# ASSESSING ANTHRACENE AND ARSENIC CONTAMINATION IN BUFFALO RIVER SEDIMENTS

By

Adrian Gawedzki

Bachelor of Arts, 2010 Ryerson University

A Major Research Paper

presented to Ryerson University

in partial fulfillment of the

requirements for the degree of

Master of Spatial Analysis (MSA)

Toronto, Ontario, Canada

## Declaration

I hereby declare that I am the sole author of this research paper.

I authorize Ryerson University to lend this research paper to other institutions or individuals for the purpose of scholarly research.

Adrian Gawedzki

I further authorize Ryerson University to reproduce this major research paper by photocopying or by other means, in total or in part, at the request of other institutions or individuals for the purpose of scholarly research.

Adrian Gawedzki

## Abstract

Anthracene and arsenic contamination concentrations at various depths in the Buffalo River were analyzed in this study. The Buffalo River is labelled as an Area of Concern (AOC) defined by the Great Lakes Water Quality agreement between Canada and the United States. It has a long history of industrial activity located in its near vicinity that has contributed to the accumulation of contamination within its sediment. The data were collected in 2005 for a feasibility study conducted by the New York State Department of Environmental Conservation (NYSDEC) with assistance from the United States Army Corp of Engineers (USACE), the Buffalo Niagara Riverkeeper (BNRK) and the United States Environmental Protection Agency (USEPA). The study was conducted to analyse the hydrology, ecology, and sediment contamination within the Buffalo River so that appropriate actions can be undertaken to restore the natural habitat of the river. An ordinary kriging spatial interpolation technique was used to calculate estimates between sample locations for anthracene and arsenic at various depths. Anthracene is known to cause damage to human skin and arsenic has been linked to lung and liver cancer. The results show that both anthracene and arsenic surface sediment (0-30cm) is less contaminated than all subsurface depths. There is variability of pollution within the different subsurface levels (30-60cm, 60-90cm, 90-120cm, 120-150cm) and along the river course, but major clusters are identified throughout all depths for both anthracene and arsenic. Surface sediment contamination for both anthracene and arsenic is lower when compared to subsurface levels, which signifies that historical contamination was greater than present day contamination.

## Acknowledgements

I would like to thank my advisor, Dr. Wayne Forsythe for his guidance throughout the project. The experience working as your research assistant has provided me with the skills needed to write this paper.

## Table of Contents

## List of Tables

## List of Figures

## List of Acronyms

AOC - Area of Concern

ASE - Average Standard Error

BNR - Buffalo Niagara Riverkeeper

CCME - Canadian Council of Ministers of the Environment

DDT - Dichlorodiphenyltrichloroethane

NYSDEC - New York State Department of Environmental Conservation

PAH - Polycyclic Aromatic Hydrocarbon

PEL - Probable Effect Level

RMSPE - Root-Mean Square Prediction Error

SQG - Sediment Quality Guidelines

SRMSPE - Standardized Root-Mean Squared Prediction Error

TEL - Threshold Effect Level

USEPA - United States Environmental Protection Agency

USACE - United States Army Corps of Engineers

# CHAPTER 1: Introduction

The Buffalo River is listed as an Area of Concern (AOC) by the Great Lakes Water Quality agreement between Canada and the United States. Cayuga Creek, Buffalo Creek, and Cazenovia Creek are the three major streams in the watershed that comprise the AOC (US EPA, 2011). The impacted area is 10 kilometres in length and contains the 2.3 kilometre stretch of the City Ship Canal (US EPA, 2011). The river is located south of the city of Buffalo and flows westward, discharging into Lake Erie. In the rivers history, large amounts of contamination have been discharged into it. In the past few years, New York State has identified three major contributors to environmental damage: ExxonMobil Corporation, Honeywell Corporation, and PVS Chemicals. These major companies had a heavy industrial presence in the vicinity of the Buffalo River and their discharges were directed into the river itself.

The Buffalo River is used as a transportation route with a large city ship canal. Residential communities, farmland, wooded areas, commercial land use, and parks makeup the land use in the rivers tributaries (US EPA, 2011). Also, the Buffalo River is a place where fishing occurs, but within the AOC, aquatic life has been harmed by PCBs, chlordane and PAHs (US EPA, 2011).

Pollution within the Buffalo River has negatively affected the aquatic ecosystem. Potential habitat areas are imperfect and limited due to contamination as invasive plant and animal species threaten diversity and quality of the rivers habitat (US EPA, 2011). The Buffalo River has a low diversity of benthic macroinvertebrates that is dominated by pollution-tolerant species (US EPA, 2011). Nelson and Hites (1980) believe that the existence of organic compounds is partially responsible for the observed tumours in fish found in the Buffalo River. The AOC has fish consumptions advisories currently in place as recent research indicates an average of 34% DELT - deformities, fin erosions, lesions, and tumors anomalies in fish, which range from a low of 14% for pumpkinseed to an extremely high 87% for brown bullhead (US EPA, 2011).

In 2005, over one-hundred different pollutants within the Buffalo River were analyzed by the New York State Department of Environmental Conservation (NYSDEC) according to Sutton (2006). Within the AOC, contaminants of concern include PCBs, PAHs, metals, and industrial organics (US EPA, 2011). This paper will focus on the contamination levels of anthracene and arsenic within the outlined study area at the surface level (0-30cm depth), and at various subsurface levels: 30-60cm, 60-90cm, 90-120cm, 120-150cm.

### 1.1 Anthracene and Arsenic

Anthracene is a polycyclic aromatic hydrocarbon (PAH) and arsenic is a metalloid. One PAH and one metalloid were chosen to get a more diverse representation of the contamination within the river. Both contaminants are known to have health effects associated with them ranging from human cancer issues to wildlife heath concerns (US EPA, 2008; Health Canada, 2006). It is important to have studied one organic substance (anthracene) and one inorganic substance (arsenic) to get a better understanding of the overall contamination of Buffalo River sediments. (Forsythe et al. (2010) conducted a study that incorporated arsenic contamination within the study area at the surface level and found clusters of concentrations that were concerning.

Due to large concentrations of toxicity within the Buffalo River, sediment removal through a dredging process is a likely option to restore the rivers health. It is important to understand the distribution of anthracene and arsenic in the Buffalo River sediment so that heavily contaminated areas can be targeted for future remediation. Outlined in the 2010 Feasibility Study for the Buffalo River are the options of dredging and sediment capping (EML, 2010). Dredging is the process of removing mass sediment, while sediment capping is the process of adding a layer of stable, uncontaminated sediment over the contaminated sediment, preventing aquatic life from directly contacting contaminated sediment. If either of these options will be used to restore the river to what it once was, specific locations where contamination is a concern need to be identified.

## 1.2 The Kriging Spatial Interpolation Technique

The kriging spatial interpolation technique is chosen as an appropriate method in determining the distribution of anthracene and arsenic concentrations within the rivers' sediment. This interpolation technique determines an unknown value between sample points based on estimations (Clark, 1979) with the advantage of providing error statistics. Traditionally, analysis was conducted using dot maps; however, they do not provide as much detail as the interpolation method.

## 1.3 Research Objectives

The objectives of this research can be organised into the following three sections:

1. To assess the distribution of anthracene and arsenic contamination in the Buffalo River sediments and identify hotspots that are heavily contaminated.
2. Determine the change in contamination levels at different depths (both surface and subsurface).

3. Compare the effectiveness of proportional circle map results to kriged map results.

### 1.4 Major Research Paper Structure

The structure of this paper is presented in a manuscript format. The first chapter provides a general introduction to the research as well as its objectives. Chapter 2 contains a literature review that is relevant to the research topic. Chapter 3 is organised as a standalone manuscript that has been submitted to the International Journal of Ecology. The manuscript contains typical journal sections including: abstract, introduction, data collection, methodology, results, discussion, and conclusion. Finally, Chapter 4 briefly outlines recommendations for future research.

# CHAPTER 2: Literature Review

## 2.1 River Pollution and Sedimentology

The Buffalo River has had a long history of heavy industrial activity located in its vicinity. Within the United States, the Buffalo River has been classified as one of the most polluted bodies of water. Research conducted by Nelson and Hites (1980) found a link between a dye manufacturing plant's discharge area located along a section of the riverbed and heavy concentrations of contamination. The authors suggest that dye-related chemicals were transferred into the Buffalo River and its sediment through leaching and runoff from the dump site (Nelson and Hites, 1980).

Historically, large corporations were able to discharge pollution directly into the riverbed. Today the lower river still sees industrial development taking place; however, some areas located along the riverbank have been abandoned (US EPA 2011). Not only are there 33 outfalls that discharge into the Buffalo River, but there are also 3 sewer system connections that extend outside the sewer district, but overflow into the river during storm events (US EPA 2011).

To effectively assess the pollution within a body of water, analyzing its sediment is proven to be effective. Miller and Orbock-Miller (2007) suggest that analyzing contamination within a body of waters' sediment is beneficial since there is less variation in pollution concentrations over time and space when compared to the water above. These sediments can be disturbed by a dredging process or through chemical breakdown. Both organic and inorganic contaminants can be found in sediment. Organic contaminants include pathogens (i.e. anthracene), microorganisms, pesticides, and polychlorinated biphenyls, while inorganic contaminants include metals, metalloids (i.e. arsenic), nutrients, and radionuclides (Miller and Orbock-Miller, 2007). This research will analyze the concentration of anthracene and arsenic within the Buffalo River sediment.

## 2.2 Anthracene

Anthracene is a polycyclic aromatic hydrocarbon (PAH). When products such as coal, oil, or gas are burned, but the burning process does not finish, PAHs are created (US EPA, 2004). Anthracene is mainly used to make dyes, plastics, and pesticides, but is also used to make smoke screens and scintillation counter crystals (US EPA, 2004). PAHs are ubiquitous in nature and have raised concerns from scientists because of their environmental impact as well as their impact on human health.

Taicheng et al. (2011) analyzed the toxilogical significance of PAHs in drinking water sources within the Pearl River Delta. The consumption of contaminated drinking water is a large issue faced by many places in the world. The authors suggest that PAHs can cause risk to humans through the natural food chain as PAHs tend to be stored in the fatty tissues of animals. The Pearl River Delta region has experienced rapid industrial and economic development causing an increase in PAH pollution levels from industrial factories (Taicheng et al., 2011). This new heavy industrial presence in the Pearl River Delta can be compared to the historical industrial presence in the Buffalo River watershed. Consumption of drinking water with anthracene can create the following symptoms in humans: headaches, nausea, loss of appetite, inflammation or swelling of the stomach and intestines (US EPA, 2004).

## 2.3 Arsenic

Arsenic is a toxic metalloid that poses many health related issues. Since it is tasteless and odourless, it is difficult to detect within drinking water. Berg et al. (2001) analyzed arsenic contamination of groundwater and drinking water in Vietnam. The study found that concentrations of arsenic within groundwater differed between seasons and the authors were able to identify districts where arsenic concentrations were above the World Health Organizations' guideline for maximum admissible arsenic concentrations (10 micrograms/L) and the Vietnamese standard for maximum admissible arsenic concentrations (50 micrograms/L). Also, the authors suggest further research needs to be conducted and actions to reduce arsenic concentrations need to be considered early to reduce the risk of chronic arsenic poisoning (Berg et al., 2001).

In similar research conducted by Smith et al. (1992), in the United States, the 50micrograms/L threshold was used to assess the risks of cancer from exposure to arsenic in drinking water. The lifetime risk of dying from liver, lung, kidney, or bladder cancer while drinking one litre per day of water contaminated with arsenic could be as high as 13 per 1000 persons at the current standard for arsenic concentration in drinkable water (Smith et al., 1992). Based on numerous American water surveys, approximately 350,000 people might drink water above the standard set by the U.S. Environmental Protection Agency (Smith et al., 1992).

## 2.4 Ordinary Kriging Analysis

Traditional methods of assessing sediment contamination were mainly analyzed by mapping sample sites and using a unique colour scheme associated to different values. With the emergence of spatial interpolation techniques, more studies began using the ordinary kriging interpolator to effectively map sediment or water contamination. The advantage that the ordinary kriging interpolator has over other interpolators is that it can be statistically validated as it generates standard error surfaces (Forsythe et al., 2010b; Jakubek and Forsythe, 2004; Johnston et al., 2001).

Furthermore, past studies conducted by Rodriguez (2010) and Forsythe et al. (2010a) assessed sediment contamination within Buffalo River sediment. The former, focused on lead and mercury concentrations at the surface and subsurface level, while the latter focused on arsenic, copper, lead, and zinc concentration at just the surface level. Both studies used the kriging interpolation technique to effectively analyze sediment contamination within the Buffalo River. Similarly, ordinary kriging was used to determine the sediment contamination in the Great Lakes in research conducted by Forsythe and Marvin (2005 and 2009), Forsythe et al. (2010b), as well as Jakubek and Forsythe (2004).

## 2.5 Threshold Effect Level and Probable Effect Level

Although using the kriging spatial interpolation technique is useful in determining the overall sediment contamination of the Buffalo River, looking at the raw results would not provide much meaning to the analysis. To assist in the interpretation of the kriged results, it is necessary to use comparative measures (Quyang et al., 2003b). In their research, Quyang et al. (2003b) compared their kriged results to a probable effect level (PEL) measure to assess the sediment quality problems in the estuarine rivers. They compared dichlorodiphenyltrichloroethane (DDT) concentrations within estuarine rivers of Central Florida to PEL values associated with DDT. With the use of the PEL measure, it was possible to identify ‘hot spots’ in Ortega River sediment where DDT concentrations were above 4.78μg $\text{kg}^{-1}$ and most concerning.

MacDonald et al. (1996) conducted their research to establish sediment quality guidelines (SQGs) for Florida coastal waters that were referenced in Quyang’s research. The SQGs were developed for 34 substances and each substance was given a threshold effect level (TEL) and PEL. Three ranges of chemical contamination were defined by the TEL and PEL values: rarely, occasionally, or frequently, which accounted for their association with adverse effects (MacDonald et al., 1996).

