Assessing Sediment Contamination in the Buffalo River

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Abstract

In the Great Lakes Water Quality agreement between Canada and the United States, the Buffalo River is listed as an Area of Concern (AoC). Contamination of water and sediment in this area from industrial and manufacturing sources has led to a degraded environment. This study analyzes surface sediment contamination by examining the contamination patterns of arsenic, lead, mercury, and nickel within a section of the Buffalo River. These particular heavy metals reveal the general patterns of contamination within the study area. The kriging spatial interpolation technique as implemented in the ArcGIS Geostatistical Analyst was utilized to generate prediction surfaces. The research shows that the river is highly contaminated by heavy metals. Pollution levels exceed sediment quality guidelines in terms of the Threshold Effect Level (TEL) and the Probable Effect Level (PEL) as defined by the Canadian Council of Ministers of the Environment (CCME).

1 Introduction

The City of Buffalo, New York is located at the eastern end of Lake Erie which is one of the Laurentian Great Lakes. Together the lakes contain one-fifth of the world's fresh surface water with only the polar ice caps and Lake Baikal in Siberia containing more (GLIN 2004).

In the Great Lakes Water Quality agreement between Canada and the United States, the Buffalo River is listed as an Area of Concern (AoC). The Buffalo River was contaminated with toxic elements as a result of decades of industrial activity in the surrounding land (SUTTON 2006). Three main contributors (ExxonMobil Corporation, Honeywell Corporation, and PVS Chemicals) to natural resource damage in the Buffalo River are being pursued for damages by the State of New York. These companies owned and operated industrial facilities along the Buffalo River (ENVIRONMENTAL NEWS SERVICE, 2009). Currently, ‘there are more than 45 inactive hazardous waste sites, 33 combined sewer overflow outfalls and several sewage systems’ located throughout the Buffalo River watershed (US EPA, 2008). These are some of the factors that contribute to the past and present pollution of the Buffalo River.

The United States Department of the Interior, the Tuscarora Nation, and the State of New York contributed to a preassessment screen for the Buffalo River (USDI ET AL. 2008). Exxon Mobil operated two different businesses along the Buffalo River. First, a dump site was operational for the purpose of disposing waste including demolition debris, tank sediments, and sewer sediments. The site was used by Mobil Oil (which merged with Exxon) until 1976 to dispose of tetraethyl lead, sludge, and other wastes (USDI ET AL.

2008), which have been found in Buffalo River sediments. Secondly, Mobil Oil operated an oil refining facility, which had its outfall discharge directly into the Buffalo River. In addition to the waste discharged into the river, a spill at the facility occurred September 2004 (USDI ET AL. 2008). PVS Chemicals controlled a manufacturing facility along the Buffalo River. The site manufactured sulphuric acid, sulphuric trioxide, nitric acid, along with other chemicals, which resulted in 10 million gallons (~38 million litres) per day of cooling water being discharged directly into the Buffalo River (USDI ET AL. 2008).

Sediment quality in this study is determined by the Threshold Effect Level (TEL) and Probable Effect Level (PEL) as defined by the Canadian Council of Ministers of the Environment (CCME). The TEL specifies concentrations where adverse biological effects are expected to occur rarely (<25%), and the PEL specifies concentrations where adverse biological effects are expected to occur frequently (>50%) (CCME 2001). The area between the TEL and PEL levels is expected to have organic irregularities occur occasionally. These guidelines are used in this study to maintain comparability with previous work done in the Great Lakes Basin (FORSYTHE ET AL. 2004; FORSYTHE & MARVIN 2005; FORSYTHE & MARVIN 2009) and collaborators in ongoing research projects.

2 Study Area and Data

The Buffalo River is part of the Buffalo Watershed, which flows westward through Buffalo, New York and empties out into Lake Erie (Figure 1). The land use in the upper basin of the river is mainly agricultural and woodland, whereas the land use in the lower basin is industrial and urban (SHREERAM 2004). This study looks at a specific section of the Buffalo River, where sediment samples were taken. Figure 2 displays the section of the river that is of importance in this study, located just south of the City of Buffalo.

