DIELDRIN CONCENTRATIONS IN GREAT LAKES SEDIMENT: SPATIAL AND TEMPORAL TRENDS

by

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ABSTRACT

This study examines the spatial distribution of dieldrin, a persistent organic pollutant previously used as an agricultural pesticide, in the sediments of the Great Lakes System. Using Environment Canada Sediment Quality data for both historical and contemporary sampling periods, graduated symbol maps were generated for Lakes Superior, Huron, St. Clair, Erie, and Ontario. Additionally, ordinary kriging was applied to the Lake Erie and Lake Ontario datasets. The use of ordinary kriging allows for a more in-depth understanding of the spatial trends occurring within the Great Lakes sediments. Cross-validation was performed to ensure that all of the interpolated surfaces were statistically valid. Results indicate low dieldrin levels with no evident point sources in both the historical and contemporary sediments of Lakes Superior, Huron, and St. Clair. This suggests that dieldrin has mainly entered these lakes via atmospheric deposition and some agricultural runoff. Dieldrin concentrations in Lake Erie have increased since the historical sampling period, indicating a shift in the spatial distribution of the contaminant. Historically, levels were higher in the eastern-most depositional basins, but contemporary data show that the western side of the lake exceeds Canadian sediment quality guidelines. The prediction surface generated in this study clearly shows that the Detroit River is a point source of contamination. Alternatively, lakewide dieldrin concentrations in Lake Ontario have appeared to decrease between sampling periods. While historically the Niagara River was a point source of contamination, levels in the Niagara Basin have been reduced. In all cases, the highest levels of dieldrin are seen in the depositional basins of the lakes, and the interpolated surfaces help in data interpretation by providing a better understanding of the spatial distribution of this contaminant.

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LIST OF ACRONYMS

AOC	Area of Concern
ASE	Average Standard Error
CCME	Canadian Council of Ministers of the Environment
EC	Environment Canada
ESRI	Environmental Systems Research Institute
GLBTS	Great Lakes Binational Toxics Strategy
GLWQA	Great Lakes Water Quality Agreement
ISQG	Interim Sediment Quality Guideline
LaMP	Lakewide Management Plan
LELaMP	Lake Erie Lakewide Management Plan
LMLaMP	Lake Michigan Lakewide Management Plan
LOLaMP	Lake Ontario Lakewide Management Plan
LSLaMP	Lake Superior Lakewide Management Plan
MPE	Mean Prediction Error
OCP	Organochlorine Pesticide
PEL	Probable Effect Level
RAP	Remedial Action Plan
RMSPE	Root-Mean-Squared Prediction Error
SMPE	Standardized Mean Prediction Error
SRMSPE	Standardized Root-Mean-Squared Prediction Error
TEL	Threshold Effect Level
USEPA	United States Environmental Protection Agency

CHAPTER 1: INTRODUCTION

1.1 The Great Lakes

Located along the border between Canada and the United States, the Great Lakes Basin covers an area of 244 000 km^2 and contains approximately 18 percent of the world's fresh surface water (USEPA, 1995). The Great Lakes system consists of lakes Superior, Michigan, Huron, St. Clair, Erie, and Ontario, and acts as a valuable resource for the millions of people residing in the basin, providing them with drinking water, hydro, and recreation. Over the course of the 20^{th} century, the Great Lakes ecosystem has become severely degraded due to industrialization, urbanization, and the introduction of toxic contaminants such as PCBs and organochlorine pesticides into the environment (USEPA, 1995). While restoration efforts have been undertaken in more recent years, contamination of both water and sediment in the lakes remains a concern.

1.1.1 Toxic Pollutants in the Great Lakes

Contaminant levels in Great Lakes sediment have been widely examined over the past number of years. Past research has shown that elevated levels of both inorganic (ie. metals) and organic (ie. pesticides) contaminants have been detected in the Great Lakes waters, sediments and biota (Allan et al., 1991; De Vault et al., 1996; Marvin et al., 2004a). In order to prevent further destruction of the Great Lakes ecosystem, several initiatives have been undertaken with the goal of restoring and maintaining the integrity of the system. These consist of several joint agreements between Canada and the United States, including the Great Lakes Water Quality Agreement, the Great Lakes Binational Toxics Strategy, and the Lakewide Management Plans that have been developed for each lake. According to the annual reports published as a requirement of these initiatives, as well as current research publications, the overall health of the Great Lakes has been improving in recent years (Marvin et al., 2004a).

1.2 Organochlorine Pesticides

Organochlorine pesticides (OCPs) are a group of persistent organic pollutants known for their toxicity. In addition to dieldrin, the focus of this study, other OCPs of note include DDT, aldrin (of which dieldrin is a breakdown product), endrin, heptachlor, mirex, chlordecone, and chlordane (Harris et al., 1966; USEPA, 1980). These compounds were widely used in the past to control pests in agricultural and urban areas until their toxicity to humans and the environment was realized (Chopra et al., 2011). Their use became heavily regulated and, in the case of dieldrin and many others, banned altogether. Due to their extreme persistence in the environment, OCPs continue to be a major concern. They tend to bioaccumulate in plants and other organisms, and biomagnify as they move up the food chain. This makes OCPs a large concern for both ecosystem and human health. Research has suggested that OCPs have detrimental effects on human health, and may be linked to the occurrence of breast cancer (Wolff et al., 1993), Parkinson's disease (Fleming et al., 1994), and have been shown to have estrogenic effects resulting in disruption of the endocrine system (Soto et al., 1994).

While deposition rates of OCPs have generally been decreasing since 1980 (Pearson et al., 1997; Wong et al., 1995), their persistence makes them difficult to eliminate and their presence will continue to be monitored. Research has shown a widespread presence of such toxins across the entire Great Lakes system (Frank et al., 1979a). Dieldrin is an OCP which has been detected in all of the Great Lakes. While the distribution of dieldrin across the Great Lakes in water (Marvin et al., 2004a), sediment (Marvin et al., 2004a; Marvin et al., 2004b), and biota (De Vault et al., 1996) has been discussed in past studies, none have incorporated geostatistical techniques for the interpolation of sediment-bound dieldrin levels lakewide.

1.3 Study Area and Data Description

1.3.1 The Great Lakes System

For this study, dieldrin data for the surficial sediments were acquired for four of the five Great Lakes (Superior, Huron, Erie, and Ontario) and Lake St. Clair. While Lake Michigan was not included in this analysis, its characteristics will be discussed here as it is an important component of the Great Lakes system. A summary of the physical characteristics of each of the lakes in the Great Lakes Basin can be seen in Table 1.1, and maps of the Great Lakes Basin, depositional areas and circulation patterns follow in Figures 1.1, 1.2 and 1.3, respectively.

1.3.1.1 Lake Superior

The most upstream of the Great Lakes is Lake Superior. It is the largest, coldest, and deepest of the Great Lakes, with an average depth of 147 metres (USEPA, 1995). Water flows into Lake Superior via many different watercourses and its main outflow is the St. Marys River. It consists of three main basins: the Eastern Basin (comprised of many long, deep troughs), the very deep Central Basin, and the shallower Western Basin,

Table 1.1: Physical Characteristics of the Great Lakes System (USEPA, 1995)

	Ave Depth (m)	Max Depth (m)	Lake Surface Area (km^2)	Land Drainage Area (km^2)	Total Area (km^2)	Volume (km^3)	Residence Time (years)
Superior	147	406	82,100	127,700	209,800	12,100	191
Michigan	85	282	57,800	118,000	175,800	4,920	99
Huron	59	229	59,600	134,100	193,700	3,540	22
St. Clair	3	6.4	694	12,616	13,310	4.17	7 days
Erie	19	64	25,700	78,000	103,700	484	2.6
Ontario	86	244	18,960	64,030	82,990	1,640	6

Figure 1.1: The Great Lakes Basin (Great Lakes Information Network, 2010)

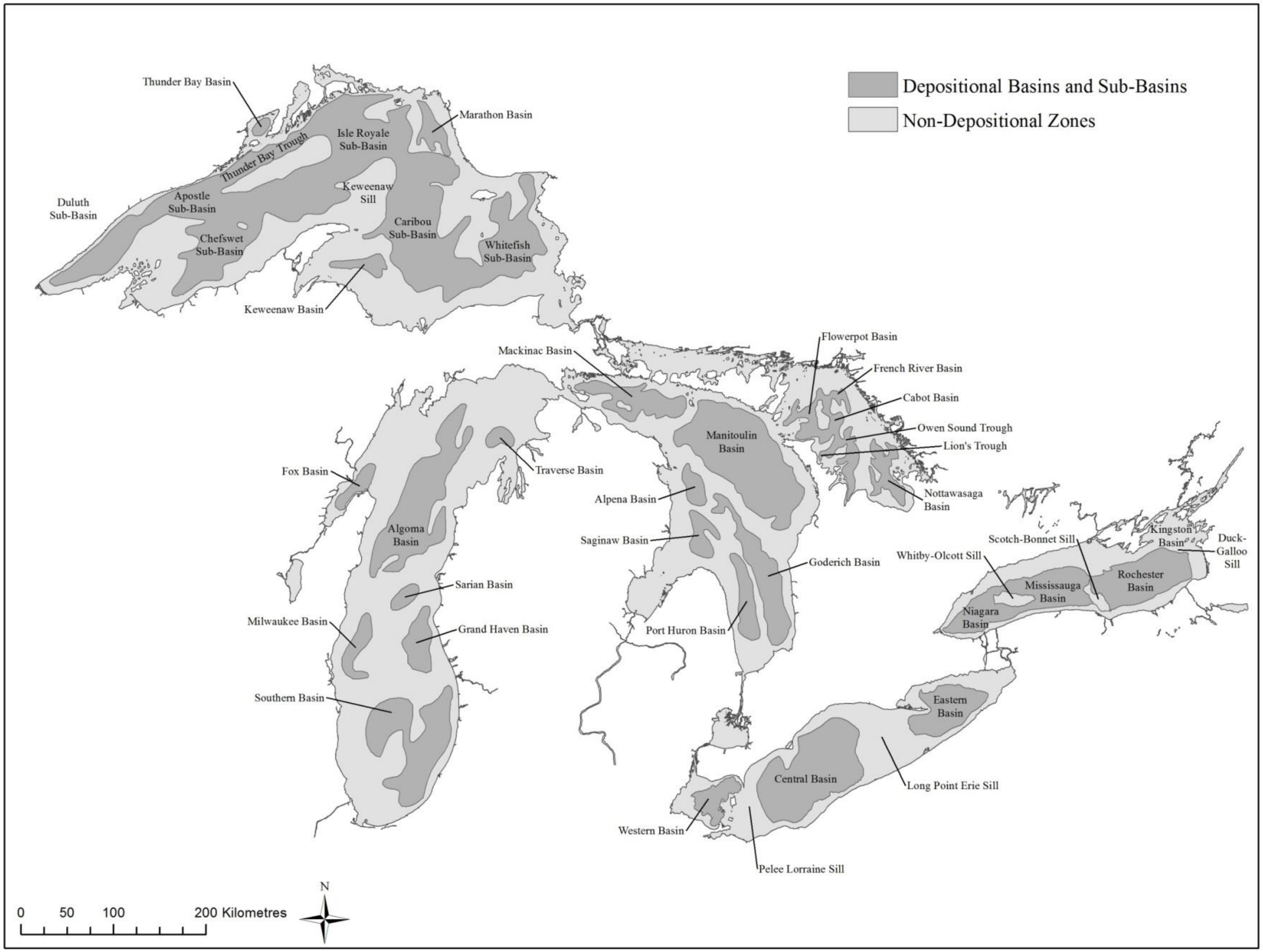

Figure 1.2: Depositional Basins and Sub-Basins in the Great Lakes

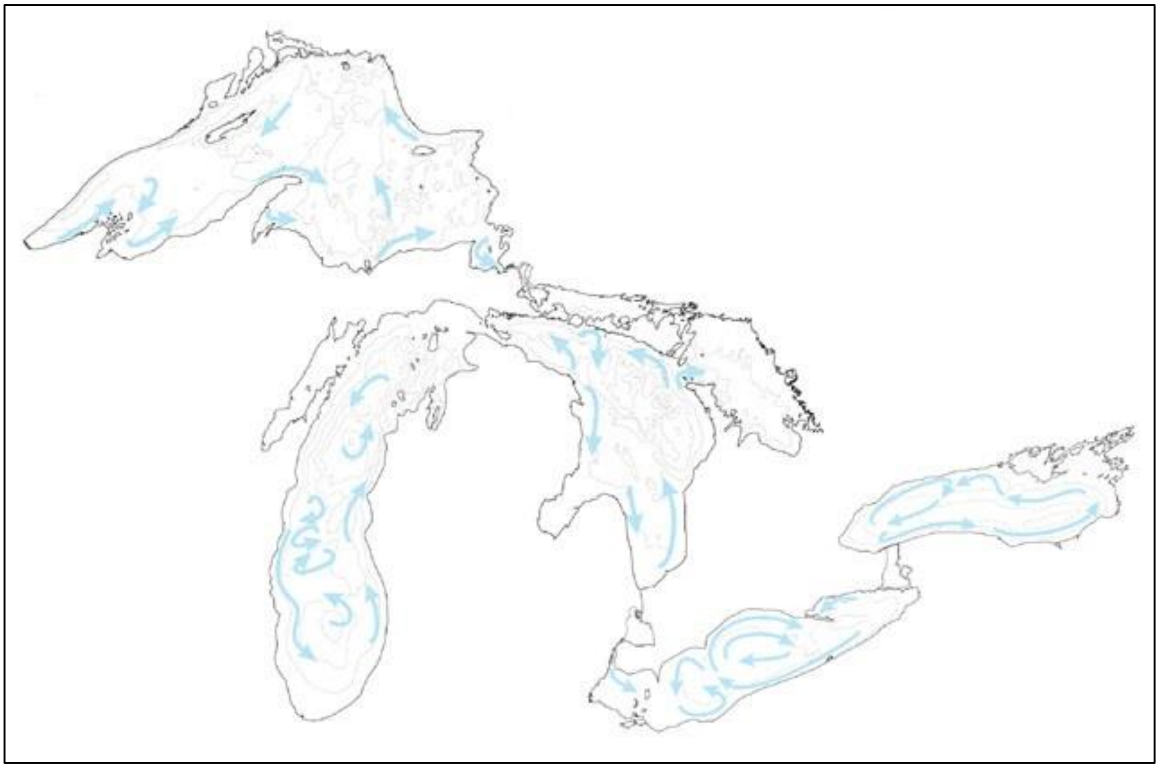

Figure 1.3: Mean summer circulation in the Great Lakes (Beletsky et al, 1999)

each of which is further divided into several sub-basins (LSLaMP, 2008). This bathymetry, in combination with its currents which flow in a generally counter-clockwise direction, result in highest sedimentation rates at the edges of the depositional basins and the bottoms of the troughs. Most (88%) of the land use in the Lake Superior watershed is forest (LSLaMP, 2008). Due to Lake Superior's extremely large surface area and remote surroundings, many of the pollutants in the lake enter via atmospheric deposition (Gewurtz et al., 2008). Relative to the other Great Lakes, the Lake Superior watershed is very sparsely populated. The largest urban areas on the Canadian shore consist of Thunder Bay and Sault Ste. Marie, Ontario, while Duluth, Minnesota is the most populated area on the American shore.

