Soil and Sediment Contamination, 22:521–531, 2013
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ISSN: 1532-0383 print / 1549-7887 online
DOI: 10.1080/15320383.2013.750266

Geospatial Estimation of Mercury Contamination in Buffalo River Sediments

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The Buffalo River Area of Concern (AOC) is associated with heavy metal pollution. This research utilized sediment core data to model the geographic distribution of mercury within surface and subsurface sediments of a section of the AOC. Using ordinary kriging, a geostatistical interpolation technique, mercury concentration prediction maps were created. Standard maps were created by interpolating a prediction surface for the entire study area. In addition, spliced maps were created by interpolating prediction surfaces for three sections of the study area and merging these together to generate a quasi-continuous surface. The latter type of map was needed in order to account for the pronounced meandering nature of the river and to explore the potential existence of regional and local mercury sedimentation patterns. The surface level results show an increased level of mercury contamination from east to west (the direction of river flow), with peak values found in the mid-region of the study area. Additionally, surface sediments were less polluted with mercury than subsurface sediments. Finally, this study highlighted several mercury contamination hotspots, which could be targeted for future sediment restoration endeavors in the AOC.

Keywords Buffalo River, mercury, kriging, contamination, sediment

Introduction

The Buffalo River is contaminated with toxic elements as a result of decades of industrial activity in the surrounding land (Sutton, 2006). The river undergoes periodic dredging, which alters natural sediment depositional patterns. A stretch of this river, known as the Buffalo River Area of Concern (AOC), is of special interest due to its high number of pollutants and pollution levels. A sediment survey conducted by the New York State Department of Environmental Conservation (NYSDEC) in 2005 analyzed more than 100 different pollutants. The above factors, when combined, provide a suitable study site to carry out the geospatial analysis of sediment pollutants.

Mercury has been used by humans from the very beginning of civilization. Traces of liquid mercury have been found in Egyptian ceremonial cups and the highly prized

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vermillion pigment, which contains mercury, was used by Romans to decorate their villas (D'Itri and D'Itri, 1977). More recently, mercury has been used in pesticides, paints, ointments, and even medical treatments (D'Itri and D'Itri, 1977).

The concentration of mercury in the environment at global and regional scales can be gauged by analyzing air, water, soil, sediment, and even glacial ice cores. There is debate over whether sediments can provide faithful information with regard to flux in pollutants, and especially that of mercury (Smol, 2008). This debate arises from the fact that natural chemical and physical processes can increase mercury concentration within sediments without the need of new additions into the system (Miller and Orbock Miller, 2007).

The environmental pollution of mercury was largely ignored until the onset of the infamous Minamata Bay (Japan) tragedy in the 1950s, when dozens of fishermen died and hundreds became permanently ill after eating mercury-contaminated fish that were caught in the bay. A prominent Japanese chemical factory was later found guilty of dumping mercury effluents into the bay (D'Itri and D'Itri, 1977). Similarly, mercury pollution in the Wabigoon-English River System (Canada) caused many native Indians to become severely ill and prompted widespread public condemnation in the 1960s (D'Itri and D'Itri, 1977). Another infamous tragedy occurred in the early 1970s, when more than 400 people died in Iraq after eating bread prepared with wheat seeds tainted with mercurial fungicides (Smol, 2008).

Mercury is naturally found in the environment where it cycles between water, soil, and air as the result of biological and chemical reactions (Botkin and Keller, 2005); however, anthropogenic emissions of mercury have added great amounts of this heavy metal to the environment. Many scientists believe that mercury pollution now threatens the health of people all around the globe (University of Wisconsin-Madison, 2006). For instance, a possible link between increased mercury pollution and increased cases of autism has been hypothesized in the scientific literature (Forsyth, 2005).

Mercury bioaccumulation starts with the conversion of mercury into methyl-mercury, usually by aquatic organisms. Methyl-mercury is then absorbed by fish tissue and finally passes to top predators where it accumulates (Botkin and Keller, 2005). It was this phenomenon that caused Minamata Bay fisherman to have up to 30,000 times more methyl-mercury in their bodies than the water systems in which they fished (D'Itri and D'Itri, 1977). Only a relative short period of ingestion of mercury-contaminated products is needed to cause severe health issues in humans. Health Canada (2007) recommends a Provisional Tolerable Daily Intake of methylmercury of 0.47 μg per kilogram of bodyweight per day for adults.

