Trace Metals in Surface Sediments of St. Clair River and Lake St. Clair, Michigan

by

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A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science
(Environmental Science)
in the University of Michigan-Dearborn
2017

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DEDICATION

To my wife Rasha Alhashem, my children Ahmed Alsaffar and Ameer Alsaffar,
and to my parents.

ACKNOWLEDGMENTS

I wish to express my sincere gratitude to my thesis advisor Dr. Sonia M. Tiquia-Arashiro for her continued guidance, advice, and support throughout the progress of this study.

I express my gratitude to the examining committee, Dr. Kent S. Murray and Dr. Yiwei Deng for their constructive criticism.

I would like to thank Mr. Fred J. Hoitash, Director, Environmental Sciences Division, RTI Laboratories, Inc for the assistance during the analytical process

I would like to express my appreciation to the U.S. Army Corps of Engineers, Detroit District, RTI laboratories, Inc and Future Net Group, Inc for their assistance and support.

Thank you

Ali Alsaffar

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
AOC	Area of Concern
ASTM	American Standard Test Method
AWCD	Average Well Color Development
CDF	Confined Disposal Facility
CLPP	community-level physiological profiles
cm	centimeter
COD	Chemical oxygen demand
CV	Coefficient of Variation
CY	Cubic Yards
DO	Dissolved Oxygen
E	East
GPS	Global Positioning System
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ID	Identification
kph	kilometer per hour
LaMP	Lake Erie Lakewide Management Plan
LC	Lake St. Clair
LWD	Low Water Datum
LOQ	Limit of Quantification
m	meter
MDEQ	Michigan Department of Environmental Quality
MDNR	Michigan Department of Natural Resources
mg/kg	Milligrams/Kilograms
mmHg	millimeter of mercury
N	North
NOAA	National Oceanic and Atmospheric Administration
NPDES	National Pollutant Discharge Elimination System
OME	Ontario Ministry of the Environment
PEC	Probable Effects Concentration

SC	St. Clair River
SD	Standard Deviation
TEC	Threshold Effect Concentration
TOC	Total Organic Carbon
USACE	United States Army Corps of Engineers
USCS	Unified Soil Classification System
USEPA	Unites States of Environmental Protection Agency
W	West
WHO	World Health Organization
WRDA	Water Resource Development Act
wt.	weight
WWTP	Wastewater Treatment Plant

ABSTRACT

St. Clair River and Lake St. Clair form the waterway connecting channel from Lake Huron to the Detroit River then drains into Lake Erie. They provide water supply for millions of people, and critical habitat for maintaining biodiversity in the aquatic environment. Previous studies reported that the contamination level in St. Clair River and Lake St. Clair sediments exceeded the allowable limits, and designated the connecting channels as Areas of Concern. Therefore, the aim of this study was to evaluate the trace metal concentrations (Ag, As, Ba, Cd, Cr, Cu, Fe, Mn, Hg, Ni, Pb, Se, and Zn) and physico-chemical properties (grain size, total solids, specific gravity, density, COD, volatile solids, and TOC) in the sediments of St. Clair River and Lake St. Clair. Sediments were collected from seven sampling locations of St. Clair River in 2009 and nineteen sampling locations of Lake St. Clair in 2010. To characterize the seasonal variation of the metabolic activities of heterotrophic microorganisms in the sediments, additional samples were collected from six locations of St. Clair River and Lake St. Clair in spring, summer, fall and winter of 2015. The analytical results indicated that the metal concentrations were unevenly distributed on the river and lake bottoms. The metal concentrations of St. Clair River sediments were lower than Lake St. Clair sediments, due to the fact that rivers such as St. Clair River, are lotic ecosystems and characterized by rapidly moving freshwater. Therefore, rivers do not accumulate much of the metals in the sediments but transport the metals to lakes where the metals concentrate. Nonetheless, the metal concentrations in sediment of the study were below the allowable regulatory limits. Comparison of metal concentrations of this study with other connecting lakes and rivers led to the conclusion that the Clinton River and Rouge River appears to be the source of contamination, and the anthropogenic factors dominated the process regulating the metal distributions within the study area. The Biolog Ecoplate assay showed that differences in heterotrophic growth and metabolic diversity between the two ecosystems were slightly significant, but the differences were more significant between sites within each ecosystem. This is likely a result of differences in sediment texture between locations and seasonal changes.

CHAPTER I - INTRODUCTION

Trace metals are one of the serious pollutants in the natural environment because of their persistence, toxicity, and bioaccumulation (Tam and Wong 2000; Brennan and Withgott, 2004). They tend to be trapped in the aquatic environment and acclimate in the sediment, and are released to the water through sediment resuspension, reduction-oxidation reactions, etc. Such process enhances the dissolved concentration of trace metals in water (Jones and Turki,1997; Brennan and Withgott, 2004; Thoung et al., 2013). Contaminated sediments are a concern not only because they act as a continuing source of potential problems for water quality and the biota in the waterways, but because they may represent a means to quantify the relationship between sources of urban runoff and water quality degradation (Murray, 1995, Eaisa, 1995).

St. Clair River and Lake St. Clair form a significant portion of the connecting channel from the upper to the lower Great Lakes. Together with the Detroit River, they provide an outlet of waters from Lake Huron into Lake Erie (USACE, 2004). Areas within each of the connecting channels of the upper Great Lakes - the St. Mary's River, the St. Clair River, Lake St. Clair, and the Detroit River have been designated `Areas of Concern' (AOC) by the International Joint Commission (Edsall et al., 1991). This has led to many studies that assessed the level of pollution in recent years largely as a result of concern about their toxicity in drinking water, significance in natural biogeochemical cycles and long term effects on human health. Contaminants have the potential to threaten the quality of the environment and human health in the Lake St. Clair watershed. These contaminants come from a variety of past and present agricultural, industrial, private, and municipal activities, and include both point and nonpoint sources of pollution. Urbanization and its accompanying industrial activities have contributed to trace metal impacts across all land use categories (industrial, commercial, and residential) and throughout the varied surface geology of the watershed (Murray, Roger, and Kaufman, 2006).

