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Temporal Trends and Origins of Lake Erie Cadmium Contamination in Relation to Sediment Substrate Type Using Multivariate Kriging Analyses

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Temporal Trends and Origins of Lake Erie Cadmium Contamination in Relation to Sediment Substrate Type Using Multivariate Kriging Analyses

Abstract

Using the kriging spatial interpolation method, Cd sediment contamination in Lake Erie from 1971 (263 samples) and 1997/1998 (55 samples) were mapped as continuous data surfaces. Although the most recent data set is two decades old, the roughly 25 year period between the two comprehensive lake-wide surveys represents a period of intense binational management action to reduce sources of contamination. To improve interpolation accuracy between two different sampling densities, auxiliary variables including lake-wide sediment substrate types were integrated into spatial analysis of Cd contamination patterns. The potential for adverse biological impacts posed by Cd sediment contamination to humans and aquatic life was measured by the threshold identified contamination along the Long Point Erie Sill and the south-western Ontario shoreline (composed predominately of glacial till) to be in the range of “practically unpolluted” by anthropogenic sources. The highest degree of anthropogenic pollution was found in regions of fine-grained materials (mud and silt). By combining Cd contamination surfaces with sediment substrate categories for analysis of anthropogenically-derived pollution, regions of the lake at higher risk for long-term sediment contamination can be targeted for continued monitoring.

Keywords

Cadmium, Kriging, Great Lakes, Sediment Contamination, Geostatistics, Spatial Analysis

1 INTRODUCTION

Cadmium (Cd) is a naturally occurring heavy metal in the earth's crust at trace levels (Wester et al. 1992). Natural concentrations of Cd in soils range from 0.06 to 1.1 $\mu\text{g/g}$ (USHHS, 2012), with a global average of 0.5 $\mu\text{g/g}$ (Kabata-Pendias and Mukherjee 2007). Particulate matter and debris resulting from forest fires, and volcanic eruptions contribute to natural inputs of Cd in the environment (Kabata-Pendias and Mukherjee 2007).

Neither humans, flora, nor fauna require Cd for metabolic functions and it is one of the most toxic metals added into our environment from anthropogenic sources (Kabata-Pendias and Mukherjee 2007). In the physical environment, Cd remains as a toxic heavy metal without biodegrading into “less harmful components” over time (Pachana et al. 2010). Long-term exposure or ingestion of Cd can result in serious human health complications (Sabo et al. 2013; Kabata-Pendias and Mukherjee 2007), ecosystem degradation (Pachana et al. 2010; Marvin et al. 2002), as well as air, water, and soil pollution (Idriss and Ahmad 2012; USHHS 2012).

Anthropogenic activities contributing to Cd pollution include (but are not limited to): metallurgy (Habashi 2011; Kot-Wasik 2005; Wester et al. 1992), industrial waste and waste management (Forsythe et al. 2016a; Dartmouth 2012; Wuana and Okieimen 2011), mining and mine tailings (Dartmouth 2012; Wuana and Okieimen 2011; Kot-Wasik 2005), agriculture and agricultural fertilizer (Forsythe et al. 2016b; Wuana and Okieimen 2011; Kot-Wasik 2005), coal power plants, and fossil fuel combustion (Dartmouth 2012; Wuana and Okieimen 2011; Kot-Wasik 2005). In 2000, the global use of Cd was 17,700 tons, 70% of which was used in the production of batteries (Kabata-Pendias and Mukherjee 2007); a common industrial and household item with a poor history of proper disposal (USHHS 2012).

This research aims to further refine multivariate kriging analysis techniques using cadmium contamination in Lake Erie as a potential indicator of a broader range of toxic contaminants with similar sources. The results will be examined within the context of Canadian Sediment Quality Guidelines for the protection of aquatic life. In addition, the examination of relationships between the presence of Cd in sediment samples and geochemical, and geomorphological characteristics of Lake Erie will be undertaken. This will enhance spatiotemporal models of lake-wide heavy metal contamination. The Index of Geoaccumulation (I_{geo}) will be utilized to investigate sediment contamination levels in combination with geostatistical (kriging) techniques for comparative analyses during the analysis period. Identifying the most vulnerable regions of Lake Erie to Cd contamination based on geochemical affinities of this heavy metal could contribute to a “weight of evidence” approach to lake-wide remediation and environmental policy implementation.

1.1 Fate of Cd Sediment Contamination in Aquatic Environments

The total amount of Cd present in sediment samples (measured in $\mu\text{g/g}$) identifies the magnitude of heavy metal contamination at specific locations. This measure, although valuable in assessing sediment contamination, is not indicative of the mobility or bioavailability of Cd within its environment (Idriss and Ahmad 2012; Prokop et al. 2003). Sorption and solubility characteristics of both heavy metals and sediment geochemistry determine the amount of Cd accessible for bioaccumulation throughout ecosystem components (Prokop et al. 2003; Adriaens et al. 2002; Luoma 1989).

Influential geochemical variables include sediment grain size, pH, and the presence of clay and organic materials (Idriss and Ahmad 2012; Adriaens et al. 2002). Bioaccumulation stemming from sediment contamination is particularly concerning as concentrations typically exceed those in the water above by several orders of magnitude (USHHS 2012; Luoma 1989). Toxicity and mobility of Cd contamination in sediments best describe this heavy metal's fate in aquatic environments (USHHS 2012; Pintilie et al. 2007). As a water pollutant, Cd is known to be more mobile than other heavy metals (Idriss and Ahmad 2012); as a sediment contaminant, the fate of Cd mobility is determined by geochemical conditions of the lake and lake bed (Pintilie et al. 2007).

1.2 Geochemical and Geomorphological Associations to Cd Contamination

Previous research has identified significant relationships between Cd and the particular geochemical conditions of contaminated sediments. Greater concentrations of heavy metal contamination (including Cd) are seen in fine-grained sediments (Adriaens et al. 2002; Marvin et al. 2002; Lick et al. 1994) near sources of industrial contamination (Kabata-Pendias and Mukherjee 2007; Marvin et al. 2002). Naturally occurring Cd is often found in coarse-grained materials such as bedrock and glacial till (Zaidi et al. 2012). Across numerous studies of aquatic environments around the world, researchers identified significant Cd contamination in sediment grain sizes measured as clay (Birch et al. 2015; USHHS 2012; Pintilie et al. 2007; Thomas et al. 1976). A relationship between Cd and pH of sediments was reported by Kabata-Pendias and Mukherjee (2007), the U.S. Department of Health and Human Services (USHHS 2012) and Idriss and Ahmad (2012) although the nature of the relationship is contested amongst researchers. Kabata-Pendias and Mukherjee (2007) suggest high mobility of Cd in sediments at pH greater than five, whereas the USHHS (2012) reports the opposite, stating that low pH values in sediment increase the mobility of Cd contamination. No significant relationship is identified between the two variables by Idriss and Ahmad (2012).

2 STUDY AREA AND DATA

Lake Erie sediments were first sampled for heavy metal contamination in 1971 by Environment and Climate Change Canada (Rukavina et al. 2013; Marvin et al. 2002). Due to the increased resource requirements associated with collecting sediment samples, and the requirement for more targeted sampling of specific offshore depositional areas, subsequent survey densities have decreased since the initial assessment. The first sediment survey collected samples from 263 locations following a 10 km by 10 km square grid pattern which decreased to 55 locations in the 1997/1998 survey (Figure 1).