The New York State Department of Environmental Conservation (NYSDEC) collected the data used in this research in 2005 (SUTTON 2006). This study will focus on four contaminants which represent the general patterns of heavy metal contamination although the dataset consisted of more than one-hundred different pollutants. The NYSDEC collected the data for the purpose of credibly determining the extent of sediment contamination within the Buffalo River. For this reason, the sediment cores were drilled systematically along regularly spaced transects (SUTTON 2006). These samples were divided into two categories: surface (including sediments consisting of core samples approximately 30cm in depth) and subsurface (including sediments consisting of core samples below a depth of 30cm). This study uses 111 surface sediment samples. The distribution of these sample points is seen in Figure 2 and remains constant for each of the contaminants studied in this project. Descriptive statistics for each contaminant are presented in Table 1.

Fig. 1: Study Area (the black rectangle indicates the location of the Buffalo River analysis area - satellite image from Google Maps together with ESRI ArcCanada 3.0 (2003) shapefiles)

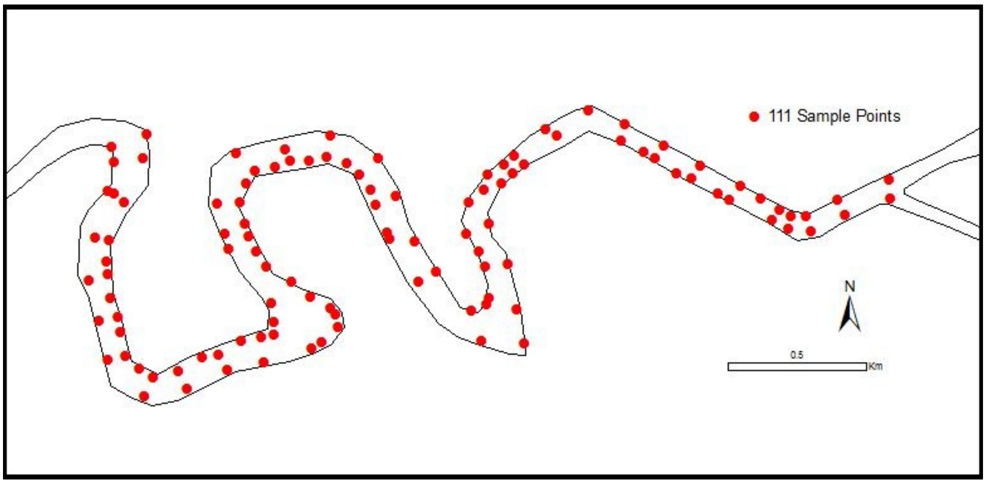

Fig. 2: The sediment sampling locations in the Buffalo River AoC

Tab. 1: Descriptive Statistics of the Contaminants

Contaminant	Minimium	Maximum	Average	Median	Standard Deviation
Arsenic	2.6	417.0	14.0	8.9	39.4
Lead	8.1	2600.0	87.1	36.3	251.9
Mercury	0.0	7.1	0.3	0.1	0.8
Nickel	11.2	53.7	29.3	29.1	6.0

3 Ordinary Kriging and Methodology

Kriging interpolation methods were initially developed for mining applications (JAKUBEK & FORSYTHE 2004). In this research, it is necessary to determine which kriging model will be used to calculate sediment contamination between all sample points within the study area. Different contaminants may require different modeling techniques to obtain the best model, based on the calculated results. In order to determine which of the three kriging methods (Spherical, Exponential, and Gaussian) should be used for the respective contaminants, all three models need to be evaluated. When selecting the options in the ArcGIS Geostatistical Wizard, the following options were used: Maximum Range: 900, Minimum Range: 300, Direction: 90, Neighbours to Include: 5, Include at Least: 1. These criteria were chosen after experimentation as they produced the most accurate results, when compared to other options. Next, the calculations for Mean Prediction Error (MPE), Average Standard Error (ASE), and Standardized Root-Mean-Square Prediction Error (SRMSPE) for each of the three models were compared. For a kriging spatial interpolation model to provide accurate predictions, the Mean Prediction Error (MPE) should be close to 0, the Average Standard Error (ASE) should be as small as possible (below 20), and the Standardized Root-Mean-Squared Prediction Error (SRMSPE) should be close to 1 (FORSYTHE ET AL. 2004). If the SRMSPE is greater than 1, there is an underestimation of the variability of the predictions and if the SRMSPE is less than 1, overestimation of the variability is the result (JOHNSTON ET AL. 2001).