Although several adverse health effects of metals have been known for a long time, exposure to trace metal is continuous and even increasing in some parts of the world, particularly in the developing countries. Being at the top of many food chains, human can be seriously affected by this biomagnification process, depending on the level of consumption of contaminated items that are lower in the food chain (Theodory, 1999).

Since sediment acts as the carrier and the potential secondary source of contaminations in aquatic ecosystems (Calmano et al. 1990; Murray et al., 1997), the degree to which it becomes a source of pollution depends on such factors, river activity (e.g., water flow rate), and the intensity of geomorphic activity of the river catchment (Martin, 2000) (Thoung et al., 2013). Therefore, the analysis of the river sediment is a very practical method to investigate the concentration of trace metals pollution in the area of concern. In the most cases, trace metal concentrations in bottom sediments are adequate indications of water pollution (Murray et al., 1997). Soluble fractions of trace elements are, in most aquatic environments, rapidly absorbed either by clay or organic compounds and deposited in sediments or they are caught by plankton and root tissues of aquatic plants. Trace metals which are absorbed and immobilized in bottom sediments constitute a potential hazard to water quality and aquatic life as they may be released as a result of physico-chemical changes. These changes are most commonly stimulated by a change in the redox conditions and by microbial activity.

1.1 Objectives of the study

(1) Evaluate the concentrations of trace metals in the sediment of St. Clair River and Lake St. Clair and to assess the concentrations of trace metals distributed in the river and lake system.

(2) Compare the data collected in this study with the data collected in previous studies on St. Clair River and Lake St. Clair sediments and with other nearest rivers and lakes as well as the USEPA Guideline for Sediment Quality.

(3) Characterize the trace metals sources (anthropogenic, geogenic) and element distribution in the river and the lake to determine what areas require further study.

(4) Determine the “metabolic fingerprint” of heterotrophic microorganisms present in the sediment samples based on the carbon source they utilize.

1.2 The Lake St. Clair Watershed

Lake St. Clair and the St. Clair River form a significant portion of the connecting channel from the upper to the lower Great Lakes. Together with the Detroit River, they provide an outlet of waters from Lake Huron into Lake Erie. The lake and river watershed area was formed during the retreat of the last glacier about 12,000 years ago, with the last significant geological modification occurring about 4,800 years ago (USACE, 2004). At that time, rising post-glacial landforms closed the upper lake system's northeast outlet and caused water to flow southward through the St. Clair River, Lake St. Clair, and the Detroit River. In the mid-1990s, residents of the Lake St. Clair watershed began to coordinate efforts to address high-profile pollution problems in the lake. These efforts swiftly elevated the lake's profile, both locally and within the Great Lakes region, and there was increasing interest in taking a comprehensive, holistic approach to managing the lake (USACE, 2004). Some residents perceived Lake St. Clair as the "forgotten lake" since it was being addressed under larger Great Lakes planning programs such as the Lake Erie LaMP, but did not have independent status or a management program specifically dedicated to it. Subsequently, Section 426 of the Water Resource Development Act (WRDA) of 1999 authorized the U.S. Army Corps of Engineers (USACE) to develop a comprehensive management plan for the St. Clair River and Lake St. Clair (Wightman, 1961; USACE, 2004).

The St. Clair River is the natural outlet from Lake Huron and flows 40 mi (64 km) in a southerly direction from Lake Huron to Lake St. Clair (Figure 1) and forms part of the international boundary between Canada and the United States (USACE, 2004). The river drops almost 5 ft. (1.5 m) from the elevation of Lake Huron to that of Lake St. Clair. The river is a relatively straight channel with artificial structures, such as riprap and retaining walls, some narrow beaches, and vegetated cliffs. Both sides of the river have highly urbanized portions (Wightman, 1961; Liu et al., 2012). The river is a significant component in the Great Lakes Waterway, with shipping channels permitting cargo vessels to travel between the upper and lower Great Lakes (USACE, 2004). Much of the shoreline on both sides of the St. Clair River is urbanized and heavily industrialized. Intensive development has occurred in and near the adjacent cities of Port Huron, Michigan and Sarnia, Ontario, at the northern end of the river. The heaviest concentration of industry (including a large petrochemical complex) lies along the Ontario shore south of Sarnia (USACE, 2004). Several communities along the St. Clair rely on the river as their primary source of drinking water. About one-third to one-half of the residents of Michigan receives their water from the St. Clair/Detroit River waterway (USACE, 2004).

The St. Clair delta on the other hand is part of the Huron-Erie Corridor which extends from the mouth of the St. Clair River through Lake St. Clair to the outlet of Detroit River (Figure 1). This is the largest delta in the Laurentian Great Lakes. It extends 18 km from the open waters of Lake St. Clair to the river and consists of massive sedimentary deposit formed by a series of radial distributaries in various stages of activity. The delta has a surface area of approximately 80 km^2 in newly emergent wetland habitat. The delta characteristics and distributaries are presented in Figure 1.

The St. Clair delta exhibits the classic "bird's foot" morphology. Landform characteristics include a number of active and relatively inactive distributary channels, interdistributary bays, and natural levee deposits. Channel depth is variable but average approximately 11 m. In mean depth of Lake St. Clair is only 3 m. Borings obtained from the United States Army Corps of Engineers (USACE) reveal that these channels are entrenched in lacustrine clays which lie beneath 13-4 m veneer of coarser deltaic sediment (Wightman, 1961; Thomas et al., 2006).