1.3.1.2 Lake Michigan

Lake Michigan, the third largest by surface area and second largest by volume, has an average depth of 85 metres and is the only Great Lake located entirely within the United States (USEPA, 1995). It is comprised two basins, a deep northern basin and shallower southern basin (Leland et al., 1973). The St. Marys River provides the main inflow into both lakes Michigan and Huron, which are connected to each other by the Straits of Mackinac. Currents flow in a clockwise direction. Land use in the northern part of the watershed is mainly forest, in contrast the southern portion of the watershed consists mostly of agricultural, industrial, and heavily populated urban areas (especially the Milwaukee and Chicago metropolitan regions) (LMLaMP, 2008).

1.3.1.3 Lake Huron

Lake Huron is the second largest of the Great Lakes by surface area and it has an average depth of 59 metres (USEPA, 1995). It is connected to Lake Michigan by the Straits of Mackinac and both of these lakes receive inflow via the St. Marys River, and while they are geographically separated, they are hydrologically the same lake (Lake Huron Action Plan, 2004). The major outflow of the lake is the St. Clair River, where it then enters Lake St. Clair and eventually the lower Great Lakes. Within Lake Huron there are four sub-basins: the main body of the lake contains the Main and Saginaw basins, while the remaining two basins are Georgian Bay and North Channel. The Lake Huron watershed has a much lower population density than the lower Great Lakes and thus fewer point sources of contamination (Lake Huron Action Plan, 2004). Nevertheless, the lake is susceptible to problems due to its large size, including atmospheric deposition of pollutants and non-point source runoff across its large watershed. Land use in the watershed consists mostly of forested area, and to a lesser extent agricultural and residential.

1.3.1.4 Lake St. Clair

Lake St. Clair, while not technically considered one of the Great Lakes, is the smallest of the lakes in the Great Lakes system. Averaging a depth of only 3 metres, it receives most (98%) of its inflow from the upper Great Lakes via the St. Clair River which forms a large delta system and wetland region at the northeastern side of the lake (USEPA, 1999). Its outflow is into Lake Erie via the Detroit River. Lake St. Clair provides an important transportation link between Lake Huron and Lake Erie, and is periodically dredged to provide clearance for large ships. Major urban centres on the lake include Detroit and Windsor. The Canadian shoreline is largely comprised of agricultural (and some urban) land use (Gewurtz et al., 2010). Relative to the other lakes in the Great Lakes system, Lake St. Clair is the most frequently used for recreational purposes, especially fishing (USEPA, 1999).

1.3.1.5 Lake Erie

Lake Erie is the smallest Great Lake by volume, with an average depth of 19 metres (USEPA, 1995). Most of the inflow into Lake Erie (80%) enters from the Detroit River, and the main outflows are the Niagara River and the Welland Canal. Circulation patterns in the lake are complex and variable (LELaMP, 2008). Lake Erie is divided into three main basins: the Western Basin (the shallowest of the basins), the Central Basin, and the Eastern Basin (the deepest). The Lake Erie watershed is heavily populated, and thus experiences many negative effects of urbanization and industrialization. It experiences high levels of sediment loading into the lake as well due to extensive agricultural practice in the watershed (LELaMP, 2008). Because of its shallowness and high amounts of anthropogenic phosphorus inputs, Lake Erie has also experienced many problems with excessive nutrient loading and eutrophication across the lake (Beeton, 2002).

1.3.1.6 Lake Ontario

Lake Ontario, the smallest of the Great Lakes by surface area, is located downstream of the other Great Lakes, and is therefore susceptible to any impairment issues occurring upstream. It has an average depth of 86 metres and a maximum depth of 244 metres (USEPA, 1995). A majority of the water entering Lake Ontario (80%) does so via the Niagara River, with the rest coming from smaller tributaries and precipitation (LOLaMP, 2008). Most of the water flowing out of the lake enters the St. Lawrence River. This flow pattern, combined with wind activity, results in the water circulating in a counter-clockwise direction within the sub-basins of the lake (LOLaMP, 2008). The main basin of Lake Ontario is divided into three sub-basins: the Niagara Basin, the Mississauga Basin, and the Rochester Basin. The temperate climate and fertile soils around the lake have resulted in much of the surrounding land (especially in the Niagara region) being used for agriculture; the other major land use type is forest in the further reaches of the watershed (LOLaMP, 2008). Millions of people reside on the Canadian side of the lake, concentrated in urban areas such as Hamilton, Toronto, and Kingston. On the American side, albeit less populated, the major urban areas include Rochester and Oswego.

1.3.2 Environment Canada Sediment Surveys

Between 1968 and 1975, all of the Great Lakes and Lake St. Clair were extensively sampled by Environment Canada in order to assess surficial sediment contamination (Marvin et al., 2003). Each of the lakes was sampled in a grid pattern, and a sediment core was acquired at each station using a mini-box core sampling procedure. The top three centimetres were then subsampled in order to be analyzed for organic contaminants, metals, grain size, and nutrients (Marvin et al., 2003, Painter et al., 2001). The purpose of this effort was to establish the current state of contamination in the Great Lakes sediments in great detail, and provide a baseline for remediation efforts.

Contemporary sediment surveys were conducted between 1997 and 2002. During these subsequent surveys, significantly fewer samples were taken. Stations were selected to focus on depositional basins and areas of fine-grained sediments, with few nearshore areas included (Forsythe et al., 2004; Marvin et al., 2004a). Figure 1.4 depicts the historical and contemporary sampling locations included for examination in this study.

The data acquired through these surveys can be used for a variety of research purposes, including sediment quality determination, examination of the spatial distribution of contaminants, and to allow for the emergence of any trends and new issues that may occur over the years, as well as the impact of any remediation efforts that have been undertaken (Marvin et al., 2004a, Marvin et al., 2004b). For a more detailed description of the sampling procedure and analytical methods for the contemporary datasets, see Marvin et al. (2003), Marvin et al. (2002) and Painter et al. (2001); for the historical datasets, refer to Frank et al. (1979a).

Due to the tendency of toxic contaminants to accumulate in the sediments, and the resulting exposure to the benthic organisms living in contact with them, sediment quality is a good indicator of the health of the entire ecosystem. At some point, the contaminants will reach a level in which adverse effects will occur within the system. Thus, sediment quality guidelines have been developed in order to provide an accepted benchmark level for the occurrence of such effects.

1.3.3 Canadian Sediment Quality Guidelines

The Canadian Sediment Quality Guidelines for the Protection of Aquatic Life can be found within the Canadian Environmental Quality Guidelines, published by the Canadian Council of Ministers of the Environment (CCME, 2001). Using available toxicity data and, where possible, a combination of two different approaches (the National Status and Trends Program approach and the spiked-sediment toxicity test approach), these benchmark levels have been defined for numerous chemicals and substances, indicating the likelihood of the occurrence of adverse biological effects when organisms are exposed to contaminated sediments (CCME, 2001).

The Canadian Sediment Quality Guidelines consist of two values, the Threshold Effect Level (TEL) and the Probable Effect Level (PEL). Below the TEL, adverse biological effects are expected to occur rarely (that is, <25% adverse effects will occur). Between the TEL and PEL is the possible effect range, in which occasional adverse effects will occur. Finally, at concentrations above the PEL, adverse biological effects are expected to occur frequently (that is, >50% adverse effects will occur).

In the event that there is a lack of sufficient data available to calculate the guideline levels for a certain contaminant using both of the recommended approaches, interim guideline levels may be derived using either a single approach or through examination of these levels in other jurisdictions. In this case, the guideline level is referred to as the Interim Sediment Quality Guideline (ISQG). Due to limited spiked-sediment toxicity data for dieldrin, an ISQG has been set in place of a TEL, however, the CCME notes that ISQGs should be applied in the same way as TELs (CCME, 2001).

1.3.3.1 Guideline Levels for Dieldrin

According to the CCME (2001), the interim sediment quality guideline level (ISQG) for dieldrin in freshwater sediments is 2.85ng/g, a level at which adverse biological effects will rarely occur, while the probable effect level (PEL) is 6.67ng/g, a level at which adverse biological effects will frequently occur. At dieldrin levels between the ISQG and PEL, adverse effects are expected to occasionally occur (CCME, 2001).

1.3.4 Available Dieldrin Data

While sediment samples were acquired for Lake Michigan, no dieldrin data were available and therefore it is not included in this study. Historical and contemporary dieldrin levels were examined in the remaining lakes. The datasets are summarized in Table 1.2, including the number of observations in each dataset falling into the ISQG and PEL threshold categories. The descriptive statistics including lakewide average dieldin concentrations for the historical and contemporary datasets can be seen in Table 1.3, and are described in the following paragraphs. Additionally, a bar chart comparing the lakewide averages by lake can be found in Figure 1.5.

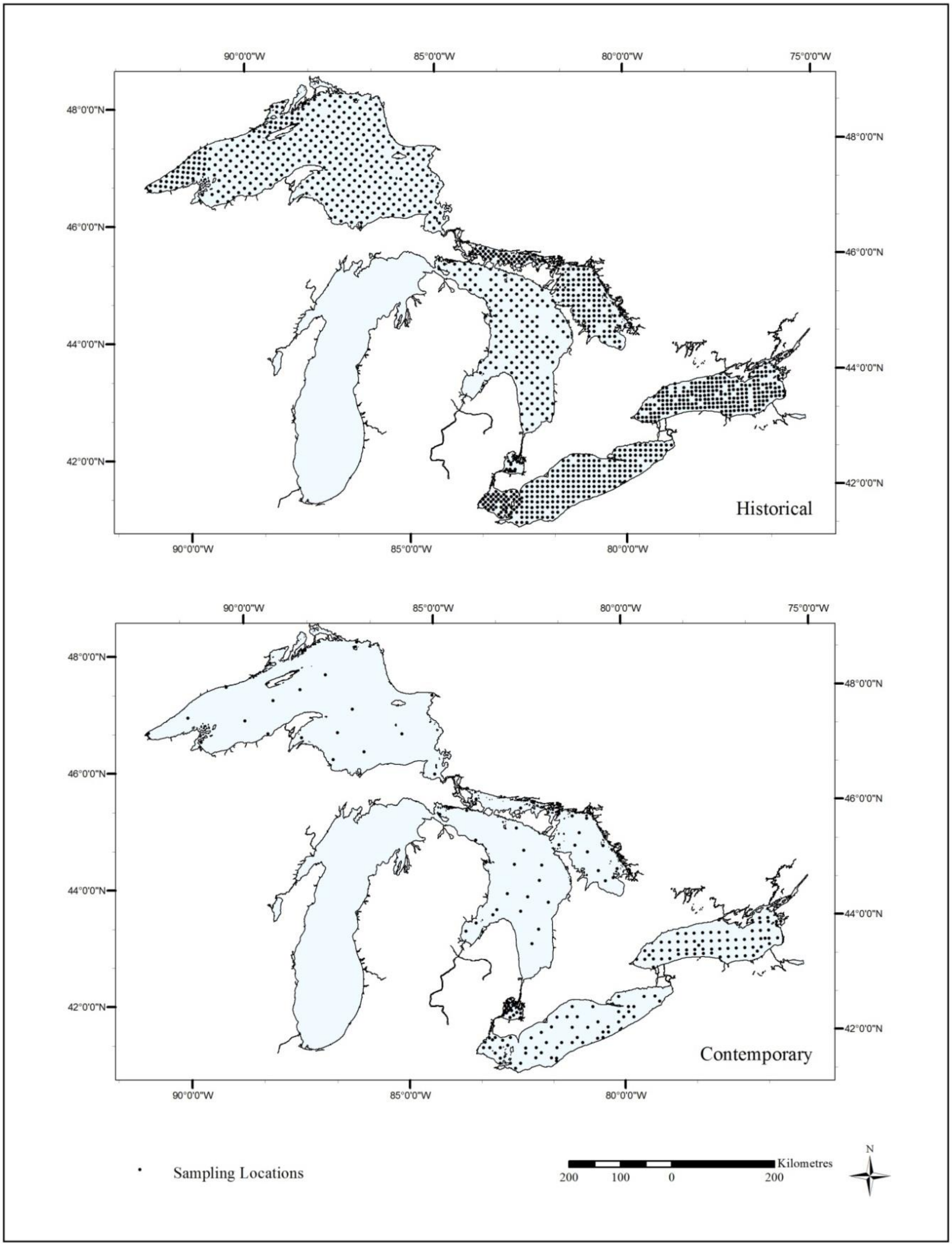

Figure 1.4: Historical and contemporary sampling locations with dieldrin data

Table 1.2: Number of sampling locations in ISQG and PEL categories

Lake	Year	# of sites	<ISQG	≥ISQG and <PEL	≥PEL
Superior	1973	405	405	0	0
Superior	2001	19	19	0	0
Huron	1969/1973	315	0	0	0
Huron	2002	33	0	0	0
St. Clair	1974	11	11	0	0
St. Clair	2001	20	20	0	0
Erie	1971	258	243	15	0
Erie	1997-1998	57	27	22	8
Ontario	1968	226	213	12	1
Ontario	1998	69	66	3	0

Table 1.3: Descriptive statistics for dieldrin concentrations in the historical and contemporary datasets

Lake	Year	#of sites	Ave (ng/g)	Min (ng/g)	Max (ng/g)	Standard Deviation	Skewness	Kurtosis
Superior	1973	405	0.04	0.00	1.90	0.18	5.75	39.79
Superior	2001	19	0.02	0.00	0.06	0.01	1.26	2.20
Huron	1969/ 1973	315	0.04	0.00	1.70	0.17	5.80	35.64
Huron	2002	33	0.07	0.00	1.03	0.18	5.22	28.74
St. Clair	1974	11	0.48	0.10	0.90	0.33	-0.19	-1.68
St. Clair	2001	20	0.10	0.02	0.27	0.07	0.97	0.63
Erie	1971	258	0.96	0.00	5.00	1.05	1.10	0.62
Erie	1997/ 1998	57	3.50	0.00	11.27	2.69	1.11	1.06
Ontario	1968	226	0.55	0.00	6.70	1.07	2.48	6.98
Ontario	1998	69	1.37	0.07	3.03	0.87	-0.01	-1.14

In Lake Superior, the mean dieldrin concentration decreased from 0.04 ng/g in 1973 to 0.02 ng/g in 2001. The historical dataset is highly skewed to the right, as indicated by the large skewness and kurtosis values. This is due to over 90% (367 of 405) of the readings being zero, or below the detection limit (the value of which is unknown). The contemporary dataset is considerably smaller at only 19 samples, and is skewed to the right as well, albeit to a much lesser extent.

