

**COMPARISON OF INTERPOLATION METHODS FOR THE SPATIAL  
MAPPING OF POLYBROMINATED DIPHENYL ETHERS IN LAKE ONTARIO**

**by**

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## **AUTHOR'S DECLARATION**

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## **ABSTRACT**

Concern over polybrominated diphenyl ethers (PBDEs) - which are used as flame retardants in a wide range of products - have risen due to its ubiquitous presence in the environment, and due to the fact that since the 1970s levels of this contaminant in North Americans has risen 100 fold (from nearly 0 parts per billion (ppb) per lipid in 1973 to between about 61.7 to 79.7 ppb per lipid currently). It has been estimated that over 100 tonnes of PBDEs are present in Great Lakes sediments. This study used geographic information systems (GIS), and spatial statistical techniques to produce various maps expressing the concentrations of three selected PBDE congeners (BDE-47, BDE-153, and BDE-209) in Lake Ontario. Two different interpolation methods, Ordinary Kriging and Inverse Distance Weighting (IDW), were also compared to see which is more effective at producing such maps when a small number of samples is available.

For the kriging analyses log-transforming the dataset produced cross-validation statistics closer to optimal, with the best models being Gaussian, Spherical, and Gaussian for BDE-47, BDE-153, and BDE-209 respectively. Comparing the Mean Prediction Error (MPE) and Root Mean Square Prediction Error (RMSPE), it was determined there may be less interpolation bias and more interpolation accuracy in the IDW analyses when the log-transformed data were used. The validity of the prediction surfaces for both interpolation methods, however, needs to be questioned. Not only was the sample size potentially too small and unevenly distributed to accurately portray the surface; default settings were used for both methods; and it is possible log-transforming the data may have improved the cross-validation statistics based on a scaling effect of the resulting

smaller values, and not necessarily from improvement in interpolation accuracy or bias. The MPE, RMSPE, and Correlation Coefficient ( $r$ ) - calculated from the actual sample location values and the prediction values for each model, were also used to directly compare the best kriging results to the IDW results. It was found that for our study, kriging was the more statistically valid interpolation method to use, although for both techniques the overall spatial trends were similar. The overall spatial patterns of PBDEs in Lake Ontario observed in this study can be explained by the location of urban centres, as well as by the circulation of the lake. Although there were limitations to this study due to the small sample size used, interpolation techniques can be helpful tools in understanding the spatial distribution of PBDEs in Lake Ontario and in the Great Lakes in general.

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## **LIST OF ACRONYMS**

ASE - Average Standard Error

Deca-BDE - Deca-bromodiphenyl ether

EQS - Environmental Quality Standard

GIS - Geographic Information Systems

HASM - High Accuracy Surface Modeling

HCB - Hexachlorobenzene

IDW - Inverse Distance Weighting

IUPAC - International Union of Pure and Applied Chemistry

LPI - Local Polynomial Interpolation

MPE - Mean Prediction Error

NY - State of New York

Octa-BDE - Octa-bromodiphenyl ether

ON - Province of Ontario

PBB - Polybrominated biphenyls

PBDE - Polybrominated diphenyl ethers

PCBs - Polychlorinated biphenyls

PEL - Probably Effect Level

Penta-BDE - Penta-bromodiphenyl ether

PNEC - Probably No Effect Concentration

PPB - Parts per billion

*r* - Correlation Coefficient

RBF - Radial Base Function

RMSPE - Root-Mean-Square Prediction Error

SPSS - Statistical Package for the Social Sciences

SRMSPE - Standardized Root-Mean-Square Prediction Error

TEL - Threshold Effect Level

## **CHAPTER 1: INTRODUCTION**

### **1.1. Polybrominated Diphenyl Ethers (PBDEs)**

Flame retardants are used in some plastics, paints, fabrics, electric and electronic equipment, upholstered furniture, non-clothing textiles, and foam products. Polybrominated Diphenyl Ethers (PBDEs) are members of a broad class of brominated chemicals used as flame retardants (United States Environmental Protection Agency, 2010). These substances are produced by the bromination of diphenyl ethers ( $O(C_6H_5)_2$ ) in the presence of a Friedel-Craft catalyst, i.e. aluminum chloride ( $AlCl_3$ ), in a solvent such as dibromomethane ( $CH_2Br_2$ ). Diphenyl ether molecules are composed of 12 carbon atoms with 10 associated hydrogen atoms, any of which can be exchanged with bromine, resulting in 209 possible PBDE substances, which are referred to as congeners ( $PBDE = C_{12}H_{10-x}Br_xO$  ( $x = 1, 2, \dots, 10 = m + n$ )) (Figure 1.1; D'Silva et al., 2004). Commercial PBDE products are not single compounds or even single congeners, but rather a mixture of congeners. These commercial PBDEs are typically produced at three degrees of bromination: 1.) Penta-bromodiphenyl ether (penta-BDE), 2.) Octa-bromodiphenyl ether (octa-BDE), and 3.) Deca-bromodiphenyl ether (deca-BDE), being classified by their average bromine content (Alaee et al., 2003; D'Silva et al., 2004). The many varying types of these different mixtures can further be divided into *higher brominated PBDEs*, which contain more than 5 bromine atoms per molecule; and *lower brominated PBDEs* - which average 1 to 5 bromine atoms per molecule, and are considered more dangerous as they bioaccumulate more efficiently (United States Environmental Protection Agency, 2010; Health Canada, 2009).

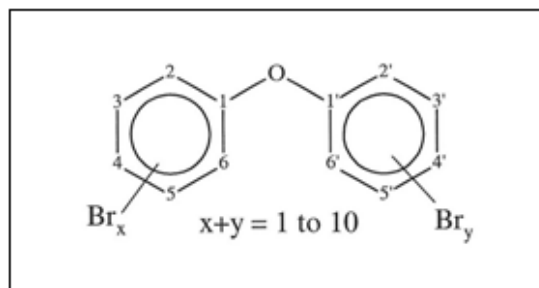


Figure 1.1: The generalized structure of brominated diphenyl ethers, (PBDE =  $C_{12}H_{10-x}Br_xO$  ( $x = 1, 2, \dots, 10 = m + n$ )). The numbers on the rings indicate carbon (C) atoms with an associated hydrogen (H) atom, with the O representing an oxygen atom. The number of bromine atoms (Br) for every possible 209 congener ranges from 1 to 10, and exchanges with the hydrogen atoms in the structure (Source: D'Silva et al., 2004).

PBDEs were first commercially produced as flame retardants in the 1970s - with their use becoming widespread due to their low cost and high compatibility - and after the manufacture of polybrominated biphenyls (PBBs) was stopped in the United States and Canada. PBB manufacturing was halted mainly due to findings that these substances were highly toxic to humans, particularly to girls exposed in utero, often causing pubertal effects to occur earlier (Gouin et al. 2005; Hites, 2006). PBDEs are classified as additive flame retardants and are simply blended or covalently bonded with polymers in an existing product, which actually makes them more likely to leach out. This leaching of PBDEs into the environment is an issue since there is mounting evidence of their environmental and health concerns (Hutzinger and Thoma, 1987; Hites, 2006). Worldwide more than 70 000 tonnes of PBDEs have been produced annually, half of this being used in the United States and Canada, including almost all of the penta-DBE manufactured (Hites, 2004). The fact that North Americans - particularly Canadians and Americans - make up almost all of the world's demand of penta-BDEs is very important and disturbing (Alaee, 2003; Ward et al., 2008). Penta-BDEs are lower brominated PBDEs, meaning that not only are they more dangerous and toxic than the higher brominated PBDEs, but they also tend to have longer half lives which mean they stay in

the environment longer and have the ability to be transported long distances (Health Canada, 2009; Wong et al., 2001; Helm et al., 2002).

Concern over PBDEs are increasing due its ubiquitous presence (Hale et al., 2003). These chemicals are considered particularly harmful by the Canadian Environmental Agency (CEPA), as they bioaccumulate in living organisms - in terms of humans doing so in blood, breast milk, and fat tissues - and last a long time in the environment (Lind et al., 2003; Environment Canada, 2009). Although there is little evidence that current levels of PBDEs in North American people are dangerous (estimated between about 61.7 to 79.7 parts per billion (ppb) per lipid), some studies have indicated that increasing levels of PBDEs may be correlated to reduced fecundity in women, and physical and mental development of young children (Scheter et al., 2005; Schreiber et al., 2010). Despite the current levels of PBDE concentration being deemed relatively low and not harmful to humans, they may threaten some wildlife and invertebrates (Kuo et al., 2010). The detected levels of PBDEs in the environment have rapidly increased since the early 1990s, and have been detected in all parts of the environment (air, water and land) (Environment Canada, 2009). A more detailed discussion of PBDEs environmental occurrence and fate, exposure and transportation, and its toxicity and transformation will be provided in the following sections.

## **1.2. Research Goals and Objectives**

This study will use geographic information systems (GIS), and spatial statistical techniques to produce various maps expressing the sediment concentrations of selected

PBDE congeners in Lake Ontario. Two different interpolation methods, ordinary kriging and Inverse Distance Weighting (IDW), will be also be compared to see which is more effective at producing such maps when a small number of samples is available. Three PBDE congeners will be selected for analysis, with the choice being done through a combination of literature review and research on their toxicity level, and their concentration in Lake Ontario and the Great Lakes system in general. Reasons why certain areas of Lake Ontario exhibit higher concentrations of the selected PBDE congeners will also be discussed, with current Canadian and International Government intervention and remediation efforts also being examined.

### **1.3. A Closer Look at the Chemistry and Commercial Use of PBDEs**

Polybrominated flame retardants, including PBDEs, are thermally labile or unstable, which enables them to act as flame retardants. PBDE congeners are identifiable by their International Union of Pure and Applied Chemistry (IUPAC) classification, and as mentioned previously using this system there are 209 theoretical congeners of PBDEs. Commercial mixtures usually only contain a few of these congeners at a level considered significant. These 209 possible congeners can be identified by their IUPAC number (1 to 209), each number related to the number and position of bromine atoms on each ring (refer to Figure 1.1) (D'Silva et al., 2004). The most common commercial preparation methods of PBDEs involve the bromination of diphenyl ethers in the presence of a catalyst. This process results in a product that contains a mixture of PDBEs with various degrees of bromination. Three commercial PBDE products are still manufactured and sold today, these being penta-bromodiphenyl ether (penta-BDE), octa-bromodiphenyl

ether (octa-BDE), and deca-bromodiphenyl ether (deca-BDE). These three different products each have their own unique properties and specific applications (Table 1.1; Ward et al., 2008). The toxicological effects of PBDE products varies with their degree of bromination. It is thought that a higher degree of bromination on the diphenyl ether molecule, the larger the actual molecule is and therefore the lesser the toxicity. Although this theory is not completely substantiated, the most toxic PBDE congeners do appear to have lesser bromination (D'Silva et al., 2004; Hardy, 2002). Internationally penta-BDEs and octa-BDEs have been unavailable since 2005. However some countries still allow the manufacturing of deca-BDEs, and current legislation in North America still allows re-processing and import of products containing all PBDE commercial types (Environment Canada, 2000; Ward et al., 2008).

Table 1.1: Chemical summary, application and Global and North American market demand for the three major commercial products of polybrominated diphenyl ethers prior to 2005 (Source: Ward, 2008).

<i>Commercial Product</i>	<i>Prominent Congeners</i>	<i>Applications</i>	<i>Global Market Demand (metric tonnes)</i>	<i>North American Market Demand (metric tonnes) (% global demand)</i>
Penta-BDE	BDE-47	polyurethane foams, textiles, furniture, insulation	7 500	7 100 (95)
	BDE-99			
	BDE-100			
Octa-BDE	BDE-183	computers, automobile trim, telephones, household appliances, fax machines	3 790	1 500 (40)
	BDE-196			
	BDE-197			
Deca-BDE	BDE-209	carpet pads, draperies, television sets, electronic casings, cable insulation, adhesives, textile coatings	56 100	24 500 (44)

Beginning in the 1950s, penta-BDEs were the first successful aromatic brominated flame-retardant formulation to be commercially produced. These substances are highly viscous liquids containing tetra (24-38%), penta (50-60%), hexa (4-8%), and hepta (minimal %) congeners. Penta-BDEs are mainly used in rigid and flexible polyurethane foams and polyurethane elastomers - which are in turn used mostly in upholstery and furnishing (D'Silva et al., 2004). The atmospheric and biological half-life of penta-BDEs is 10 to 20 and 19 to 119 days respectively, which indicates that these substances have the potential for long range and transboundary transport and resilience (Wong et al., 2001; Helm et al., 2002). Some studies have suggested that penta-BDEs are able to activate the *Ah*-receptor, to reduce hepatic vitamin A levels, and induce cancer by intragenic recombination. These substances have also been shown to potentially act as thyroxin competitors, which is an important hormone responsible for metabolism regulation (Hallgren et al., 2001).

The commercial mixtures of octa-BDEs are a combination of hepta (44%), octa (31 to 35%), penta / hexa (11%), nona (10%), and decabromo (0.5%) congeners. The initial thoughts on octa-BDEs was that their toxicity hazard was low from acute exposure, although it has been shown that they can cause developmental toxicity from ingestion (Dagani et al., 2002). The lower brominated congeners present in octa-BDEs commercial mixtures have been found widely in the environment, biota and sediments (D'Silva et al., 2004; World Health Organization, 1994).



Deca-BDEs are currently the most widely used commercial PBDE product (refer to Table 1; Ward et al., 2008). These substances are composed of deca (77%), nona (22%), and octa (0.8%) congeners, although some products are composed almost entirely of deca-BDE congeners (D'Silva et al., 2004). These types of PBDEs are the only mixtures in which limited toxicological information is known with respect to humans. However, due to its large molecule size and molecular mass, it has been shown to be minimally absorbed from the gastrointestinal tract of mammals and not likely to bioaccumulate. Deca-BDEs have been shown at high dose levels to be a carcinogen and to have mutagenic potential - having caused increased cases of hepatocellular adenomas and thyroid adenomas and carcinomas in tests on mice and rats (Darnerud et al., 2001). Despite these finds on the toxicity of deca-BDEs, these substances are considered less potent than other PBDE mixtures - including penta-BDEs and octa-BDEs (U.S. Department of Health and Human Services, 1987).

#### **1.4. Transportation, Occurrence and Toxicity of PBDEs in the Environment**

PBDE mixtures are non-covalently bonded additives in a huge number of manufactured goods, and because of this they have the ability to leach into the environment throughout the lifetime of the product (Hites, 2006). They can also enter the environment through point sources via accidental discharge or other means, and the detection of PBDEs in homes and work environments shows that people are being exposed to a continual source of PBDE contamination (D'Silva et al., 2004; Barontini et al., 2001). PBDEs and their derivative compounds leach into the environment from plastics in appliances, foam in upholstery, television and computers, and fibers of carpets

and drapes. These substances also leach out during processing and recycling, or combustion. The covalent bonds which hold PBDEs to a specific product eventually weaken, resulting in the PBDE being released and available to bond to other molecules and substances (D'Silva et al., 2004; Hites, 2006). Depending on what type of product the PBDE is bonded to and where it is located, the leached PBDE can find its way and persist in dust and other atmospheric samples, river and lake sediments, soils, and eventually in humans and other living organisms (D'Silva et al., 2004). The environmental distribution of PBDE congeners is not equivalent to those of commercial mixtures - this perhaps being explained by sunlight decomposing some congeners, free radicals, or biological attack. It is likely that based on congener physiochemical characteristics (and based on the polymer mixture they are contained in), individual congeners have different rates of environmental release, fate and transport (D'Silva et al., 2004; Sjodin et al., 2001).