Although the most recent data set is two decades old, the roughly 25-year period between the two comprehensive lake-wide surveys represents a period of cooperative binational management action to reduce sources of chemical contamination to the Great Lakes. The sediment sampling surveys are also the most comprehensive datasets that are available and they provide a robust basis for future survey design (Mitchell et al. 2018; Forsythe et al. 2016a; Forsythe and Marvin 2009). As a result, differences in the occurrence and distribution of cadmium between the 1971 and 1997/1998 surveys as determined using the multivariate kriging analyses are representative of reductions in loadings from primary anthropogenic sources.

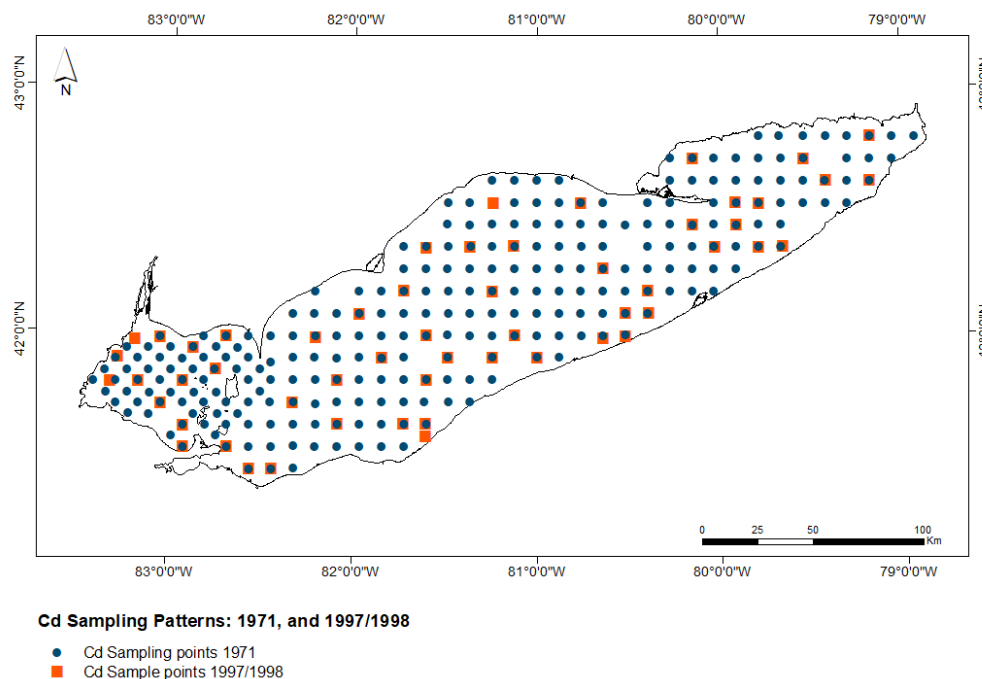


Figure 1. Sampling locations from the 1971 and 1997/1998 sediment surveys.

In Lake Erie, the average natural concentration of Cd in lake sediments is $<1 \mu\text{g/g}$ (Marvin et al. 2003). The mean Cd sediment contamination throughout the lake has exceeded this threshold since 1971 (Table 1).

Table 1. Descriptive statistics of Cd sediment contamination samples from Lake Erie.

| Year | Sample No. | Min. ($\mu\text{g/g}$) | Max. ($\mu\text{g/g}$) | Mean ($\mu\text{g/g}$) | Standard Dev. | Variance |
|-----------|------------|--------------------------|--------------------------|--------------------------|---------------|----------|
| 1971 | 263 | 0 | 10.8 | 2.36 | 1.48 | 2.2 |
| 1997/1998 | 55 | 0 | 4 | 1.23 | 0.93 | 0.87 |

2.1 Cd Contamination in Lake Erie

The Lake Erie watershed is entirely encompassed by the emerging Great Lakes Megaregion (RPA 2008; Figure 2) developed by “the extraordinary dynamics [of] such an enormous and powerful concentration of people and activities” (Murphy 1962). Lake Erie is the smallest Great Lake by volume (484 km³; GLIN 2016), situated between southern Ontario, Canada and the northern borders of Ohio, Pennsylvania, and New York in the United States. Intensive and haphazard urbanization, agricultural and industrial practices have been an environmental and ecosystem concern since the 1960’s (Ashworth 1987). Detroit, Michigan and Cleveland, Ohio are known sources of historical industrial pollution to Lake Erie and its basin (Marvin et al. 2002).

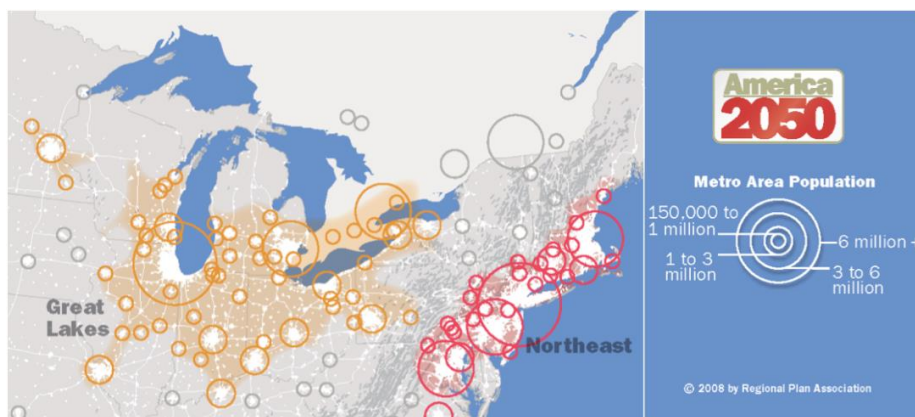


Figure 2. The Great Lakes Megaregion encompasses the entire Lake Erie watershed, extending inland to several major American cities, and municipal regions of southwestern Ontario (RPA 2008).

2.2 Sediment Substrate Classification

The western, central and eastern basins of Lake Erie are unique glacial, and geomorphic features physically divided by glacial moraines (Morang et al. 2011; Thomas et al. 1976). Depths decrease offshore, and from the western to eastern basin, remaining relatively flat throughout the central basin (Dusini et al. 2009; NGDC 1999). Thomas et al. (1976) describe a coarsening of sediment grains from the western to eastern basins apart from fine-grained sediments from shoreline erosion located in the deepest regions of the eastern basin. This eastward trend in sediment coarsening can be attributed to the prevailing west/southwest winds across Lake Erie, and the amount of wind-wave energy created across the expansive central Basin (Dusini et al. 2009; Thomas et al. 1976). Lake Erie contains a wide range of sediment grain sizes including glacial till (0.004 to <256 μm), bedrock (≥ 256 mm), sand (62.5 μm to 2 mm), gravel (2 to <256 mm), and clay (0.98 to 3.9 μm) (Haltuch et al. 2000). Figure 3 displays a Lake Erie substrate map originally created by Haltuch et al. (2000) from data collected by Lewis (1966) and Rasul et al. (1997).

Lake Erie can be further categorized into depositional and transport zones. Depositional basins (outlined in Marvin et al. 2002) are represented by substrate regions identified as “mud”. Fine sediment (0.98 to 3.9 μm) dominates the deep, offshore depositional basins (Thomas et al. 1976) including silts and clays according to the Wentworth Scale of Grain Sizes (Table 2 - Williams et al. 2011). Increasingly larger grain sizes are in shallower waters of the transport, or non-depositional zones (Marvin et al. 2002; Thomas et al. 1976) including the Pelee-Lorraine Ridge, and the Long Point-Erie Sill separating the western and central basins, and the central and eastern basins, respectively. Within seven kilometers of the shoreline is considered the littoral transport zone dominated by larger materials like sands, gravel, and glacial till (Morang et al. 2011; Dusini et al. 2009; Thomas et al. 1976). The distribution of substrates throughout Lake Erie is also indicative of lake-wide patterns of grain size and relative distribution. These spatial patterns are also representative of the relationships between grain sizes, lake circulation, wave-wind energy and overall movement of sediment types throughout the basin (Morang et al. 2011; Thomas et al. 1976).

