A GEOCHEMICAL SURVEY AND WATER QUALITY MODELLING STUDY OF THE LAKE ST. CLAIR WATER SYSTEM

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THE ALLEGORY OF
PARADISE THAT
IS PROMISED FOR THE
RIGHTEOUS IS THIS:

IT HAS RIVERS OF
UNPOLLUTED WATER……

‘Al Quran (47:15)

ABSTRACT

Lake St. Clair is a small semi-circular lake located between Lake Huron and Lake Erie. A significant portion of Lake St. Clair is bounded by parts of the Metro-Detroit and Greater Windsor areas. A review of past studies showed that no significant study of Lake St. Clair water chemistry has been conducted in the recent past. Therefore no updated database for the lake existed. It was therefore decided to undertake a geochemical study of the water in Lake St. Clair to determine the water quality of Lake St. Clair with respect to heavy metals and certain other trace elements. Water sampling took place in the months of July, August and September of 1998. Analysis of the water samples was conducted using an Inductively Coupled Plasma Mass Spectrometer and an Inductively Coupled Plasma Optical Emission Spectrometer. A GIS database was developed to carry out spatial analysis of the results. The results were used to simulate a water quality model of the lake. Results of the Geochemical survey indicate that the Clinton River appears to be a significant source of contamination. Comparison of these results with the water quality model led to the conclusion that desorption and atmospheric deposition are playing an important role for certain elements. It is expected that this study would help further the understanding of the Lake St. Clair contamination puzzle.

DEDICATION

To my parents, supervisor and friends.

ACKNOWLEDGEMENTS

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1- INTRODUCTION

The quality of water that we ingest as well as the quality of water in our lakes, streams, rivers and oceans is a critical parameter in determining the overall quality of our lives. Water quality is determined by the solutes and gases dissolved in the water, as well as the matter suspended in and floating on the water. Water quality is a consequence of the physical and chemical state of the water as well as any alterations that may have occurred as a consequence of human activity. The usefulness of water for a particular purpose is determined by the water quality. If human activity alters the water quality, so that it is no longer fit for uses for which it was previously suitable, the water is said to be polluted. So, water pollution may be defined as the artificially induced degradation of natural water quality (Fetter, 1994).

A significant portion of Lake St. Clair is bounded by parts of the Metro-Detroit and Greater Windsor areas. Lake St. Clair is critical for a large number of activities for the people living in its vicinity, such as domestic, recreational, agricultural and industrial uses. Lake St. Clair is emptied by the Detroit River, which then drains into Lake Erie. Thus it is important for the people living in its vicinity as well as those living and using the water downstream to know about the present and future state of the water quality of Lake St. Clair.

It was therefore decided to undertake a geochemical study of the water in Lake St. Clair to determine the water quality of Lake St. Clair with respect to heavy metals and certain other trace elements. The methodology involved four stages;

- the collection of water samples from the lake;
- preparation of the water samples for analysis;

- instrumental analysis by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) and ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) and finally;
- construction of a water quality model using the WIN/WASP+ (Windows Water Quality Analysis Software Program) program.

Two methods of sample preparation were undertaken. This was to compare the resulting data. One involved the standard filtration of the water samples using a vacuum filtration procedure to remove suspended particles larger than 0.45μ, whereas the other consisted of centrifuging the water at a rate of 10,000 RPM (rotations per minute) to remove suspended solids. The purpose of centrifuging the samples was to see whether it would better serve the purpose of preparation as compared to filtration, or not.

1.1 LITERATURE REVIEW

This literature review was carried out to summarize work conducted in research areas relevant to this thesis project. The review focused on studies concerning the distribution of heavy and trace metals in Lake St. Clair and modelling projects carried out in the same lake. Studies reviewed for this purpose are summarized in the following sub-sections.

1.1.1 HEAVY AND TRACE METAL DISTRIBUTIONS IN LAKE ST. CLAIR

Concerns have arisen about the extent of contamination in the Great Lakes region. This has led to many studies that assessed the level of pollution in the water and sediments of the area (Goldberg et al., 1981; Hoff, 1994; Wong et al., 1995). The primary objective of these studies was to quantify the amount of heavy metal loading of the system and to investigate the sources and pathways of metal loading (Hoff, 1994; Shaw et al., 1990). Contamination of Lake St. Clair sediments was investigated by Rossman and Borres (1988) and Thomas et al. (1975), who found that the sediments contained high concentrations of heavy metals. These high values pose a threat to the water quality of Lake St. Clair.

Mudroch and Hill (1989) collected sediment cores from Lake St. Clair in 1985 and in the St. Clair River in 1986 to investigate the horizontal and vertical distribution of Hg in the sediments. They found that the Hg concentrations in the sediments of Lake St. Clair decreased with depth.

Toms (1999) studied the Hg and methylHg in the sediments of Lake St. Clair. Overall he found that Hg levels had decreased over the 13 years since the last study of that nature was conducted. Maximum concentrations have dropped from levels > 3µg/g to 0.9 µg/g. He felt that the measured Hg was deposited recently and due to anthropogenic factors.

Shwetz (1998) analyzed sediments from Lake St. Clair and the Detroit River to determine amounts of Pb, Zn, Ni, Cu and Cr. She found that the highest concentrations of Pb, Zn, Cu and Cr and the second highest concentrations of Ni were obtained from a sample near the center of Lake St. Clair. She felt that this suggests the site is a repository for metal accumulation. She also found that Lake St. Clair sediment possessed the less easily extractable forms of metals than Detroit River sediments, associated with the organic and reducible sediment phases.

Theodory (1998) studied zebra mussels to determine heavy metal (Fe, Zn and Mn) pollution. He found that average concentrations of the heavy metals Fe, Zn and Mn in the mussel shells were 149 ± 102, 9 ± 8 and 14 ± 7 ppm (parts per million) respectively. Other studies, carried out in Lake Erie and the other Great Lakes, employed molluscs as biomoniters to investigate pollution trends of heavy metals in industrial and urban areas (Al-Aasm et al., 1998; Elder and Collins, 1991). Such organisms can accumulate heavy metals in their tissues and biomagnify existing levels in the aquatic environment (Amiard et al., 1986; Broman et al., 1991; Coleman et al., 1986; Sadiq and Alam, 1992). Recent studies have also dealt with heavy metal concentrations in mussels and the associated sediments. A significant relationship was found between heavy metal concentrations of the sediments and that of associated mussels, where an increase in the metal content of the sediment was accompanied by an increase in the metal content of the mussel tissues (De Gregori, 1996; McConchie and Lawrence 1991; Stoepler 1992). This type of research helped develop bioaccumulation models to assist in the development of hydrodynamic and pollutant fate models for the Great Lake waters.

1.1.2 MODELLING OF THE LAKE ST. CLAIR/ST. CLAIR RIVER WATER SYSTEM

Chapra (1997) writes that in contrast to flowing waters, lakes were not emphasized in the early years of water-quality modelling. However, starting in the 70's it was recognized that their use for water supply, hydropower and flood control was highly significant. Modelling of lake phenomena has since been pursued by many scientists and engineers.

In 1984 scientists at the National Water Research Institute at the Canada Center for Inland Waters in Burlington modelled the fate of seven volatile hydrocarbons in Lake St. Clair. Halfon et. al. (1990) simulated the fate of bromodichloromethane, carbon tetrachloride, chloroform, Freon 12, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene. They used the TOXFATE model coupled with a hydrodynamic model. The model was driven by estimated contaminated loads, by which is meant pollution input, and used meteorological data during May and June 1984. Results were compared with data collected at 51 lake stations on 18-21 June 1984. The predicted model results were compared with observed relative amounts of the seven hydrocarbons in the lake during the four day period. The comparison showed good concurrence between the two sets of results. This study showed that if appropriate loading values were available to the TOXFATE model, it could reliably predict the fate of these hydrocarbons in Lake St. Clair. Furthermore the model could be used to simulate different scenarios of increased and decreased loadings over a limited time span. This would be done by using hypothetical loadings, and if wind data and water temperatures conditions were available in real time. the model could be used to follow an actual spill in the St. Clair River.

Ibrahim (1986) completed a simulation of pollutant transport responses to loading and weather variations in Lake St. Clair. The United States Environmental Protection Agency (USEPA) TOXIWASP model was used to simulate interactions between sediments and contaminants. The model was verified by comparing the simulated results with measured levels of HCB (hexachlorobenzene) in the St. Clair River and similarly with measured concentrations of Cd in the Detroit River. The field sampling for these measurements were carried out in the summers of 1984 and 1985. His results for Cd indicated high levels in most bottom layers of water in Lake St. Clair and the Detroit River (up to 0.225 micrograms/kg). He felt that these high levels of Cd were the result of atmospheric deposition. Furthermore, he speculated that the source of this atmospheric Cd was the Wayne County Industrial Complex in Michigan.

Lang et. al. (1988) carried out a modelling project for Lake St. Clair that involved total phosphorus. An unbiased ratio estimator technique was used to estimate annual loads and variances from monitored hydrologic areas. During the late 70's Lake Huron was a major source of phosphorus, accounting for approximately 52% of the total load. Hydrologic area loads accounted for 43% whereas the other smaller tributaries besides the St. Clair River accounted for the rest. It was observed that over the entire 6 year period examined, the lake's total input and output of phosphorus were nearly equal. It was concluded that there was no significant net source or sink of phosphorus in Lake St. Clair during the 1975-80 period.

A numerical circulation and transport model was used to simulate water currents and their trajectories in Lake St. Clair by Schwab et al in 1989. Results from the model were compared to three different types of measurements, namely, (1) 910 mean currents from an array of fixed currents meters, (2) currents measured from a ship during seven synoptic surveys of the lake, and (3) trajectories of satellite-tracked drifting buoys during four different experiments. The model was then used to predict the effects of storms on the residence time of water entering the lake from eight tributaries and the probable horizontal distribution in the lake of water from a particular tributary. Results showed that although the average residence time for water of the lake is about 9 days, actual residence times range from less than 2 days to over 30 days depending on wind conditions. The calculated distribution patterns of water from various tributaries coincide closely with observed distributions of some water quality parameters and biota.

A modelling study in which the response of the St. Clair River and an aquatic food chain in Lake St. Clair to the release of hexachlorobenzene (HCB) and octachlorostyrene (OCS), from the "chemical valley of Sarnia" was predicted by Barycka (1988). Results were calibrated with 1985 field measurements. The model indicated that a plume of contaminated water from multiple sources in the Sarnia area travels along the Canadian shoreline and empties into Lake St. Clair via the Chenal Ecarte and the South Channel. It was found that, for both contaminants, about 20% of the total loading is lost in the river due to various processes affecting the toxic pollutant. It was also predicted that a change in concentrations found in fish would occur due to bioaccumulation.

Two computer mass-balance models were applied by Tomczak (1998) to the St. Clair River. He studied the release rate of HCB, which is thought to be stored in the sediments of the St. Clair River. The models indicated that ship traffic increases the bottom shear stress and sediment resuspension potential by approximately a factor of 2 and thus is the most important factor in the disturbance and resuspension of sediments. Predicted depth-averaged HCB concentrations in the water column were low. The high river flow rate was noted to cause export of HCB into Lake St. Clair at a rate of 15 grams/day. The chemical export into the lake was predicted to decrease to about 11grams/day within 10 years provided there are no additional inputs during this time. The model predicted that with the help of remediation, the release of HCB from the sediments would decrease to 1.5 grams/day (or 10% of present value) by the year 2010.

Summarizing the above two sub sections (i.e. sections 1.1.1 and 1.1.2), one can conclude that previous studies of Lake St. Clair show that most of the heavy metal and trace element content present in the lake are stored in the sediments. Results indicate continued recent introduction of Hg (Toms, 1999). Bio-accumulation of these metals and elements in aquatic life was found to be a direct result of their storage in the sediments. Modelling of Lake St. Clair also revealed the same results. It is also noted that a thorough water quality database of the Lake St. Clair waters was not available.

1.2 STUDY AREA

The geographic setting, description, climate, geological background and hydrological and hydrogeological aspects of the study area are described in the following sub-sections.

1.2.1 GEOGRAPHIC SETTING, PHYSIOGRAPHY AND CLIMATE

Lake St. Clair is located between the St. Clair River and the Detroit River as can be seen in Figure 1.1. It is a shallow, sub-circular lake located within the Lake Huron - Lake Erie corridor, with a surface area covering 1,190 km^2. Lake St. Clair is situated between longitudes W 82°23' and W 82°55' and latitudes N 42°15' and N 42°45'. The lake stretches 42 km at its longest (north-south) transect and 38 km (east-west) at its widest point. The St. Clair River is the major tributary draining into Lake St. Clair, which in turn, flows into the Detroit River: the Detroit River drains into Lake Erie. At the northeastern portion of the lake is an extensive delta system, which is the largest within the Great Lakes. Numerous distributary channels carry St. Clair River water through the delta into Lake St. Clair, as can be seen in Figure 1.1. The southern and eastern shorelines of Lake St. Clair are extensively urbanized whereas the marshy northern and western shorelines are flanked by farms and used for hunting purposes.

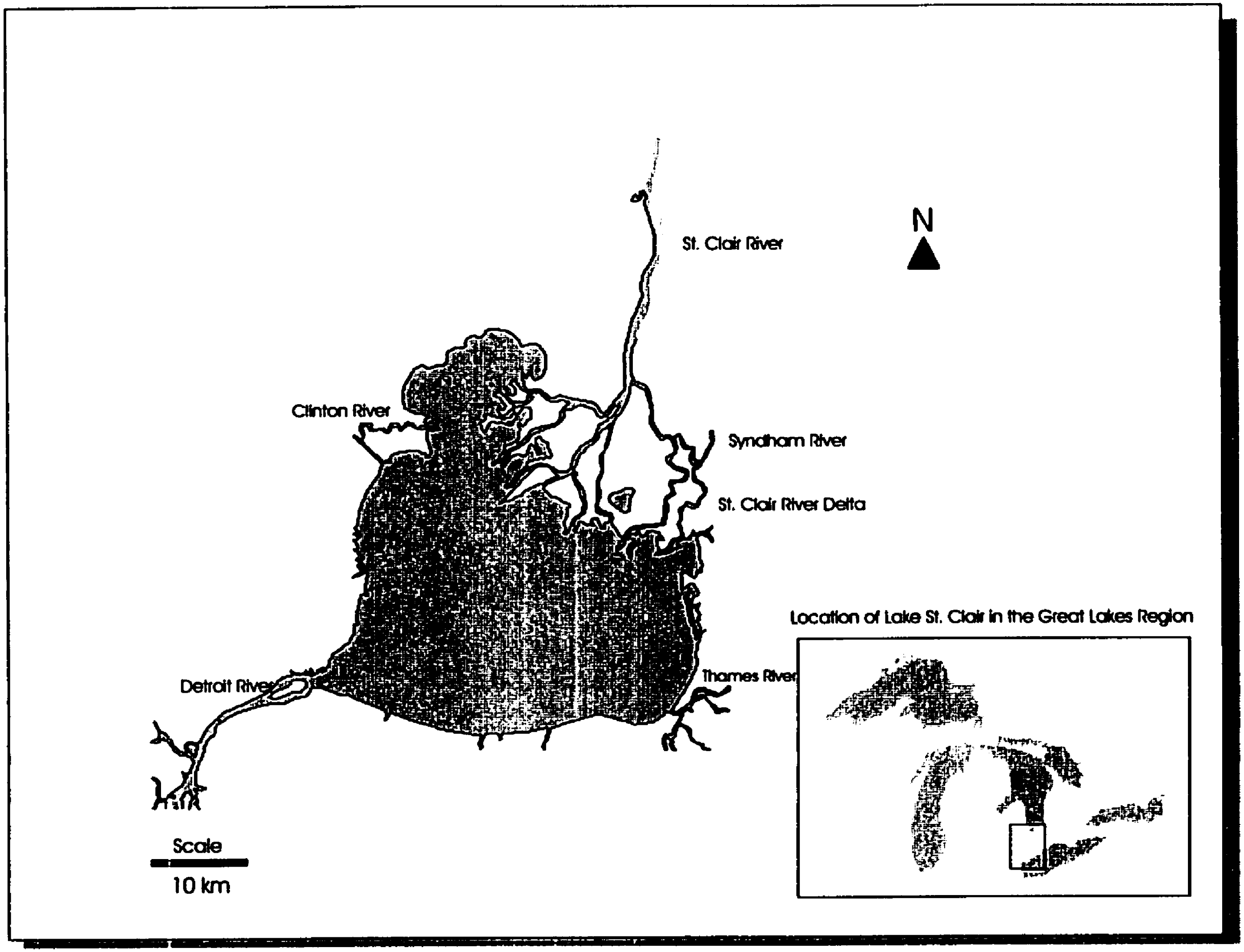


Figure 1.1 Location Map of Lake St. Clair and Tributaries

The physiography of Lake St. Clair is unique amongst the Great Lakes, as it is the shallowest. It has an average depth of only about 3.6 meters. The extreme long-term fluctuation in the lake level of ± 1-meter is also very large by comparison with its depth. The lake has a very large hydraulic flow-through (5400 m^3/s) which results in an average retention time of approximately one week (Ibrahim, 1986).

Lake St. Clair is affected by strong and unstable wind conditions especially during the spring and fall periods. The speed and direction of wind-generated currents can change very rapidly. During the winter months of January and February, Lake St. Clair may be completely or partially covered by ice. But in recent years, due to the relatively warm weather, this has not been the case. In addition to wind, the following factors also contribute to the dynamics of the lake: surface runoff, atmospheric precipitation, inflow from the St. Clair River and the outflow to the Detroit River (Ibrahim, 1986).

Three main continental air mass types influence the study area. One air mass (composed of warm, moist air) flows north from the Gulf of Mexico. This moist air causes most of the precipitation in the area. Cold dry air, from northern Canada, also enters the study area. It is responsible for relief from the heat in the summer. In the winter it sends a harshly cold biting blast over the area. The third air mass originates over the Pacific Ocean. It is usually a dry, moderately cool body of air. Local weather effects due to the presence of Lake Erie and Lake Huron also affect the study area. Temperatures are moderated, humidity is high, rain and snowfall are enhanced and wind flow is modified by the presence of Lake Erie and Lake Huron (Bolsenga and Herdendorf, 1993).

The highest average monthly temperatures occur during July while the coldest are during January and February. Extreme temperatures range from -29° to 38° C. The mean annual precipitation is 95 cm.

1.2.2 GEOLOGICAL BACKGROUND

The sediments in the rivers and lakes of southern Ontario should be discussed in the context of regional geology, geomorphology and cultural geography. The general geology of the area is given in Figure 1.2. When it is considered that the sediments of Lake Ontario and Lake Erie contain 90 to 99% mineral matter (Thomas et al, 1976), the local and regional geology and geomorphology define the nature of the sediment which is being eroded. Regional bedrock geology in the lower Great Lakes region consists primarily of Paleozoic sedimentary assemblages overlapping a crystalline Precambrian basement exposed in the northern reaches of the Great Lakes Basin. The metamorphosed assemblage of sedimentary and igneous suites of the Precambrian basement underlie a relatively unaltered Paleozoic veneer of limestone, shale, dolomite and sandstone in southwestern Ontario.

The regional drainage into Lake St. Clair and the Detroit River has no surface exposure of rock. The drainage basins of Lake St. Clair and the Detroit River, lie within Quaternary deposits (up to 92m in thickness) deposited during the waning stages of the Pleistocene glaciation. Over the last one million years the topography of southern Ontario has altered drastically. The surficial sediment and landforms are a product of the last major ice advance and retreat during the Wisconsinan Stage when gigantic ice sheets invaded from Labrador and the Quebec highlands. This was due to 4 lobes emanating from and retreating to the depressions occupied by Lake Ontario, Lake Erie, the central

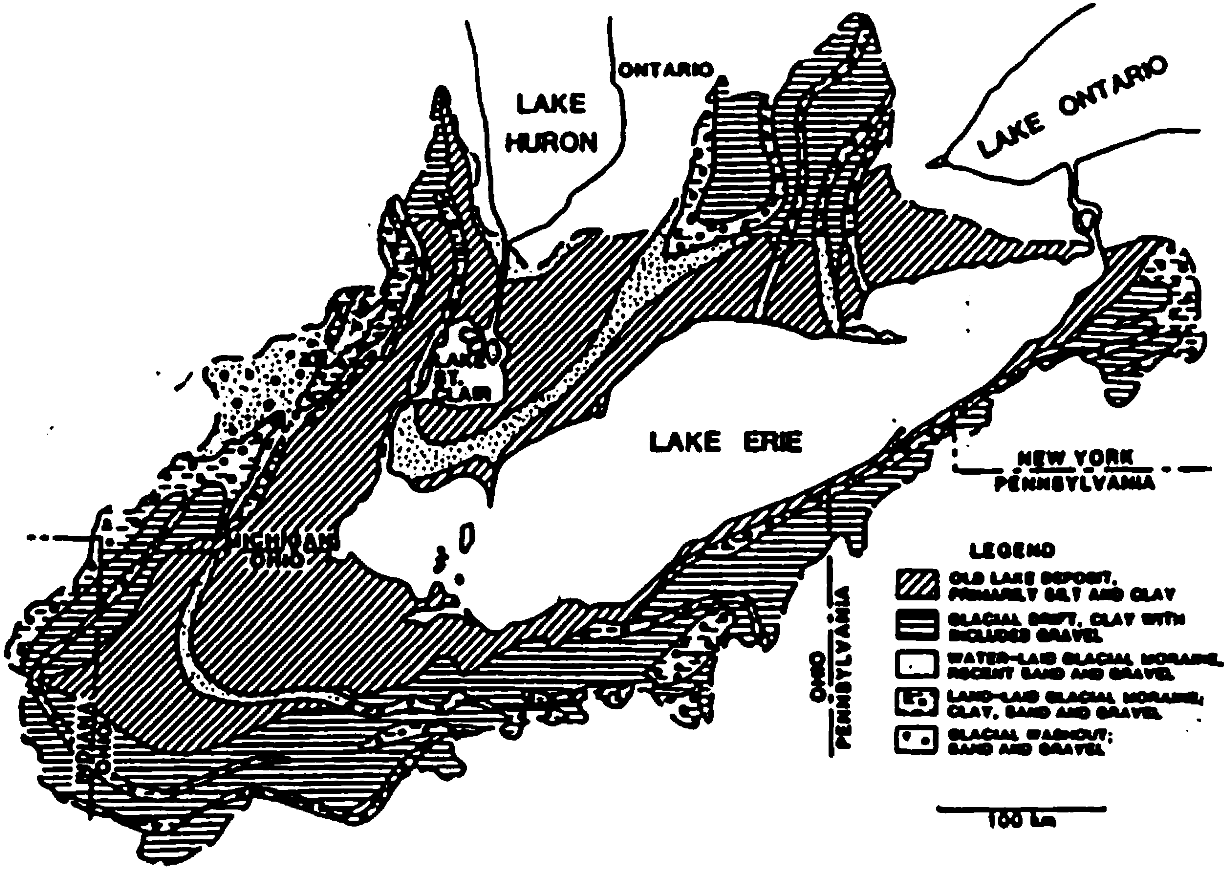


Figure 1.2 Surface geology map of the Lake St. Clair Region (Bolsenga and Herdendorf, 1993)

part of Lake Huron and Georgian Bay. The distribution of moraines, drumlins, eskers and ancient shorelines delineate the minor physiographic regions of southwestern Ontario today (Barnett, 1985). A belt of late to post-glacial lake bottom clays and sand plains and spillways mark the top of the regional stratigraphic sequence. Thin sand deposits rim the east and south shores of Lake St. Clair and the banks of the upper Detroit River. Extensive clay plains encircle these sand deposits; glacial clays are also found along the lower St. Clair River and the drainage area of the lower Detroit River (Stone and Sanderson, 1992).

1.2.3 HYDROLOGICAL AND HYDROGEOLOGICAL ASPECTS

The St. Clair Delta is the largest delta in the Great Lakes region and is located at the mouth of the St. Clair River. The high flow rate of the St. Clair River, averaging about 5200 m^3/s, inhibits the deposition of fine-grained material on its bottom. Being the fastest flowing river in the area, it is actively incising downward into hard stony glacial clays. Firm, hard, glacial, lacustrine clays were found to exist in some parts of the river channel (Ibrahim, 1986). Sediment transported along the St. Clair River substrate consists of these eroding glacial clays and medium to coarse sands and gravels. The deltaic islands of the St. Clair Delta wedge outward over the glacial lacustrine clays and silts of the Lake St. Clair substrate. Only the western part of the delta is actively forming today, fed by sediments transported by the St. Clair River branching into distributary channels referred to as the North, Middle and South channels.

Input into Lake St. Clair includes the St. Clair River as well as the Clinton River on the American side. The Clinton River drains Oakland and Macomb counties in

Michigan. On the Canadian side the main tributaries are the Syndham and Thames Rivers. The Syndham River drains Lambton and Middlesex counties in Ontario. It funnels water and sediment from almost 1000 square miles of glacial clay plain. The Thames River drains an area of clay plain downstream of London, Ontario spread over 2,200 square miles. The pattern of recent sediment accumulation in Lake St. Clair conforms to lake bathymetry. The thickest sediments have accumulated in the lake center. Lake St. Clair is however overall considered to be a non-depositional lake. The average post-glaciation sediment thickness outside the delta is minimal, ranging from 3.5 to 7 cm (Thomas et al., 1975, Mudroch and Hill, 1975). Cs-137 dating points to stratigraphic inhomogeneity in the sediment; recent sediment having mixed with older sediment. Results from Cs-137 studies also indicated a 3-6 year residence time for sediments in Lake St. Clair. The main bulk of the sediment is transported rapidly down to Lake Erie through the Detroit River.

2- SAMPLING

To study the water quality of Lake St. Clair with respect to heavy metals and certain other trace element contents, water samples were collected from selected sites in the lake. Sample site selection, preparation for sampling, sampling, the immediate procedures following sampling and sample treatment are discussed in the following sub sections.

2.1 SAMPLE SITE SELECTION

Site selection for sampling was based on several different criteria. First, the sites were selected according to the current circulation patterns of the lake. The intention was to cover those locations through which incoming waters from the St. Clair River pass through to the Detroit River as well as those which lie beyond this main flow of the lake. Lake St. Clair was split up into 10 segments which was required to simulate a water quality model of the lake. A segment map for Lake St. Clair is shown in Figure 2.1. A rough grid-like sampling scheme was set up with 22 sample sites across the lake, 3 sites in the delta (sites 3,6 and 7) and one location in the St. Clair River (site 5). No water sample was collected from segment 3 because of field error. Water samples from the delta and river were collected to determine the metal concentrations of water entering the lake from its main input. Specific locations such as the mouth of Clinton River, the bay located in the north-east of the top portion of the lake and the area near the start of the Detroit River were also pinpointed as areas where sample sites were desired for modelling. These desired sites were plotted on a navigational chart (NOAA #14850, 48TH edition, 1:60,000) and from this, co-ordinates were obtained and programmed as

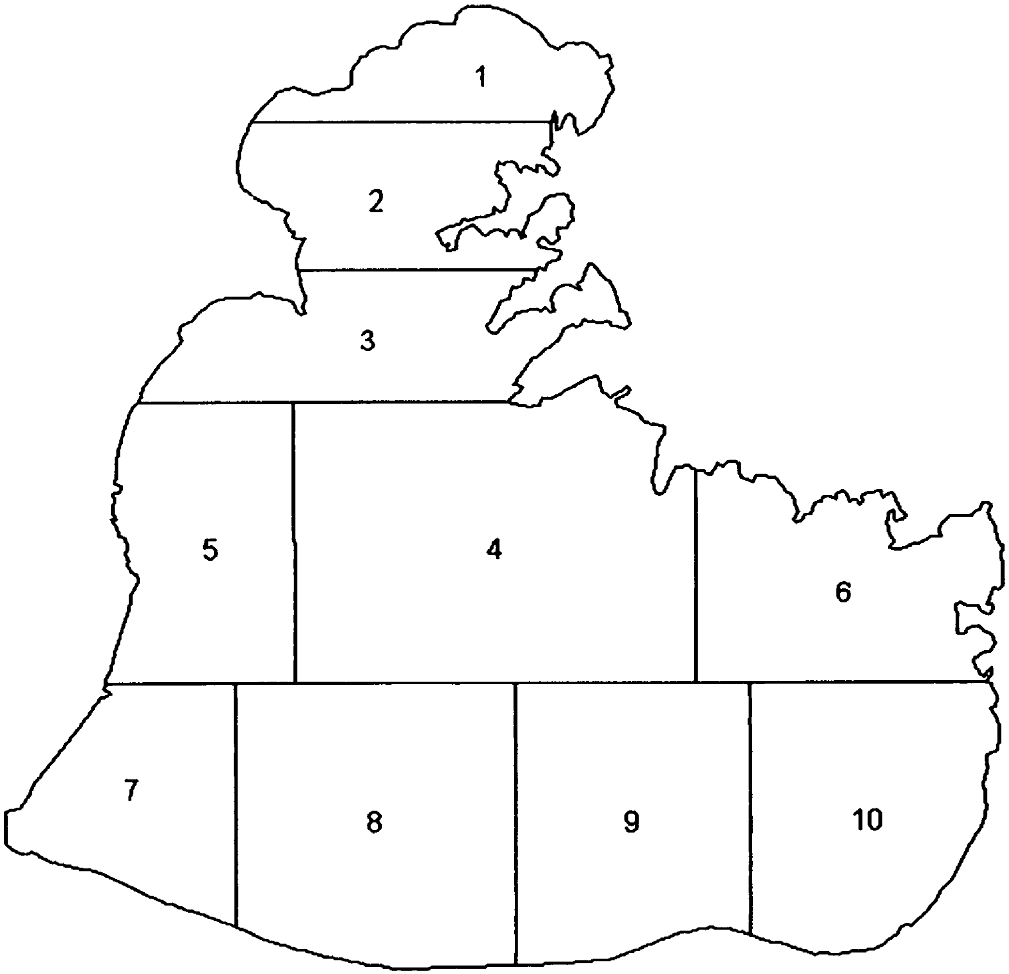


Figure 2.1 Segment ID Map

waypoints in a hand-held Global Positioning System unit (GPS) receiver (Garmin GPS 45XL). The sample site locations are shown in Figure 2.2. Sample site co-ordinates are given in Appendix 1.

