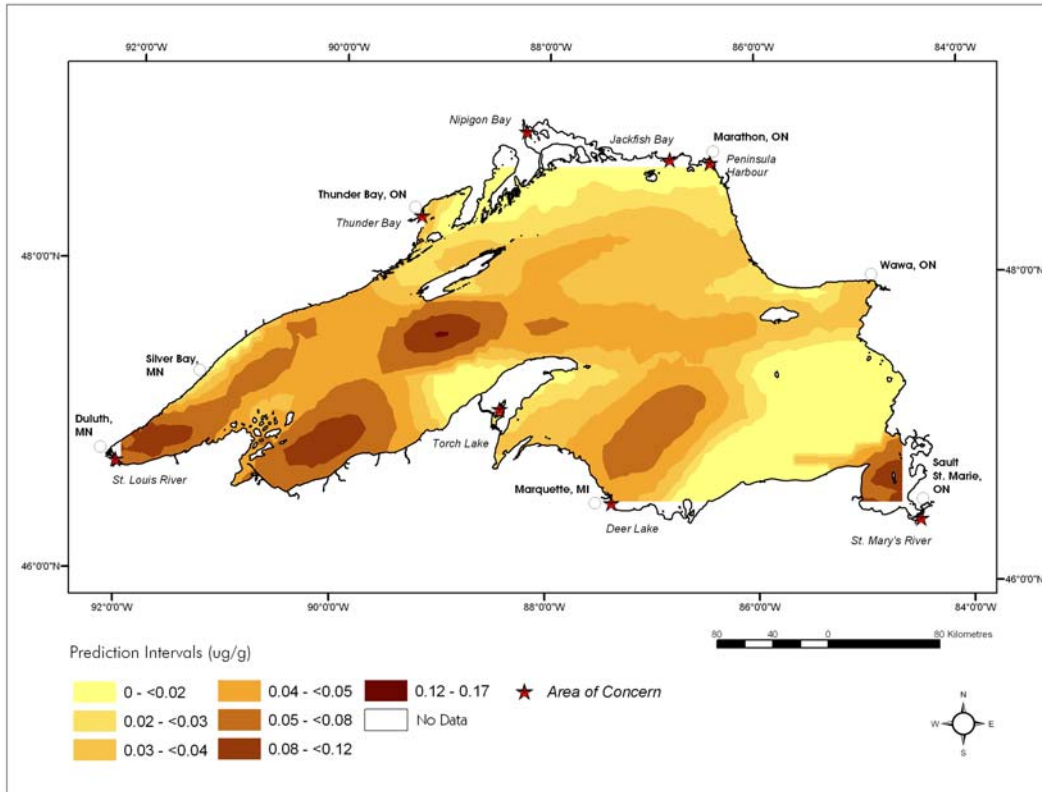FIGURE 4.27: Uranium (U)

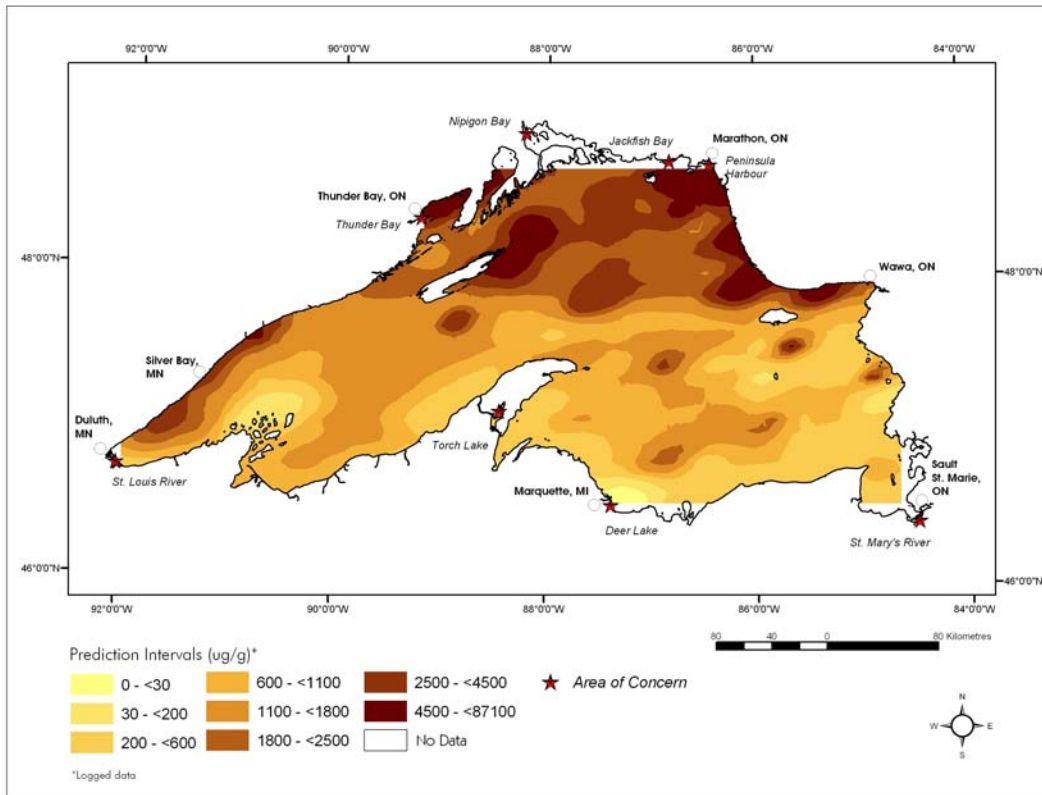FIGURE 4.28: Silver (Ag)