Mercury has an affinity for fine-grained organic sediments and thus usually does not move too far away from its point source (Smol, 2008). Mercury is found in an elemental and organic form, known as methyl-mercury. The latter form is of greater environmental concern due to its high mobility and propensity to bioaccumulate in living organisms (Smol, 2008).

TEL and PEL

This paper uses the threshold effect level (TEL) and probable effect level (PEL) as defined by the Canadian Council of Ministers of the Environment (CCME) as indicators of sediment quality in freshwater sediments. The TEL indicates the concentration below which adverse biological effects are expected to occur rarely ($<25\%$), while the PEL indicates a concentration above which adverse biological effects are expect to occur frequently ($>50\%$) (Canadian Council of Ministers of the Environment, 2001). The range between TEL and

PEL is known as the possible effect range (PER) and biological abnormalities are expected to occur occasionally within this range.

The main objective of this paper was to assess the spatial distribution of mercury. This was achieved by producing prediction surface maps using the kriging spatial interpolation technique. This technique allows locations within the AOC that have pollution levels below the TEL, between the TEL and the PEL, and above the PEL to be identified. The AOC has a long history of periodic dredging (US EPA, 2008a). In fact, in 2003 the AOC was dredged for the last time before sediment samples were collected in 2005 (Sutton, 2006). It is likely that dredging alters the natural sedimentation patterns within the AOC.

The segment of the AOC studied in this paper has a pronounced meandering pattern. In general terms, a meandering river is characterized by having alternate accumulations of sediments called point bars, which are opposite to deeper areas called pools, which are in turn separated by shallower and longer areas called riffles (Miller and Orbock Miller, 2007). Because of the meandering nature of the river, it was necessary to determine if the best way to interpolate mercury concentration values was to use the entire length of the river or divide it into regional sections. The former approach requires the development of a global kriging model whereas the latter requires several regional kriging models.

It should be noted that most pollutants do not yet have official Canadian TEL values; instead these pollutants have an interim sediment quality guideline (ISQG). The ISQG acts as a temporary value until the full battery of toxicology tests are carried out and a TEL designation is published (Canadian Council of Ministers of the Environment, 2001). This paper used the ISQG values as a proxy for the TEL values of mercury. Mercury has a TEL of 0.17 μg/g and a PEL of 0.486 μg/g.

Study Area

The Buffalo River runs through to the City of Buffalo, which is located in New York State (USA) near the Canadian border (Figure 1). This river flows east to west and discharges into Lake Erie. The land use in the upper basin of the river is mainly agricultural and woodland, whereas land use in the lower basin is industrial and urban (Inamdar, 2004). Stream bank erosion, especially due to ice scouring, is an important contributor to sediment build-up in the Buffalo River, which receives about 86,000 tons of sediment each year from its three watersheds (Inamdar, 2004).

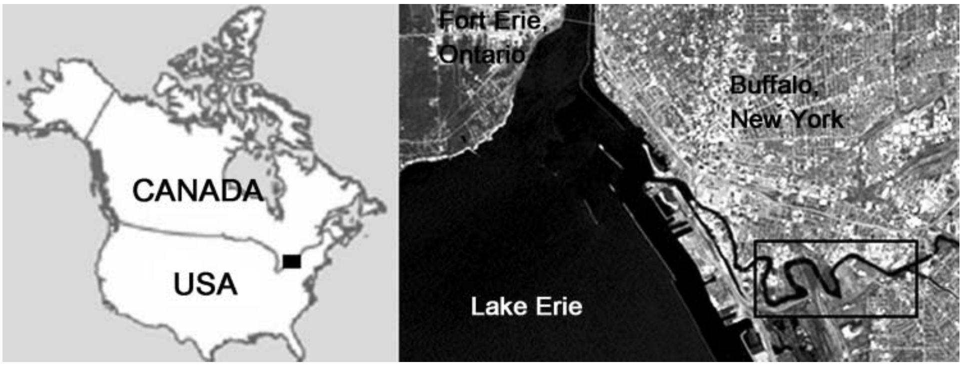

Figure 1. The Buffalo River Study Area (the hollow black box denotes study area extent).