2.2 SAMPLING

Steps taken for preparation for sampling are given in Appendix 2. Sampling took place on the 13th and 14th of July, the 14th of August and 23rd of September, 1998. In ideal conditions it would have been best to carry out all the sampling on the same date or over several consecutive days. But due to the limitations caused by availability of the boat (Great Lakes Institute Mon Ark), the sampling was carried out on the above mentioned dates. The water samples were collected by the use of an instrument called the Van Dorn sampler used to collect water samples from different measured depths. The water samples were poured into pre-washed 500mL polyethylene bottles. Initially it was intended that 3 samples be taken from each site. Samples from the bottom layer were collected from a depth of 0.5 meters from the bottom, samples from the middle layer were collected at a depth halfway to the bottom and surface layer samples were collected from a depth of 0.5 meters from the surface. During the collection of the water samples it was felt that at some sites the water was too shallow to take 3 samples. For a depth of 3.5 meters or less, two water samples were taken (except in the case of sample site # 1, at that time the decision of taking 2 water samples for such depths had not yet been made). For a depth of less than 1.5 meters, 1 water sample was collected. Table 2.1 shows the number of samples taken and the depth for each sample site, as well as the date of sample collection. At sample site # 27 only 2 samples

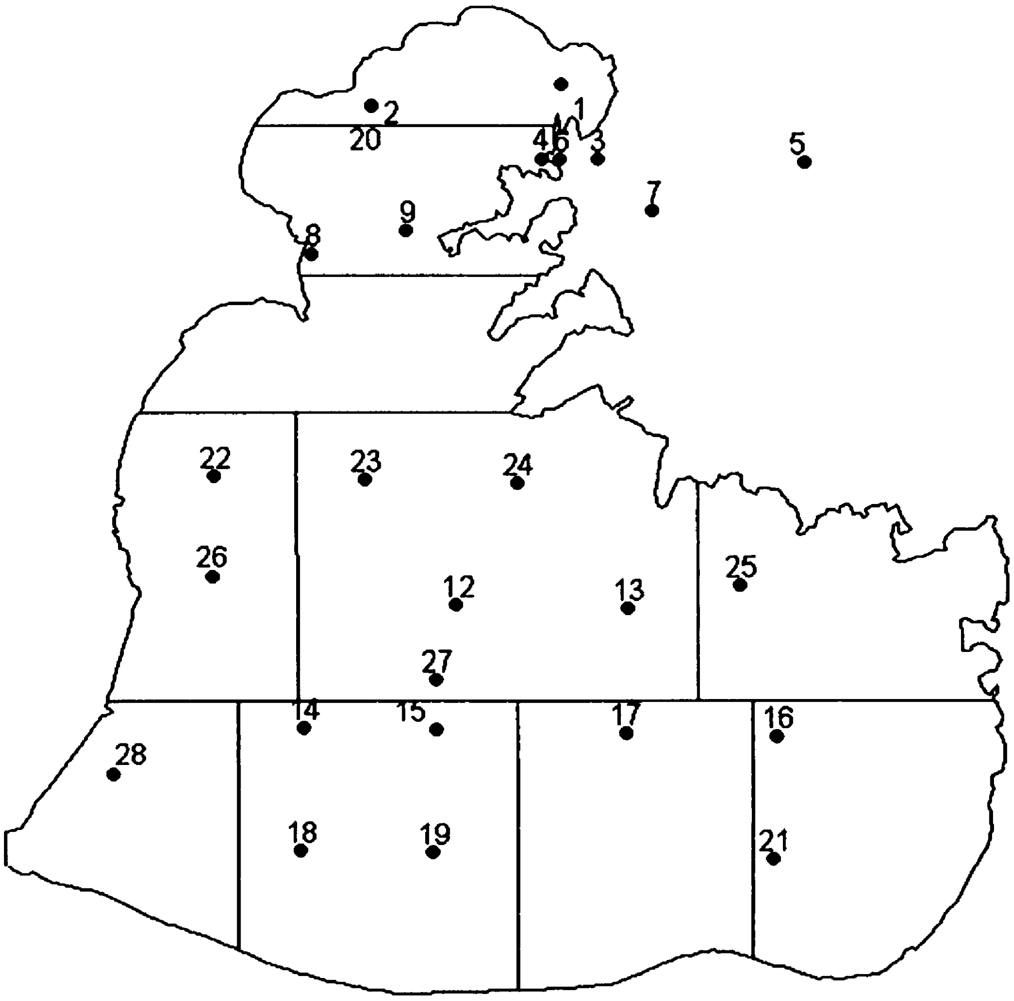


Figure 2.2 Sample site location Map, Lake St. Clair

Site #	Number of Samples Collected	Depth	Sampling Date	Site #	Number of Samples Collected	Depth	Sampling Date
1	3	2.44	14/08/98	16	2	4.88	14/07/98
2	2	2.44	14/08/98	17	3	5.18	14/07/98
3	3	10.7	14/08/98	18	3	3.66	13/07/98
4	3	9.45	14/08/98	19	3	4.57	13/07/98
5	3	13.7	14/08/98	20	3	2.44	14/08/98
6	1	1.22	14/08/98	21	3	3.96	14/07/98
7	3	11.6	14/08/98	22	2	4.57	23/09/98
8	1	1.22	14/08/98	23	3	5.49	23/09/98
9	2	3.35	14/08/98	24	3	4.57	23/09/98
12	3	5.79	13/07/98	25	2	2.74	23/09/98
13	3	4.57	14/07/98	26	3	4.27	23/09/98
14	3	5.49	13/07/98	27	2	5.79	23/09/98
15	3	5.18	13/07/98	28	3	4.57	23/09/98

Table 2.1 Sample sites, samples collected at each site, depths (meters) at each site and date of visit to the site

were taken in spite of the greater depth due to a field error. A total of 9 bottles, filled with Milli-Q water, were also taken into the field to serve as field blanks.

2.3 SAMPLE TREATMENT

Initially water samples brought back from the field were stored in a walk-in refrigerator at a temperature of 4^0C, after which the water samples were split into two separate sets of samples.

2.4 SAMPLE PREPARATION

The two sets of water samples were prepared independently of each other for analysis. The methods of preparation are described below.

2.4.1 Sample Preparation by Filtration

One set of samples was filtered through 0.45 μm filter papers to remove larger particles suspended in the water. A method of vacuum filtration was used since the pores in the filter paper were too fine for the water to pass through without the help of vacuum suction. The water samples were then treated with concentrated nitric acid so as to make up a 1% acid concentration in the water sample and then stored again at a temperature of 4^0C for analysis. The filtration work was done in December 1998-January 1999. The steps involved in the filtration are given in Appendix 3.

2.4.2 Sample Preparation by Centrifuging

The second set of samples was prepared by centrifuging at a rate of 10,000 revolutions per minute for 10 minutes each. This was to remove most of the larger suspended particles. The test tubes and storage bottles used in this process were acid washed by the same procedure that was applied on the field bottles. The steps involved are given in Appendix 4.

The centrifuge process took place in the months of August, September and October 1998.

3- ANALYTICAL METHODOLOGY

Elemental analyses of the water samples were made using two complimentary multi-element analytical instrument methods; Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). *Instrument analyses were provided by the Metals Laboratory at the Great Lakes Institute for Environmental Research. ICP-MS data for filtered and centrifuged samples are given in Appendices 5 and 6 respectively. ICP-OES data on major cations (Ca, K, Mg, Na and Zn) for filtered and centrifuged samples are given in Appendices 7 and 8 respectively.

3.1 DATA QUALITY

3.1.1 Filtered Samples

To test the quality of the data obtained, eight field blanks and a sample of the standard SLRS-3 (National Research Council Canada) were analysed. A comparison was made between the values obtained from the ICP-MS for SLRS-3 and the certified values for this standard.

Table 3.1 shows the data for the field blanks. One of the field blanks was lost during analysis. Means, standard deviations, elemental detection limits, relative standard deviations (RSD) and quantification limits (QL) have been calculated for all elements analysed by the ICP-MS. Detection limits were calculated as = 3*(standard deviation of the field blanks) and quantification limits were calculated as = 10*(detection limits).

**Concentrations were calculated with the assumption that density of solutions is 1g/cm^3, thus they have been labelled micrograms/kg.*

Table 3.1 Means, standard deviations (STD), detection limits (DL), relative standard deviations (RSD) and quantification limits (QL) for Field Blanks, filtered samples by ICP-MS (micrograms/kg)

Blank name	FB 1	FB 2	FB 3	FB 4	FB 5	FB 6	FB 7	FB 8		Mean	STD	DL	RSD (%	QL
Li	0.0020	0.0021	0.0023	0.0004	0.0006	0.0003	0.0009	0.0009		0.0012	0.0009	0.003	72	0.027
V	0.0595	0.0739	0.0264	0.0387	0.0319	0.0259	0.0175	0.0204		0.037	0.0200	0.06	54	0.60
Cr	0.2168	0.3613	0.0598	0.1177	0.0387	0.0414		0.0082		0.12	0.1268	0.39	105	3.90
Mn	0.0443	0.0508	0.0098	0.1044	0.0047	0.0197	0.0264			0.032	0.0343	0.103	106	1.03
Co	0.0026	0.0015	0.0014	0.0013	0.0000	0.0009				0.0014	0.0009	0.0028	68	0.0279
Ni	0.0624	0.0060	0.0142	0.0029	0.0278					0.021	0.0278	0.083	130	0.83
Cu	0.0266	0.0585	0.0042	0.0228	0.0252	0.0196				0.027	0.0196	0.059	71	0.59
Zn	0.1622	0.1849	0.0919	0.1080	0.2039	0.4217	0.8069	0.5984		0.32	0.2615	0.78	81	7.8
Se	0.3277	0.3164	0.0052	0.1666	0.0703	0.0867	0.1059	0.1270		0.15	0.1155	0.35	77	3.46
Rb	0.0035	0.0034	0.0045	0.0019	0.0044	0.0025	0.0026	0.0034		0.0033	0.0009	0.0027	28	0.0273
Sr	0.0140	0.0252	0.0250	0.0448	0.0119	0.0194	0.0178			0.02	0.0120	0.036	59	0.36
Y	0.0001	0.0001	0.0000							0.000093	0.00004	0.00013	46	0.0013
Mo	-0.0013	-0.0028	-0.0025	-0.0047	-0.0036	-0.0037	-0.0043	-0.0015		-0.00305	0.0013	0.00380	241	0.0380
Cd	0.3191	0.0434	0.0586	0.0420	0.0172	0.0260	0.1159			0.084	0.1159	0.35	137	3.48
Te	0.0131	0.0154	0.0100	0.0227	0.0107	0.0209	0.0111			0.012	0.0088	0.026	72	0.264
Cs	0.0007	0.0001		0.0002	0.0006	0.0006	0.0002	0.0001		0.0003	0.0003	0.00084	93	0.0084
Ba	0.0007	0.0001		0.0002	0.0006	0.0006	0.0002	0.0001		0.0003	0.0003	0.00084	93	0.0084
La	0.0007	0.0001		0.0002	0.0006	0.0006	0.0002	0.0001		0.049	0.0640	0.19	132	1.9207
Pb	0.1545	0.0305	0.0560	0.1185	0.0705					0.00056	0.0002	0.00061	36	0.0061
U	0.0006	0.0005	0.0006	0.0005	0.0007	0.0009	0.0002	0.0004						

Note: *Blank data indicates negative values*

Table 3.3 shows the comparison between the certified values and the data obtained from the analysis for the standard SLRS-3 (filtered) for all the elements analysed as well as the data obtained for three samples of SLRS-3 run with the centrifuged samples. As can be seen, the values show a very good agreement between the two sets. There is a difference of 1.1 part per billion (micrograms/kg) for Sr. For Cd the difference is as low as 0.011 micrograms/kg. In the case of Mo the difference is 0.005 micrograms/kg. Figure 3.1 shows the comparison between the sets of values.

3.1.2 Centrifuged Samples

To test the quality of the data obtained, eight field blanks, 3 samples of the standard SLRS-3 and 4 samples of the standard SLRS-4 were analysed. Basic statistics were applied to the values obtained for the field blanks. Comparisons were made between values obtained from ICP-MS for SLRS-3 and SLRS-4 and the certified values for these standards.

Table 3.2 shows the data for the field blanks. Four of the field blanks were lost during analysis. Means, standard deviations, elemental detection limits, relative standard deviations and quantification limits have been calculated for all elements analysed by the ICP-MS. Table 3.3 shows the comparison between the certified values and the data obtained from the ICP-MS analysis for 3 samples of the standard SLRS-3 as well as data for a sample of SLRS-3 run with the filtered water samples. The results are shown for all the elements analysed. As can be seen the values show a very good agreement between the two sets. Figure 3.1 shows the graphical comparison between the means of the values obtained from the ICP-MS and the certified values. All the values for the various

Table 3.2 Means, standard deviations (STD), detection limits (DL), relative standard deviations (RSD) and quantification limits (QL) for Field Blanks, centrifuged samples by ICP-MS (micrograms/kg)

Sample Name	FB1	FB2	FB3	FB4	Mean	STD	DL	RSD(%)	QL
Lithium	0.0061	0.0023	0.0029	0.0103	0.0054	0.004	0.0110	68	0.1
Vanadium	0.0119	0.0062	0.0082	0.0089	0.0088	0.002	0.0070	27	0.07
Chromium	0.0964	0.0737	0.0308	0.0395	0.0601	0.03	0.0914	51	0.9
Manganese	0.0449	0.0240	0.0199	0.0232	0.0280	0.01	0.0342	41	0.3
Cobalt	0.0138	0.0131	0.0102	0.0107	0.0120	0.002	0.0053	15	0.1
Nickel	0.0760	0.0457	0.0294	0.0145	0.0414	0.03	0.0790	64	0.8
Copper	0.0201		0.0216		0.0209	0.001	0.0033	5	0.03
Zinc	0.9259	0.1945	0.5217	0.3687	0.5027	0.31	0.9365	62	9.4
Arsenic	0.0045	0.0019	0.0035	0.0049	0.0037	0.001	0.0040	36	0.04
Rubidium	0.0015	0.0050	0.0050	0.0045	0.0040	0.002	0.0051	43	0.05
Strontium			0.0273	0.2042	0.1157	0.13	0.3753	108	3.75
Yttrium	0.0001	0.0003	0.0001	0.0001	0.0001	0.0001	0.0003	63	0.003
Molybdenum	0.0080	0.0075	0.0103	0.0076	0.0083	0.001	0.0039	16	0.04
Cadmium	0.0054	0.0057	0.0031	0.0035	0.0044	0.001	0.0039	30	0.04
Caesium			0.0001	0.0001	0.0001	0.00003	0.0001	35	0.001
Barium	0.0017	0.0118	0.0005	0.0285	0.0106	0.01	0.0389	122	0.39
Lanthanum	0.0004	0.0005	0.0002	0.0004	0.0003	0.0001	0.0003	32	0.003
Lead	0.3193	0.0205	0.1562	0.2158	0.1779	0.12	0.3742	70	3.7
Bismuth			0.0003	0.0007	0.0005	0.0002	0.0007	47	0.01
Thorium	0.0002	0.0005	0.0001	0.0001	0.0002	0.0002	0.0006	81	0.01

Note: *Blank data indicates a negative value.*

Sample	SLRS-3	SLRS-3-1	SLRS-3-2	SLRS-3-3	Mean	Std. Dev	RSD(%)	Certified Values
	filtered	centrifuged	centrifuged	centrifuged				
V	0.28	0.32	0.32	0.31	0.32	0.0056	1.75	0.3
Cr	0.17	0.39	0.37	0.38	0.38	0.0091	2.41	0.30
Mn	4.11	3.82	3.64	3.68	3.72	0.09	2.50	3.9
Co	0.062	0.068	0.067	0.067	0.067	0.001	1.280	0.027
Ni	1.24	1.38	1.36	1.37	1.37	0.009	0.64	0.83
Cu	1.41	1.52	1.49	1.58	1.53	0.050	3.25	1.35
Zn	1.17	1.38	1.44	1.17	1.33	0.14	10.56	1.04
As	0.81	0.78	0.74	0.76	0.76	0.020	2.67	0.72
Sr	29.19	30.97	30.13	30.47	30.52	0.42	1.37	28.1
Mo	0.18	0.21	0.19	0.19	0.20	0.011	5.76	0.19
Cd	0.002	0.011	0.012	0.017	0.013	0.003	23.631	0.013
Ba	13.83	13.06	12.93	13.03	13.01	0.070	0.53	13.4
Pb	0.03	0.063	0.07	0.14	0.09	0.044	48.15	0.068
U	0.05	0.043	0.04	0.04	0.04	0.001	2.18	0.045

Table 3.3 Comparison between ICP-MS data and Certified values for SLRS-3 (micrograms/kg)

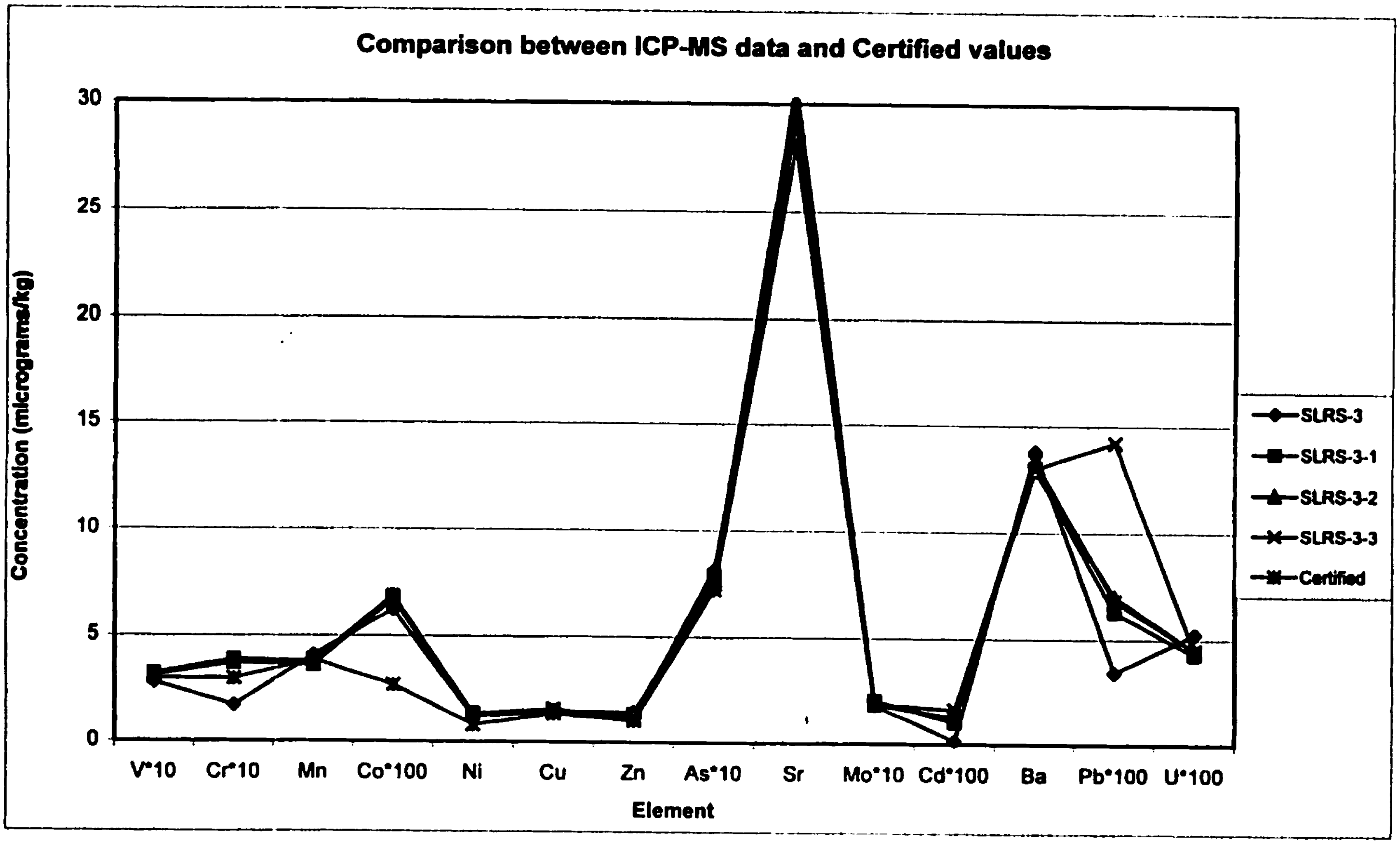


Figure 3.1 Comparison between ICP-MS data and Certified values for SLRS-3 in filtered(SLRS-F) and centrifuged analyses

elements show a good match except Co, which has a known molecular ion interference that has not been corrected for.

Table 3.4 shows the comparison between the certified values and the data obtained from the ICP-MS analysis for 4 samples of the standard SLRS-4. Again the comparison shows that the data quality is good. Figure 3.2 shows the graphical comparison between the means of the values obtained from the ICP-MS and the certified values. Again, all the values for the various elements match well, again with the exception of Co. Precision (RSD) for most elements is between 1 and 5 % for both SLRS-3 and SLRS-4 (Tables 3.3 and 3.4).

3.2 WATER QUALITY MODELLING OF LAKE ST. CLAIR

A water quality model of Lake St. Clair was constructed using the WIN/WASP+ Water Quality Analysis Software Program. The majority of secondary data required for the simulation of the model of Lake St. Clair was obtained from a NOAA (National Oceanic and Atmospheric Administration) Data Report, 1980. Other sources of information are The Great Lakes: an atlas and resource book (1987) as well as the Lake Erie and Lake St. Clair Handbook (1993).

The model was run for dissolved Sr, Mo and Cd. The reason behind choosing these particular metals was the fact that they showed significant variations in behaviour across the lake and were expected to depict the behaviours of various other metals in the lake. Sr being a highly soluble element is expected to be representative of other such metals. Mo and Cd are transition metals and were chosen to represent them in this

	SLRS4-1	SLRS-4-2	SLRS-4-3	SLRS-4-4	Mean	Std. Dev	RSD(%)	Certified Values
Vanadium	0.35	0.35	0.35	0.34	0.347	0.006	1.73	0.32
Chromium	0.40	0.40	0.38	0.36	0.384	0.017	4.43	0.33
Manganese	3.28	3.34	3.26	3.22	3.275	0.053	1.60	3.37
Cobalt	0.076	0.073	0.074	0.073	0.074	0.0016	2.20	0.033
Nickel	1.33	1.28	1.26	1.23	1.275	0.041	3.18	0.67
Copper	1.85	1.87	1.84	1.84	1.849	0.016	0.84	1.81
Zinc	0.86	0.79	0.78	1.34	0.94	0.27	28.6	0.93
Arsenic	0.75	0.75	0.75	0.74	0.747	0.003	0.45	0.68
Strontium	28.09	27.61	27.12	27.21	27.5	0.44	1.61	26.3
Molybdenum	0.210	0.206	0.206	0.204	0.206	0.0024	1.15	0.21
Cadmium	0.01083	0.01067	0.01105	0.01086	0.01085	0.00016	1.44	0.012
Barium	12.57	12.57	12.21	12.43	12.45	0.17	1.37	12.2
Lead	0.073	0.076	0.128	0.079	0.089	0.026	29.3	0.086
Uranium	0.051	0.052	0.051	0.053	0.052	0.0011	2.08	0.050

Table 3.4 Comparison between ICP-MS data and Certified values for SLRS-4, centrifuged samples (micrograms/kg)

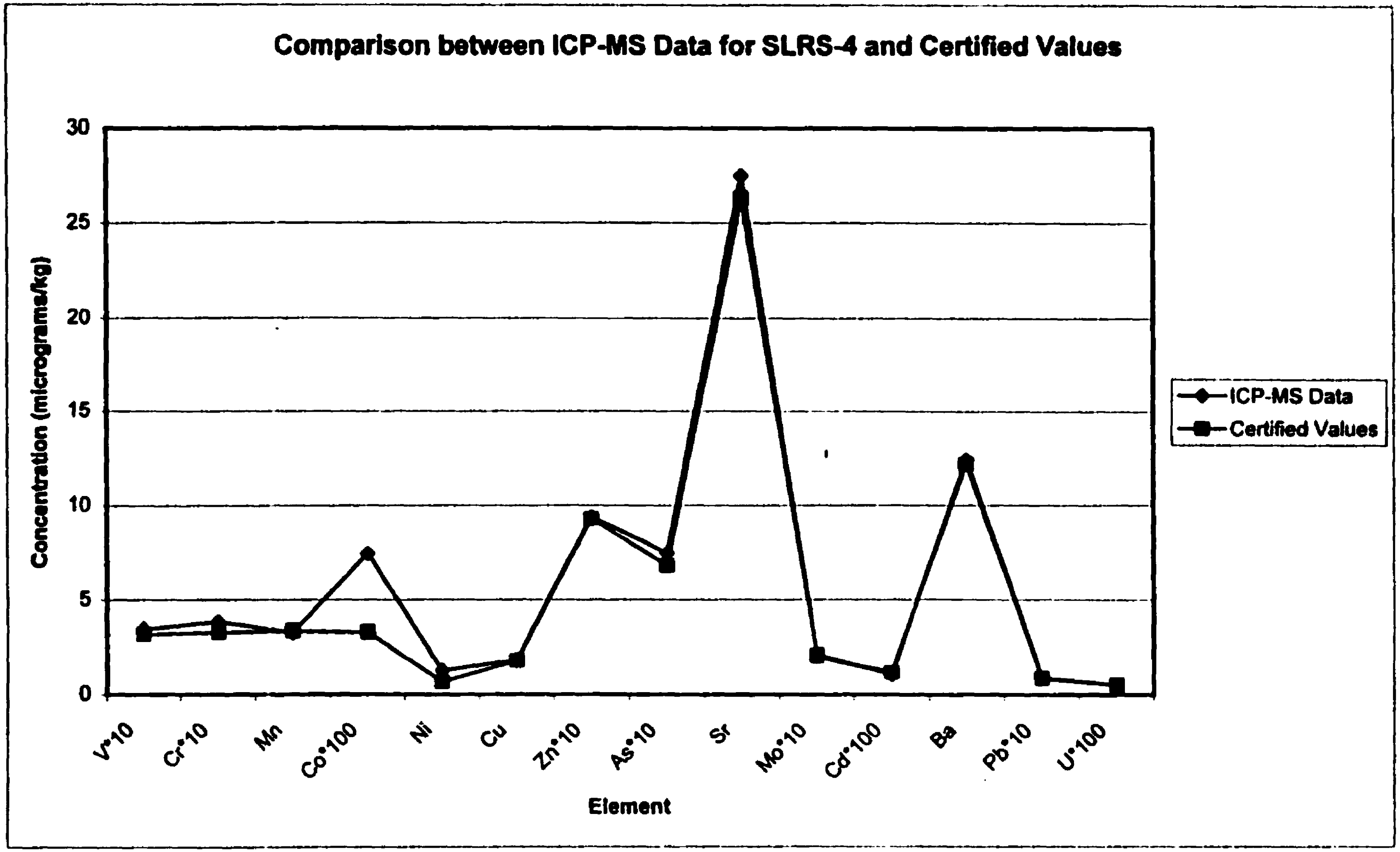


Figure 3.2 Comparison between ICP-MS data and Certified values for SLRS-4 in centrifuged analysis

project. The purpose was to compare the results of the modelling with observed results of the geochemical survey as discussed in Chapter 5.

3.2.1 THE WIN/WASP+ WATER QUALITY ANALYSIS SIMULATION PROGRAM

WIN/WASP+ (Windows Water Quality Analysis Software Program) was used to simulate a water quality model of Lake St. Clair. It is an enhanced version of the USEPA Water Quality Analysis Simulation Program (WASP). It was obtained from the AScI Corporation, located in Virginia, USA. It is used to model water quality of surface water bodies. It is a finite element model, which calculates the dispersion and advection of chemicals in a water body. At the core of the WIN/WASP+ modelling framework are the WASP simulation models for eutrophication (EUTRO) and for toxic chemicals (TOXI). These models use the same algorithms as the USEPA version known as TOXIWASP, which is described below (AScI WIN/WASP+ Users' Manual, 1997).

TOXIWASP is a dynamic model used for the simulation of transport and fate of toxic chemicals in water bodies. TOXIWASP formulates variable chemical degradation rates from the chemical characteristics of a compound and the environmental parameters of the aquatic system. TOXIWASP calculates total chemical concentrations explicitly every time for each time step for every segment, including surface water and subsurface water. The chemical concentrations are affected by the same fore-mentioned process as well as by degradation, sediment-water dispersion and percolation. There is no allowance for lateral migration of the chemical within the bed. The input data for the transport model is specified on the basis of monitoring or predictions from hydrodynamic models.