FIGURE 4.29: Sulfur (S)
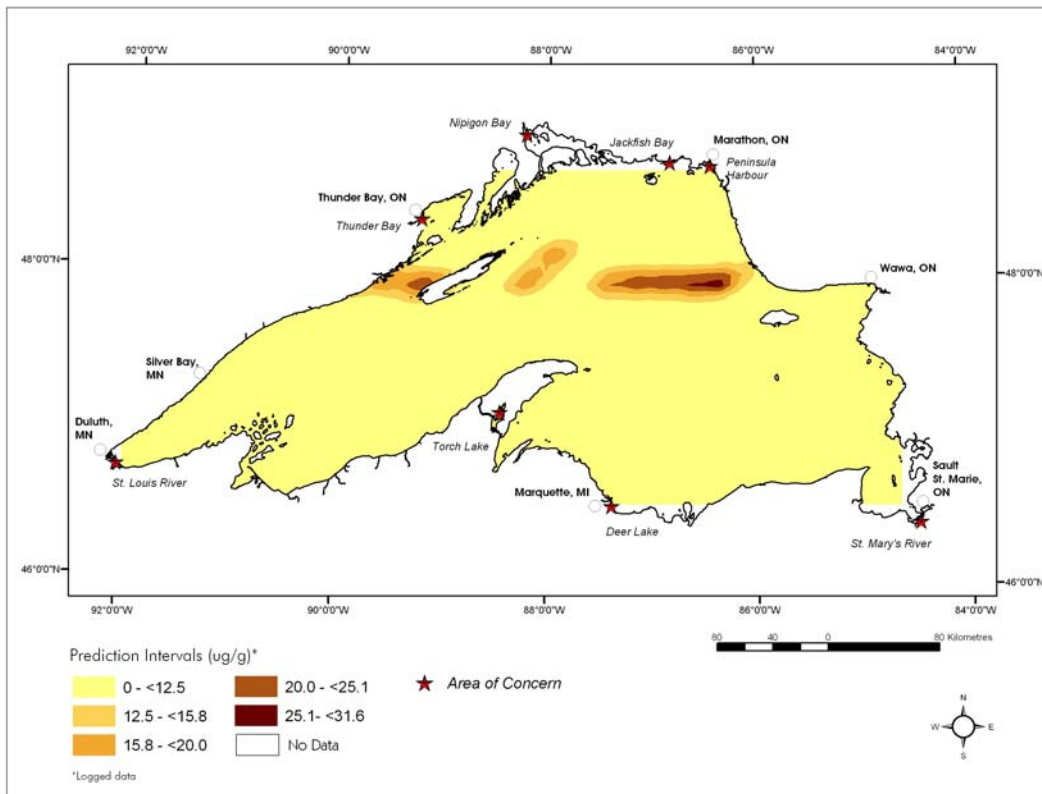
FIGURE 4.30: Calcium (Ca)
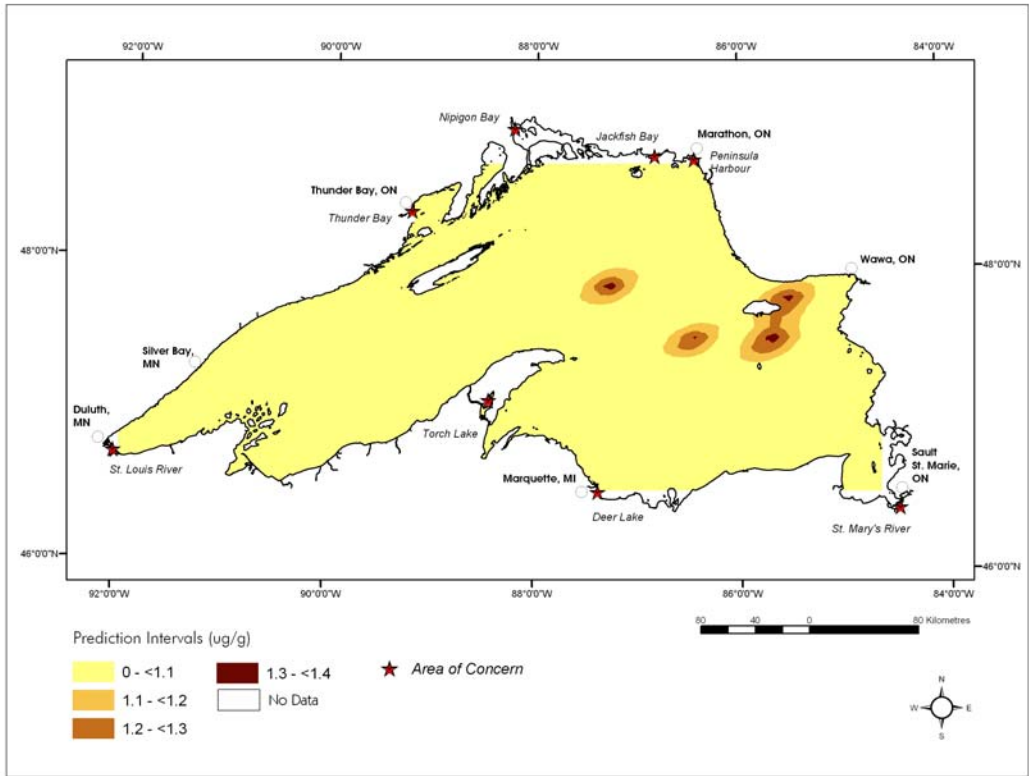

FIGURE 4.31: Selenium (Se)