On a global scale, PBDEs have been measured and detected in high levels in soil and sediments (Zhu and Hites, 2005), air and house dust (Sjodin et al., 2001), and biological samples (Hale et al., 2003). It has been determined that PBDE levels in North Americans have increased nearly 100 fold since the 1970s, increasing from near 0 ppb per lipid in 1973 to between about 61.7 and 79.7 ppb per lipid currently (Schechter et al., 2005). North Americans have the highest global PBDE body concentrations, averaging over 20 times that of Europeans, which is mainly due to the large market demand for products (that contain PBDE) in North America (Hites, 2004). Studies indicate that health hazards of PBDE may be significant, with pregnant women and developing fetuses being particularly at risk (Schreiber et al., 2010). Based on the evidence of cancer being caused

in animals by deca-BDE, these substances have been designated as possible human carcinogens. In terms of such studies performed on animals, PBDEs have been shown to delay hatching and depress the swimming and feeding rates of fish (Timme-Laragy et al., 2006), as well as cause neural effects and cardiac arrhythmia (Lema et al., 2007). Experiments exposing rodents to PBDEs have also found that neo-natal exposure can impair motor skills, learning and memory (Eriksson et al., 2002), induce immuno-toxicity (Martin et al., 2007), disrupt endocrine functioning (Hallgren and Darnerud, 2002), and effect reproductive development (Kuriyama et al., 2005). PBDEs have low water solubility, are highly lipophilic - which refers to a chemical compound's ability to dissolve in fats, oils and lipids, and are considered to have low volatility (D'Silva et al., 2004). This means that PBDEs - although highly effective at stopping fires from occurring and undoubtedly having saved many lives, are able to resist environmental, biological and chemical degradation which causes them to linger in humans, biota and the environment. It is believed that certain PBDE congeners can persist without breaking down for years, potentially even decades, meaning there is high potential for exposure and transport of these chemicals long distances and across national and international boundaries. The half lives of these substances within humans is thought to be from weeks to several years, while in the environment estimates of some PBDE congener half lives are in the range of two to ten years (D'Silva et al., 2004).

Studies which have investigated the toxicological effects of PBDEs on humans are quite scarce. There is, however, recent evidence of PBDEs having adverse effects on human health and reproduction, with children potentially being particularly at risk to

adverse health effects (Schreiber et al., 2010). Documentation of the transfer of PBDE contamination from mothers to fetal tissues during pregnancy has been documented (Lind et al., 2003; Schechter et al., 2007), with infants and young children also being potentially exposed to early PBDE contamination through nursing and house dust (Harrad et al., 2008). A major pathway of human exposure to PBDEs is thought to be through the eating of contaminated food, as PBDEs have been detected in a large variety of fish, meat and dairy products in North America and Europe (Schechter et al., 2007; D'Silva et al., 2004; Bocio et al., 2003). The use of fertilizers and other bio-solids in agricultural practices that are contaminated with PBDEs is thought to be another potential contributor to food contamination (Hale et al., 2001). Human exposure is definitely not solely caused by the ingestion of PBDE contaminated food however, with exposure also from using PBDE-containing products, the changing of liquid PBDE to gas (volatization) from incinerated and landfill waste, wastewater treatment plants releasing PBDEs which find their way into rivers and lakes, and inhalation of house dust contaminated with PBDEs (Darnerud et al., 2001; La Guardia et al., 2007). It is also worth noting that the ambient concentrations of PBDEs are far higher in urban areas than in rural and remote regions (Hoh and Hites, 2005).

### **1.5. PBDEs in the Great Lakes**

The main source of PBDE contamination in the Great Lakes is the same as it is for many aquatic systems - this being through atmospheric deposition (Hale et al., 2003). As mentioned previously, PBDEs can find their way into the Great Lakes through the disposal and recycling of products that contain PBDEs, deposition from tributaries and

wastewater treatment plants, and from manufacturing outputs. Once these substances are in the lake sediments they can be disturbed and absorbed by living organisms in the lake, with humans eventually being exposed again in such organisms that are eaten. Humans can also be re-exposed to PBDEs from sediment contamination if these sediments are disturbed and the water is then used for drinking or agricultural practices (Ward et al., 2008; La Guardia et al., 2007). It has been estimated, via the use of dated sediment cores, that approximately 100 tonnes of PBDE are present in sediments of the Great Lakes (Song et al., 2005; Zhu and Hites, 2005). Most of this 100 tonnes of PBDE sediment contamination within the Great Lakes is of the deca-BDE congener BDE-209. BDE-209 is a large molecule which is quite immobile, not possessing the same transport ability as some of the lower brominated compounds. However, lower brominated PBDEs - more specifically penta-BDE congeners, are common in ambient air and biota with the most common congeners being BDE-47, -99, -100, -153, and -154 (Hites, 2004).

Fish in the Great Lakes and rivers which drain into them have been tested and found to contain PBDEs (Zhu and Hites, 2004). Higher-order predators such as salmon and trout, which are popular species for anglers and recreational fishers, have had total PBDE concentration loads between 1 000 to 3 000 ng/g (1 000 000 to 3 000 000 pg/g) lipid weight (Hites, 2004). Although currently the environmental PBDE levels in fish are considered to be safe for human consumption, PBDE levels globally and in the Great Lakes continue to rise, and these substances do indeed accumulate in animal lipids and muscle. It has been suggested that the quality standard required to protect human health from adverse effects caused by the eating of PBDE-contaminated food is 1 mg/kg/day

(mg of PBDE per kg of food eaten per day). This quality standard works out to 1 000 000 pg/g/day (pg of PBDE per g of food eaten per day), and was calculated mainly on the effects of penta-BDEs (Darnerud et al., 2001; Hites, 2004). This quality standard figure, although quite high, is encouraging because penta-BDEs are no longer available and their concentrations in the Great Lakes are not as high as other PBDE congeners. Also the levels mentioned previously for the PBDE in salmon and trout were total PBDE levels (Hites, 2004), so concentrations of the more dangerous penta-PBDEs are likely far lower. Health Canada suggests eating foods such as vegetables, fruit, and whole grains which have lower levels of PBDEs than meat, dairy and fish products (Health Canada, 2009).

Over the past 20 years, PBDE levels in fish and birds in the Great Lakes have exponentially increased from nearly 0 ng/g lipid weight in 1980, to an average between about 500 000 and 1 100 ng/g (500 000 1 100 000 pg/g) lipid weight in 2000 (Luross et al., 2002; Norstrom et al., 2002). In this time period PBDE concentrations in these biota have doubled about every three years, although for some of the lakes these trends seem to be leveling off (Zhu and Hites, 2004). Despite this plateau of PBDE levels in fish and birds, if the current degree of increases in the Great Lakes continues at its present rate they may exceed the upper limit of levels deemed safe for the consumption of fish (Darnerud et al., 2001). There is also evidence to suggest that locations along the Great Lakes that are adjacent to areas that are heavily urbanized and industrialized have higher PBDE contamination levels, and thus may be more vulnerable (Hites, 2004). This may mean that future investigations should focus on these more vulnerable areas of the Great Lakes to allow a more accurate assessment of the extent and effects of PBDE

contamination. Results from this study may be able to identify such vulnerable areas of PBDE sediment contamination (for the selected PBDE congeners) in Lake Ontario.

## **1.6. Interpolation Techniques**

In its most general term, interpolation is a statistical technique which predicts or estimates unknown data values using known data values. There are many different types of interpolation techniques, although all such techniques are based on the assumption that spatially distributed objects are spatially correlated, or that things located closer to one another have similar characteristics. These processes can be used to estimate unknown values for any geographic point data, albeit to predict precipitation, elevation, noise levels, and in our case sediment contaminant concentrations (Haining et al., 2010).

### **1.6.1. Kriging Analysis**

In geostatistics, kriging is a general term used for a range of spatial best linear unbiased predictor (BLUP) least-squares methods of spatial interpolation. This analysis gives predictions, but also the kriging errors or kriging variances at each prediction location (Haining et al., 2010). The original formula for linear kriging - which is now known as ordinary kriging, is the most robust and widely used method. Ordinary kriging assumes the mean is unknown, but constant, and that the random field is locally stationary. In this method, the estimate at any location  $s_0$ ,  $Z(s_0)$ , is a weighted linear combination of the data:

$$Z(s_0) = \sum_{i=1}^n \{\lambda_i z(s_i)\} \quad (1)$$

The weights  $\lambda_i$ , are chosen to minimize the kriging variance. To ensure the estimates are unbiased, the weights are constrained to sum to a total of 1 (Haining et al., 2010; Webster and Oliver, 2007). Ordinary kriging then models a spatial surface in deviations from a constant mean, where these deviations are correlated spatially (Forsythe and Marvin, 2005; Krivouchko and Gotway, 2004). Kriging has been elaborated and built upon to be applied to increasingly complex problems since its original formulation. Disjunctive and indicator kriging are nonlinear forms which provide probabilities whose attribute values are above or below a given threshold. Such techniques have been used quite widely in risk assessments of contaminated sites based on the threshold values of certain serious contaminants (Brus et al., 2002).

When one performs kriging analysis there are cross-validation statistics produced, which provide accuracy measures for the predictions made that must be considered in order for the results to be viewed as valid or reliable. Failure to meet the standards of these statistics indicates that the predictions made by the kriging procedure are biased, or not centred on the true values (Krivouchko and Gotway, 2004). These cross-validation statistics include Mean Prediction Error (MPE), Root-Mean-Square Prediction Error (RMSPE), Average Standard Error (ASE), the similarity between the RMS and ASE  $|\text{RMS} - \text{ASE}|$ , and Standardized Root-Mean-Square Prediction Error (SRMSPE). For any dataset being used to perform kriging there are  $n$  number of sites, with the MPE, ASE and RMSPE mathematically determined by the measured values  $Z(x_i)$  and the prediction values  $Z^*(x_i)$  in the following equations (Shi et al., 2009):

$$MPE = \frac{1}{n} \sum_{i=0}^n \{Z^*(x_i) - Z(x_i)\} \quad (2)$$



$$ASE = \frac{1}{n} \sum_{i=1}^n \{|Z * (xi) - Z(xi)|\} \quad (3)$$

$$RMSPE = \sqrt{\frac{1}{n} \sum_{i=1}^n \{Z * (xi) - Z(xi)\}^2} \quad (4)$$

The MPE is a measure of the interpolation bias and should have a value as close to 0 as possible. The RMSPE and the ASE are interpolation accuracy measures and should also be as low as possible, although a value <20 is often considered valid. If RMSPE and ASE values are higher than 20 the predictions made by the kriging analysis are diverging too far from the measured locations (Shi et al., 2009; Jakubek and Forsythe, 2004; Forsythe and Marvin, 2005). On top of this the RMSPE and ASE should be as similar to one another as possible, which is expressed as the |RMSPE - ASE| statistic - and is literally the ASE subtracted from the RMSPE. If the ASE is greater than the RMSPE the variability of the predictions are overestimated, and an underestimate oppositely results if the RMSPE is greater than the ASE. Finally in order for the SRMSPE to be valid it should have values approaching 1. If the SRMSPE is greater than 1, an underestimation in the variability of predictions occurs, while an overestimation of the variability of predictions occurs if the SRMSPE is less than 1 (Jakubek and Forsythe, 2004; Forsythe and Marvin, 2005).

### 1.6.2. Inverse Distance Weighting (IDW)

Inverse Distance Weighing (IDW) is a simple interpolation method that estimates cell values by averaging sample data point values in the neighbourhood of each processing cell. As the name of the interpolation technique suggests, the weighting factor of this technique are based solely on a function of the distance between the point of interest, and the sampling points. Points exhibit more influence, or weight, the closer they

are to the centre of the cell being predicted. Essentially this means IDW implements the assumption that areas closer to one another are more alike than farther away areas (Ashraf et al., 1997). Although there are few decisions one has to make regarding model parameters in IDW, there are several things to consider. The Power Function ( $p$ ) is one parameter that needs to be considered in IDW, with the optimal power value determined by minimizing the Root-Mean-Square Prediction Error (RMSPE). Weights used in IDW are proportional to the inverse distance raised to the  $p$ , which results in the weights decreasing rapidly as the distance increases. How quickly these weights decrease is directly dependent on the value of  $p$ . Very high  $p$  values will result in only a few immediately surrounding points influencing the prediction, while a  $p$  value of 0 will result in no decrease with distance and thus the prediction being the mean of all the measured values (Sun et al., 2009; Ashraf et al., 1997). Taking these factors into account, IDW estimates the value of a point of interest,  $Z$ , using the following equation:

$$Z = \frac{\sum_{i=0}^n \frac{1}{(D_i)^p} Z_i}{\sum_{i=0}^n \frac{1}{(D_i)^p}} \quad (5)$$

where  $Z_i$  is the value of a sampling point (sample location in our study),  $D_i$  is the distance between the interpolated and sampled values,  $n$  is the number of sample points, and  $p$  being the Power Function (Sun et al., 2009).

Another factor that is quite important in IDW is the search neighbourhood. Since this model assumes that objects which are closer together are more alike than farther away objects, these farther away objects will have little relationship with the value of a prediction location. It is common to limit the number of measured values used in predicting unknown location values by specifying this search neighbourhood. The shape

of the search neighbourhood is also important, and is influenced by the data being used and the surface being created. Dividing the search neighbourhood into sectors means maximum and minimum constraints are applied individually to each sector, while the weights used for predicting a location are still at the centre. Output surfaces produced by this interpolation method are sensitive to the presence of outliers, resulting in clustering - or "bulls eyes" around data locations. There is also no assessment of prediction errors in a statistical format when using IDW. This method is convenient, however, in that no assumptions are required of the data used, few decisions are required to produce the prediction surfaces, and it is often useful for newcomers to interpolation (Sun et al., 2009; Ashraf et al., 1997).

### 1.6.3. Relevant Research Conducted using Kriging Analysis

Several studies have been conducted that use ordinary kriging to analyze the spatial distribution of sediment contaminant concentrations in the Great Lakes. These studies looked at the spatial distribution of contaminants such as hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs), lead (Pb), and mercury (Hg) among others (Jakubek and Forsythe, 2004; Forsythe and Marvin, 2005; Forsythe et al., 2004). These studies mentioned utilizing ordinary kriging analysis, which is the one of the two interpolation methods which will be used in this study to map PBDE congener sediment concentrations in Lake Ontario.

#### 1.6.4. Relevant Research Conducted using IDW

IDW is used very little on its own in studies regarding sediment contaminant concentration. It has been used, however, in many studies which look at comparing different interpolation techniques either to themselves, or to proposed new mapping techniques. Shi et al. (2009) compared such classical methods including kriging, IDW, and splines to a more recently developed and apparently accurate surface modeling technique called High Accuracy Surface Modeling (HASM). These interpolation techniques were used and compared in their ability to model soil pH in China. This study compared cross-validation statistics of Average Standard Error (ASE) and RMSPE, and although the HASM was found to be more accurate, it was also found that ordinary kriging was more accurate than IDW, which is of interest concerning the present study. Sun et al. (2009) conducted a similar study, comparing interpolation methods for modeling temporal and spatial variations in groundwater in northwest China. This study compared IDW, Radial Basis Function (RBF), and various kriging methods. Comparing RMSPE statistics and Correlation Coefficients ( $r$ ) for the measured values and the predicted values for each method, they found that ordinary kriging was the optimal method for this application. Other such interpolation comparison studies have been conducted to investigate different techniques' ability to map climatic variables such as precipitation and temperature (Zhang and Srinivasan, 2009; Attorre et al., 2007), heavy metals in agricultural soils (Meng et al., 2008), and various soil properties of agricultural plots used to cultivate lettuce (Panagopoulos et al., 2006) - with kriging being the most effective interpolation technique to employ for each of these studies. Despite this extensive research on PBDEs and interpolation comparison, no such interpolation

comparison seems to have been conducted with respect to PBDEs in Lake Ontario and the rest of the Great Lakes.

#### 1.6.5. Spatial Mapping of PBDEs in Great Lakes Sediments

Although there is much recent research and literature on the increase in PBDE concentrations in the environment and in humans (D'Silva, 2004; Hites, 2004; Lind et al., 2003; Schecter et al., 2007), no such spatial analysis of these chemicals in the Great Lakes - more specifically Lake Ontario, and interpolation method comparison has been conducted. Many studies have measured the amount of PBDE sediment concentration locally in the Great Lakes, and in water bodies around the world (Guzzella et al., 2008; Song et al., 2005). Guzzella et al. (2008) measured PBDE concentrations in the Lake Maggore basin - a heavily industrialized and densely populated area in Italy and Switzerland, from 2005 to 2006. Song et al. (2005) assessed the levels of PBDE concentration in Lake Ontario and Lake Erie in 2002. Both studies showed that the dominant PBDE congener was BDE-209. Looking at the data already provided for this study it appears that BDE-209 has some of the highest concentrations in the samples sites from Lake Ontario, which is perhaps good reason to consider this congener for analysis in this project. Although the studies mentioned did measure selected PBDE congener concentrations from their respected locations, there is little spatial analysis of the data. Their methods included taking the concentrations and averaging these values or providing a range of values, then comparing them to previous year's estimates. Song et al. (2005) interestingly did provide PBDE concentration values at various depths for each

sediment core sample taken, but their overall analysis also used average values and ranges of values.