Log-transformations are generally used for skewed distributions; therefore, it would be appropriate to perform this function on sediment contaminants that are not normally distributed. Although log-transformations are not always used when kriging skewed distributions, HOULDING (2000) and JOHNSTON ET AL. (2001) support the idea of using them. They believe kriging is successful when values (e.g. sample points) are normally distributed and if they are not, they need to be transformed (HOULDING 2000; JOHNSTON ET AL. 2001). Moreover, CLARK (1979) argues that normality is not necessary for kriging; however, prediction errors rely on normality (CLARK 1979). Based on these opinions, it may not be universally acceptable to transform non-normal data prior to performing a kriging spatial interpolation; however, it is recommended as the kriged results may closely resemble the true distribution between sample points.

4 Analysis and Results

Once it was determined whether raw data or logged data were best suited for analysis, the kriging calculations were mapped. The predictions were each divided into nine vector classes with TEL and PEL isolines. The vector classes are organised into three groups: below TEL, TEL to PEL, and above PEL. Because some of the contaminants did not possess values within these created categories, a specific tonal scheme was used for each class, allowing for an accurate comparison of results. These 9 classes are represented by ascending light to dark tones, where the lightest tone is given to the lowest value and the darkest tone attributed to the highest value. Once the logged contaminants were kriged, their classes were then converted to their original form, where they could be compared with the TEL and PEL indicators of sediment contamination. This process helped to visually interpret how contaminated the Buffalo River is, which may not be evident when looking at the data values independently.

The results of the four contaminants analyzed in this research are presented below. Each contaminant is analyzed in terms of overall pollution level and the associated spatial distribution. In addition, the contamination levels are analyzed in relation to the TEL and PEL levels. The MPE, ASE, and SRMSPE results are presented in Table 2.

Tab. 2: Kriging Cross Validation Results for the Buffalo River

Contaminant	Model	MPE	ASE	SRMSPE
Arsenic (log)	Exponential	0.2457	0.2479	0.9600
Lead (log)	Exponential	0.3702	0.3908	0.9425
Mercury	Gaussian	0.0023	0.8800	0.9771
Nickel	Exponential	0.2083	6.6900	0.8450

4.1 Arsenic

The spatial distribution of arsenic is seen in Figure 3. The data were log-transformed to obtain suitable estimation outcomes. The majority of the study area contains arsenic concentrations between the TEL and PEL, making the river generally contaminated with arsenic. In the eastern (up-river) and central sections there are small areas where arsenic concentrations are below the TEL. More importantly, there are three small clusters where the concentrations are above the PEL. Although, these are the areas where adverse biological effects are likely to occur, the entire AoC needs to be further studied as majority of the river has arsenic concentrations above the TEL.

4.2 Lead

Sediment contamination of lead in the Buffalo River falls between the TEL and PEL boundaries as seen in Figure 4. As with arsenic, the data were log-transformed to provide the predictions. Lead contamination is not dispersed evenly throughout the study area as there are high concentrations located in the central and western sections of the AoC. The eastern area predominately has a low concentration of lead, which is in contrast to the western area where there is a presence of moderate concentrations of lead. In addition, there are scattered TEL isolines located throughout the study area.