FIGURE 4.32: Molybdenum (Mo)
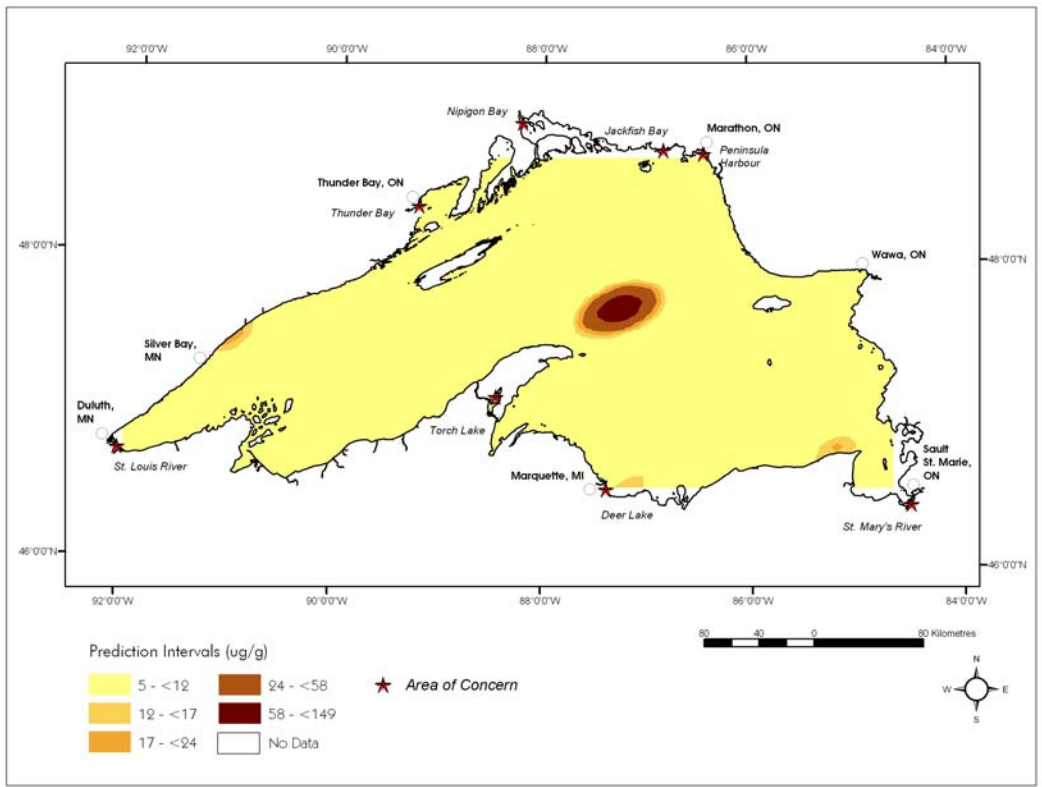
FIGURE 4.33: Tin (Sn)
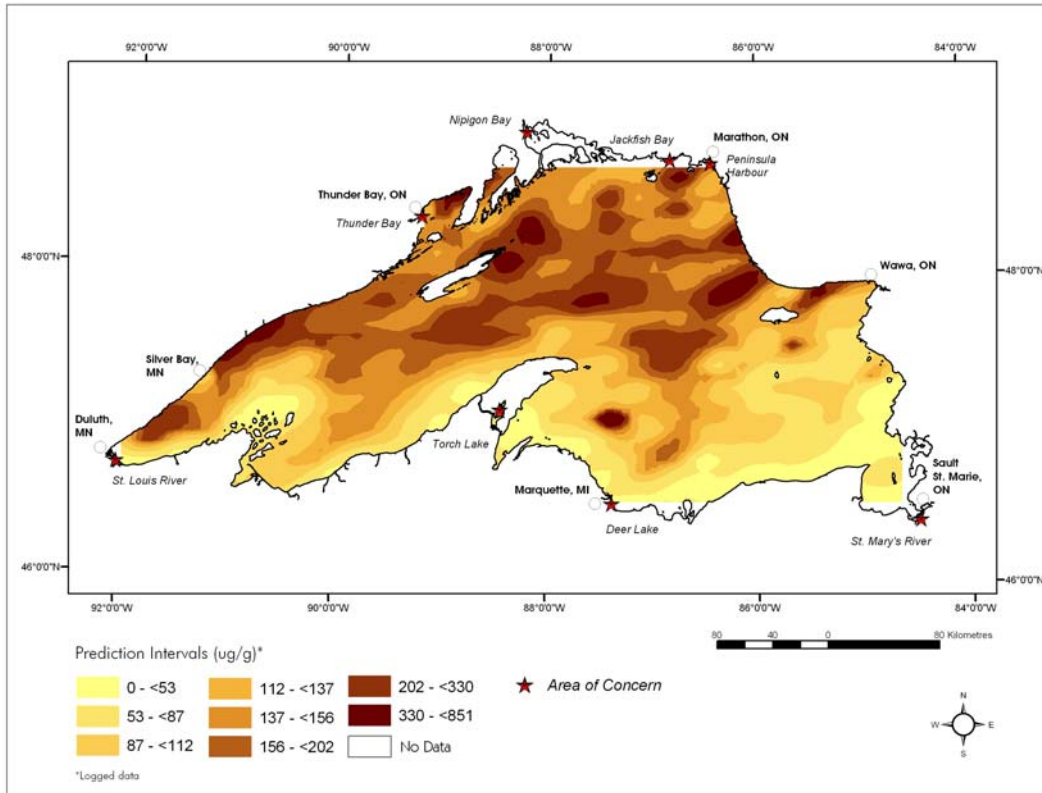
FIGURE 4.34: Strontium (Sr)
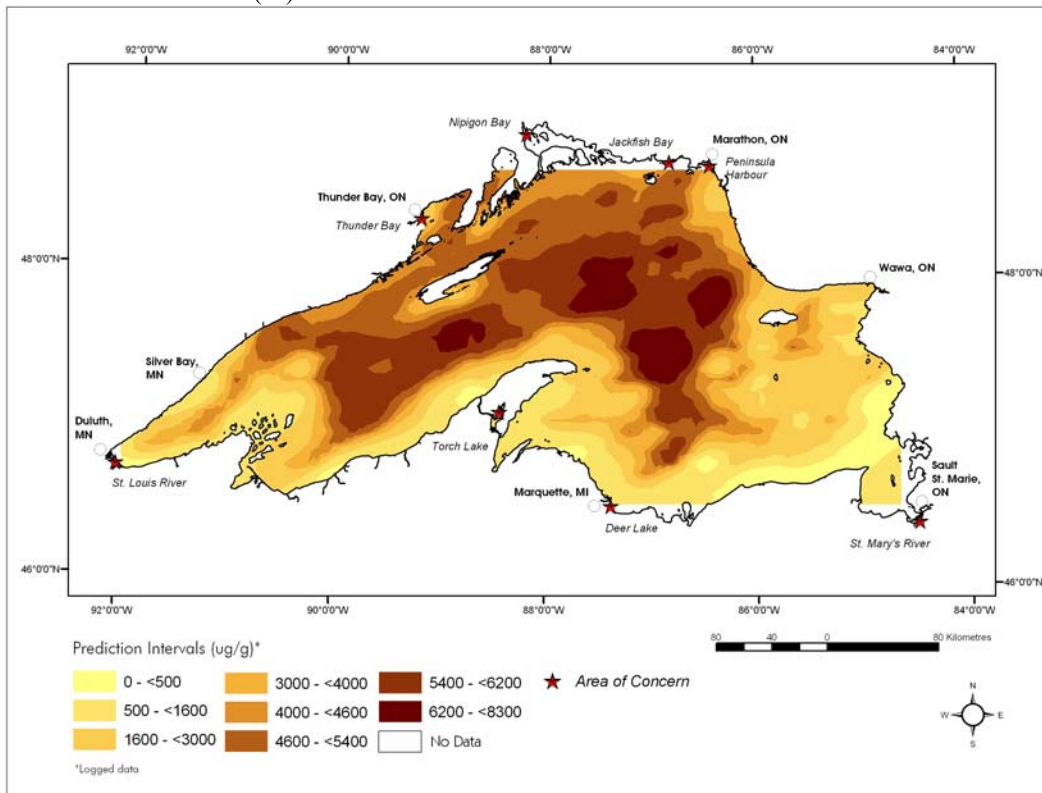
FIGURE 4.35: Potassium (K)