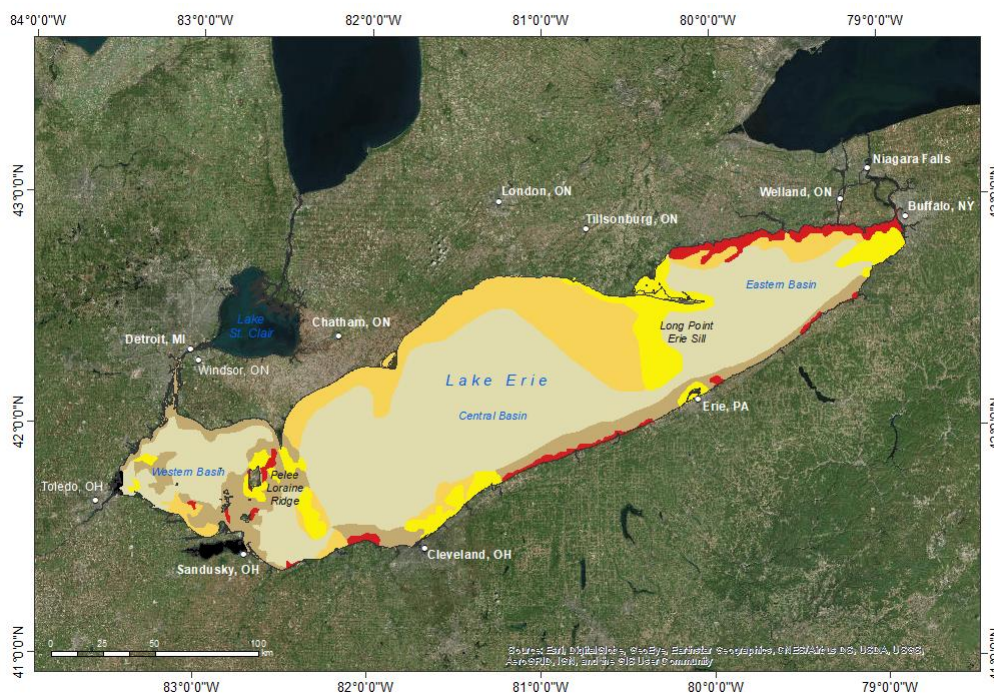


Figure 3. Lake Erie substrates, re-drawn from (Haltuch et al. 2000).

Table 2. The Wentworth (1922) Scale of Grain Sizes (Williams et al. 2011).

| Phi (ϕ) | Size (mm) | Wentworth Scale |
|----------------|----------------------|------------------------------|
| ≥ -8 | 256 mm | Boulders |
| -6 to -8 | 64 to <256 mm | Cobbles |
| -1 to -6 | 2 to <64 mm | Pebbles (granules to coarse) |
| 4 to -1 | 62.5 μ m to <2mm | Sand (very fine to coarse) |
| 8 to 4 | 3.9 to <62.5 μ m | Silt (very fine to coarse) |
| 10 to 8 | 0.98 to <3.9 μ m | Clay |

3 METHODOLOGY

Previous research used spatial analysis techniques in concert with Geographic Information Systems (GIS) - based statistical analyses to assess temporal changes in sources and loadings of contaminants to several of the Laurentian Great Lakes (Mitchell et al. 2018; Forsythe et al. 2016a; Forsythe et al. 2016b; Forsythe and Marvin 2009; Forsythe and Marvin 2005). Using these techniques, the production of statistically valid concentration estimates based on interpolated point data was possible and provided a better understanding of the occurrence and distribution of contaminants over large areas of open-lake depositional environments.

The results of this research provide for an improved understanding of the impact of anthropogenic contamination sources on open-lake environs and enable more directed monitoring and effective use of resources to track progress toward reducing the presence of toxics in the Great Lakes. Observations from previous analyses of Great Lakes sediment data sets have justified the focus on sampling of offshore depositional basins in more recent surveys as reductions in loadings of contaminants from historically

contaminated areas have been reduced, resulting in more diffuse distributions of contamination mostly confined to open-lake areas (Mitchell et al. 2018; Forsythe et al. 2016a; Forsythe et al. 2016b; Forsythe and Marvin 2009; Forsythe and Marvin 2005).

3.1 Kriging

The kriging spatial interpolation method as implemented in the ArcGIS software (Esri 2017), was used to create continuous data layers from Cd point data from the 1971 and 1997/1998 surveys. Ordinary kriging was used to estimate the concentration of Cd in lake sediments at unsampled locations for both datasets. The parameters used to model the distributions for both years are presented in Table 3. These were determined through experimentation, goodness of model fit based on semivariograms, and estimation error outputs (Figure 4).

Table 3. Kriging parameters used for modeling the 1971, and 1997/1998 datasets.

| Year | Distribution Model | Major Range (m) | Minor Range (m) | Direction (°) | Lag Distance (m) |
|-----------|--------------------|-----------------|-----------------|---------------|------------------|
| 1971 | Spherical | 100,000 | 50,000 | 90 | 30,832 |
| 1997/1998 | Gaussian | 100,000 | 50,000 | 90 | 30,001 |

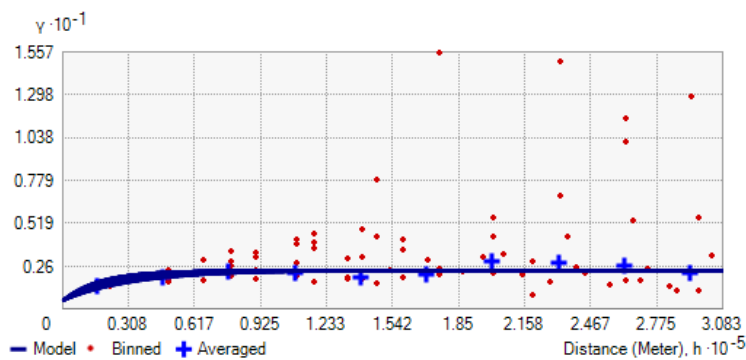


Figure 4. Example semivariogram illustrating the fit of an Exponential model to the 1971 Cd dataset.

The cross-validation statistics (Table 4) determine the amount of agreement between an interpolated value, and the measured value at the sample location (Li and Heap 2008; Ouyang et al. 2003). Valid kriging models provide accurate interpolated values when the Mean Prediction Error (MPE) is near 0, the Average Standard Error (ASE) is smaller than 20, the Standardized Root-Mean-Squared Prediction Error (SRMSPE) is near 1, and the MPE and ASE are similar (Forsythe et al. 2016b; Simpson and Wu 2014; Johnston et al. 2003). Predictive models with an MPE greater than and less than 0 represent under- and overestimation of kriged values in comparison to the actual measured values (Forsythe and Marvin 2005; Osburn 2000). Underestimation of variability in the kriged surfaces are identified when the SRMSPE is >1, while a SRMSPE <1 represents an overestimation of variability (Forsythe et al. 2016b; Johnston et al. 2003).