TOXIWASP is a modelling program designed to provide WASP users with the capability for simple dynamic simulations of chemicals. It can be used for cases requiring more dynamic transport and loading capabilities. TOXIWASP is more suited to stratified lakes and reservoirs, large rivers, estuaries and coastal waters (User's Manual for TOXIWASP, 1983).

3.2.2 BASIC MATHEMATICAL OVERVIEW OF TOXIWASP

TOXIWASP is dynamic chemical model that can be applied to water quality problems in streams, lakes, reservoirs, estuaries and coastal waters. It requires that the water body being modelled be split up into segments. It uses a compartment approach whereby segments can be arranged as shown in Figure 3.3.

Pollutant transport is based on user-specified flow and dispersive mixing between segments. TOXIWASP calculates time varying concentrations using an explicit numerical solution to the mass flux form of the one dimensional advective dispersion equation:

$$\Delta M_j/\Delta t = {}^{n}\Sigma_{i=1}[Q_{ij}C_i + E_{ij}A_{ij}(\Delta C/L)_{ij}] + W_j - KV_j \tag{1}$$

where,

M = constituent mass

C = constituent concentration, ML^{-3}

Q = water flow, L^3T^{-1}

E = longitudinal dispersion, L^2T^{-1}

A = cross-sectional area

L = characteristic length, L

W = mass loading, MT^{-1}

K = kinetic degradation or transformation rate, $ML^{-3}T^{-1}$

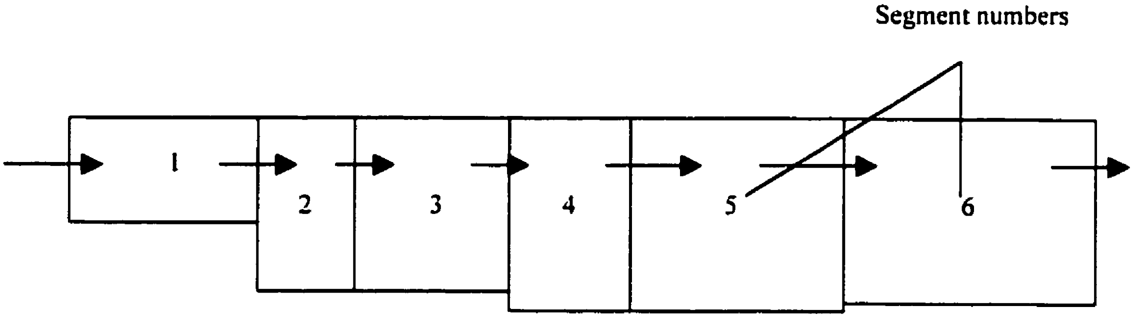
V = segment volume L^3

j = segment number

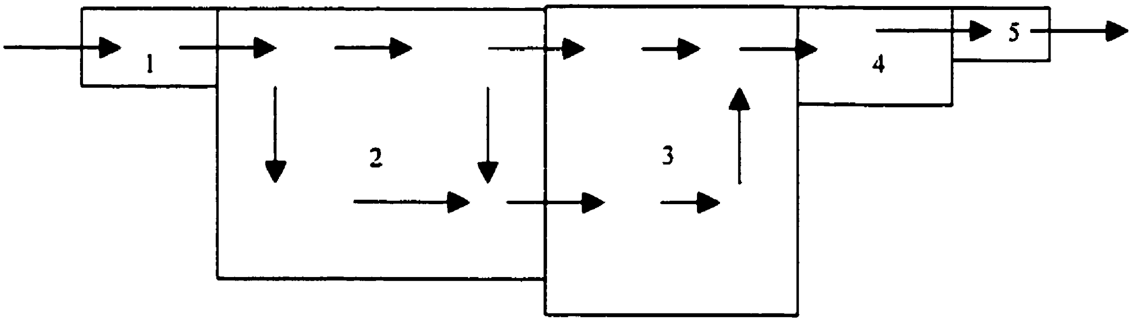
i = adjacent segments

ij = interface between segment j and adjacent segment i

For a river the segments are shown as follows,



Similarly for a lake the segmentation is as follows,



→ **represents directional flow of water**

3.3 Examples of TOXIWASP Network Configurations

The differential equation that solves for water-borne chemicals, written in the general concentration, is as follows

$$\partial C/\partial t = u\partial C/\partial x + \partial/\partial x(E\partial C/\partial t) + W/V - K + S \qquad (2)$$

where,

C = concentration of chemical, ML^{-3}

u = flow velocity of water, LT^{-1}

W = mass loading of chemical, MT^{-1}

S = net exchange of chemical with bed

K = kinetic degradation or transformation rate, $ML^{-3}T^{-1}$

x = longitudinal distance

t = time

From the chemical characteristics of the compound and the environmental parameters of the system, TOXIWASP formulates a total transformation rate (User's Manual).

The three dimensional differential describing the distribution of the total chemical is:

$$\partial C/\partial t = \partial/\partial x(E_x\partial C/\partial x) + \partial/\partial y(E_y\partial C/\partial y) + \partial/\partial z(E_z\partial C/\partial z) -$$

$$\partial u_xC/\partial x - \partial u_yC/\partial y - \partial u_zC/\partial z + S \qquad (3)$$

where,

C = concentration of total chemical, ML^{-3}

E = dispersion coefficient, L^2T^{-1}

u = velocity, LT^{-1}

S = sources/sinks due to reactions and transfers or direct addition/removal of the chemical

x, y, z = co-ordinate directions representing three dimensions

To carry out the simulation TOXIWASP requires that the water body being modelled be split up into segments. The central difference approximation of space derivatives in the mass balance equations is applied. Assuming the completely mixed finite segments, the distribution of the total chemical for water segment i (which is between segments j and l) is expressed as follows:

$$\mathbf{V_i dC_i/dt = \Sigma_j Q_{j,i} C_i - \Sigma_k Q_{i,k} C_i + \Sigma_j (E_{i,j} A_{i.j}/L_{i.j})(C_j - C_i) -}$$

$$\mathbf{Ws_{i,l} A_{i,l} fp_i C_i + Wu_{l,i} A_{i,l}\, fp_l C_l + (E_{i,l} A_{i.l}/L_{l,j})(fd_l C_l - fd_i C_i) + S} \quad \mathbf{(4)}$$

Where:

V_i = volume of segment i, L^3

C_i = total concentration in segment i, ML^{-3}

$Q_{j,i}$ = hydrodynamic flow from segment j to segment i, L^3T^{-1}

$Q_{i,k}$ = hydrodynamic flow from segment i to segment k, L^3T^{-1}

$E_{i,j}$ = dispersion coefficient between segments i and j, L^2T^{-1}

$L_{i,j}$ = mixing lengths of segments i and j, L

$Ws_{i,l}$ = settling velocity of particulates from segment i to segment l, LT^{-1}

$Wu_{l,i}$ = resuspension velocity from segment l to segment i to segment l, LT^{-1}

fd/fp = fraction of dissolved/particulate contaminant

S = sources/sinks due to reactions and transfers or direct addition/removal of the chemical

For the time derivative in the above equation, a forward difference approximation is used:

$$\mathbf{C_i^{n+1} = C_i^n + (dC_i^n/dt)\Delta t} \qquad \mathbf{(5)}$$

This above relationship states that the concentration at time n+1 is equal to the concentration at time n plus the derivative evaluated in time n multiplied by the time step Δt (Barycka, 1988).

3.2.3 LIMITATIONS OF WIN/WASP+

The nature of WIN/WASP+ computer program is such that it calculates the three dimensional flow. The simulation for the model does not take into account atmospheric deposition of pollutants. At the same time it does not calculate the loss of polluting substances to the food chain. In this study it was used to calculate the dispersion, transport and flushing out rates of selected metals dissolved in Lake St. Clair waters with respect to time. Data used for the simulations was temporal in nature. It was assumed that constant amounts of polluting elements were entering the lake. Seasonal temperature changes were not taken into account. Due to a lack of data no sensitivity analysis was applied. For that reason it is impossible to tell how accurate the modelling results are.

3.2.4 MODEL SIMULATION

To set up my simulation of the Lake St. Clair Water system there were several initial steps involved. They include Input Parameterization, Systems definition, Segmentation, Segment Parameters, Dispersion, Flows, Boundaries, Loads, Print Intervals, Time Functions, Constants and the Validity Check. The sources of the various parameters and constants required for the simulation are given below in Table 3.5. Details for these parameters and constants are given in Appendix 9.

Parameter/Constant		**Source**
Water velocities		Ibrahim, 1986
Water volumes		GIS analysis
Water Temperature		Bolsenga and Herdendorf, 1993
Hydrological Parameters		Bolsenga and Herdendorf, 1993
Limnological Constants		Chapra, 1998
Limnological Parameters		NOAA Report, 1980
Chemical Constants		Stumm and Morgan, 1996

Table 3.5 Sources of various parameters and constants

These steps are briefly described below in the following sub-sections.

Input Parameterization

In the WIN/WASP+ Water Quality Analysis Software Program a new input data set requires that an input parameterization data entry be filled out. This provides the basic information that is needed by the program to parameterize the other data entry windows and forms that are to follow. It is here that the modeller informs the program about what type of WIN/WASP+ input he/she is going to be creating.

Data Set Description

This field provides a one-line descriptor for the defined input data file. This helps to indicate what sort of project the input data set is being prepared for and also it may indicate the study area and type of study.

Model Type

In this field the program allows the user to specify which WIN/WASP+ model type (EUTRO or TOXI – EUTRO stands for entrophication model and TOXI stands for toxic model) the data set is being created. In this case the TOXI option was selected.

Restart Options

WIN/WASP+ provides the user with the ability to use restart files between simulation runs. A restart file is a "snap-shot" of the model conditions at the end of the model run. This "snap-shot" can be used for a future model run. In this case the restart option was selected.

Date and Times

Here the user must specify the starting time and date. In this particular study the starting time was artificially defined as 1-1-1998.

Hydrodynamics

There are three flow options available for WASP. They are:

1) WASP will calculate net transport across a segment interface that has opposing flow. WASP will net the flows and move the mass from the segment that has higher flow leaving. If the opposing flows are equal no mass is moved.
2) Pertains to mass and water being moved without regard to net flow.
3) This option is used when linking WASP to a hydrodynamic model.

In this particular simulation option 2 was selected.

Systems

The system data entry form allows the user to define system specific information. A system in WIN/WASP+ is a state variable within the model. The state variables depend entirely on the model. The modeller controls the number and type of systems to be modelled. For example in this study the three systems modelled independently are Sr, Mo and Cd.

Systems Options

There are three options for this field: Simulated, Constant and Bypassed. These three options pertain to the systems being modelled. In this case the simulated option was selected for the systems in the model.

Density

This field allows the modeller to specify the density of each contaminant being modelled. In this case, since concentrations of the contaminants were so low, this option was ignored.

Segmentation Screen

This data entry form allows the modeller to define the number of segments that will be considered during the simulation. The segments were devised so as to simulate the best estimation of average flows in the lake annually. Average water velocities were entered for each segment. An average velocity of 0.03 m/s was assumed for the lake waters. Segments have volume, environmental and constituent concentrations associated with them. The segment data entry form has four tables associated with them: 1) Segment Definition, 2) Environmental Parameters, 3) Initial Conditions, 4) Fraction of contaminant dissolved. Each table was filled with the specific particulars regarding the study. It is here that the parameter values like pH, water temperature etc. were entered for the segments. Also the initial concentrations of the modelled chemicals were indicated.

Dispersion

The dispersion-input screen is a complex screen that contains four tables. Here the exchanges of water between the different segments in terms of volumes flowing out from and into another are defined.

Exchange Fields

This table allows the choice of two types of exchange. They are surface water exchange and pore water exchange. In this case the surface water option was selected. This is because only surface water quality was being modelled.

Dispersion Function

The dispersion between the different segments is set for the model to calculate during its execution. It is here that segment connectivity is defined. Mixing lengths and the cross sectional area, reflecting the area through which mixing occurs are also defined here. Appropriate entries were made according to the set up of the segments.

Flows

This set of tables works in exactly the same way except that evaporation/precipitation are also included and the transport of the chemicals is defined. The proper adjustments were made to carry out the simulations.

Boundaries

Here the boundary concentrations were specified for each of the segments. The boundary segments were automatically determined by WIN/WASP+ when the transport functions were defined. WIN/WASP+ requires that a boundary concentration be specified for every system that is being simulated for every boundary segment. These steps were carried out keeping in mind congruency.

Loads

Loads are entered for each of the simulated chemical systems for given segments. The amounts of water with the loads were defined for the model making an estimate to achieve concurrence with observed results.

Constants

This data entry group specified the constants for the water constituents being simulated by the WIN/WASP+ model. Specified values applied over the entire network for the whole simulation.

Validity Check

Once all the required data were placed in their respective fields and the model construction properly realized, a validity check was carried out to make sure there were no troubles or errors in the data input set. This was done to determine whether or not the data was correct and within the dimensioned capabilities of the model.

4- ANALYTICAL RESULTS

Water samples were collected to be representative of the surface, middle and bottom layers of water of the lake. Sample sites, samples collected from each site, depth at each site and date of field visit to the site are given in Table 2.2. Locations of sample sites are given in Figure 2.2. The results from ICP-MS for both filtered and centrifuged samples are given in Appendices 5 and 6 respectively.

4.1 RESULTS OBTAINED FROM ICP-MS ANALYSIS

Only data from the ICP-MS for filtered water samples was analysed. Data for the centrifuged samples was obtained only a week and a half before the submission deadline for this work. This was due to problems occurring in instrument calibration. Therefore reliable data was not obtained till nearly the completion of this work. An overview of the analytical data for many of the elements is provided in histograms of the data in Figure 4.1 (a, b, c and d). The ranges for these plots have been adjusted in size to cover some very high concentrations for certain elements (e.g. Zn and Cr in Figure 4.1d). Figure 4.1a shows the histogram for the value ranges observed for Ba and Sr. Except for one instance, most of the values for Ba lie between 11.0 and 16.0 micrograms/kg. The anomalous value was found in the sample from site # 8. Here a concentration of 25.2 micrograms/kg was observed. The maximum value range was two times the minimum value range. Values obtained for Sr follow a similar pattern. Most of the observed concentrations were seen to be between 60 and 72 micrograms/kg. However there was dispersion in value ranges as can be seen in the figure. Higher values were observed. The highest observed value was again seen at sample site 8. Here a value of 119

Figure 4.1a

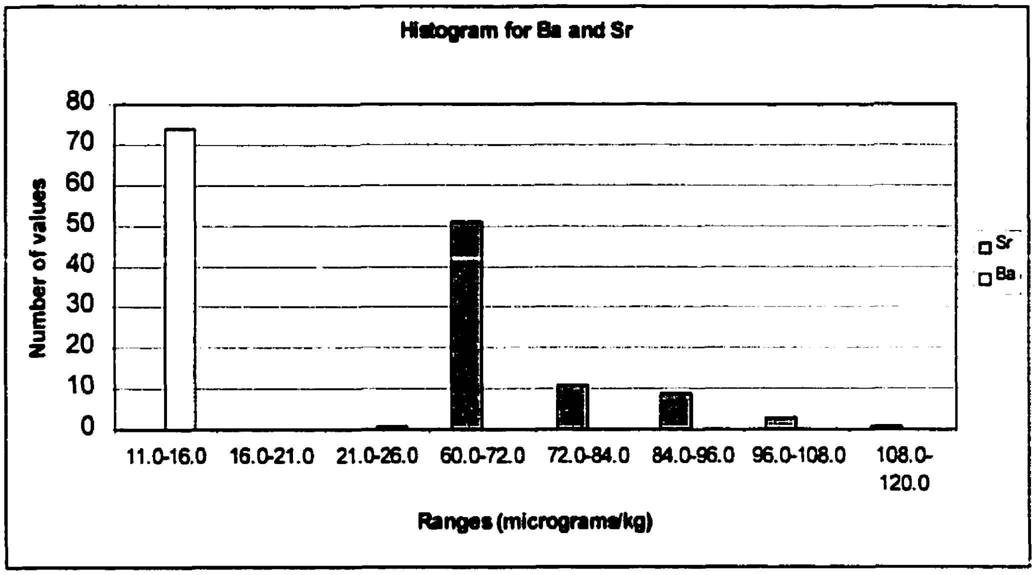


Figure 4.1b

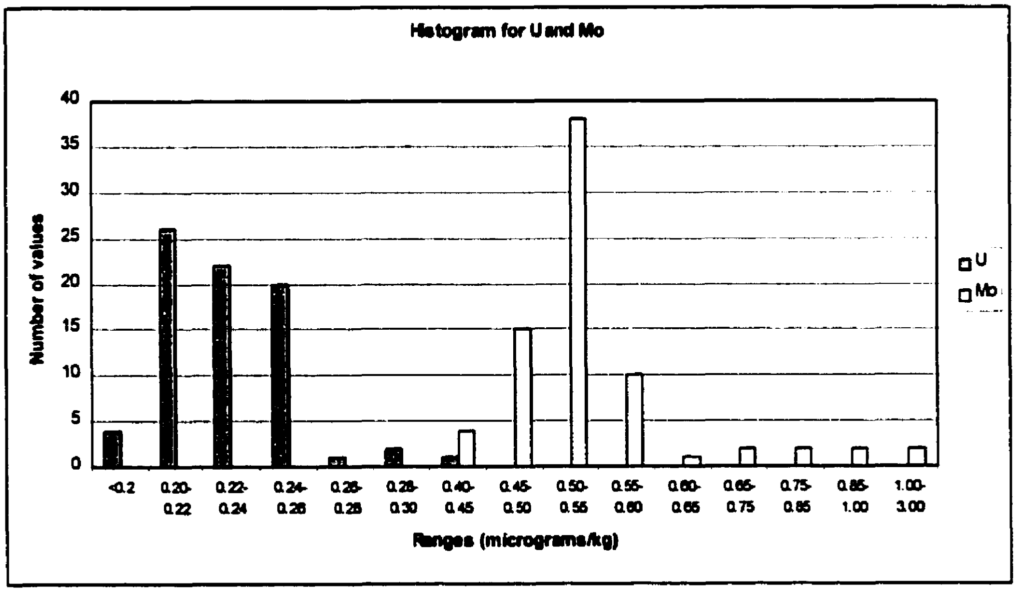


Figure 4.1c

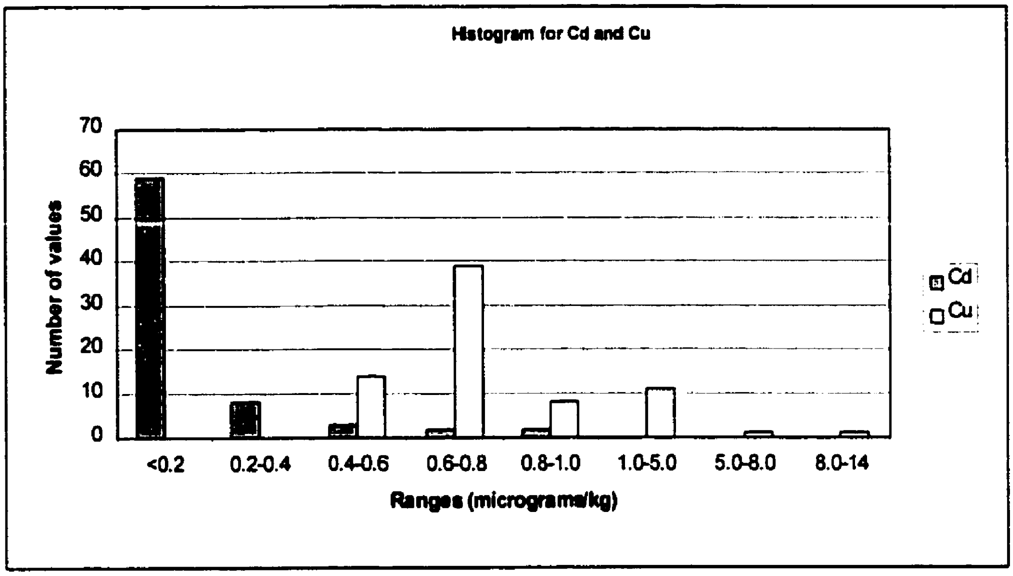
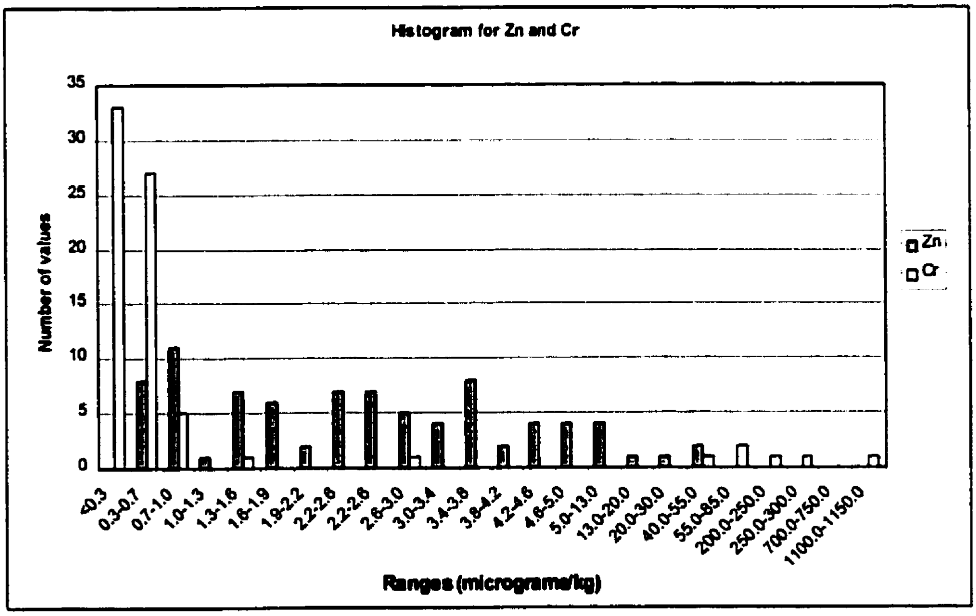


Figure 4.1d



micrograms/kg was found. As in the case of Ba, the maximum value range was twice the minimum value range. Figure 4.1b shows the histogram for the value ranges observed for U and Mo. Both show similar patterns. Most of the values for U fall between 0.20 and 0.26 micrograms/kg. Four concentrations less than 0.2 micrograms/kg were observed. Observed concentrations were dispersed across larger ranges as well as can be seen in the figure. Interestingly enough the highest observed concentration was for the sample from site # 8. Here a concentration of 0.43 micrograms/kg was observed. The maximum value range for U was 4 times the minimum value range. In the case of Mo most of the values fall in between 0.50 and 0.55 micrograms/kg. Values less than and greater than these values were seen. More or less the patterns are similar to those shown by U. The Maximum value range was 4 times the minimum value range. Figure 4.1c shows the histogram for Cd and Cu values. Value range dispersion for both show a distinct similarity to each other. Most observed concentrations of Cd were less than 0.2 micrograms/kg. A limited number of higher concentrations were also seen. The highest value observed was observed at site # 14. Maximum concentration range for Cd was four times higher than the minimum concentration range. Cu concentrations showed variations similar to Cd. Most values lay between 0.6 and 0.8 micrograms/kg. Again values were dispersed across higher ranges. Maximum concentration observed was 13.6 micrograms/kg. This value was observed at site # 25. Maximum concentration range was, as in the case of Cd, 4 times the minimum concentration range. Figure 4.1d shows the histogram for Zn and Cr values. Zn concentrations were dispersed over a large array of concentration ranges. Minimum concentrations were less than 0.3 micrograms/kg. The maximum concentration found was 48.71 micrograms/kg. This value was observed at sample site 28. Cr concentrations were also dispersed. Minimum concentration observed was 0.33 micrograms/kg. Relatively speaking, enormously large maximum concentration of 1106.79 micrograms/kg was found. This value was for the sample from site # 25.

To analyse these results spatially, both laterally and vertically in the lake, it was required that a GIS (Geographic Information System) database be constructed. Details regarding the construction of this database are given in Appendix 10. The results obtained from the analysis of the filtered water samples from the ICP-MS were imported into a GIS database. From here the concentrations were plotted for the samples from three layers of water in Lake St. Clair. These concentrations were contoured by the use of the GIS software ARCVIEW to give contour maps of the concentrations of selected metals in Lake St. Clair. To show anomalous concentrations for the selected metals across the lake waters contour intervals were decided after taking the difference between the maximum and minimum concentrations for each element and dividing the difference by four.

Although concentrations for many metals were obtained, contour maps are plotted for only three metals. They are Sr, Mo and Cd. These metals were selected as examples because they have very different geochemical properties and show different distributions, as seen in Figure 4.1, and will be modelled to demonstrate the behaviours of various metals in the lake.

4.1.1 RESULTS FOR FILTERED WATER SAMPLES

STRONTIUM

The contour maps for concentrations of Sr obtained from the analysis of the filtered set of samples are given as Figures 4.2, 4.3 and 4.4. All maps were prepared on the basis of data given in Appendix 5. Contour intervals were chosen to show the significant concentration variations across the lake.

Figure 4.2 shows the variations in concentration for Sr in the surface water layer of Lake St. Clair. The map has a contour interval of 13 micrograms/kg. Sr concentrations are less than 81 micrograms/kg across much of the lake. There is however a small increase in the southern and central region. At sample site #12 concentrations are seen to increase to a value greater than 94 micrograms/kg. However there appears to be a much higher concentration near site # 8. The map shows increasing concentrations of Sr in this region. This is believed to be due to input from the Clinton River, which releases its water into Lake St. Clair near site # 8.

Figure 4.3 shows the variations in concentration for Sr in the middle water layer of Lake St. Clair. The map has a contour interval of 15 micrograms/kg. Concentrations in most of the southern region were found to be greater than 80 micrograms/kg but less than 95 micrograms/kg. In the central area as well as the waters in the vicinity of the start of the Detroit River were found to be less than 80 micrograms/kg. However, in this case again a concentration increase is seen towards site # 8 (note this is the same analysis as only one sample was collected from this site). The map shows increasing concentrations of Sr in this region. This, as mentioned before, is believed to be due to input from the Clinton River.

Figure 4.2 Contour Map of observed concentrations of Strontium in surface layer-Lake St. Clair

Figure 4.3 Contour Map of observed concentrations of Strontium in middle layer-Lake St. Clair

Figure 4.4 Contour Map of observed concentrations for Strontium in bottom layer-Lake St. Clair

Figure 4.4, shows the variations in concentration for Sr in the bottom water layer of Lake St. Clair. The map has a contour interval of 15 micrograms/kg (parts per billion). As can be seen in the map slightly lower concentrations were observed from the results. Most areas of the lake showed concentrations ranging between 76 micrograms/kg and 91 micrograms/kg. The same concentration increase was witnessed at site # 8 as was seen in the previous two maps.

Sr concentrations did not vary much with depth as can be seen from the comparison of the Figures 4.2, 4.3 and 4.4, although on average, concentrations in the bottom layer were a little less than those observed in the middle and surface layers. This indicates that the behavior of Sr is not significantly affected by differing conditions at different depths.

MOLYBDENUM

The contour maps for concentrations of Mo obtained from the analysis of the filtered set of samples are given as Figures 4.5, 4.6 and 4.7. All maps were prepared on the basis of data given in Appendix 5. Contour intervals were chosen so as to show the significant concentration variations across the lake.

Figure 4.5 shows the variations in concentration for Mo in the surface water layer of Lake St. Clair. The map has a contour interval of 0.6 micrograms/kg. Concentrations ranged between 0.5 and 1.1 micrograms/kg across the greatest part of the surface waters of the lake. A higher concentration for the single sample from site # 8 is again noted. Here the concentration is above 3.0 micrograms/kg.