60
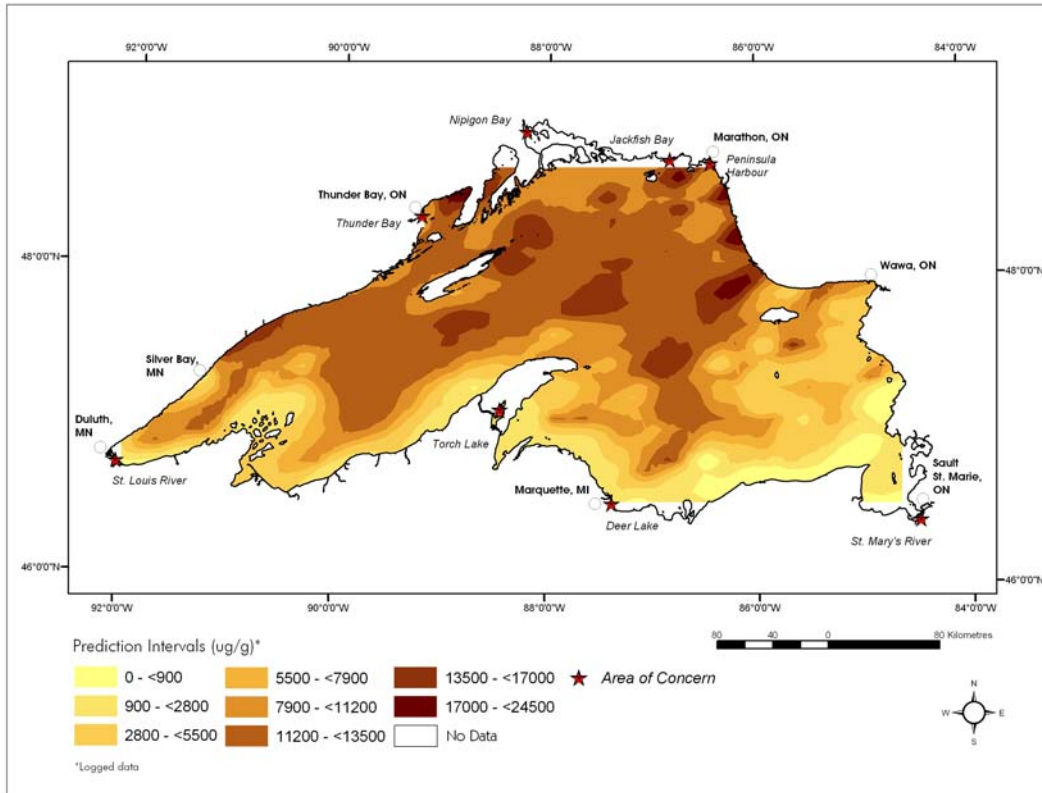
FIGURE 4.36: Magnesium (Mg)
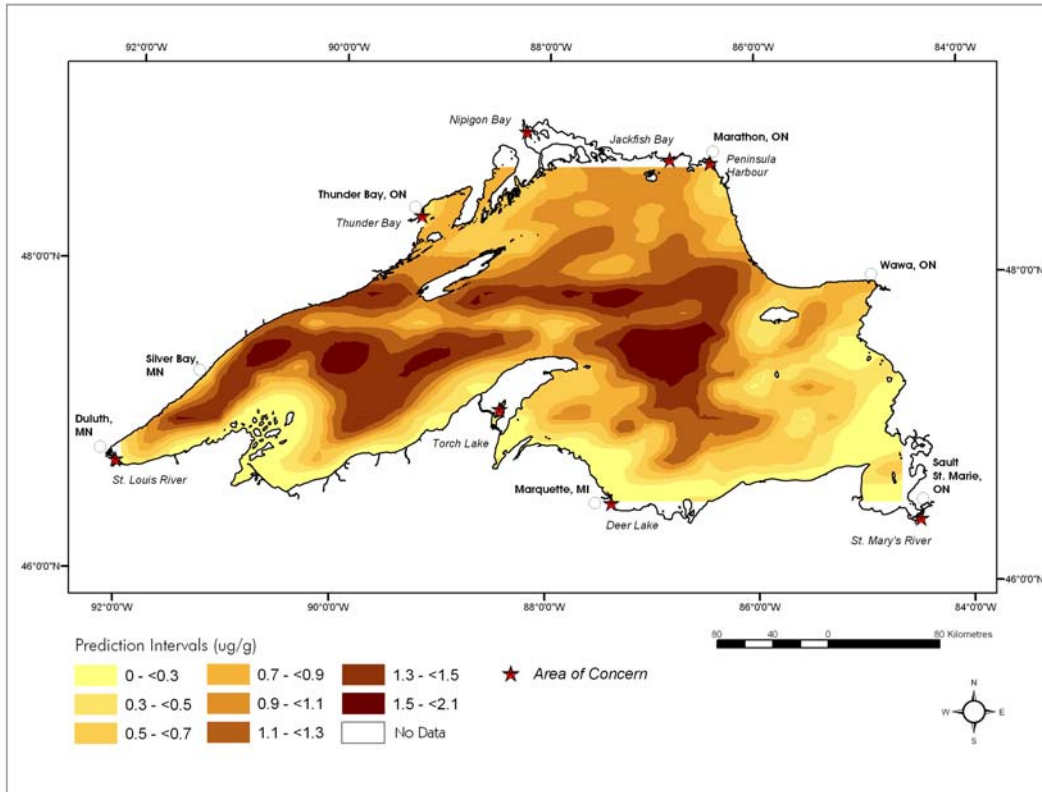
FIGURE 4.37: Beryllium (Be)