Table 4. Kriging cross-validation statistics of the 1971 and 1997/1998 sediment surveys.

| Year | MPE ($\mu\text{g/g}$) | RMSPE ($\mu\text{g/g}$) | SRMSPE ($\mu\text{g/g}$) | ASE ($\mu\text{g/g}$) | RMSPE-ASE ($\mu\text{g/g}$) |
|-----------|----------------------------|------------------------------|-------------------------------|----------------------------|----------------------------------|
| 1971 | 0.003 | 1.125 | 0.995 | 1.120 | 0.005 |
| 1997/1998 | -0.009 | 0.933 | 0.996 | 0.938 | -0.005 |

The Canadian Council of Ministers of the Environment (CCME) have established thresholds of freshwater sediment contamination based on the likelihood of the concentration to create harmful biological conditions (Forsythe and Marvin 2009; CCME 1999). Measured Cd contamination $<0.6 \mu\text{g/g}$ marks the Threshold Effect Level (TEL), at which harmful biological effects are not likely to occur (Forsythe and Marvin 2009; CCME 1999). Measured Cd contamination $\geq 3.53 \mu\text{g/g}$ denotes the Probable Effect Level (PEL), where adverse biological effects are likely to occur (Forsythe and Marvin 2009; CCME 1999). Cd concentrations measured between the TEL and PEL should be of temporal concern, as the measurement may increase or decrease between sampling surveys.

3.2 Index of Geoaccumulation (I_{geo})

The I_{geo} Index was an additional method utilized in this research to identify pollution intensity. Müller (1969) devised the first scale of measurement for heavy metal contamination in aquatic sediments (Gupta et al. 2014). The research was applied to contaminated sediments of the Rhine River (located in Western Europe) relative to water quality standards of the International Association of Waterworks in the Rhine Catchment (IAWR); this index of geoaccumulation (I_{geo}) is now a widely accepted measure of sediment enrichment (Birch et al. 2015; Gupta et al. 2014).

From a single sediment sample, the Index of Geoaccumulation identifies the amount of anthropogenic contamination relative to the background, or natural presence of the same metal (Förstner et al. 1993). I_{geo} calculates sediment enrichment by:

$$I_{\text{geo}} = \log_2(C_n/1.5B_n) \quad (1)$$

where C_n is the measured concentration of metal contamination, B_n is the measured background concentration of the same metal, which is multiplied by a factor of 1.5 to correct for lithologic effects (Gupta et al. 2014; Sabo et al. 2013). Sediment cores, dating back before anthropogenic influences, are used to measure and identify the background concentration of specific metals (Birch et al. 2015). Background concentrations of Cd in Lake Erie were measured at $<1 \mu\text{g/g}$ in all three basins (Marvin et al. 2003).

I_{geo} contamination values are ranked on a scale from 0 to 6, and then “graded” (Förstner et al. 1993) by the intensity of anthropogenic contamination (Gupta et al. 2014). The I_{geo} classification established by Müller (1981) is presented in Table 5. For reference, Förstner et al. (1993) determined the highest I_{geo} class (6) to be 100-fold greater than B_n .

Table 5. Index of geoaccumulation and pollution classifications (Müller 1981).

| Index of Geoaccumulation (I_{geo}) | I_{geo} Class | Pollution Intensity |
|--|-----------------|------------------------|
| >5 | 6 | Very strong pollution |
| >4-5 | 5 | Strong to very strong |
| >3-4 | 4 | Strongly polluted |
| >2-3 | 3 | Moderately to strongly |
| >1-2 | 2 | Moderately polluted |
| >0-1 | 1 | Unpolluted to moderate |
| <0 | 0 | Practically unpolluted |

4 RESULTS AND DISCUSSION

Cadmium as a non-essential heavy metal contaminant in Lake Erie, must be tracked spatially and temporally to anticipate potentially harmful ecosystem conditions.

4.1 Change Detection

To quantify and assess the degree and spatial extent of change in Cd sediment contamination, a change detection analysis was employed between the 1971 and 1997/1998 interpolated kriging surfaces. First, the 1971 interpolated layer was clipped to the extent of the 1997/1998 interpolation since the smaller sampling density of the 1997/1998 dataset resulted in different spatial interpolation extents. Next, to simplify the output change categories, Cd intervals for both time periods were aggregated to represent areas <TEL, \geq TEL to <PEL, and \geq PEL (Table 6). The contamination categories were then reclassified into unique numerical identifiers; for the 1971 dataset, <TEL was reclassified to 100, \geq TEL to <PEL to 200, and \geq PEL to 300. The 1997/1998 dataset was also reclassified as <TEL to 1, \geq TEL to <PEL to 2, and \geq PEL to 3. When added together using the Raster Calculator in ArcGIS (Esri 2017), unique combinations of the 8 numerical identifiers allowed for categorization of the output into degrees of Cd contamination change between 1971 and 1997/1998. All possible change combinations are listed in Table 7.

Table 6. Cd values organized by whole contamination intervals.

| Contamination Intervals <TEL ($\mu\text{g/g}$) | Contamination Intervals \geq TEL to <PEL ($\mu\text{g/g}$) | Contamination Intervals \geq PEL ($\mu\text{g/g}$) |
|---|---|---|
| 0 - <0.20 | \geq 0.6 - <1.58 | \geq 3.53 - <4.51 |
| \geq 0.2 - <0.40 | \geq 1.58 - <2.55 | \geq 4.51 - <5.48 |
| \geq 0.4 - <0.60 | \geq 2.55 - <3.53 | \geq 5.48 |

Table 7. Calculated contamination change categories and their meanings.

| Change Category | Description |
|-----------------|---|
| 101 | No change, <TEL |
| 102 | <TEL in 1971 to \geq TEL to <PEL in 1997/1998 |
| 103 | <TEL in 1971 to \geq PEL in 1997/1998 |
| 201 | \geq TEL to <PEL in 1971 to <TEL in 1997/1998 |
| 202 | No change, \geq TEL to <PEL |
| 203 | \geq TEL to <PEL in 1971 to \geq PEL in 1997/1998 |
| 301 | \geq PEL in 1971 to <TEL in 1997/1998 |
| 302 | \geq PEL in 1971 to \geq TEL to <PEL in 1997/1998 |
| 303 | No Change, \geq PEL |

4.2 Spatial Analysis

Three areas of elevated contamination were identified from interpolation of the 1971 Cd survey (Figure 5). Along the southern extent of the central basin, two areas off the shores of Cleveland and Ashtabula, Ohio were identified to contain Cd sediment contamination $\geq 3.53 \mu\text{g/g}$ or \geq PEL. Even greater concentrations of Cd were predicted from the lower reaches, and mouth of the Detroit River discharging into the western basin of Lake Erie. Cd contamination in this location is likely to exceed $5.48 \mu\text{g/g}$, more than 1.5x the PEL. In total, Cd contamination \geq PEL is estimated to represent $3,246 \text{ km}^2$, or 13% of Lake Erie sediments within the study boundaries. Moderate levels of sediment contamination were estimated in over 80% of the $21,277.75 \text{ km}^2$ Lake Erie study area. Cd concentrations from 0.6 to $3.53 \mu\text{g/g}$ dominate most of the central basin, and the entirety of the eastern basin. Along portions of the Pelee-Lorraine Ridge, and the Long Point-Erie Sill are the lowest estimated concentrations of Cd contamination ranging from 0.6 to $<2.55 \mu\text{g/g}$.

The 1997/1998 sediment survey predicted lower overall Cd contamination values across the lake (Figure 6). Nearly 90% of the lake's study area was estimated to have contamination values \geq TEL to <PEL; the range of Cd values \geq TEL to <PEL in the 1997/1998 contamination map do not exceed $2.55 \mu\text{g/g}$ in contrast to the maximum interval measurement of $<3.53 \mu\text{g/g}$. Sediment contamination <TEL was identified in $2,581 \text{ km}^2$, or 10.5% of the study area, exclusively in the eastern basin. Interestingly, the southern shore of the central basin experienced higher concentrations of Cd nearest Cleveland and Ashtabula, Ohio, than any other area of the lake. This spatial pattern was also visible in the distribution of sediment contamination from the 1971 survey, although clearly not of the same magnitude in 1997/1998.