Although there are many studies comparing the ability of different interpolation techniques to map spatial trends, such research has not been done for PBDE sediment concentrations and when only a smaller sample size is available - although using small sample sizes may raise questions to the reliability and validity of the results. However, the lack of research in this area is evidence that studies such as this one can and should be used to map PBDE concentrations in the Great Lakes, and in any other medium where this contaminant is present.

## **CHAPTER 2: DATA AND METHODOLOGY**

### **2.1. Study Site and Dataset**

Lake Ontario has the smallest surface area (19 010 km<sup>2</sup>) of the five Great Lakes, with a volume of 1 640 km<sup>3</sup> - which is actually three times that of Lake Erie (Forsythe and Marvin, 2005). The waters of Lake Erie via the Niagara River and Welland Canal are what primarily feed into Lake Ontario, with its overall drainage basin covering large portions of Ontario, Canada and New York State in the United States. A large majority (~93%) of Lake Ontario's water is drained northeast via the St. Lawrence River (Lake Ontario Management Plan, 1998). Densely populated, urban industrial centres are found on Lake Ontario's western and northern shores, including Toronto, ON and Hamilton, ON. The eastern and southern shores contained within the United States however, are much less populated and have less overall urbanized area (U.S. EPA, 1995). Water circulation in Lake Ontario, for the most part, flows in a counter-clockwise direction with a smaller clockwise flowing gyre in the northwest portion of the lake (Figure 2.1) (Beletsky et al., 1999).

Data were obtained from 22 monitoring (n = 22) sites throughout Lake Ontario (Figure 2.2). When Environment Canada conducted this field collection from sites throughout Lake Ontario, it did so for many more sites than the 22 which are being used in this study. Unfortunately these data were not able to be obtained and implemented into this study, which prompted the shift in focus from strictly using kriging analysis to map PBDE concentrations in Lake Ontario in 2008, to comparing the ability of kriging analysis and IDW to map PBDE sediment concentrations in Lake Ontario when only a

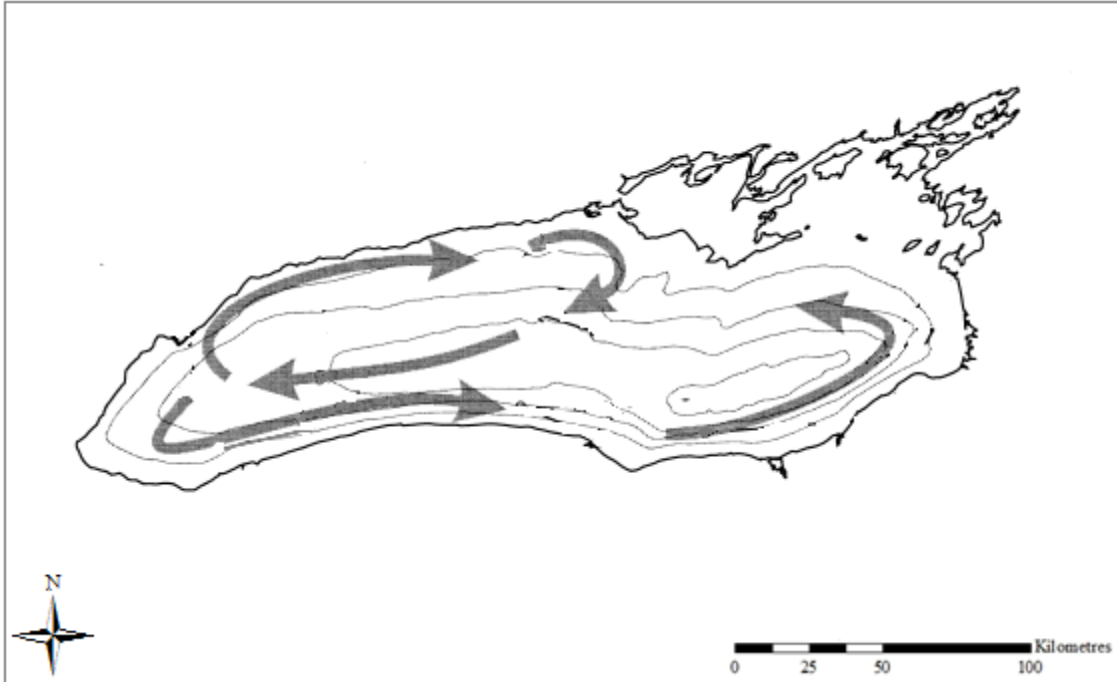


Figure 2.1: Annual circulation in Lake Ontario. The dark grey arrows indicate the overall circulation pattern of the lake, while the thinner light grey lines indicate 50 metre isobaths (Source: Beletsky et al., 1999).

small sample size is available. From Figure 2.2 it can be seen that many of the sampling sites are clustered in the southwestern portion of Lake Ontario. In fact 11 of the 22 sampling sites are clustered in this region near Hamilton, ON, Toronto, ON and St. Catharines, ON, with the remaining 11 sites scattered through the remainder of the lake.



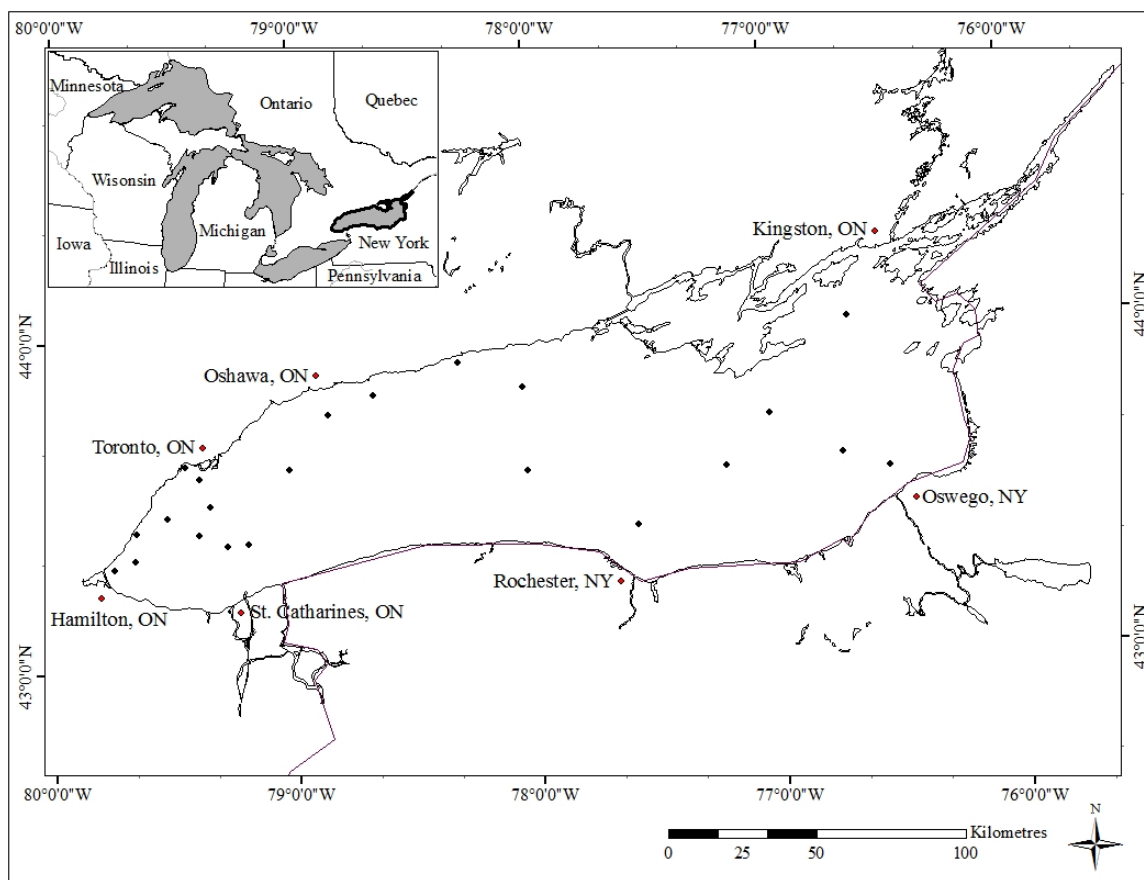


Figure 2.2: Lake Ontario study site and its surrounding locations, as well as the sample locations within Lake Ontario, 2008. The sample locations are indicated on the map by the black dots, and represent where the PBDE samples were taken from the lake.

## **2.2. Data Collection**

Using a mini box corer, sediment samples were collected throughout Lake Ontario. Such sediment sampling processes involve a box corer being deployed from a vessel. The device is lowered vertically until it reaches the sediment surface, at which point the box corer - which is fixed at the lower end of a plunger - is triggered and the sample taken. As the corer is removed from the sediment surface, a spade swings underneath to stop any sediment loss. This sediment sampling method is designed for limited disturbance of the sediment surface (Macias-Zamora et al., 1999). The data from the 22 sample locations used in this study (refer to Figure 2.2) were part of a large

sampling effort that took place in 2008/2009. Sample locations were chosen primarily based on where higher PBDE concentrations were expected to be found, which can explain why so many were clustered in the southwestern portion of Lake Ontario near urban centres. The top 3 cm of the sediment samples which were collected were themselves then sub-sampled, and later analyzed for metals, grain size, nutrients, and organic contaminants - including the 41 PBDE congeners included in the dataset used in this study. Following protocol described by Marvin et al. (2003), all of the samples were frozen before being transported to a laboratory for analysis. The sediment samples were analyzed in a laboratory and the concentrations were determined for 41 PBDE congeners at the 22 sample locations. These concentrations were measured in pg/g (picogram of PBDE per gram of dry sediment).

### **2.3. Selection of PBDE Congeners which will be Analyzed and Mapped**

As mentioned previously specific PBDE congeners were selected and their spatial distribution investigated in this project. The congeners which were decided for inclusion in this project were done so based on their potential toxicity and their concentration in Lake Ontario based on the data provided. D'Silva's (2004) study identified 23 PBDE congeners as important in terms of their inclusion in future analytical studies. These PBDE congeners were labeled as important based on 3 factors: 1.) Being of environmental importance - meaning they are likely to occur at high concentrations in the environment, 2.) Being of toxicological importance - meaning they may be highly toxic and potentially pose a significant health risk, and 3.) Being of scientific interest.

The twenty three PBDE congeners D'Silva (2004) thought fulfilled the importance criteria mentioned above were BDE-15, 17, 28, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 119, 126, 138, 153, 154, 166, 183, 190, and 209. Of the 41 PBDE congeners provided, 16 of these are included in the 23 D'Silva (2004) identified as important. A total of three of these PBDE congeners were selected for analysis in this study. The spatial patterns of BDE-209 (decabromodiphenyl ether) will definitely be investigated in this study. This congener is the main component in deca-BDE commercial products and is widely accepted as the dominant depository congener. Studies have found BDE-209 to be much more prominent than other congeners in homes and commercial buildings, and office furnishings and computers in both North America and Europe (Harrad et al., 2008). Due to BDE-209 being such a large, heavily and hydrophobic molecule it is also the most abundant congener in inland and lake sediments, as well as in rainwater (Song et al., 2005; tar Schure and Larsson, 2002). Despite the molecule's large size, BDE-209 has also been shown to bioaccumulate in fish and food webs, although at a lesser rate than lower brominated congeners (Zhu and Hites, 2004). Current studies looking at the toxicity of BDE-209 have shown that at high levels in mice it can cause permanent changes in spontaneous behavior after neonatal exposure, with the effects appearing to worsen with age (Eriksson et al., 2002). Solvated BDE-209 has also been shown to debrominate via sunlight or other radiant energy to lower brominated, and potentially more toxic congeners in soil, sand, and sediments (Soderstrom et al., 2004). Similar debromination of BDE-209 has been observed in fish as well (Zhu and Hites, 2004). These reasons combined with BDE-209 being the congener with the greatest sediment concentration in Lake Ontario in the dataset provided (average of 12 884.36 pg/g sediment) (Table 2.1),

and it being the most abundant congener in many other studies, is why it will be investigated in this study.

The second PBDE congener whose spatial distribution in the sediments of Lake Ontario will be looked at is BDE-153 (hexabromodiphenyl ether). Being a significant component in penta-BDE commercial mixtures, this congener is one of the most abundant PBDE congeners and is detectable in many biota (D'Silva et al., 2004). BDE-153 has been detected at quite high levels in human liver samples, human blood, human placenta, and in human breast milk (Thomsen et al., 2002). This congener has also been measured in human adipose tissue from cancerous breasts at high levels, as well as in human patients with non-Hodgkin's lymphoma (She et al., 2000). From 1978 to 1993 the concentration of BDE-153 has also increased over 300% in Great Lakes fish (0.15 to 47.3 ng/g lipid, or 15 to 47 300 pg/g lipid) (Luross et al., 2002; Zhu and Hites, 2004). Dioxin-like activity of BDE-153 has also been noted in mice, with this congener inducing deficits in learning, memory functioning, and alterations in spontaneous behavior (Eriksson et al., 2001). For these reasons, and in conjunction with the fact that in the dataset provided this congener had a relatively high average sediment concentration (223.45 pg/g sediment) (Table 2.1), is why the spatial distribution of BDE-153's sediment concentration in Lake Ontario will be investigated.

The final PBDE congener which will be investigated for its spatial patterns in Lake Ontario sediments is BDE-47 (tetrabromodiphenyl ether). This congener is one of the as the most abundant in the environment, and it is also moderately toxic (Darnerud et

al., 2001). This is likely due to the fact that it is a large component in many commercial PBDE mixtures, particularly in penta-BDE products. BDE-47's abundance in the environment may also be due to the fact that among brominated diphenyl ethers, it has the most thermodynamically stable conformation. BDE-47 may also be the most stable byproduct left from the debromination of unstable, higher-brominated congeners in the environment (D'Silva et al., 2004). In many food webs BDE-47 has been found at the highest levels, and has been measured in elevated levels in human breast milk and tissue, human placenta, human blood, human adipose, and human liver (Thomsen et al., 2002). This congener has higher levels than any other PBDE in marine creatures and fish-feeding animals (Luross et al., 2002; Zhu and Hites, 2004). In terms of BDE-47 concentrations in sediments, in the last 20 years this congener has increased by a factor of 20 (Hale et al., 2003). Perhaps the most concerning aspect of BDE-47 is its toxicity, being shown to reduce levels of the thyroid hormone (Hallgren and Darnerud, 2002) and to be a neurotoxin which hinders development in mice and rats (Eriksson et al., 2001). The aforementioned information on BDE-47, particularly its toxicity, identifies it as being the most toxic of the PBDE congeners analyzed in this study - its abundance, and the fact it has a high average sediment concentration in the data set which will be used in this study (817.07 pg/g sediment) (Table 2.1), is why this congener will be included for analysis in this study.

The Canadian federal government has developed guidelines or thresholds with respect to contaminant concentrations in the Great Lakes, and bodies of water in general (Canadian Council of Ministers of the Environment, 1999). Based on studies performed

Table 2.1: Polybrominated diphenyl ether (PBDE) congeners which will be analyzed in this study. Also provided is the average, minimum, maximum and standard deviation for each congener's Lake Ontario sediment concentration. The values provided are in picogram of PBDE congener per gram of dried sediment (pg/g).

<i>PBDE congener</i>	<i>Average</i>	<i>Minimum</i>	<i>Maximum</i>	<i>Standard Deviation</i>
BDE-47	817.07	26.70	1 730.00	559.79
BDE-153	223.45	9.00	510.00	163.09
BDE-209	12 884.36	306.00	29 200.00	7 984.16

on water quality and sediment chemistry the Canadian government specifies the threshold effect level (TEL) - which is the level of contaminant concentration below that adverse biological effects are expected to occur rarely, and the probably effect level (PEL) - which is the level of contaminant concentration if above that adverse biological effects are expected to occur often (Canadian Council of Ministers of the Environment, 1999). However, there are currently no such Canadian Sediment Quality or Provincial Quality Guidelines for PBDEs or for brominated flame retardants in general. However, in 2005 the European Union developed Environmental Quality Standards (EQS) for penta- and deca-BDEs, which conveniently encompass the three PBDE congeners being looked at in this study. These set standards represent probably no effect concentrations (PNECs) - which is the concentration below which exposure to a substance is not expected to cause adverse effects (European Union, 2005a,c). Two such methods were used to arrive at the EQS: one using the lowest no observed effect concentration (NOEC) from sediment toxicology tests and applying an assessment factor, and another using equilibrium partitioning models to predict a PNEC for sediments using water toxicology data. This means that for both penta- and deca-BDEs two such PNEC values were given, and since neither have definitively been agreed upon both will be considered in this study

(European Union, 2005a,c). The values of these PNECs for the PBDE congeners examined in this study are given in Table 2.2.