61
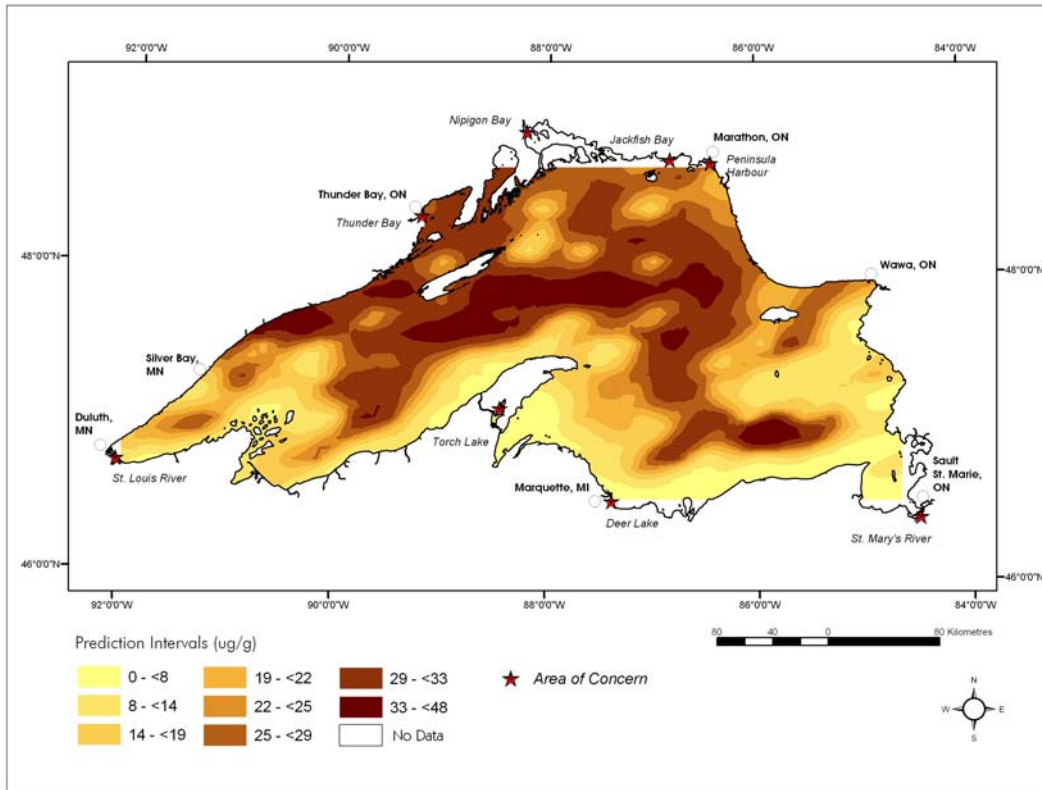
FIGURE 4.38: Cobalt (Co)
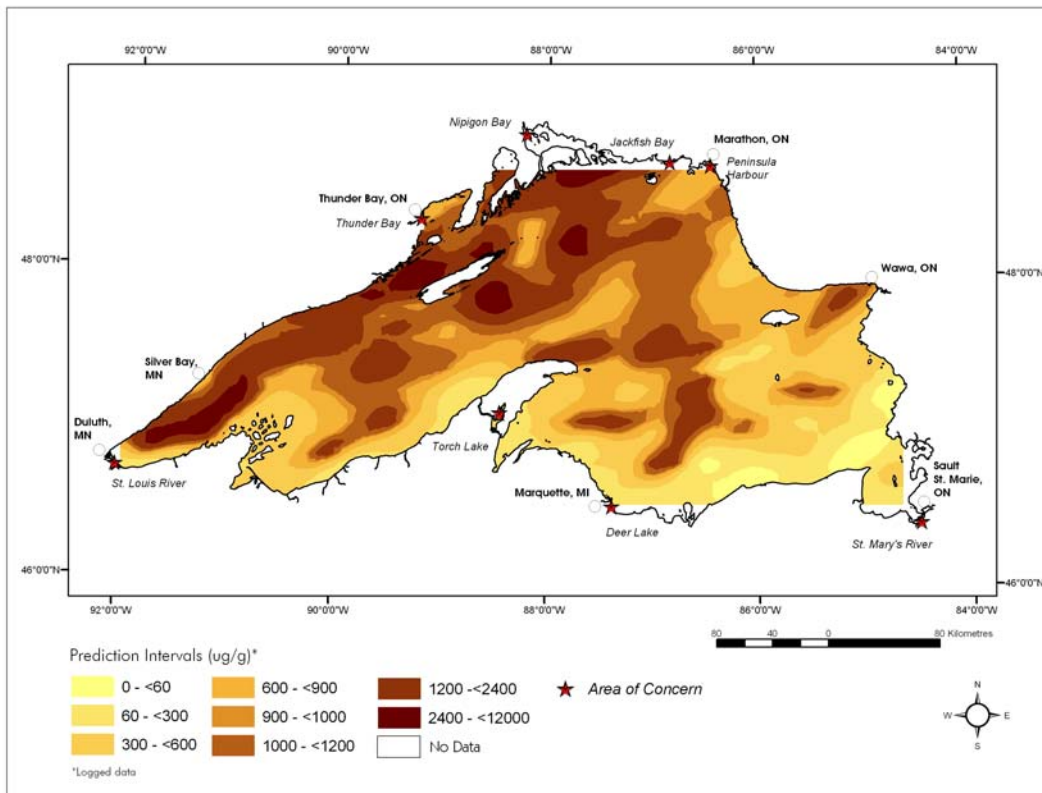
FIGURE 4.39: Manganese (Mn)