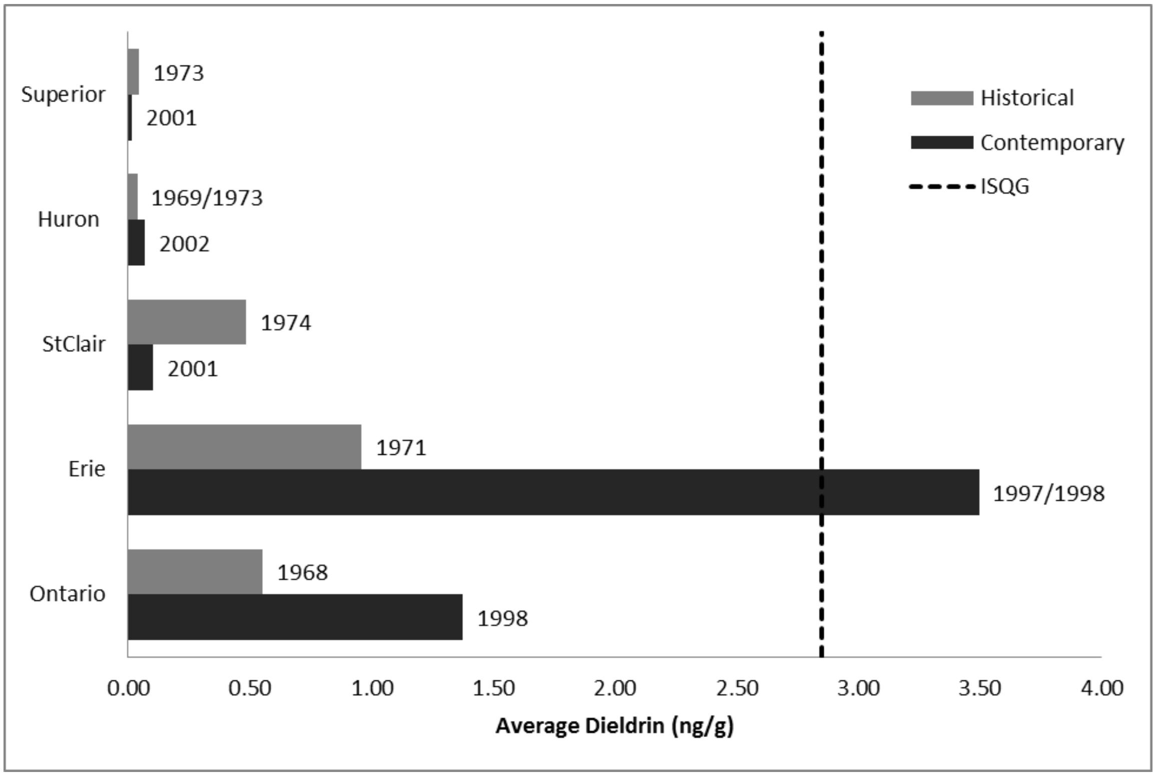

Figure 1.5: Lakewide average dieldrin concentrations

The mean dieldrin concentration for Lake Huron increased slightly between the two sampling periods, from 0.04 ng/g in 1969/1973 to 0.07 ng/g in 2002. Again, both of the Lake Huron datasets exhibit very large values for skewness and kurtosis, indicating their distributions are strongly skewed to the right for the same reasons mentioned above.

Lake St. Clair has the highest mean dieldrin concentrations of these three lakes, and, as in Lake Superior, the mean levels decreased over time from 0.48 ng/g in 1974 to 0.10 ng/g in 2001. Both of the Lake St. Clair datasets are much closer to a normal (Gaussian) distribution.

In Lake Erie, the multiple readings above the ISQG and PEL are cause for concern. The average dieldrin concentration in Lake Erie increased between the two sampling periods, from 0.96 ng/g to 3.50 ng/g. In 1971, 5.8% of the dieldrin readings fell above the ISQG, while in 1997/1998, 38.6% were above ISQG and and additional 14.0% were above the PEL. The skewness and kurtosis values for each of these datasets is in an acceptable range, and therefore their distributions are fairly normal.

Likewise, the average dieldrin concentration in Lake Ontario rose from 0.55 ng/g to 1.37 ng/g. In the historical dataset, 5.3% of the readings exceeded the ISQG, while one reading exceeded the PEL. In the contemporary dataset, 4.3% of the readings exceeded the ISQG with none above the PEL, however, the mean concentration is higher due to the many zero readings in the historical dataset.

Lakes Erie and Ontario are the only ones in which dieldrin levels were recorded above the 2.85 ng/g ISQG, and therefore it is these two lakes that were examined in greater detail through the creation of a prediction surface using the ordinary kriging technique. The remaining lakes, while all displaying some dieldrin presence, had low average levels and due to the low readings, would have been difficult to display on a surface or would not meet the requirements for geospatial interpolation.

1.4 Research Objectives

The objectives of this study are:

1) use existing data that were acquired by Environment Canada to examine the spatial distribution of dieldrin concentrations in the surficial sediments of the Great Lakes and Lake St. Clair;

2) use ordinary kriging to determine the best model for creating a prediction surface estimating dieldrin concentrations in those lakes that demonstrate levels of concern (ie. above the ISQG);

3) examine any differences between the spatial distribution of dieldrin concentrations historical (1968-1974) and contemporary (1997-2002) datasets.

CHAPTER 2: LITERATURE REVIEW

2.1 Dieldrin

Dieldrin, an organochlorine pesticide, was first produced in 1948 and is a known contaminant in the Great Lakes basin. Synthetically formed and first introduced into the environment in the early 1950s, it was widely used as an agricultural insecticide up until the 1970s for the control of corn, potato and fruit pests (Environment Canada, 2005a). Besides the direct application of dieldrin to crops and soil, it also entered the environment as a breakdown product of aldrin, another widely used insecticide used to eliminate corn-targeting worms and termites (USEPA, 1980). By the year 1970, use had decreased to approximately 11 million pounds (USEPA, 1980). Aldrin, which was considerably less expensive to produce than dieldrin, was used at a much higher rate since it targeted many of the same pests (USEPA, 1980; Jorgenson, 2001).

In the mid-1960s, production of aldrin and dieldrin peaked in the United States at approximately 20 million pounds per year, and at this time was the second most used agricultural pesticide after DDT (Jorgenson, 2001). In Canada, peak use of aldrin and dieldrin occurred in the early 1960s (Agriculture Canada, 1973). The USEPA restricted the use of aldrin and dieldrin in 1974, including banning spray and dusting application methods and any use which results in a discharge to waterways, as well as banning domestic production of the chemicals (USEPA, 2003), however use of aldrin could still be registered for direct soil application for termite control (USEPA, 1980). Since 1987, there has been no registered use of aldrin or dieldrin in the United States (USEPA, 2003). The use of aldrin and dieldrin was similarly restricted in Canada in the mid-1970s, with all registered uses discontinued in 1984 (Jorgenson, 2001). According to the Great Lakes Binational Toxics Strategy, there has been no known use of dieldrin in the Great Lakes basin since 1997 (Canada) and 1998 (United States) (Waffle and Smith, 2008). While both chemicals have been banned in most developed countries since the 1980s, aldrin is still used in some parts of the world, including Malaysia, Thailand, Venezuela, and some parts of Africa (Jorgenson, 2001; Environment Canada, 2005a).

Dieldrin, like other organochlorine pesticides, is hydrophobic in nature and does not readily dissolve in water. Rather, it has an affinity for organic particulate matter (Jorgenson, 2001). Therefore, it readily binds to soil and has made its way into lake sediments through a slow migration into groundwater and through surface runoff from treated soils (CCME, 2001; Doong et al., 2002; USEPA, 2003), while relatively lower levels are found in water (USEPA, 2003). Other means of transport included aerial dispersion via spray drift or following volatilization (CCME, 2001). The ability of dieldrin to be transported over long distances, in combination with its persistence, has become a large concern in recent years as dieldrin has been detected in areas where it has never been used. For example, dieldrin residues have been found in the air, wildlife, and throughout the food webs of the Canadian Arctic (Hargrave et al., 1992; Norstrom et al., 1998; Hung et al., 2002). Dieldrin was shown to be entering the Great Lakes via wet precipitation during a study occurring in the late 1980s, with the highest concentrations occurring in the lower Great Lakes in the spring and summer (Chan et al., 1994).

2.1.1 Bioavailability of Dieldrin

Bioaccumulation is the process by which a substance is taken up into the tissues of a living organism, such as a plant or animal. This can occur as uptake directly from the water or through consumption of food already containing the substance (Jorgenson, 2001). Dieldrin has a high solubility in fats, which allows it to become stored in the fatty tissues of animals, as well as in plants, and its persistence means that it will bioaccumulate in organisms and biomagnify as it moves up the food chain, eventually making its way into humans (USEPA, 2003; LMLaMP, 2008).

Due to its bioaccumulative and toxic properties, dieldrin has been targeted for virtual elimination by the USEPA and Environment Canada under the Great Lakes Binational Toxics Strategy (Gulezian and Epstein, 1997). Progress has been made towards this goal, as Great Lakes Binational Toxics Strategy reports have indicated an overall decreasing trend for dieldrin levels in Lake Trout and bivalves across all of the lakes (Waffle and Smith, 2008). While dieldrin levels in the tissues of biota are declining, the increased accumulation in the sediment of Lake Erie (as seen in this study) remains a concern.

2.1.2 Ecosystem and Health Effects

Because dieldrin is concentrated in sediments, it poses a significant threat to benthic organisms living there. It makes its way into the tissues of benthic micro- and macroinvertebrates, and as a result its presence in the ecosystem can lead to a decrease in species richness and abundance (via reproductive health failure), as well as increased mortality rates (CCME, 2001; Jorgenson, 2001). It has been found to be especially bioaccumulative in earthworms, mussels, and most of all, fish (Jorgenson, 2001). The USEPA (1980) found that aldrin/dieldrin was acutely toxic to freshwater fish and invertebrates at concentrations as low as 2.5 µg/L, and that plants are more resistant than other organisms.

In addition to these adverse effects in the aquatic ecosystem, acute and chronic dieldrin exposure to humans (through water, air, and ingestion of contaminated food) can result in effects such as headache, dizziness, nausea, vomiting, uncontrollable muscle movements, neurological damage, birth defects and respiratory illness (USEPA, 2003; Chopra et al., 2011). Dieldrin is a known endocrine disruptor and have been shown to have estrogenic effects resulting in reproductive issues in both females and males (Soto et al., 1994), and infants can be especially susceptible because dieldrin can be passed on from mother to child through breast milk (Stevens et al., 1993; USEPA, 2003). Aldrin and dieldrin are listed as possible carcinogens by the USEPA, due to strong evidence of carcinogenity in mice, and the lack of available human data (USEPA, 2003; Jorgenson, 2001).

2.2 Further Investigation Into Great Lakes Contamination

The large size of the Great Lakes has not prevented them from responding negatively to the environmental effects of industrialization, agriculture, and a multitude of other anthropogenic activities. They have become contaminated with metals and persistent toxic chemicals, and while actions are being taken to restore the Great Lakes to their original condition, recovery is slow and ongoing. Nevertheless, it is promising to note that all of the Great Lakes have shown the same trend of declining contamination levels, though recently the rates of decline have begun to level off (Environment Canada, 2005b).

2.2.1 *Lake Superior*

Lake Superior's large size and location have allowed it to remain the least contaminated of the Great Lakes, however, it faces several challenges related to its large surface area and depth. A combination of atmospheric deposition and the lake's long retention time (191 years) allow contaminants to accumulate and they remain in the system for a long period of time. Organochlorine contaminants, including dieldrin, have been detected in Lake Superior (Kucklick and Baker, 1998). Over the past 30 years, most contaminants in the water and fish have been declining (Environment Canada, 2005b). Despite a trend of decreasing contaminant levels in the lake, recent research has shown that mercury and PCB levels have accumulated in fish and birds to levels higher than those in the lower Great Lakes (LSLaMP Annual Report, 2011).

Specifically regarding the Environment Canada Sediment data, studies into the presence of OCPs and PCBs in the historical (1973) dataset determined that levels were either extremely low or undetectable across the entire lake (Frank et al., 1980). Dieldrin was detected in only 9% of the samples, and the mean lakewide concentrations of the toxin were particularly low and displayed no discernable spatial pattern. Dieldrin levels in Lake Superior at this time were found to be considerably lower than those in the remaining downstream lakes (Frank et al., 1980). When compared with the contemporary (2001) data, the declining contaminant levels in the water and surficial sediments show that progress is being make towards rehabilitation goals in spite of the problems that remain (Marvin et al., 2004a; LSLaMP Annual Report, 2011).

2.2.2 Lake Michigan

Lake Michgan suffered rapid contamination from OCPs in its southern basin following World War II (Allan et al., 1991). According to the Lake Michigan historical (1975) EC data, OCPs and PCBs were found at levels two to four times higher in the depositional zones when compared with the rest of the lake. Generally, levels of these contaminants were higher than in Lake Superior, yet much lower than those in the downstream lakes (Frank et al., 1981). Dieldrin was detected in 48.3% of the samples, being marginally higher in the depositional basins, and its spatial distribution suggested widespread sources of the toxin into the lake, likely due to high agricultural inputs of aldrin and dieldrin in the eastern watersheds of Lake Michigan (Frank et al., 1981). DDT, dieldrin, and aldrin were the most commonly used insecticides in the Lake Michigan watershed prior to 1966, resulting in their widespread distribution across the lake (Leland et al., 1973).

As in all of the Great Lakes, Lake Michigan follows the same general trend of declining contaminant levels, with sediment contamination being the highest in the depositional basins (Allan et al., 1991). Marvin et al. (2004a) found that mercury levels in this lake are among the lowest of the Great lakes, however elevated levels of lead in the sediment are concerning. Dieldrin has been identified as a critical pollutant in Lake Michigan (LMLaMP, 2008).

2.2.3 *Lake Huron, Georgian Bay, and North Channel*

Lake Huron's contaminant inputs come from a variety of sources, including atmospheric deposition, industrial point sources, agricultural runoff, and hazardous leachates from landfills (Allan et al., 1991).

The historical EC Sediment Survey datasets for Lake Huron were collected in the main body of Lake Huron in 1969 and in Georgian Bay and North Channel in 1973. An analysis of OCP and PCB levels in the surficial sediments found residues much higher in the depositional zones, a comparable pattern as found in the upstream Great Lakes (Frank et al., 1979b). Georgian Bay and the North Channel demonstrated a higher percentage of samples with detectable dieldrin readings than the main body of the lake, however mean dieldrin levels across each of these areas were low (Frank et al., 1979b).

Since that time, dieldrin in Lake Huron has seen a trend of general decline over the years, and it has been shown to have significantly declined in the tissues of lake trout since 1982 (LELaMP, 2008). According to Environment Canada (2005b), general contaminant levels in fish and wildlife of Lake Huron have decreased since the 1970s.

2.2.4 *Lake St. Clair*

As in all of the Great Lakes, Lake St. Clair experienced degradation of both water and sediment quality largely due to the numerous point sources of industrial pollution located upstream in the St. Clair River, especially south of Sarnia, Ontario (Griffiths et al., 1991). Most contaminants have been found to enter the St. Clair River as industrial and municipal discharges and spills (Griffiths et al., 1991). In the late 1960s, elevated levels of mercury were found in fish from the St. Clair River and Lake St. Clair, resulting in fishing bans and becoming a driving force behind the extensive EC sediment surveys (Marvin et al., 2004a; Gewurtz et al., 2010).

The historical (1974) EC Sediment Quality data for Lake St. Clair indicates the presence of dieldrin in less than a quarter of the samples, with the Detroit River being a major source of the contaminant (Frank et al., 1977). Aside from dieldrin, a multitude of other toxic contaminants have been detected in the sediments of Lake St. Clair and the Detroit River, acting as a major contributor to the degradation of Lake Erie (Allan et al., 1991; Marvin et al., 2002; Jia et al., 2010).

2.2.5 Lake Erie

As mentioned above, upstream sources have played a major role in the contamination of the western portion of Lake Erie. Its shallow depth and low volume result in warm temperatures making it very biologically productive, and it has experienced periods of intense eutrophication due to high nutrient loads. Lake Erie also experiences high levels of sediment loading via erosion, agricultural runoff, and point-source contamination due to the high population living in its basin (LELaMP, 2008).