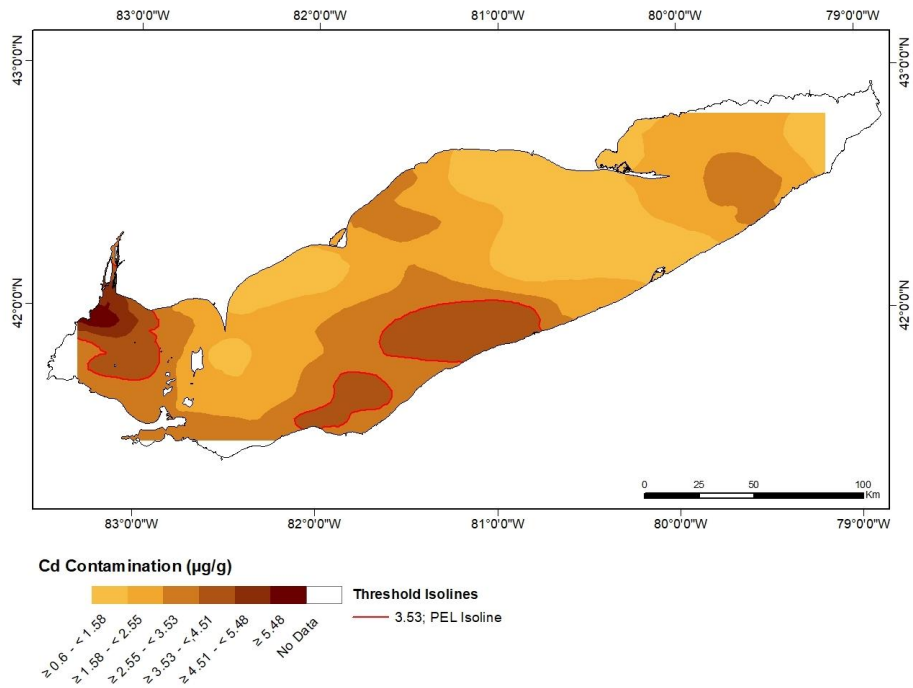


Figure 5. Kriging results of the 1971 Cd contamination in Lake Erie.

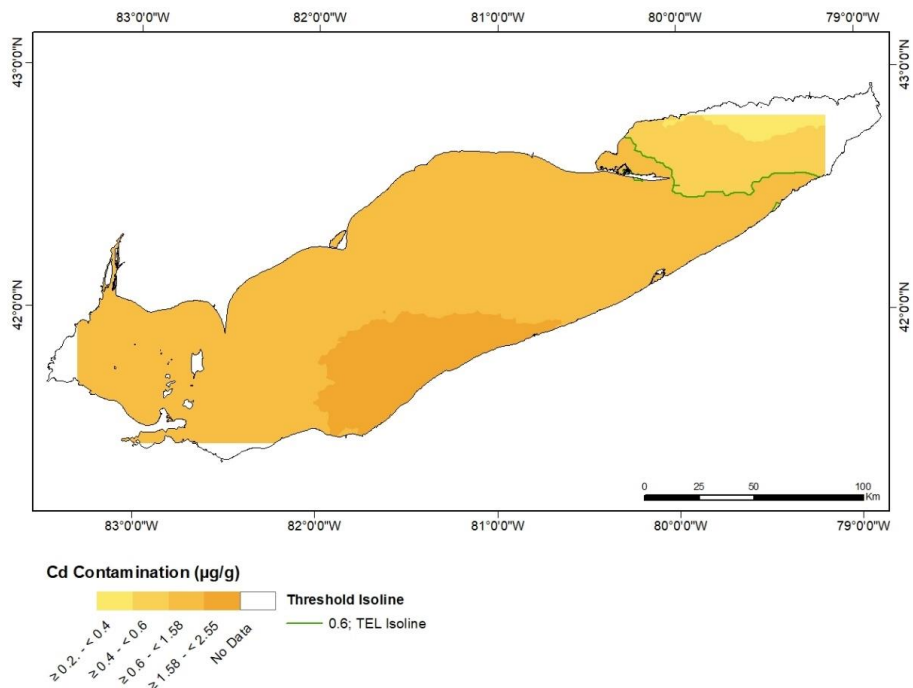


Figure 6. Kriging results of the 1997/1998 Cd contamination in Lake Erie.

The result of detecting spatiotemporal change in sediment contamination between 1971 and 1997/1998 is presented in Figure 7. The seemingly simplistic result was to be expected considering the contamination patterns presented in the 1971 and 1997/1998 maps. Areas of elevated sediment contamination identified from the 1971 survey were reduced to Cd values measuring \geq TEL to $<$ PEL in 1997/1998. The greatest magnitude of change was calculated near the mouth of the Detroit River, over an expanse of 1,554.75 km² or 6% of the study area. Here sediment contamination was estimated to exceed more than 5.48 $\mu\text{g/g}$ in 1971. Cd concentrations ranging from 3.53 to 10.8 $\mu\text{g/g}$ in 1971 decreased to a range of 0.6 to 1.57 $\mu\text{g/g}$ in 1997/1998, reducing the range of Cd contamination in these sediments from 7.27 $\mu\text{g/g}$ (1971) to 0.96 $\mu\text{g/g}$ (1997/1998). In addition to the reduced Cd levels in the eastern basin by 1997/1998, approximately 24% of the study area reported a downward contamination trend from Cd values \geq PEL, to \geq TEL to $<$ PEL. Between the two survey periods, the majority of the lake (18,593 km²) maintained a consistent level of Cd contamination at the \geq TEL to $<$ PEL interval.

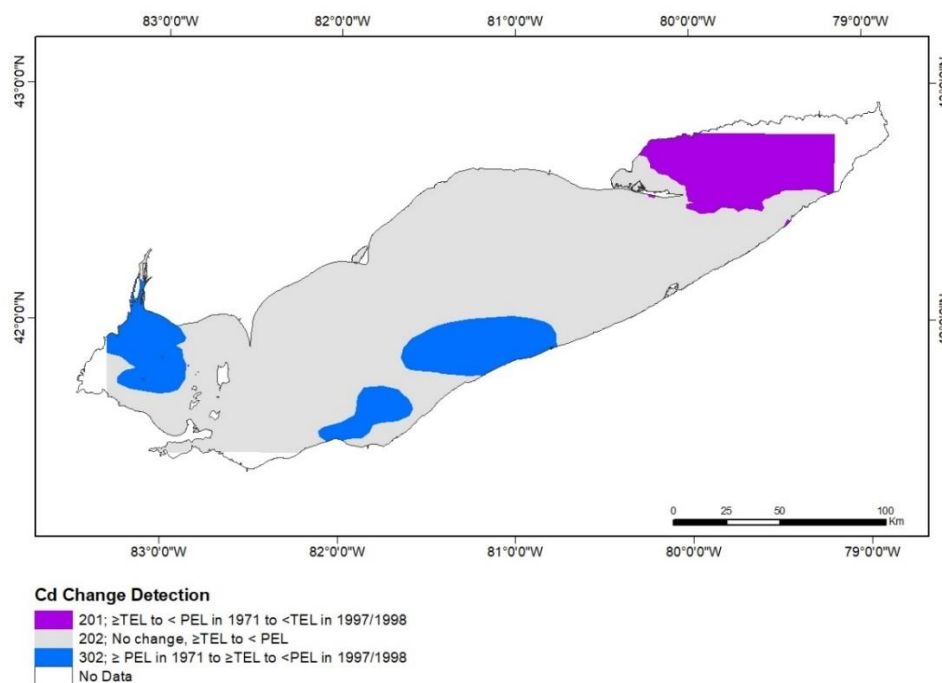


Figure 7. Change in Cd contamination concentrations and extent between 1971 and 1997/1998.