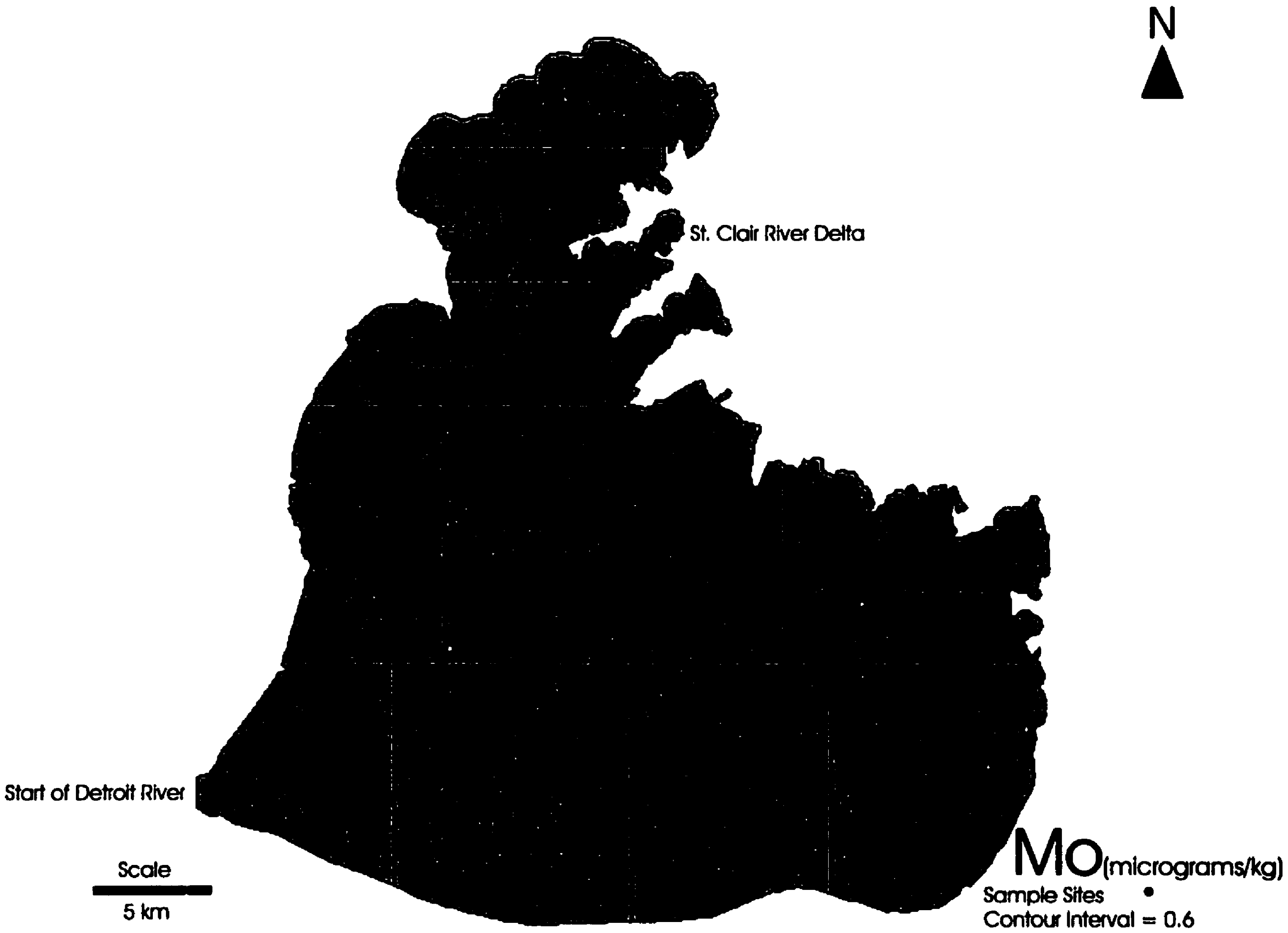


Figure 4.5 Contour Map of observed concentrations for Molybdenum in surface layer-Lake St. Clair

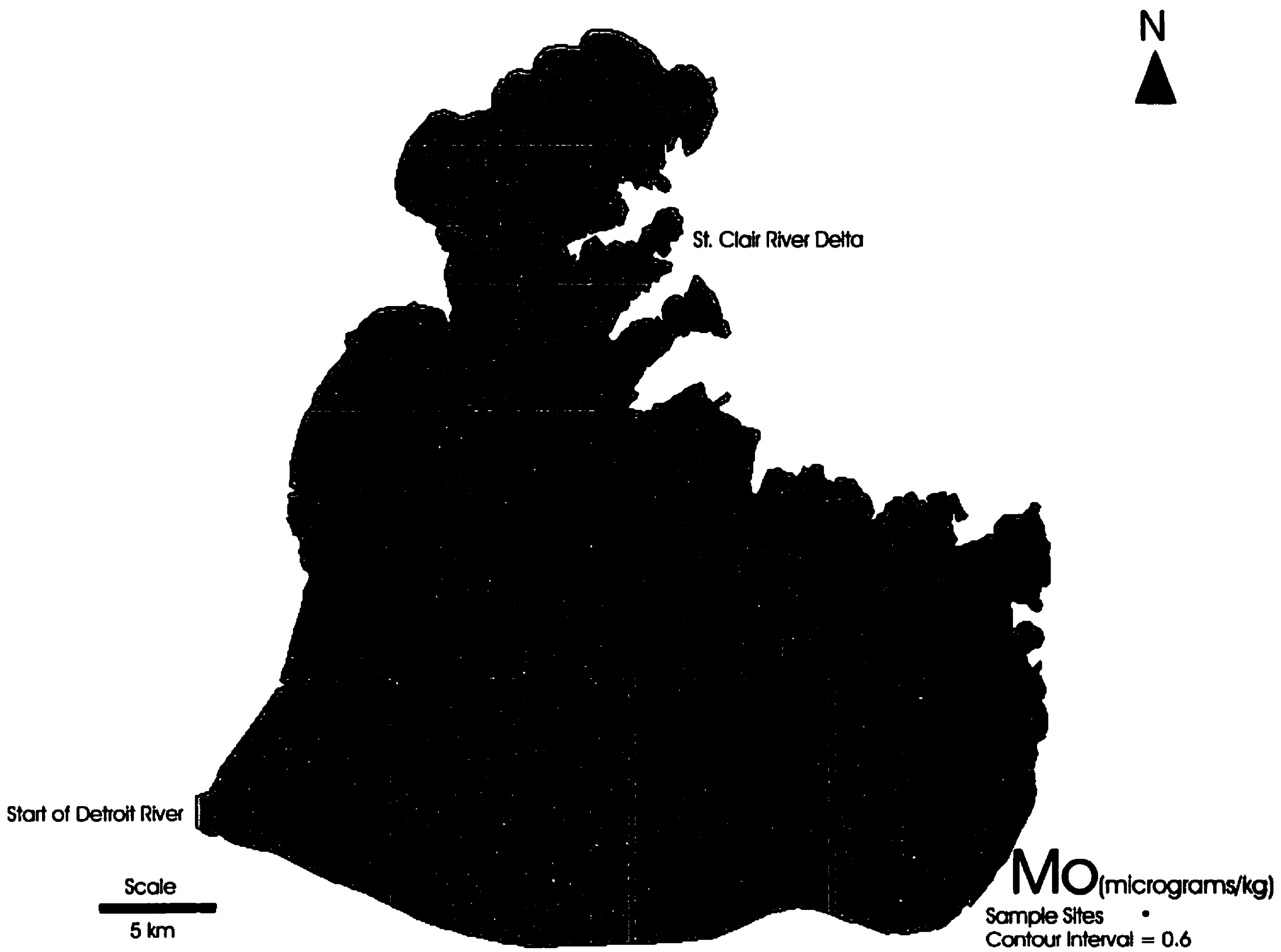


Figure 4.6 Contour Map of observed concentrations of Molybdenum in middle layer-Lake St. Clair

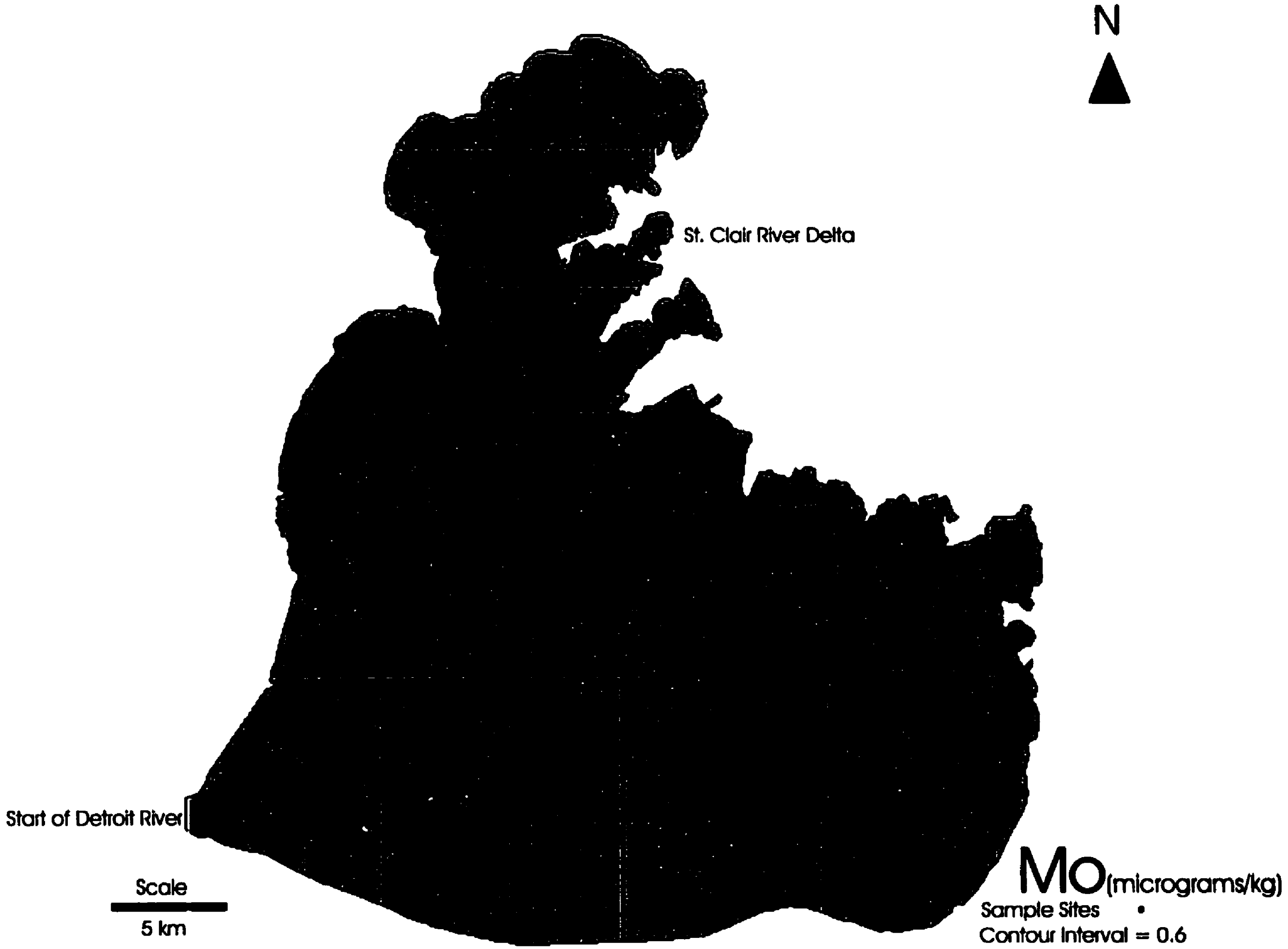


Figure 4.7 Contour Map of observed concentrations for Molybdenum in bottom layer-Lake St. Clair (ppb)

Figure 4.6 shows the variations in concentration for Mo in the middle waters of Lake St. Clair. The map has a contour interval of 0.6 micrograms/kg. Most of the lake shows concentrations lying in the 0.5 - 1.1 micrograms/kg range. However, two anomalous zones were found in the lake. One was at the previously noted site # 8 and the other in at site # 25. At site # 25, a value of 1.6 micrograms/kg was measured.

Figure 4.7 shows the variations in concentration for Mo in the bottom waters of Lake St. Clair. The map has a contour interval of 0.6 micrograms/kg. Again it is noted that most the lakes' bottom waters show concentrations lying in the range of 0.5 – 1.1 micrograms/kg. Two anomalous zones were found at sites 8 and 25. At site # 25 a value of 2.6 micrograms/kg was found.

If one compares the results shown in Figures 4.5, 4.6 and 4.7 for the different layers of water for Lake St. Clair, it is notable that, other than for site # 8, the higher concentrations of Mo were found in the bottom and middle layers of the lake as compared to the surface layer.

CADMIUM

The contour maps for concentrations of Cd obtained from the analysis of the filtered set of samples are given as Figures 4.8, 4.9 and 4.10. All maps were prepared on the basis of data given in Appendix 5. Contour intervals were chosen so as to show the significant concentration variations across the lake.

Figure 4.8 shows the variations in concentration for Cd in the surface water layer of Lake St. Clair. The map has a contour interval of 0.18 micrograms/kg. The northern and extreme western parts of the lake show concentrations less than 0.18 micrograms/kg. The same is the case for the localities around sample sites 13, 21 and 25. Two 'hot spots'

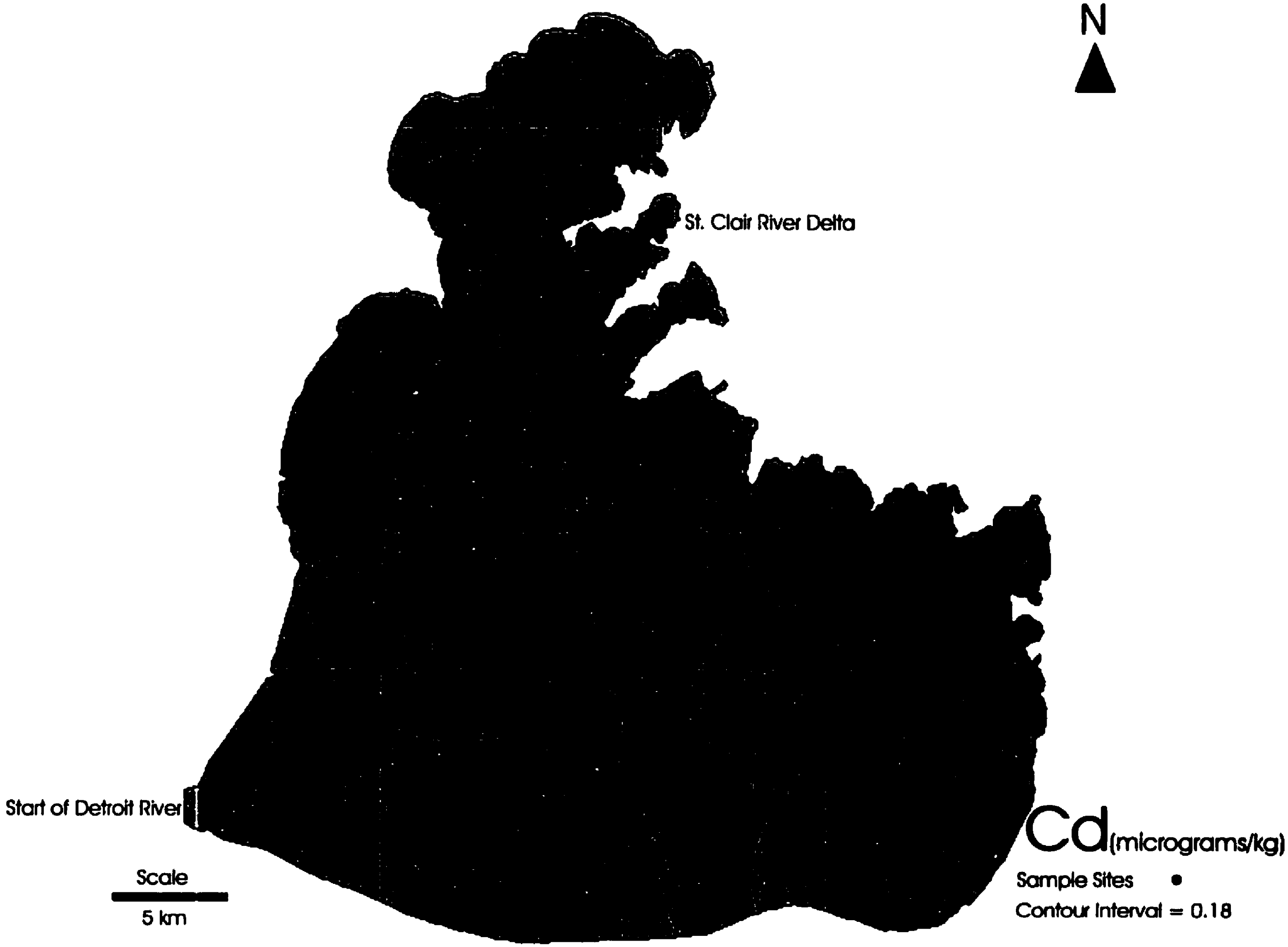


Figure 4.8 Contour Map of observed concentrations for Cadmium in surface layer-Lake St. Clair

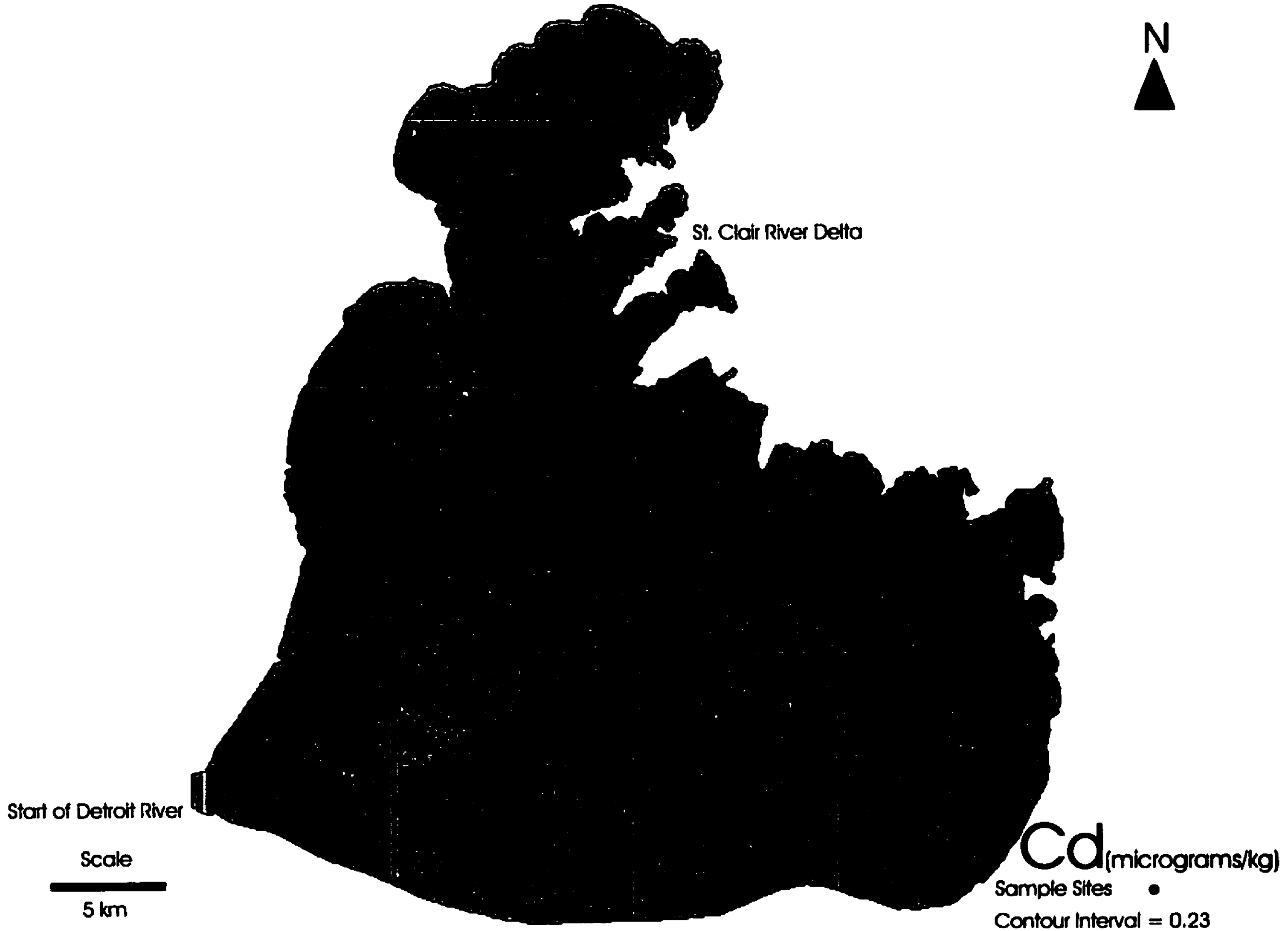


Figure 4.9 Contour Map of observed concentrations for Cadmium in middle layer-Lake St. Clair

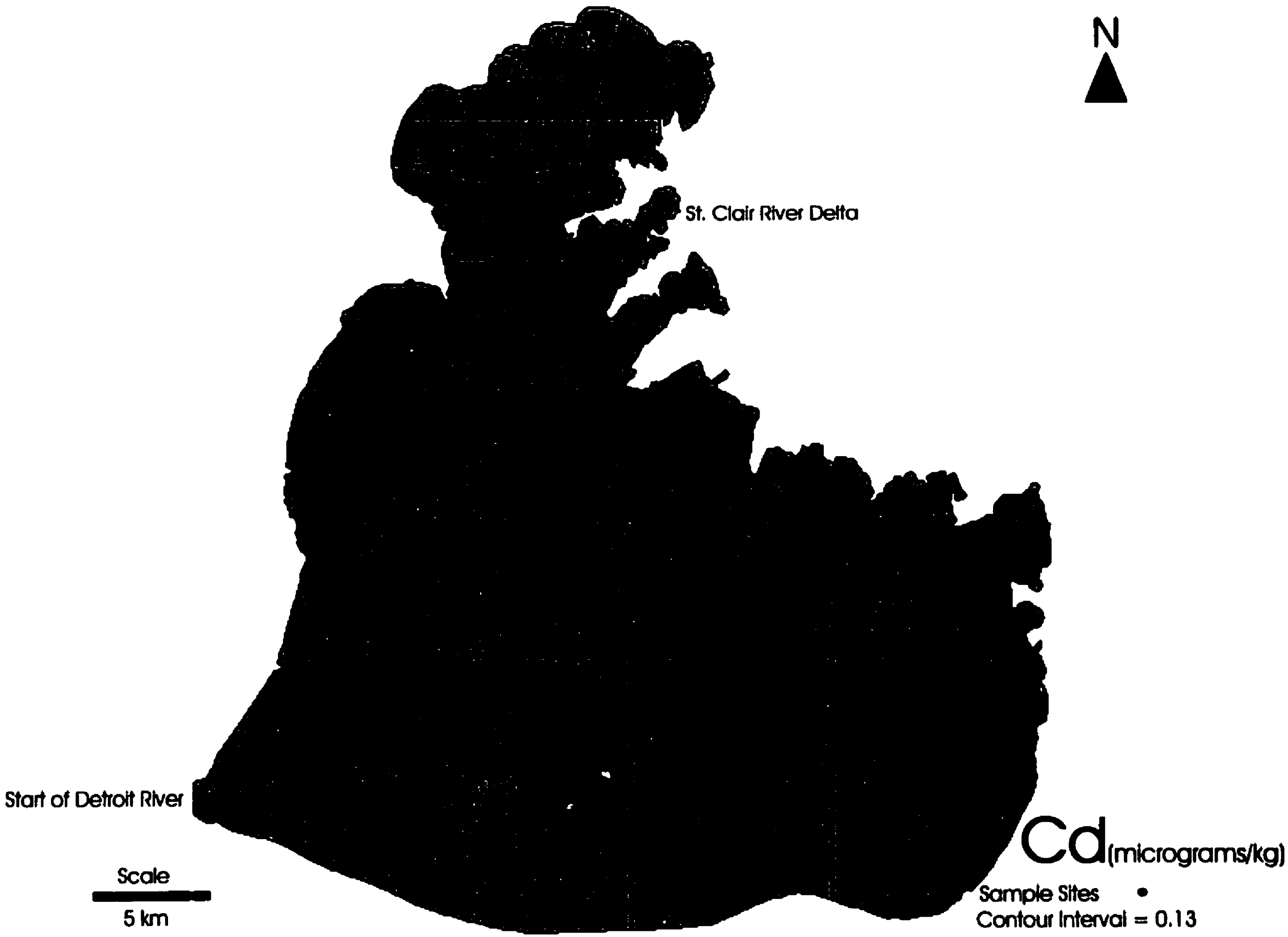


Figure 4.10 Contour Map of observed concentrations for Cadmium in bottom layer-Lake St. Clair

were noted. One of them was sample site # 16 and the other 'hot spot' was found at sites # 12, 27. Concentrations of Cd increased in these areas to above 0.54 micrograms/kg.

Figure 4.9 shows the variations in concentration for Cd in the middle layer of Lake St. Clair water. The map has a contour interval of 0.23 micrograms/kg. The figure shows that there are two hot spots. One lies at site # 14 and the other lies at site # 16. At site # 14 Cd concentrations in excess of 0.70 micrograms/kg were observed. At site # 16 concentrations greater than 0.47 micrograms/kg were found. Values were found to be less than 0.24 micrograms/kg for the rest of the lake.

Figure 4.10 shows the variations in concentration for Cd in the bottom layer of Lake St. Clair water. The map has a contour interval of 0.13 micrograms/kg. Values less than 0.13 micrograms/kg were found in a greater part of the lake except at sites # 13, 20 and 26. At sites # 13 and 26 concentrations in excess of 0.26 micrograms/kg were found. At site # 20 a concentration greater than 0.39 micrograms/kg was observed.

A comparison of the contour maps for Cd concentrations in the different layers of water (i.e. Figures 4.8, 4.9 and 4.10) showed that there are concentration changes with depth and that certain sites showed higher concentrations for lower depths whereas others showed higher concentrations at the surface.

5- DISCUSSION

Discussion of the analytical results and the water quality modelling of Lake St. Clair are given in the following sub-sections. Except in section 5.3, only ICP-MS data for the filtered water samples are analysed for reasons mentioned in section 4.1.

5.1 RESULTS OF GEOCHEMICAL ANALYSIS FOR LAKE ST. CLAIR WATERS

Results of the geochemical analysis of water samples from Lake St. Clair revealed concentration distributions across the lake. Sr, Mo and Cd are specifically discussed below, as they were selected for the simulation of a water quality model for Lake St. Clair.

STRONTIUM

Results given in Appendix 5 showed Sr concentrations in Lake St. Clair waters to be between 63 and 110 micrograms/kg. Sr exists at a level of about 0.02% in the Earth's crust. It is introduced into surface waters by the weathering of rocks or by the discharge of wastewater from industries using Sr compounds. Small concentrations of Sr may be of benefit to animals, but high concentrations are toxic, as they may upset the metabolism of Calcium and Phosphorus (Dojlido and Best, 1993). The source of higher Sr in Lake St. Clair appears to be the Clinton River. In humans there have been no cases of Sr poisoning. Thus drinking water standards allow for a relatively large amount (2 ppm) of Sr to be present.

MOLYBDENUM

Results given in Appendix 5 showed Mo concentrations in Lake St. Clair waters to be between 0.5 and 3.0 micrograms/kg. Mo exists in nature in the form of the minerals molybdenite and wulfenite. It is mainly used in the manufacture of hardened steels as a cayalyst. Mo salts are also used in the manufacture of glass, ceramics, pigments and fertilizers. It is present in wastewaters from these industries. Mo is essential to the growth of plants in very small amounts but can be toxic to grazing animals (Dojlido and Best, 1993). Thus drinking water standards allow for amounts of up to 500 micrograms/kg. A significant source of Mo in Lake St. Clair appears to be the Clinton River.

CADMIUM

Results given in Appendix 5 showed Cd concentrations in Lake St. Clair waters to be between 0.0004 and 0.94 micrograms/kg. Cd does not exist in nature as the native metal but principally as the sulphide ore greenockite, which is found associated with sphalerite. Cd enters the environment in the wastewaters of industries using Cd such as the plastics, electroplating and Nickel-Cd battery industries. Another anthropogenic source is discharge from the iron and steel industry (Dojlido and Best, 1993). Cd is toxic to almost all human body systems. It is stored in the liver and kidneys. Cd can induce can induce kidney disease and pulmonary edema. The drinking water standard for Cd is 1 micrograms/kg. According to the results of this study the water of Lake St. Clair falls under that limit, but the highest sample is very close to the limit.

5.2 MEAN, MINIMUM AND MAXIMUM CONCENTRATIONS IN LAKE ST. CLAIR

Table 5.1 shows the mean, minimum and maximum concentrations among all the samples collected in this study. These values are those obtained from the ICP-MS analysis of the filtered water samples. As can be seen in Table 5.1 average concentrations of Sr, Mo and Cd are 75.8, 0.6 and 0.13 micrograms/kg. Also shown in the table are the Canadian Water Quality Standard maximum values for the Protection of Aquatic Life as prescribed by Environment Canada (1999). Values obtained for Ni, Mo, As, Se, Pb and Tl fall below the prescribed water quality values. Average concentrations of Cr and Cd are higher than values given in the guidelines. It should be pointed out that maximum concentrations for Chromium and Nickel were found to be very high. These high values were found at sample site # 25.