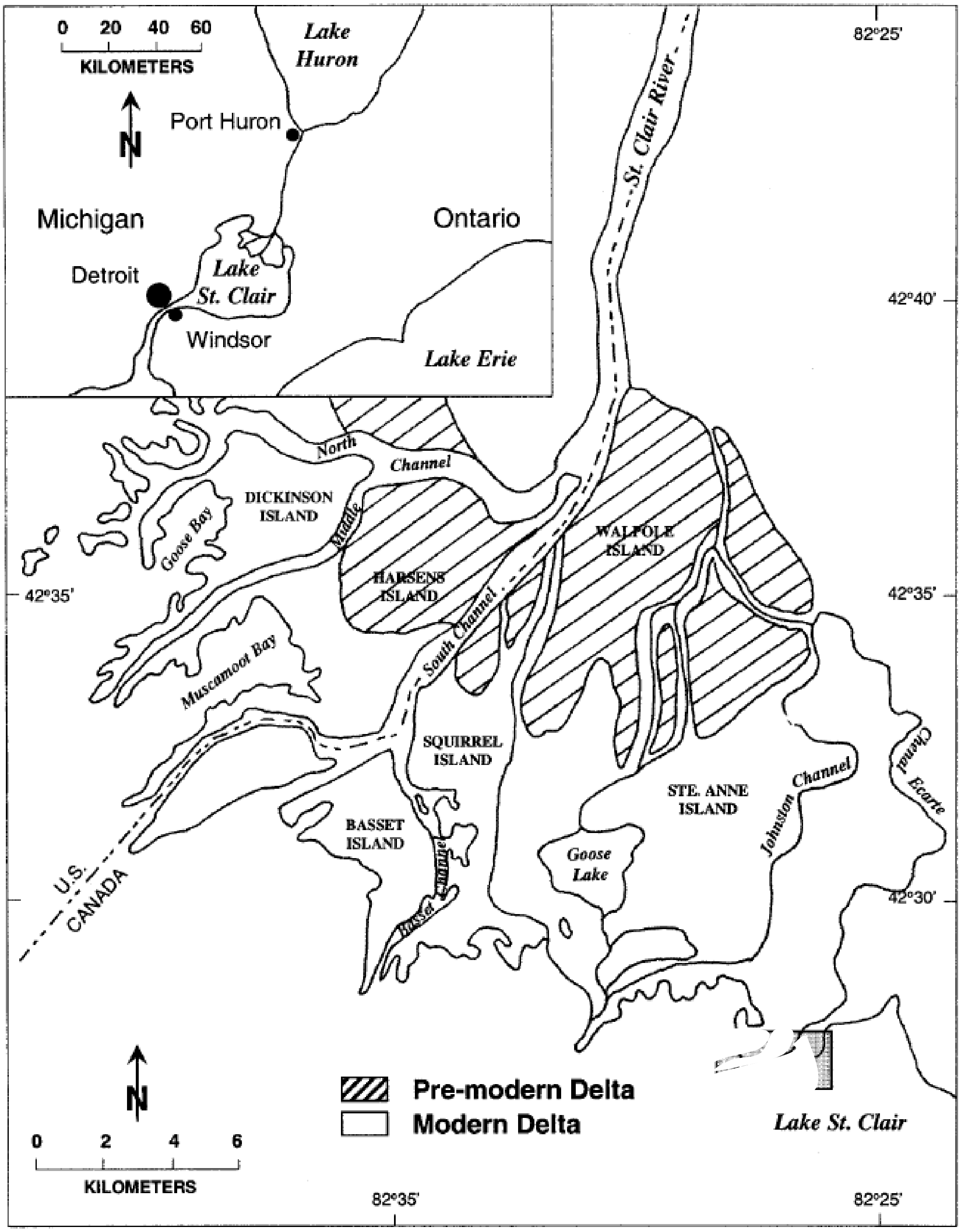


Figure 1. The St. Clair River delta showing the pre-modern and modern surface and the delta distributaries (Adapted from Ralph and Jaworski, 1982).

Lake St. Clair is a shallow, sub-circular lake located within the Lake Huron-Lake Erie corridor, with a surface area covering 190 km^2. 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. 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 (Shwetz, 2004). Approximately 98% of the water entering Lake St. Clair comes from the upper Great Lakes, which have a combined drainage basin of 56,603 mi^2 (146,600 km^2). Water remains in the river only 21 hours before draining into Lake St. Clair. The annual average discharge is 182,000 ft^3/sec (5,150 m^3/sec) based on historical records. The flow rate averages around 182,000 cubic feet per second (5,200 m^3/s), and the drainage area is 223,600 square miles (579,000 km^2) (US. Geological Survey, 2011). This takes into account the combined drainage areas of Lakes Huron, Michigan, and Superior. Although, during extremes it has been as high as 232,000 ft^3/sec (6,570 m^3/sec) and as low as 106,000 ft^3/sec (3,000 m^3/sec) for a particular month. Extreme flows are usually caused by periods of abnormally high or low water supplies from lakes Superior, Michigan and Huron. Ice buildup in the lower river also causes flows to be significantly reduced for weeks at a time (USACE, 2004).

Lake St. Clair drains into the Detroit River and subsequently into Lake Erie. The Detroit River runs about 32 miles and drops nearly 3 ft. (1 m). Ice build-up in the Detroit River in winter months occasionally can hold water back in Lake St. Clair. Like the St. Clair River, plant growth during the spring-autumn period can also materially reduce the Detroit River's outflow capacity, causing changes in circulation patterns on Lake St. Clair. In addition, during rare occasions of extreme storm surges toward the west end of Lake Erie, the Detroit River has been known to virtually stop and even reverse in direction for a few hours.