The AOC is characterized by its heavy industrial pollution, which is mostly found in contaminated sediments as the industries that were present in the AOC for decades are now largely gone (Sutton, 2006). These polluted sediments, both surface and subsurface, together with runoff and atmospheric deposition account for most of the sources of new contamination (US EPA, 2008a). Within the vicinity of the AOC and throughout the Buffalo River watershed there are more than 45 inactive hazardous waste sites, 33 combined sewer overflow outfalls, and several sewage systems. All of these factors also contribute to the ongoing pollution of the AOC (US EPA, 2008a). Despite these issues, Preddice (2009) reports that no fish kills were observed in the Buffalo River for the 2000–2009 period. Fish consumption advisories are, however, in effect for the river as outlined by the US EPA (2008b).

Data

The data used in this study were collected by the New York State Department of Environmental Conservation in 2005. The original data consist of more than 100 different pollutants; however, this study only used the data available for mercury. The data were divided into two types: surface and subsurface sediments. Surface sediments mostly consisted of the top 15 cm of the core; however, a few 30 cm composite cores were also part of the dataset. Subsurface sediments consisted of all other samples deeper than 30 cm. Surface samples emphasize the current (2005) and ambient conditions of the biological active strata, whereas subsurface samples emphasize the history of pollutant depositional patterns (Sutton, 2006).

All sediment core sampling was performed from the Great Lakes National Program Office vessel “RV Mudpuppy.” It is equipped with a differential Global Positioning System (GPS) that allows for sub-meter accuracy in the determination of sampling locations (Sutton, 2006). The sediment samples were collected using a vibro core unit (Sutton, 2006) that can collect cores up to 4.5 meters (15 feet) in length. The sample cores were prepared, cut, and specific sample collections were made (Sutton, 2006). Analysis of the contaminants contained within the cores was performed by Severn Trent Laboratories (STL). The exact procedures and analytical methods are outlined in Sutton (2006). In addition to mercury, analyses of Semi Volatile Organic Compounds (SVOCs), pesticides, other metals, and Polychlorinated Biphenyls (PCBs) were undertaken.

This study used 111 surface and 166 subsurface samples from a total of 182 cores, meaning that a single core can have one or more data values associated with it. The geographical distribution of the surface sample points can be seen in Figure 2 for both global and regional kriging models. Figure 3 shows the distribution of subsurface sample points at four depth levels. Each depth level has a different sample size, as not all sediment cores were sampled at the same depth intervals. Depth 1 (30–60 cm) has 33 samples, Depth 2 (60–90 cm) has 34 samples, Depth 3 (90–120 cm) has 49 sample points, and Depth 4 (120–150 cm) has 50 samples. The depth interval in centimeters is an approximation of the original units, which were recorded in feet by the NYSDEC. In terms of subsurface samples, only these four datasets were used to carry out ordinary kriging analyses. Table 1 shows the data characteristics for mercury at all depths.

Methodology

Ordinary kriging is a well-tested method used to investigate the geographic distribution of pollutants in sediments. Forsythe et al. (2004), Forsythe and Marvin (2009), and Forsythe

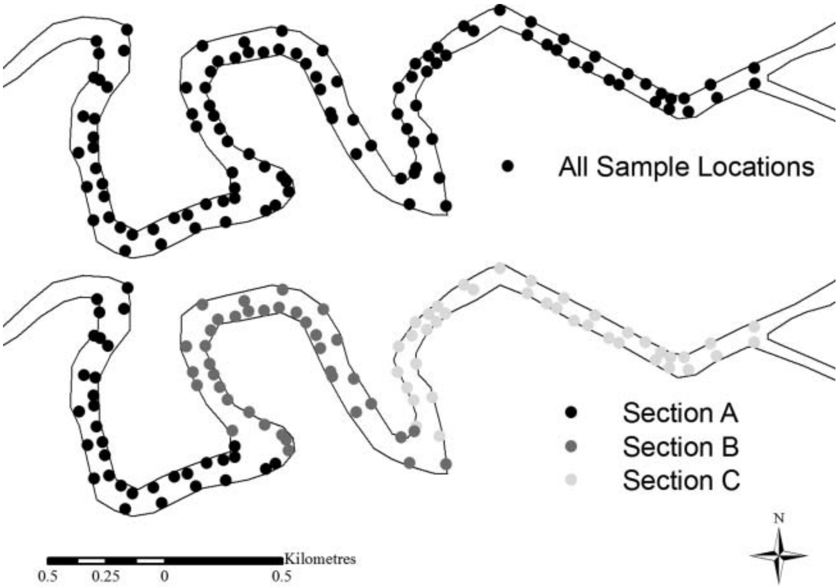

Figure 2. 2005 sample locations at surface level for both global and regional kriging models.

et al. (2010) utilized kriging to examine sediment contamination patterns in the Great Lakes Basin. Riverbed pollution patterns were also identified using a kriging approach by Gawedzki and Forsythe (2012) and Ouyang et al. (2002; 2003a; 2003b).