Dieldrin levels in Lake Erie’s historical (1971) dataset show a trend of increasing contamination from the Western to Eastern basins (Frank et al., 1977). Contemporary sediment quality data were examined by Marvin et al. (2002). In contrast to the historical data, the results indicated increasing sediment quality in a north-eastward direction, with the Western Basin displaying the poorest sediment quality. The authors found that both metals and other contaminants shared a similar distribution across the lake, and that concentrations of metals have declined since the historical sampling period. Additionally, Marvin et al. (2004b) examined sediment quality in the lower Great Lakes via a sediment quality index. Thirty-four compounds were examined during this study with sediment quality results similar to previously mentioned, with an overall trend of decreasing sediment quality towards the south-western portion of the lake.

2.2.6 Lake Ontario

Lake Ontario receives inputs of industrial and municipal effluent from the Niagara River, which drains into the southwestern side of the lake. Additionally, it receives large amounts of agricultural and urban runoff, and there are several large industrial centres located on its shores, including Toronto and Hamilton in Ontario, and Rochester, NY (Allan et al., 1991). Dieldrin has been deemed a critical pollutant in the Lake Ontario Lakewide Management Plan due to its persistence and bioaccumulative effects (LOLaMP, 2008).

The presence of OCPs in Lake Ontario (1968) was examined by Frank et al. (1979a). OCPs appeared to be concentrated within the three main depositional basins of the lake (the Niagara, Mississauga, and Rochester basins). Specifically concerning dieldrin, this study found the presence of dieldrin in approximately 40% of the total samples, and the highest levels were found in the Niagara Basin.

Contemporary (1968) Lake Ontario sediment quality was also examined by Marvin et al. (2002, 2004b) in the studies described in the previous sections. Sediment quality in Lake Ontario was found to be lower in Lake Ontario than in Lake Erie, with the poorest quality sediments being located within the three depositional basins, consistent with historical observations. Similarly to Lake Erie, the concentration of metals in the surficial sediments has declined in recent years. The results obtained by Marvin et al. (2004a) are also consistent with these patterns.

According to the Lake Ontario LaMP, there has been a reduction in toxic inputs from the Niagara River between 1960 and 1990, and PCB levels have been declining in fish and wildlife, including an 80-90% reduction in dieldrin in herring gull eggs (LOLaMP, 2008).

2.2.7 Remediation Efforts

First signed in 1972, the Great Lakes Water Quality Agreement (GLWQA) is a commitment between Canada and the United States recognizing the declining health of the Great Lakes system. It was revised in 1978 and amended in 1987. According to this agreement, the countries will work together “to restore and maintain the chemical, physical and biological integrity of the waters of the Great Lakes Basin Ecosystem” (Bruce and Higgins, 1987). It has a focus on the reduction of pollutant inputs into the system and the restoration and enhancement of Great Lakes water quality.

In order to meet the goals set out in the GLWQA and its amendments, Lakewide Management Plans (LaMPs) have been developed for lakes Superior, Michigan, Erie, and Ontario (LSLaMP, 2008; LMLaMP, 2008; LELaMP, 2008; LOLaMP, 2008). The Lake Huron Binational Partnership has been formed which operates in a similar fashion to the LaMPs except that it prioritizes obvious lakewide issues and applies less focus on types of impairment, causes, loading sources and reporting (Lake Huron Action Plan, 2004). Within each of the Great Lakes, Areas of Concern (AOCs) have been identified in which extreme environmental degradation has occurred and are in need of special attention due to their degree of impairment. Remedial Action Plans (RAPs) have been developed for each of these AOCs in order to set out strategies and goals that will allow the AOCs to be removed from the list, as well as monitoring the progress of the remediation efforts (Gurtner-Zimmermann, 1995). To date, four of the 43 AOCs have been delisted. Figures 2.1 and 2.2 depict the watersheds for lakes Erie and Ontario, indicating major cities and AOCs. There are 12 AOCs located within the Lake Erie watershed, and 8 in the Lake Ontario watershed.

The Great Lakes Binational Toxics Strategy (GLBTS) is another joint commitment between Environment Canada and the United States Environmental Protection Agency aimed at the reduction and elimination of bioaccumulative persistent toxic substances in the Great Lakes basin (Gulezian and Epstein, 1997). By 2008, a majority of the original goals had been met, dealing with a reduction or elimination of Level 1 substance (identified by both countries to be chemicals of concern/ critical pollutants) releases into the Great Lakes Basin ecosystem (Waffle et al., 2008).

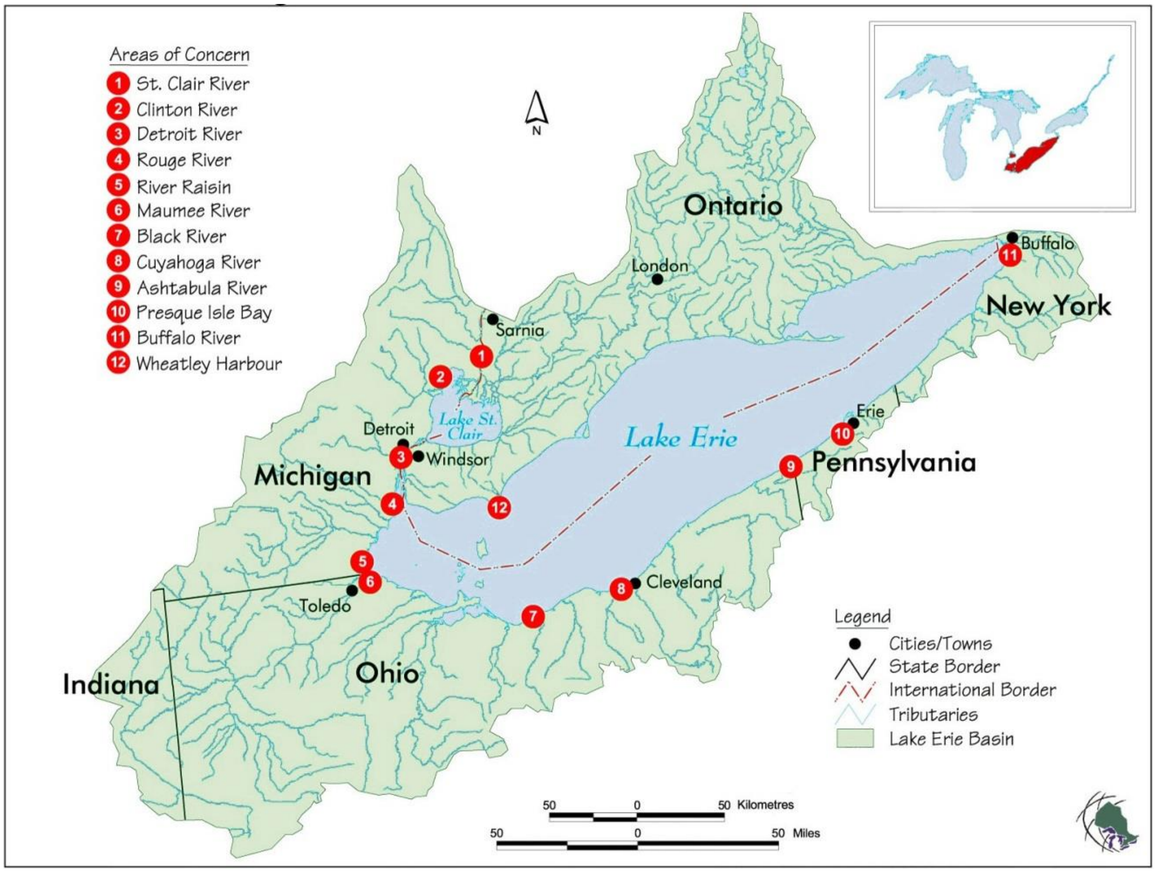

Figure 2.1: Lake Erie drainage basin and areas of concern

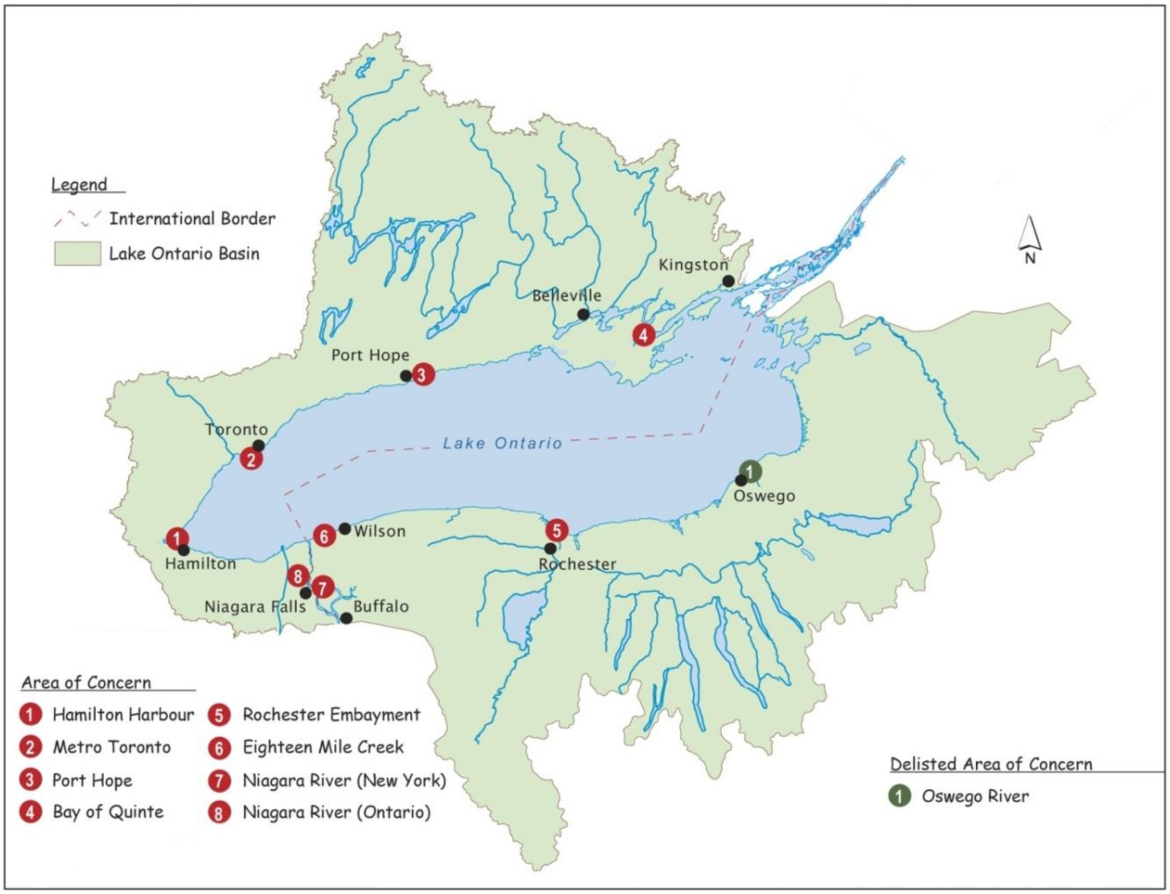

Figure 2.1: Lake Ontario drainage basin and areas of concern

2.3 Examination of Pollutant Levels in the Environment

A major drawback of working with environmental data is that the attributes in question are often continuous rather than discrete, for example elevation, precipitation, or contaminant levels in soil. As a result, samples are often acquired at a limited number of locations within the study area due to financial and time constraints. While valuable information about the surface can be obtained through statistical analysis of these point measurements, it can be extremely difficult to visualize spatial trends in the data, and often values in locations other than those sampled are of interest.

There are several different methods useful for visualizing the spatial distribution of environmental data. One simple way is to display the point locations on a map, altering the size or colour of the symbol with respect to the values of a particular attribute. This technique has been successfully used in sediment contamination studies. Spatial and temporal variation in mercury and dieldrin concentrations across the Great Lakes sediments were mapped using a graduated colour scale (Marvin et al., 2004a), and similarly, a variety of persistent organic pollutants were examined in Lake Erie sediments using graduated symbols (Marvin et al., 2004b). In both of these cases, the maps provided valuable insight into how the contaminants were distributed across the regions. Graduated symbol maps are presented in this paper for all of the lakes, and is especially useful in cases where contaminants show little spatial autocorrelation or range in values. However, it would often be useful to know the values of the attribute across the whole surface of the study area in order to examine any spatial trends that might be present in the data and allow for a more complete analysis of the dataset.

Spatial interpolation can be done using two different methods. Deterministic methods are created using mathematical techniques, and contours are created based on the extent of similarity or degree of smoothing. Examples of deterministic methods are inverse distance weighting and radial basis functions (ESRI, 2010). Geostatistical methods incorporate statistical models and spatial autocorrelation when creating the prediction surface (ESRI, 2010). Such techniques, including kriging and cokriging, have been applied to continuous environmental datasets with much success in recent years (Atteia et al., 1994; Tao, 1995; Jakubek and Forsythe, 2004).

2.3.1 Environmental Applications of Kriging

As previously described, geostatistical techniques are commonly used when working with environmental datasets. Originally developed for use in mining, kriging has been successfully applied in numerous other areas, including agriculture, meteorology, and hydrogeology (Gilbert and Simpson, 1985; Webster and Oliver, 2007).

There are numerous examples of the application of kriging techniques for examining spatial trends of contaminant levels in the surficial sediments of water bodies. For example, Ouyang et al. (2003a and 2003b) used kriging to map the spatial distribution of mercury and DDT, respectively, in river environments. This technique has also been used to examine contaminant distribution in the Great Lakes basin specifically. Forsythe et al. (2004) used a kriging approach to compare mercury and lead in the sediments of the lower Great Lakes and found that, while not statistically valid in all cases, the results allowed conclusions to be drawn with respect to the sources of contaminant loadings into the lakes. Additionally, Forsythe and Marvin (2005) used a similar approach to analyze the distribution of several contaminants in the lower Great Lakes. The kriging approach has also been used to examine historical changes between lead and mercury concentrations in lakes Huron, Erie, and Ontario (Forsythe and Marvin, 2004; Forsythe and Marvin, 2009).

CHAPTER 3: METHODOLOGY

3.1 Kriging

3.1.1 History and Theory of Kriging

Developed by D.G. Krige, a mining engineer, kriging is a technique used for interpolating values at unsampled points across a continuous surface where only a number of point values are known (Webster and Oliver, 2007). By applying this technique to the dataset, a raster prediction surface can be created, providing an estimated value for all unsampled locations. Kriging takes into account spatial autocorrelation between data points as a function of distance, assuming that near points will be more similar than those farther away (ESRI, 2010). This provides a more accurate estimation than deterministic methods as spatial trends in the data can be accounted for. This is especially important when working with sediment contamination because there are many factors that can affect depositional patterns such as wind, currents, and bathymetry.

Another major benefit of kriging is that it allows for the amount of error in the interpolation to be examined, thereby providing a measure of validity. Error is minimized in kriging if sampling is done in a regular grid pattern, and clustering of points will reduce accuracy (Webster and Oliver, 2007).

3.1.2 Ordinary Kriging

Ordinary kriging has proven very successful in many applications, including mapping sediment contamination, and will be used for this study. It is the most robust and frequently used kriging method (Isaaks and Srivastava, 1989), and it assumes that the mean is constant and unknown (Webster and Oliver, 2007). Ordinary kriging uses a weighted linear combination of the data, with the goal of minimizing error variance. The weights are calculated based on proximity of adjacent points as well as their configuration, for example, if points are clustered their individual weight will be reduced (Webster and Oliver, 2007).