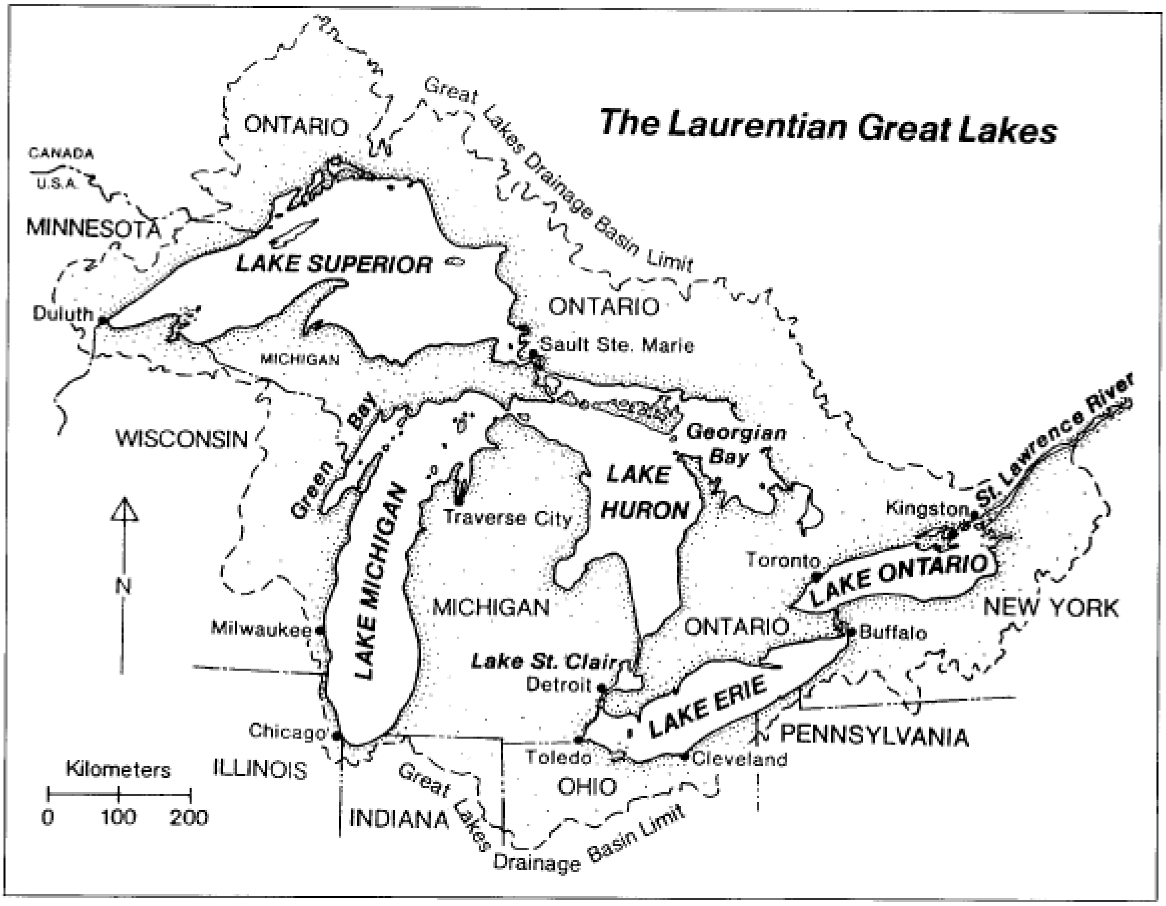


Figure 2. The Laurentian Great Lakes (Adapted from Herdendrof, 1992).

The Detroit River is a 35km long channel forming the international boundary between Canada and the United States (Figure 1& 2). The river flows from Lake St. Clair and drains into Lake Erie (Shwetz, 2004). The upper Detroit River riverbanks are extensively urbanized and are lined by municipal, recreational and industrial facilities (Quinn, 1988). The lower Detroit River, especially from Zug Island southward to Grosse lie, is an industrial valley of steel and petrochemical plants. The river is an intensive shipping route, and serves as the water source for industrial and municipal needs. Consequently, numerous industrial and municipal discharges drain into the river from both sides (Shwetz, 2004).

Within the river are a series of islands that are also used extensively for recreational and industrial purposes. Fighting Island and Grosse lie have been used as disposal sites for waste products from the manufacture of caustic soda and soda ash (predominantly gypsum). Mud and Grassy Island have been used as disposal sites for dredged sediment (Shwetz, 2004).

1.3 Sediment Mobility and Bed Armoring in the St. Clair River

Sediment transport is the movement of solid particles (sediment), typically due to a combination of gravity acting on the sediment, and/or the movement of the fluid in which the sediment is entrained. Sediment transport occurs in natural systems where the particles are clastic rocks (sand, gravel, boulders, etc.), mud, or clay; the fluid is air, water, or ice; and the force of gravity acts to move the particles along the sloping surface on which they are resting. Sediment transport due to fluid motion occurs in rivers, oceans, lakes, seas, and other bodies of water due to currents and tides (Ackers and White, 1973).

The most common modes of sediment transport in rivers are bedload and suspended load. Bed load moves by rolling, sliding, and hopping (or saltating) over the bed, and moves at a small fraction of the fluid flow velocity. Bedload is generally thought to constitute 5-10% of the total sediment load in a stream, making it less important in terms of mass balance. However, the bed material load (the bedload plus the portion of the suspended load which comprises material derived from the bed) is often dominated by bedload, especially in gravel-bed rivers. This bed material load is the only part of the sediment load that actively interacts with the bed. As the bed load is an important component of that, it plays a major role in controlling the morphology of the channel (Fernandez-Luque and van Beek, 1976).

Suspended load is carried in the lower to middle parts of the flow, and moves at a large fraction of the mean flow velocity in the stream (Ackers and White, 1973). A common characterization of suspended sediment concentration in a flow is given by the Rouse profile. The Rouse profile characterizes sediment concentrations because the Rouse number includes both turbulent mixing and settling under the weight of the particles. Turbulent mixing results in the net motion of particles from regions of high concentrations to low concentrations. Because particles settle downward, for all cases where the particles are not neutrally buoyant or sufficiently light that this settling velocity is negligible, there is a net negative concentration gradient as one goes upward in the flow. The Rouse Profile therefore gives the concentration profile that provides a balance between turbulent mixing (net upwards) of sediment and the downwards settling velocity of each particle (Ackers and White, 1973).

Changes in the supply of sediment to streams can have wide-ranging effects on the form and function of fluvial ecosystems. For example, inputs of large volumes of sediment, often from landslides and bank erosion associated with rare, large storms, can result in channel aggradation, filling of pools, channel widening, and/or streambed fining (Kelsey, 1980; Roberts and Church, 1986; Knighton, 1991; Madej, 1995).