Moreover, other studies conducted by Forsythe et al. (2010a), Forsythe and Marvin (2009), Rodriguez (2009), and Jakubek and Forsythe (2004) all used TEL and PEL measures set by the Canadian Council of Ministers of the Environment (CCME) to add meaning to their studies. Whether the study areas were as large as one of the great lakes, or smaller in size like the Buffalo River, the TEL and PEL parameters proved to provide adequate meaning to each study. This research will use both TEL and PEL as measures to assess the sediment contamination of the Buffalo River, similar to the above listed research. In addition, this makes comparison between previous research conducted on sediment contamination in the Buffalo River possible.

# CHAPTER 3: Manuscript

## ASSESSING ANTHRACENE AND ARSENIC CONTAMINATION WITHIN THE BUFFALO RIVER SEDIMENT

### 3.1. Abstract

Anthracene and arsenic contamination concentrations at various depths in the Buffalo River were analyzed in this study. The Buffalo River is labelled as an Area of Concern (AOC) defined by the Great Lakes Water Quality agreement between Canada and the United States. It has a long history of industrial activity located in its near vicinity that has contributed to the accumulation of contamination within its sediment. The data were collected in 2005 for a feasibility study conducted by the New York State Department of Environmental Conservation (NYSDEC) with assistance from the United States Army Corp of Engineers (USACE), the Buffalo Niagara Riverkeeper (BNRK) and the United States Environmental Protection Agency (USEPA). The study was conducted to analyse the hydrology, ecology, and sediment contamination within the Buffalo River so that appropriate actions can be undertaken to restore the natural habitat of the river. An ordinary kriging spatial interpolation technique was used to calculate estimates between sample locations for anthracene and arsenic at various depths. Anthracene is known to cause damage to human skin and arsenic has been linked to lung and liver cancer. The results show that both anthracene and arsenic surface sediment (0-30cm) is less contaminated than all subsurface depths. There is variability of pollution within the different subsurface levels (30-60cm, 60-90cm, 90-120cm, 120-150cm) and along the river course, but major clusters are identified throughout all depths for both anthracene and arsenic. Surface sediment contamination for both anthracene and arsenic is lower

when compared to subsurface levels, which signifies that historical contamination was greater than present day contamination.

**Keywords:** Kriging, Buffalo River, Sediment, Contamination, Anthracene, Arsenic

### 3.2. Introduction

The Buffalo River is labelled as an Area of Concern (AOC) defined by the Great Lakes Water Quality agreement between Canada and the United States and will experience a proposed $39 million cleanup (Tokasz, 2010). Both private and public investors are part of this major cleanup effort that is set to begin in the spring of 2011. The major contributors to the cleanup effort include the United States Environmental Protection Agency (USEPA), the New York State Department of Environmental Conservation (NYSDEC), the United States Army Corps of Engineers (USACE), and the Buffalo Niagara Riverkeeper (BNRK). The plan outlines the removal of almost a million cubic yards of contaminated sediment (Tokasz, 2010) through a dredging process.

Both anthracene and arsenic have health concerns associated with them so areas with heavy contamination in the rivers sediment are concerning. Anthracene is a polycyclic aromatic hydrocarbon (PAH) and arsenic is a metalloid. Both contaminants will be analyzed to better depict the true contamination within Buffalo River sediments.

#### *Anthracene*

Anthracene generally enters a person’s body through breathing contaminated air; however, one can be exposed to it by eating or drinking food and water that is contaminated. Degradation of benthos, loss of fish and wildlife habitat, and health concerns related to consumption of the river’s carp are some of the concerns related to the contamination of the Buffalo River (Inamdar, 2004). Once in your body, anthracene can target fat tissues, or organs including the kidneys, and liver (US EPA, 2008).

Djomo et al. (1995) conducted a controlled experiment with Zebrafish to analyze their uptake and depuration of PAHs including anthracene. Two controlled tanks were used, one with clean water, the other with contaminated water. The results indicate that a rapid uptake of contamination is noticed within the zebrafish when exposed to the contaminated tank. Anthracene had the highest uptake rate in zebrafish within the first 24 hours when compared to other PAHs studied.

Baumard et al. (1997) conducted research on PAHs in sediments and mussels in the western Mediterranean Sea. Twenty-three sample locations were used in the study to report on 26 PAHs. The authors found that, PAHs with low molecular weight, such as anthracene were mainly absorbed as dissolved compounds rather than absorbed by particulate matter through the digestive route (Baumard et al., 1997).

### *Arsenic*

Arsenic is tasteless and odourless in drinking water, making it difficult to detect by a consumer. Health Canada and the International Agency for Research on Cancer consider arsenic a human cancer-causing agent. With long term exposure to arsenic, some effects include: thickening and discoloration of the skin, nausea and diarrhea, decreased production of blood cells, abnormal heart rhythm and blood vessel damage, or numbness in the hands and feet (Health Canada, 2006). Concentrations of arsenic in the Buffalo River surface sediment are mostly between the TEL and PEL levels (Forsythe et al., 2010a).

Berg et al. (2001) conducted a study that analyzed the human health threat of arsenic contamination in groundwater and drinking water in Red River, Vietnam. The study area of Hanoi consisted of sixty-eight sample locations from private tubewells and 8 sample locations from the major drinking water plants. The average arsenic concentration was 159mg/L in rural groundwater samples from private small scale tubewells, while the groundwater that was used directly as drinking water in a highly affected rural area, had average arsenic concentration levels of 430mg/L. (Berg et al., 2001). The results indicate that chronic arsenic poisoning is a significant risk to millions of people who are consuming untreated groundwater.

Guha Mazumder et al. (2000) analyzed arsenic level in drinking water and the prevalence of skin lesions in West Bengal, India. The arsenic level in 7683 participant's drinking water was measured in addition to their keratosis and hyperpigmentation levels. The results indicated that there is a relationship between arsenic levels in water and skin lesions, specifically, "high amounts of arsenic in the tubewell water were associated with keratosis and hyperpigmentation" (Guha Mazumder et al., 2000). The mean arsenic concentration was 210mg/L for individuals that did not have any skin lesions. Also, there were cases where participants had skin lesions and low levels of arsenic in their drinking water. The authors suggest that the reasoning may be related to the source of water; therefore, these individuals were likely to be exposed to arsenic in their drinking water from places outside the sample locations such as their workplace (Guha Mazumder et al., 2000).

### *TEL and PEL*

The Canadian Council of Ministers of the Environment (CCME) has identified two measures, Threshold Effect Level (TEL) and the Probable Effect Level (PEL) that are effective in assessing contamination. Contamination concentrations below the TEL are where adverse biological effects are expected to occur rarely, while concentrations above the PEL are where adverse biological effects are expected to occur frequently. Forsythe and Marvin (2009), Forsythe et al. (2010a), and Rodriguez (2009) all used PEL and TEL values in their research. Kriged results were categorized into three separate groups: below TEL, TEL to PEL, and above PEL, with three class ranges in each group. This gives meaning to the results as they can be compared to the guidelines set by the CCME (Forsythe and Marvin, 2009; Rodriguez, 2009). The TEL is 46.9ng/g, and the PEL is 245ng/g for anthracene, while the TEL is 5.9ug/g and the PEL is 17ug/g for arsenic.

### *Study Area*

The Buffalo River (Figure 3.2.1) is a tributary to Lake Erie in the City of Buffalo, New York. Lake Erie is one of the five Laurentian Great Lakes which 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). The Buffalo River is better known as part of the Buffalo Creek in the western New York area; however, within the vicinity of the City of Buffalo, it is known as the Buffalo River. This watershed has two main tributaries: Cazenovia Creek and Cayuga Creek. The total drainage area for the Buffalo River watershed is approximately 440 square miles (US EPA, 2011).

**Figure 3.2.1.** Area of Concern. The section of the Buffalo River that is located within the highlighted rectangular box, serves as the study area for this project. Data source: Google Maps (2009)

The Buffalo River has a long history of heavy industrial activity that spans decades and has raised concerns about the river's contamination. Canfield et al. (1996), Forsythe et al. (2010), as well as Irvine and Pettibone (1993) suggest the Buffalo River AOC has been negatively affected by industrial activity, leading to the contamination of its sediments. The river was used as a dumping ground for all types of waste with discharges connected directly to the river. ExxonMobil Corporation, Honeywell Corporation, and PVS Chemicals are major contributors to the Buffalo River's environmental damage and are being pursued for these damages (Tokasz, 2010). Contamination within the Buffalo River sediment is not uniform. There are sections of the Buffalo River that have high pollution levels, above the TEL and PEL for multiple contaminants including lead, nickel, and mercury (Forsythe et al., 2010a).

## 3.3. Data Collection

The data for this study were collected in 2005 by the New York State Department of Environmental Conservation with assistance from the United States Army Corp of Engineers, the Buffalo Niagara Riverkeeper and the United States Environmental Protection Agency (Sutton, 2006). Sediment core samples were collected to assess the impairment of habitat due to chemical contamination of shallow sediments, chemical contamination in recently deposited sediments, and historical chemical contamination in undisturbed sediment (Sutton, 2006).

Both surface (core samples up to 30cm in depth) and subsurface sediment (core samples below a depth of 30cm) will be analyzed. During collection, a sampling bias was exercised towards areas known to be affected by tributaries, outfalls, and other industrial sources or historical spills (Sutton, 2006). Previously sampled areas were also considered for comparison purposes. A total of 182 sample cores were extracted from the Buffalo River. This study will use 111 surface samples seen in Figure 3.3.1 and 166 subsurface samples seen in Figure 3.3.2. Each sample point could have more than one data value associated due to a variation of contamination at different depths.

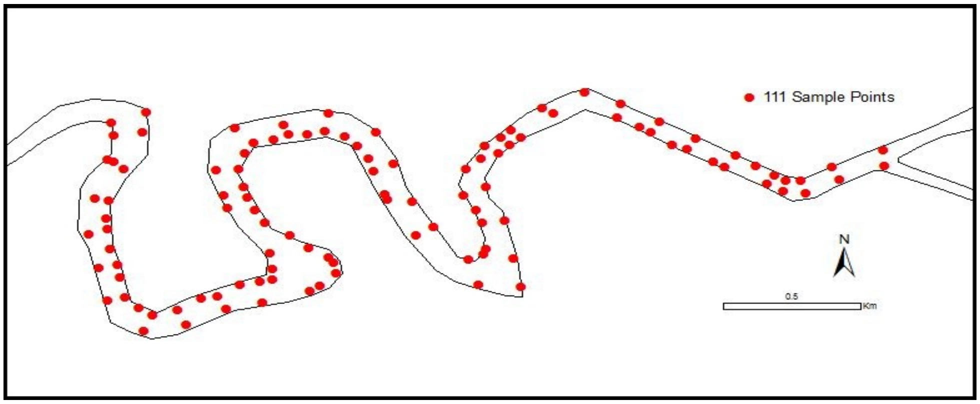

**Figure 3.3.1.** Distribution of sample points within the study area for surface sediments.
Data source: NYSDEC (2008)

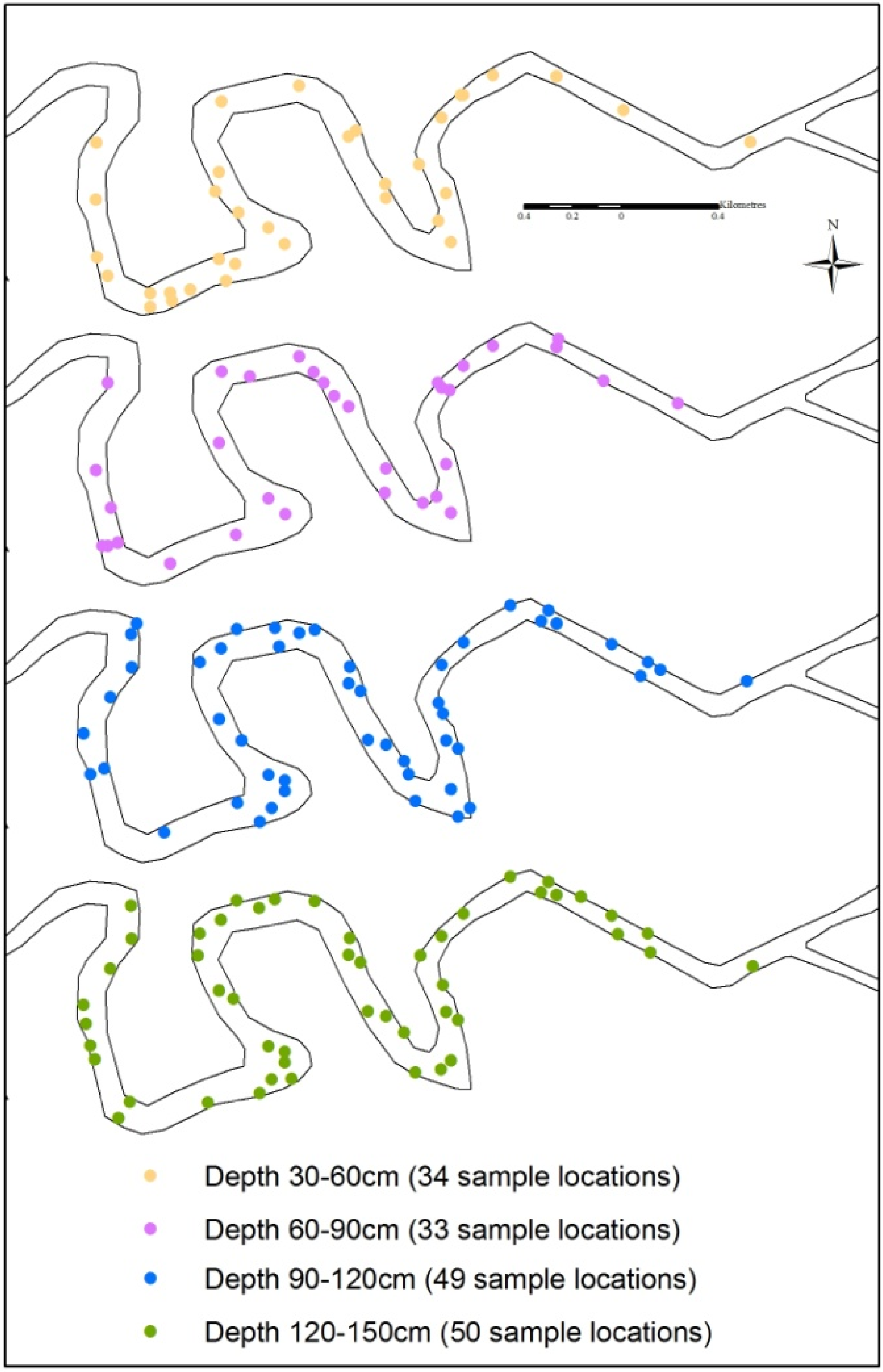

**Figure 3.3.2.** Distribution of sample points within the study area for subsurface sediments. Data source: NYSDEC (2008)

The data characteristics for anthracene and arsenic can be seen in Table 3.3.1 and Table 3.3.2 respectively. One important note is that there is a large difference between the number of samples taken at the surface level and the number of samples taken at various subsurface depths. Although 166 subsurface samples were obtained (more than the surface samples), these were divided among four subsurface groups, each of which was independently analyzed. Additionally, it is interesting to see that for both anthracene and arsenic, the average contamination of each is slightly lower at the surface level when compared to the subsurface depths. Thus, it is more effective to analyze the sediment contamination of the Buffalo River at surface and subsurface levels to get the best representation of its true contamination.