Figure 4.40 shows the same contamination data as Figure 4.13 for the nickel distribution. Now that all of the kriging surfaces have been presented, Figure 4.40 is shown as an example of how the sediment contamination data would be displayed if ordinary kriging was not used to interpolate the point data and create a continuous surface of information. The point data are provided using the Canadian Sediment Quality Guideline values for nickel: TEL (16 ug/g) and PEL (75 ug/g).
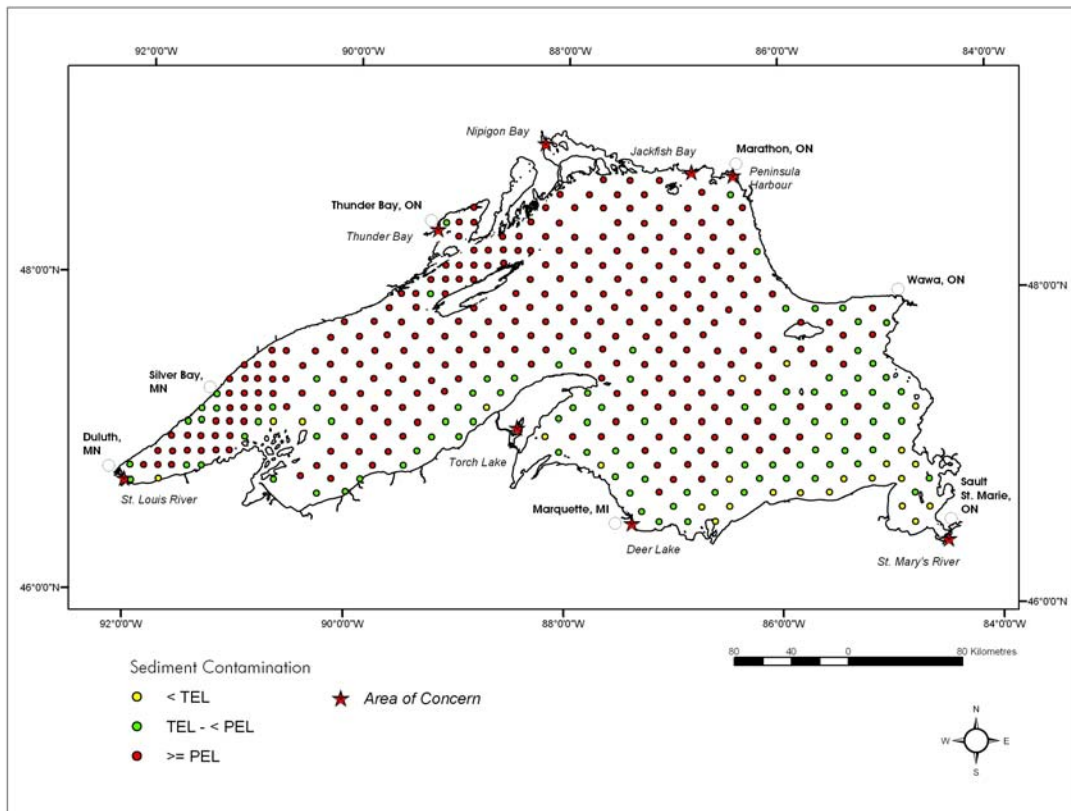
FIGURE 4.40: Point data distribution of Nickel (Ni)