Liu (2012) described a numerical modeling approach with field data to investigate the possibility of sediment movement in the St. Clair River and assess the likelihood of morphological change under the current flow regime. A two-dimensional numerical model was used to study flow structure, bed shear stress, and sediment mobility/armoring over a range of flow discharges. Boundary conditions for the numerical model were provided by detailed field measurements that included high-resolution bathymetry and three-dimensional flow velocities. The results indicate that, without considering other effects, under the current range of flow conditions, the shear stresses produced by the river flow are too low to transport most of the coarse bed sediment within the reach and are too low to cause substantial bed erosion or bed scour. However, the detailed maps of the bed show mobile bed forms in the Upper St. Clair River that are indicative of sediment transport. Relatively high shear stresses near a constriction at the upstream end of the river and at channel bends could cause local scour and deposition. Ship-induced propeller wake erosion also is a likely cause of sediment movement in the entire reach.

1.4 Surface Geology and Stratigraphy of Lake St. Clair and St. Clair River

The Lake St. Clair shoreline (including islands) is 413 km long, divided between Michigan (230km) and Ontario (183km) (Robinson, 1977). The size distribution of surficial sediments has been mapped recently by Rukavina (1987). Muddy sand is the major bottom type particularly in the central part of the lake (Figure 3). Well sorted sand is deposited as an outwash of the delta and a gravel-sand mixture occurs along the south shore. Clay-rich sediments occur in the west-central part of the basin. Average thickness of modern sediments is 13 cm with thicker layers of sand (30-50 cm) along the delta front and mud (20-30 cm) in the west-central part of the main basin.

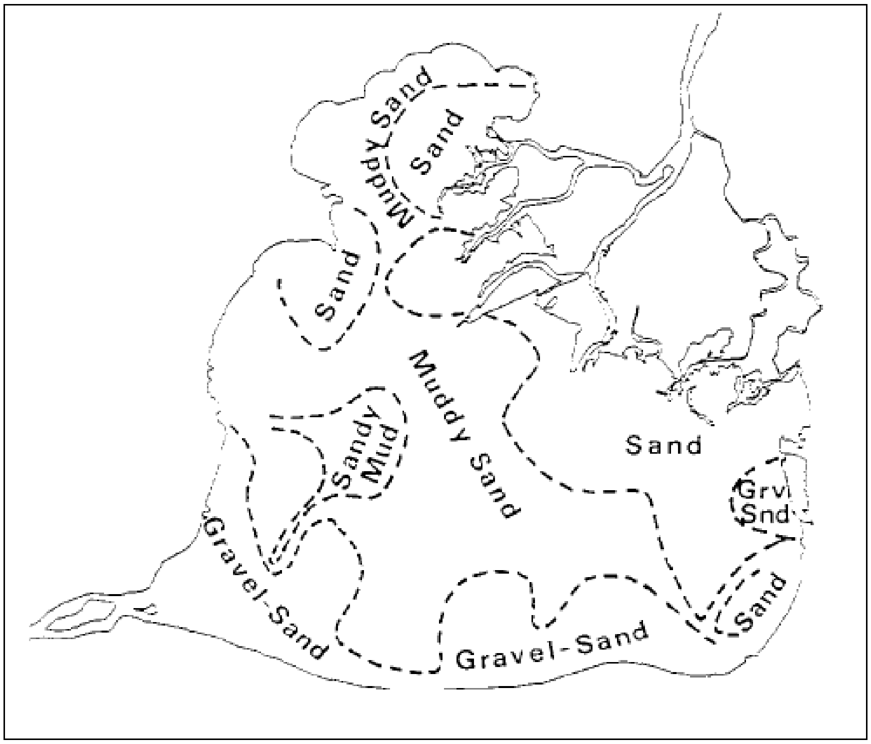


Figure 3. Distribution of sediment types in Lake St. Clair (Adapted from Rukavina, 1987).

The surface sediment of rivers and lakes of southern Ontario and western Michigan should be discussed in the context of regional geology (Din, 1999), geomorphology and cultural geography. The Lake St. Clair-Detroit River system is underline by middle and Upper Devonian and by lower Mississippian rocks. The oldest rocks are the dolomites of the Detroit River formations and the limestone of the Dundee Formation, found near the mouth of the Detroit River (Bolsenga and Herdendrof, 1993). Soil in the extensive flatlands of the Lake Erie basin are characteristically dominated by poorly drained and relatively impervious clays, derived from old lake sediments and glacial drift (Figure 4). When it is considered that the sediment of Lake Ontario and Lake Eire contain 90% to 99% mineral matter (Thomas et al., 1976), the local and regional geology and geomorphology define the nature if 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 underlies a relatively unaltered Paleozoic veneer of limestone, shale, dolomite and Sandston in Southwestern Ontario.

The eastern and southern St. Clair County is located on the Erie-Huron lowland and has been covered by several glacial lake sub stages of the Wisconsin (Pleistocene age) glacial stage (Brown, 1963). The glacial sediments are composed mainly of glacial lake clay, with discontinuous lenses of glacio-fluvial (rivers/streams associated with glaciation) and glacio-lacustrine (lakes associated with glaciation) sands and gravel occurring in the lower portions of the sediments (Brown, 1963). Some till plain deposits are found around Lakeport and to the northeast. The thickness of the glacial deposits averages 100ft. (range 50-160ft.), and may be thicker in bedrock valleys. Although groundwater is generally a difficult resource to obtain in St. Clair county, water is derived from the basal portions of the deposits primarily from the sand/gravel lenses. Regionally, groundwater flows towards the St. Clair River, or its tributaries such as the Black River (Gillespie, et al., 1989).