Table 2.2: Selected PBDE congeners and European Union Environmental Quality Standards. Given are these standards developed using two different methods. The first probably no effect concentration (PNEC 1) was developed using the lowest no observed concentration (NOEC) from sediment toxicology tests and applying an assessment factor, while the second (PNEC 2) used equilibrium partitioning models and water toxicology data. The PNECs are given in milligrams of PBDE per kilogram of dried sediment (mg/kg) and in picograms of PBDE per gram of dried sediment (pg/g) (Source: European Union, 2005a,c).

<i>PBDE Congener</i>	<i>PBDE Commercial Classification</i>	<i>PNEC 1</i>		<i>PNEC 2</i>	
		<i>mg/kg</i>	<i>pg/g</i>	<i>mg/kg</i>	<i>pg/g</i>
DBE-47	penta-BDEs	0.31	310 000	16.7	16 700 000
DBE-153					
DBE-209	deca-BDE	384	384 000 000	34.5	34 500 000

#### **2.4. Statistical Methods - Data Preparation**

Before the dataset worked with in this study was subject to any statistical and GIS analysis, it first had to be checked for its normality. This process was done using Statistical Package for the Social Sciences (SPSS) version 15. First the three PBDE congeners which were selected for this study were log 10 transformed. After this both the non-transformed and log-transformed data's descriptive statistics were investigated (Table 2.3). Although the descriptive statistics were analyzed at the same time for both the non-transformed and log-transformed data, for both interpolation techniques the non-transformed data was used first followed by the log-transformed data. This was done for both interpolation techniques, as kriging cross-validation statistics should be looked at first using non-transformed data, with transformed data being used if the non-transformed data do not satisfy these statistics. Log-transforming a dataset is helpful since it will usually remove outliers, skewness or kurtosis. Ideally one wants the skewness - which is

a measure of how well the data are distributed, of a variable to be 0 or as close to 0 as possible. If the skewness of a variable's probability distribution is greater than 1 it means its distribution is positively, or right-skewed. Conversely if the skewness of a variable's probability distribution is less than -1, its distribution is negatively, or left-skewed. In either case, if the skewness of a variable is greater than 1 or less than -1 it needs to be transformed. Kurtosis is a measure of the "peakedness" of a probability distribution of a variable, which one ideally wants around 3 or lower (Bluman, 2008).

Looking at the non-transformed and log-transformed descriptive statistics for BDE-47, BDE-153, and BDE-209 in Table 2.3, it can be seen that log-transforming the dataset actually degraded the skewness and kurtosis statistics. Prior to log-transforming the data all the skewness values were close to 0, and nor were any of the kurtosis values objectionable. However, after the data were log-transformed all the skewness values were less than -1, indicating the data were now negatively-skewed. Despite the fact that log-transforming the data made them less normally distributed, this process was still done for later use in the kriging and IDW analyses. Kriging, which does not necessarily require a dataset to be normally distributed, was performed first on the non-transformed data. After the kriging cross-validation statistics were investigated for the non-transformed data it was decided whether the use of the log-transformed data was required. It is likely however that log-transforming the dataset will improve the cross-validation statistics associated with kriging analysis (Dennis et al., 2009; Forsythe and Marvin, 2005).



Table 2.3: Descriptive statistics for the non-transformed and log-transformed dataset for the selected PBDE congeners: BDE-47, BDE-153, and BDE-209.

<i>Descriptive Statistic</i>	<i>Non-Transformed</i>			<i>log-Transformed</i>		
	<i>BDE-47</i>	<i>BDE-153</i>	<i>BDE-209</i>	<i>BDE-47</i>	<i>BDE-153</i>	<i>BDE-209</i>
Mean	817.07	223.45	12 884.36	2.730	2.175	3.954
Minimum	26.70	9.00	306.00	1.430	0.950	2.490
Maximum	1 730.00	510.00	29200.00	3.240	2.710	4.470
Std. Deviation	559.80	34.77	1 702.23	0.510	0.473	0.478
Skewness	0.075	0.512	-0.007	-1.204	-1.046	-1.642
Kurtosis	-1.314	-0.823	-0.798	0.676	0.587	2.902

## **2.5. Statistical Methods - Kriging Analysis**

Along with the dataset containing the concentrations of PBDE congeners, ESRI shapefiles of Lake Ontario, major surrounding cities, and station locations were also used. The data for each congener, both non-transformed and log-transformed, were joined to the station locations shapefile so that analysis could begin. With these shapefiles opened within ArcGIS v. 9.3, kriging was performed by accessing the "Geospatial Analyst" toolbar, and then "Geostatistical Wizard". When the Geostatistical Wizard was accessed, ordinary kriging was selected as the "Method", and the appropriate attribute, e.g. BDE-209 selected. For each congener three models were investigated: 1.) Spherical, 2.) Exponential, and 3.) Gaussian. Each model produces a different ordinary kriging interpolation, differing prediction errors for semivariograms, and the cross-validation statistics that are produced for each model had to be investigated to select the best fit model. Within the "Semivariogram/Covariance Modeling" step of the kriging process the "Major range" was set to 100 000, the "Minor range" to 50 000, and the "Direction" to 90 (for Lake Ontario). The next step in the kriging process was the "Search Neighbourhood" step. Not much was changed here, with the "Neighbours" to include set to 5, "Include at least" to 1, and the "Sector type:" set to 4 with a 45 degree offset. These values were used

as default settings as described in Dennis et al. (2009). With this done the prediction surface was ready to be created and the cross-validation statistics were recorded

For all three PBDE congeners the PNEC values were far higher than any of the observed interval values, with BDE-209 having the highest maximum value of 29 200 pg/g , well below the lower PNEC 2 value of 34 500 000 pg/g for deca-BDEs. Even the PNEC 1 value for penta-BDEs at 310 000 pg/g was far higher than the maximum values for either BDE-47 and BDE-153, with BDE-47 having the higher maximum value of these two congeners at 1 730 pg/g. Due to this isolines showing these PNEC values could not be illustrated for all PBDE congeners. All three PBDE congeners were analyzed using the three model types (Spherical, Exponential and Gaussian), and for each congener these were modeled using the non-transformed and log-transformed data. The cross-validation statistics were recorded for each of these model types and congeners, and would be used later to determine which model type and data type (non-transformed or log-transformed) were most appropriate. For the prediction surfaces the number of classes was initially set to nine, divided manually into appropriate ranges depending on the concentration values for each PBDE congener.

## **2.6. Statistical Methods - Inverse Distance Weighting**

The methodology process for the IDW portion of this study was somewhat more simple than the kriging portion. Using the same shapefiles utilized in the kriging analysis in ArcGIS v. 9.3, the "Geostatistical Analyst" toolbar was accessed, then again the "Geostatistical Wizard". The "Methods" type here was set to Inverse Distance Weighting,

and the Attribute again the desired congener data. When the "Set Parameters" box came up, the "Neighbours to include:" was set to 5, "Include at least:" was set to 1, and the "Sector type:" was set to 4 with a 45 degree offset, as this is what was done in the kriging analysis and these two methods will be compared later. The "Power Function" was set by the "Geostatistical Wizard" at 2, and when this power function is used the process is known as the inverse distance square weighted interpolation, it was left as such. The "Cross Validation" step was the final step in this process, and only two statistics were provided in this case; these were the prediction error statistics of "Mean" (MPE), and "Root-Mean-Square" (RMSPE). These were recorded to later compare them to the appropriate kriging cross-validation statistics. Like when performing the kriging analysis, no isolines were needed in these maps as the PNEC values were higher than any observed values. Once the intervals were set and the prediction surface layer was exported as a vector, the vector layer was clipped to only include data within Lake Ontario. This process was performed for all three PBDE congeners, and using the non-transformed and log-transformed data types. The same process used in the kriging analyses of dividing the classes in the prediction surfaces was applied to the IDW prediction surfaces.

## **2.7. Statistical Methods - Comparison of Analyses**

Once the kriging model types, i.e. Gaussian, Spherical or Exponential, were selected for each PBDE congener, they could then be compared directly to the IDW prediction surfaces created. This was done by following the methodology of the Sun et al. (2009) study, which compared interpolation methods to model the temporal and spatial variations of groundwater in northwest China. Sun et al. (2009) evaluated the accuracy of

the various methods by comparing the RMSPE and the Pearson Correlation Coefficient ( $r$ ) of the measured values and the predicted values of each interpolation method. This is what will be done in this instance individually for each congener, although the MPE will also be added to the comparison, as it is calculated by ArcGIS along with the RMSPE when conducting IDW. In order to calculate the  $r$  for each PBDE congener, first the actual and predicted values calculated in the "Cross Validation" step from each kriging and IDW procedure were recorded. These values were then imported into SPSS and the  $r$  was calculated using the "Analyze" option, selecting "Correlate" and "Bivariate" and inputting the appropriate variables. This was performed using each congener, although only the log-transformed data were used in the interpolation method comparison as they produced valid cross-validation statistics (discussed in Chapter 3). These  $r$  values, as well as the MPE and RMSPE values (determined and recorded previously) were analyzed together to directly compare the kriging and IDW results for each PBDE congener.

## **CHAPTER 3: RESULTS**

In this section of the study the results of the kriging and IDW analyses will be discussed and compared to one another. Before this however, the cross-validation statistics need to be looked at for the kriging analyses for the three selected PBDE congeners (for both the non-transformed and log-transformed data). These statistics will be analyzed, and the most appropriate model for each congener will be selected and used to produce a prediction surface. Following this the results of the IDW analyses will be presented.

### **3.1. Kriging Analyses**

#### **3.1.1. Kriging Cross-Validation Statistics for BDE-47, BDE-153, and BDE-209**

In order to select the most appropriate and accurate model type for each PBDE congener investigated in this study, the cross-validation statistics needed to be considered. As can be seen from Table 3.1, the cross-validation for the non-transformed BDE-47 data are not valid. Although the MPE stats are quite close to 0 for each model type, the RMSPE and ASE are all far greater than 20, and the SRMSPE values are not as close to 1 as the log-transformed values. Log-transforming the data in this instance, although not making the dataset itself more normal in its distribution, improved the validity of the cross-validation statistics. Since all three model's cross-validation statistics were valid, the best model type was selected by counting which one had the most statistics closest to the ideal. Based on this it was determined that the Gaussian model was the most appropriate to create kriging prediction surfaces for BDE-47. The Gaussian model produced an MPE closest to 0 (0.008439), both the RMSPE and ASE were well

below 20, and the SRMSPE was also closest to 1 (0.9764). The fact that the ASE was greater than the RMSPE for the Gaussian model, and the fact that the SRMSPE was under 1, means that the variability in the predictions made were overestimated slightly. This was the case for all the models tested for BDE-47.

Table 3.1: Cross validation statistics for the non-transformed and log-transformed BDE-47 data. These statistics are shown for the three model types investigated: Spherical, Exponential, and Gaussian. Bolded portions of the table indicate the values which best satisfied cross-validation statistic types. This bolding process was only done for the log-transformed data as the model selected based on this would be used by default for the non-transformed data.

<i>Data Type</i>	<i>Model</i>	<i>Mean Prediction Error (MPE)</i>	<i>Root-Mean-Square Prediction Error (RMSPE)</i>	<i>Average Standard Error (ASE)</i>	<i>Similarity of RMSPE &amp; ASE  RMSPE - ASE </i>	<i>Root-Mean-Square Standardized Prediction Error (SRMSPE)</i>
BDE-47	Spherical	-3.825	448.8	525.2	-76.4000	0.8857
	Exponential	8.441	490.9	545.1	-54.2000	0.9281
	Gaussian	-4.894	471.5	526.9	-55.4000	0.9219
log-transformed BDE-47	Spherical	0.01554	0.3226	0.3508	-0.0482	0.8534
	Exponential	0.02052	0.3508	0.3728	<b>-0.0220</b>	0.9666
	Gaussian	<b>0.008439</b>	0.3133	0.3454	-0.0321	<b>0.9764</b>

The cross validation statistics for the non-transformed BDE-153 data were not valid (Table 3.2). For the three kriging models tested - Spherical, Exponential and Gaussian, the MPE values were somewhat close to 0, but the RMSPE and ASE values were well over 20. On top of this the |RMSPE - ASE| and SRMSPE values for the log-transformed data were closer to optimal as well. From the bolded values in Table 3.2, it can be seen that the Spherical model best satisfied the cross-validation statistics for the log-transformed data. This model produced a MPE closest to 0 (-0.000641), a |RMSPE - ASE| closest to 0 (0.0139), and a SRMSPE closest to 1 (1.017). These Spherical model statistics, which show that the RMSPE is greater than the ASE, and the SRMSPE is

greater than 1, indicate that slight underestimation in the variability of the predictions occurred.

Table 3.2: Cross validation statistics for the non-transformed and log-transformed BDE-153 data. These statistics are shown for the three model types investigated: Spherical, Exponential, and Gaussian. Bolded portions of the table indicate the values which best satisfied cross-validation statistic types. This bolding process was only done for the log-transformed data as the model selected based on this would be used by default for the non-transformed data.

<i>Data Type</i>	<i>Model</i>	<i>Mean Prediction Error (MPE)</i>	<i>Root-Mean-Square Prediction Error (RMSPE)</i>	<i>Average Standard Error (ASE)</i>	<i>Similarity of RMSPE - ASE /RMSPE - ASE/</i>	<i>Root-Mean-Square Standardized Prediction Error (SRMSPE)</i>
BDE-153	Spherical	-11.73	154.4	154.5	-0.1000	0.9843
	Exponential	-7.607	141.8	141.1	0.7000	0.9696
	Gaussian	-12.28	163.9	153.7	10.2000	1.039
log-transformed BDE-153	Spherical	<b>-0.0006405</b>	0.3845	0.3706	<b>0.0139</b>	<b>1.017</b>
	Exponential	0.01338	0.3907	0.3728	0.0179	1.054
	Gaussian	-0.005231	0.4155	0.3619	0.0536	1.125

As was the case for the previous two PBDE congeners, the cross-validation statistics for the non-transformed BDE-209 data were not valid. The MPE values for the three models for this congener were all well over 0, being off by nearly over 100 for each model. The RMSPE and ASE values were also extremely high, well over the cutoff value of 20. The log-transformed data produced cross-validation statistics which were valid (Table 3.3). The Gaussian model produced a MPE closest to 0 (0.00744) and a SRMSPE closest to 1 (0.9638), while the Exponential model produced a  $|RMSPE - ASE|$  closest to 0 (-0.0055). Therefore the Gaussian model was selected for the kriging analysis as its best satisfied 2 of the 3 cross-validation statistics, while the Exponential model only best satisfied 1 cross-validation statistic. The ASE for the Gaussian model was larger than the

RMSPE, and the SRMSPE was less than 1 as well, which indicates that there was an overestimation in the variability of predictions made by this model.

Table 3.3: Cross validation statistics for the non-transformed and log-transformed BDE-209 data. These statistics are shown for the three model types investigated: Spherical, Exponential, and Gaussian. Bolded portions of the table indicate the values which best satisfied cross-validation statistic types. This bolding process was only done for the log-transformed data as the model selected based on this would be used by default for the non-transformed data.