**Table 3.3.1.** Anthracene Sediment Sampling Location Statistics for the Buffalo River (ng/g)

| Depth | No. of Sites | Min | Max | Average | SD |
|---|---|---|---|---|---|
| Surface 0-30cm | 111 | 1.28 | 4.08 | 2.158198 | 0.510365 |
| Sub 30-60cm | 34 | 1.76 | 4 | 2.686471 | 0.720371 |
| Sub 60-90cm | 33 | 1.81 | 4 | 2.778182 | 0.767284 |
| Sub 90-120cm | 49 | 1.41 | 5.04 | 2.661429 | 0.845193 |
| Sub 120-150cm | 50 | 1.59 | 5.04 | 2.6866 | 0.875787 |

**Table 3.3.2.** Arsenic Sediment Sampling Location Statistics for the Buffalo River (ug/g)

| Depth | No. of Sites | Min | Max | Average | SD |
|---|---|---|---|---|---|
| Surface 0-30cm | 111 | 0.41 | 2.62 | 0.979009 | 0.241724 |
| Sub 30-60cm | 34 | 0.51 | 2.55 | 1.17 | 0.364966 |
| Sub 60-90cm | 33 | 0.8 | 1.82 | 1.120303 | 0.259959 |
| Sub 90-120cm | 49 | 0.64 | 2.21 | 1.104694 | 0.331035 |
| Sub 120-150cm | 50 | 0.83 | 2.21 | 1.1676 | 0.345691 |

### 3.4. Methods

An ordinary kriging spatial interpolation technique was used to assess the surface and subsurface sediment contamination of the Buffalo River as it pertains to Anthracene and Arsenic. The analysis was run independently on each of the two contaminants and their associated subsurface depths. The kriging geospatial technique was originally developed for the mining industry to estimate ore reserves, but has been effectively been used to estimate sediment contamination (Forsythe et al., 2001b; Bailey and Gatrell, 1995; Johnston et al., 2001).

Since the Buffalo River meanders, the kriged prediction error maps for the entire study area may not be a true representation of the contamination within the Buffalo River. The technique "uses statistical models that are based on the assumption that spatial autocorrelation exists within a collection of sampled points" (Forsythe et al., 2010b; Quyang et al., 2003). Rodriguez (2009) in his research found that the prediction error maps for mercury and lead contamination in the entire Buffalo River study area did not differ much from the results of the prediction error maps for three separate sections of the river.

The major advantage that the ordinary kriging technique has over other interpolation methods is that it can be statistically validated as it generates standard error surfaces (Forsythe et al., 2010b; Jakubek and Forsythe, 2004; Johnston et al., 2001). The most adequate parameters to use when performing a kriging interpolation for the Buffalo River study area through the geostatistical wizard in ESRI's ArcMap are as follows: Maximum Range: 900; Minimum Range: 300; Direction: 90; Neighbours to Include: 5; Include at Least: 1 (Forsythe et al., 2010a). These criteria were chosen after experimentation as they produced the most accurate results, when compared to other options. The maximum and minimum distances take into account the distance between sampling points. The direction parameter was set to 90 to account for both downstream and upstream meanders. Increasing the number of neighbours to include from 5 could decrease the spatial autocorrelation among measured points. Since there is a small number of sample points at the various subsurface depths, the including at least parameter was not increased from 1. To achieve the most ideal kriging results, the most appropriate kriging method (Spherical, Exponential, or Gaussian) should be evaluated. To determine the best model, the ideal criteria are as follows:  the mean should be as close to 0 as possible, the root-mean square prediction error (RMSPE) and average standard error (ASE) should be similar and both should not be not more than 20, while smaller values are more ideal, and the standardized root-mean squared prediction error (SRMSPE) should be as close to 1 as possible (Forsythe et al., 2010b; Forsythe and Marvin, 2009; Jakubek and Forsythe, 2004). If the RMS and ASE are greater than 20, then the actual values at each of the sampled locations are not close to the predicted values at those locations (Forsythe et al., 2010b; Forsythe and Marvin, 2009; Jakubek and Forsythe, 2004). When the SRMSPE is greater than 1, then the variability of predictions is underestimated and when the SRMSPE is less than 1, then the variability of predictions is overestimated (Forsythe and Marvin, 2005; Johnston et al., 2001).

A log transformation may need to be conducted if the kriging error results are not statistically valid. Although it is not necessary to log transform data used by the kriging interpolator, data that are normally distributed are better suited for kriging analysis (Forsythe et al., 2010). Quyang et al. (2004) recommends log transformations for nonnormally distributed datasets because the skeweness warrants some type of standardization. Missing values within the dataset need to be assigned a generic value, not zero, to ensure that they are omitted from the transformations and results. A base ten log function, “LG10()” in SPSS was used to standardize the data.

### *Log-Transformations*

After running the ordinary kriging spatial interpolator on the anthracene data, the best suited models were not statistically valid at the surface or subsurface levels so they were log-transformed. Table 3.4.1 shows the log-transformed cross validation statistics for anthracene at all depths, which are all considered to achieve the most suitable kriging statistics as defined in research conducted by Forsythe et al., (2010b), Jakubek and Forsythe (2004), and Johnston et al., (2001). The best suited model chosen at various depths included all three models considered: Spherical, Exponential, and Gaussian. The variability of predictions is slightly underestimated at subsurface depths of 60-90cm and 90-120cm, while the variability of predictions is slightly overestimated at surface level and subsurface depths at 30-60cm and 120-150cm.

**Table 3.4.1.** Kriging Log-Normalized Data Cross Validation Statistics for Anthracene

| Depth | Model | MPE | ASE | SRMSPE |
|---|---|---|---|---|
| Surface 0-30cm | Exponential | 0.004554 | 0.515 | 0.9837 |
| Sub 30-60cm | Gaussian | 0.0398 | 0.8171 | 0.9847 |
| Sub 60-90cm | Spherical | 0.003769 | 0.7406 | 1.027 |
| Sub 90-120cm | Exponential | 0.01351 | 0.3492 | 1.024 |
| Sub 120-150cm | Gaussian | 0.009402 | 0.8895 | 0.9954 |

After running the ordinary kriging spatial interpolator on the arsenic data, the best suited models were not statistically valid at the surface or subsurface levels, except at a subsurface depth of 60-90cm. It was decided to log transform all the depths to maintain consistency when comparing the results between the depths. The cross validation results can be seen in Table 3.4.2. Again these results are considered to achieve the most suitable kriging statistics. Similar to the case for anthracene, the best models varied for the different depths and included: Spherical, Exponential, and Gaussian. Further, the models slightly underestimated the variability of prediction at all depths except for the 60-90cm subsurface depth.

**Table 3.4.2.** Kriging Log-Normalized Data Cross Validation Statistics for Arsenic

| Depth | Model | MPE | ASE | SRMSPE |
|---|---|---|---|---|
| Surface 0-30cm | Gaussian | 0.000212 | 0.2364 | 1.028 |
| Sub 30-60cm | Spherical | 0.02332 | 0.3507 | 1.03 |
| Sub 60-90cm | Spherical | 0.001421 | 0.2854 | 0.9491 |
| Sub 90-120cm | Exponential | 0.00177 | 0.3492 | 1.024 |
| Sub 120-150cm | Exponential | 0.001712 | 0.3566 | 1.018 |

## 3.5. Results

### *Anthracene*

The surface sediment contamination of anthracene is depicted in Figure 3.5.1. The surface contamination is least contaminated when compared to the subsurface levels. The majority of the river appears to be contaminated between the TEL and PEL levels. Although the portions of the river that fall between these TEL and PEL levels are of interest, the areas where contamination is above the PEL level are most concerning. There is a small cluster of heavy contamination in the central portion of the river. High levels of anthracene contamination here are located on both sides of the meander. Also, a smaller section in the northern portion of the study area is contaminated above the PEL level. The immediate areas surrounding these sections of the river that are above the PEL are still heavily contaminated and are near the probable effect levels. There are no TEL isolines in Figure 3.5.1 because concentration levels for anthracene are all above this level. Figure 3.5.2 shows the sample locations and contamination levels for anthracene at the surface level. Since there are 111 sample locations in the study area, the proportional circle map appears slightly cluttered. Likewise, majority of the sample points have anthracene concentrations between the TEL and PEL (46.9ng/g and 245ng/g) making the map appear somewhat uniform. Variation in contamination concentrations between sample points in this class is difficult to identify. Further, there are samples taken that have anthracene concentrations below the TEL; however, these are few in number and are scattered throughout the study area.

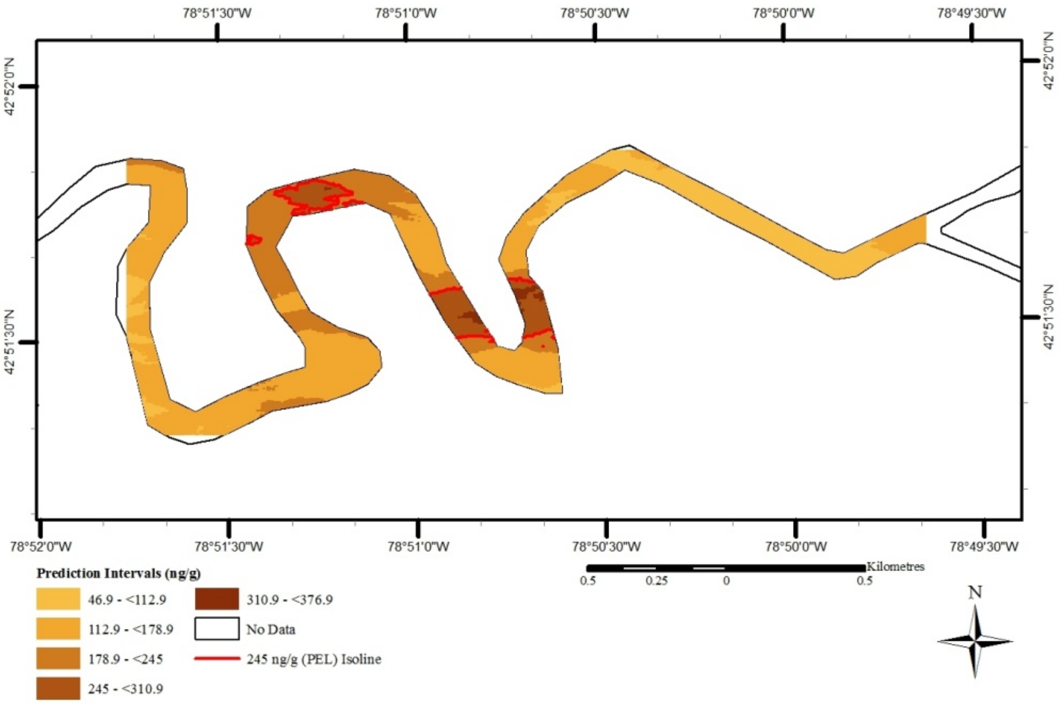

**Figure 3.5.1.** 2005 kriged anthracene log-normal concentrations at surface level

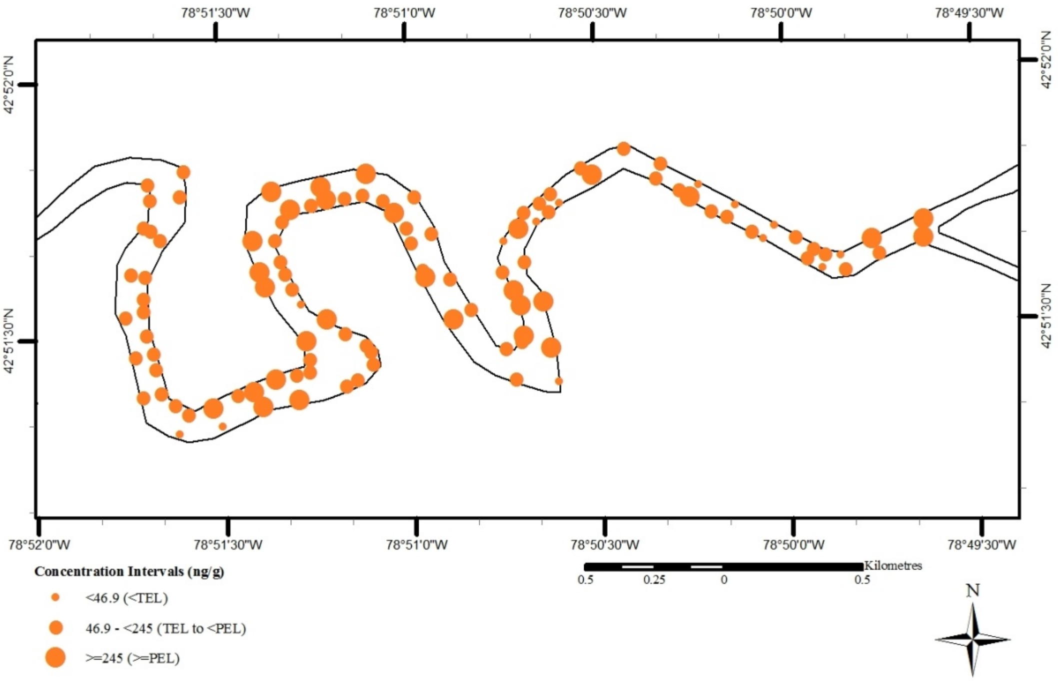

**Figure 3.5.2.** 2005 anthracene log-normal concentrations at surface level

The subsurface sediment contamination of anthracene at a subsurface depth of 30-60cm can be seen in Figure 3.5.3. This layer of sediment is located directly under the surface sediment. The contamination at this depth is more severe than that of the surface level. There is only a small PEL isoline located in the western section of the study area that separates a small northern portion that is contaminated between the TEL and PEL and the rest of the river that is contaminated above the PEL. Further, there is a very small portion of the river in the north-central section that is below the PEL, and classified between 112.9ng/g and 178.9ng/g, but it surrounded by heavier contamination. What is most concerning is that not only is the majority of contamination above the PEL at this depth, but most of the river falls in the final kriged class, which has contamination greater than or equal to 376.9ng/g. Since the pollution is so heavy here, there is no surprise that there are no TEL isolines and no segment of the river is below that TEL. The sample locations of anthracene contamination at a depth of 30-60cm can be seen in Figure 3.5.4. The majority of sample locations have anthracene contamination levels above the PEL and are dispersed throughout the entire river. There are no sample locations at this depth that have anthracene concentrations below the TEL.