Since high concentrations of Mo and Sr were found at sample site # 8, near the mouth of the Clinton River a simple calculation of the average concentrations across Lake St. Clair excluding this value from this site was made for comparison purposes. These concentrations are given in Table 5.2. When the two sets of values in Tables 5.1 and 5.2 were compared it was found that average concentrations of Sr, Mo and Ba were slightly reduced whereas the average concentrations of the other remained unchanged. Table 5.3 shows average concentrations in the St. Clair River and Lake St. Clair waters as well as the average concentrations of waters entering the Detroit River. The average concentrations for the St. Clair River are the mean of those water samples taken from the St. Clair River and the St. Clair River delta. These concentrations were calculated from values obtained from the analysis of water samples collected from sites 3, 5, 6 and 7. The

Element	Lithium	Vanadium	Chromium	Manganese	Nickel	Cobalt
Minimum	1.0	0.2	0.1	0.01	0.5	0.1
Maximum	2.7	6.2	1107	101	703	24.1
Mean	1.2	0.4	33	3.2	22.0	0.9
Maximum/Mean	2.2	15.7	33.2	31.5	32.0	27.9
Cdn WQ Guideline	-	-	8.9	-	150	-
Element	Copper	Zinc	Selenium	Rubidium	Arsenic	Strontium
Minimum	0.5	0.4	0.4	0.7	0.4	61
Maximum	13.6	49	1.4	1.4	1.4	119
Mean	1.1	4.3	0.5	0.9	0.6	75.8
Maximum/Mean	12.1	11.4	2.5	1.7	2.3	1.6
Cdn WQ Guideline	4	30	1	-	5	-
Element	Yttrium	Molybdenum	Barium	Cadmium	Antimony	Thorium
Minimum	0.00	0.4	12	0.0004	0.11	0.0002
Maximum	0.02	2.9	25	0.94	0.22	0.01
Mean	0.01	0.6	13	0.13	0.1	0.004
Maximum/Mean	2.53	4.9	1.9	7.01	1.79	1.74
Cdn WQ Guideline	-	73	-	0.02	-	-
Element	Lanthanum	Lead	Thallium	Uranium	Caesium	
Minimum	0.001	0.001	0.001	0.19	0.000	
Maximum	0.024	0.29	0.006	0.43	0.004	
Mean	0.004	0.08	0.004	0.2	0.002	
Maximum/Mean	5.92	3.48	1.77	1.89	2.31	
Cdn WQ Guideline	-	7	0.8	-	-	

Table 5.1 Miniumum, maxiumum and mean concentrations for Lake St. Clair and the St. Clair River water in micrograms/kg (filtered samples)

Element	Lithium	Beryllium	Cobalt	Copper	Vanadium	Chromium
Minimum	1.0	0.0002	0.13	0.46	0.19	0.102
Maximum	1.4	0.008	24	14	6.2	1107
Mean	1.2	0.003	1	1	0.39	34
Cdn WQ Guideline	-	-	-	4	-	8.9
Element	Manganese	Nickel	Strontium	Yttrium	Zinc	Selenium
Minimum	0.007	0.5	61	0.004	0.35	0.37
Maximum	100.55	703	96	0.024	49	0.84
Mean	3	22	75	0.010	4	0.53
Cdn WQ Guideline	-	150	-	-	30	1
Element	Rubidium	Arsenic	Caesium	Lead	Molybdenum	Barium
Minimum	0.65	0.36	0.0005	0.001	0.43	12
Maximum	0.94	1.31	0.004	0.29	2.6	16
Mean	0.86	0.58	0.002	0.083	0.57	13.2
Cdn WQ Guideline	-	5	-	7	73	-
Element	Cadmium	Antimony	Lanthanum	Uranium	Bismuth	Thallium
Minimum	0.0004	0.11	0.001	0.19	0.0002	0.001
Maximum	0.94	0.14	0.024	0.29	0.30	0.006
Mean	0.14	0.12	0.004	0.22	0.096	0.003
Cdn WQ Guideline	0.02	-	-	-	-	0.8

Table 5.2 Minimum, Maximum and Mean Concentrations excluding the Site at the mouth of the Clinton River (micrograms/kg)

St. Clair River													
Element	Lithium	Beryllium	Vanadium	Chromium	Manganese	Nickel	Cobalt	Copper	Zinc	Selenium	Rubidium	Arsenic	Strontium
Mean	1.23	0.0031	0.24	25.4	2.6	15.56	0.63	0.83	2.1	0.52	0.83	0.533	66
Element	Yttrium	Molybdenum	Barium	Cadmium	Antimony	Caesium	Thorium	Lanthanum	Thallium	Lead	Bismuth	Uranium	
Mean	0.0092	.0.502	13	0.118	0.117	0.002	0.00005	0.0038	0.0027	0.104	0.112	0.210	
St. Clair Waters													
Element	Lithium	Beryllium	Vanadium	Chromium	Manganese	Nickel	Cobalt	Copper	Zinc	Selenium	Rubidium	Arsenic	Strontium
Mean	1.25	0.0030	0.42	34.9	3.3	23.19	0.91	1.18	4.7	0.55	0.87	0.601	78
Element	Yttrium	Molybdenum	Barium	Cadmium	Antimony	Caesium	Thorium	Lanthanum	Thallium	Lead	Bismuth	Uranium	
Mean	0.0098	0.627	14	0.138	0.122	0.002	0.00452	0.0041	0.0037	0.081	0.094	0.231	
Water entering Detroit River													
Element	Lithium	Beryllium	Vanadium	Chromium	Manganese	Nickel	Cobalt	Copper	Zinc	Selenium	Rubidium	Arsenic	Strontium
Mean	1.27	0.0031	0.27	0.2	1.0	0.67	0.15	0.92	18.2	0.41	0.90	0.617	70
Element	Yttrium	Molybdenum	Barium	Cadmium	Antimony	Caesium	Thorium	Lanthanum	Thallium	Lead	Bismuth	Uranium	
Mean	0.0137	0.532	14	0.043	0.126	0.003	0.00667	0.0104	0.0046	0.104	0.107	0.245	

Table 5.3 Average Concentrations in St. Clair River, Lake St. Clair Waters and water entering Detroit River (micrograms/kg)

average concentrations of water entering the Detroit River were calculated from the results of analysis of the three water samples taken from sample site # 28. Table 5.3 shows that average concentrations of Li, Be, V, Cu, Se, Rb, As, Y, Ba, Cd, Mo, Sb, Cs, Tl, Pb, Bi and U remain relatively consistent throughout the waters across the study area. On the other hand Sr shows higher average concentrations in the lake waters as compared to both the St. Clair River Delta and water entering the Detroit River. A lower average concentration of Manganese was observed in waters entering the Detroit River whereas higher average concentrations of Cr were seen in the lake waters.

The results discussed in this sub-section agree with the findings of Rossman and Borres (1988) and Thomas et al. (1975) who found that the sediments contained high concentrations of heavy metals in Lake St. Clair. In 1975 Kemp et al. found that Lake Erie is being fed with metals pollutants from Lake St. Clair via the Detroit River. This scenario seems to continue to persist in the light of the findings discussed above. Another interesting comparison can be made with the findings of Mudroch and Hill (1989) who collected sediment cores from Lake St. Clair to investigate the vertical distribution of Hg in the sediments. They found that Hg concentrations decreased with depth. According to the results found in this study of the Lake St. Clair waters, it was seen that in the case of Sr there was little variation in concentration with depth. On the other hand Mo was found to be in higher concentrations with depth (closer to the sediments) and Cd showed higher concentrations with depth at some sample sites while at others it did not. It is worthy to note that higher Cd concentrations were observed in the deeper waters at sites located where known hot spots for high metal contents in sediments exist. This is interesting since it agrees with the findings of Ibrahim (1986) who found that high levels of Cd were present in the bottom water layer of Lake St. Clair.

5.3 COMPARISON BETWEEN ICP-MS RESULTS OBTAINED FOR FILTERED AND CENTRIFUGED SAMPLES

Figures 5.1, 5.2, 5.3, 5.4 and 5.5 show the comparisons between ICP-MS results obtained for filtered and centrifuged samples for samples 7, 8, 25, 27 and 28. Selection of site # 7 was made since it is present in the St. Clair River Delta. Site # 8 was selected for comparison, as it is present near the mouth of the Clinton River. Sample Site # 25 was selected as it is present near the St. Clair River Delta. Site # 27 was chosen since it is located in roughly the centre of the lake. Site # 28 was selected as it gives a set of values for concentrations entering the Detroit River. The graphs were plotted on semi-log scales. The results of all the samples showed good comparisons for Sr, U, Ba, Cd, Mo, Rb, As, Zn, La, Pb, Co, Li and Cu. In the case of samples 8, 27, 28 the comparisons for the other elements were also in good agreement. This suggests that both methods of preparation of the water samples (i.e. by filtration and centrifuge) are valid for this type of study. On the other hand for values obtained for samples 7 and 25 there were differences in the case of Cr, Mn, Co and Ni. The differences are far outside of any analytical error as discussed in the last chapter. It is interesting to note that sample 7 was taken from inside the St. Clair River Delta and sample 25 was taken from a spot close to the same delta. In both cases the filtered samples have higher concentrations than the centrifuged ones. It is possible that small particles containing these base metals passed through the filters (standard

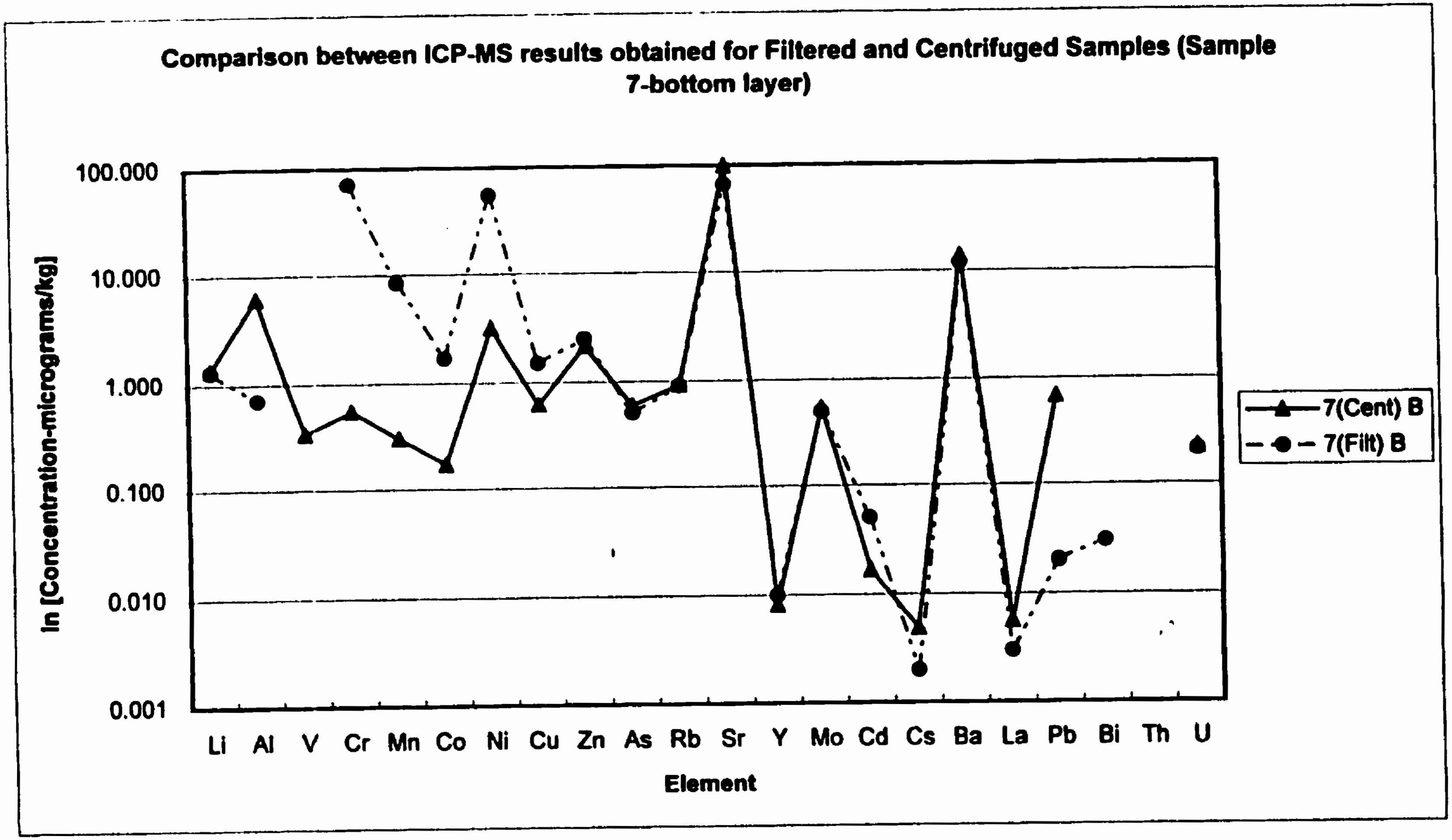


Figure 5.1 Comparison between ICP-MS values for Filtered and Centrifuged Samples (Sample Site 7)

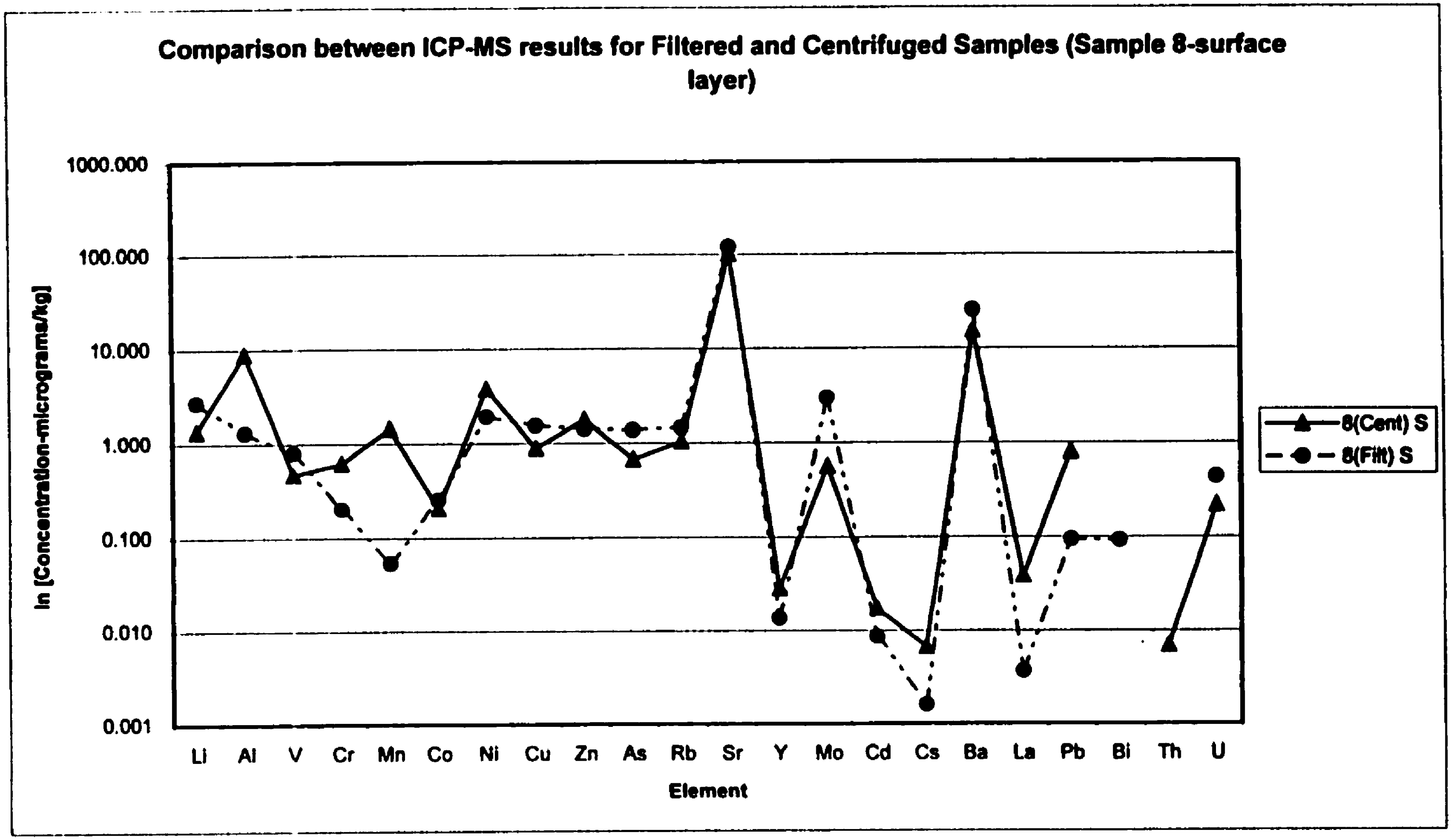


Figure 5.2 Comparison between ICP-MS values for Filtered and Centrfuged Samples (Sample Site 8)

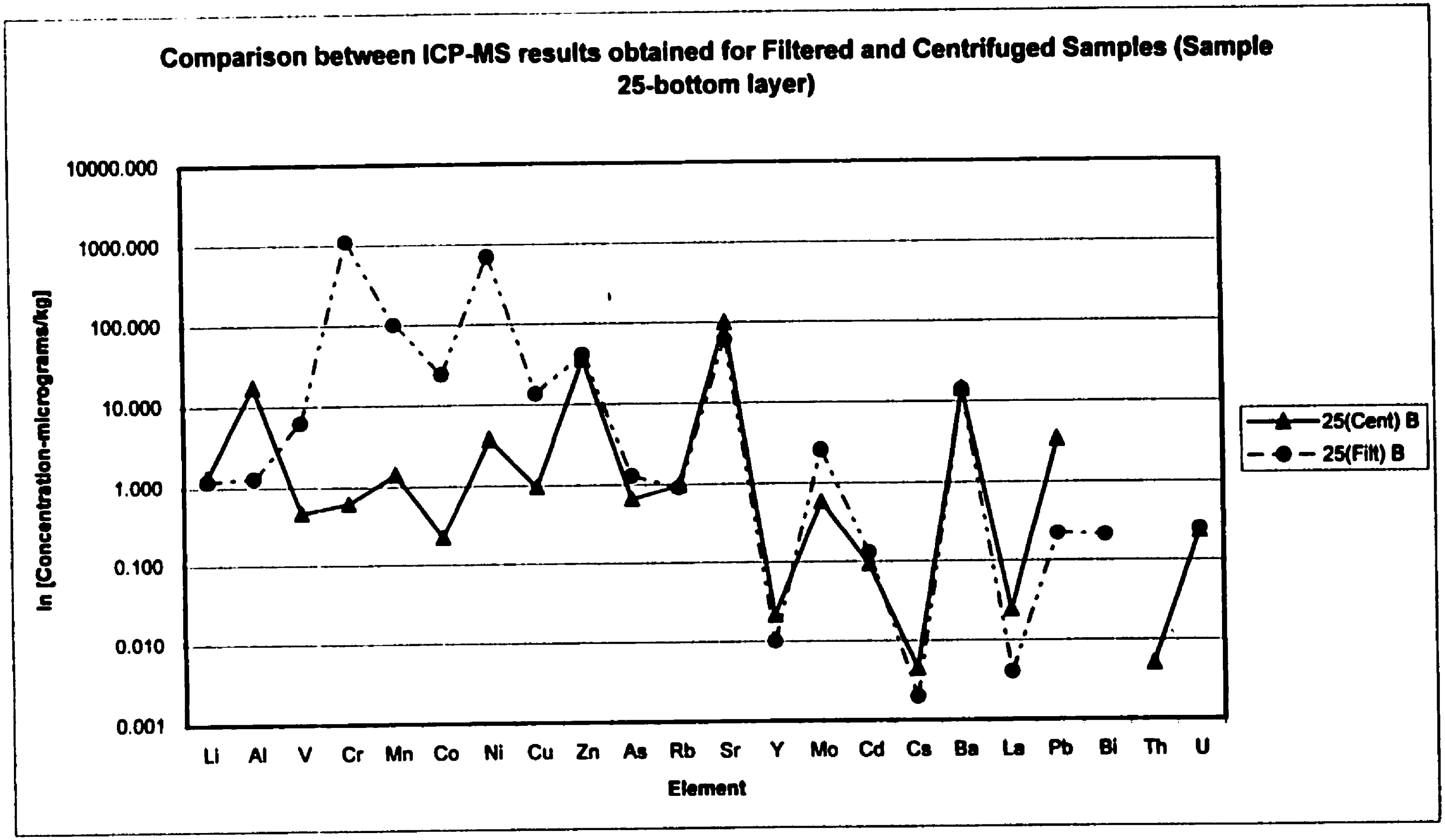


Figure 5.3 Comparison between ICP-MS values for Filtered and Centrifuged Samples (Sample Site 25)

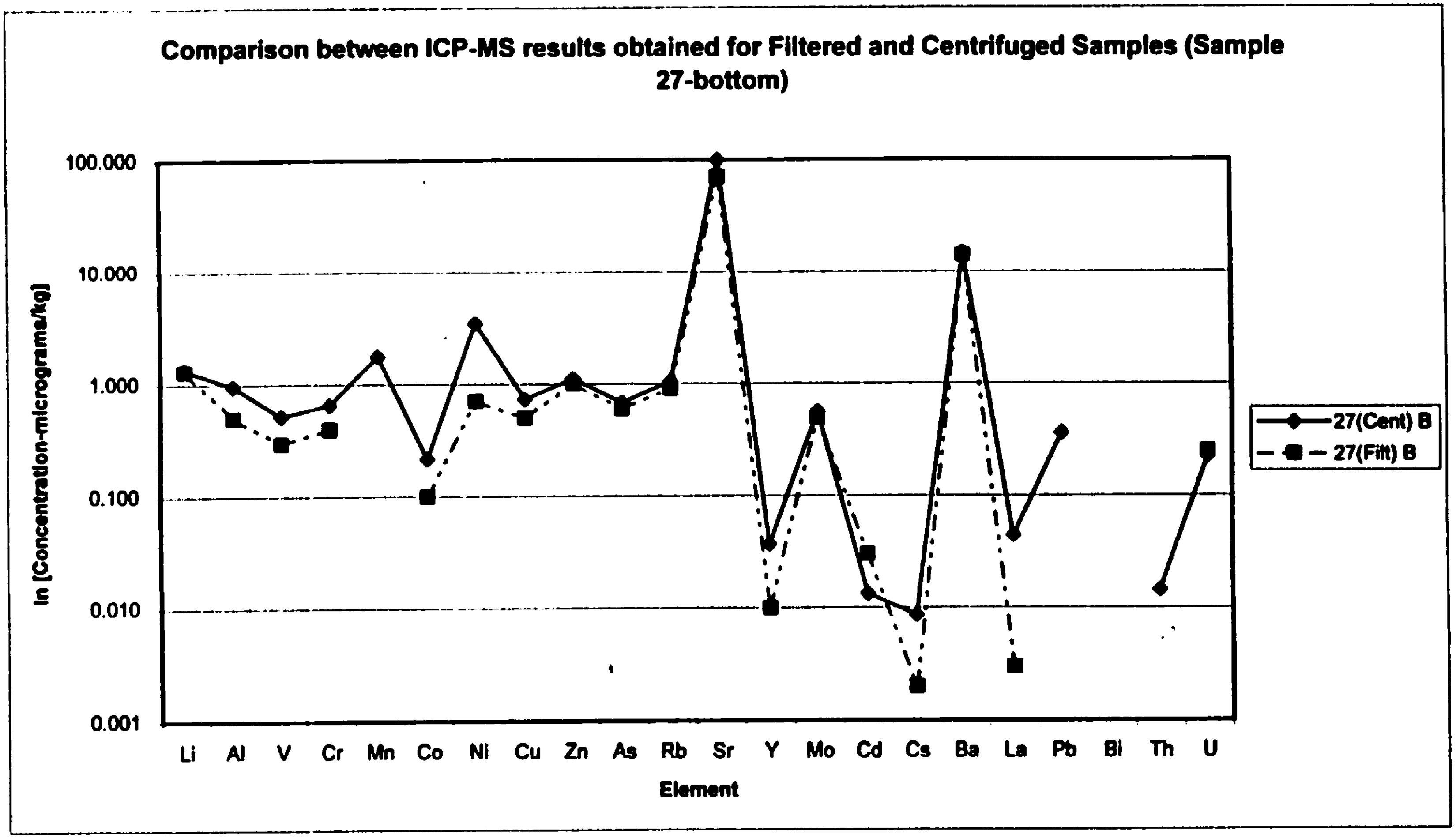


Figure 5.4 Comparison between ICP-MS values for Filtered and Centrfuged Samples (Sample Site 27)

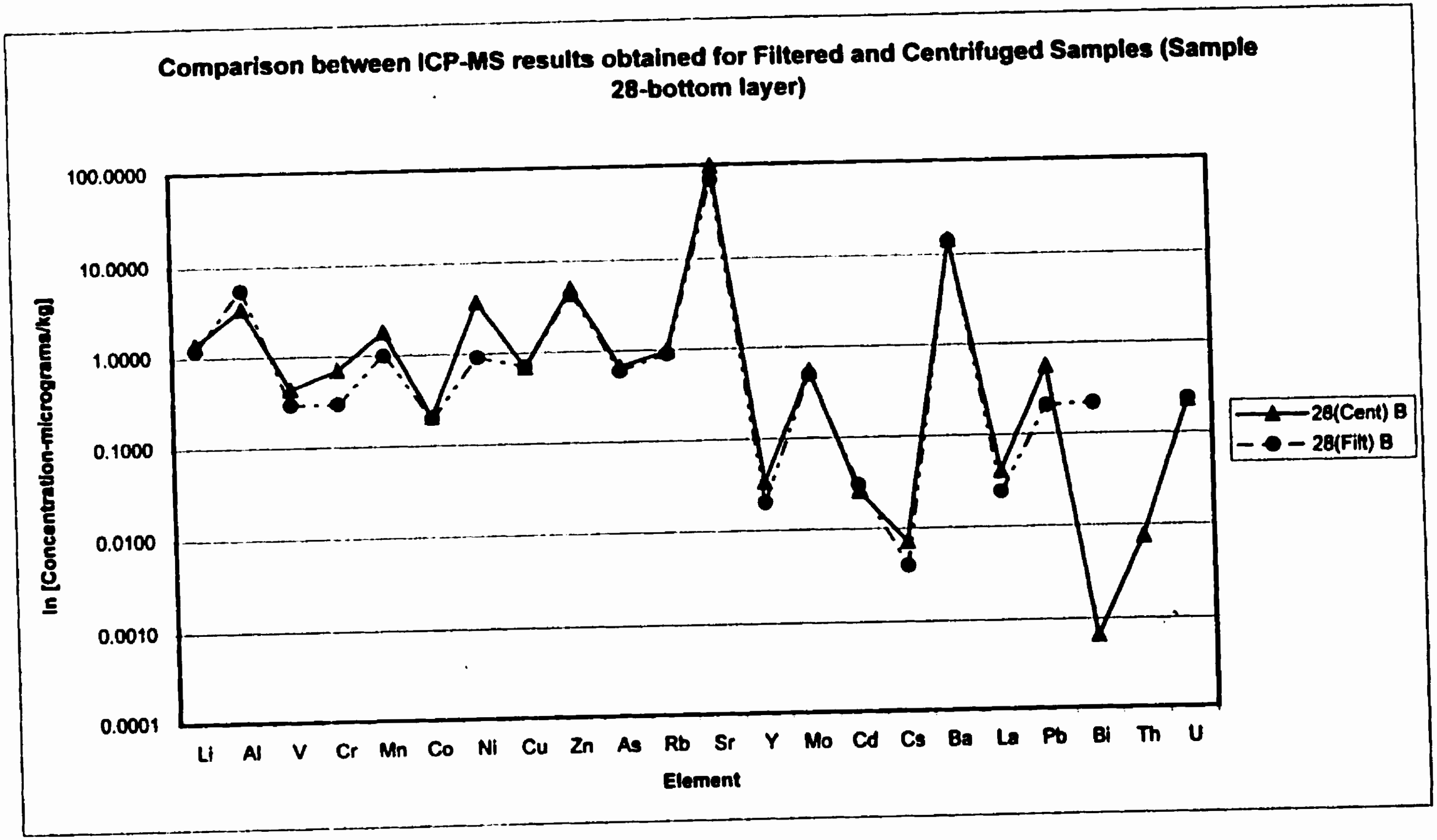


Figure 5.5 Comparison between ICP-MS values for Filtered and Centrifuged Samples (Sample Site 28)

method for obtaining "dissolved" concentrations) but where removed by the strong centrifuging.

5.4 RESULTS AND DISCUSSION OF WATER QUALITY MODELLING OF LAKE ST. CLAIR WATERS

A water quality model of the Lake St. Clair waters was constructed using the Water Quality Analysis Program (WIN/WASP+). The model was firstly run for steady state. For the steady state simulations constant concentrations of the selected metals are assumed to be entering the lake from the St. Clair River. Values for these concentrations were calculated from results obtained for samples from sites 3, 5, 6 and 7 (Table 5.3). The next step was running the model for no input of contaminants, i.e. only "clean" water entering the lake. The third step was running the model for present conditions using data from analysis of samples collected during the geochemical survey. The modelling focussed on three metals i.e. Sr, Mo and Cd. The results of these modelling procedures are given below.

5.4.1 STEADY STATE MODEL

Steady state models were simulated for initial concentrations and in coming waters from the St. Clair River for Sr, Mo and Cd. The results are discussed below. Time taken to achieve steady state is discussed for Segment 7. The water in Segment 7 drains into the Detroit River. The time taken for this segment to achieve steady state gives the time for the whole of the lake to achieve steady state.

STRONTIUM

A steady state model was run for Lake St. Clair for Sr. Initial concentrations were taken from various sites present in the particular segments. The model was run for a nominal starting date of January 1, 1998. Concentrations of incoming waters from the St. Clair River were taken as 68 micrograms/kg (Table 5.3). The purpose of this model was to determine the time the lake to achieve a steady state concentration. The results of this simulation can be seen in Figure 5.6a. Average concentration of Sr in Segment 7 increased and decreased for a period of two weeks before reaching steady state after 4 weeks. The initial increase was due to the high concentrations of Sr in water from the Clinton River flushing out of the system.

MOLYBDENUM

A similar steady state model was run for Lake St. Clair for Mo. Concentrations of incoming waters from the St. Clair River were taken as 0.54 micrograms/kg (Table 5.3). The results of this simulation for Segment 7 can be seen in Figure 5.6b. Average concentration of Mo in Segment 7 decreased and increased for a period of 8 days before finally reaching steady state after 2 months.

CADMIUM

A steady state model was also run for Lake St. Clair for Cd. Concentrations of incoming waters from the St. Clair River were taken as 0.05 micrograms/kg. The results of this simulation can be seen in Figure 5.6c. Average concentration of Cd in Segment 7 increased initially for the first three days and then decreased steadily before reaching steady state after 5 weeks.