<i>Data Type</i>	<i>Model</i>	<i>Mean Prediction Error (MPE)</i>	<i>Root-Mean-Square Prediction Error (RMSPE)</i>	<i>Average Standard Error (ASE)</i>	<i>Similarity of RMSPE - ASE /RMSPE - ASE/</i>	<i>Root-Mean-Square Standardized Prediction Error (SRMSPE)</i>
BDE-209	Spherical	-136.7	7298	8070	-772.0000	0.9233
	Exponential	98.67	7356	7763	-407.0000	0.9803
	Gaussian	-111.6	7367	8048	-681.0000	0.9319
log-transformed BDE-209	Spherical	0.00882	0.3671	0.3794	-0.0123	0.9601
	Exponential	0.02369	0.3802	0.3857	<b>-0.0055</b>	0.9589
	Gaussian	<b>0.007436</b>	0.3589	0.3741	-0.0152	<b>0.9638</b>

### 3.1.2. Kriging Prediction Surfaces for BDE-47 using a Gaussian Model

Since only the log-transformed data for BDE-47 - and all the congeners investigated in this study as a whole, produced valid cross-validation statistics the model selected based on the log-transformed data was also used for the non-transformed data. The non-transformed data were used in the kriging analysis just to compare the prediction surfaces produced by the two data types. The prediction surfaces are shown for the non-transformed BDE-47 data (Figure 3.1) and the log-transformed BDE-47 data (Figure 3.2). The Gaussian model was selected for both these prediction surfaces based on the cross-validation statistics for the log-transformed data. Looking at Figure 3.1 there is a definite pattern of increase in BDE-47 as one moves westward across the lake, particularly in the



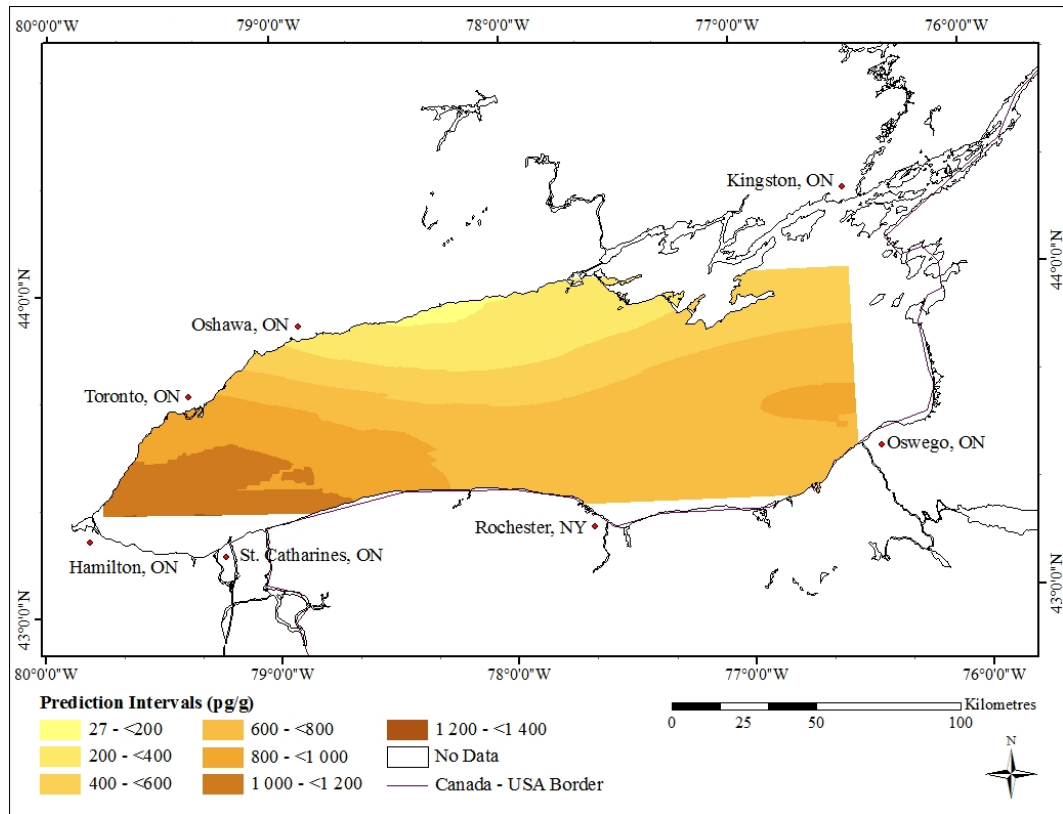


Figure 3.1: Kriging analysis of non-transformed BDE-47 using a Gaussian Model for Lake Ontario, 2008.

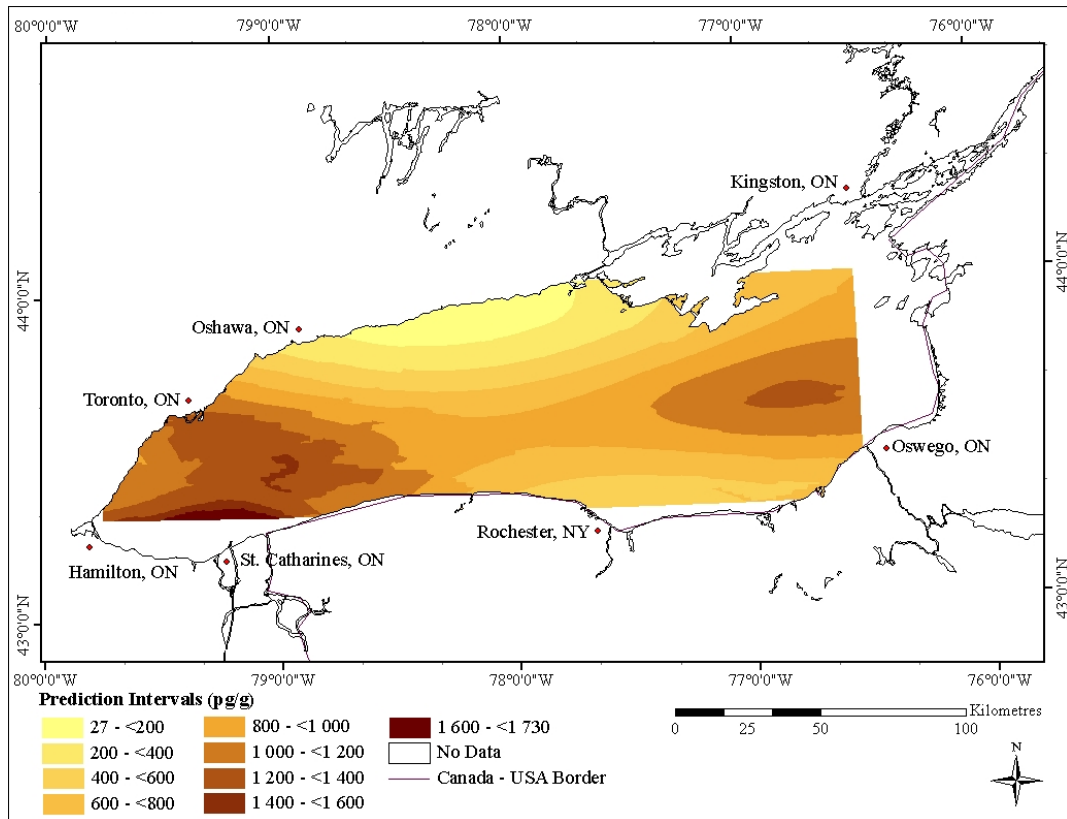


Figure 3.2: Kriging analysis of log-transformed BDE-47 using a Gaussian Model for Lake Ontario, 2008.

southwest of Lake Ontario towards Toronto, ON and Hamilton, ON. Southeast of Toronto all the data is displayed in the 1 000 - < 1 200 and 1 200 - < 1 400 pg/g concentrations. Starting from about 30 km northeast of Toronto, ON and 80 km northeast of St. Catharines, ON is a large band of 600 - < 800 pg/g which moves from the higher bands of BDE-47 concentration east across the Lake towards Oswego, NY. North of this 600 - < 800 pg/g band are two thin bands of BDE-47 of 400 - < 600 pg/g and 200 - < 400 pg/g which move across the lake east to west from Oshawa, ON towards Kingston, ON. A small area of Lake Ontario near Oswego, NY sees the BDE-47 concentration increase to 600 - < 800 pg/g.

Similar overall patterns in BDE-47 distribution in Lake Ontario are seen in the log-transformed data (Figure 3.2), although based on the cross-validation statistics it is clear that this prediction surface may yield more accuracy. In the southwest portion of Lake Ontario is an area of high BDE-47 concentration. This patch begins, like in the non-transformed data prediction surface, about 30 km northeast of Toronto, ON and 80 km northeast of St. Catharines, ON, and ranges from 1 000 - < 1 200 to 1 600 - < 1 730 pg/g, increasing as one moves southeast towards Hamilton, ON and St. Catharines, ON. Similar patterns of decreased BDE-47 concentrations exist for the rest of the lake, as in the non-transformed prediction surface, as one moves north towards Oshawa, ON and south towards Rochester, NY from the centre of Lake Ontario. The lowest levels are seen in the north-central portion of the lake close to Oshawa, ON. There is a second band of BDE-47 increase towards Oswego, NY where two rings of 1 000 - < 1 200 and 1 200 - < 1 400 pg/g of BDE-47 concentration are seen. It suggested through the kriging cross-

validation statistics that the use of log-transformed data is perhaps more useful in mapping BDE-47 sediment concentration in Lake Ontario.

### 3.1.3. Kriging Prediction Surfaces for BDE-153 using a Spherical Model

The prediction surface produced by the kriging results of the non-transformed BDE-153 data was quite basic and easy to interpret (Figure 3.3). Two areas of higher BDE-153 concentrations are visible this prediction surface, the first in the northeast portion of Lake Ontario from Oswego, NY north towards Kingston, ON. BDE-153 concentrations from 195 - < 260 pg/g are seen here increasing to 260 - < 325 pg/g north towards Kingston, ON. A second higher area of BDE-153 concentration is seen in the southwest portion of Lake Ontario. From about 25 km northeast from Toronto, ON south to about 80 km northeast of St. Catharines, ON is where this second region begins. The BDE-153 here is mostly 195 - < 260 pg/g with small areas near Toronto, ON and a larger region towards Hamilton, ON of 260 - < 325 pg/g. The areas of Lake Ontario in between these two areas of higher BDE-153 concentration are largely between 130 - < 195 pg/g, with a reasonably large region near Oshawa, ON along the northern shore of the lake between 65 - < 130 pg/g.

Figure 3.4 shows the BDE-153 kriging prediction surface for the log-transformed data. Similar overall spatial patterns for the two data types were observed, although the more optimal cross-validation statistics indicate that the log-transformed BDE-153 prediction surface may be more accurate. The same two regions to the northeast and southwest of Lake Ontario exhibit the highest concentrations of BDE-153. To the

northeast the concentration increases north east towards Kingston, ON to 390 - < 455 pg/g. The area of high BDE-153 concentration in the southwest starts from about 10 km west of Oshawa, ON south to about 60 km northeast of St. Catharines, ON, and stretches southeast to Hamilton, ON. The outer area of this region range from 195 - < 260 pg/g increasing to 325 - < 390 pg/g around Toronto, On and towards Hamilton, ON. The lowest concentrations were found (9 - < 65 and 65 - < 130 pg/g) in the north-central part of Lake Ontario, with mid-ranges from Oshawa, ON extending southeast towards Rochester, NY of 130 - < 260 pg/g.

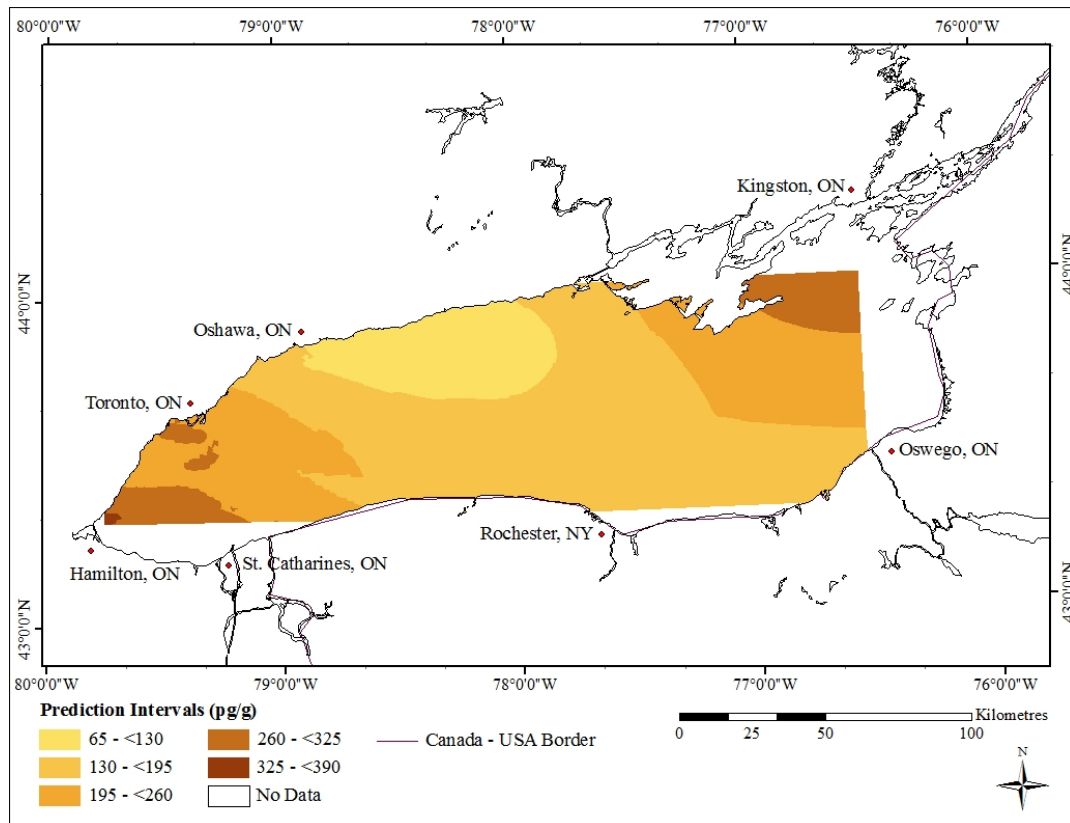


Figure 3.3: Kriging analysis of non-transformed BDE-153 using a Spherical Model for Lake Ontario, 2008.

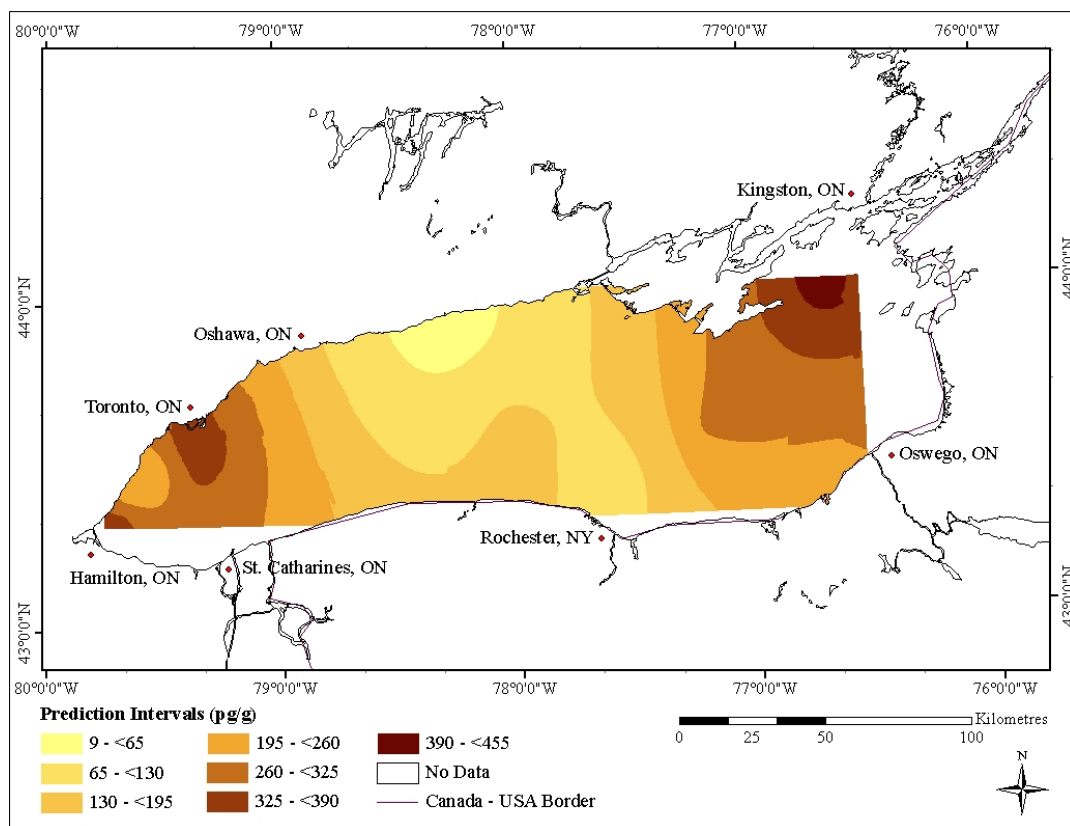


Figure 3.4: Kriging analysis of log-transformed BDE-153 using a Spherical Model for Lake Ontario, 2008.