4.3 DISCUSSION

One of the prevailing patterns observed in the results is that higher concentrations of contaminants are found in depositional basins, particularly the deeper basins: Thunder

Bay Trough, Duluth, Isle Royale and Caribou sub-basins. The International Joint Commission (1989) asserts that 95% of the contaminants that enter Lake Superior come from long-distance atmospheric deposition. It is also a major input mechanism for heavy priority elements such as mercury, cadmium, copper, zinc, and lead- all of which showed higher distributions in the depositional basins. It should not be surprising then, to have surfaces without any indication of a point-source input such as Se, Mo, and Sn. However, some contaminants were found both in depositional basins as well as in shoreline areas indicating that some contaminants are more closely associated with regional watershed activities.

Point-source locations that could be identified from the surfaces include Silver Bay, Minnesota located on the North Shore of Lake Superior (90 km northeast of Duluth), Thunder Bay, Keweena Peninsula, and the northeast Canadian shoreline from Marathon to Wawa, Ontario. The town of Silver Bay, was built by the Reserve Mining Company when its taconite processing plan was incorporated in 1956. The processing of ore to obtain the desired metal results in the creation of large quantities of waste rock (tailings), liquid effluent, and/or smoke. All three of these waste forms are rich in various types of metals (Kemp et al., 1978). Several compound surfaces (CaO, MgO, Na_2O, TiO_2) as well as Co, Sr, Ca, and Mg were found particularly affected by Silver Bay's taconite tailings. Taconite, being a source of iron, also affected the distribution of this contaminant.

Mercury is currently on Lake Superior's critical contaminants list affecting all of Lake Superior's AOCs. Back in 1973, it is clear that Thunder Bay was where mercury posed the biggest problem. High anthropogenic loadings of Hg are most likely due to large inputs from pulp and paper plants in the Thunder Bay area making it the best example

from this study of a point pollution source, though it also maintains the depositional trend. Taconite production also continues to be a substantial source of mercury emissions in the U.S. part of the basin (LaMP, 2002) which helps explain the second area in Lake Superior where mercury concentrations exceed its TEL, downstream from Silver Bay.

Given the great areal expanse of Lake Superior, the two concepts of anthropogenic inputs from point-sources and long-distance atmospheric inputs are not incompatible, the combination of which can be clearly seen in many of the surfaces. Kerfoot et al. (1999), explain that depositional basins far offshore could be heavily influenced by atmospheric inputs, at the same time that nearshore discharges gradually work their way toward the centre of Lake Superior with appreciable time lags.

Since the underlying message throughout this study emphasizes the complexity and poorly understood cycling and distribution of contaminants, the following two examples deviate from what has been understood thus far.

The silver distribution, described as unusual in the results sections, does not display the pattern of high concentrations in depositional basins. Point sources may be the main contributing source for silver since the highest concentrations are occurring near the AOCs in Lake Superior. This may be the case since silver is known to have restricted atmospheric mobility (Kerfoot et al., 1999). Though one would expect that with time, silver would be transported to depositional basins.

The distributions of copper also proved surprising. Copper in Lake Superior sediments has been suspected to come from the intensively mined regions of the Keweenaw Peninsula, Thunder Bay, Marathon, and Sault Ste. Marie (Kemp et al., 1978). In fact one of the great North American metal mining rushes of copper occurred on the Keweena

Peninsula. Between 1850 and 1929, the Keweenaw district was the second largest producer of copper in the world (Kerfoot and Robbins, 1999). But according to the results, the copper surface with the only area above the PEL does not show up near these point-sources. This suggests that some contaminants can be transported considerable distances from their original sources.

In order to interpret chemical data, it is useful to compare the data to some kind of standard. Contaminants that had CSQGs provided interesting information and insight into which contaminants were already problematic by our current standards in 1973. Mercury has already been mentioned, but it was a localized problem mainly in Thunder Bay. Nickel and chromium both however occur at levels above their respective PELs over most of Lake Superior followed by zinc and cadmium with levels above their respective TELs. In the other spectrum, arsenic, a by-product of nonferrous metal (lead, zinc, and copper) mining and smelting operations (U.S. EPA, 1997), was the only contaminant in the priority heavy metals group that occurred entirely below its TEL (though 24 sampling points exceeded the TEL). Revisiting the cross-validations results arsenic was underestimated though to a much lesser degree than the rest of the heavy metals, perhaps because arsenic is fairly evenly distributed across the lake sediments. The model's ability to correctly assess its variability was one of the worst in the entire data set, which helps explain the surface pattern that was created. Arsenic was the only heavy metal not displaying patterns that in some way conformed to the bathymetry of the lake. It is not understood why arsenic is behaving differently, but perhaps it relates to its chemical composition. While the rest of the priority heavy metals fall under the chemical series of 'transitional metals', arsenic is a 'non-metal'.

With the exception of mercury, the other critical pollutants available in this study proved to be similar in several ways. Though dieldrin was the least of a concern with concentrations falling well below its TEL, aroclor and DDE followed close behind with slightly higher concentrations occurring near the two urban centres of Duluth and Thunder Bay. That these critical pollutants are linked to anthropogenic origins makes sense since PCB production, though now banned, was found in commercial, industrial and electrical equipment, as well as being incidentally produced through as many as 200 chemical processes (LaMP, 2002). DDE and the PCB aroclor are likely to be associated with historical nonpoint source runoff from agricultural fields and forested areas, the latter being dominant in the Lake Superior Watershed.