The bedrock surface can be described as mainly flat-lying with minor undulations dipping gently east towards the St. Clair River. Other factors which may influence bedrock topography (Brown, 1963) include: (1) pre-glacial, differential weathering and erosion due to lithological differences; (2) pre-glacial erosion channels; and (3) glacial erosion dependent on ice movement and rock type. With the exception of a few east-west trending erosional valleys such as the one underlying the lower tier of sections in Fort Gratiot Township, 7N-17E, there are no distinct or striking features in the bedrock topography, and it is not reflected at the surface, nor greatly affected by deeper structures in the Dundee/Detroit River (Brown, 1963).

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 (Din, 1999).

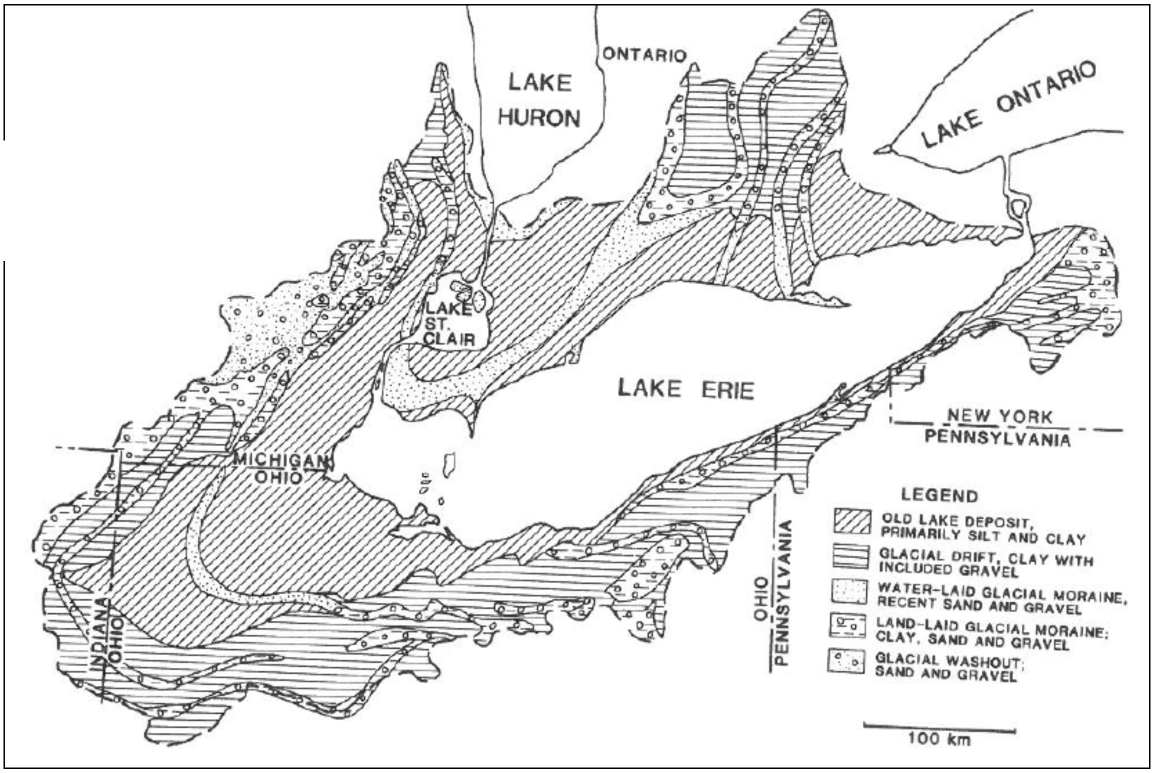


Figure 4. Surface Geology Map of the Lake St. Clair Region (Adapted from Bolsenga & Herdendrof, 1993).

The first definitive work on the St. Clair delta was carried out by Cole (1903) for the Michigan State Geological Survey. Cole's studies determined that the delta was deposited on top of the deep water proglacial lake clay and that the sediment was derived from wind current action along the shores of Lake Huron. This work was confirmed years later by Duane (1967). Barrell (1912) discussed the environmental setting of the delta, referring to it as an example setting of the delta which formed a shallow basin of constant level with weak wave action. A further review was published by Leverett and Taylor (1915), they interpreted the geologic and geomorphic history of delta in terms of the development of the drainage system on the Great Lake basin during Wisconsin times. Hough (1958) provided a historical background for the various lake stages based on relative age dating and radiometric techniques. Shortly thereafter, Wightman (1961) studied the geographic characteristics of the St. Clair River region. He attempted to establish a late Quaternary chronology for the formation of delta based in radiometric techniques.

1.5 Environmental Health of St. Clair Watershed

Many contaminants have the potential to threaten the quality of the environment and human health in the Lake St. Clair watershed. These contaminants come from a variety of past and present agricultural, industrial, private, and municipal activities, and include both point and nonpoint sources of pollution. Point source contamination is pollution that comes from an easily identifiable source, such as outfall pipes from industrial or municipal wastewater treatment plants. Nonpoint source pollution comes from indistinguishable or hidden sources, such as failing septic systems, leaking underground storage tanks, atmospheric deposition, and runoff from lawns, agricultural fields, parking lots and roadways (USACE, 2004). Industrial and municipal point sources are generally well regulated and are no longer the largest threat to the St. Clair River and Lake St. Clair ecosystem. However, accidental as well as illegal industrial/municipal releases, including discharges of untreated sewage during major weather events due to system overload, still occur. Municipal storm water remains a large pollutant source that has been traditionally unregulated (USACE, 2004). Agriculture utilizes much of the land in the Ontario portion of the watershed, as well as a significant portion of the tributary land in St. Clair County, Michigan. Agricultural impacts in the U.S. portion of the watershed tend to be localized (USACE, 2004).

1.4.1. Habitat and Biodiversity

Lake St. Clair is productive and provides favorable habitat for a large and diverse biota (Leach, 1991). Over the last 150 years, the Lake St. Clair region has undergone a dramatic transformation from open space and wetlands to agriculture and urban development, which now dominate the landscape. This conversion has resulted in drained wetlands, loss of tall grass prairie, fragmented forest habitats, increased sedimentation, excess nutrient loading, and dredged aquatic habitats. Lake St. Clair's original shoreline has been altered significantly during the last century, resulting in decreased populations of fish and wildlife, especially species that require undisturbed shoreline for critical portions of their life cycle (Leach, 1991; USACE, 2004).