Figure 5.6a

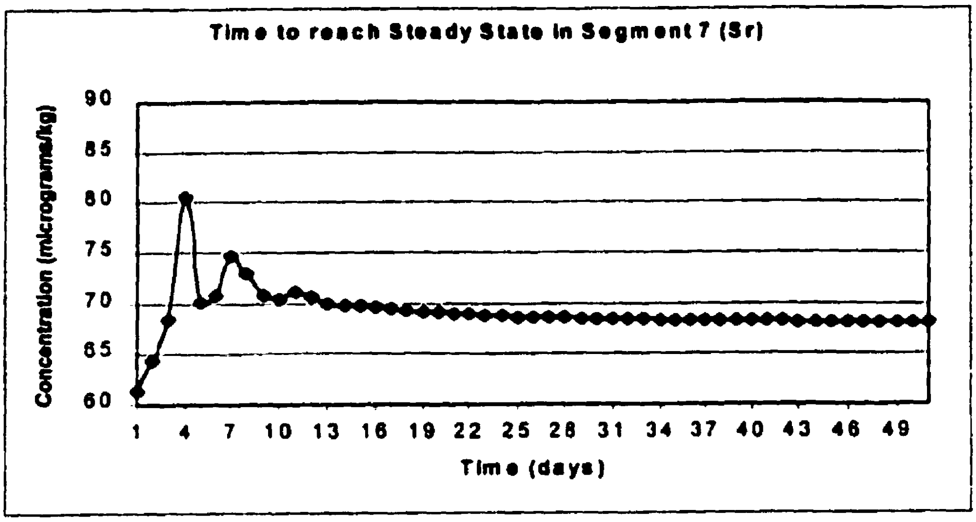


Figure 5.6b

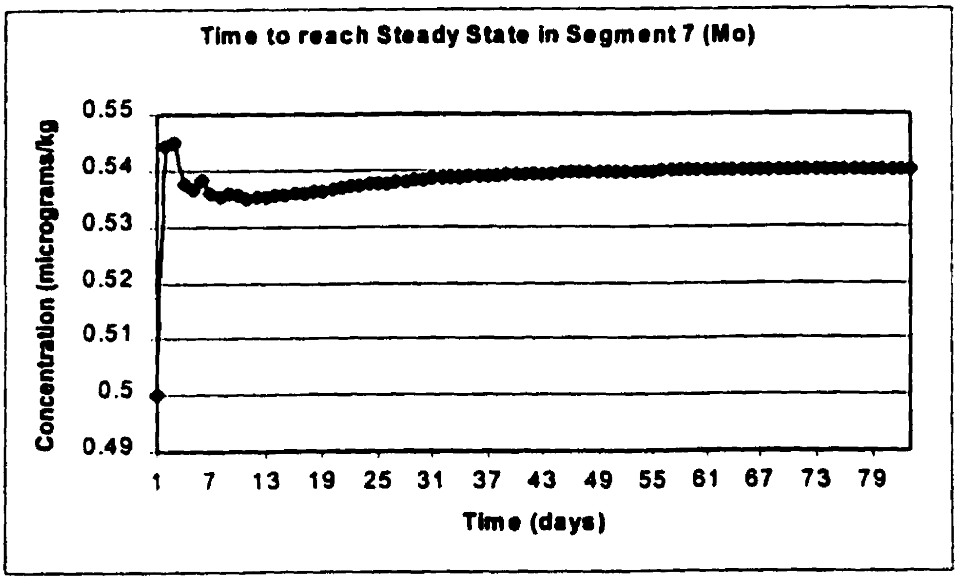
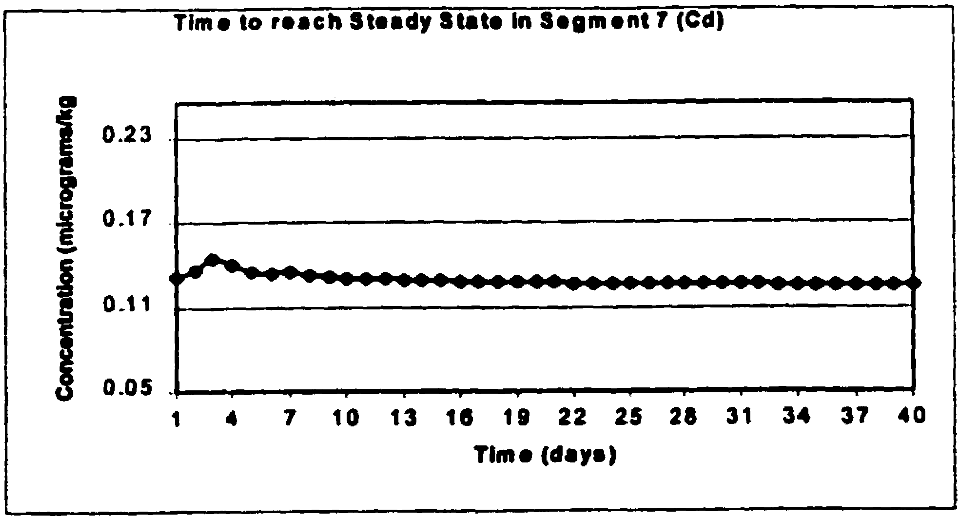


Figure 5.6c



5.4.2 REDUCTION TIME OF PRESENT CONCENTRATIONS

The WIN/WASP+ model was then used to estimate the time for the present metal contaminants to flush out totally from the lake. Again the simulations were run taking January 1, 1998 as the nominal starting date. The results of these simulations for Sr, Mo and Cd are discussed below.

STRONTIUM

Decay of Sr concentrations with time as predicted by the WIN/WASP+ model are given in Figures 5.7 for Segments 3,4 and 7 respectively. Segment 3 is discussed because water from both the Clinton and St. Clair Rivers is entering it. Segment 4 is discussed because it is the largest segment. Segment 7 is discussed due to the fact that the water in this segment drains into the Detroit River and the time taken for Sr to flush out of this segment more depicts the time for the whole of the lake to flush out Sr. Since the decay is exponential the concentration would reach exactly zero after an infinite time. But the results do tell us when the concentration will reach a relatively infinitesimally small amount. Flushing out time depends on the volume of the segment as well as water velocity in each segment. Also in some of the segments it is seen that initially there are increases in concentration before decreases set in. This is so because of the fact that there is connectivity between the segments and the concentration changes in each are not independent of the others. Water in each segment is interacting and mixing with water of the other segments. Segmentation was performed for modelling purposes but does not indicate independent water systems across the lake.

Figure 5.7a

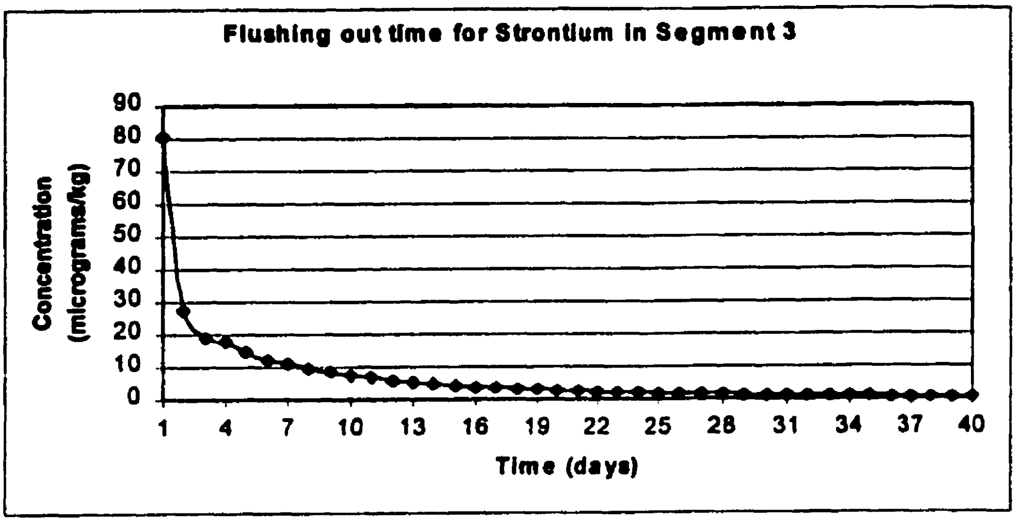


Figure 5.7b

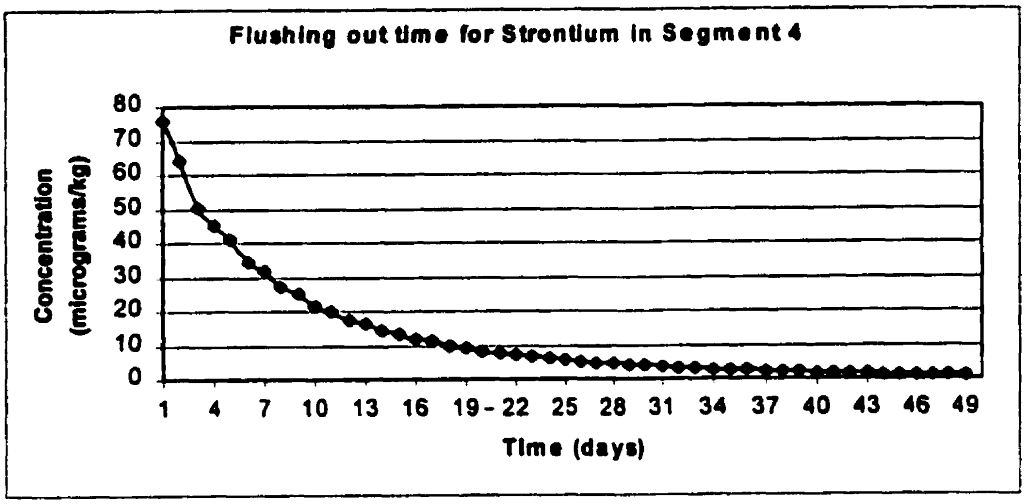


Figure 5.7c

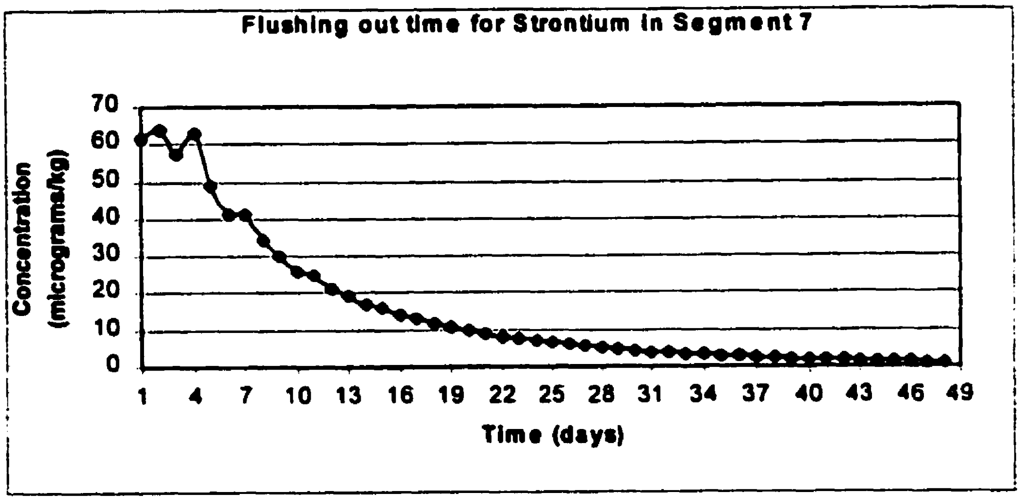


Figure 5.7a depicts the decay of Sr concentrations in Segment 3. It is noted that for the first few days there is a sharp decrease in concentration after which the rate of decay is steadier and flushing out is completed in 40 days. In Segment 4 the flushing out takes place almost exponentially as can be seen in Figure 5.7b. Total time taken for flushing out is estimate as 49 days. Segment 7 shows some interesting results (Figure 5.7c). Initially there is an increase in concentration of up to 65 micrograms/kg. Then there is a sharp decrease after which again there is a sharp increase. This all takes place within 7 days. After a few weeks there is again a slight increase and then the decrease in concentration continues uninterrupted. Total flushing out time is approximately 76 days.

MOLYBDENUM

Decay of Mo concentrations with time as predicted by the WIN/WASP+ model are given in Figures 5.8 for Segments 3,4 and 7 respectively.

Figure 5.8a depicts the decay of Mo concentrations in Segment 3. The decay of concentration takes place approximately exponentially, flushing out is approximately completed in 50 days. In Segment 4, Mo concentration, flushes out roughly exponentially as can be seen in Figure 5.8b. Total time taken for flushing out is estimate as 50 days. Segment 7 shows some interesting results. Initially there no decrease in concentration. Then there is a sharp increase after which there again is a slight increase after 5 days. After this increase, almost steady decrease in concentration of Mo sets in. This all takes place within 7 days. This can be seen in Figure 5.8c. After a few weeks there is again a slight increase and then the decrease in concentration continues uninterrupted. Total flushing out time is approximately 50 days.

Figure 5.8a

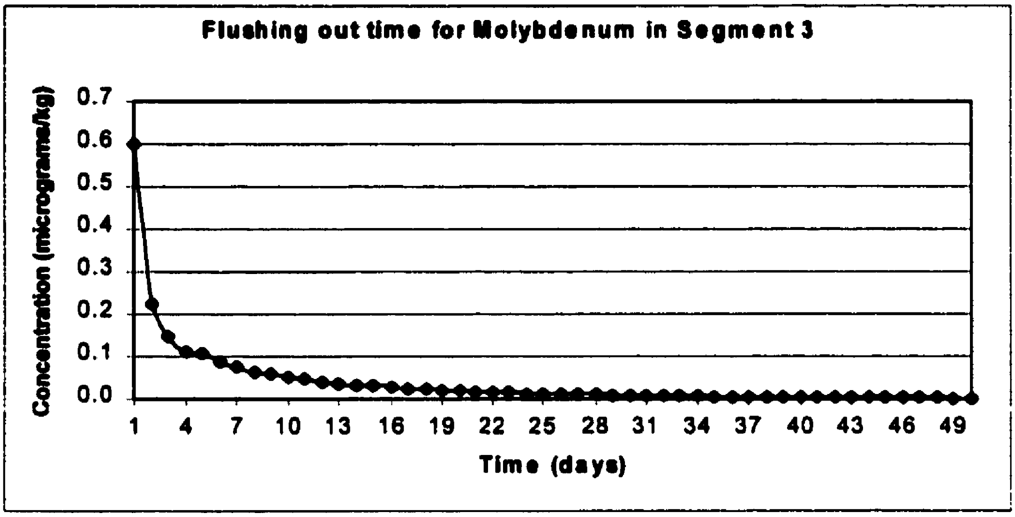


Figure 5.8b

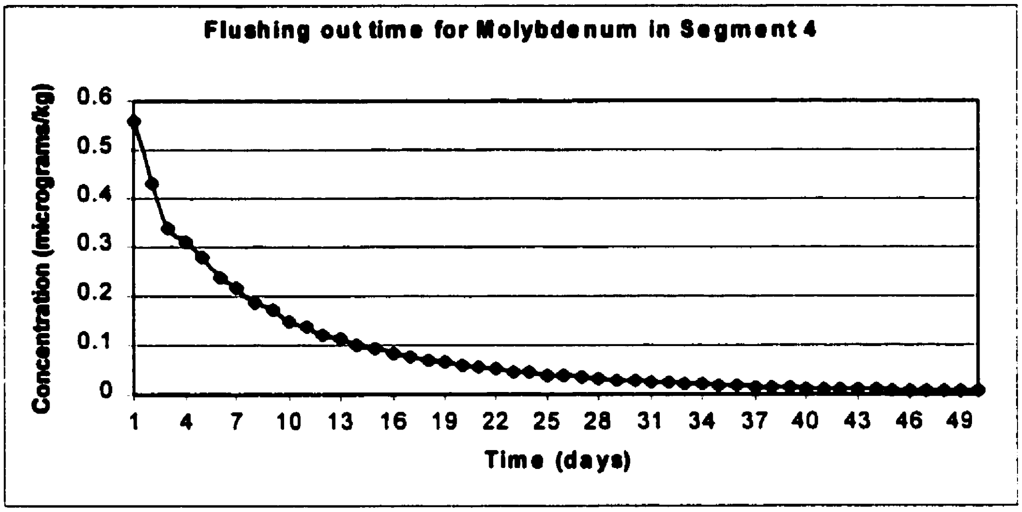
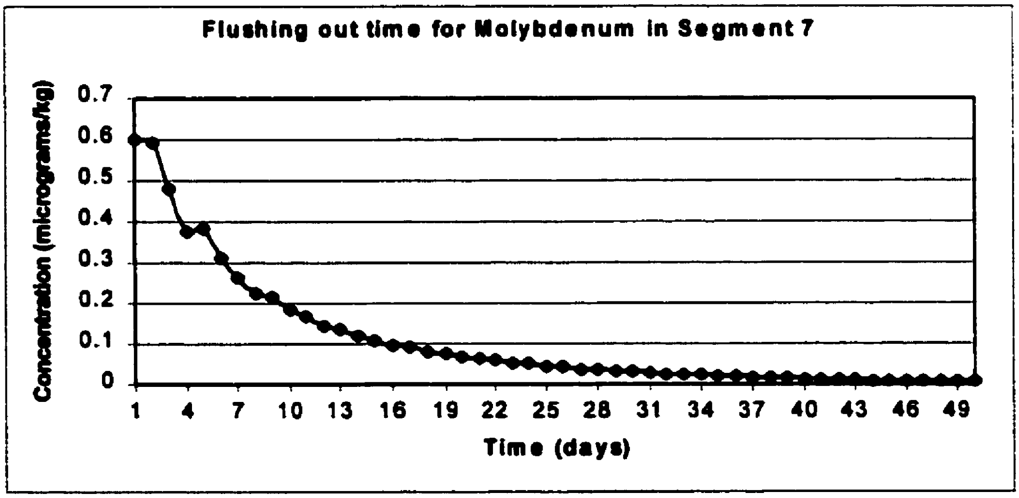


Figure 5.8c



CADMIUM

Decay of Cd concentrations with time as predicted by the WIN/WASP+ model are given in Figures 5.9 for Segments 3,4 and 7 respectively.

Figure 5.9a depicts the decay of Cd concentrations in Segment 3. It was seen that Cd concentration decreased exponentially. Decay is relatively steady and approximately total flushing out is completed in 41 days. In Segment 4, after a drastic increase in concentration from 0.02 micrograms/kg to almost 0.12 micrograms/kg, the flushing out takes place more or less exponentially as can be seen in Figure 5.9b. Total time taken for flushing out is estimated as 51 days. In Segment 7 initially there is an increase in concentration of up to 0.10 micrograms/kg. After which there is a sharp decrease which steadies out after a period of 8 days. This can be seen in Figure 5.9c. The concentration of Cd then decreases steadily. Total flushing out time is approximately 49 days.

Summarizing the results discussed in this sub-section, it was observed that if pollution of the lake was to totally halted, it would take almost three weeks for the lake to flush out substantially. Contamination levels would decrease to infinitesimally small amounts in 7 weeks. It was also found that Sr levels decrease at a slower rate as compared to Mo and Cd.

5.4.3 COMPARISON BETWEEN OBSERVED AND PREDICTED CONCENTRATIONS

The WIN/WASP+ simulated model of Lake St. Clair was used to run a simulation of what were thought to be the present conditions to predict average concentrations that should ideally be present in the different segments of the lake. Atmospheric deposition,

Figure 5.9a

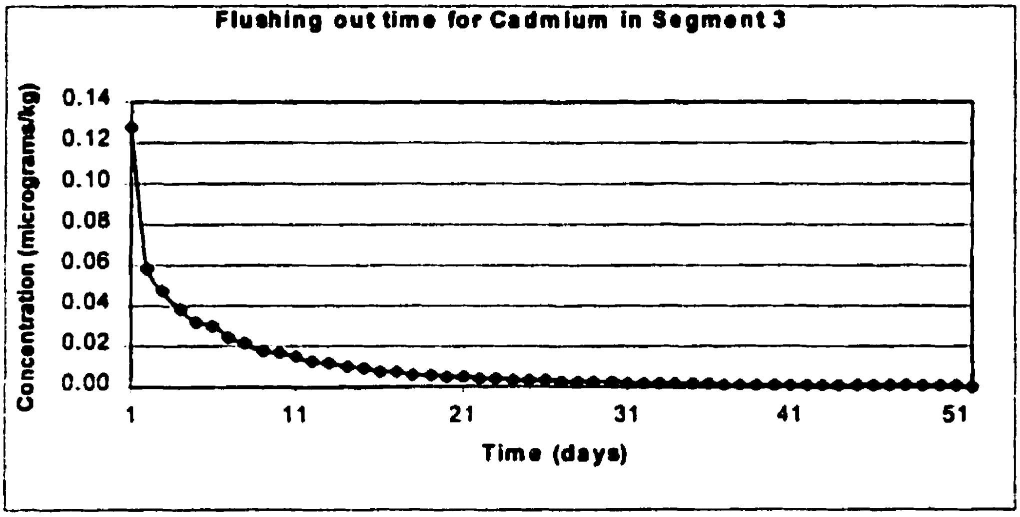


Figure 5.9b

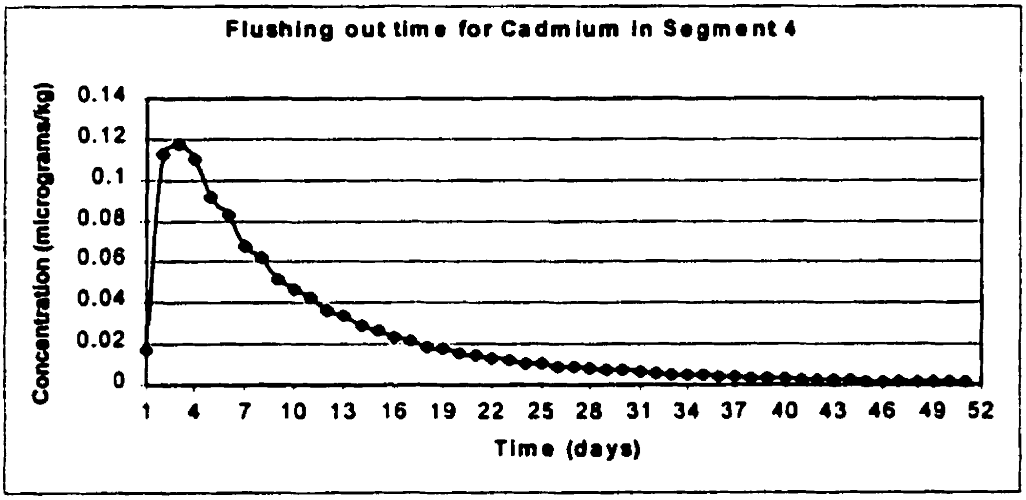
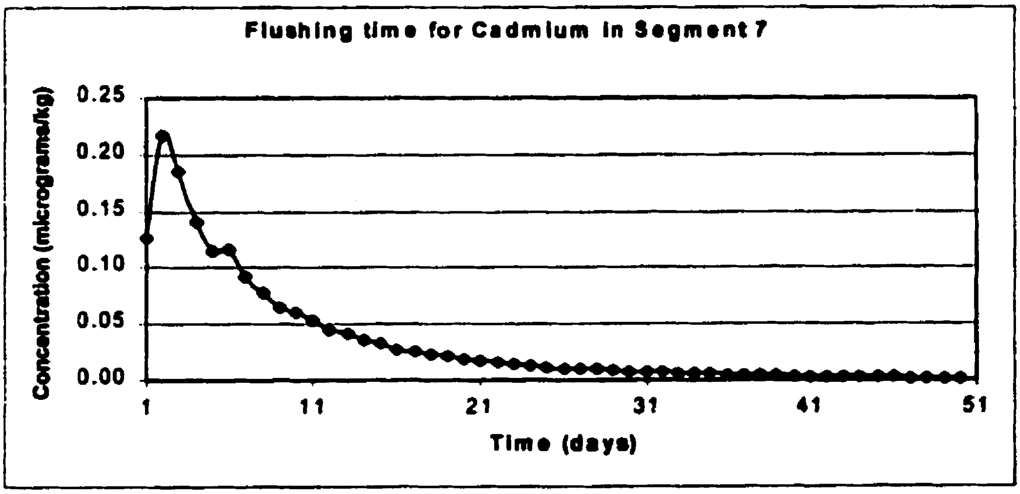


Figure 5.9b



surface run off, sediment re-suspension and sources other than the St. Clair and Clinton Rivers were ignored. Concentrations of water from these two rivers were taken from results of the survey. Water samples were actually taken from the St. Clair River whereas in the case of the Clinton River results of the analysis performed on the water sample from site # 8 near the mouth of the Clinton River were used to assume concentrations from the Clinton River. Flow of water from the Clinton River was taken as 2% of the amount of flow from the St. Clair River. This value was determined from the handbook on Lake St. Clair (Bolsenga and Herdendorf, 1993). These simulations were run for Sr, Mo and Cd. The comparisons between observed and predicted results are discussed below.

STRONTIUM

The observed and predicted average concentrations of Sr are given in Table 5.4. Figure 5.10 depicts the histogram for this comparison. In Segment 1 the average observed concentration was 82 micrograms/kg whereas the predicted concentration is 68 micrograms/kg. In Segment 2 observed concentration was 87 micrograms/kg and in Segment 3 the observed concentration was 79 micrograms/kg. Predicted concentrations in Segments 2 and 3 are 68 and 89 micrograms/kg. Thus in Segments 1 and 2 predicted concentrations were less than observed observations whereas in Segment 3 the opposite was the case. In Segments 4,5 and 6 the observed average concentrations were 75, 70 and 90 micrograms/kg whereas the predicted concentrations in these segments were 82, 86 and 80 micrograms/kg. Thus it can be seen that predicted values in Segments 4 and 5 were higher than those observed in the survey. In the case of Segment 6 observed values were higher. Observed values for Segments 7,8,9 and 10 were 64, 90, 68 and 63 whereas

Segment	Observed Concentration	Predicted Concentration
1	82	68
2	87	68
3	79	89
4	75	82
5	70	86
6	90	80
7	64	83
8	90	82
9	68	82
10	63	80

Table 5.4 Comparison between observed and predicted concentrations of Strontium (micrograms/kg)

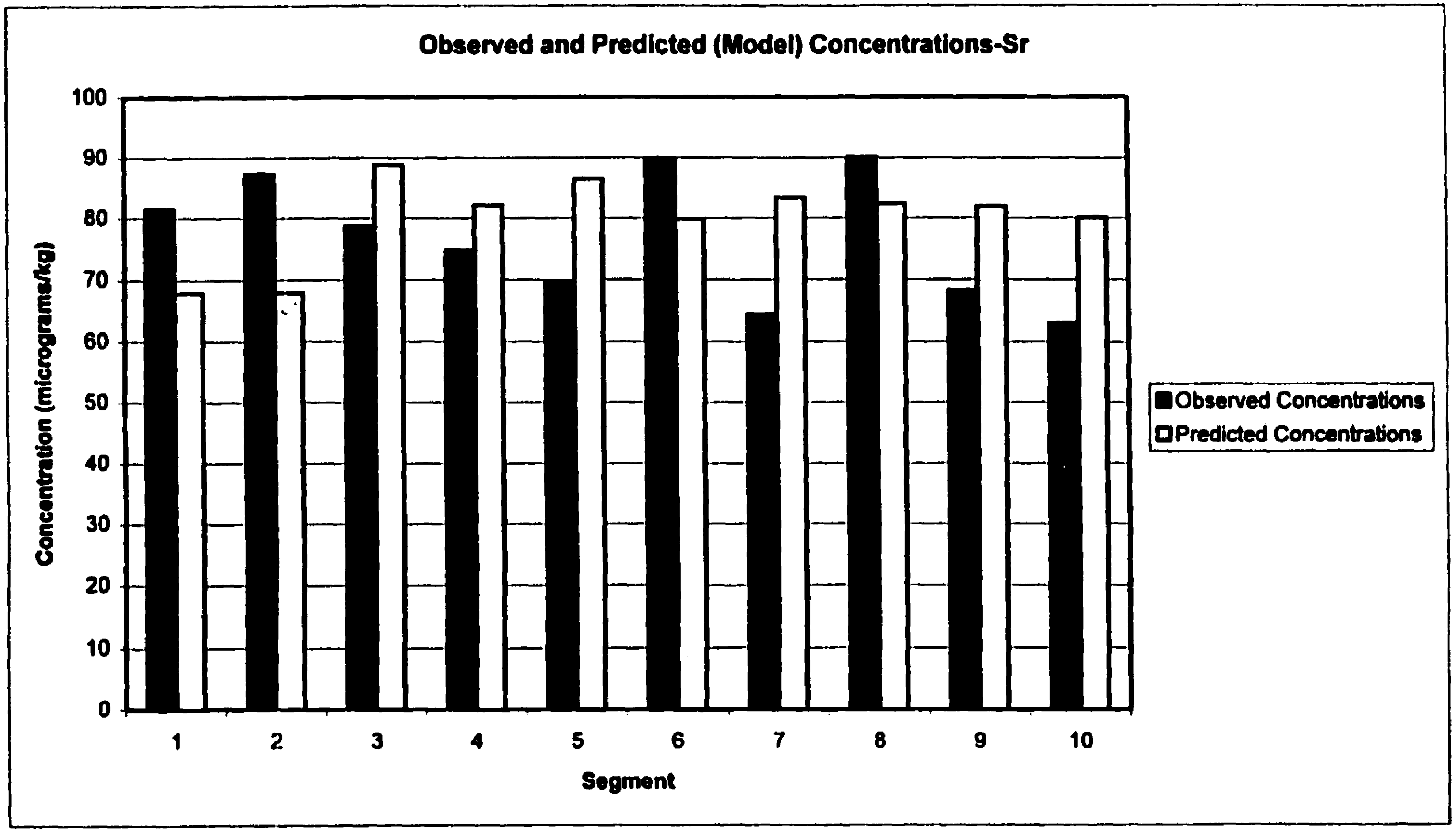


Figure 5.10 Comparison between Observed and Predicted Concentrations for Segments (Sr)

predicted values for these segments were 83, 82, 82 and 80 micrograms/kg respectively. Thus it can be seen that observed values were higher in Segments 7, 9 and 10 while in Segment 8 the opposite was the case.