Among contaminants with distributions largely influenced by atmospheric deposition, the lowest concentrations were found to occur along the U.S. shoreline. Kerfoot and Robbins (1999) explain that of all the Laurentian Great Lakes, Lake Superior contains the strongest development of a separate coastal regime, chemically and biologically distinct from cooler offshore waters. Particularly, along the U.S. shoreline where the shallowest areas are found in conjunction with faster currents (due to less dense warmer waters) that probably prevent heavy metal deposition.

Tin is another example with poorer cross-validation results and a less trustworthy surface. The surface generated for tin is merely a visual of a few discrete areas in Lake Superior where tin was found by the sampling survey. No positive autocorrelation is present for tin.

5.1 CONCLUSIONS

The water chemistry of Lake Superior is determined by the geology and climate of its drainage basin, anthropogenic inputs, bathymetry, circulation patterns, thermal regime, and biological processes. By being able to display the distribution of 34 contaminants, this study has provided a glimpse of where and why these contaminants have come to be contained in sediments. The kriging procedure used in this study included preliminary data analysis (summary statistics and frequency histograms), structural data analysis (log transformation of data, empirical semivariogram, semivariogram model, and cross validation), and point kriging estimation.

Lake Superior has in the past been viewed as a pristine environment when compared to the other Laurentian Great Lakes. But this study has shown that with regards to contaminant cycling, it is not under assault solely from long distance atmospheric discharges. This ecosystem has seen its fair share of disturbances by several sources of point pollution and by 1973 anthropogenic activity had already produced elevated and potentially problematic concentrations of the priority heavy metals nickel and chromium. The study showed that generally, it is the western shoreline of Lake Superior, home to two of the most populous urban centres (Thunder Bay, ON and Duluth, MN) that is the most affected by point source pollution. Mercury levels were above suggested guidelines, in Thunder Bay from pulp and paper industry where it was used as a slimicide; the origin of various contaminants in the Duluth sub-basin were seen to originate from taconite tailing inputs from Silver Bay; while Duluth and the St. Louis River AOC showed problematic levels of DDE as well as higher concentrations of most heavy metals

concentrating in the Duluth sub-basin. Not a surprising area for point source pollution contribution since at one time this area held the record of being the greatest coal port in the world (U.S.EPA, 1997).

With ordinary kriging as the optimal interpolation model, the estimated spatial distributions of the contaminated sediment illustrated several recurring patterns, some of which could be explained by the characteristics of the Lake Superior basin. Athough some of the results require further investigation, a better idea of the distribution of contaminated sediments in Lake Superior as it was in 1973 was presented.

A lognormal probability distribution was found to appropriately estimate the distribution of the contaminants. In this study, a logarithmic transformation was not applied on datasets that included zeros, in order to avoid dealing with undefined values. However, unless the data set has too many zeros, log kriging is recommended. In this case, zeros can be excluded from the data set by assigning them as missing or as no data values. Alternatively, a different transformation can be employed (ie. the HyperLog (HL) transform, a log-like transform that admits negative, zero, and positive values).

Ordinary kriging proved to be a valuable tool in the analysis of the spatial distribution of the 34 contaminants available in this study. The challenge of kriging is to approximate a model that will best serve the data set. The cross validation results indicated that most datasets, particularly the heavy metals tend to be underestimated. However, even this drawback can prove to be beneficial as it helps to distinguish typical or natural behaviour among groups of contaminants such as the heavy metals or more specifically, the transitional metals (of which arsenic is not a part of). Data sets found to be overly underestimated by the kriging analysis may suggest there are discreet areas of high

contamination, particularly as is the case with this historical data and the more numerous point sources of pollution that may have existed 30 years ago. Models that overestimated the results were exclusively seen with the group of organometallic compounds, whose concentrations are expressed as true percentages. Lack or limited point sampling in the bays and vicinity of all AOCs with the exception of Thunder Bay, prevented surface results from being generated in these areas. The distribution of many of the data sets, particularly those most influenced by atmospheric deposition, showed a clear pattern relating to depositional basins that would have been harder to gauge and interpret if just point data were analyzed. Since kriging helps overcome the problem of having a limited number of sample points, this study concurs with previous studies that ordinary kriging is a useful tool for the statistical analysis of continuous data.

5.2 LIMITATIONS

The main limitation of the data was the insufficient spatial distribution of measured sampling locations along seven of the eight areas of concern in Lake Superior. A more sufficient distribution of sampling locations along these areas would have made an analysis of these areas possible.

It is beneficial to have a reference of contamination levels in order to place the results within practical context. This was possible for only 11 of the contaminants in this study since Canadian Sediment Quality Guidelines are not available for many contaminants.

It is also important to keep in mind general limitations inherent to modelling. A model is in essence an abstraction of reality, thus the simplifications required may lead to models

being somewhat unrepresentative of reality. This was observed, particularly in the case of the heavy priority metals that in general were underestimated.

5.3 RECOMMENDATIONS

This paper used the first large scale lake-wide contamination data set available for the sediments in Lake Superior. Similar methods (Forsythe and Marvin, 2005; Forsythe et al., 2004; Jakubek and Forsythe, 2004) have been used in the past to better understand sediment contamination in the lower Great Lakes. This study expands upon that research and confirms that the methods previously used also provide successful results on a much larger study area and data set. The data used in this study are over thirty years old and since the onset of this investigation, more recent data have become available. The results from this study provide baseline information on contamination distribution for future work in Lake Superior. It is recommended that log transformations continue to be employed with appropriate modification if the dataset consists of zero values. It is also recommended to attempt cokriging with bathymetry data to make better predictions since this paper has shown that a relationship exists between sediment contamination and depositional basins.

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