Kriging is a geostatistical method and produces interpolation surfaces that are unbiased and exact (Clark, 1979; Wackernagel, 2003). In practical terms, unbiased means that the residuals' average is very close to zero, whereas exact means that estimated values are very close to the sampled values. Unlike other interpolation techniques, ordinary kriging provides a prediction error surface which allows for a sound assessment of predicted values. The most adequate parameters to use in ESRI's ArcGIS Geostatistical Wizard when performing a kriging interpolation for the Buffalo River based on experimentation are: Maximum Range: 900; Minimum Range: 300; Direction: 90; Neighbors to Include: 5; Include at Least: 1.

In general terms, the best kriging model is that which has the mean prediction error (MPE) closest to zero, the smallest root-mean square prediction error (RMSPE), the average standard error (ASE) closest to the RMSPE and not greater than 20, and the standardized

Table 1
Mercury sediment sampling location statistics for the Buffalo River (μg/g)

Depth (cm)	No. of Sites	Min	Max	Average	SD
0–30	111	0.017	7.1	0.29	0.84
30–60	34	0.020	9.5	1.11	1.96
60–90	33	0.026	6.9	1.14	1.74
90–120	49	0.026	10.9	0.95	2.10
120–150	50	0.026	14.7	1.28	2.82

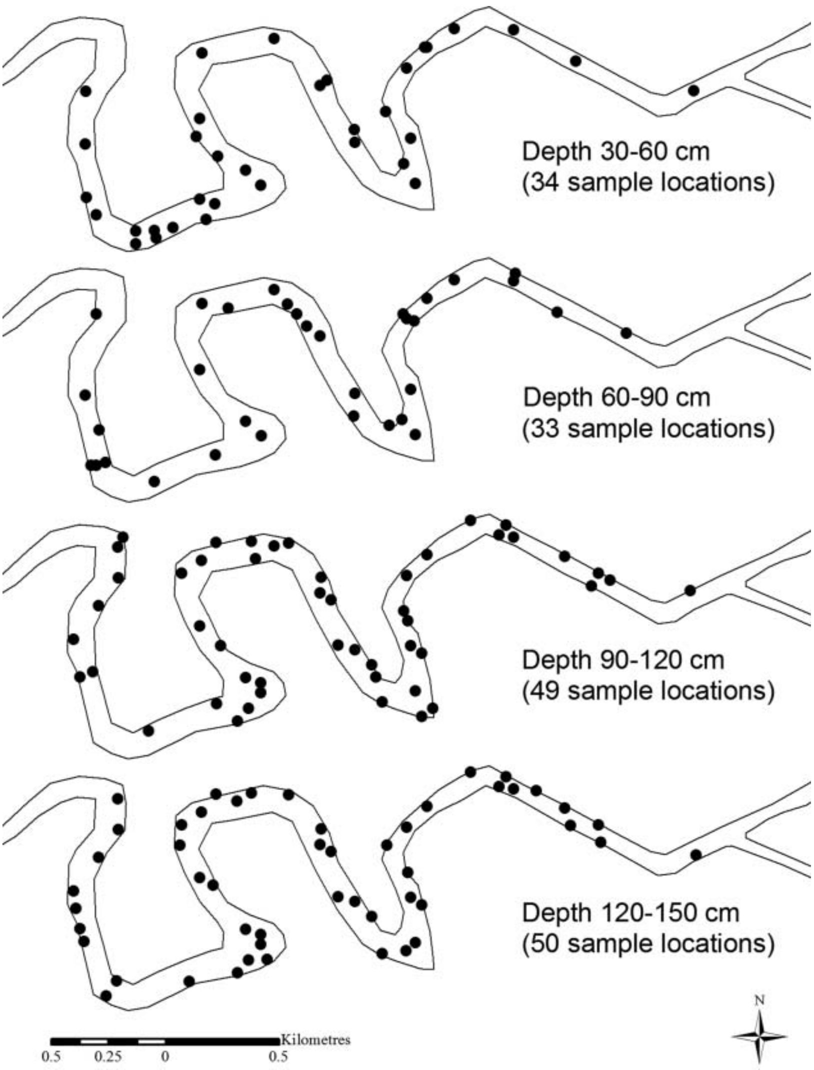

Figure 3. 2005 sample locations at all subsurface levels.

root-mean squared prediction error (SRMSPE) closest to one (ESRI, 2001). These four prediction error parameters served as the basis to selecting the best semivariogram model for kriging and the most suited models at each depth that can be seen in Table 2.