The model used for ordinary kriging is as follows:

$$Z(s) = \mu + \varepsilon(s) \tag{1}$$

Where Z is the concentration at location s, the unknown mean is represented by μ, while $\varepsilon(s)$ is the autocorrelated error at location s (Atteia et al., 1994; ESRI, 2010).

3.1.3 Log Transformation

Environmental datasets frequently do not demonstrate a Gaussian (normal) distribution, but rather positively skewed, especially when dealing with contaminant levels which often occur at very low concentrations. While normality in the dataset is not required when performing ordinary kriging (Ouyang et al., 2005), there some debate in the literature as to whether it is required to produce the best results. For example, some argue that the best results are achieved if the data are normally distributed, and transformation of the data is required if they are skewed or contain outliers (Johnston et al., 2001; Ouyang et al., 2003a).

In this study, the datasets were examined for normality using histograms, Q-Q plots and measures of skewness and kurtosis. Ordinary kriging models were fit to both untransformed and log-transformed data. In all cases, the untransformed datasets provided error statistics (discussed in sections 3.1.7 and 3.1.8) that were within acceptable limits and provided meaningful kriging results. The untransformed datasets were therefore used for the creation of the prediction surfaces presented later in this paper.

3.1.4 Semivariogram and Model Selection

An empirical semivariogram must be constructed in order to look for spatial autocorrelation in the data. If a dataset demonstrates spatial autocorrelation, it means that the relationship between the points is such that near points have more similar values than points a greater distance apart. The semivariogram plots the distance between each pair of points against half of the variance between the points squared (Johnston et al., 2001). When exploring the data, several important characteristics must be looked at. The range is the distance at which semivariance stops increasing with increasing distance between points (indicating a lack of spatial autocorrelation). The sill is the semivariance value at the range. The nugget is the y-intercept of the graph. When the nugget is greater than 0, it indicates that at extremely small distances there is some small amount of variance, which can be attributed to error or some source of variation (ESRI, 2010).

In creating the semivariogram, there are often so many pairs of points that it can become difficult to interpret. In order to overcome this, ArcGIS uses binning, a process by which the pairs of locations are grouped together according to their distance apart. Therefore, the semivariogram displays the average distance and semivariance for each bin, rather than for each pair of points individually (ESRI, 2010).

Once the semivariogram is created, the next step is to select a model that best fits it. Three different model types have been deemed the most appropriate for kriging sediment contamination (Dennis et al., 2009). Therefore, the Spherical, Gaussian, and Exponential models were tested for each dataset in this study. The best model was chosen by examining how well the model fit the shape of the semivariogram, as well as the cross-validation error statistics. Additionally, anisotropy was incorporated into the modeling process to improve results.

3.1.5 Anisotropy

The default kriging model when working with the Geostatistical Analyst is an isotropic model. However in many cases, especially when dealing with waterways, spatial variation may not be the same in all directions. This is extremely important to consider when interpolating hydrological data, as winds and currents can have a large effect on sedimentation patterns. The phenomenon is known as anisotropy. After the angle of the anisotropic axis is determined, it can be incorporated into the variogram model to improve its accuracy (Johnston et al., 2001). For the purposes of this study, anisotropic angles of 70º for Lake Erie and 90º for Lake Ontario were incorporated into the model after being deemed most accurate by Dennis et al. (2009).

When running the kriging model for the datasets in this study, the anisotropy parameter was set to true, thereby allowing an angle and major and minor range to be specified. By altering the values for these parameters, the intensity of the anisotropic influences are specified. The major and minor range were selected through experimentation and examination of error statistics, with the values used by Dennis et al. (2009) and a visual examination of the data distribution as guidelines.

3.1.6 Search Neighbourhood

Because kriging is applied in cases where spatial autocorrelation exists within the dataset, it is fair to assume that measured values nearer to the prediction location have a larger influence on its actual value than those more distant. This is especially true if the dataset is spread over a large area, as is the case in this study. Thus, most of the weight in the kriging equation is assigned to the nearest points, and the more distant points can be eliminated altogether from the calculations, as they are likely to exhibit little, if any, influence on the actual value (Johnston et al., 2001). Within the Geostatistical Analyst, this is accomplished by defining the search neighbourhood. By default, the search neighbourhood is circular in shape, but due to the introduction of anisotropic influences, the search neighbourhood becomes an ellipse whose size and orientation are defined by the input parameters of major range, minor range, and direction. The sector type can also be altered to help reduce bias, and in this case 4 sectors with 45º offset was used. This means that within each of these sectors, the maximum nearest neighbours within each sector will be included in the calculation. This will allow for points to be more spread out in the direction of anisotropic influence (ie. along the major range). Previous research into the application of ordinary kriging to predict sediment contamination levels has determined that the optimal search neighbourhood when using these specific datasets is a maximum of 5 neighbours and a minimum of 1 neighbour (Dennis et al., 2009). Therefore, this is the search neighbourhood that was applied when running all models in this study.

3.1.7 Cross-Validation

Once a model is applied to the dataset, cross-validation is performed to determine how accurate those particular parameters were at predicting values at the unsampled locations. By looking for the model with the least error associated with it, one can select the most accurate variogram model and proceed with the interpolation using that particular model (Isaaks and Srivastava, 1989). Cross-validation can be performed using the Geostatistical Analyst, within the Geostatistical Wizard. During the cross-validation process, each known value is removed systematically and the model is used obtain a predicted value at that particular location (ESRI, 2010; Isaaks and Srivastava, 1989). By comparing this prediction with the measured value, the error associated with each model is calculated and presented within the Geostatistical Analyst, and can be viewed graphically in the form of various plots, and numerically as a set of error statistics. A scatter plot (prediction plot) is produced that plots measured values against predicted values. The best fit line through these points will generally be slightly less than one (a slope of one would indicate no error), due to the fact that small values tend to be overpredicted and large values tend to be underpredicted (ESRI, 2010). Similarly, an error plot is produced in which the measured values are subtracted from the predicted values, and a standardized error plot where these values are divided by the estimated kriging standard errors. Lastly, a QQ plot is produced which shows how the standardized error differs from a normal distribution. The closer the points fall to a straight line, the closer the errors are to being normally distributed (ESRI, 2010).

In addition to the graphs described above, error statistics are provided as follows: a count of the number of samples used in the calculations, the mean error - the average difference between the measured and predicted values, which should be close to zero if the estimates are unbiased (Atteia et al., 1994), the root mean square error (the square root of the variance), the average standard error, the mean standardized error (which should be small, as it is a measure of how precise the prediction is - Atteia et al., 1994), and the root mean square standardized error (if this is greater than one then the variability is underestimated and vice versa).

3.1.8 Characteristics of an Accurate Model

The selection of the appropriate model for the data is determined by examining the error statistics following the cross-validation process. Ideally, the mean and the standardized mean prediction error (SMPE) will be close to 0, which would indicate that the prediction errors are unbiased. Additionally, in a good model the root-mean-squared prediction error (RMSPE) will be small, the average standard error (ASE) will be close to the RMSPE, and the standardized root-mean-squared prediction error (SRMSPE) will be close to 1. If the SRMSPE is greater than one then the variability is underestimated, and vice versa (ESRI, 2010). Furthermore, the RMSPE and ASE should not be greater than 20 (Dennis et al., 2009). In this study, these statistics were examined in all cases and were used to aid in the estimation of the best-fit model for the semivariogram.

CHAPTER 4: RESULTS AND DISCUSSION

For each of the lakes with available dieldrin data, graduated symbol maps were produced for both the historical and contemporary untransformed datasets to provide a visualization of the spatial distribution of the data and the changes that have occurred during the two sampling periods. The ISQG and PEL were indicated where applicable. Because dieldrin concentrations in many of the lakes are quite low, spatial trends in the data can be difficult to visualize (Gewurtz et al., 2007), especially in the contemporary datasets where sampling locations were relatively limited. These maps are discussed in detail in the following sections. Additionally, due to the wider range of contaminant levels, including many above the sediment quality guidelines, prediction surfaces were generated for lakes Erie and Ontario to allow for a better understanding of the spatial trends of the data. The kriging results and discussion can be found in Section 4.2.

4.1 Graduated Symbol Map Results

4.1.1 Lake Superior

The graduated symbol maps for Lake Superior can be seen in Figure 4.1. While dieldrin levels were extremely low across the lake, with no readings falling above or near to the ISQG, the historical Lake Superior dataset appears to demonstrate some spatial autocorrelation. Slightly elevated levels appear to be concentrated in several of the depositional sub-basins, especially in the southern portion of the Caribou Sub-Basin, the Isle Royale Sub-Basin, and at the western edge of the Chefswet Sub-Basin. These patterns are consistent with the tendency of OCPs to adsorb to fine grained sediments

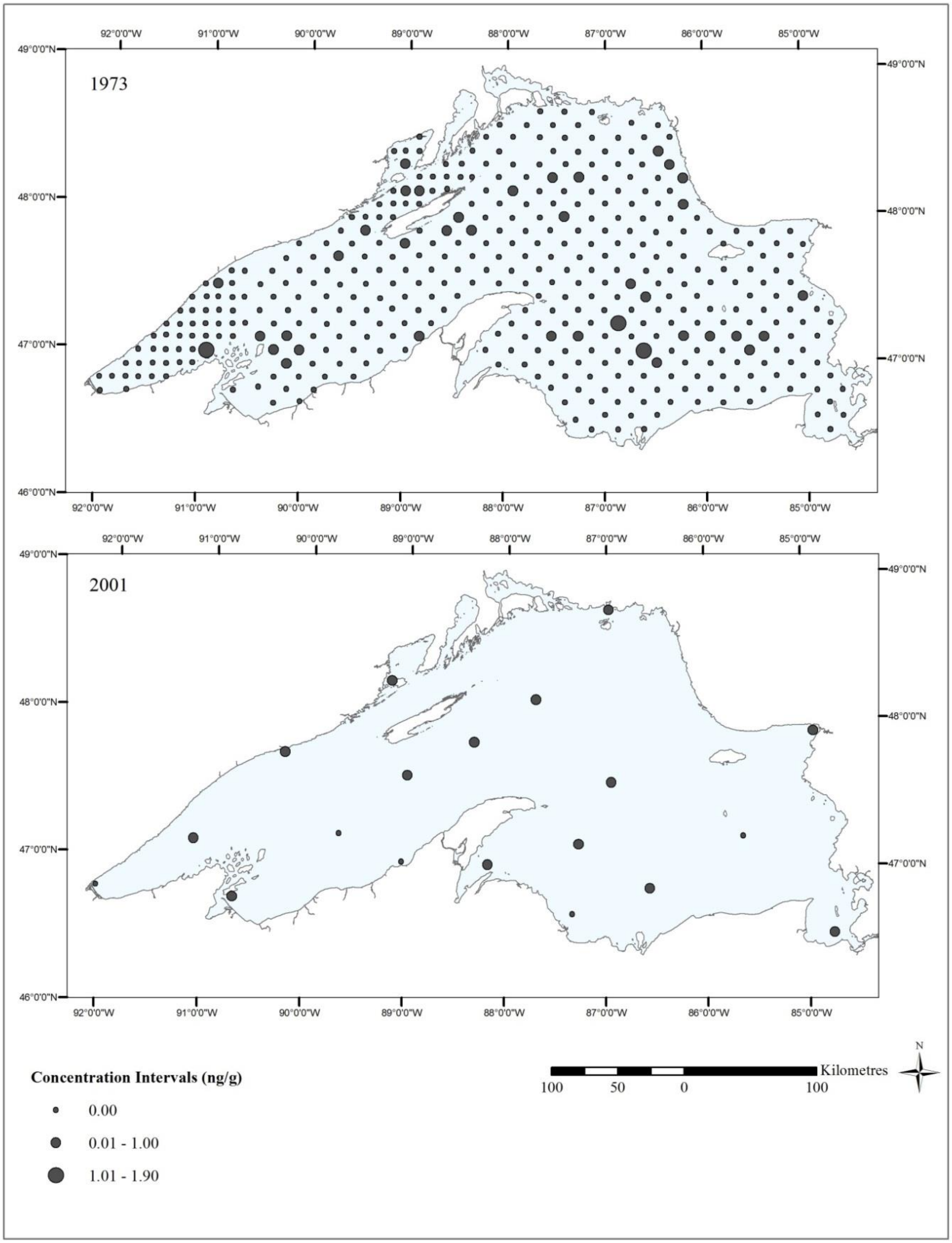

Figure 4.1: Dieldrin graduated symbol map results for Lake Superior, 1973 and 2001

which settle in the depositional basins. Several low readings were recorded in Thunder Bay and the Thunder Bay Trough, possibly implicating Thunder Bay as a point source. However, due to the extremely low concentrations, it is difficult to draw any conclusions with regards to spatial trends. These findings are consistent with those of Frank et al. (1980). The contemporary dataset is significantly smaller with only 19 sites associated with dieldrin data. These locations are spread throughout the lake and are all extremely low, not exceeding 0.06 ng/g. While the lakewide average is much lower than in the historical dataset, no strong conclusions about temporal trends can be drawn due to the lack of contemporary data. In both cases, no clear point sources of the contaminant are evident, reflecting a high degree of atmospheric deposition (LSLaMP, 2008). Overall, Lake Superior appears to be the least contaminated of the Great Lakes with respect to dieldrin, largely due to the limited agricultural land use in its watershed (Glooschenko et al., 1976).