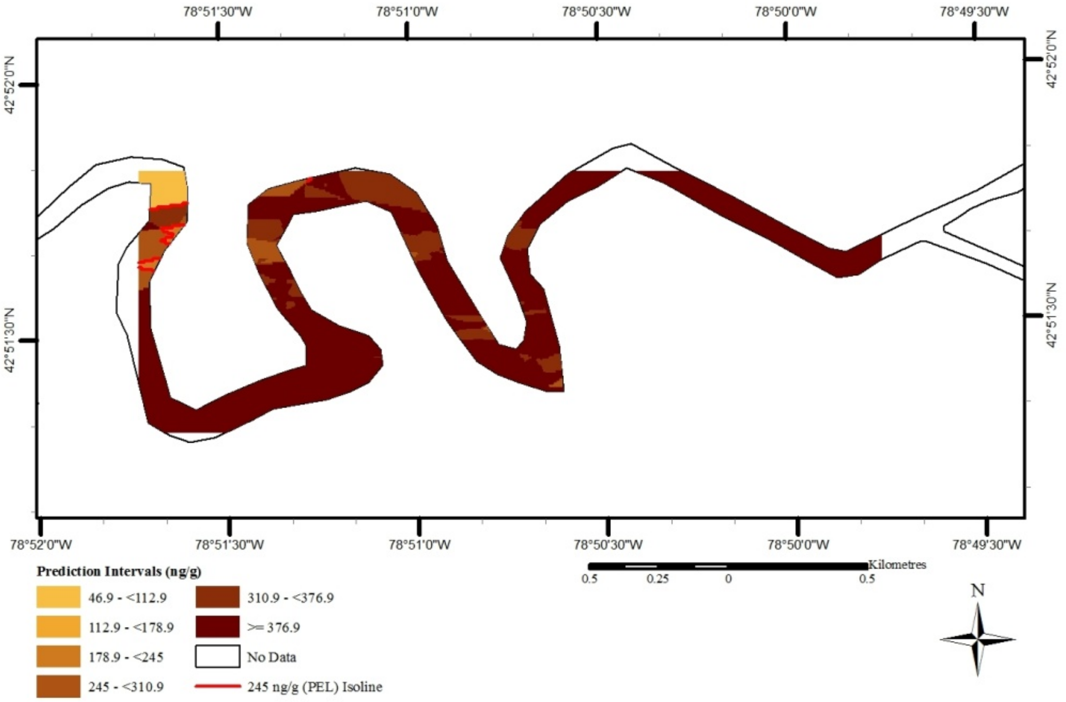

**Figure 3.5.3.** 2005 kriged anthracene log-normal concentrations at a depth of 30-60cm

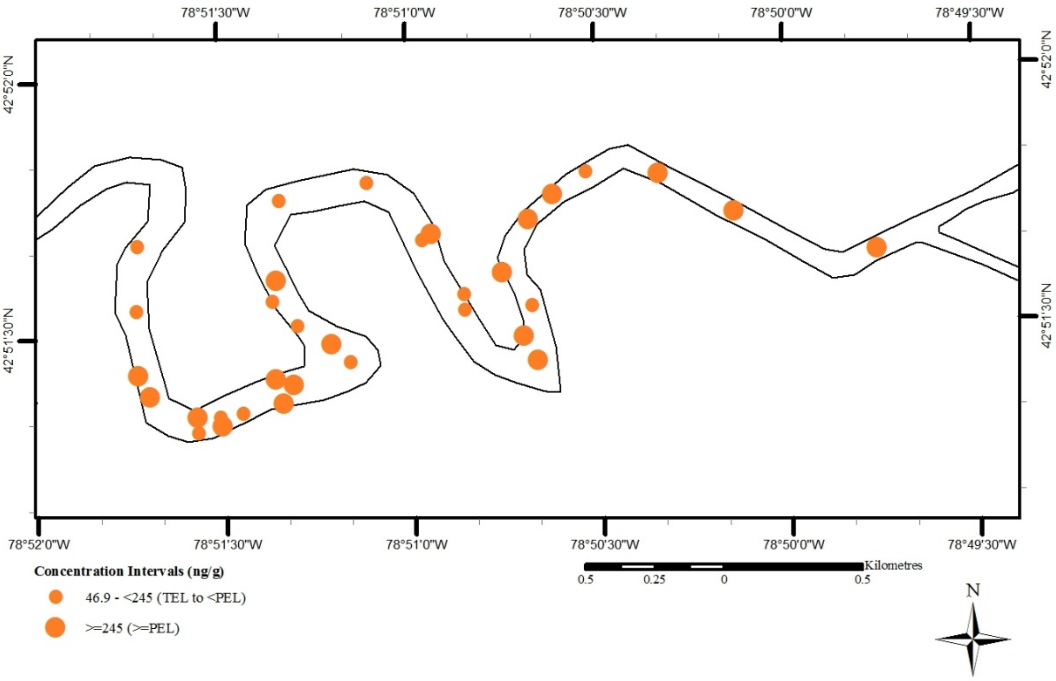

**Figure 3.5.4.** 2005 anthracene log-normal concentrations at a depth of 30-60cm

Figure 3.5.5 shows the distribution of anthracene contamination at a subsurface depth of 60-90cm. The contamination at this depth appears to be less contaminated when compared to the depth above. The central segment of the river is heavily contaminated above the PEL at the highest class, greater than or equal to 376.9ng/g. The eastern portion and part of the western portion of the river are less contaminated as contamination falls between the TEL and PEL, but then increase in contamination concentrations. The increase to heavy contamination is fairly sudden as the sections classified between 245ng/g and 376.9ng/g is very small. Further the least contaminated areas, between 46.9ng/g and 112.9ng/g, are located in the western and eastern sections of the river and are small. The contamination in these areas is still above the TEL, thus, no sections of the river at this subsurface depth is classified below the TEL and considered to have minimal contamination. Figure 3.5.6 shows the distribution of sample locations for anthracene contamination at a subsurface depth of 60-90cm. The central section of the river has the most sample points with contamination levels for anthracene above the PEL. The eastern section of the river contains a few sample locations at this depth, all of which are between the TEL and PEL.

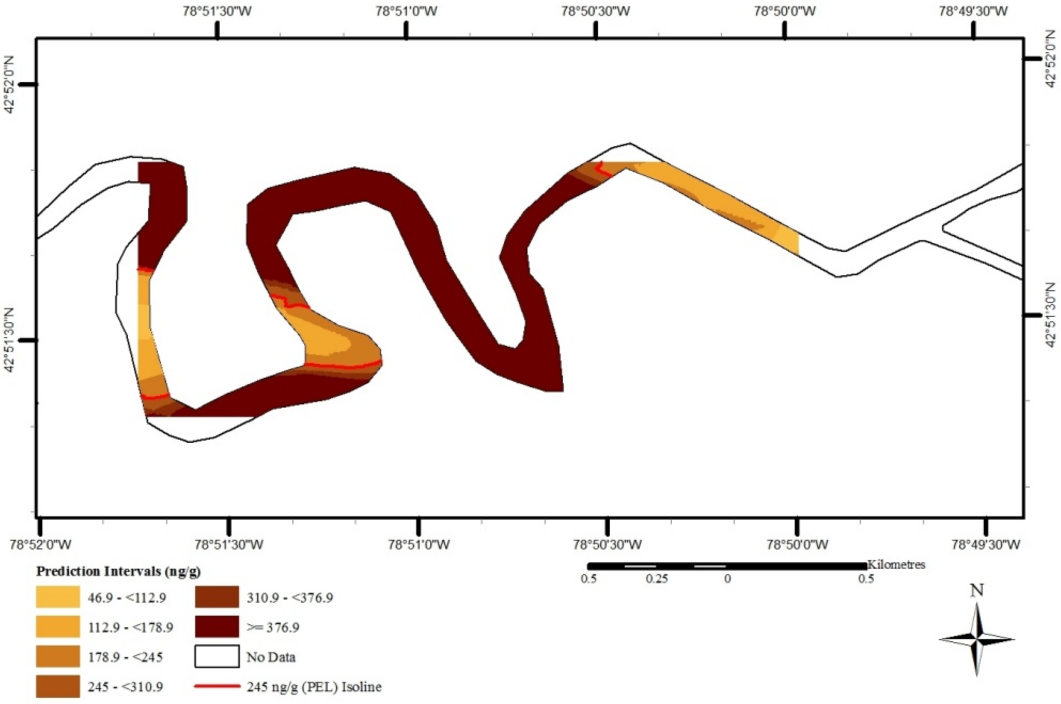

**Figure 3.5.5.** 2005 kriged anthracene log-normal concentrations at a depth of 60-90cm

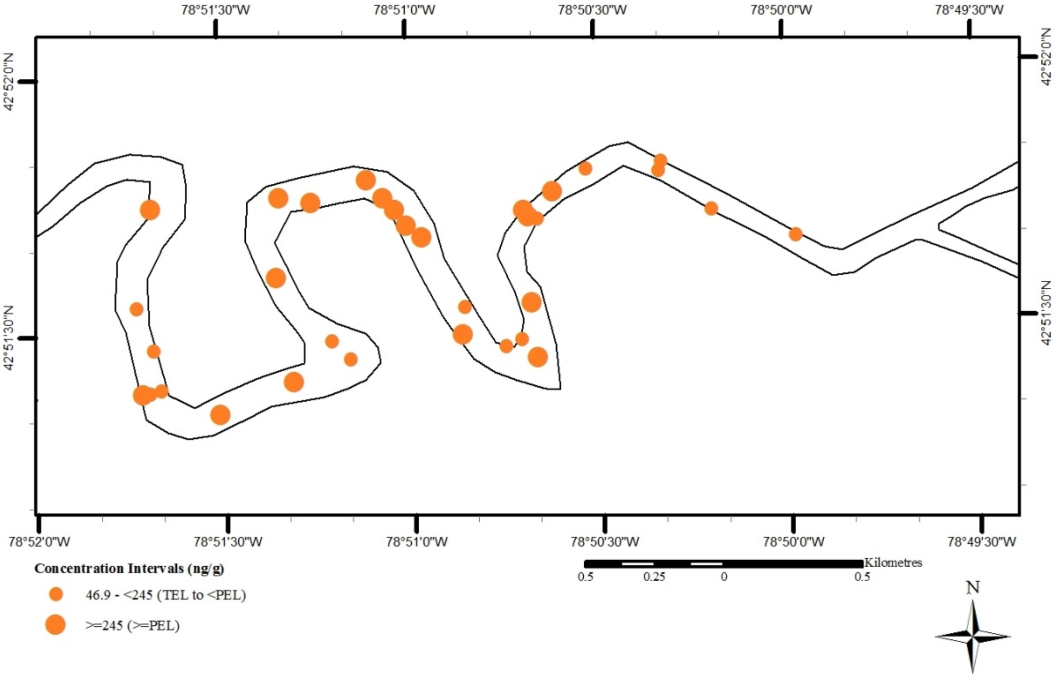

**Figure 3.5.6.** 2005 anthracene log-normal concentrations at a depth of 60-90cm

The subsurface sediment contamination of anthracene at the next subsurface depth of 90-120cm is seen in Figure 3.5.7. At this depth, the contamination follows a similar pattern to that of the above depth at 60-90cm. The central portion of the river is heavily contaminated with anthracene as it is greater than or equal to 376.9ng/g. The south central section of the river has a small area that is classified between the TEL and PEL, as this section is less contaminated than the depth above. Although the area directly above is still contaminated above the PEL, it is not as contaminated as the above depth since a small section here is between the 245ng/g and 376.9ng/g range. Also, the eastern portion of the river is mostly between the TEL and PEL, but does contain a small portion above the TEL. Moreover, the western segment of the river is more contaminated than the above depth with a much smaller pocket between the TEL and PEL, but decreases in the south-western area. Again, no portion of the river at this depth is contaminated below the TEL, thus still remaining a concern. Figure 3.5.8 shows the sample locations at a subsurface depth of 90-120cm for anthracene. With more sample points than at previous depths, the map appears to be cluttered. Using proportional circles to display anthracene concentrations, you are limited to the number of classes you can select to effectively display the data. Thus, only three classes have been chosen that are deciphered by circle size, which is less than the number of classes used in Figure 3.5.7, which effectively displays six classes.