Results and Discussion

Figure 4 shows the predicted distribution of mercury contamination in Buffalo River surface sediment using 111 sample locations with the global model while Figure 5 shows the same, using a regional kriging model with three spliced sections. Mercury shows a global trend of low values in the eastern region and high values in the western region of the study area. Similar observations can be made using the spliced map regional model. Also, an area of

Table 2
Kriging data cross validation statistics for mercury

Depth (cm)	Model	MPE	RMSPE	ASE	SRMSPE
0–30	Gaussian	0.0057	0.856	0.909	0.943
30–60	Exponential	−0.1791	1.998	1.621	1.168
60–90	Gaussian	0.0237	1.782	1.872	0.954
90–120	Spherical	0.0243	2.283	2.319	1.004
120–150	Exponential	0.0227	3.235	3.110	1.042

very high values exists in the central section of the AOC in both models. Contamination levels appear to be slightly higher in the central section of the AOC using the regional model when compared to the global kriging model; however, these two models produce prediction surfaces that are very similar in nature by identifying key hotspots where contamination levels are above the PEL. One main difference is that the global kriging model identifies an area in the northwest section of the Buffalo River as heavily contaminated, whereas the regional model does not show heavy contamination in the same area. Since this area is at the edge of the AOC, this difference may be caused by a lack of sample locations on the left side of the meander. Thus, in the regional model, the semivariogram incorporates a contaminated sample point on the opposite side of the meander that may affect contamination predictions in the western portion of the AOC.

Figure 6 shows the distribution of mercury contamination within Buffalo River sediments at four different subsurface depths: 30–60 cm, 60–90 cm, 90–120 cm, and 120–150 cm. At the first subsurface depth, 30–60 cm, there are numerous small TEL

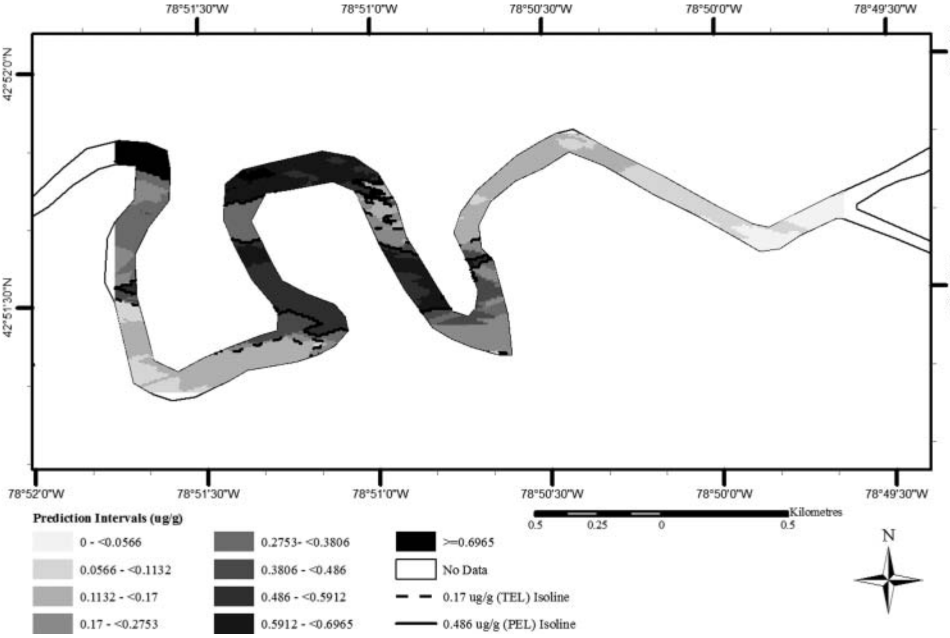

Figure 4. 2005 kriged mercury concentrations at surface level.