Kriging of Cd concentrations and calculating I_{geo} values were completed simultaneously, but were analysed separately. The Raster Calculator was used to calculate the I_{geo} value for the 1971 and 1997/1998 datasets (Esri 2017). The I_{geo} layer was classified by the Sediment Accumulation Index (Müller 1981) with intervals ranging from <0 = “practically unpolluted” to >5 = “very strong pollution” (Table 3). The same method of change detection was applied to the I_{geo} maps from both years, just as it was employed with the kriged maps. The classified I_{geo} maps for 1971 and 1997/1998 were analyzed with the interpolated concentration maps, and the substrate map featured in Figure 8.

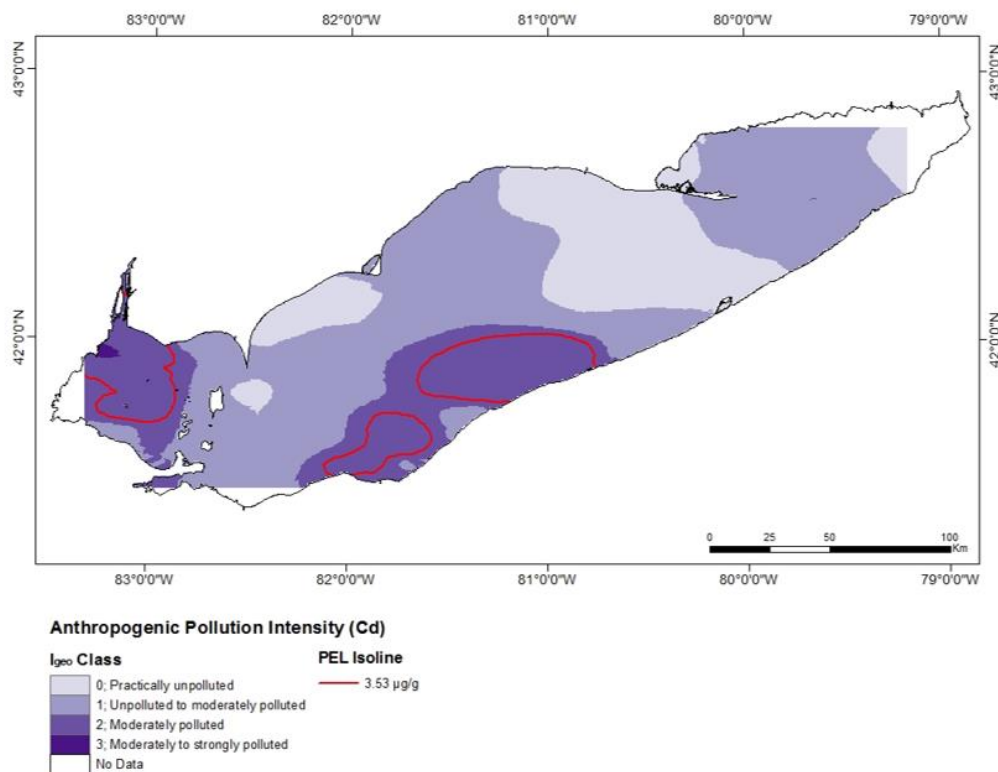


Figure 8. Anthropogenic pollution intensity measured by the index of geoaccumulation in contrast to the PEL isoline for the 1971 Cd dataset.

From the 1971 survey, sediment along the Long Point-Erie sill was determined to be “practically uncontaminated” ($I_{geo}=0$) with Cd aside from that occurring naturally. This level of pollution intensity was also identified in a section of the eastern basin, and along the northwestern shore of the central basin. Contamination levels \geq TEL to $<$ PEL ranging from 1.58 – 3.53 µg/g were classified as “unpolluted to moderately polluted” ($I_{geo}=1$) by the sediment accumulation index. I_{geo} indices calculated “moderate pollution” (5,573.25 km²) that exceeded the isoline boundaries of Cd concentrations predicted to be \geq PEL (3,246 km²) in 1971. For example, the highest values of anthropogenic Cd were identified in sediments at the mouth of Swan Creek, MI, southwest of the Detroit River inlet to Lake Erie. Cd concentrations were predicted to exceed 5.48 µg/g from the 1971 survey; a subset of this highly contaminated sediment was identified to be “moderately to strongly polluted” from anthropogenic sources of Cd alone.

Where Cd sediment contamination was predicted to be $<$ TEL in the 1997/1998 survey, the I_{geo} index also measured the levels of contamination in this region to be “practically uncontaminated” (Figure 9). This degree of pollution intensity suggests that traces of Cd in eastern basin sediments are naturally occurring. Along the southern shore of the central basin, most Cd values predicted between 1.58 and $<$ 2.55 µg/g were measured to contain “unpolluted to moderately polluted” sediments on the I_{geo} index. Several small areas of “unpolluted to moderately polluted” sediment stand out against the “practically uncontaminated” state of the western basin; most notably the approximate 36 km² area near the mouth of Swan Creek.

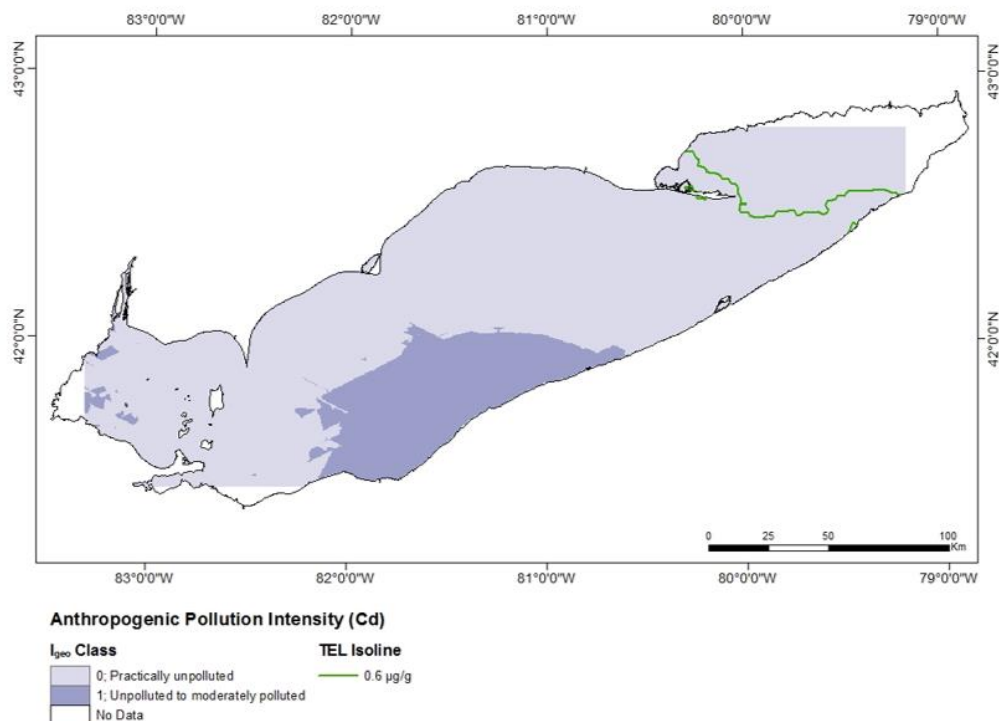


Figure 9. Anthropogenic pollution intensity measured by the index of geoaccumulation in contrast to the PEL isoline for the 1997/1998 Cd dataset.