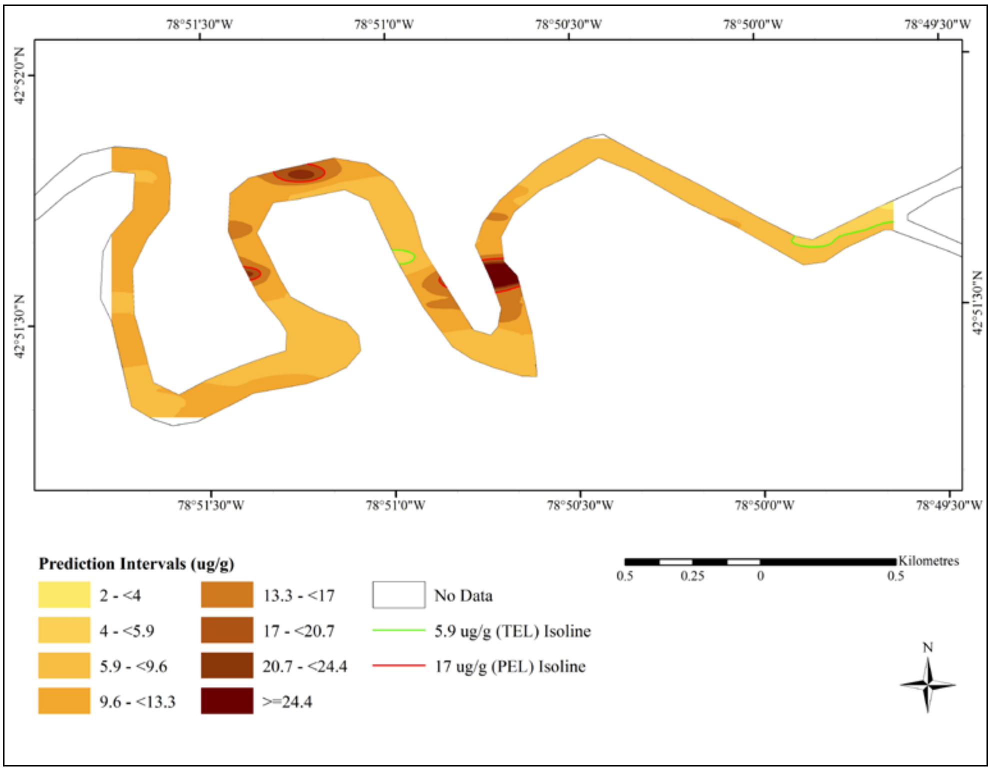

Fig. 3: Arsenic Kriging Results for the Buffalo River 2005

4.3 Mercury

The spatial distribution of mercury in the AoC sediment is portrayed in Figure 5. There is a high concentration of mercury contamination in the central and western portions of the study area. The Buffalo River has the largest areas of severe mercury contamination when it is compared to the other contaminants studied. This could be a result of years of contamination build-up as mercury was released into the river and flowed westward with the rivers current, eventually settling in its current location.