MOLYBDENUM

The observed and predicted average concentrations of Mo are given in Table 5.5. Figure 5.11 depicts the histogram for this comparison In Segment 1 the average observed concentration was 0.8 micrograms/kg whereas the predicted concentration is 0.5 micrograms/kg. In Segment 2 the observed concentration was 0.8 micrograms/kg and in Segment 3 the observed concentration was also 0.8 micrograms/kg. Predicted concentrations in Segments 2 and 3 are 0.5 and 1.5 micrograms/kg. Thus in Segments 1 and 2 predicted concentrations were less than observed observations but higher for Segment 3. In Segments 4,5 and 6 the observed average concentrations were 0.5, 0.5 and 1.6 micrograms/kg whereas the predicted concentrations in these segments were 1.3, 1.4 and 1.3 micrograms/kg. Thus it can be seen that predicted values in Segments 4 and 5 are greater than observed in the survey whereas in Segment 6 the opposite is true. Observed values for Segments 7,8,9 and 10 were 0.6, 0.5, 0.5 and 0.6 whereas predicted values for these segments were 1.3, 1.2, 1.2 and 1.3 micrograms/kg respectively. Thus it can be seen that observed values were lower in Segments 7, 8, 9 and 10.

CADMIUM

The observed and predicted average concentrations of Cd are given in Table 5.6. Figure 5.12 depicts the histogram for this comparison. In Segment 1 the average observed concentration was 0.06 micrograms/kg whereas the predicted concentration is 0.05 micrograms/kg. In Segment 2 observed concentration was 0.03 micrograms/kg and in

Segment	Observed Concentration	Predicted Concentration
1	0.79	0.54
2	0.84	0.54
3	0.78	1.54
4	0.51	1.26
5	0.51	1.44
6	1.62	1.32
7	0.60	1.32
8	0.52	1.28
9	0.50	1.28
10	0.60	1.32

Table 5.5 Comparison between observed and predicted concentrations of Molybdenum (micrograms/kg)

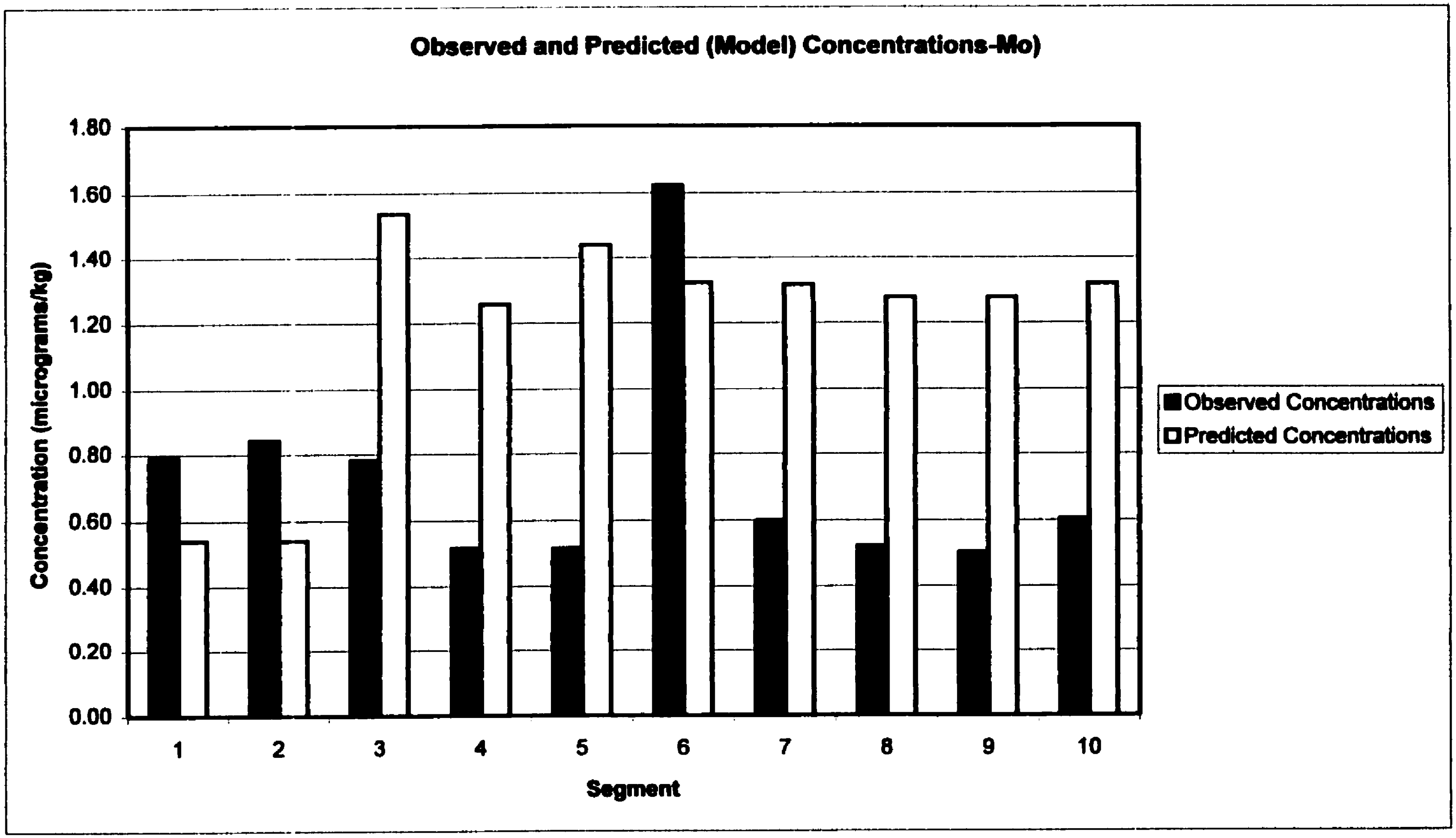


Figure 5.11 Comparison between Observed and Predicted (Model) Concentrations Segmentwise

Segment	Observed Concentration	Predicted Concentration
1	0.06	0.05
2	0.03	0.05
3	0.04	0.06
4	0.22	0.06
5	0.06	0.06
6	0.05	0.06
7	0.06	0.06
8	0.18	0.06
9	0.29	0.06
10	0.10	0.06

Table 5.6 Comparison between observed and predicted concentrations of Cadmium (micrograms/kg)

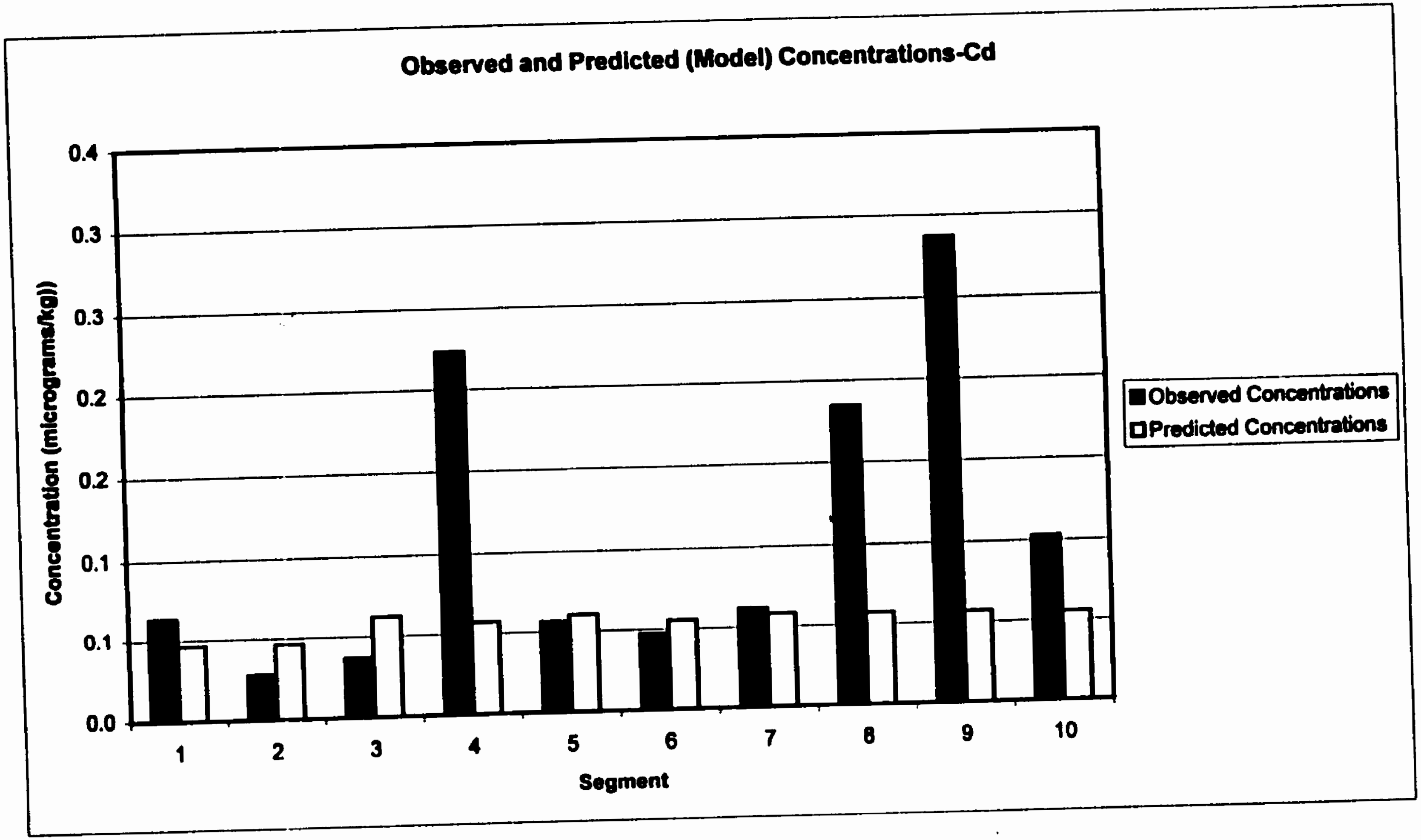


Figure 5.12 Comparison between Observed and Predicted (Model) Concentrations Segmentwise-Cd

Segment 3 the observed concentration was 0.04 micrograms/kg. Predicted concentrations in Segments 2 and 3 are 0.05 and 0.06 micrograms/kg. Thus in Segments 2 and 3 predicted concentrations were greater than observed observations whereas in Segment 1 the opposite was the case. In Segments 4,5 and 6 the observed average concentrations were 0.22, 0.06 and 0.05 micrograms/kg whereas the predicted concentrations in these segments were 0.06, 0.06 and 0.06 micrograms/kg. Thus it can be seen that the observed value in Segments 4 was higher than that predicted by the model. In the case of Segment 5 and 6 observed and predicted values were very close. Observed values for Segments 7,8,9 and 10 were 0.06, 0.18, 0.29 and 0.10 micrograms/kg whereas predicted values for these segments were 0.06 in each case. Hence observed values were higher in Segments 8, 9 and 10 while in Segment 7 both predicted and observed values concurred.

There are two main possibilities to that account for the differences in values. One is that in some segments re-suspension from the sediments has increased the concentration where the values observed are higher than those predicted. Chapra (1997) writes that waves on a water body's surface caused by winds causes sub-surface water to move in circular eddies, whose energy is dissipated at the bottom. This stirs up the sediments, which are re-suspended in the water. This may cause the metals attached to the suspended solids to be desorbed in the water. This would lead to a higher observed concentration. The same phenomenon may explain instances of lower observed concentrations. The sorption of the dissolved metals to form complex ligands also known as chemical sorption, may be taking place with the metals being adsorbed on to the surfaces of suspended particles, which may settle at the bottom or have been filtered out. Strumm and Morgan (1996) write that adsorption, the accumulation of matter at the solidwater interface, is the basis for most surface-chemical processes. They further state that atoms, molecules and ions exert forces on each other at the interface causing surface complex reactions like surface hydrolysis resulting in the formation of coordinate bonds at the surface of the suspended sediments between metals and with ligands. Ion exchange is also a factor that is affecting the concentration of metals dissolved in Lake St. Clair. Tomczak (1998) found, during his modelling of the St. Clair River that ship traffic increases the bottom stress and he concluded that it is another important factor in sediment re-suspension. This factor was also not taken into consideration during the modelling.

The second reason that may be behind these discrepancies is the concentration of in coming waters may not be constant and may vary with time. Thus, since a constant loading was used in the modelling a difference was found between simulated and observed values. As mentioned before atmospheric loading, surface runoff and other sources besides the St. Clair and Clinton Rivers were ignored. The differences observed in the modelling indicate that inputs are present, which are not in the model.

6- CONCLUSIONS

This study consisted of a geochemical survey and the simulation of a water quality model of Lake St. Clair. The following conclusions were made from this study.

1. The Clinton River appears to be a significant source of contamination to Lake St. Clair. Efforts should be made to monitor and treat the waste water that is allowed to drain in to the Clinton River.
2. Results revealed that Li, Se, As, Sr, Y, Ba, Sb, Th, Pb, Tl and Cs show limited dispersion in values. Maximum/mean ratios for these elements were less than 4. This proves that these elements are conservative in nature. Mo, Cd and La values showed some dispersion. Maximum/mean ratios for these elements were 4.8, 7.2 and 6 respectively. The Clinton River appears to be a source of Mo in the lake. As far as Cd was concerned atmospheric deposition is thought to be major factor. V, Cu and Zn displayed greater dispersion. Maximum/mean ratios for these elements were 15.5, 12.4 and 11.4 respectively. It was concluded that desorption is responsible. The largest amount of dispersion was seen for Co (26.8), Mn (31.6), Ni (32) and Cr (33.5). Desorption or unknown inputs in the lake may be responsible for these relatively large ratios.
3. Average concentrations obtained for Al, Ni, Mo, As, Se, Pb and Tl fall within the values prescribed by the Canadian Water Quality Guidelines for the Protection of Aquatic Life. Average concentrations of Chromium and Cd are higher than values given in the guideline.

4. Two hot spots of Cd were observed from the analysis of the filtered water samples. One of them was at sample site # 16 and the other 'hot spot' was found at sites # 12, 27. Analysis of the centrifuged water samples showed high amounts of certain metals at sample site # 25 as well as in the 'hot spots' found in the filtered data.
5. The water quality model predicts that it would take Lake St. Clair 6 weeks for the contamination levels to decrease to a negligible level if hypothetically speaking contamination of Lake St. Clair were to immediately stop.
6. Discrepancies between average concentrations predicted by the model for the different segments and actual observed average concentrations pointed towards other sources of contamination than those modelled, including a significant role for re-suspended sediments and possibly atmospheric input.
7. Further studies of this nature should be carried out determine seasonal changes in concentrations of the lake and also to conduct detailed mapping for concentrations of these metals. For this purpose sample sites should be strategically selected with special focus on waters near the Clinton River, the central area of the lake and within the St. Clair River Delta. The problem of collecting water samples over such a large and complex lake at a point in time also need to be solved if realistic models are to be constructed.

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APPENDICES

APPENDIX 1

SAMPLE SITE LOCATIONS

Sample Site #	**Latitude**	**Longitude**
	X-coord	**Y-coord**
1	42.66 degrees North	82.65 degrees West
2	42.65 degrees North	82.75 degrees West
3	42.63 degrees North	82.63 degrees West
4	42.63 degrees North	82.66 degrees West
5	42.63 degrees North	82.52 degrees West
6	42.63 degrees North	82.65 degrees West
7	42.61 degrees North	82.60 degrees West
8	42.59 degrees North	82.78 degrees West
9	42.60 degrees North	82.73 degrees West
12	42.45 degrees North	82.70 degrees West
13	42.45 degrees North	82.61 degrees West
14	42.40 degrees North	82.78 degrees West
15	42.40 degrees North	82.71 degrees West
16	42.40 degrees North	82.53 degrees West
17	42.40 degrees North	82.61 degrees West
18	42.35 degrees North	82.78 degrees West
19	42.35 degrees North	82.71 degrees West
20	42.65 degrees North	82.75 degrees West
21	42.35 degrees North	82.53 degrees West
22	42.50 degrees North	82.83 degrees West
23	42.5 degrees North	82.75 degrees West
24	42.5 degrees North	82.67 degrees West
25	42.46 degrees North	82.55 degrees West
26	42.46 degrees North	82.83 degrees West
27	42.42 degree North	82.71 degrees West
28	42.38 degrees North	82.88 degrees West

Sample site co-ordinates

APPENDIX 2

PREPARATION FOR SAMPLING

Before conducting the field sampling the field bottles were pre-washed. The washing took place in seven stages;

- firstly the bottles were soap washed
- next, the bottles were placed in an acid bath after rinsing with Milli-Q water
- they were then allowed to sit in the acid bath for 24 hours
- from the acid bath the bottles were transferred into a water bath which contained Milli-Q water
- there they remained for another 24 hours
- the water bottles were then removed from the water bath and rinsed with Milli-Q water
- finally the bottles were placed in a clean fume hood for 24 hours where they were allowed to dry in HEPA filtered air.

The acid bath consisted of 13% nitric acid. The Milli-Q water is prepared by the MILLIPORE, Milli-Q RG with output at 18.2 MΩ. The feed water for the Milli-Q system was distilled water.

APPENDIX 3

FILTRATION PROCEDURE

The steps involved in the filtration are as below:

- Rinsed filtration unit and filter paper with 1% HNO_3 3 times
- Rinsed filtration unit and paper with Milli-Q water 3 times
- Rinsed recovery flask (pyrex) with Milli-Q water 2 times
- Rinsed filtration unit, filter paper and recovery flask with water sample
- Filtered sample into the recovery flask from which the filtered sample was poured into 60mL polyethylene bottles
- Filter paper was removed and a new paper was placed for the next sample
- Cleaning procedure was repeated

The filtered water samples were then acidified as mentioned above.

APPENDIX 4

CENTRIFUGE PROCEDURE

The steps involved in sample preparation by centrifuging are given below:

- water samples were poured into acid washed 30mL polycarbonate test tubes, approximately 20mL of the water samples were poured for each run
- the tubes were spun in the centrifuge at a rate of 10,000 revolutions per minute for 10 minutes each
- the above two steps were repeated two times for each sample so as to make up 50mL
- after centrifuging the test tube containing the sample was emptied into acid washed storage bottles (60mL polyethylene bottles) with extreme caution so as not to disturb the sediment pellet left as a result of the centrifuging
- the centrifuged water samples were then treated with concentrated nitric acid and then stored again at a temperature of 4^0C for analysis. An amount equivalent to 1% of the total of the water sample of concentrated nitric acid was added (1% of 50mL = 0.5mL)
- the sample was then stored in a walk-in fridge at 4°C.

APPENDIX 5

ICP-MS DATA FOR FILTERED WATER SAMPLES

Sample Site	1	1	1	2	2	2	3	3	3	4	4	4	5	5	5	6	6	6	7	7	7	8	9	9	9
Layer	B	M	S	B	M	S	B	M	S	B	M	S	B	M	S	B	M	S	B	M	S	S	B	M	S
Lithium	1.24	1.33	1.24	1.25	1.24	1.25	1.22	1.26	1.27	1.21	1.25	1.28	1.15	1.22	1.35	1.19	1.19	1.19	1.27	1.24	1.18	2.75	1.29	1.31	1.33
Vanadium	0.32	0.27	0.27	0.24	0.25	0.24	0.23	0.27	0.25	0.27	0.21	0.22	0.22	0.28	0.32	0.19	0.19	0.19	<RDL	0.24	<RDL	0.75	0.24	0.26	0.27
Chromium	0.39	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	0.41	<RDL	0.50	<RDL	<RDL	<RDL	<RDL	0.43	<RDL	<RDL	<RDL	70.99	<RDL	231.28	<RDL	<RDL	<RDL	<RDL
Manganese	0.01	0.09	0.03	0.01	0.02	0.07	0.02	0.03	0.03	0.04	0.04	0.03	0.03	0.14	0.02	0.03	0.03	0.03	8.42	0.05	21.97	0.05	0.05	0.05	0.06
Cobalt	0.15	0.17	0.16	0.15	0.16	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.13	0.15	0.16	0.15	0.15	0.15	1.72	0.14	4.38	0.25	0.16	0.16	0.16
Nickel	2.72	3.03	2.67	2.58	2.63	2.62	2.70	2.65	2.65	2.69	2.68	2.65	2.66	2.70	2.79	2.80	2.80	2.80	61.07	2.58	146.49	4.32	2.74	2.74	2.74
Copper	0.62	0.99	0.75	0.70	0.72	0.77	0.52	0.54	0.63	0.82	0.66	0.75	0.67	0.57	0.57	0.53	0.53	0.53	1.49	0.56	2.79	1.54	0.62	0.62	0.63
Zinc	4.76	8.35	1.07	3.09	2.08	1.13	3.73	1.63	1.34	4.21	3.09	1.45	4.77	2.58	0.58	0.95	0.95	0.95	2.47	2.52	2.94	1.41	1.82	1.22	0.62
Rubidium	0.84	0.87	0.88	0.88	0.88	0.85	0.83	0.84	0.84	0.83	0.84	0.88	0.86	0.84	0.89	0.77	0.77	0.77	0.87	0.84	0.89	1.44	0.86	0.87	0.87
Arsenic	0.58	0.59	0.55	0.55	0.55	0.64	0.55	0.57	0.51	0.60	0.49	0.51	0.57	0.54	0.56	0.48	0.48	0.48	0.50	0.53	0.64	1.36	0.55	0.57	0.58
Strontium	71	70	72	69	70	68	68	68	68	68	68	69	67	67	70	63	63	63	67	67	66	119	71	71	72
Yttrium	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02
Molybdenum	0.49	0.51	0.53	0.51	0.52	0.49	0.48	0.48	0.49	0.46	0.50	0.48	0.48	0.48	0.53	0.43	0.43	0.43	0.53	0.44	0.82	2.95	0.49	0.50	0.51
Cadmium	0.10	0.10	0.02	0.02	0.02	0.06	0.06	0.14	0.02	0.03	0.02	0.01	0.80	0.15	0.00	0.01	0.01	0.01	0.05	0.04	0.15	0.01	0.01	0.01	<RDL
Antimony	0.12	0.12	0.11	0.13	0.12	0.12	0.11	0.12	0.11	0.12	0.12	0.12	0.11	0.11	0.12	0.12	0.12	0.12	0.11	0.12	0.12	0.22	0.12	0.12	0.12
Cesium	0.00	0.00	0.002	0.003	0.002	0.002	0.002	0.002	0.002	0.002	0.003	0.003	0.001	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.003	0.002	0.003	0.002	0.002
Barium	13.3	13.4	13.6	13.6	13.6	12.9	13.0	12.7	12.9	12.7	12.8	13.0	12.7	12.8	13.5	11.9	11.9	11.9	12.4	12.6	13.0	25.2	13.0	13.1	13.1
Lanthanum	0.00	0.00	0.002	0.004	0.003	0.003	0.004	0.004	0.005	0.003	0.005	0.005	0.003	0.004	0.003	0.004	0.004	0.004	0.003	0.004	0.004	0.004	0.004	0.003	0.003
Thallium	0.00	0.00	0.003	0.004	0.003	0.004	0.002	0.003	0.004	0.002	0.003	0.003	0.003	0.002	0.005	0.002	0.002	0.002	0.003	0.001	0.003	0.005	0.003	0.003	0.002
Lead	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	0.26	<RDL	0.21	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	0.29	<RDL	<RDL	<RDL	<RDL
Bismuth	<RDL	0.07	<RDL	<RDL	<RDL	0.09	<RDL	0.04	0.10	0.29	0.12	0.22	0.07	<RDL	<RDL	<RDL	<RDL	<RDL	0.03	0.13	0.30	0.09	0.01	0.01	0.01
Thorium	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	0.01	0.01	0.01	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL
Uranium	0.22	0.21	0.21	0.23	0.22	0.23	0.21	0.21	0.20	0.21	0.22	0.22	0.23	0.22	0.23	0.19	0.19	0.19	0.21	0.21	0.23	0.43	0.20	0.21	0.21

ICP-MS data for filtered water samples(micrograms/kg)

Sample Site	12	12	12	13	13	13	14	14	14	15	15	15	16	16	17	17	17	18	18	18	19	19	19	20	20
Layer	B	M	S	B	M	S	B	M	S	B	M	S	B	M	B	M	S	B	M	S	B	M	S	B	M
Lithium	1.06	1.14	1.14	1.25	0.99	1.01	1.07	1.09	1.07	1.25	1.16	1.18	1.16	1.24	1.19	1.16	1.14	1.25	1.12	1.26	1.21	1.15	1.35	1.29	1.19
Vanadium	0.35	0.39	0.55	0.60	0.33	0.36	0.23	0.33	0.29	0.37	0.33	0.31	0.39	0.37	0.25	0.29	0.33	0.23	0.31	0.32	0.35	0.36	0.39	0.38	0.36
Chromium	0.79	0.99	1.71	2.61	0.90	0.72	0.50	0.64	0.46	0.67	0.54	0.55	0.59	0.46	0.99	0.42	0.57	0.43	<RDL	0.33	0.49	0.48	0.65	0.56	0.50
Manganese	0.08	0.14	0.11	0.11	0.01	0.01	0.09	0.05	0.12	0.07	0.20	0.06	0.01	0.06	0.16	0.06	0.17	0.08	0.12	0.07	0.02	0.04	0.04	0.04	0.03
Cobalt	0.17	0.19	0.18	0.20	0.15	0.15	0.18	0.16	0.16	0.18	0.16	0.17	0.15	0.16	0.17	0.16	0.16	0.17	0.16	0.17	0.16	0.15	0.17	0.18	0.15
Nickel	3.43	4.44	4.39	3.41	2.50	2.58	3.08	2.87	2.78	2.95	2.82	2.71	2.34	2.52	2.89	3.08	2.89	2.78	2.85	2.81	2.64	2.61	2.80	2.73	2.47
Copper	0.66	0.89	1.86	0.75	0.49	0.60	0.92	0.60	0.65	0.81	0.62	0.63	0.68	0.65	0.73	1.07	0.63	0.81	1.01	0.66	0.65	0.63	0.61	0.68	0.62
Zinc	4.75	7.87	25.88	4.54	0.82	0.49	0.90	2.70	1.31	1.84	3.61	0.87	2.45	1.83	3.21	3.29	0.93	0.59	2.48	0.45	1.16	1.83	0.35	1.49	1.49
Rubidium	0.88	0.91	0.94	0.87	0.79	0.83	0.76	0.84	0.89	0.82	0.84	0.85	0.81	0.81	0.85	0.86	0.86	0.72	0.91	0.83	0.83	0.81	0.85	0.84	0.82
Arsenic	0.42	0.37	0.41	0.38	0.49	0.42	0.55	0.46	0.50	0.48	0.54	0.54	0.60	0.55	0.43	0.59	0.56	0.36	0.60	0.56	0.57	0.63	0.58	0.62	0.66
Strontium	88	93	95	96	91	86	91	85	84	79	78	75	87	82	82	84	84	84	87	86	88	85	84	84	85
Yttrium	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Molybdenum	0.50	0.51	0.55	0.57	0.52	0.52	0.54	0.53	0.53	0.53	0.50	0.50	0.52	0.57	0.51	0.51	0.53	0.54	0.56	0.57	0.55	0.56	0.53	0.56	0.55
Cadmium	0.08	0.29	0.72	0.32	0.06	0.15	0.16	0.94	0.24	0.01	0.01	0.004	0.05	0.58	0.06	0.42	0.24	0.15	0.09	0.01	0.08	0.01	0.01	0.51	0.07
Antimony	0.11	0.12	0.12	0.11	0.11	0.11	0.11	0.11	0.12	0.13	0.12	0.11	0.11	0.11	0.11	0.12	0.11	0.11	0.13	0.12	0.12	0.12	0.12	0.12	0.12
Caesium	0.003	0.003	0.004	0.002	0.001	0.001	0.002	0.002	0.002	0.001	0.002	0.003	0.001	0.001	0.001	0.002	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.000
Barium	14.0	13.4	13.6	13.2	13.0	12.9	15.5	13.0	13.2	13.7	13.7	13.3	12.2	13.0	12.7	13.0	12.7	12.0	12.8	12.7	12.8	12.8	12.7	13.0	12.8
Lanthanum	0.003	0.004	0.004	0.002	0.001	0.002	0.009	0.002	0.003	0.004	0.006	0.004	0.001	0.002	0.004	0.003	0.002	0.005	0.005	0.003	0.002	0.002	0.001	0.002	0.002
Thallium	0.006	0.005	0.004	0.002	0.003	0.003	0.005	0.004	0.005	0.003	0.004	0.003	0.002	0.002	0.004	0.003	0.003	0.003	0.003	0.003	0.003	0.004	0.003	0.004	0.004
Lead	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL
Bismuth	0.19	0.12	0.03	<RDL	<RDL	<RDL	0.11	0.16	0.00	0.06	0.03	0.04	<RDL	<RDL	0.00	0.02	<RDL	0.00	0.15	0.00	<RDL	0.03	<RDL	0.01	<RDL
Thorium	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL
Uranium	0.23	0.20	0.20	0.20	0.21	0.21	0.22	0.20	0.21	0.19	0.20	0.20	0.22	0.22	0.20	0.21	0.21	0.21	0.23	0.24	0.23	0.23	0.24	0.24	0.24

ICP-MS data for filtered water samples(micrograms/kg)