At the mouth of the Swan Creek, a small section of Lake Erie was identified to have Cd contamination \geq PEL in 1971, and a higher I_{geo} Index value than surrounding areas in 1997/1998 (Figure 10). These research findings align with previous studies which used enrichment factors to establish connections between patterns of sediment contamination and historic anthropogenic activities in the lower Great Lakes (Marvin et al. 2002).

Prior to the enactment of the Great Lakes Water Quality Agreement (GLWQA), the Great Lakes Steel Co., Allied Chemical Corp., Ford Motor Co., and Scott Paper Co. were identified as sources of industrial, inorganic and organic pollution in the Detroit River, Huron River and Swan Creek (USEPA 1965). Until 1967, spoils from the dredging of navigational routes in the Detroit River were often dumped into the open waters of Lake Erie (USAED 1974); the impacts of dredging activities were acknowledged for their economic benefits regardless of environmental degradation (Miller 1998).

4.3 Raster Overlay and Sediment Substrate Analysis

To assess the patterns and relationships amongst Cd contamination and sediment substrate types, both the 1971 and 1997/1998 predicted contamination maps were reclassified to $<$ TEL, \geq TEL to $<$ PEL, and \geq PEL contamination intervals. When overlaid with sediment substrate types, strong patterns of Cd contamination appear in regions of the lake dominated by clay, silt, and glacial till.

In 1971, contamination \geq PEL represented 3,246 km² or 13% of the study area (Figure 11). When overlaid with the substrate map, 90.44% of contamination \geq PEL was

identified in regions dominated by mud (68.86%) and sand/mud (21.58%). The remaining 9.56% of the study area with contamination \geq PEL was identified in regions of bedrock (3.74%), sand/gravel (3.54%), and glacial till (1.66%). The majority of Cd contamination in 1971 was predicted to range from \geq TEL to $<$ PEL, representing 21,227.75 km² or 87% of the study area; the presence of contamination values $<$ TEL was not identified in the 1971 survey.



Figure 10. Extent of anthropogenic contamination identified by the I_{geo} Index around the tributaries of Swan Creek and the Huron River in the western basin of Lake Erie. I_{geo} class=3, 1971, outlined in dark purple; I_{geo} class=1, 1997/1998, outlined in light purple (Esri 2017).

Again, most of the contamination values \geq TEL to $<$ PEL were identified in substrate regions dominated by mud (56.55%), as well as glacial till (20.85%). The remaining contamination \geq TEL to $<$ PEL was identified in sand/mud (10.96%), sand/gravel (9.28%), bedrock (1.9%), and no data ($>$ 1%). Surface area (km²) coverage of Cd contamination \geq TEL to $<$ PEL and \geq PEL by substrate type are presented in Table 8.

Similar relationships were identified between Cd contamination, mud, and glacial till from the 1997/1998 survey (Figure 12). In 1997/1998, contamination \geq TEL to $<$ PEL represented 21,937.5 km² or 89% of the study area; the presence of contamination values \geq PEL was not identified from the 1997/1998 survey. The majority of Cd contamination \geq TEL to $<$ PEL was identified in substrate regions of mud (56.71%) while the same range of contamination was found in glacial till covering 18.74% of the study area. The remaining contamination \geq TEL to $<$ PEL was identified in sand and mud (13.63%), sand and gravel (9.18%), bedrock (1.39%), and no data ($>$ 1%).

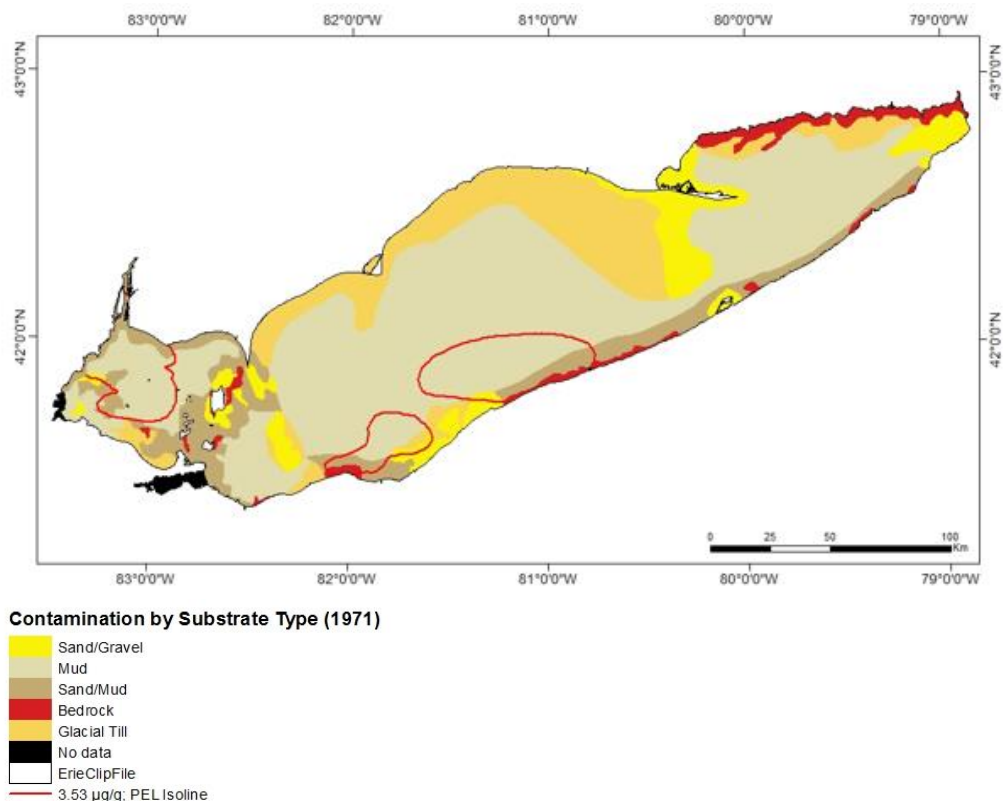


Figure 11. Cd contamination \geq TEL to $<$ PEL and \geq PEL from the 1971 dataset by substrate type.

Table 8. Surface area (km²) coverage of Cd contamination \geq TEL to $<$ PEL and \geq PEL by substrate type from the 1971 dataset.

| Substrate Type | $<$ TEL (km ²) | \geq TEL to $<$ PEL (km ²) | \geq PEL (km ²) |
|----------------|----------------------------|--|-------------------------------|
| Mud | n/a | 12,033.25 | 2,021.5 |
| Sand/Mud | | 2,331 | 633.5 |
| Sand/Gravel | | 1,975 | 115 |
| Glacial Till | | 4,435.5 | 54 |
| Bedrock | | 404 | 121.25 |

Almost exclusively in the eastern basin, Cd contamination $<$ TEL represents 2,581 km², or 11% of the study area. The majority (70.75% of the study area) of sediments contaminated with Cd $<$ TEL were identified in substrate regions of mud. Low levels of contamination were also found in regions dominated by glacial till (15.57%), as well as bedrock (8.6%), sand and gravel (3.12%), sand and mud (1.85%), and no data ($>$ 1%). Surface area (km²) coverage of Cd contamination and $<$ TEL and \geq TEL to $<$ PEL by substrate type are presented in Table 9.