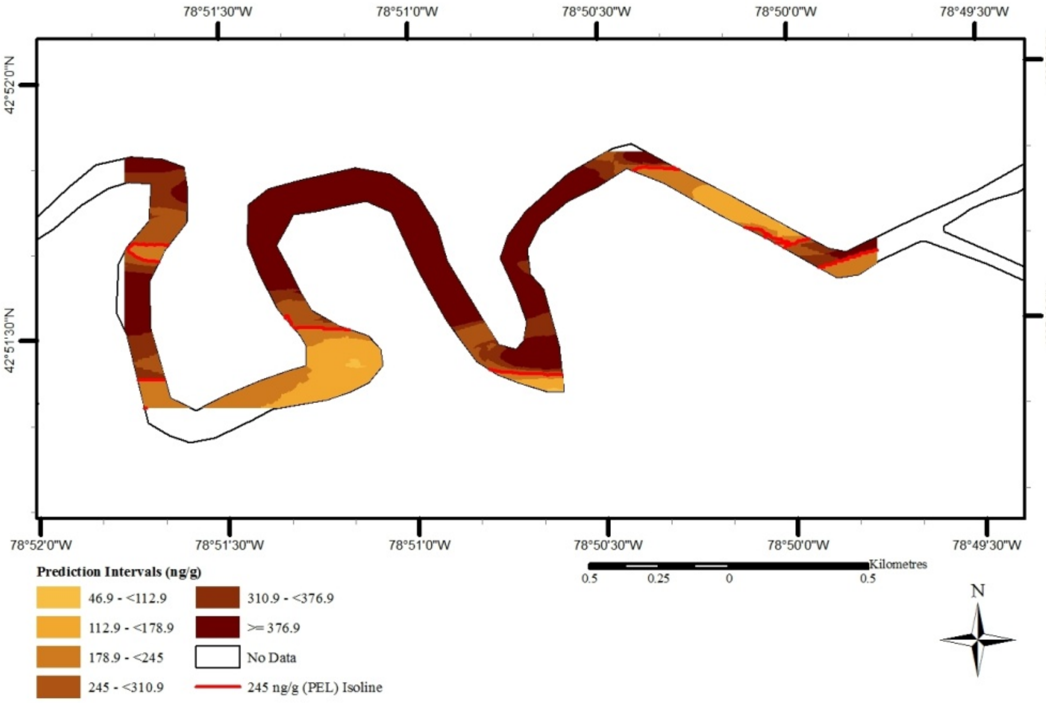

**Figure 3.5.7.** 2005 kriged anthracene log-normal concentrations at a depth of 90-120cm

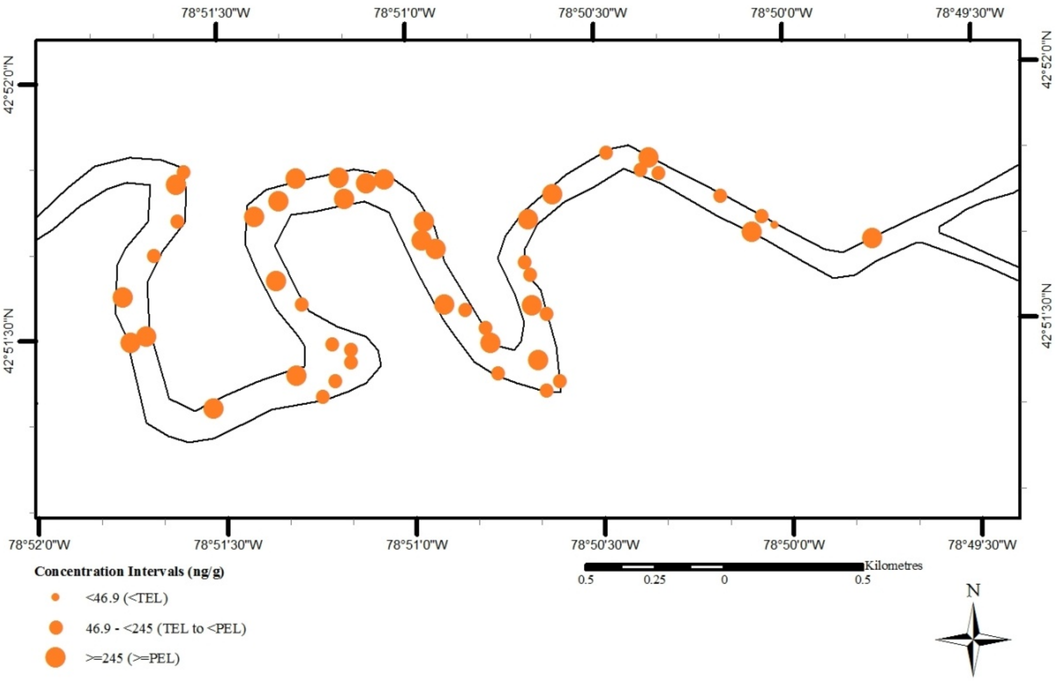

**Figure 3.5.8.** 2005 anthracene log-normal concentrations at a depth of 90-120cm

Figure 3.5.9, shows the distribution of sediment contamination of anthracene at the deepest subsurface depth of 120-150cm. Again, the pattern of anthracene distribution at this depth is similar to the two depths above. The central section of the river is heavily contaminated above the PEL. Most of this portion is contaminated at a concentration greater than or equal to 376.9ng/g. Similar to the above depth, which is slightly different than at the 60-90cm depth, there is a small section in the south-central area that is a little less contaminated and just below the PEL. Further, the eastern section of the river is less contaminated than the central section as the concentrations are between the TEL and PEL, but the contamination level here is still concerning. Also, the south-west section of the river is mostly contaminated between the TEL and PEL, with only a small area of anthracene concentrations above the PEL. The north-west section of the river is heavily contaminated with contamination levels similar to that of the central portion of the river. Figure 3.5.10 shows the central section of the Buffalo River has the most sample locations at a subsurface depth of 120-150cm that are above the PEL. Also, there is a single sample location that has an anthracene concentration below the TEL which is also located close to another sample point that has an anthracene concentration above the PEL. This part of the river appears to be a transition zone from above to below the PEL.

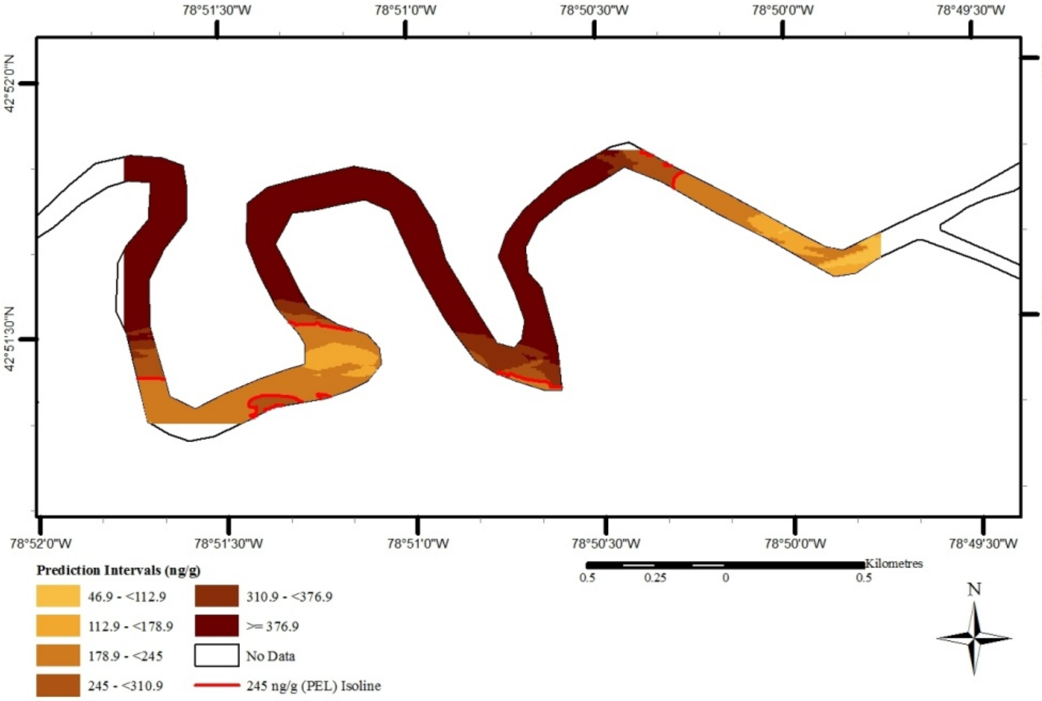

**Figure 3.5.9.** 2005 kriged anthracene log-normal concentrations at a depth of 120-150cm

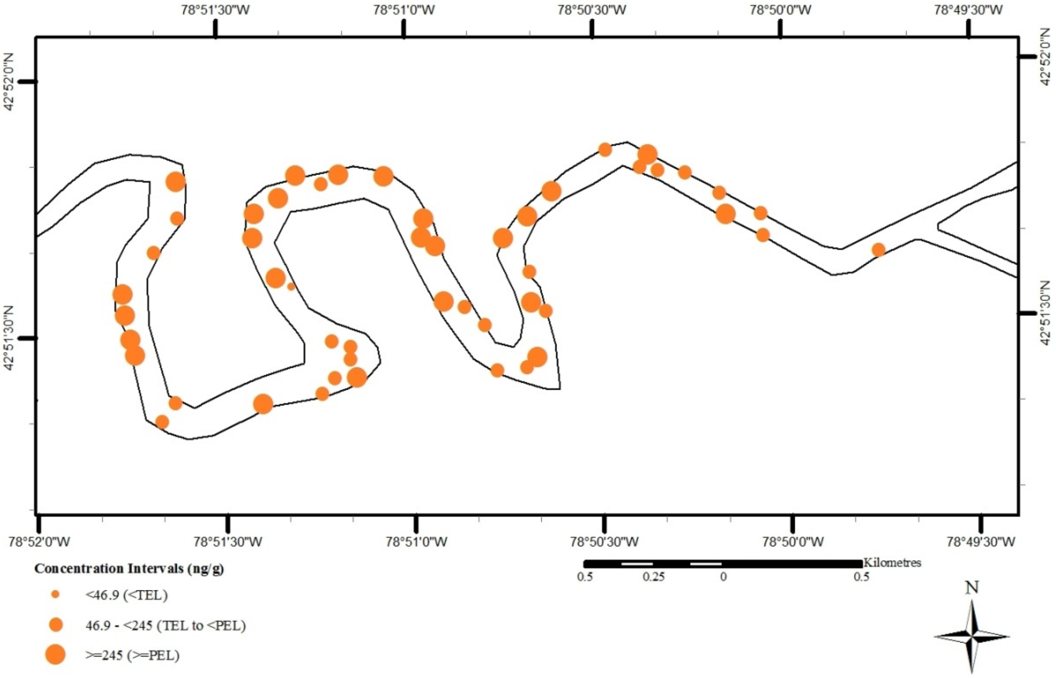

**Figure 3.5.10.** 2005 anthracene log-normal concentrations at a depth of 120-150cm

*Arsenic*

The surface sediment contamination of arsenic is depicted in Figure 3.5.11. Similarly to the case with anthracene, the surface contamination is least contaminated when compared to the subsurface levels. The Buffalo River is less contaminated with arsenic when compared to anthracene. The eastern section of the river has a TEL isoline, which was not present for anthracene contamination concentrations at the surface or any subsurface levels. This small area has arsenic concentrations just below the TEL. Further, the arsenic concentrations at the surface level appear to be fairly uniform throughout the river. Although the river appears less contaminated with arsenic when compared to anthracene, concentrations here are mostly categorized between the TEL and PEL and still concerning as adverse biological effects are likely to occur. Furthermore, the central section of the river has a small area that is above the PEL and is most alarming; however, the concentrations of arsenic here are just above the PEL and not too heavily contaminated. Figure 3.5.12 shows the distribution of arsenic concentrations by sample locations. There is a small cluster of sample locations in the east that have concentrations below the TEL. These points contribute to the creation of a TEL isoline in the kriged map. There are other sample locations in the central section of the river that have arsenic concentrations below the TEL; however, they are surrounded by more heavily contaminated sample locations, which prevent the creation of a TEL isoline.