Changes to the Lake St. Clair ecosystem to accommodate agricultural, residential, municipal, industrial, commercial, recreational and commercial shipping activities, along with introductions of invasive species, have led to declines in habitat quality and native species distribution and abundance. Today, the shoreline of the St. Clair system displays sharply contrasting land uses. Portions of the Upper St. Clair River are heavily industrialized. On the Canadian side, between Sarnia and Corunna, Ontario, oil and chemical companies occupy much of the river shoreline. In Michigan, industrialization of the shoreline is mainly centered at Port Huron. Along the Ontario shoreline of Lake St. Clair, wetlands and agriculture dominate, whereas in Michigan the entire shoreline is highly urbanized (USACE, 2004).

Chemical is general tend to bioaccumulate in aquatic organisms and reach higher concentration than in the ambient water (Wang et al., 2011; Theodory, 1999). This phenomenon of increasing concentration of chemicals persists throughout the food web, resulting in the biomagnification of those chemicals up to a million times their initial concentration in water. Therefore, the top predators can bioaccumulate high concentrations of certain toxic chemicals that can be the underlying cause of major deformities and even death in some cases. The bioaccumulation process is dependent upon the bioavailability of trace metals. Bioavailability, which is a quantities measure of the incorporation of trace metals by organisms, is in turn linked to metal speciation (Theodory, 1999). The bioavailability of trace elements to both unicellular and higher organisms is the result of complex reactions between the ligands present in the aqueous medium and those of living cells. Practically, all fractions of trace elements, truly dissolved and associated with suspended particulate matter, may be bioavailable to aquatic organisms (Alina et. al., 2007).

1.4.2. Human Health

Drinking water from the St. Clair River and Lake St. Clair is safe but potentially vulnerable to accumulate contaminants chemicals from agricultural runoff, and emerging issues related to microbial and chemical contaminants. There are potential problems with contamination due to pollution from various point and nonpoint sources, which can be exacerbated by the weather. The lake and its watershed must continue to be protected to ensure a continued safe source of drinking water (USACE, 2004). The shortage of safe and accessible drinking water will become a major challenge in many parts of the world. While, bottled water is widely available in both industrialized and developing countries and many consumers use it as a safer alternative to tap water, it may represent a significant cost to the consumers. Consumers may have various reasons for purchasing bottled drinking water such as taste, convenience or fashion, but for many consumers, safety and potential health benefits are important considerations (WHO, 2001; Badr et. al., 2011).

In addition to recreational fishing and hunting, the lake is also used for swimming, boating. Lake St. Clair and the St. Clair River provide a safe supply of drinking water to millions of residents in Michigan and Ontario, and are among the most heavily used recreational areas in the Great Lakes for fishing, boating and swimming. Many people on both sides of the U.S.-Canadian border are concerned about the potential health risks associated with pollutants in these water bodies. These concerns are underscored by beach closures and fish consumption advisories, as well as potential threats to drinking water (Leach, 1991; USACE, 2004).

Although several adverse health effects of metals have been known for a long time, exposure to trace metal is continuous and even increasing in some parts of the world, particularly in the developing countries. Link is known about interactions among the various trace metals during their co-exposure through drinking water and their net combined toxic implication in humans and animals (Badr et. al., 2011). The causes for these public health concerns vary, but citizen response is unified: people want full use of local water resources without risks to their health. The pollutants that raise public health concerns can be broadly divided into two categories: long-term persistent chemicals and disease-causing bacteria. These pollutants can threaten human health if people drink contaminated water, eat contaminated fish or swim in contaminated water (USACE, 2004). Being at the top of many food chains, human can be seriously affected by this biomagnification process, depending on the level of consumption of contaminated items that are lower in the food chain (Theodory, 1999).

1.4.3. Land Use

Land use has a direct and major impact on the environmental quality of the Lake St. Clair watershed. Increased impervious surfaces in urban areas and loss of natural vegetation associated with land use changes adversely affect surface water quality and quantity by increasing runoff and associated contaminants. The loss of natural habitat associated with land use change has critically impacted the biodiversity and ecosystems in the watershed. Programs are needed to help mitigate these impacts and to manage growth in the region (Wightman, 1961; Theodory, 1999; USACE, 2004). In Ontario, the heavily concentrated industrial and residential development along the upper portion of the St. Clair River produced water quality and sediment problems that have been the focus of the St. Clair River Remedial Action Plan. The largely rural Lake St. Clair watershed is impacted mostly by agricultural development with some urban development (Wightman, 1961; Theodory, 1999; USACE, 2004).

The contamination of agricultural soil with trace metals has been an important area of research due to the potential risk to public health associated with intake of trace metals (Wei and Yang 2010, Eaisa, 1995, Saud, 2014). Trace metals are potentially toxic to crops and people and may enter the human body through inhalation of dust, direct ingestion of soil and consumption of food plants grown in metal-contaminated soil (Sridhara et. al., 2008 and Wantong et. al., 2011).

1.6 Heavy Metals in Aquatic Environments

The term “heavy metal” refers to any metallic chemical element that has a relatively high density and is toxic or poisonous. Heavy metals are at least five times as dense as water. Generally, heavy metals have densities above 5 g cm^{-3} (Hawkes, 1997) and cannot be degraded or destroyed. Thus, they persist in all compartments of the environment. Some heavy metals such as Cu, Zn, Fe, Ni, Mo and Co are essential for the growth and metabolism of organisms at low concentrations. In contrast, many other heavy metals have no essential biological function (e.g., Pb, Sn, Cd, Al, Hg) but can accumulate in the biomass and can freely transfer from one organism to another through the food chain (Irena and Ajit, 2010). Heavy metals typically occur in low or trace amounts in the environment and all have the potential to provoke toxic effects in organisms at concentrations within a few orders of magnitude. Although some of these metals are essential as micronutrients, their high concentration in the food chain can cause toxicity and environmental impacts and endanger aquatic ecosystems (Irena and Ajit, 2010).