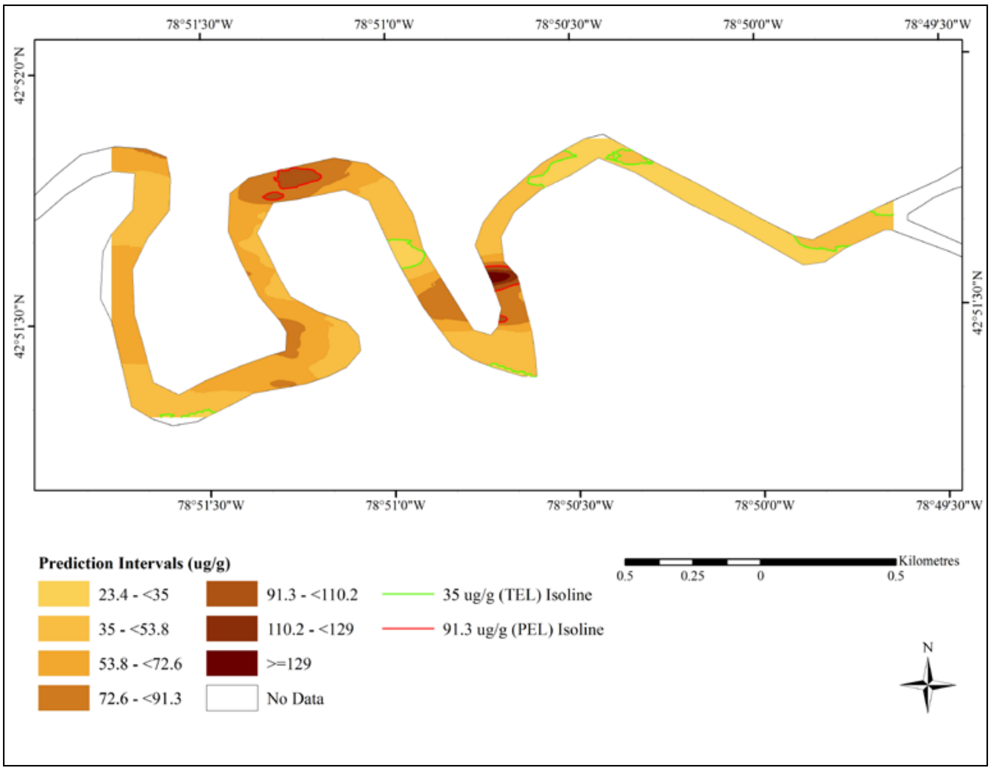

Fig. 4: Lead Kriging Results for the Buffalo River 2005

4.4 Nickel

The Buffalo River is contaminated with nickel as seen in Figure 6. There is only one small section in the east where nickel concentrations are below the TEL. The majority of the river is contaminated with nickel between the TEL and PEL, which is a concern. Also, there are 9 PEL isolines scattered throughout the central and eastern sections of the Buffalo River with one major cluster of high concentrations of nickel contamination in the sediment. Although visually the nickel concentrations do not appear as contaminated as the mercury concentrations, it can be argued that the general contamination throughout the AoC is more severe in the case of nickel.

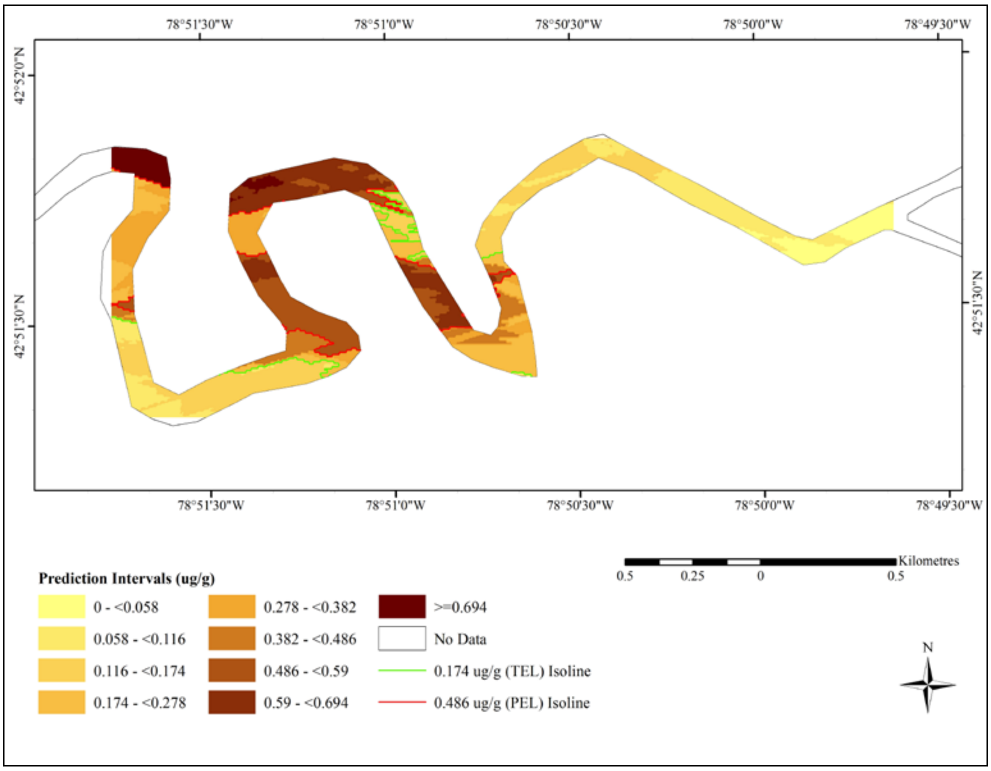

Fig. 5: Mercury Kriging Results for the Buffalo River 2005

5 Conclusion

This research was conducted to determine pollutant levels in the Buffalo River. With the use of data provided by the NYSDEC, a kriging spatial interpolation technique determined the spatial distribution of sediment contamination in the study area. Analysis of four contaminants provided a good measure of the true contamination of the Buffalo River. Mapping the geographic distribution of these contaminants shows areas where high concentrations of contaminants are located. Kriging results for each contaminant showed sections of the study area where contamination was above the TEL and more importantly the PEL. Large portions of the study area have contaminant concentrations between the TEL and PEL for arsenic, lead, mercury, and nickel. Based on these observations, the river is indeed highly contaminated and these pollution issues should be addressed. Within the Buffalo River, there are PEL hotspots located in the central area for most contaminants and these areas should be of greatest concern when dealing with future restoration.