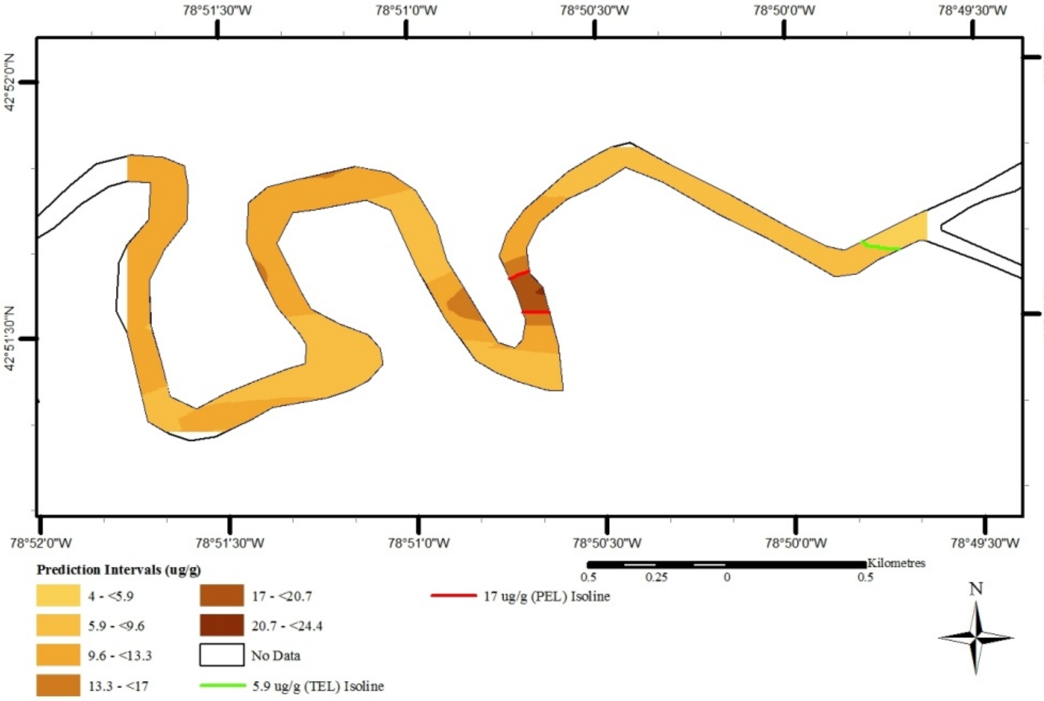

**Figure 3.5.11.** 2005 kriged arsenic log-normal concentrations at surface level

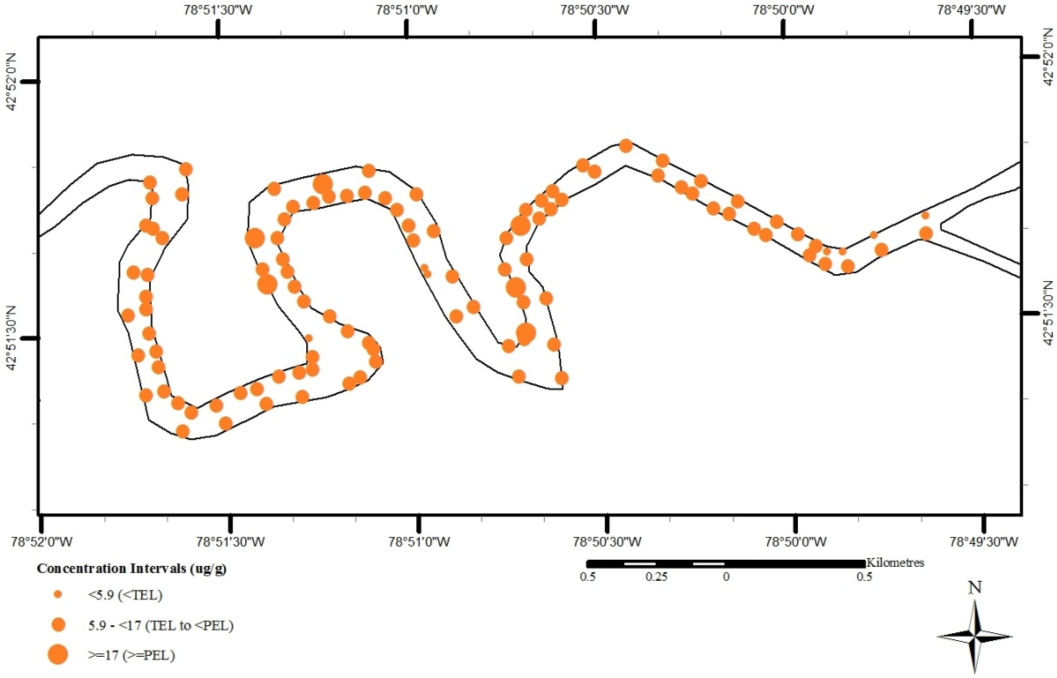

**Figure 3.5.12.** 2005 arsenic log-normal concentrations at surface level

Figure 3.5.13 shows the arsenic concentrations at a subsurface depth of 30-60cm, which is just below the surface level. Arsenic contamination at this depth is more severe when compared to the surface level above. There are clusters of heavy contamination scattered throughout the river. Similar to the above depth, the central section of the river is mostly contaminated between the TEL and PEL with a larger cluster of arsenic contamination above the PEL. This level of contamination is located on both the downstream and upstream sections. Also, there is a large area in the eastern portion of the river that is heavily contaminated above the PEL at concentrations greater than or equal to 24.4ug/g. Moreover, the western portion of the river has a sudden change in contamination as the southern section is contaminated above the PEL, while the northern section has a small area contaminated below the TEL. Furthermore, Figure 3.5.14 shows the distribution of sample locations and concentration of arsenic contamination at a subsurface depth of 30-60cm. There are few sample locations located in the eastern section of the river, with two points showing arsenic concentration levels above the PEL. The western section of the river has two sample points with arsenic concentrations below the TEL that are separated by more heavily contaminated sample points.

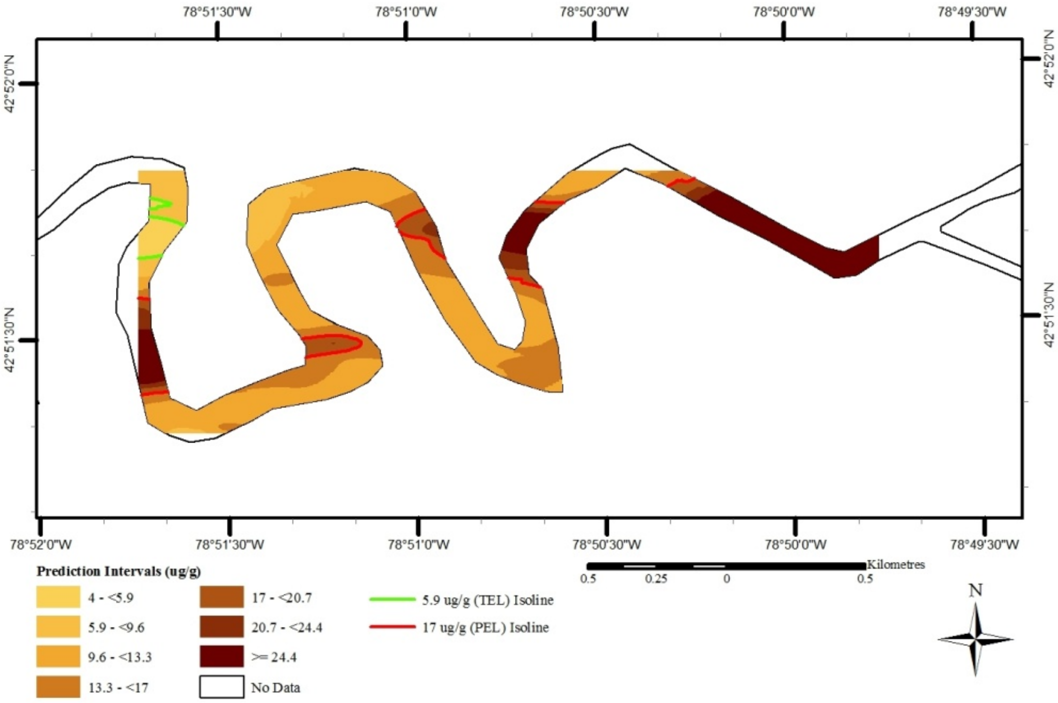

**Figure 3.5.13.** 2005 kriged arsenic log-normal concentrations at a depth of 30-60cm

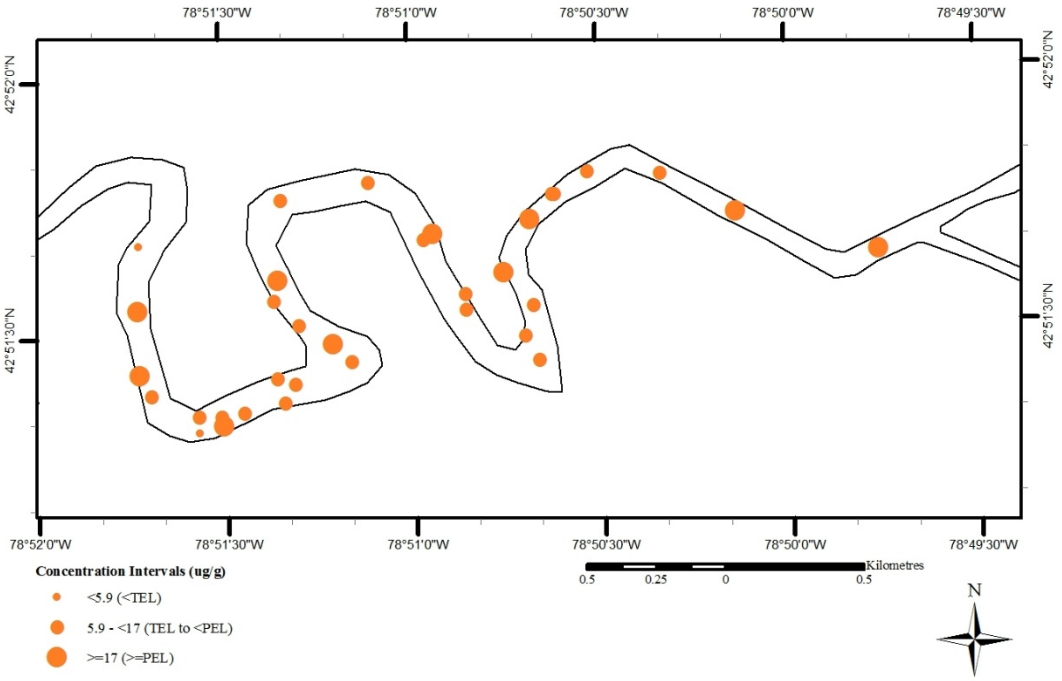

**Figure 3.5.14.** 2005 arsenic log-normal concentrations at a depth of 30-60cm

Figure 3.5.15 shows the distribution of arsenic at a subsurface depth of 60-90cm. This is the upper most depth that does not contain any TEL isolines. The concentrations of arsenic within the rivers' sediment follow a uniform pattern throughout. Majority of the river at this depth has arsenic concentrations between 9.6ug/g and 17ug/g. The heaviest contamination and largest classification grouping is concentrated in the central section of the river. The south-western and eastern portions of the river are slightly less contaminated, but contamination levels are still between the TEL and PEL. Also, there are clusters of small areas where arsenic contaminations are above the PEL and are most concerning. These are mostly located in the central section of the river, where contamination is heaviest, but are also present in the north-western section of the river. Figure 3.5.16 shows the distribution of sample locations for arsenic concentrations at a subsurface depth of 60-90cm. There are no sample points that have arsenic concentrations below the TEL. The sample locations are dispersed throughout the river and with fewer sample locations, there are more gaps between points. This proportional circles map does not relay the contamination levels well when compared to the kriged maps since viewers are required to estimate the contamination levels between points.

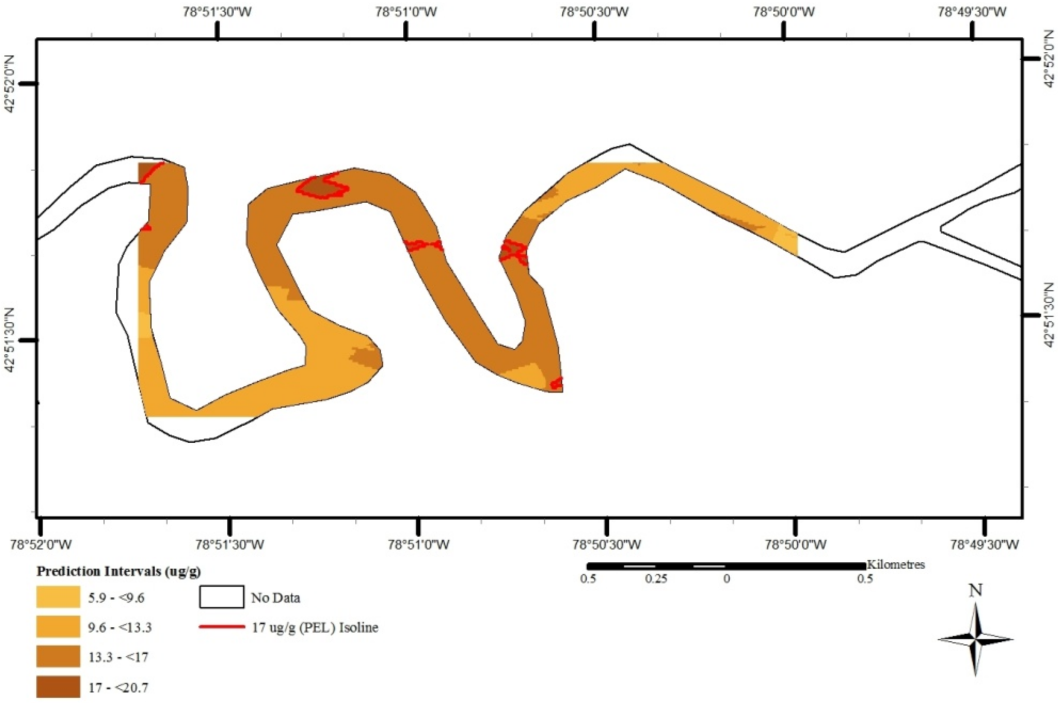

**Figure 3.5.15.** 2005 kriged arsenic log-normal concentrations at a depth of 60-90cm

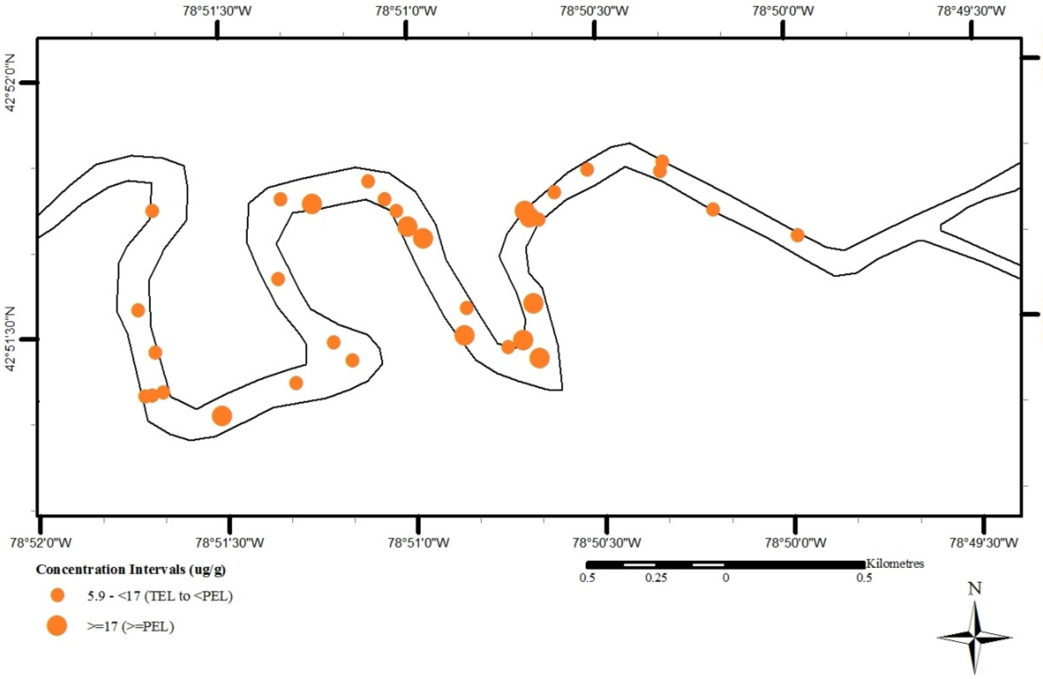

**Figure 3.5.16.** 2005 arsenic log-normal concentrations at a depth of 60-90cm

The subsurface sediment contamination of arsenic at the next subsurface depth of 90-120cm is seen in Figure 3.5.17. Contamination concentrations differ throughout the river at this depth, but contamination levels are above the TEL in all areas. The heaviest arsenic contamination at this depth is located in the central section of the river. The upstream portion here is more contaminated with a large area above the PEL when compared to the downstream portion, which has smaller clusters of heavy contamination above the PEL. Also, there are PEL isolines located in the western section of the river, where there is a small pocket of heavy contamination. Further, the eastern section of the river is less polluted with arsenic as concentrations are between 9.6ug/g and 17ug/g. Figure 3.5.18 shows the distribution of sediment sample locations for arsenic at a subsurface depth of 90-120cm. Many samples taken in the central section of the river have arsenic concentrations above the PEL. Specifically, the northern part of this central section has a cluster of sample points above the PEL, appearing to be severally contaminated. When compared to Figure 3.5.17, the kriged map only shows a small PEL isoline located in this northern section.