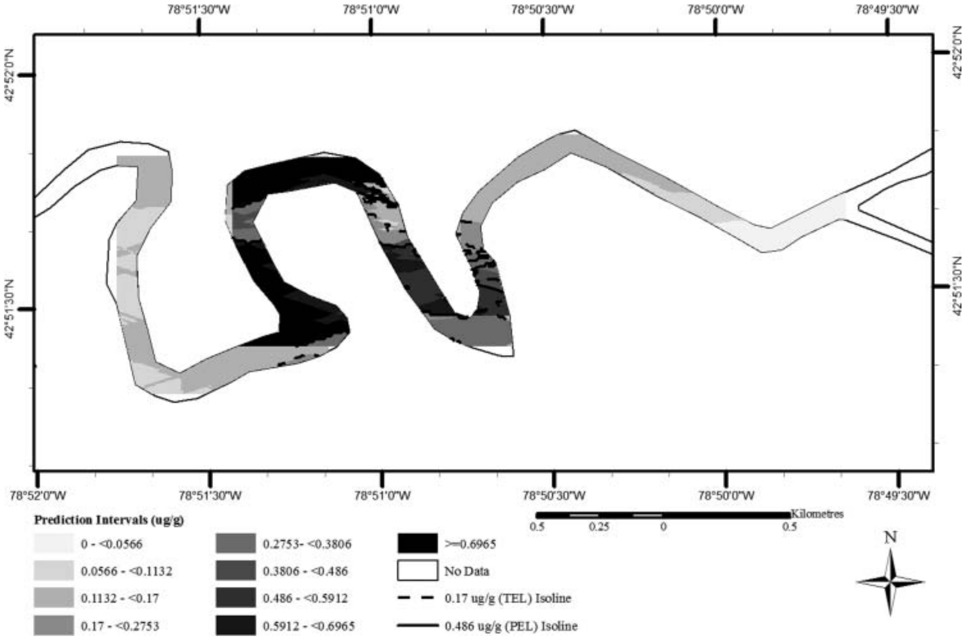

Figure 5. 2005 kriged mercury concentrations at surface level (spliced map).

isolines scattered throughout the AOC. The PEL isolines indicate areas of heavy contamination with large clusters of heavily polluted sediment dispersed throughout the entire AOC. At the depth of 60–90 cm, the majority of the sediment is heavily contaminated as most of the central and eastern sections are above the PEL. What is most remarkable is that contamination levels are not just above the PEL, but at levels much greater than the PEL. There is only one small section in the southwestern portion of the AOC where contamination levels are below the TEL and between the TEL and PEL. At the depth of 90–120 cm, heavily contaminated regions are mainly located in the central and western section of the AOC and account for the majority of the surface area. The southwestern and easternmost portions of the Buffalo River have TEL isolines that encompass small areas where contamination is not so problematic. Finally, at the depth of 120–150 cm, the majority of the Buffalo River is contaminated above the PEL. The eastern portion of the river has some TEL isolines which separate less contaminated sediment from areas between the TEL and PEL. Similar to the depths above, the central section of the AOC is heavily contaminated above the PEL. In addition, the western section of the river is mainly contaminated at levels above the PEL. There is no evident chronological pattern that exists when comparing contamination patterns at all depths. The most contaminated (above the PEL) hotspot that is present at all depths is located in the central section of the AOC.

The collection and analysis of sediment cores is a costly undertaking. As mentioned previously, some of the patterns located on the edge of the study area may differ somewhat from the actual situation. The collection of more core samples in future surveys would assist in a greater understanding of spatial distributions as it may be possible to further define and localize hotspots. Prediction error surfaces that were created in the kriging analyses also allow for the identification of possible future sampling locations where somewhat higher error values indicate the possible need for additional core samples.