### 3.1.4. Kriging Prediction Surfaces for BDE-209 using a Gaussian Model

The overall appearance of the kriging prediction surfaces using a Gaussian model (for both non- and log-transformed data) for BDE-209 are very similar to that already discussed for BDE-47. Obviously these prediction surfaces differ in the concentration levels, as BDE-209 is present at much higher levels than BDE-47. Figure 3.5 shows the prediction surface using the non-transformed BDE-209 data. The southwest area of Lake Ontario has higher concentrations of BDE-209 (14 000 - < 17 500 pg/g). A second band of relatively high BDE-209 concentration (10 500 - < 14 000 pg/g) makes up a large portion of the remainder of Lake Ontario, extending from Toronto, ON east up towards Kingston, ON and down to Oswego, NY. A smaller area making up the remainder of Lake Ontario in the north-central area of the lake, from about 40 km southwest from

Oshawa, ON to about 100 km southwest of Kingston, ON, has lower BDE-209 concentration, with the lowest beginning near Oshawa, ON along northern shore at 3 500 - < 7 000 pg/g.

Similar overall patterns can be seen in the log-transformed BDE-209 data (Figure 3.6), although higher concentrations are observed throughout the whole lake using these data, and the interpolations are perhaps more accurate based on the cross-validation statistics. An area of relatively high BDE-209 concentration can be seen in the northeast of Lake Ontario towards Kingston, ON and Oswego, NY - ranging from 14 000 - < 17 500 pg/g and 17 500 - < 21 000 pg/g. A second area of high BDE-209 concentration can be viewed in the southwest of Lake Ontario beginning from about 120 km southeast from St. Catharines, ON along the southern shore and Toronto, ON along the northern shore, stretching southeast towards Hamilton, ON. This area ranges in BDE-209 concentration from 14 000 - < 17 500 pg/g to 24 500 - < 28 000 pg/g, with the highest levels being in the middle of cluster and south towards Hamilton, ON and St. Catharines, ON. Two areas of lower BDE-209 concentration exist along north-central shoreline and an area in the southeast of Lake Ontario, with concentrations ranging from 7 000 - < 10 500 pg/g to 306 - < 3 500 pg/g, decreasing as one moves towards the lake's shoreline in both areas.

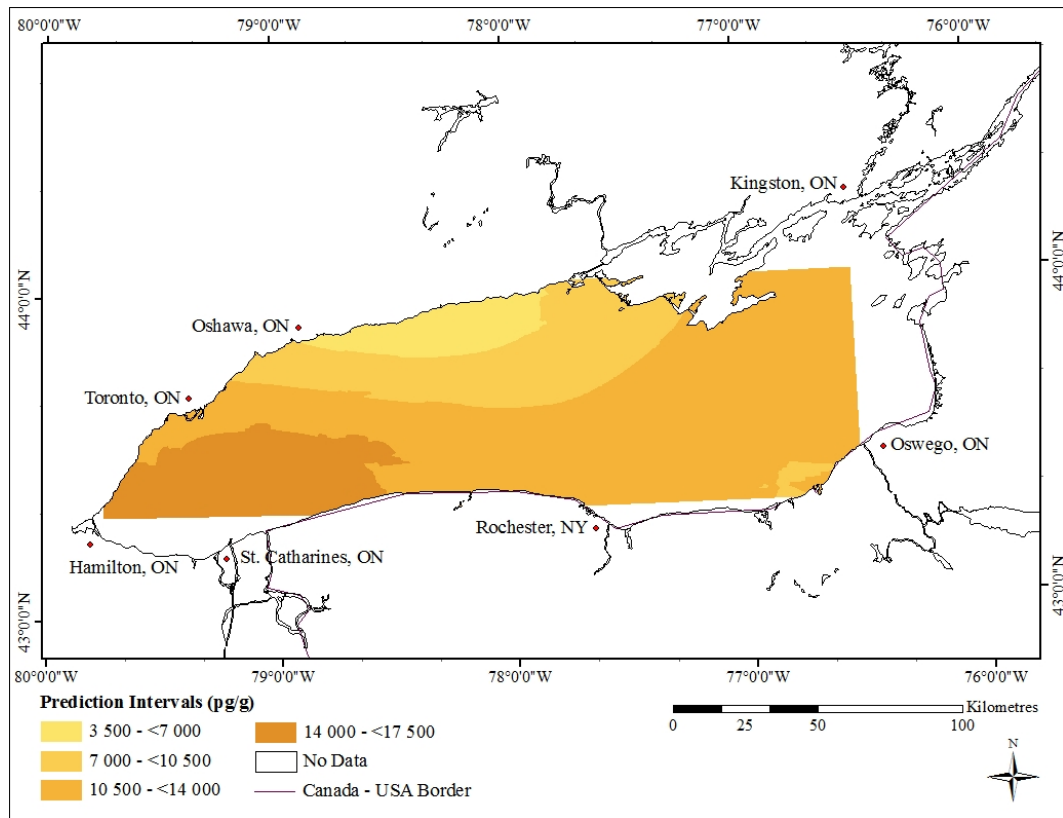


Figure 3.5: Kriging analysis of non-transformed BDE-209 using a Gaussian Model for Lake Ontario, 2008.

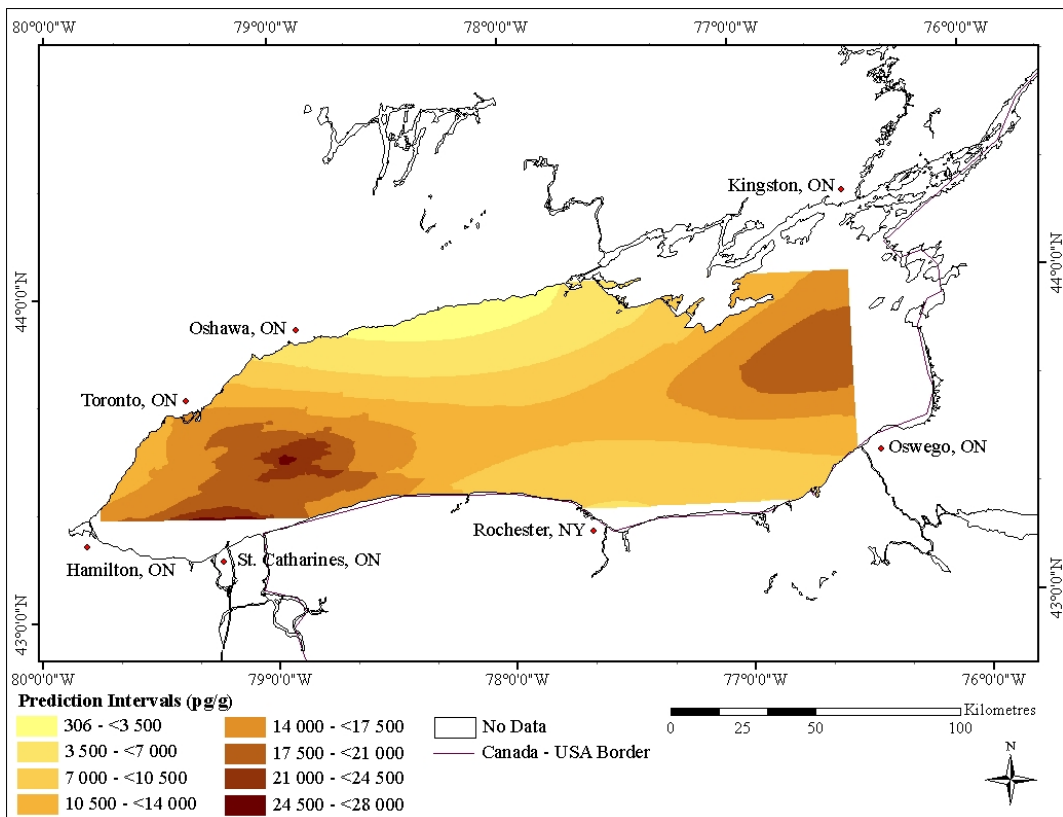


Figure 3.6: Kriging analysis of log-transformed BDE-209 using a Gaussian Model for Lake Ontario, 2008.

### 3.1.5. Implications of Kriging Cross-Validation Statistics and Prediction Surfaces

For all three congeners, log-transforming the data may have resulted in more effective mapping of PBDE sediment concentration in Lake Ontario. Transforming the data as such resulted in more ideal cross-validation statistics, and thus interpolations with more accuracy and less bias. However, for all three PBDE congeners the accuracy of the interpolations needs to be carefully questioned due to the paucity and uneven distribution of the data points. The fact that log-transforming the data actually degraded the skewness and kurtosis statistics, and thus skewed the distribution, is an important detail to consider. Log-transforming the data actually converted them into smaller values, which also may have incorrectly improved the cross-validation statistics, which is another issue that needs to be investigated further in the Discussion sections to come.

## **3.2. Inverse Distance Weighting**

### 3.2.1. IDW Statistics for BDE-47, BDE-153, and BDE-209

The statistics produced during the IDW process suggest that log-transforming the data increased the validity of the predictions surfaces. The MPE and RMSPE for the non-transformed BDE-47 prediction surface was 64.65 and 472.20 respectively, while for the log-transformed BDE-47 prediction surface these same statistics were 0.04907 and 0.3801 respectively. For BDE-153, the MPR and RMSPE for the non-transformed prediction surface was 7.465 and 141.8 respectively, while for the log-transformed prediction surfaces these same values were 0.03768 and 0.3789 respectively. Finally, for BDE-209 the MPE and RMSPE calculated for the non-transformed prediction surface



was 919.5 and 7 907 respectively, while for the log-transformed prediction surface these same statistics were 0.04947 and 0.4056 respectively

### 3.2.2. IDW Prediction Surface for BDE-47

Looking at the two prediction surfaces created using IDW for the non-transformed BDE-47 data (Figure 3.7) and the log-transformed BDE-47 data (Figure 3.8), they appear to have more or less the same overall contaminant concentration patterns. Both show the highest BDE-47 concentrations of 1 400 - < 1 600 pg/g and 1 600 - < 1 730 pg/g near Toronto, ON, Hamilton, ON, and St. Catharines, ON, decreasing gradually to 600 - < 800 pg/g eastward towards Oshawa, ON. The central portion of Lake Ontario from about Oshawa, ON along the northern shore to about 40 km east of Rochester, NY along the southern shore has the lowest BDE-47 concentrations in both the non-transformed and log-transformed prediction surface. Here the contaminant's concentration ranges from 27 - < 200 pg/g and 400 - < 600 pg/g, with the lowest levels being along the north-central shore of the lake in this region. Further southeast past this central region of the lake BDE-47's concentration levels increase again from 600 - < 800 pg/g to up to 1 200 - < 1 400 pg/g in some areas. Both non-transformed and log-transformed IDW prediction surfaces exhibited signs of clustering, or "bulls eyes", although these were somewhat more apparent and exaggerated in the non-transformed prediction surface. These clusters were particularly obvious in the southwest portion of Lake Ontario near Toronto, ON and Hamilton, ON. It can almost be expected for such clustering to occur in the prediction surfaces for both data types, considering that there were only 22 sample locations and that the data were skewed in their distribution.

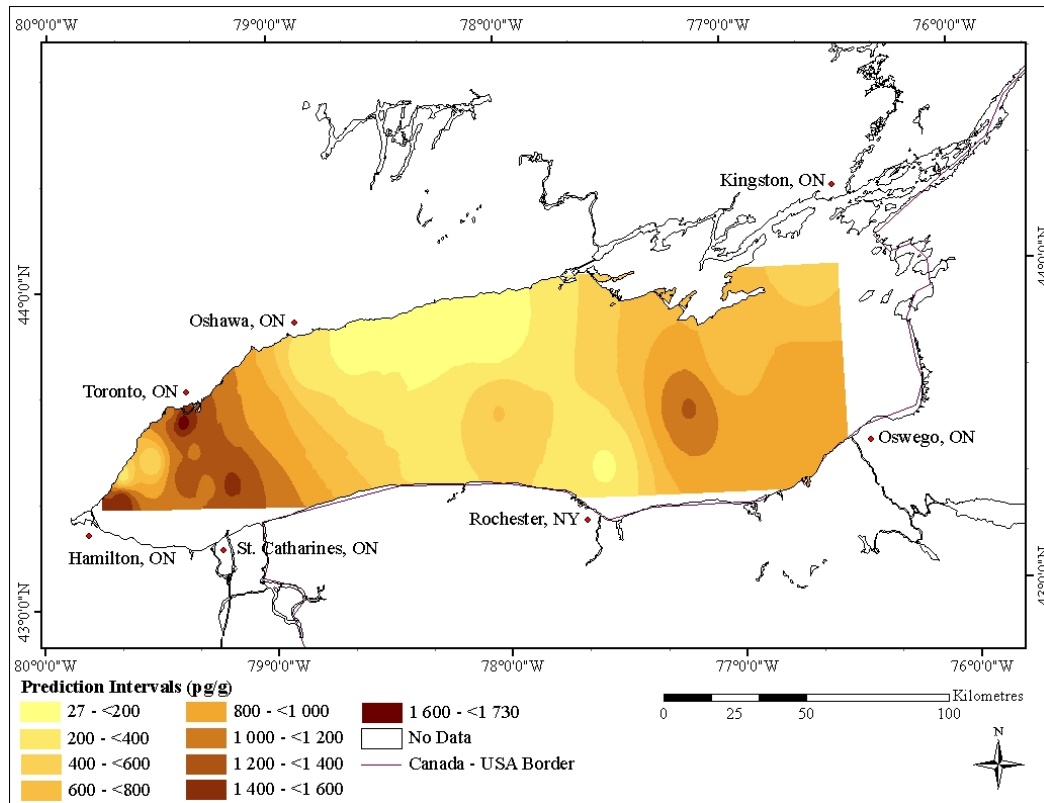


Figure 3.7: Inverse Distance Weighting analysis of non-transformed BDE-47 for Lake Ontario, 2008.

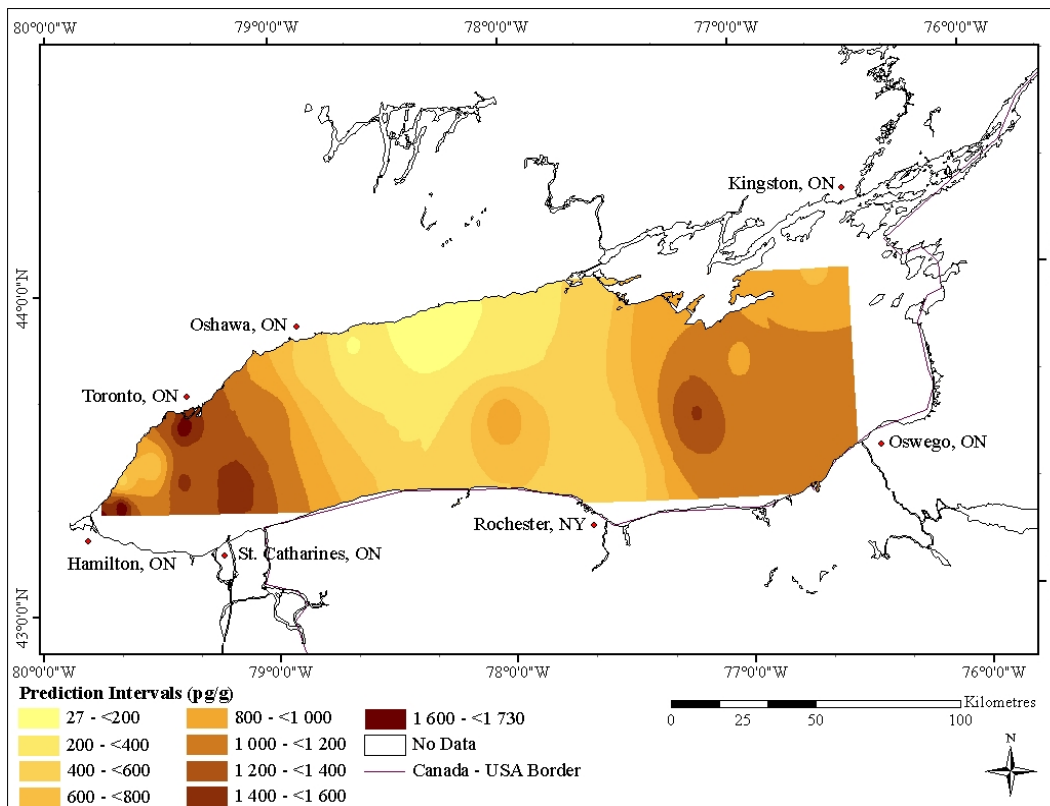


Figure 3.8: Inverse Distance Weighting analysis of log-transformed BDE-47 for Lake Ontario, 2008.