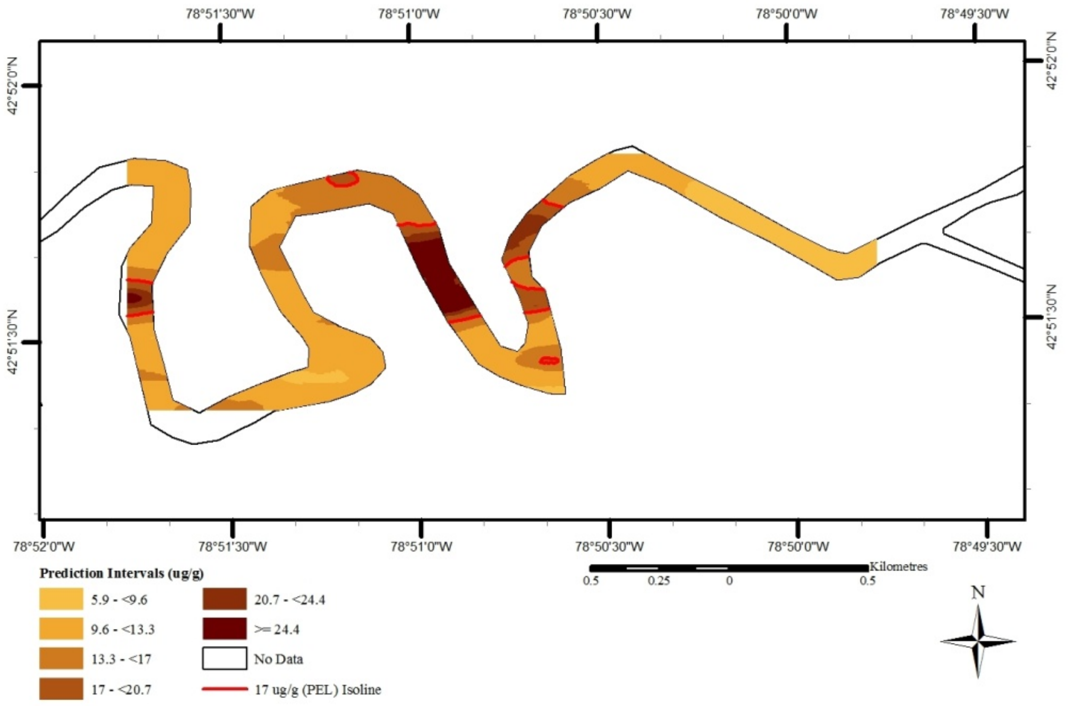

**Figure 3.5.17.** 2005 kriged arsenic log-normal concentrations at a depth of 90-120cm

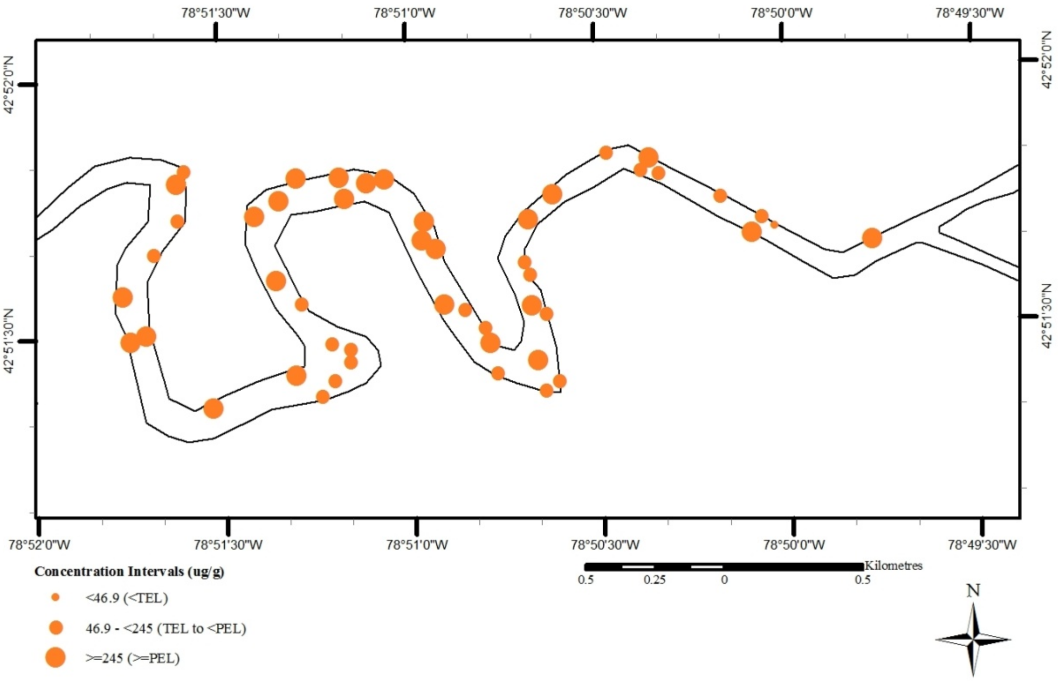

**Figure 3.5.18.** 2005 arsenic log-normal concentrations at a depth of 90-120cm

Figure 3.5.19, shows the distribution of arsenic concentrations within the rivers' sediment at the deepest subsurface depth of 120-150cm. Similar to the depth above, the central section of the river at this depth is polluted the most with arsenic. The contamination is heavier here as the PEL isolines encompass larger areas both on the downstream and upstream sections of the central part of the river. Further, the western section of the river has heavy arsenic contamination at this depth that is similar to that of the above depth. The area here that has arsenic concentrations greater than or equal to 17ug/g is larger than the above depth and decreases more gradually. Also, the eastern portion of the river is similarly contaminated to the depth above with arsenic concentrations ranging between the TEL and PEL. The sample locations and concentrations of arsenic at a subsurface depth of 120-150cm can be seen in Figure 3.5.20. There are no sample locations at this depth that have arsenic concentrations below the TEL. Sample locations with arsenic contamination above the PEL are mainly concentrated in the central section of the river, but are present in the western section as well. When comparing Figures 3.5.19 to 3.5.20, the distribution of contamination follows a similar pattern, but the kriged map in Figure 3.5.19 is more detailed.

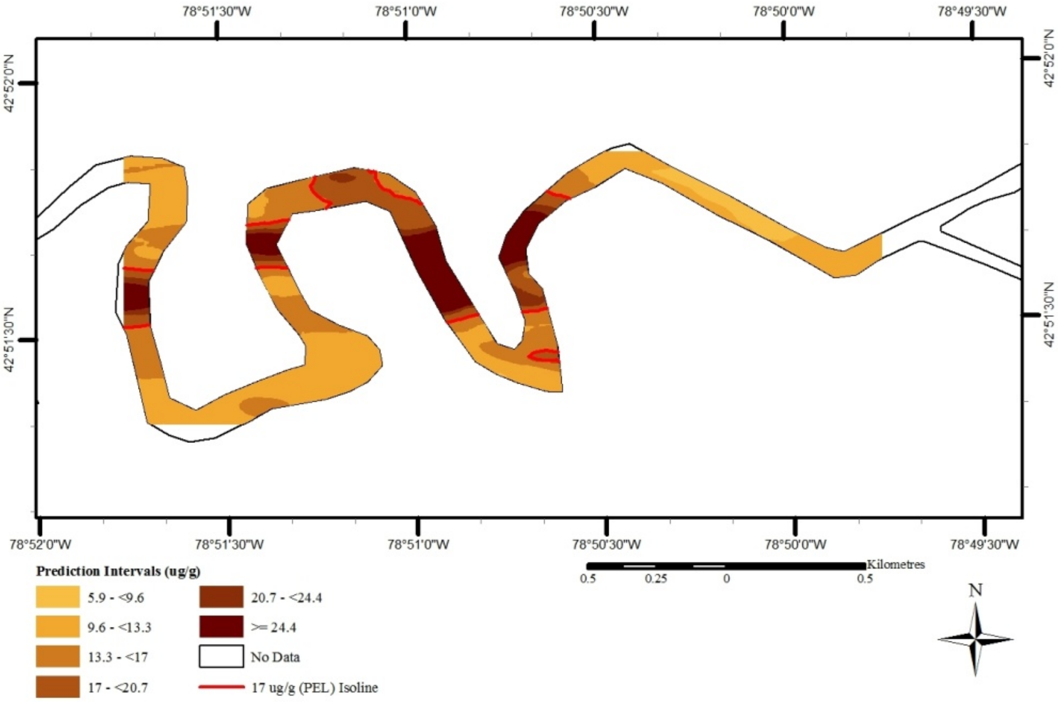

**Figure 3.5.19.** 2005 kriged arsenic log-normal concentrations at a depth of 120-150cm

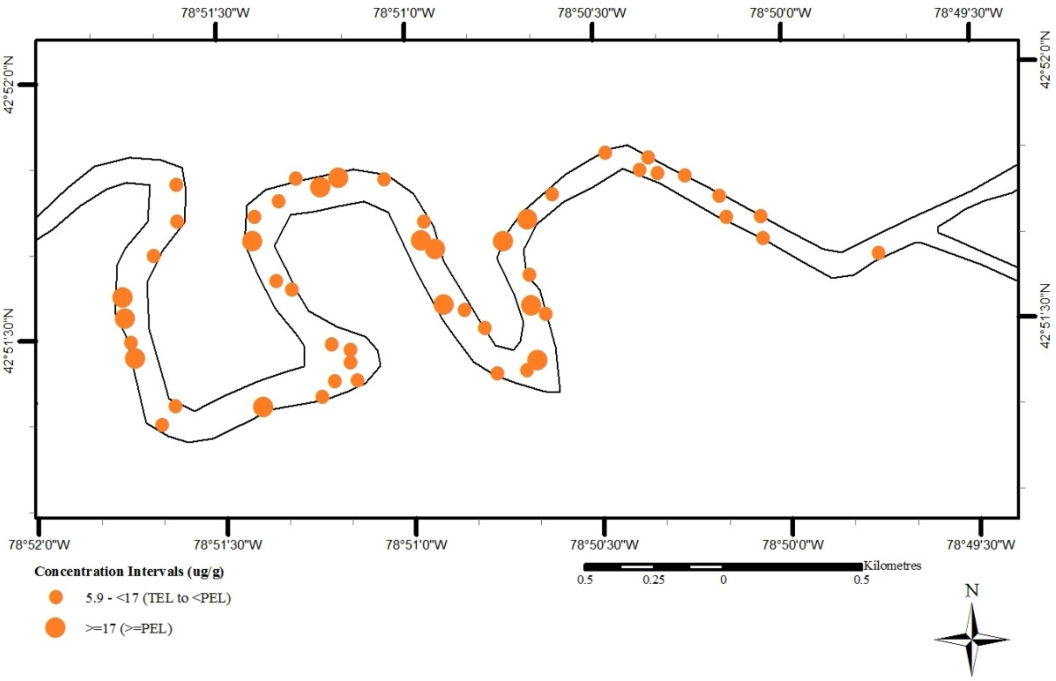

**Figure 3.5.20.** 2005 kriged arsenic log-normal concentrations at a depth of 120-150cm

## 3.6. Discussion

The Buffalo River is heavily contaminated with anthracene and arsenic. Areas with contamination concentrations that are above the PEL are most concerning, while areas that have contamination concentrations between the TEL and PEL are less concerning, but still important. Areas below the TEL, which are few in this study, do not pose a great threat to the aquatic ecosystem. The distribution of sample locations between the three chosen class divisions can be seen in Table 3.6.1 for anthracene and in Table 3.6.2 for arsenic. Generally, the river is more heavily contaminated with anthracene when compared to arsenic. Anthracene concentrations above the PEL are a lot larger in proportion to concentrations between the TEL and PEL when compared to arsenic.

**Table 3.6.1.** Number of Anthracene Sediment Sampling Locations in Relation to TEL and PEL Categories

| Depth | No. of Sites | <TEL | ≥TEL and <PEL | ≥PEL |
|---|---|---|---|---|
| Surface 0-30cm | 111 | 13 | 69 | 29 |
| Sub 30-60cm | 34 | 0 | 16 | 18 |
| Sub 60-90cm | 33 | 0 | 15 | 18 |
| Sub 90-120cm | 49 | 1 | 22 | 26 |
| Sub 120-150cm | 50 | 1 | 24 | 25 |

**Table 3.6.2.** Number of Arsenic Sediment Sampling Locations in Relation to TEL and PEL Categories

| Depth | No. of Sites | <TEL | ≥TEL and <PEL | ≥PEL |
|---|---|---|---|---|
| Surface 0-30cm | 111 | 7 | 98 | 6 |
| Sub 30-60cm | 34 | 2 | 22 | 10 |
| Sub 60-90cm | 33 | 0 | 23 | 10 |
| Sub 90-120cm | 49 | 2 | 37 | 10 |
| Sub 120-150cm | 50 | 0 | 36 | 14 |

Anthracene concentrations at the surface level are lower when compared to the various subsurface depths. As seen in Table 3.6.1, there are more sample points within the ≥TEL and <PEL class than the ≥PEL class at the surface level; however the opposite pattern exists at the subsurface depths. The drastic change in contamination levels here may be attributed to PAHs binding with sediment rather than staying on the surface. Also, current conditions, being 2005, of biological active strata are identified by surface sediments, while subsurface sediments represent the history of contaminant depositional patterns (Sutton, 2006). Further, the subsurface distribution of anthracene appears to be fairly uniform throughout all depths. One underlying pattern that appears to exist is that anthracene contamination within the Buffalo River sediment is greatest at a subsurface depth of 30-60cm and then tends to gradually decrease within deeper sediment. This can be seen by comparing Figures 3.5.1 through 3.5.10.