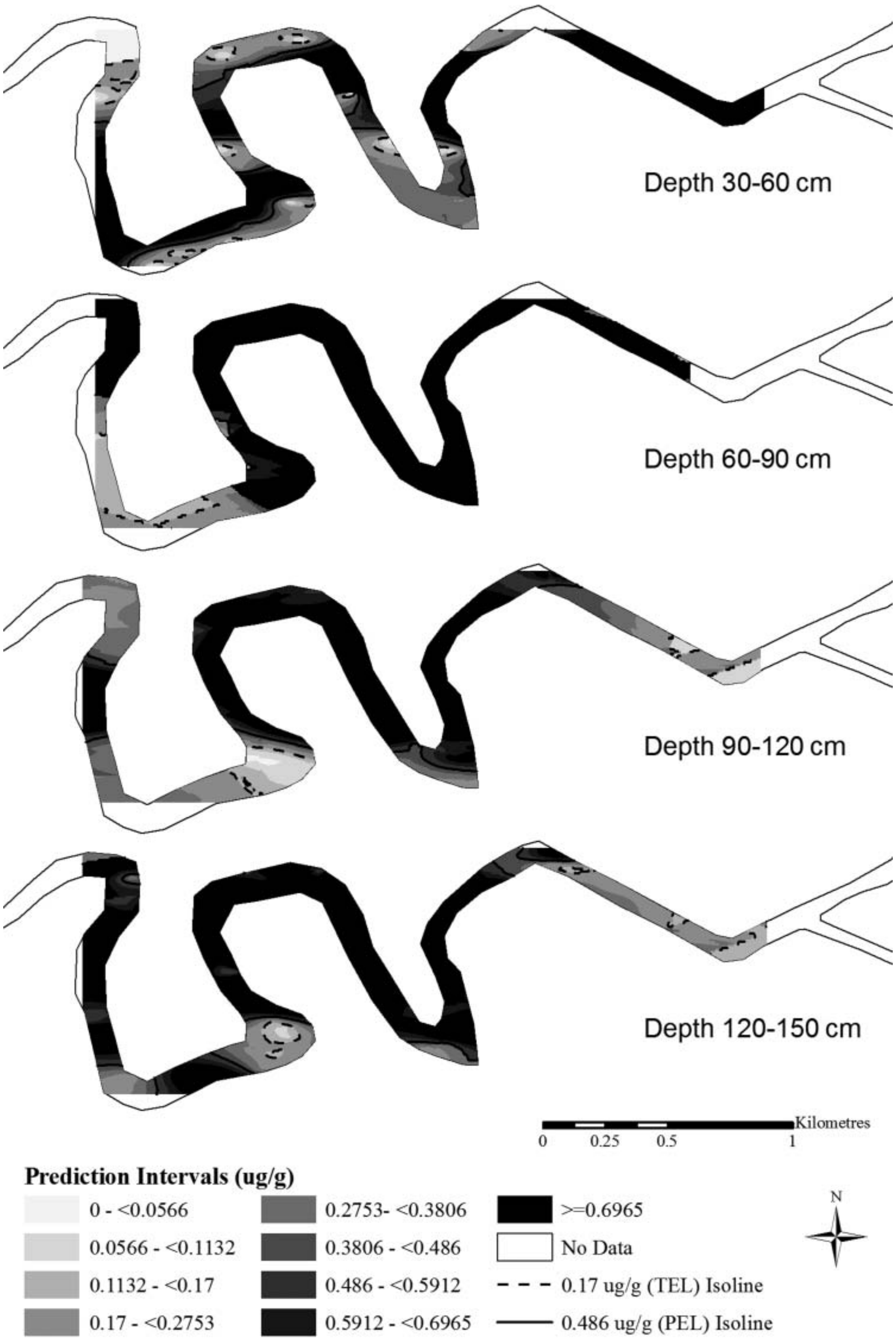

Figure 6. 2005 kriged mercury concentrations at various subsurface depths.

Conclusions

The pattern of deposition for mercury found in the Buffalo River varies based on depth. Generally, the southwest section of the river is least contaminated. Heavily contaminated concentrations of mercury are clustered in the central region of the study area at all depths. Any plans for remedial and restorative work in the Buffalo River Area of Concern should focus on this region, which encompasses large PEL hotspots identified in the prediction maps. Identifying key areas with heavy contamination can be economically valuable as the process of dredging is costly.

Documenting the geographical distribution of mercury sheds light on the location of major areas of pollution and possibly into the sources of pollution. To achieve the latter, more detailed studies are required in terms of mapping the location of past and present sources of potential pollution along the banks of the Buffalo River. Also, contamination levels at the surface level are lower when compared to all subsurface depths, suggesting that historical industrial activity contributed to the contamination of the Buffalo River.

This study showed that kriging is a very effective tool in the creation of prediction surfaces for irregularly shaped study areas. There is value in creating regional maps since they highlight important regional and local variations, which can be overlooked if only global maps are used; however, these differences, for mercury surface sediment contamination, are minimal. It should be noted that kriged section maps could not be produced at subsurface levels because there were not enough sample locations to develop valid kriging models. The results seem reasonable when the kriged maps are compared to the proportional circle maps. The main advantage is that kriging allows for the full contaminant distribution to be assessed and analyzed.

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