### 3.2.3. IDW Prediction Surface for BDE-153

Similar to the IDW non-transformed and log-transformed prediction surfaces for BDE-47, those produced for BDE-153 were also quite similar (Figures 3.9 and 3.10). There were two areas, one in the southwest and another to the northwest of Lake Ontario where the highest BDE-153 concentrations were observed. The area in the southwest of the lake began from Oshawa, ON along the northern shore and about 80 km northeast of St. Catharines, ON along the southern shore with a concentration of 130 - < 195 pg/g, increasing westward and peaking at 325 - < 455 pg/g and 455 - < 510 pg/g near Toronto, ON and Hamilton, ON. The northeast BDE-153 high concentration zone began about 50 km east of Rochester, NY with a concentration of 130 - < 195 pg/g and increased in a northeastern direction towards Kingston, ON - again peaking at the 390 - < 455 pg/g and 455 - < 510 pg/g concentration level. Lower concentrations of 65 - < 130 pg/g were seen in the central portion of Lake Ontario, with the lowest concentrations being observed along the northern shore of this area of the lake at 9 - < 65 pg/g. The same clustering around high value sample locations which were observed in the IDW prediction surfaces for BDE-47 were seen in the IDW prediction surfaces for BDE-153, and again these were somewhat more pronounced and obvious in the non-transformed prediction surface - particularly near Toronto, ON and Hamilton, ON in the southwest.

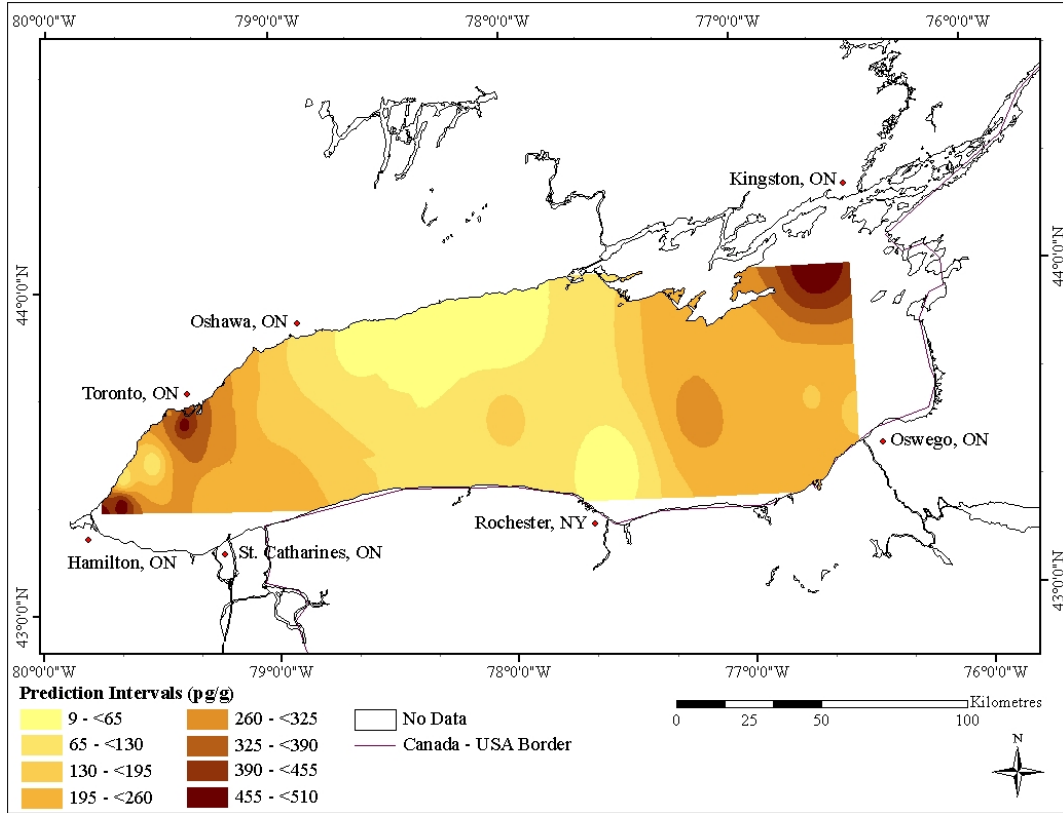


Figure 3.9: Inverse Distance Weighting analysis of non-transformed BDE-153 for Lake Ontario, 2008.

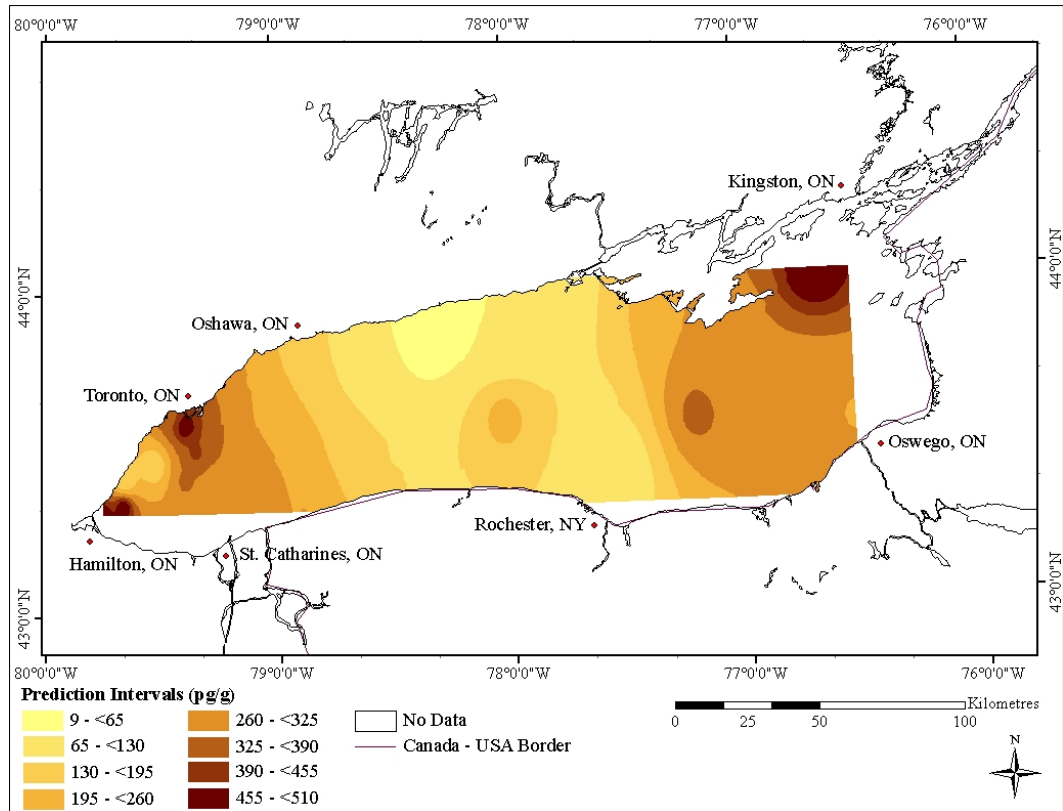


Figure 3.10: Inverse Distance Weighting analysis of log-transformed BDE-153 for Lake Ontario, 2008.

#### 3.2.4. IDW Prediction Surface for BDE-209

The IDW prediction surfaces produced for the non-transformed BDE-209 data and the log-transformed BDE-209 data (Figures 3.11 and 3.12), although quite similar, probably differed from one another the most compared to the IDW prediction surfaces produced for the other PBDE congeners. Both non-transformed and log-transformed prediction surfaces for BDE-47 and BDE-153 contained the same number of prediction intervals, while for BDE-209 the log-transformed prediction surface contains one more, this being at the upper level of concentration as well. Both prediction surfaces for BDE-209, however, did have two areas of Lake Ontario which showed high contaminant concentration levels. The first of these areas was in the southwest of the lake, beginning from Oshawa, ON along the northern shore and about 120 km northeast of St. Catharines, ON along the southern shore, with a concentration of 7 000 - < 10 500 pg/g. West of here the BDE-209 concentration increased to an upper limit of 21 000 - < 24 500 pg/g and 24 500 - < 28 000 pg/g near Toronto, ON and Hamilton, ON, although in the log-transformed prediction surface a small region near Hamilton, ON expressed a BDE-209 concentration of 28 000 - < 29 200 pg/g. About 100 km west of Rochester, NY along the southern shore and 120 km southwest of Kingston, ON along the northern shore is where the second high BDE-209 concentration zone began, with the lower levels being at 7 000 - < 10 500 pg/g, increasing northeast towards Kingston, ON to 14 000 - < 17 500 pg/g. Two small pockets of lower BDE-209 concentration of 3 500 - < 7 000 pg/g were seen around Rochester, NY and Oshawa, ON, with the lowest concentrations being observed in the north-central portions of Lake Ontario at 306 - < 3 500 pg/g. The IDW prediction surfaces for this congener also exhibited the most apparent and numerous clusters, likely

caused by sampling location sites having BDE-209 levels far higher than elsewhere in the lake. Many of these clusters were located in the southwest portion of the lake near Toronto, ON and Hamilton, ON, although several are also present in the central and eastern portions of the lake near Rochester, NY and Oswego, NY respectively.

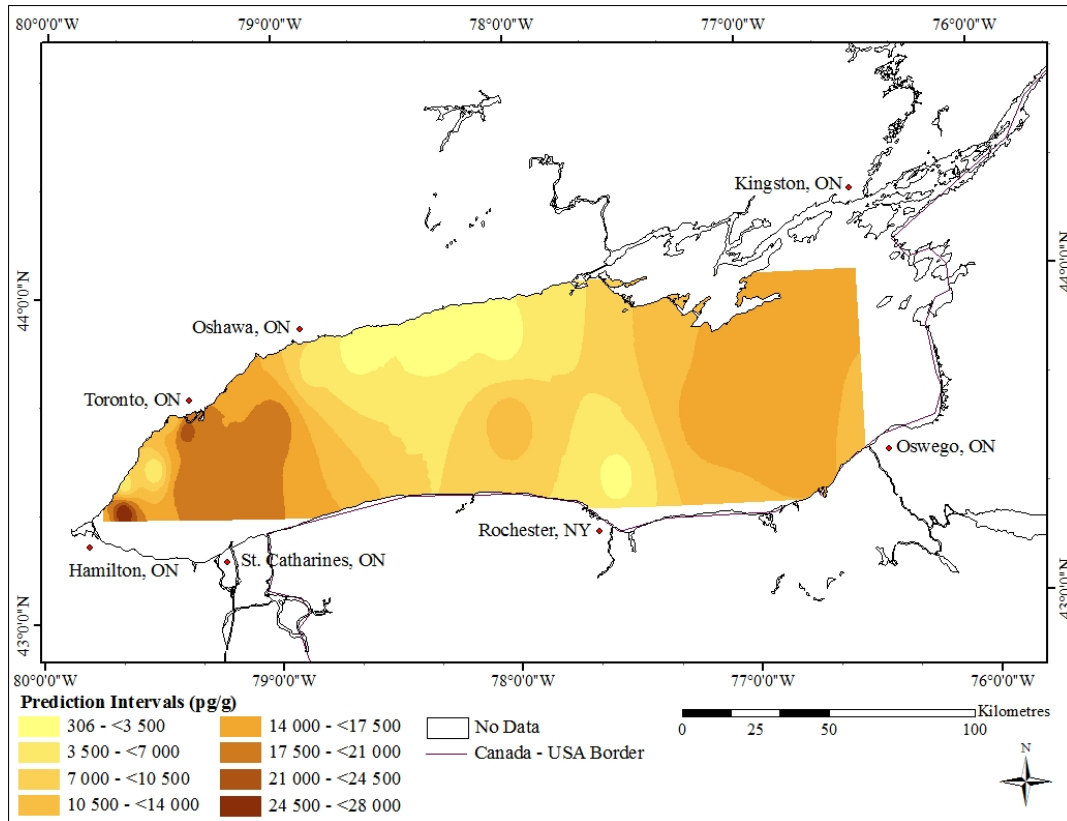


Figure 3.11: Inverse Distance Weighting analysis of non-transformed BDE-209 for Lake Ontario, 2008.

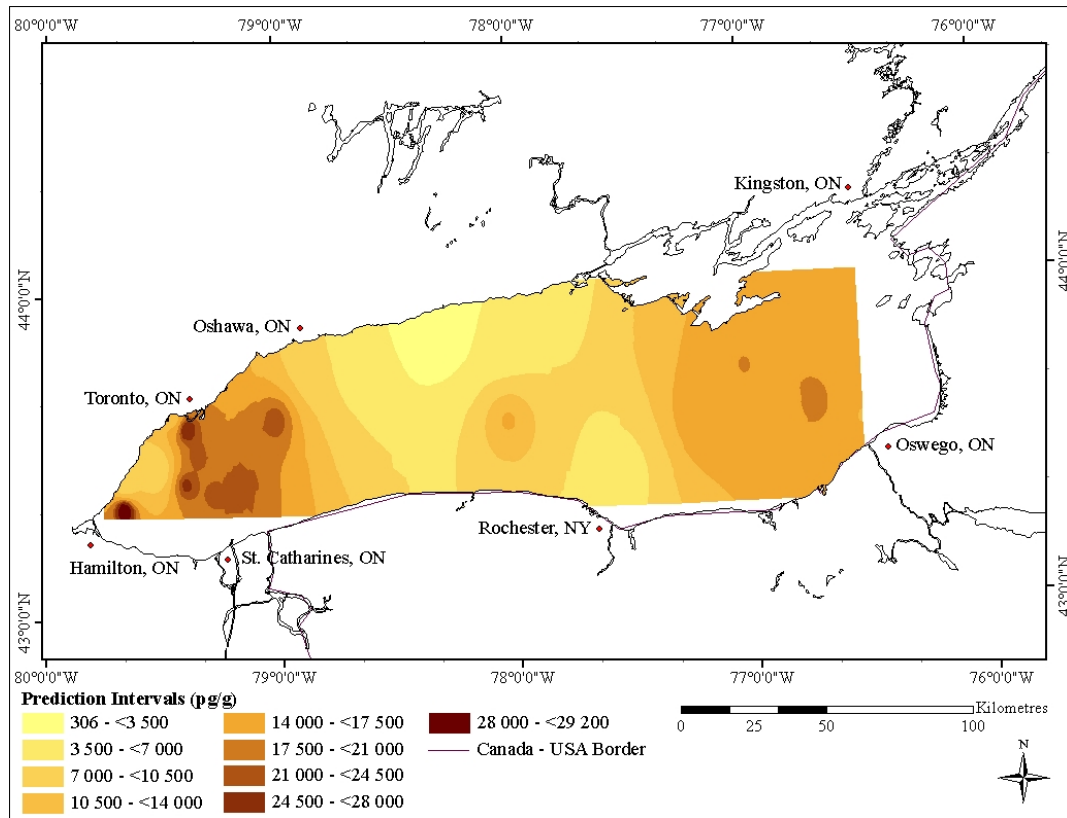


Figure 3.12: Inverse Distance Weighting analysis of log-transformed BDE-209 for Lake Ontario, 2008.

### 3.2.5. Implications of IDW Statistics and Prediction Surfaces

Similarly to the results for the kriging analyses, the MPE and RMSPE calculated for IDW were closer to 0 when the log-transformed data were used. This indicates that there may have been less interpolation bias and more accuracy when using the log-transformed data, and that this may be an important step when running IDW. However, such results depend on the dataset being used, and this step should not be considered mandatory when performing IDW. The prediction surfaces for both data types seem to be affected by clustering, likely representative of outliers in the dataset. The results from the IDW prediction surfaces also need to be considered against the fact that the interpolations may not be completely realistic due to the small sample size; the uneven distribution of these sample locations; and since log-transforming the data may reflect

improved statistics based on a scaling effect of the produced smaller values, and not necessarily an improvement in interpolation accuracy or bias.

### **3.3. Comparison of Interpolation Methods**

From the previous Results sections it was determined that log-transforming the dataset may have resulted in more statistically valid prediction surfaces for all PBDE congeners, when running both kriging and IDW analyses. Further analysis of the cross-validation statistics from the kriging analysis determined that the ideal model for BDE-47, BDE-153, and BDE-209 was Gaussian, Spherical, and Gaussian respectively. Direct comparison of which interpolation method was more appropriate, effective, and accurate for each congener was now possible. This was done by comparing the log-transformed kriging results (for the aforementioned model types) for each PBDE congener against the log-transformed IDW results individually. The MPE, RMSPE, as well as the Correlation Coefficient ( $r$ ) - which was calculated from the actual sample location values against the predicted values for each model, were used as a basis for comparison. As was mentioned, the MPE and RMSPE should be as close to 0 as possible, and the closer the  $r$  is to 1 the better as this indicates more correlation between the actual sample location values, and the ones predicted by the interpolation method. The results of such comparisons are shown in Table 3.4.