4.1.2 Lake Huron, Georgian Bay, and North Channel

Historical and contemporary graduated symbol maps for Lake Huron, Georgian Bay, and North Channel are depicted in Figure 4.2. The trends visible here are similar to those seen in Lake Superior. In the historical dataset, only a very small percentage (8%) of the locations in the main body of the lake exhibit any detectable trace of dieldrin, and those that do all fall well below the ISQG. There are not enough measureable readings to deduce the presence of any spatial autocorrelation. However, most of the detections appear to occur in the Mackinac Basin and in Saginaw Bay. Glooschenko et al. (1976)

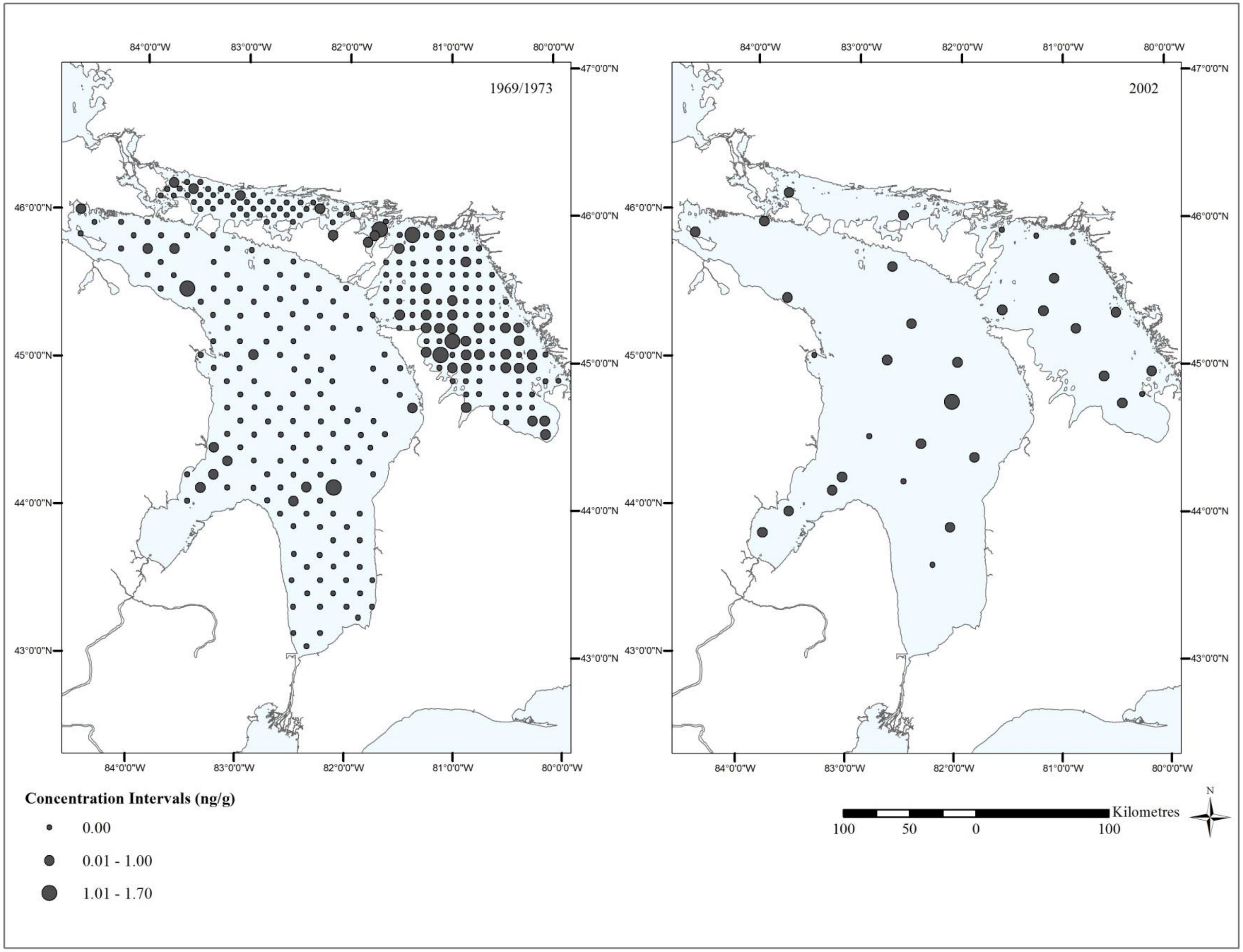

Figure 4.2: Dieldrin graduated symbol map results for Lake Huron, Georgian Bay and North Channel, 1969/1973 and 2002

reported dieldrin as the main pesticide in the St. Marys River, providing an explanation for dieldrin presence of the contaminant in both the Mackinac Basin and the North Channel, where traces of dieldrin were also detected. Estimations of agricultural aldrin and dieldrin use in the land surrounding Saginaw Bay were relatively high at >0.010 points per acre in 1966 (Nowell et al., 2006), suggesting that agricultural runoff and erosion played a role in deposition in this area of Lake Huron. Additionally, elevated dieldrin readings were recorded across the depositional regions of Georgian Bay in the 1973 dataset. Detectable amounts of dieldrin were present at 70% of the sampling sites in Georgian Bay. One explanation for this phenomenon is the historical use of organochlorine pesticides in the Muskoka Lakes region of Ontario, where these compounds were applied by spray application until the mid-1960s for biting fly control in these recreational areas (Miles and Harris, 1973; Agriculture Canada, 1973). Furthermore, the use of organochlorine pesticides in the Lake Huron watershed on corn, soybean and small grain crops was fairly intense up until the late 1960s (Glooschenko et al., 1976). A significantly fewer number of samples were taken during the contemporary sampling period and again no discernible patterns can be seen, although in this case dieldrin was detected in 76% of samples taken in the main body, indicating a slight increase likely due to atmospheric deposition. In Georgian Bay, the contemporary data are difficult to compare to the historical dataset due to the much sparser sampling locations, but low levels are seen across the bay. Overall, dieldrin levels in Lake Huron are low due to the fact that most of its inflow comes from Lake Superior, the least contaminated of the Great Lakes (Reinert, 1970).

4.1.3 Lake St. Clair

The graduated symbol maps for Lake St. Clair can be seen in Figure 4.3 along with those for Lake Erie. In both the contemporary and historical datasets, all values are too low to discern any spatial autocorrelation. The urban-agricultural land around the City of London drains into Lake St. Clair via the Thames River. This area has historically experienced large amounts of pesticide application, with DDT and dieldrin found in the highest quantities in Thames River water samples in 1971 (Miles and Harris, 1973). In fact, most of the land on the Canadian side of Lake St. Clair is used for agricultural purposes, and dieldrin inputs are likely carried to the lake via agricultural runoff and erosion (USEPA, 1999; Gewurtz et al., 2010). The St. Clair River AOC, located in the St, Clair River watershed, is a highly industrialized area which may have played a role in some of the OCP inputs into the lake, however no published evidence of aldrin/dieldrin production or use in this area could be found. The extremely short residence time (7 days) of the water in Lake St. Clair, as well as the periodic dredging of the lake, prevents much accumulation of those contaminants entering from upstream areas. This has resulted in increased detection of insecticide residues in the Detroit River and the western basin of Lake Erie, just downstream of Lake St. Clair (Miles and Harris, 1973).

4.1.4 Lake Erie

The lower Great Lakes clearly exhibit a much higher degree of benthic impairment than those upstream. The western basin of Lake Erie is the first portion of the Great Lakes system that has any readings over the ISQG, and this can be seen in both the historical (1971) and contemporary (1997/1998) graduated symbol maps.

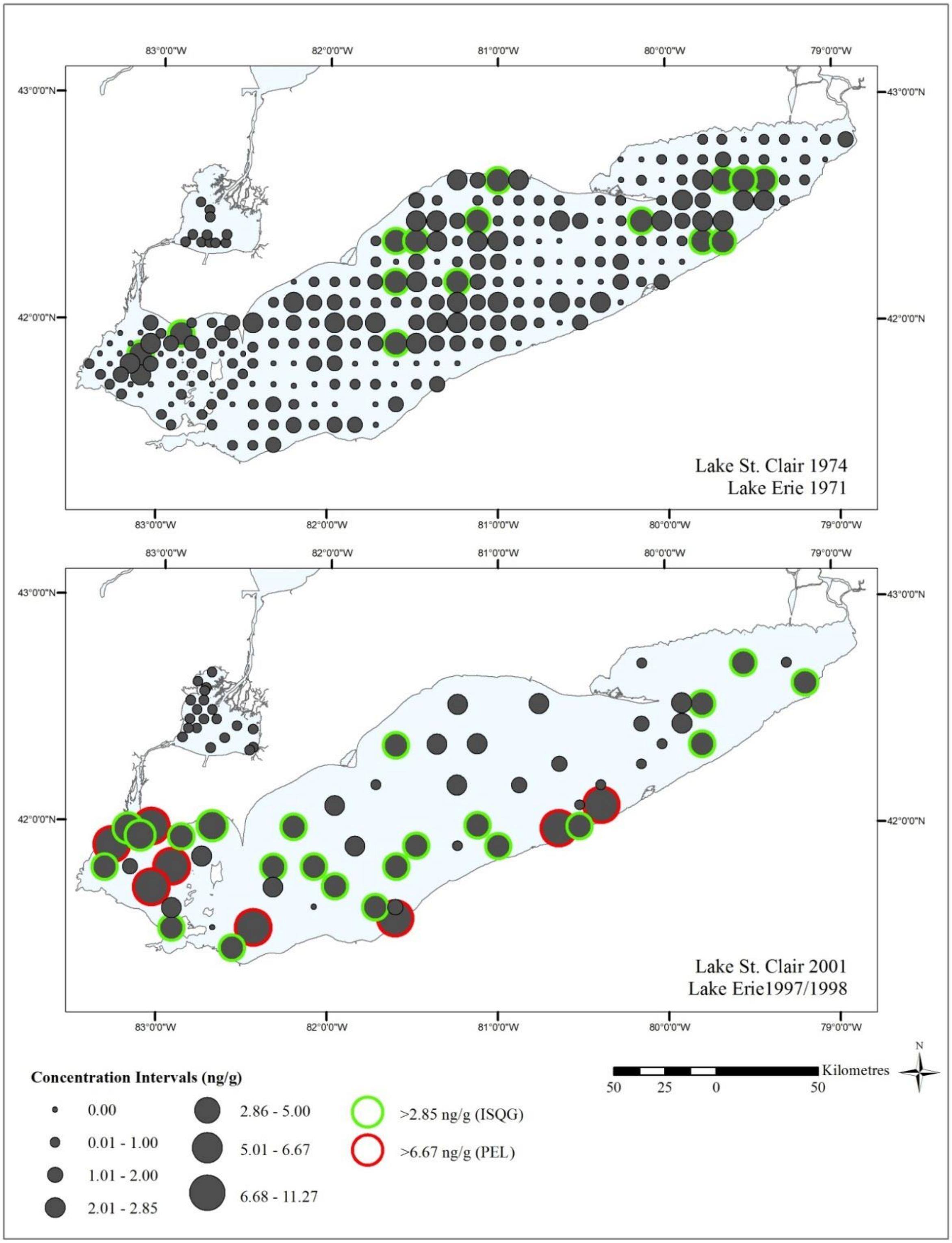

Figure 4.3: Dieldrin graduated symbol map results for Lake St. Clair (1974 and 2001) and Lake Erie (1971 and 1997/1998)

In the historical graduated symbol map, there is some discernible spatial autocorrelation of the elevated values, which seem to be most concentrated in the three depositional basins of the lake. This is to be expected because contaminants tend to adsorb to fine-grained sediments, which settle in the deep basins (Marvin et al., 2002). Most of the readings above the ISQG fall into the Central and Eastern Basins, with two instances occurring at the mouth of the Detroit River. Historically, the Detroit River has been shown to be a significant source of dieldrin into Lake Erie (Frank et al., 1977), and water samples taken in 1974 indicate that dieldrin was the main pesticide occurring in its waters (Glooschenko et al., 1976). A second major source of OCPs into Lake Erie resulted from the intensive application to tobacco and corn crops in Norfolk County and parts of surrounding counties (Elgin, Oxford, Brant, and Haldimand) on the north shore of the lake (Harris et al., 1966; Frank et al., 1977). This area (the Big Creek watershed, which drains 280 square miles into Long Point Bay) has been widely examined with respect to the occurrence of DDT and dieldrin in water, fish and sediments (Miles and Harris, 1971; Frank et al., 1974a; Frank et al., 1974b). Between the years of 1968 and 1971, 8-9% of the aldrin and dieldrin applied in Ontario was applied to the Big Creek watershed (Frank et al., 1974b), and this time period reflected a decrease in use over previous years due to increased tolerance of certain pests and a switch to DDT as the primary method of pest control (Frank et al., 1974a). The intensive use of dieldrin in this watershed provides an explanation for the high readings in the Eastern Basin in 1971. Frank et al. (1977) reported that at this time, 62% of the annual dieldrin loading into Lake Erie was into the Eastern Basin. The elevated dieldrin levels recorded in the Central Basin can be attributed to runoff from the agricultural land north of the basin, which has historically been used for vegetable crops (Miles and Harris, 1971). Additionally, aldrin and dieldrin were widely used in agricultural areas in watersheds south of the lake, with levels exceeding 0.010 pounds per acre along much of the shore in 1966 (Nowell et al., 2006). In the contemporary map, a much higher level of impairment is obvious with many values above both the ISQG and the PEL. These maps clearly represent rising contamination levels over time, the opposite trend reported by Marvin et al. (2002), who saw a decline in all contaminants assessed during this time period. In contrast to the historical data, a different spatial pattern exists with many of the highest values occurring in the Western Basin and along the southern shore of the lake. The Detroit River appears to be a major source of dieldrin contamination, which is consistent with other reports (Marvin et al., 2002). The shift in the spatial distribution of the contamination levels can be attributed to several factors. Sediment loads from the Detroit River tend to remain in the Western Basin, with minimal transport across the lake (Marvin et al., 2002). This is due to both bathymetry and the two-gyre circulation pattern in the lake (seen in Figure 1.3), and has resulted in large amounts of accumulation in the Western Basin as the years progressed. Additionally, the high OCP occurrence in the Eastern Basin was historically attributed to the high agricultural uses of the compounds. Since they have not been applied since the 1970s, dieldrin levels in the Eastern Basin have begun to diminish (Marvin et al., 2002).

4.1.5 Lake Ontario

The graduated symbol maps for Lake Ontario can be seen in Figure 4.4. These datasets also contain many dieldrin readings above the ISQG indicating that dieldrin

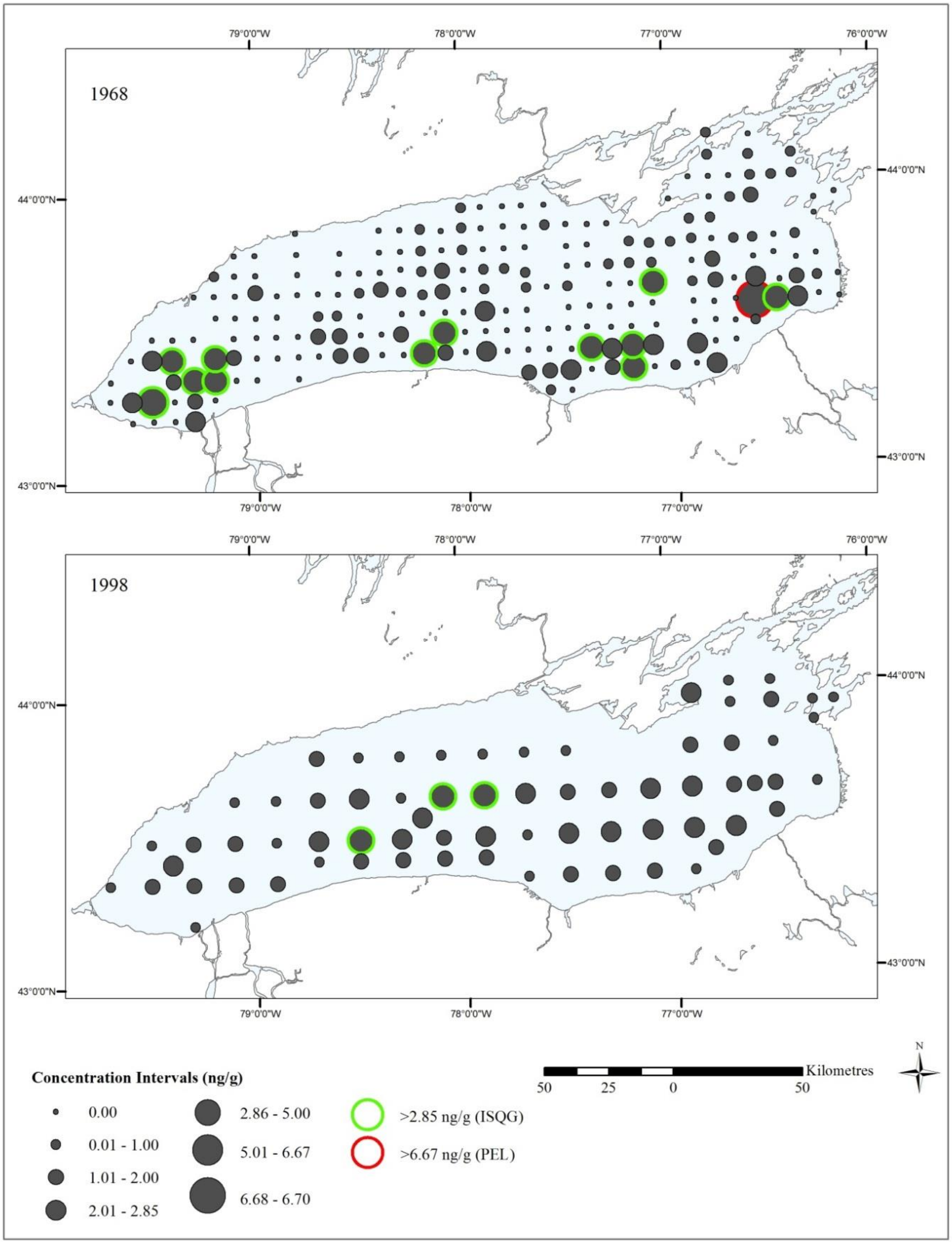

Figure 4.4: Dieldrin graduated symbol map results for Lake Ontario, 1968 and 1998

continues to be a concern for this lake. While the historical dataset contains a higher number of readings above the ISQG, the lakewide average for the contemporary dataset is much higher than in the historical one (1.37 vs. 0.55 ng/g, respectively), indicating a possible increase over time. The problem with this is that the contemporary sampling focused on the depositional zones where the contaminant was most likely to be found, thereby inflating the average and making it difficult to directly compare the data.