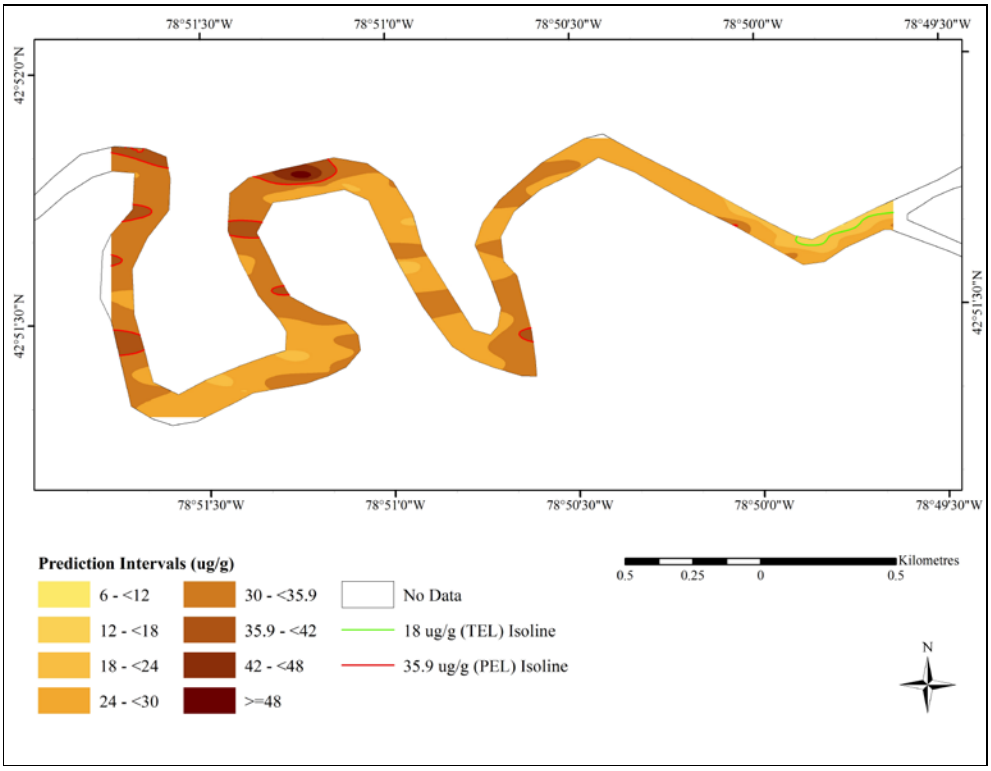

Fig. 6: Nickel Kriging Results for the Buffalo River 2005

The analysis did not incorporate the geomorphic features of the river bed. There may be pools and other features that affect the deposition locations of the contaminants. An important factor in discerning the depositional patterns would also be to consider the effect of periodic dredging in the Buffalo River (RODRIGUEZ, 2009). Ordinary kriging assumes an unknown but constant mean; that is, the mean is not a function of location only the error (JOHNSTON ET AL., 2001). Since the AoC has many meanders, this assumption may not be valid. Nonetheless, the flexibility of ordinary kriging is likely to produce relatively accurate predictions (RODRIGUEZ, 2009).

Finally, the data used for this research was retrieved from core sampling that only provides averages, which means that there is a loss of information (MILLER AND ORBOCK MILLER, 2007). This is portrayed as a single value and does not include the range of contaminant concentrations that exist within the core. Thus, the prediction maps presented in this paper may under predict the real number and extent of TEL and PEL isolines (RODRIGUEZ, 2009).

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