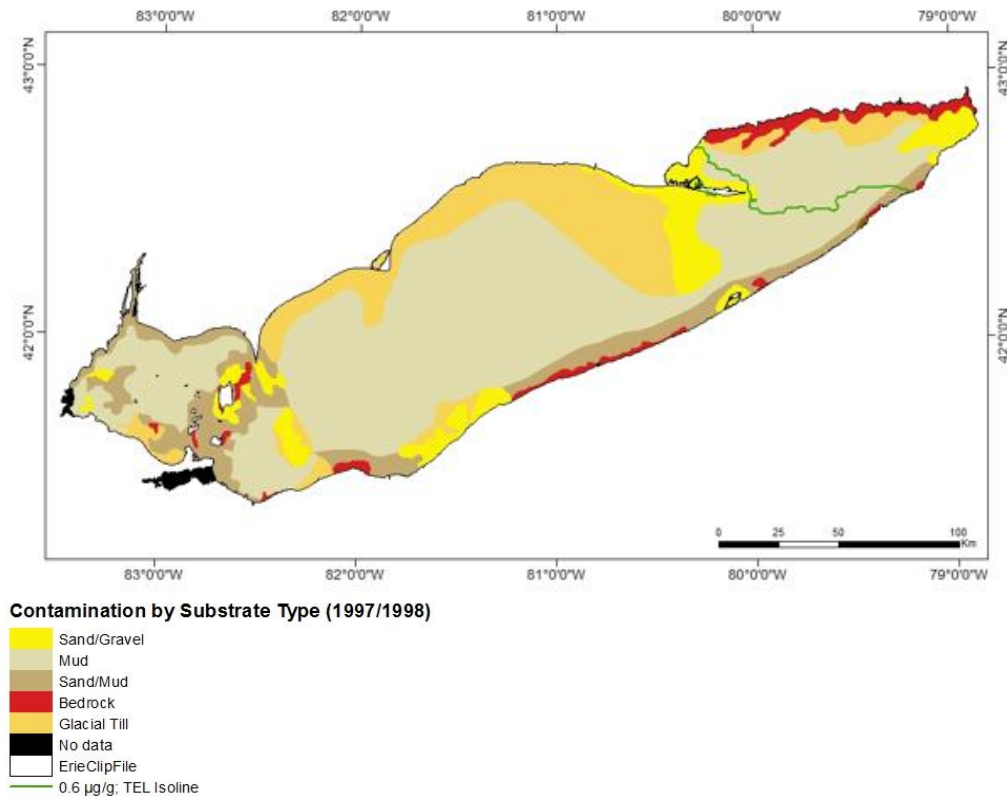


Figure 12. Cd contamination <TEL and ≥TEL to <PEL from the 1997/1998 dataset by substrate type.

Table 9. Surface area (km²) coverage of Cd contamination <TEL and ≥TEL to <PEL by substrate type from the 1971 dataset.

| Substrate Type | <TEL (km ²) | ≥TEL to <PEL (km ²) | ≥PEL |
|----------------|-------------------------|---------------------------------|------|
| Mud | 1,826 | 12,440.50 | n/a |
| Sand/Mud | 47.75 | 2,990.50 | |
| Sand/Gravel | 80.5 | 2,014.5 | |
| Glacial Till | 401.75 | 4,111.75 | |
| Bedrock | 222 | 304.25 | |

The GLWQA has likely been the driving force in heavy metal pollution reduction in all four American shoreline states (Michigan, Ohio, Pennsylvania and New York) and the Canadian Province of Ontario (IJC 1972). Since 1972, the GLWQA has strived to “restore and maintain the chemical, physical, and biological integrity of the Great Lakes Basin Ecosystem” (IJC 2002). Interpolated sediment contamination maps show a lake-wide trend of decreasing Cd levels ≥PEL from 1971 to 1997/1998. By 1997/1998, 89.4% of the interpolated area was predicted to contain Cd contamination levels between the ≥TEL to <PEL threshold; sediment in the remaining area (almost exclusively in the eastern basin) was measured to be contaminated with Cd <TEL, and below the background levels of naturally occurring Cd. Specifically, the GLWQA is a form of administrative law, which intends to alter human behavior towards environmental stewardship and responsibility in the Great Lakes Basin (Tran 2009; IJC 1994; IJC 1982), another potential factor leading to the overall lake-wide decline in Cd contamination.

Since natural background levels of Cd in Lake Erie are measured at $<1 \mu\text{g/g}$, the $\geq\text{TEL}$ to $<\text{PEL}$ threshold of contamination is subject to interpretation of Cd values ranging from $>0.6 \mu\text{g/g}$ to $<1 \mu\text{g/g}$. Contamination values in this range are considered to be naturally occurring traces of Cd, and are not likely to pose adverse biological effects, being so close to the TEL. That being said, Cd values above $1 \mu\text{g/g}$ and $<\text{PEL}$ are increasingly likely (up to $<3.53 \mu\text{g/g}$) to cause adverse biological impacts from anthropogenic sources (I_{geo} values >1).

All Cd contamination identified to be $\geq\text{PEL}$ in 1971 is also suggested to be of anthropogenic origins by the I_{geo} Index. Overlay analysis identified these regions of high contamination to be in substrates dominated by mud. Moderate levels of Cd contamination ranging from $\geq\text{TEL}$ to $<\text{PEL}$ in 1971 were predominately located in glacial till substrates. Since glacial till is a medium for naturally occurring Cd, it was not surprising to identify contamination values ranging from 0.6 to $<1 \mu\text{g/g}$ along the Long Point-Erie Sill, and the northwestern shoreline of Lake Erie. Anthropogenically sourced contamination in 1997/1998 was identified by the I_{geo} Index along the Ohio shorelines outside of the traditionally industrial city of Cleveland, Ohio whereas the eastern basin of Lake Erie measured contamination $<\text{TEL}$ and as “practically uncontaminated” by the I_{geo} Index.

5 CONCLUSIONS

The results of this research further refined spatial analysis techniques for a broad range of toxic contaminants with similar sources. The visualization of Cadmium pollution patterns was improved and the use of the Threshold Effect Level and Probable Effect Level assisted in identifying regions of Lake Erie where adverse environmental effects were likely to pose health risks to aquatic life. When compared against the Geoaccumulation Index, high-risk regions (i.e. greater than or equal to the Probable Effect Level) fell within the boundaries of anthropogenically sourced Cadmium contamination. When sediment substrate characteristics were integrated into overlay analyses, interpolated Cadmium contamination surfaces were generated that added additional context with respect to polluted sediment distribution between 1971 and 1997/1998. They effectively assess spatial and temporal changes in sources of sediment contamination throughout the lake. The levels of Cadmium contamination in fine-grained sediments which pose the greatest risk of adverse biological impacts (greater than or equal to the Probable Effect Level) are likely the result of direct pollution originating from human activities.

Spatiotemporal models of lake-wide heavy metal contamination were enhanced through this research. The identification of the most vulnerable regions of Lake Erie related to Cadmium contamination based on geochemical affinities contributes to a “weight of evidence” approach that can be useful for lake-wide remediation efforts and environmental policy implementation. The results weigh heavily in favor of long-term sediment remediation efforts and environmental policy implementation specifically in the western Lake Erie basin and along the Ohio shoreline. Excessive sediment contamination from anthropogenic sources was revealed throughout Lake Erie after considering naturally occurring levels of Cadmium (less than $1 \mu\text{g/g}$). Patterns of contamination less than the Threshold Effect Level and greater than or equal to the Probable Effect Level are strongly reflected by the distribution of geoaccumulation indices. The geoaccumulation classes also provide some context related to Cadmium

contamination greater than or equal to the Threshold Effect Level to less than the Probable Effect Level.

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