The historical graduated symbol map for Lake Ontario depicts a similar distribution as for Lake Erie, with a pattern of increased readings in the depositional basins. Due to the circulation patterns of the lake, contaminants tend to be fairly evenly distributed lakewide (Marvin et al., 2002). Possible sources of historical OCP contamination into Lake Ontario vary. Based on a visual examination of the graduated symbol map, the Niagara River appears to be a point source of dieldrin. This has been confirmed in the literature (Marvin et al., 2002) and is likely due to the intensive use of aldrin in the Niagara Peninsula, which was approximately 10 600 kg per year in 1968 and 1969 (Frank et al., 1979). Hamilton Harbor has also been considered as a possible point source due to the high contaminant levels found in the eggs of colonial waterbirds and turtles in this area (Weseloh et al., 1995; Bishop et al., 1996), however no data from Hamilton Harbour was available for this study. Aldrin and dieldrin were also applied at a moderate level to land on the southern side of the lake (Nowell et al., 2006), as well as areas north of the lake. For example, these insecticides were used intensively for vegetable production in the area north of Toronto, Ontario, and appeared in sediments of adjacent streams in the late 1960s, and have been detected in the area around Belleville, Ontario, where land is used for potato and vegetable production (Frank et al., 1974b). In the contemporary (1998) graduated symbol map, while it exhibits few values above the ISQG, dieldrin levels appear to be moderate across the lake with little spatial autocorrelation. In contrast to Lake Erie, the water in Lake Ontario circulates on a lakewide basis (see Figure 1.3), allowing sediment to be redistributed across the lake more evenly. Due to the discontinuation of aldrin/dieldrin use for agricultural purposes in the Lake Ontario watershed, a decrease in contamination is expected. However, as mentioned previously, the focus on the depositional basins during the contemporary sampling period makes comparison difficult.

4.2 Kriging Results

The cross-validation error statistics are presented in this section, along with the resulting prediction surfaces for Lakes Erie and Ontario. Classes and colours have been set so that the historical and contemporary maps are on the same scale and therefore dieldrin levels and temporal changes can be more easily compared.

4.2.1 Cross-Validation Results

Following the selection of the best model for each dataset, cross-validation results were recorded and are presented in Table 4.1. Based on the following statistics, the error for each model used fell into acceptable ranges and therefore each of these resulting prediction surfaces represent a relatively accurate interpolation of the available data. The low mean error values indicate that the predictions are unbiased, a major assumption of ordinary kriging; the SRMSPE values are close to one, indicating that the standard errors are accurate (though slightly overestimated); and the predictions are close to the measured values, as indicated by the low (and similar) RMSPE and ASE values

(Johnston et al., 2001). The Lake Erie contemporary data produced the least accurate surface with an MPE of -0.123 and the higher RMSPE an ASE values (2.620 and 2.650, respectively).

Table 4.1: Cross-validation results

Lake	Year	MPE	RMSPE	SRMSPE	ASE	|RMS-ASE|	Model
Erie	1971	0.002	0.948	0.987	0.960	0.012	Exponential
Erie	1997/ 1998	-0.123	2.620	0.990	2.650	0.030	Spherical
Ontario	1968	0.004	1.003	0.972	1.035	0.032	Exponential
Ontario	1998	0.034	0.756	0.963	0.781	0.025	Exponential

4.2.2 Lake Erie

The kriging results for the historical (1971) Lake Erie data are shown in Figure 4.5. The prediction surface for this dataset clearly depicts that dieldrin concentrations were highest in the three depositional basins of the lake. A clear trend of increasing contamination can be seen from the Western to the Eastern basins. Though approximately 6% of the measured concentrations fell between the ISQG and PEL, the entire prediction surface does not depict any areas above the ISQG. The areas with the highest dieldrin concentrations are found within the two largest and deepest basins of the lake (the Central Basin and the Eastern Basin), as well as an area with slightly elevated levels at the Detroit River, suggesting a loading source into the lake. This has been attributed to agricultural runoff into the north shore of Lake Erie, with contaminants moving into the Eastern Basin (Frank et al., 1977). The error statistics for this dataset indicate an accurate model. The MPE is very close to zero (0.002), the RMSPE and ASE are both small and of similar value (0.948 and 0.960, respectively), and the SRMSPE is 0.987, indicating that the prediction might be slightly overestimated. Of all the kriged surfaces presented in this study, the Lake Erie historical estimation is likely the most accurate overall. This is

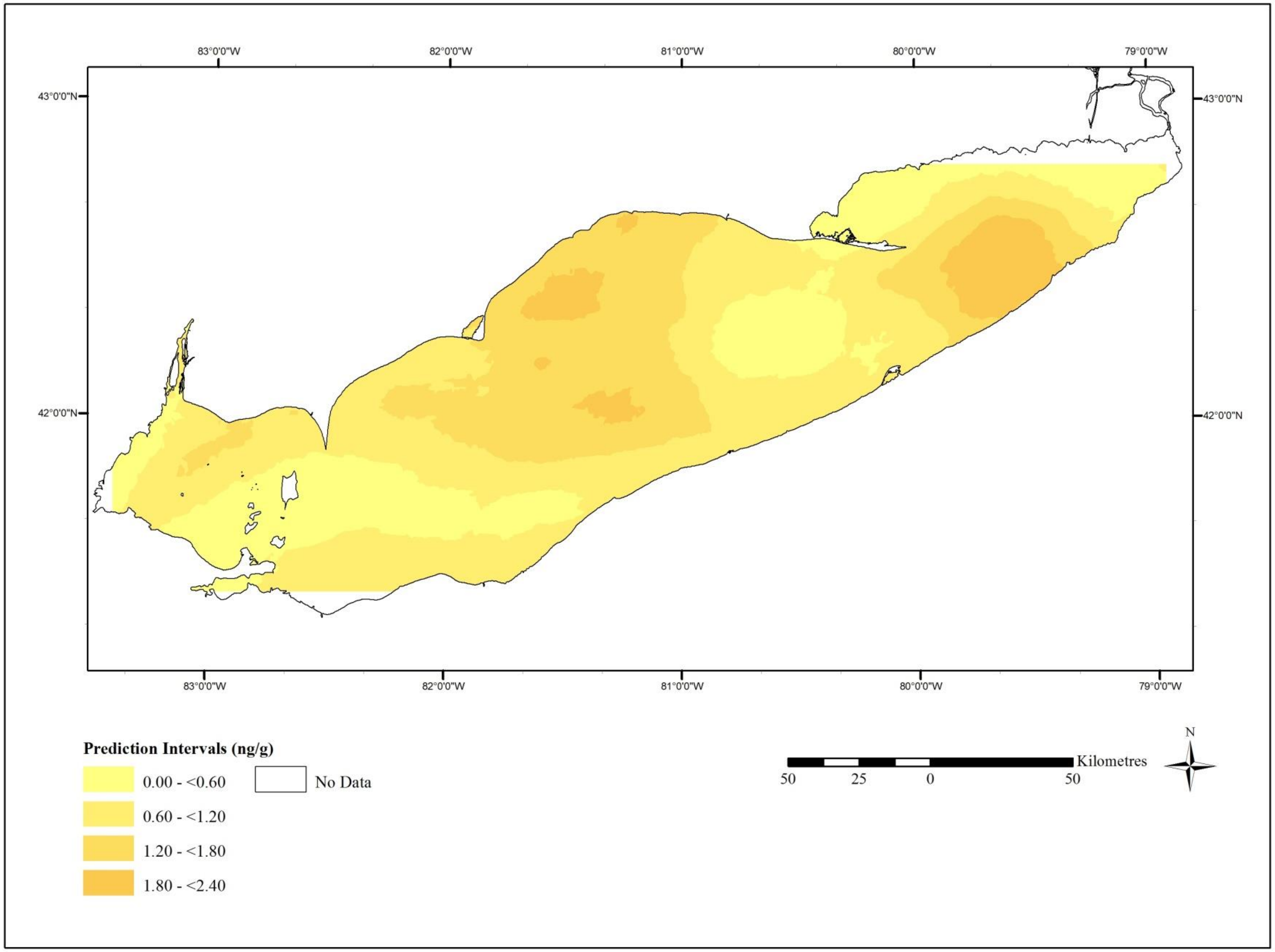

Figure 4.5: Dieldrin kriging results for Lake Erie 1971

due to the large number of sampling locations available for analysis (258 across the lake) and they were arranged in a regular grid pattern, which is ideal for minimizing error (Webster and Oliver, 2007).

The resulting prediction surface for the contemporary (1997/1998) Lake Erie dataset can be seen in Figure 4.6. These results indicate a substantial portion of the lake had sediment containing dieldrin levels above the ISQG of 2.85 ng/g, indicating a moderate level of impairment. Although estimations on the western side of the lake were approaching the PEL of 6.67 ng/g, there is no area on the prediction surface that exceeds this level. In contrast, the point data used in the analysis contained approximately 46% of the locations above the ISQG, with an additional 8% of the locations above the PEL. This indicates that the most extreme contamination values are under-represented on the prediction surface. According to the kriging results, the sediment on the western side of the lake was clearly more contaminated with dieldrin. Concentrations tend to decrease from west to east, though they still appear to be higher within the Central and Eastern basins relative to their surrounding non-depositional zones. This is consistent with the pattern seen in the graduated symbol map. The results clearly indicate that the Detroit River is a major source of dieldrin to the lake. As previously described, the Detroit River receives much agricultural runoff from the Canadian side of its watershed, which can help to explain the elevated levels of dieldrin in this area. The fact that the western basin exhibits the highest degree of contamination aligns with more recent reports that there is not a significant amount of transport of contaminants in an eastward direction after they are loaded from the Detroit River (Marvin et al., 2002). As described for the historical dataset, the error statistics for this model fall into an acceptable range, however the MPE

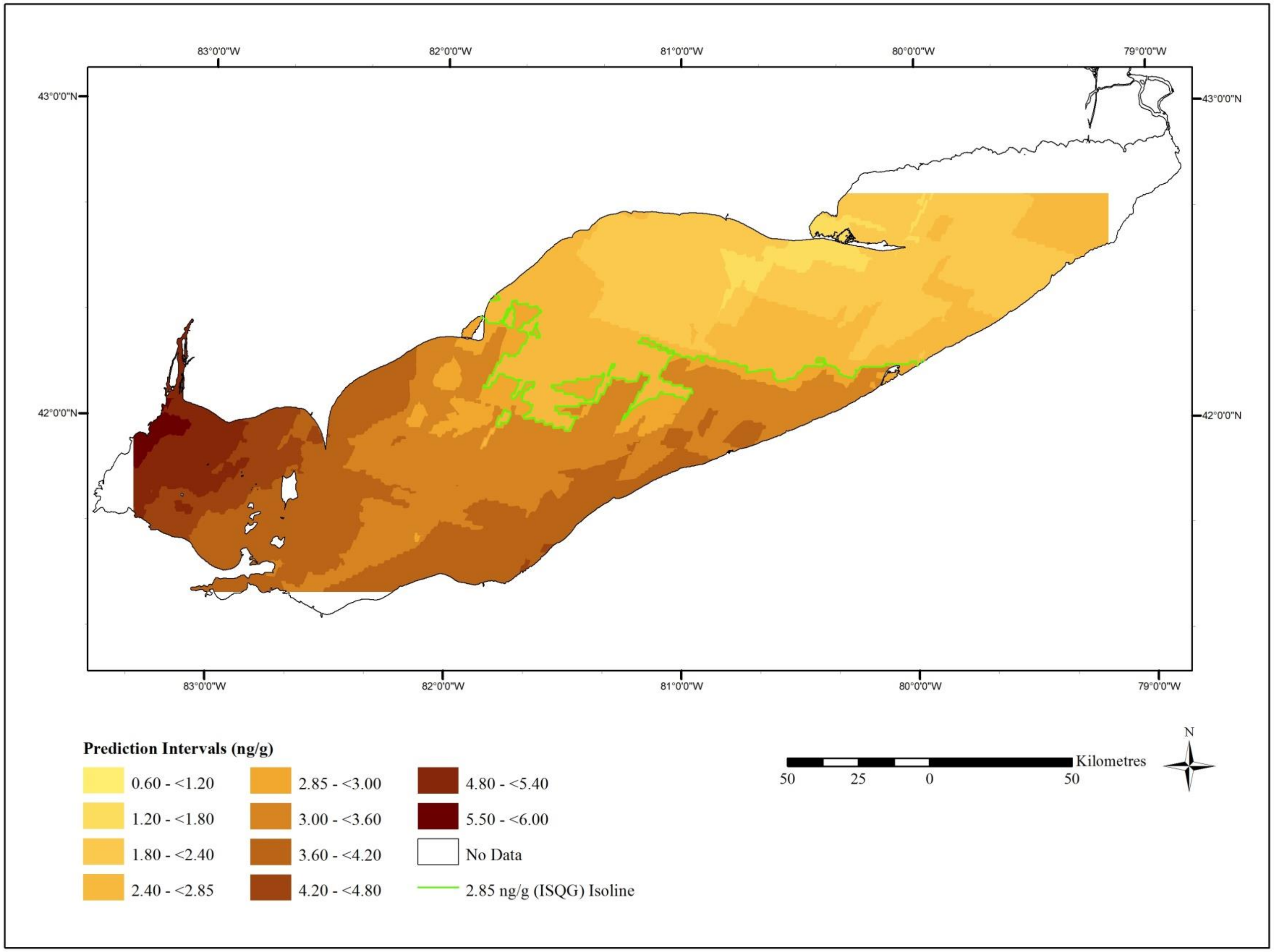

Figure 4.6: Dieldrin kriging results for Lake Erie 1997/1998

of -0.123 is the highest of the maps presented in this study. The SRMSPE is 0.990, indicating a slight overestimation of the prediction. As in the historical results, the RMSPE and ASE are low and similar. The prediction surface for the Lake Erie contemporary dataset is clearly not as smooth as the historical surface. This can be attributed to the increased influence of the closest neighbours on the prediction (ESRI, 2010). In order to smooth out the surface, parameters such as the nugget and lag size could have been altered when modeling the semivariogram, however the defaults were used to ensure consistency for comparisons.