One important note is that Table 3.6.1 may not show this pattern distinctly, which is attributed to just grouping sediment samples into the chosen classes; however, this information does not show exact sediment core concentration. Just because subsurface level 30-60cm and 60-90cm are proportionally similar in Table 3.6.1, does not mean contamination levels are exact because one depth could have most of those sample points recorded closer to the TEL while the other depth would have those samples recorded closer to the PEL. The kriging spatial interpolation technique eliminates this issue, making kriging more effective than viewing traditional proportional circle maps. When comparing the kriged maps to the proportional circle maps in Figures 3.5.1 through 3.5.20, the kriged maps show more information. With proportional circle maps, the viewer needs to guess or estimate how contamination levels vary between sample locations, which are what the kriged maps display.

Arsenic concentrations within the Buffalo River sediment differ when comparing surface contamination to subsurface contamination. Forsythe et al. (2010a) incorporated arsenic surface contamination in their research. Results in this paper are identical to those published in their research. Figure 3.5.11 shows that the majority of the river is contaminated with arsenic between the TEL and PEL, with most values closer to the TEL, signifying that contamination is concerning, but not as severe when compared to anthracene or other metals in Forsythe et al. (2010a) research. If the surface level is only used to analyse the severity of contamination within the river, the true distribution of contamination may not be known. Arsenic, a metal, tends to bind with particles which then deposit into the sediment, meaning that above water would have lower concentration of arsenic than the subsurface sediment (Smol, 2008). No obvious pattern can be seen when comparing the subsurface depths in Figures 3.5.13 through 3.5.20, except that key areas of concern can be identified.

Moreover, these key areas of concern can be identified in both anthracene and arsenic contamination maps. The reason why these areas are important is because they represent the highest concentrations of contamination, which is above the PEL, making adverse biological effects likely to occur. Also, since dredging is occurring to restore the rivers' health, these heavily contaminated areas need to be identified and suggested as sites to be dredged. Figures 3.5.1 through 3.5.20 identify the central section of the Buffalo River study area as the most concerning, with contamination levels above the TEL on both the downstream and upstream sections of the river. Also, the western upriver section is concerning as all subsurface depths show PEL isolines, with large portions of anthracene concentration greater than or equal to 376.9ng/g. Further, four of out of the ten kriged maps display PEL isolines in the eastern section of the river, which appears to be the least contaminated. This could be attributed to the fact that the river flows westward and any remaining dredged sediment may have already flowed down river.

### 3.7. Conclusion

This research was completed to determine the extent of contamination within the Buffalo River. The New York State Department of Environmental Conservation collected the data used in this research. Both anthracene and arsenic concentrations were mapped using the kriging spatial interpolation technique to identify areas where sediment contamination was most concerning. Analysing a PAH and metalloid presented a good measure of the real contamination within Buffalo River sediments.

The Buffalo River was more contaminated with anthracene as compared to arsenic. The surface layer is a lot less contaminated than the subsurface layers in both cases, which can be linked to the labelling of the Buffalo River as an Area of Concern by the Great Lakes Water Quality Agreement between Canada and the United States. Since, more quality control measures have been implemented by the government, including holding major corporations accountable for the environmental damage. Current discharges and other sources of contamination have decreased which can be attributed to less contamination of the surface layer; however, historic contamination still plays a factor as deeper sediments are heavily contaminated. Based on the results of the study, it can be concluded that the Buffalo River should still be an area of concern as historical contamination is still present within the rivers' sediment and appropriate actions to be taken to restore its health. Dredging may be a good option in restoring the natural habitat of the river, and key areas outlined in this research should be considered as suitable sites.

# CHAPTER 4: Recommendations and Future Research

Although analyzing anthracene and arsenic concentrations at various depths within the Buffalo River sediment was a good measure of assessing the rivers' overall contamination, future research could be conducted on other contaminants. Assessing the distribution of DDT, PCBs, copper, and other contaminants within the different sediment depths could benefit the analysis. A more in depth study can be performed on the geomorphology of the river to see if the generic makeup of the meandering river could be linked to varying contamination levels.

Furthermore, key areas that have been heavily contaminated with anthracene and arsenic have been identified in this research. Future research could try and link these areas with sources of pollution and try to determine if any relationships exist between them and discharge sites located throughout the river. The identified heavily contaminated hotspots for both anthracene and arsenic are most concerning and should be considered for future remedial actions. Since contamination is heavy for both contaminants studied in these hotspots, it is recommended that these areas get dredged, rather than have the sediment capped. Dredging is an expensive process; however having identified selected areas of concern would decrease the investment needed to undergo a larger remedial project.

Current conditions of the Buffalo River can be assessed by analyzing surficial contamination while historical contamination can be identified by analyzing subsurface contamination (Sutton, 2006); however, this may be misleading since the Buffalo River has previously been dredged. The inclusion of past dredging sites may also be considered important as the process disturbs the overall health of the entire river. Presently, it would be difficult to assess exactly how old the rivers sediment is without fully understanding the impact of past remedial actions.

Additionally, Rodriguez (2009) considered the possibility that the meanders in the Buffalo River could present misleading kriging results. He was not able to find any major differences between the kriged results for lead and mercury throughout the entire Buffalo River compared to the kriged results for lead and mercury on sections of the Buffalo River. Additional research should be conducted on the effects of using the kriging spatial interpolation technique on a study area that meanders. The kriging spatial interpolation technique uses nearby sample location to predict contamination in a continuous area. Since sections of the river on opposite sides of meanders may have different contamination levels, it may be important to interpolate these areas individually. This may be difficult accomplish with the present subsurface dataset as there may not be enough sample locations to effectively interpolate separate sections of the Buffalo River based on its meanders.

Further research on kriging sections the Buffalo River for different contaminants at various depths may be beneficial although you would need more sample points for this. If re-sampling takes place in future years, it should closely mirror the current sample locations in addition to newer sample locations. This would provide the opportunity for a comparative study to monitor the success of the remedial actions taken. Also, if re-sampling occurs, it would be beneficial to extract pollutant concentration at all depths for each sample location. If this is completed, then concentrations for different contaminants can be aggregated. These aggregated contamination levels could then show the overall sediment contamination in a specific area and could also be kriged. With the current dataset, this is not possible since different layer depths have sample locations unevenly distributed.

## REFERENCES

Bailey, T.C., and A.C. Gatrell. 1995. *Interactive Spatial Data Analysis*, Longman Group Limited.

Baumard P., H. Budzinski, and P. Garrigues. 2009. Polycyclic Aromatic Hydrocarbons in Sediments and Mussels of the Western Mediterranean Sea. *Environmental Toxicology and Chemistry, 17* (5), 765-776.

Berg, M., H. Tran, T. Nguyen, H. Pham, R. Schertenleib, and W. Giger, 2001. Arsenic Contamination of Groundwater and Drinking Water in Vietnam: A Human Health Threat. *Environmental Science and Technology, 35*(13), 2621-2626.

Canfield, T. J., J.F. Dwyer, J.F. Fairchild, P.S. Haverland, C.G. Ingersoll, N.E. Kemble, D.R. Mount, T.W. LaPoint, G.A. Burton, and M.C. Swift. 1996. Assessing Contamination in Great Lakes Sediments Using Benthic Invertebrate Communities and the Sediment Quality Triad Approach. *Journal of Great Lakes Research, 22*(3), 565-583.

Clark, I. 1979. *Practical Geostatistics.* Essex: Applied Science Publishers.

Djomo, J. E., P. Garrigues, and J.F. Narbonne. 2009. Uptake and Depuration of Polycyclic Aromatic Hydrocarbons from Sediment by the Zebrafish (Brachydanio Rerio). *Environmental Toxicology and Chemistry, 15*(7), 1177-1181.

ENVIRON International Corporation, MACTEC Engineering and Consulting, Inc., LimnoTech (EML). 2010. *Feasibility Study for the Buffalo River, New York.* Buffalo: Buffalo River Great Lakes Legacy Act Project Coordination Team.

Forsythe, K.W., and C.H. Marvin. 2005. Analyzing the Spatial Distribution of Sediment Contamination in the Lower Great Lakes, *Water Quality Research Journal of Canada, 40*(4), 389-401.

Forsythe, K. W., and C.H. Marvin. 2009. Assessing Historical Versus Contemporary Mercury and Lead Contamination in Lake Huron Sediments. *Aquatic Ecosystem Health and Management, 12*(1), 101-109.

Forsythe, K.W., A. Gawedzki, and P.S. Rodriguez. 2010a. Assessing Sediment Contamination in the Buffalo River. In: Strobl, J., T. Blaschke, and G. Griesebner (Eds.) *Proceedings of the 22nd Symposium for Applied Geographic Information Processing (Angewandte Geographische Informationsverarbeitung XXII), AGIT 2010*. July 7-9, 2010. Salzburg, AUSTRIA. Herbert Wichmann Verlag, Hüthig GmbH and Co. KG, Heidelberg, Germany. pp. 606-615.

Forsythe, K.W., K. Paudel, and C.H. Marvin. 2010b. Geospatial Analysis of Zinc Contamination in Lake Ontario Sediments. *Journal of Environmental Informatics, 16*(1), 1-10.

Great Lakes Information Network (GLIN). 2004. *Great Lakes Facts and Figures*. Retrieved May 17, 2011, from: htpp://www.great-lakes.net/lakes/ref/lakefact.htm

Guha Mazumder, D. N., R. Haque, N. Ghosh, B. K. De, A. Santra, D. Chakraborti, and A. H. Smith. 2000. Arsenic levels in drinking water and the prevalence of skin lesions in West Bengal, India. *International Journal of Epidemiology, 29*(6), 1047-1052.

Health Canada. 2006. *Arsenic in Drinking Water*. Retrieved May 18, 2011, from: http://www.hc-sc.gc.ca/hl-vs/iyh-vsv/environ/arsenic-eng.php

Inamdar, S. 2004. *Sediment Modeling for the Buffalo River Watershed.* Buffalo: Great Lakes Center. 1-59.

Irvine, K. N., and G.W. Pettibone. 1993. Dynamics of Indicator Bacteria Populations in Sediment and River Water Near a Combined Sewer Outfall. *Environmental Technology, 14* (6), 531-542.

Jakubek, D.J., and K.W. Forsythe. 2004. A GIS-based Kriging Approach for Assessing Lake Ontario Sediment Contamination, *The Great Lakes Geographer*, *11*(1), 1-14.

Johnston K., J.M. VerHoef, K. Krivoruchko, and N. Lucas. 2001.*Using ArcGIS geostatistical analyst*. Redlands: Environmental Systems Research Institute.

MacDonald, D., S. Carr, F. Calder, E. Long, and C. Ingersoll. 1996. Development and Evaluation of Sediment Quality Guidelines for Florida Coastal Waters. *Ecotoxicology, 5*(4), 253-278.

Miller, J.R. and S.M. Orbock-Miller. 2007. *Contaminated Rivers - A geomorphological-geochemical approach to site assessment and remediation.* Dordrecht: Springer.

Nelson, R.C., and R.A. Hites. 1980. Aromatic Amines in and Near the Buffalo River. *Environmental Science and Technology*, *14*(9), 1147-1149.

Ouyang, Y., J. Higman, D. Campbell, and J. Davis. 2003a. Three-dimesnisonal Kriging Analysis of Sediment Mercury Distribution: A Case Study. *Journal of the American Water Resources Association*, *39*(3), 689-702.

Ouyang, Y., J. Higman, J. Thompson, T. O'Toole, and D. Campbell. 2002. Characterization and Spatial Distribution of Heavey Metasl in Sediment from Cedar and Ortega Rivers Subbasin. *Journal of Contaminant Hydrology, 54*(1), 19-35.

Ouyang, Y., P. Nkedi-Kizza, R.S. Mansell, and J.Y. Ren. 2003b. Spatial Distribution of DDT in Sediments from Estuarine Rivers of Central Florida. *Journal of Environmental Quality, 32*(5), 1710-1716.

Rodriguez, P. 2009. *Assessing the Geographic Distribution of Mercury and Lead in Buffalo River Sediments.* Unpublished Master of Spatial Analysis Major Research Paper: Department of Geography, Ryerson University.

Sutton, G. P. 2006. *Buffalo Sediment Study.* New York State Department of Environmental Conservation, Buffalo.

Smith, A.H., C. Hopenhayn-Rich, M.N. Bates, H.M. Goeden, I. Hertz-Picciotto, H.M. Duggan, R. Wood, J.M. Kosnett, and M.T. Smith. 1992. Cancer Risks from Arsenic in Drinking Water. *Environmental Health Perspectives*, *97*, 259-167.

Smol, J. P. 2008. *Pollution of Lakes and Rivers – A Paleoenvironmental Perspective* (2nd Edition). Malden: Blackwell Publishing.

Taicheng, A., M. Qiao, G. Li, H. Sun, X. Zeng, and J. Fu. 2011. Distribution, Sources, and Potential Toxicological Significance of PAHs in Drinking Water Sources within the Pearl River Delta. *Journal of Environmental Monitoring, 13*(5), 1457-1463.

Tokasz, J. 2010, Dec 14. Group intent on Buffalo River cleanup; $39 million plan targets removal of contaminants. *Buffalo News*, p. B5.

US EPA. 2004. *Anthracene Fact Sheet*. Retrieved April 29, 2011, from: http://www.epa.gov/wastes/hazard/wastemin/minimize/factshts/anthrace.pdf.

US EPA. 2011. *Buffalo River Area of Concern*. Retrieved July 7, 2011, from: http://www.epa.gov/glnpo/aoc/buffalo.html