Sample Site	**20**	**21**	**21**	**21**	**22**	**22**	**23**	**23**	**23**	**24**	**24**	**24**	**25**	**25**	**25**	**26**	**26**	**26**	**27**	**27**	**27**	**28**	**28**	**28**	**RDL**
Layer	**S**	**B**	**M**	**S**	**M**	**S**	**B**	**M**	**S**	**B**	**M**	**S**	**B**	**M**	**S**	**B**	**M**	**S**	**B**	**M**	**S**	**B**	**M**	**S**	
Lithium	1.30	1.35	1.37	1.36	1.31	1.41	1.42	1.16	1.24	1.14	1.30	1.22	1.21	1.24	1.27	1.21	1.18	1.31	1.31	1.27	1.30	1.24	1.34	1.21	**0.003**
Vanadium	0.39	0.43	0.52	0.27	0.24	0.27	0.25	0.23	0.26	<RDL	0.25	0.22	6.16	<RDL	<RDL	0.25	0.26	0.29	0.31	<RDL	0.27	0.28	0.27	0.24	**0.06**
Chromium	0.49	0.50	0.64	0.43	0.39	0.45	<RDL	<RDL	<RDL	53.12	<RDL	<RDL	1106.73	595.07	83.41	<RDL	<RDL	<RDL	<RDL	297.64	<RDL	<RDL	<RDL	<RDL	**0.37**
Manganese	0.14	0.14	0.05	0.07	<RDL	0.01	0.01	<RDL	0.01	6.30	0.01	<RDL	100.55	55.32	10.10	0.60	<RDL	<RDL	<RDL	<RDL	<RDL	0.99	<RDL	<RDL	**0.103**
Cobalt	0.16	0.16	0.16	0.17	0.15	0.16	0.16	0.14	0.15	1.30	0.15	0.15	24.10	13.06	2.03	0.14	0.14	0.16	0.15	6.61	0.15	0.15	0.16	0.14	**0.004**
Nickel	2.66	2.67	2.61	2.81	2.76	2.87	3.01	2.43	2.47	46.46	2.78	2.56	813.14	442.37	71.61	2.45	2.49	2.65	2.60	222.50	2.63	2.56	2.67	2.34	**0.346**
Copper	0.80	2.82	0.71	0.75	0.70	0.64	0.84	0.75	0.60	1.21	0.70	0.63	13.60	7.67	1.75	0.63	0.53	0.56	0.54	4.11	0.55	0.72	0.46	1.57	**0.073**
Zinc	0.88	12.04	2.86	2.00	4.42	1.31	4.09	2.73	0.90	4.97	2.40	0.95	40.95	21.79	2.64	3.99	2.36	0.64	1.04	11.12	0.45	4.25	1.78	48.71	**0.78**
Rubidium	0.81	0.65	0.71	0.90	0.92	0.94	0.94	0.86	0.90	0.92	0.84	0.88	0.90	0.91	0.92	0.85	0.86	0.92	0.91	0.89	0.88	0.89	0.91	0.91	**0.003**
Arsenic	0.64	0.56	0.78	0.54	0.60	0.63	0.62	0.57	0.60	0.66	0.55	0.60	1.31	1.01	0.70	0.64	0.63	0.65	0.63	0.83	0.65	0.62	0.60	0.63	**0.09**
Strontium	83	86	84	73	70	70	72	69	70	71	68	69	61	66	71	68	69	71	71	68	70	69	72	70	**0.04**
Yttrium	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	**0.0004**
Molybdenum	0.54	0.71	0.73	0.49	0.54	0.53	0.52	0.47	0.51	0.55	0.47	0.50	2.62	1.62	0.62	0.47	0.51	0.51	0.49	1.07	0.51	0.54	0.53	0.53	**0.004**
Cadmium	0.15	0.02	0.09	0.01	0.05	0.01	0.02	0.01	0.25	0.03	0.06	0.22	0.13	0.09	0.06	0.28	0.12	0.01	0.03	0.40	0.71	0.03	0.02	0.09	**0.004**
Antimony	0.11	0.12	0.12	0.11	0.13	0.14	0.12	0.12	0.12	0.13	0.11	0.12	0.14	0.14	0.13	0.12	0.13	0.13	0.13	0.13	0.13	0.12	0.12	0.13	**0.01**
Caesium	0.001	0.001	0.001	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.002	0.002	0.002	0.002	0.002	0.004	0.003	0.003	**0.001**
Barium	12.4	12.1	12.1	13.3	14.1	14.2	14.2	13.4	13.6	13.8	13.1	13.4	13.5	13.7	13.9	13.8	14.3	14.5	14.3	13.8	13.8	14.0	14.0	14.0	**0.02**
Lanthanum	0.002	0.008	0.003	0.005	0.008	0.004	0.004	0.003	0.004	0.004	0.003	0.003	0.004	0.008	0.012	0.003	0.004	0.004	0.003	0.006	0.003	0.024	0.003	0.004	**0.001**
Thallium	0.004	0.003	0.004	0.003	0.005	0.003	0.004	0.004	0.005	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.005	0.004	0.004	0.005	0.005	0.004	**0.001**
Lead	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	0.22	<RDL	<RDL	<RDL	0.23	<RDL	<RDL	<RDL	0.19	0.21	<RDL	<RDL	**0.19**
Bismuth	0.04	0.03	0.12	<RDL	0.17	<RDL	0.12	0.00	0.14	<RDL	<RDL	0.01	0.21	0.16	0.11	0.07	0.27	<RDL	<RDL	0.19	0.21	0.22	<RDL	<RDL	**0.002**
Thorium	<RDL	<RDL	<RDL	<RDL	0.01	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	**0.001**
Uranium	0.24	0.29	0.29	0.21	0.24	0.24	0.26	0.23	0.23	0.24	0.22	0.23	0.25	0.25	0.25	0.24	0.25	0.25	0.25	0.25	0.24	0.24	0.24	0.25	**0.001**

ICP-MS data for filtered water samples(micrograms/kg)

APPENDIX 6

ICP-MS DATA FOR CENTRIFUGED WATER SAMPLES

Sample Site	1	1	1	2	2	2	3	3	3	4	4	5	5	5	6	7	7	7	8	9	9	9	12
Layer	S	B	M	S	B	M	B	M	S	B	M	S	M	B	S	M	B	S	S	S	M	B	M
Lithium	1.27	1.40	1.37	1.32	1.29	1.45	1.27	1.34	1.44	1.32	1.29	1.30	1.35	1.30	1.27	1.29	1.36	1.30	1.33	1.30	1.35	1.33	1.31
Vanadium	0.26	0.45	0.43	0.38	0.39	0.40	0.37	0.36	0.38	0.33	0.30	0.37	0.37	0.36	0.35	0.33	0.33	0.38	0.46	0.31	0.38	0.33	0.35
Chromium	0.83	0.47	0.51	0.53	0.51	0.52	0.56	0.51	0.51	0.49	0.46	0.55	0.54	0.51	0.51	0.56	0.54	0.56	0.61	0.55	0.49	0.88	0.56
Manganese	0.03	1.42	1.44	0.65	0.40	0.35	1.39	1.59	1.62	0.35	0.64	1.06	0.87	1.16	0.60	0.39	0.30	0.35	1.42	0.45	0.51	0.73	0.39
Cobalt	0.16	0.20	0.19	0.17	0.17	0.17	0.19	0.19	0.19	0.18	0.16	0.19	0.18	0.17	0.18	0.18	0.17	0.18	0.20	0.17	0.17	0.17	0.20
Nickel	3.28	3.30	3.53	3.39	3.40	3.12	3.55	3.33	3.35	3.50	3.28	3.40	3.30	3.17	3.50	3.43	3.16	3.45	3.73	3.30	3.19	3.88	4.38
Copper	0.54	0.76	0.96	0.68	0.75	0.83	0.71	0.64	0.67	0.68	0.63	0.69	0.64	0.60	0.62	0.70	0.61	0.69	0.88	2.00	0.64	0.60	0.97
Zinc	4.79	5.74	5.55	4.74	7.39	0.37	5.20	2.99	1.41	6.37	4.42	1.25	3.61	4.15	4.03	4.10	2.12	6.24	1.75	1.67	4.44	5.32	9.83
Arsenic	0.66	0.64	0.66	0.60	0.59	0.64	0.61	0.59	0.57	0.59	0.55	0.59	0.61	0.60	0.58	0.59	0.59	0.59	0.67	0.60	0.59	0.59	0.60
Rubidium	0.90	0.94	0.94	0.91	0.89	0.86	0.96	0.92	0.91	0.89	0.86	0.92	0.92	0.93	0.88	0.91	0.91	0.88	1.02	0.91	0.89	0.88	0.94
Strontium	96	97	96	97	95	104	99	95	96	95	94	97	98	96	95	97	99	96	100	98	96	94	102
Yttrium	0.00	0.03	0.02	0.01	0.02	0.01	0.02	0.03	0.03	0.01	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.03	0.01	0.01	0.02	0.02
Molybdenum	0.57	0.54	0.53	0.54	0.55	0.59	0.52	0.52	0.51	0.53	0.51	0.50	0.55	0.54	0.53	0.51	0.53	0.52	0.55	0.52	0.52	0.51	0.53
Cadmium	0.02	0.04	0.02	0.08	0.06	0.01	0.03	0.02	0.02	0.04	0.03	0.01	0.02	0.03	0.05	0.05	0.02	0.05	0.02	0.02	0.05	0.05	0.21
Caesium	0.002	0.006	0.005	0.004	0.003	0.001	0.006	0.007	0.006	0.003	0.003	0.004	0.004	0.004	0.003	0.003	0.005	0.002	0.007	0.002	0.003	0.003	0.003
Barium	14.24	14.31	14.26	14.04	14 02	13.30	14.30	14.00	13.68	13.70	13.52	14.07	13.96	14.07	13.83	13.88	13.78	13.85	15.06	13.80	14.02	14.01	14.30
Lanthanum	0.00	0.03	0.03	0.01	0.01	0.01	0.03	0.03	0.03	0.01	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.04	0.01	0.01	0.01	0.01
Lead	0.00	0.36	0.41	4.20	3.20	0.07	0.37	0.43	0.48	0.62	0.52	0.29	0.35	0.33	3.30	3.74	0.68	3.54	0.79	0.52	3.51	3.23	0.15
Bismuth	<RDL	0.0032	0.0010	<RDL	<RDL	<RDL	<RDL	<RDL	0.0021	0.0015	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	0.0008	<RDL
Thorium	0.0021	0.0090	0.0059	0.0022	0.0029	0.0024	0.0079	0.0074	0.0067	0.0016	0.0021	0.0069	0.0035	0.0064	0.0026	0.0022	0.0018	0.0012	0.0069	0.0019	0.0028	0.0031	0.0017
Uranium	0.27	0.24	0.23	0.19	0.24	0.26	0.22	0.22	0.23	0.23	0.23	0.22	0.23	0.24	0.22	0.22	0.22	0.23	0.21	0.23	0.23	0.22	0.24

ICP-MS data for centrifuged water samples(micrograms/kg)

Sample Site	12	13	13	13	14	14	15	15	15	15	15	16	16	17	17	17	17	18	18	18	19	19	20
Layer	B	M	S	B	S	M	S	S	M	B	B	B	M	B	B	B	M	B	M	S	M	B	B
Lithium	1.32	1.27	1.33	1.34	1.34	1.32	1.38	1.28	1.36	1.42	0.01	1.38	1.35	1.35	0.00	1.33	1.38	1.39	1.28	1.37	1.31	1.35	1.36
Vanadium	0.33	0.36	0.35	0.34	0.41	0.35	0.50	0.43	0.44	0.44	0.01	0.42	0.48	0.48	0.00	0.34	0.40	0.59	0.44	0.63	0.43	0.41	0.44
Chromium	0.63	0.56	0.50	0.54	0.56	0.50	0.66	0.83	0.57	0.56	0.05	0.50	0.55	0.68	0.04	0.50	0.52	0.71	0.54	0.55	0.59	0.50	0.63
Manganese	1.40	0.42	0.31	0.40	0.58	0.37	2.66	0.50	1.94	2.08	0.02	0.47	0.56	3.38	0.02	0.44	1.68	3.75	0.72	0.57	0.47	0.41	0.69
Cobalt	0.19	0.18	0.17	0.16	0.18	0.17	0.22	0.19	0.20	0.19	0.01	0.16	0.16	0.22	0.01	0.18	0.18	0.23	0.18	0.18	0.20	0.17	0.19
Nickel	4.31	3.51	3.43	3.03	3.51	3.36	3.91	3.88	3.63	3.47	0.05	3.04	3.14	3.90	0.02	3.72	3.60	3.89	3.35	3.44	3.67	3.35	3.50
Copper	2.07	0.74	0.79	0.66	0.73	0.94	0.84	0.71	0.89	0.83	0.02	0.86	0.82	0.91	<RDL	0.76	1.34	0.94	0.84	0.84	0.86	0.93	0.84
Zinc	29.89	3.57	0.72	1.59	5.11	2.04	2.88	2.82	2.88	2.33	0.26	1.73	2.74	2.71	0.13	5.26	3.56	0.80	1.45	0.57	1.68	1.26	1.41
Arsenic	0.58	0.58	0.57	0.58	0.63	0.61	0.63	0.67	0.61	0.65	0.00	0.68	0.67	0.64	0.00	0.59	0.62	0.77	0.69	0.67	0.69	0.65	0.69
Rubidium	0.96	0.88	0.89	0.89	0.94	0.91	1.05	0.96	1.01	1.02	0.00	0.87	0.88	1.01	0.00	0.91	0.96	0.97	0.92	0.90	0.92	0.88	0.91
Strontium	101	101	102	103	99	102	105	101	105	105	0	102	102	104	0	101	102	108	109	107	110	105	107
Yttrium	0.01	0.01	0.01	0.01	0.01	0.02	0.04	0.02	0.03	0.03	0.00	0.01	0.01	0.03	0.00	0.01	0.02	0.07	0.02	0.02	0.02	0.02	0.01
Molybdenum	0.54	0.56	0.55	0.57	0.55	0.55	0.56	0.57	0.55	0.55	0.01	0.58	0.58	0.55	0.01	0.54	0.55	0.57	0.59	0.60	0.59	0.59	0.60
Cadmium	0.39	0.26	0.16	0.12	0.03	0.03	0.08	0.01	0.05	0.03	0.00	0.04	0.03	0.08	0.00	0.06	0.39	0.02	0.02	0.01	0.02	0.01	0.35
Caesium	0.002	0.002	0.002	0.002	0.003	0.003	0.009	0.003	0.008	0.006	0.000	0.002	0.003	0.007	0.000	0.003	0.004	0.009	0.002	0.002	0.002	0.002	0.002
Barium	14.15	13.71	13.76	13.86	14.82	14.04	14.98	15.15	14.56	14.66	0.01	13.18	14.21	14.07	0.00	14.43	14.21	13.57	13.78	13.63	13.73	13.37	13.62
Lanthanum	0.01	0.01	0.01	0.01	0.01	0.01	0.05	0.01	0.03	0.04	0.00	0.01	0.01	0.04	0.00	0.01	0.02	0.08	0.02	0.01	0.01	0.01	0.01
Lead	0.22	0.17	0.12	0.20	0.96	0.13	0.24	0.24	0.24	0.21	0.01	0.11	0.41	0.33	0.01	0.13	0.39	0.20	0.10	0.12	0.06	0.20	0.21
Bismuth	<RDL	0.0009	<RDL	<RDL	0.0017	<RDL	<RDL	<RDL	0.0009	0.0015	<RDL	<RDL	0.0010	<RDL	<RDL	<RDL	<RDL	0.0011	0.0016	<RDL	<RDL	<RDL	<RDL
Thorium	0.0009	0.0023	0.0013	0.0111	0.0031	0.0014	0.0075	0.0026	0.0163	0.0075	0.0016	0.0040	0.0024	0.0085	0.0014	0.0120	0.0069	0.0101	0.0030	0.0030	0.0021	0.0043	0.0027
Uranium	0.24	0.23	0.24	0.25	0.23	0.24	0.23	0.23	0.24	0.24	<RDL	0.25	0.26	0.24	<RDL	0.25	0.26	0.25	0.25	0.26	0.24	0.25	0.25

ICP-MS data for centrifuged water samples(micrograms/kg)

Sample Site	20	20	21	21	21	22	22	23	23	23	24	24	24	25	25	26	26	27	27	28	28	28	RDL
Layer	M	B	M	S	B	S	M	B	S	M	B	M	S	S	B	M	B	M	B	M	S	B	
Lithium	1.35	1.39	1.43	1.48	1.54	1.30	1.34	1.37	1.41	1.35	1.32	1.35	1.40	1.32	1.33	1.28	1.35	1.39	1.34	1.33	1.36	1.37	0.01
Vanadium	0.47	0.42	0.62	0.61	0.61	0.44	0.41	0.44	0.42	0.46	0.38	0.39	0.38	0.50	0.46	0.53	0.49	0.57	0.52	0.44	0.44	0.44	0.01
Chromium	0.57	0.50	0.62	0.69	0.53	0.87	0.77	0.57	0.53	0.65	0.66	0.63	0.55	0.63	0.60	3.65	0.74	0.81	0.66	0.64	0.58	0.69	0.09
Manganese	0.75	0.57	0.63	0.73	0.98	0.84	0.94	1.62	1.43	1.44	1.12	1.60	1.19	1.32	1.41	3.15	1.76	3.34	1.77	1.19	1.07	1.76	0.03
Cobalt	0.20	0.17	0.17	0.18	0.17	0.19	0.18	0.19	0.19	0.21	0.20	0.18	0.18	0.21	0.22	0.47	0.24	0.25	0.22	0.20	0.19	0.20	0.01
Nickel	3.46	3.13	3.13	3.26	3.10	3.40	3.40	3.43	3.39	3.74	3.86	3.41	3.32	3.99	3.74	13.69	4.10	3.82	3.48	3.58	3.49	3.60	0.08
Copper	1.01	0.91	0.82	1.21	0.93	0.84	0.74	0.81	1.00	0.77	0.96	0.83	0.79	1.16	0.95	0.80	0.73	0.81	0.73	0.67	0.69	0.68	0.003
Zinc	1.92	0.53	2.69	8.31	2.10	4.01	9.97	5.37	1.95	4.18	8.71	8.50	4.81	7.37	35.71	6.11	2.95	2.16	1.11	2.76	0.88	4.88	0.94
Arsenic	0.70	0.69	0.82	0.82	0.84	0.67	0.63	0.65	0.67	0.69	0.63	0.62	0.60	0.66	0.65	0.67	0.68	0.72	0.68	0.66	0.64	0.66	0.004
Rubidium	0.88	0.86	0.75	0.76	0.73	1.04	0.95	0.97	0.97	1.02	0.97	0.97	0.93	0.97	0.96	1.04	1.05	1.10	1.05	0.98	0.96	0.97	0.01
Strontium	106	105	106	107	107	102	95	97	97	102	98	98	96	99	99	101	102	102	99	99	96	97	0.38
Yttrium	0.02	0.02	0.01	0.01	0.02	0.03	0.02	0.03	0.03	0.03	0.02	0.03	0.02	0.02	0.02	0.03	0.03	0.06	0.04	0.02	0.02	0.03	0.0003
Molybdenum	0.59	0.61	0.78	0.78	0.80	0.56	0.54	0.55	0.56	0.58	0.53	0.53	0.52	0.58	0.57	0.58	0.55	0.58	0.56	0.55	0.55	0.55	0.004
Cadmium	0.07	0.15	0.03	0.04	0.04	0.04	0.08	0.03	0.02	0.02	0.06	0.07	0.04	0.08	0.09	0.03	0.02	0.02	0.01	0.02	0.01	0.03	0.004
Caesium	0.002	0.002	0.002	0.002	0.002	0.005	0.006	0.006	0.007	0.006	0.005	0.006	0.005	0.004	0.004	0.007	0.007	0.012	0.009	0.006	0.006	0.007	0.000
Barium	13.68	13.50	12.61	12.41	13.16	15.10	14.49	14.39	14.07	14.56	14.40	14.03	13.73	14.57	14.23	15.30	15.12	14.90	14.64	14.06	13.83	14.32	0.04
Lanthanum	0.01	0.01	0.01	0.01	0.02	0.03	0.03	0.03	0.04	0.03	0.03	0.04	0.03	0.05	0.02	0.03	0.03	0.08	0.04	0.03	0.03	0.04	0.0003
Lead	0.47	0.21	0.23	0.39	0.16	3.05	5.92	0.32	0.45	0.45	3.53	4.42	3.26	5.15	3.36	0.59	0.53	0.37	0.36	0.34	0.33	0.56	0.37
Bismuth	0.0154	<RDL	0.0029	0.0007	<RDL	<RDL	<RDL	<RDL	<RDL	0.0009	<RDL	<RDL	<RDL	<RDL	<RDL	0.0016	<RDL	0.0014	<RDL	0.0017	<RDL	0.0007	0.0007
Thorium	0.0038	0.0046	0.0042	0.0037	0.0045	0.0067	0.0061	0.0089	0.0081	0.0084	0.0054	0.0077	0.0046	0.0036	0.0050	0.0077	0.0148	0.0158	0.0143	0.0068	0.0071	0.0075	0.001
Uranium	0.25	0.25	0.31	0.30	0.32	0.22	0.23	0.24	0.23	0.22	0.22	0.23	0.23	0.23	0.23	0.22	0.23	0.23	0.22	0.22	0.23	0.23	0.001

ICP-MS data for centrifuged water samples(micrograms/kg)

APPENDIX 7

ICP-OES DATA FOR FILTERED WATER SAMPLES

Sample Site	1	1	1	2	2	2	3	3	3	4	4	4	5	5	5
Layer	B	M	S	S	B	M	B	M	S	B	M	S	B	M	S
Calcium	26800	26200	26500	26700	26900	26500	26400	26900	26800	25900	26400	26300	25900	26400	26900
Potassium	959	910	949	953	<RDL	1008	887	1002	934	918	909	914	948	988	2327
Sodium	3881	3850	3927	3776	3841	3834	3827	3767	3797	3826	3797	3754	3841	3867	3891
Magnesium	7695	7495	7497	7725	<RDL	7703	7681	7489	7384	7375	7803	7589	7789	7462	12298
Zinc	<RDL	<RDL	<RDL	<RDL	3	<RDL	4	1	1	9	<RDL	5	5	3	<RDL
Sample Site	6	6	6	7	7	7	8	9	9	9	12	12	12	13	13
Layer	S	M	B	B	M	S	S	B	M	S	B	M	S	B	M
Calcium	24200	24200	24200	26300	25700	26500	34700	26600	26600	26700	27200	26200	26600	26700	26900
Potassium	727	920	993	971	994	950	969	1037	987	980	1016	1002	1043	985	955
Magnesium	6842	7655	7577	7453	7430	7561	7452	7603	7583	7848	7689	7694	7860	7878	7754
Sodium	3907	3838	3511	3854	3787	3814	21992	5005	5015	3895	3924	3959	4059	3909	3957
Zinc	3	1	<RDL	3	2	4	1	2	1	1	<RDL	1	21	<RDL	<RDL
Sample Site	13	14	14	14	15	15	15	16	16	17	17	17	18	18	18
Layer	S	B	M	S	B	M	S	B	M	B	M	S	B	M	S
Calcium	26600	29700	27100	26900	26800	27400	27000	25700	24600	26200	27700	27100	27700	27500	27000
Potassium	965	1068	953	987	944	927	947	929	932	998	998	938	889	1092	1148
Magnesium	7843	7825	7571	7561	7548	7782	7377	7852	7990	7890	7890	7377	7899	7894	8082
Sodium	3958	4003	3927	3972	3820	3887	3769	<RDL	<RDL	3822	3980	4019	23	<RDL	4144
Zinc	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	<RDL	2	<RDL
Sample Site	19	19	19	20	20	20	21	21	21	22	22	23	23	23	24
Layer	B	M	S	B	M	S	B	M	S	M	S	M	S	B	S
Calcium	28100	27400	27900	26900	26300	26700	25700	25300	26400	27800	28100	27100	26900	28000	26500
Potassium	940	961	962	997	967	907	929	991	952	1022	988	1009	999	988	1027
Magnesium	8098	7987	8158	8110	7906	7968	8200	8350	8568	7579	7771	7478	7745	7942	7888
Sodium	4122	4182	4369	4164	4151	4123	4081	4151	4357	3890	3980	3895	3937	4039	<RDL
Zinc	<RDL	<RDL	<RDL	1	<RDL	<RDL	<RDL	<RDL	1	4	3	4	<RDL	<RDL	<RDL
Sample Site	24	24	25	25	25	26	26	26	27	27	27	28	28	28	RDL
Layer	M	B	B	M	S	B	M	S	B	M	S	B	M	S	
Calcium	26000	27000	27800	27300	26800	26800	27500	27700	27600	27500	27700	27300	27400	27600	
Potassium	1011	1045	1059	963	1028	997	1013	923	945	972	<RDL	<RDL	<RDL	<RDL	50
Magnesium	7794	7772	7649	7882	7757	7808	7921	7690	7756	7784	<RDL	<RDL	<RDL	<RDL	1
Sodium	3833	3888	4151	3973	3981	3954	3873	3874	3915	3817	3864	3915	3882	3851	50
Zinc	2	7	55	3	4	2	<RDL	<RDL	<RDL	5	1	<RDL	4	<RDL	1

ICP-OES Data for filtered water samples(micrograms/kg)

APPENDIX 8

ICP-OES DATA FOR CENTRIFUGED WATER SAMPLES

Sample Site	12	12	12	13	13	13	14	14	14	15	15	15	16
Layer	B	M	S	B	M	S	B	M	S	B	M	S	B
Calcium	26700	27700	27300	27800	27300	26900	27700	27500	26900	27500	27500	27400	23800
Iron	4	3	3	3	3	3	32	5	34	41	42	68	8
Potassium	843	884	919	883	829	881	856	819	898	881	881	864	785
Magnesium	7704	7932	7841	7916	7849	7742	7861	7931	7742	7776	7767	7777	7679
Sodium	3839	4013	3996	3896	3894	3868	3899	3901	3929	3805	3777	3825	3914
Sample Site	16	17	17	17	18	18	18	19	19	19	20	20	
Layer	M	B	M	S	B	M	S	B	M	S	B	M	
Calcium	24000	27300	26100	26500	24200	26500	25800	26500	25800	25700	24600	24700	
Iron	13	61	28	6	8	85	13	10	5	4	7	7	
Potassium	822	882	869	873	821	899	891	897	854	853	834	947	
Magnesium	7896	7752	7548	7426	8133	7841	7935	7874	7738	7857	8248	8314	
Sodium	4048	3795	3793	3697	4275	3918	4028	3998	3902	3989	4780	4854	

ICP-OES data for centrifuged water samples(micrograms/kg)

APPENDIX 9

MODELLING PARAMETERS/CONSTANTS

Volumes calculated for the model are given below and were calculated by GIS analysis using the software ARCVIEW.

Segment	**Volume(m^3)**
1	36955100
2	122426000
3	202292000
4	1187240000
5	402494000
6	406629000
7	345922000
8	776197000
9	639113000
10	588624000

An average velocity of 0.3m/s was used for the lake. Average velocities for the segments used for the model are given below. These values were assumed on the basis of current patterns in the lake. The source of this data was Dr. Ibrahim's PhD dissertation.

Segment	**Velocity(m/s)**
1	0.3
2	0.3
3	0.5
4	0.6
5	0.6
6	0.1
7	0.5
8	0.4
9	0.2
10	0.1

Hydraulic flow and total amount of water input was also taken from the same source.

A list of remaining parameters and constants as well as their sources is given below.

Parameter/Constant		**Source**
Water temperature		Measured in field
Rearation coefficient		Chapra, 1997
Dissolved organic carbon		Chapra, 1997
Chlorophyll-a		Chapra, 1997
PH		Measured in field
Bacteria concentration		Chapra, 1997
Light extinction coefficient		Chapra, 1997

Log$_{10}$ of octanol-water partition coefficient		Strumm and Morgan, 1996
Log$_{10}$ of organic carbon partition coefficient		Strumm and Morgan, 1996
Partitioning parameter of chemical onto solids		Strumm and Morgan, 1996
Solids independent partition coefficient for sorption		Strumm and Morgan, 1996
Molecular weight		Periodic table
Ionization constants		Chapra, 1997

APPENDIX 10

DEVELOPMENT OF GEOGRAPHIC INFORMATION SYSTEM DATABASE

To carry out this project it was imperative to create database that contained the desired geographical information concerning the project area. Also coverages were required of Lake St. Clair to carry out the model execution and to view results on a map/coverage. The GIS also was used to make calculations of area, volumes and depths for the lake and each of the individual segments. The GIS analysis of the study area was carried out in five steps.

Step # 1

In the first step the NOAA map from 1995 for Lake St. Clair was digitized in ArcInfo. The boundaries were initially outlined and then nodes were added for the depth points of the lake. The coverage was then edited for errors. Segment outlines were digitized. The final coverage was cleaned and saved for the next steps.

Step # 2

A database was created for the lake in ArcView. Depth values for each of the depth nodes were added. Afterwards the coverage was contoured according to the bathymetry of the lake. The contoured maps were split up into the separate maps for each of the individual in ArcInfo.

Step # 3

The individual contoured maps of each of the segments were imported into MapInfo. Here areas for polygons were obtained.

Step # 4

The areas were used to calculate volumes for the segments in the database in ArcView. The final coverage and database was saved for use in the modelling procedures.

Step # 5

During the entry of data into the WIN/WASP+ the GIS coverage and database were studied using ArcExplorer.

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