A comparison of the historical and contemporary prediction surfaces shows a substantial temporal change in the distribution. Whereas the historical data indicated increasing levels in an eastward direction with a clear pattern of dieldrin deposition in the three major basins of the lake, the contemporary data shows a reversed trend. Over the 27 years between sampling periods, the amount of dieldrin in the sediments has clearly increased. This can be attributed to the continued use of dieldrin in high quantities in the region for approximately 15 years after the historical data were collected, and this persistent chemical is still making its way into the sediments via runoff and atmospheric deposition.

4.2.3 Lake Ontario

Figure 4.7 depicts the prediction surface for the historical (1968) Lake Ontario dataset. The pattern is similar to that of Lake Erie in that the highest concentrations of dieldrin are found in the depositional basins of the lake. The area displaying the highest degree of impairment is the Niagara basin. In this representation of the data, there are no

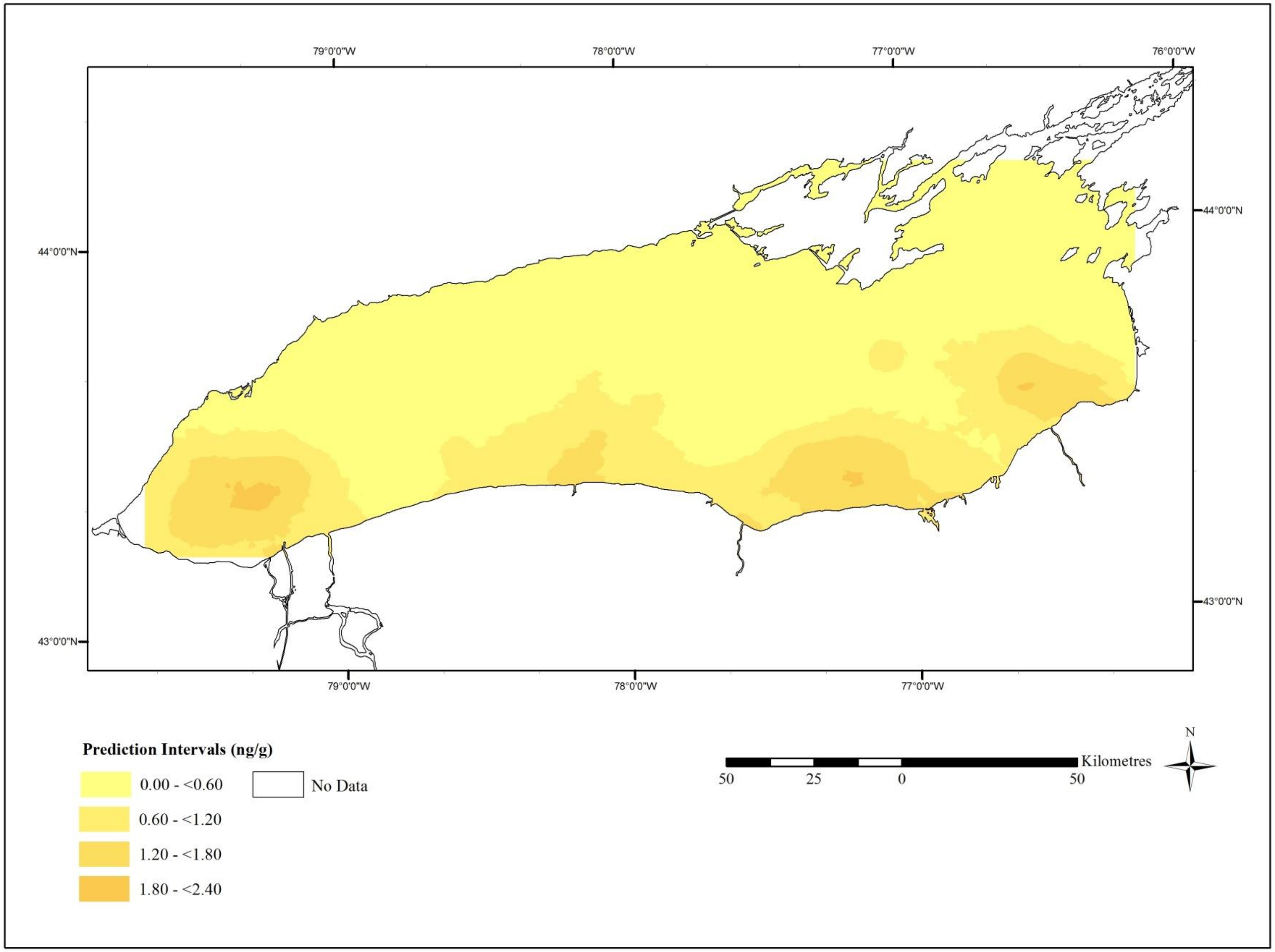

Figure 4.7: Dieldrin kriging results for Lake Ontario, 1968

areas estimated at levels over the ISQG. In contrast, almost 15% of the point measurements included in the calculation fell above the ISQG, and one of them even exceeded the PEL, albeit only slightly. The exceptionally high dieldrin readings in the Niagara basin are consistent with historical patterns of aldrin application in the Niagara Peninsula, which was very high until use was terminated here in 1970 (Frank et al., 1979). As with both of the Lake Erie results, the cross-validation error statistics are indicative of an accurate model.

The contemporary (1998) prediction surface for Lake Ontario can be seen in Figure 4.8. The areas with the highest levels of dieldrin are still the depositional basins of the lake, with the Rochester and Mississauga basins being the most impaired. According to this prediction, dieldrin contamination has declined in the sediments of the Niagara Basin. In contrast to the contemporary spatial patterns in Lake Erie, where much of the contamination was concentrated on the western side of the lake, Lake Ontario exhibits patterns of deposition across the three main basins of the lake. This is likely due to the counter-clockwise circulation patterns in Lake Ontario that allow contaminants to be transported to a greater extent lakewide (Marvin et al., 2002). While the error statistics are good for this model as well with an MPE of 0.034, the deviation from the grid sampling pattern and focus on depositional zones may have resulted in some overestimation in the non-depositional zones. Overall, the SRMSPE of 0.963 indicates the prediction surface might be slightly overestimated.

Though not as significant as in Lake Erie, temporal changes in the distribution can be seen in Lake Ontario as well. Dieldrin levels appear to have been reduced a great deal around the mouth of the Niagara River in the Niagara Basin of the lake. According to the

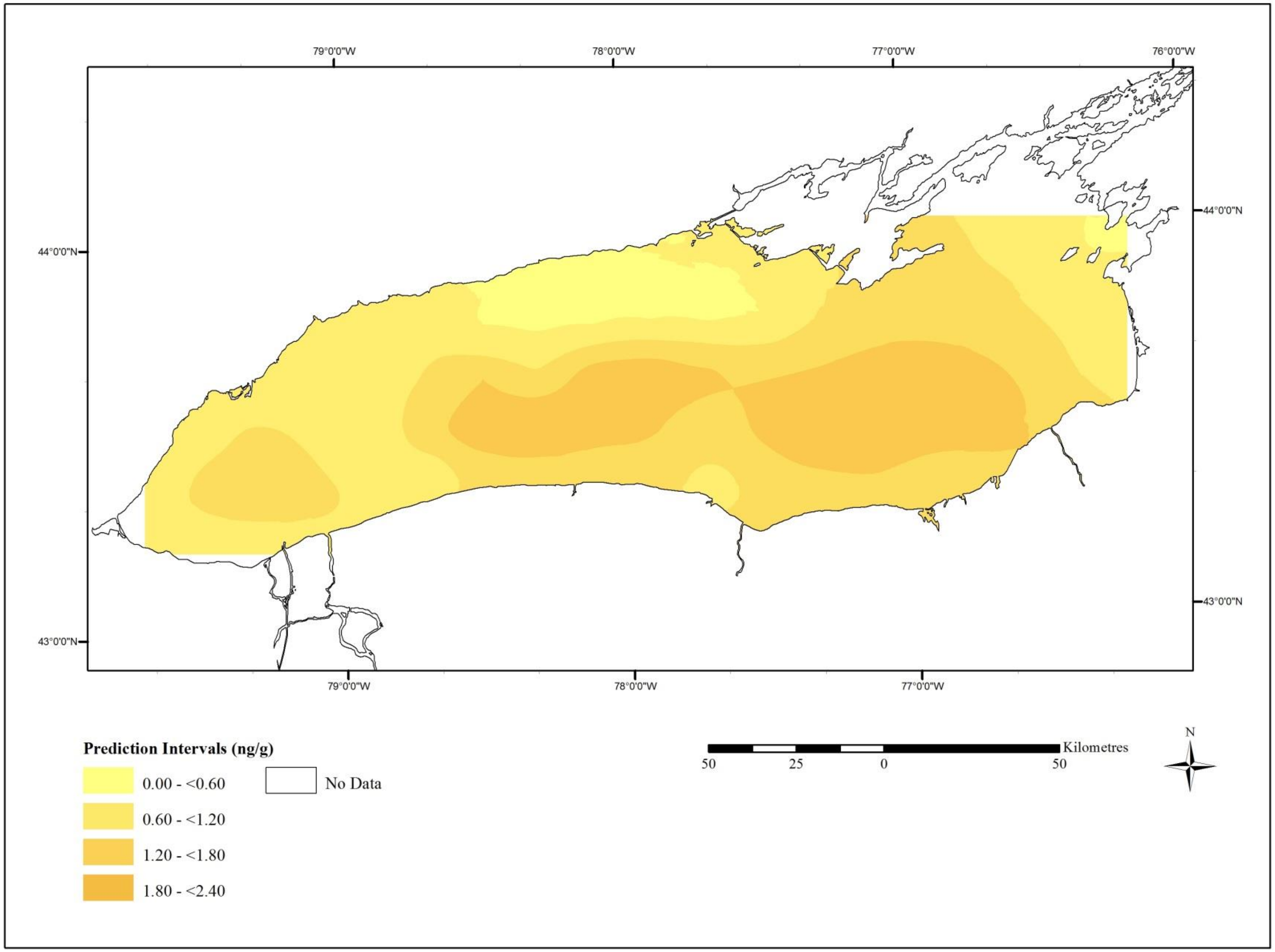

Figure 4.8: Dieldrin kriging results for Lake Ontario, 1998

Lake Ontario LaMP, toxic inputs into Lake Ontario from the Niagara River declined from 1960 to 1990, which at least partially explains the temporal change in this region of the lake. Both the Mississauga and Rochester Basins show a comparable degree of impairment as in the historical prediction.

4.3 Potential Sources of Error

Several factors must be taken into consideration when assessing the accuracy of the kriging analyses. The first issue is the decision of whether to log-transform the data prior to undertaking ordinary kriging. In most of the cases presented in this study, this was not an issue because skewness and kurtosis values fell within an acceptable range and log-transformation was not necessary. However, the Lake Ontario 1968 dataset presented a problem in this respect. It displayed a skewed distribution as indicated by elevated skewness and kurtosis values (2.48 and 6.98, respectively), therefore transformation of the data may initially be deemed appropriate. In this case, the untransformed dataset was used for analysis upon closer examination of the data. Since the log of zero is undefined, any records with values of zero would be removed from the analysis following transformation. Therefore, only 39% of the original Lake Ontario historical dataset would have been included for kriging analysis of the log-transformed dataset. The removed records would be those containing the lowest dieldrin values in the lake, and this would likely have reduced the accuracy of the prediction surface by creating overestimation in these areas. Additionally, the exclusion of the records containing values of zero would have led to a deviation in the regular grid pattern of the sampling locations, with large gaps appearing in the Lake Ontario contemporary dataset in the non-depositional zones. Because the most accurate results are obtained when samples are collected on a grid, this may have also had an impact on accuracy (Webster and Oliver, 2007).

Another discrepancy when directly comparing the historical and contemporary kriging results is the focus depositional locations in the contemporary datasets (Marvin et al., 2004a). Because it is the fine grained sediments in the depositional basins that toxic contaminants tend to adsorb to (Frank et al., 1977), this bias likely inflated the overall average dieldrin concentration of the dataset. The nearshore zones of the prediction surface are likely to be much less accurately estimated than the deeper basins.

CHAPTER 5: CONCLUSIONS

The Great Lakes system has become severely degraded over the past century largely due to industrialization and the manufacture and application of agricultural pesticides. While many of these toxic contaminants, including dieldrin, have been banned since the 1980s, their persistence has allowed them to remain in the system, sometimes at levels that are detrimental to the benthic ecosystem and the organisms they bioaccumulate within.

This study has aided in the interpretation of sediment-bound dieldrin distribution across the Great Lakes and Lake St. Clair. Graduated symbol maps were produced for each of the included lakes, allowing for some interpretation and comparison of contaminant amounts and temporal trends. The results of ordinary kriging in several of the datasets have provided a much clearer indication of the processes occurring in the lakes. In several of the datasets, point sources can be identified and the depositional patterns are evident. Substrate type, sedimentation patterns, and surrounding land use all appear to play a large role in the spatial distribution of dieldrin in sediment. While some potential sources of the contaminant have been identified, many areas of pesticide use are not reported in the literature, especially use in urban and industrial areas.

While all of the lakes included in this study exhibited some dieldrin contamination in both the historical and contemporary surveys, the concentrations in Lakes Superior, Huron, and St. Clair all fall well below the ISQG and are less concerning than those in the lower Great Lakes. The lack of spatial autocorrelation seen in the data of the upper lakes supports the literature regarding contaminant levels and potential sources. Dieldrin levels are quite low across these lakes and sources appear to be non-point for the most part, entering mostly via atmospheric deposition in Lake Superior in addition to agricultural runoff further downstream in the system. While some spatial autocorrelation can be seen in the graduated symbol maps for the lower Great Lakes, generation of the prediction surfaces using ordinary kriging allow for a better interpretation of spatial trends. The kriging results clearly show that dieldrin tends to accumulate within the depositional basins of Lakes Erie and Ontario, a trend less easily seen using dot maps alone. In Lake Erie, the distribution has changed over time. The historical results indicate no obvious point sources but do show a clear pattern of increased levels in the depositional basins, especially the Central and Eastern basins likely due mainly to agricultural runoff. By the time the contemporary data had been collected, a very distinct change in the spatial distribution was evident. The resulting prediction surface indicates that the Detroit River has become a major source of dieldrin loading into Lake Erie. In Lake Ontario, the reverse pattern is seen. While in the historical dataset dieldrin levels were most elevated in the Niagara Basin around the mouth of the Niagara River, the contemporary data indicates that this loading in this area may have decreased and the contaminated sediments have settled in the deeper Mississauga and Rochester basins.

Through comparison of the proportional circle maps and prediction surfaces, as well as examination of the cross-validation error statistics, the ordinary kriging results have proven to be quite accurate though in all cases the model slightly overestimated the distribution. All results were statistically valid. Due to the more intensive sampling pattern in the depositional zones of the lakes, these areas likely produce more accurate predictions than in the nearshore and non-depositional zones. Overall, the results of this study have allowed for an increased understanding of how this persistent chemical is distributed across the Great Lakes system.

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