For each PBDE congener the MPE and RMSPE values are far closer to 0 for the kriging analysis than for the IDW. The  $r$  values produced by the kriging analysis for BDE-47 and BDE-209 are also significantly higher than those produced by the IDW.



Surprisingly, despite having a far lower MPE and RMSPE for its kriging results, BDE-153 had a higher  $r$  value from the IDW prediction surface than from the kriging analysis prediction surface. All of the  $r$  values were significant to a factor of 0.05 (95%). Although depending on the characteristics of the data being used and the area being analyzed, it appears that when a smaller sample size is used, kriging may be a more accurate and statistically valid interpolation method to use when mapping PBDE sediment concentration in Lake Ontario.

Table 3.4: Direct comparison between the kriging prediction surfaces and the IDW prediction surfaces. Shown are the Mean Prediction Error (MPE), Root-Mean-Square Prediction Error (RMSPE), and the Correlation Coefficient ( $r$ ) - measured using the actual measured log-transformed sample location values and the predicted log-transformed values. All of the  $r$  values are significant to 0.05 (95%) factor.

<b>Interpolation / Model / PBDE congener</b>	<b>Mean Prediction Error (MPE)</b>	<b>Root-Mean-Square Prediction Error (RMSPE)</b>	<b>Correlation Coefficient (<math>r</math>)</b>
Kriging / Gaussian / 47	0.008439	0.3589	0.778
IDW / 47	0.04907	0.3801	0.654
Kriging / Spherical / 153	-0.0006405	0.3133	0.549
IDW / 153	0.03768	0.3789	0.581
Kriging / Gaussian / 209	0.007436	0.3845	0.637
IDW / 209	0.04947	0.4056	0.500

## **CHAPTER 4: DISCUSSION**

The overall goal of this research project was to analyze the spatial patterns of selected PBDE congeners in Lake Ontario, and to investigate whether kriging or IDW was the better interpolation method to utilize with the small sample size used. Through the analysis of cross-validation statistics it was determined, with the dataset used in this study, that when running kriging or IDW one may achieve better accuracy and statistical validity when log-transforming the data. This may not be the case for all instances however, and may vary depending on the data being used. Specifically for the three selected PBDE congeners, the ideal kriging model to utilize in this instance was Gaussian for BDE-47 and BDE-209, while for BDE-153 the best kriging model was Spherical. By directly comparing MPE, RMSPE and the Correlation Coefficient ( $r$ ) individually for kriging and IDW, it was determined that kriging may be the better interpolation method to utilize for the spatial mapping of PBDEs in Lake Ontario when using a smaller-than-ideal sample size. The kriging results were more statistically valid than those of IDW, with direct comparison of the maps produced by the two interpolation methods also favouring kriging. The prediction surface produced by IDW were affected quite significantly by the presence of outliers in the data, being seen with the appearance of "bulls eyes" around very high and low sample location points. This is due to the fact that IDW is an exact interpolator, which means the method only uses exact values from sample locations to make predictions for an unknown area (Ashraf et al., 1997; Sun et al., 2009). Kriging on the other hand assumes an unknown, but constant mean, with estimates for any location based on weights that are chosen to minimize the kriging variance (Ashraf et al., Haining et al., 2010; Webster and Oliver, 2007). It would have been

interesting to see if the same results would have occurred provided with a dataset with a more robust number of sample locations. If more sample locations existed it is possible IDW may have produced more accurate results.

Kriging analysis is probably the most robust and widely used interpolation method in general (Haining et al., 2010). In this study it likely outperformed IDW since kriging assumes the mean is unknown, but still constant, and that the random field is locally stationary. This means kriging assumes the distance, direction, or both, between sample points reflect spatial correlation, and can be used to explain the variation in the surface. The weights used in kriging are chosen to minimize the variance, with these weights being constrained to 1 to ensure the estimates made are unbiased, while in IDW weights are determined by input points, each which have local influence on predictions made that lessen with distance away from the prediction location (Haining et al., 2010; Webster and Oliver, 2007; Panagopoulos et al., 2006). Using these weights the kriging produces a spatial surface in deviations from a constant mean, where these deviations are spatially correlated (Forsythe and Marvin, 2005; Krivouchko and Gotway, 2004).

Since kriging is such a strong and accurate interpolation model, it is not surprising that it has been utilized to analyze the spatial distribution of sediment contaminants in the Great Lakes such as hexachlorobenzene (HBC), polychlorinated biophenyls (PCBs), lead (Pb), and mercury among many others (Jakubek and Forsythe, 2004; Forsythe and Marvin, 2005; Forsythe et al., 2004). There have also been quite a few studies that investigate the ability of various interpolation methods to spatially map anything from

climatic variables such as temperature and precipitation (Zhang and Srinivasan, 2009; Attorre et al., 2007), to soil pH (Shi et al., 2009) and the spatial variation of groundwater (Sun et al., 2009). However, in the aforementioned interpolation comparison studies the sample sizes utilized were considerably larger than the 22 used in the present study. Sun et al.'s (2009) study of temporal and spatial variation in groundwater sampled from 48 sites, Shi et al.'s (2009) study of soil pH had a very robust sample size of 150, while Attorre et al.'s (2007) study utilized data from 201 precipitation measuring stations and 102 temperature measuring stations. In kriging the variogram - which has a very important role in the calculation of prediction variances, is calculated from sample points. If this variogram is calculated using too few data points it may be too erratic, with the resulting variation being very large. It is therefore important to establish how large of a sample size is needed to produce an acceptable estimate of the variogram. There is no real set number to how large such a sample size should be, although it has been suggested that variograms based on fewer than 50 data points are of little value (Webster and Oliver, 1992). Webster and Oliver (1992) have also suggested that a sample size of at least 100 is needed, with 150 sample points calculating variograms deemed satisfactory, while using up to 225 or more sample points will usually be reliable.

Perhaps using co-kriging - which is an interpolation technique that can improve kriging prediction surfaces if the distribution of a secondary variable that has been more extensively sampled is known - may have improved the results. If this second variable is well correlated with the initial variable, which would be PBDE in our case, it can be used in this interpolation technique to improve the less extensively sampled variable (Haining

et al., 2010). Such a study was conducted by Pang et al. (2009) to spatially map soil copper (Cu) in China. Using previously sampled soil organic matter data as a secondary, or ancillary, variable accuracy was far higher when using co-kriging than when simply using kriging. The RMSPE was improved and the  $r$  between the predicted and measured values increased significantly when using co-kriging over kriging, even when the sample size was reduced by 10% (Pang et al., 2009). Future studies looking to map PBDE sediment concentrations could be designed similarly to Pang et al.'s (2009), which could potentially make up for the cost and difficulty of acquiring upwards of 100 to 225 sediment samples - which is suggested as needed by Webster and Oliver (1992). Although ideally a large number of sediment samples should be utilized, perhaps sampling from areas expected to have higher PBDE concentrations - as was done in this study, coupled with data from more intensively sampled sediment contaminants could improve future results.

A comparison study such as the present one has not been done that looks at the ability of kriging and IDW to produce prediction surfaces when using a smaller-than-ideal sampling size. A dataset of only 22 sample locations was used in this study, so the results from this paper may shed light onto which interpolation method is ideal when confronted with such an obstacle. A small sample size can result from a number of factors ranging from improperly sampled data, lack of funds, lost or misplaced data, or the simple fact that gathering data from enough sample sites was physically impossible. Based on the figures suggested by Oliver and Webster (1992), perhaps it is not surprising that not many interpolation comparison studies have been done using small sample sizes.

Although in this study kriging was found to be more accurate than IDW based on cross-validation statistics, and the  $r$  value calculated for each of the three PBDE congeners, perhaps the sample size was too small. The variogram may have been incorrectly calculated, resulting in far too much variation. Also, log-transforming the data may have also influenced the cross-validation statistics incorrectly. Not only did doing this skew the dataset, but the improvements in the cross-validation statistics may have been due to the transformation lowering the values, and not from actual improvements in interpolation accuracy or bias.

#### **4.1. Possible Reasons for Observed Kriging PBDE Patterns**

Although the overall spatial patterns were discussed for the kriging and IDW prediction surfaces, these were done individually by PBDE congener, with little to no actual comparison or analysis of overall patterns in the PBDE distribution in Lake Ontario. Looking back to the log-transformed kriging prediction surfaces for BDE-47 (Figure 3.2), BDE-153 (Figure 3.4), and BDE-209 (Figure 3.6) there are some spatial patterns worth noting and discussing further. There are two clear areas of higher PBDE concentrations for all three congeners. The first is in the southwest portion of Lake Ontario, being particularly high near the urban centres of Toronto, ON, Hamilton, ON, and to some degree St. Catharines, ON. A second area of Lake Ontario with higher PBDE concentration is the northwest portion of the lake towards Kingston, ON and Oswego, NY. The central portions of Lake Ontario, particularly towards the northern and southern shores are where lower PBDE concentrations were observed. These observations mirror others studies which suggest areas along the Great Lakes that are adjacent to heavily

urbanized and industrialized cities have higher PBDE contamination levels, and perhaps require more attention and monitoring than other areas (Hites, 2004). In future studies, due to the high cost of undertaking such sediment samples, efforts could focus on areas near large urban centres.

As was mentioned in the early chapters of this paper, PBDEs have many ways of finding their way into the environment, albeit via accidental discharge; leaching from plastic appliances; foam upholstery; televisions and computers; fibers and drapes; and during processing and recycling practices (D'Silva et al., 2004; Barontini et al., 2001). In terms of how PBDEs end up in aquatic ecosystems - and for our interest Lake Ontario and the rest of the Great Lakes, the main source of PBDE contamination is through atmospheric deposition (Hale et al., 2003). PBDEs can also find their way into the Great Lakes through the disposal and recycling of products containing the contaminant, deposition from tributaries and wastewater treatment plants, and from manufacturing outputs (Ward et al., 2008; La Guardia et al., 2007). These modes of input into the Great Lakes can help explain why higher concentrations of PBDEs were observed near urban areas. Not only are the large, major urban areas found in southwest Lake Ontario and to some extent eastern Lake Ontario (obvious urban point sources of PBDE input), but they are also located near rivers and tributaries undoubtedly adding further contamination near these regions. Upstream sources including Lake Erie also likely contribute to the PBDE levels in Lake Ontario.

The circulation of Lake Ontario could also help explain some of the observed spatial patterns of PBDEs in this paper. Lake Ontario's circulation is characterized by a counter-clockwise direction, with a smaller clockwise rotating gyre in the northwest portion (refer to Figure 2.1). Looking at this overall water circulation and the isobaths displayed for Lake Ontario and comparing this to the kriging prediction surfaces for BDE-47 (Figure 3.2), BDE-153 (Figure 3.4), and BDE-209 (Figure 3.6), the higher PBDE concentrations were observed in the shallower regions of the lake to the southwest and northeast. The lake's currents could have been carrying these contaminants and depositing them into these shallow regions. The gyre present in the northwest portion of the lake could also have contributed to the high PBDE concentrations in the region, as the two overall currents collide and suspend the sediments which eventually settle in the region's shallower waters.

#### **4.2. Government Intervention and Future Considerations on PBDEs in the Great Lakes**

The alarming presence of PBDE in the environment, as well as the unknown long-term effects of this contaminant on human health, was enough for the Canadian government to take action on the matter (Schechter et al., 2007; Schreiber et al., 2010; Ward et al., 2008). The Canadian Environmental Protection Act of 1999 prohibited the manufacturing of any PBDE or any resin, polymer or other mixture containing PBDE. However, this Act does still allow PBDE or resins, polymers and other mixtures that contain PBDEs to be re-processed as long as it is done in a manner where no release of the substance occurs, and as long as it is disposed in a way that abides by the laws of the



jurisdiction where they will be disposed. The allowing of re-processing could potentially be detrimental in that PBDEs could be released due to negligence. This act also does not prohibit the import of PBDEs for use as raw materials, in semi-finished goods, and in finished products (Environment Canada, 2000; Ward et al., 2008).

Other current Canadian initiatives include "The Environmental Choice Program", started in 1988 this program established environmental criteria for laptop and desktop computers. This initiative encourages the reduced use of hazardous substances (including PBDEs); designing for recycling, efficiency, reduced packaging, and ergonomic considerations. Companies are awarded an Environment Canada's ecolabelling program certification if they demonstrate the aforementioned criteria (Environment Canada, 2009). Many companies are also voluntarily attempting to manage PBDE release by trying to avoid the use of deca-BDEs (BDE-209) commercial mixture in the manufacturing of semi-finished and finished goods in Canada. Similar such international action has been taken as penta-BDEs and octa-BDEs have been internationally unavailable since 2005. However some countries still allow the manufacturing of deca-BDEs (BDE-209) (Environment Canada, 2000).

Although the Canadian government has taken some action on the manufacturing of PBDES, the Canadian government has yet to set any sediment quality guidelines for PBDEs. As mentioned earlier the European Union has set PNECs in sediments for penta- and deca-BDEs (which cover all three of the PBDE congeners investigated in this study). The observed levels in this study however were far under these European Union PNECs,

with the highest observed BDE-209 concentration of 29 200 pg/g being well under the PNEC 1 and PNEC 2 for deca-BDEs of 384 000 000 pg/g and 34 500 000 pg/g, respectively. The highest levels of BDE-47 of 1 730 pg/g are also well under the PNEC 1 and PNEC 2 for penta-BDEs of 310 000 pg/g and 16 700 000 pg/g, respectively. Despite these encouraging figures, Canada still has to set such threshold values, since the full health effects of PBDEs on humans, fish and birds, and other wildlife are not known. Further research needs to be done on PBDEs in this respect as well as on the spatial distribution of such substances in lake and river sediments, soil, the atmosphere, and where large populations of people live. The results of this study are just a small part of what PBDE research needs to be done.

## **CHAPTER 5: CONCLUSIONS**

The huge increase in PBDEs in Lake Ontario, and the Great Lakes system in general, since the 1970s and particularly since the 1990s are solely due to human activities. The overall pattern of higher PBDE sediment concentrations in the southwest and northeast of Lake Ontario near the large urban centres of Toronto, ON, Hamilton, ON and St. Catharines; and Kingston, ON and Oswego, NY respectively, can be attributed mainly to the proximity of these cities to Lake Ontario. The circulation of the lake may also explain some of the observed patterns of PBDEs in this study. Although there has been government intervention on controlling PBDEs both locally and internationally, the ability of PBDEs to last for long periods of time in the environment, the unknown long-term health effects of the substance, and the fact that North America has a large majority of the global market demand for PBDEs makes the continued research and spatial monitoring of this contaminant necessary.

Two interpolation methods - ordinary kriging and IDW were also compared for their ability to map the spatial distribution of BDE-47, BDE-153, and BDE-209. Statistically valid results were obtained using the log-transformed dataset. A closer comparison of the log-transformed cross-validation statistics and the Correlation Coefficient ( $r$ ) for the prediction surfaces produced by the two interpolation methods was also performed. This comparison showed that for the most part kriging was the more statistically valid interpolation method to employ. A comparison of the actual prediction surfaces themselves also favoured the kriging method, as the IDW prediction surfaces contained clusters likely due to outliers in the data, which could also have been caused by

the uneven distribution and small number of sampling locations. The overall spatial trends revealed from the two interpolation methods were quite similar however, so the use of IDW as perhaps a preliminary tool to quickly grasp an idea of PBDE distribution or other sediment contamination concentration should not entirely be overlooked. The use of kriging to map the spatial trends of PBDEs in Lake Ontario for data obtained in 2008 can be an effective communication tool, although in this study the sample size was perhaps too inadequate and unevenly distributed. It is also possible the improved cross-validation statistics when the data was log-transformed did not solely reflect improvements in interpolation accuracy and bias, and may have been due to an invalid variogram calculated by a sample size that was too small. Despite the limitations of this study, further research into the mapping of sediment contamination in the Great Lakes, other bodies of water, soil, and other medium will no doubt be made easier by using such GIS tools. Such interpolation techniques should be utilized more extensively due to their effectiveness, low cost, ease of which they produce spatial distribution maps, and potential to influence future management options and decisions.

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