Heavy metals in aquatic environments have been intensively studied in recent years largely as a result of concern about their toxicity in drinking water, significance in natural biogeochemical cycles and long term effects on human health. Much of the recent research on heavy metals lakes, rivers and streams (Irena and Ajit, 2010), has been concerned with the fisheries of these systems. However, most domestic and industrial wastes are discharged to streams and rivers. As waters containing these effluents are used increasingly for agricultural, industrial and recreational uses as well as for drinking water, a more thorough understanding of the distribution, fate and cycling within both the abiotic and biotic components of 1otic environments is increasingly important. As a consequence, the actual and potential adverse effects of heavy metals in drinking water on human health have become a subject of considerable research (Irena and Ajit, 2010). The investigation of the entry sources, effects, and control of these pollutants in aquatic environments have also been the research focus of environmental scientists.

Heavy metals are one of the serious pollutants in the natural environment because of their persistence, toxicity, and bioaccumulation (Tam and Wong 2000; Brennan and Withgott, 2004). They tend to be trapped in the aquatic environment and acclimate in the sediment, and are released to the water through sediment resuspension, reduction-oxidation reactions, etc. Such process enhances the dissolved concentration of trace metals in water (Jones and Turki; Wright and Mason, 1999; Brennan and Withgott, 2004; Thoung et al., 2013). Since sediment acts as the carrier and the potential secondary source of contaminations in river system (Calmano et al. 1990), the degree to which it becomes a source of pollution depends on such factors, river activity (e.g., water flow rate), and the intensity of geomorphic activity of the river catchment (Martin, 2000) (Thoung et al., 2013). Therefore, the analysis if the river sediment is a very practical method to investigate the concentration of trace metals pollution in the area of concern.

In the most cases, trace metal concentrations in bottom sediments are adequate indications of water pollution. Soluble fractions of trace elements are, in most aquatic environments, rapidly absorbed either by clay or organic compounds and deposited in sediments or they are caught by plankton and root tissues of aquatic plants. Generally, the speciation of trace metals in sediments is very similar to that in soil. Trace metals which are absorbed and immobilized in bottom sediments constitute a potential hazard to water quality and aquatic life as they may be released as a result of physico-chemical changes. These changes are most commonly stimulated by a change in the redox conditions and by microbial activity.

1.7 Environmental Assessment of Sediment Quality

Areas within each of the connecting channels of the upper Great Lakes - the St. Mary River, the St. Clair River, Lake St. Clair, and the Detroit River have been designated `Areas of Concern by the International Joint Commission (Edsall et al., 1991). Elevated sediment concentrations of iron and zinc in the St. Mary's River and of mercury in the St. Clair and

Detroit rivers contributed to the designation of Areas of Concern in those waters (GLWQB, 1983). This has led to many studies that assessed the level of pollution in the water and sediment of the area (Goldberg et al., 1983; Hoff 1994; Wong et al., 1995). The primary objective of these studies was to quantify the amount of the trace metal loading of the system and to investigate the sources and pathways of metal loading (Hoff 1994).

In 1985, Edsall (Edsall et al., 1991) conducted a comprehensive survey of trace metal contaminants in the sediments within each of the connecting channels, from the head of the St. Mary's River to the mouth of the Detroit River. The purpose of the survey was to determine the distribution of cadmium, chromium, copper, lead, mercury, nickel, and zinc in the connecting channels of the upper Great Lakes and to identify locations where metal concentrations exceeded the criteria of the U.S. Environmental Protection Agency (USEPA) for open-water disposal of polluted sediments (Table 1).

Table 1. Criteria for sediment concentration of metals established by the Ontario Ministry of the Environment (OME) and USEPA. All units in µg g^{-1} (International Joint Commission, 1982).

Metal	OME	USEPA		
		Non-polluted	Moderate pollution	Heavy pollution
Mercury	0.3	<1.0	-	>1.0
Cadmium	1.0	-	-	>6
Chromium	1.0	<25	25-75	>75
Copper	25.0	<25	25-50	>50
Nickel	25.0	<20	20-50	>50
Lead	50.0	<40	40-60	>60
Zinc	100.0	>90	90-200	>200

Edsall study (1991) revealed widespread metal contamination of the sediments. Concentrations of cadmium, chromium, copper, lead, mercury, nickel, and zinc each exceeded USEPA sediment pollution guidelines at one or more stations throughout the study area. Sediments were polluted more frequently by copper, nickel, zinc, and lead than by cadmium, chromium, or mercury. Sediments with the highest concentrations of metals were found (in descending order) in the Detroit River, the St. Mary's River, the St. Clair River, and Lake St. Clair.

Of the seven metals measured, chromium, nickel, copper, zinc, and lead were the most common sediment contaminants throughout Edsall (1991) study area (Table 2). Chromium levels exceeded USEPA pollution criteria in only the St. Mary's River and Detroit River and Lake St. Clair (Table 2). Although moderate chromium contamination was common to all areas of the St. Mary's River and Detroit River, heavily contaminated sediments were limited mostly to the lower Detroit River.

Table 2. Number of stations in the Upper Great Lakes connecting channels where sediment concentrations of metals exceeded moderate (M) or heavy (H) pollution criteria of USEPA. Number of stations in each channel is shown in parentheses (Adapted from Edsall et al., 1991).

Metal	St. Mary's River (125)*		St. Clair River (35)*		Lake St. Clair (43)*		Detroit River (47)*		All channels Combined (250)*	
	M	H	M	H	M	H	M	H	M	H
Mercury	0	0	0	0	0	2	0	4	0	6
Cadmium	0	0	0	0	0	0	0	2	0	2
Chromium	69	1	0	0	2	0	19	4	90	5
Copper	38	4	14	1	5	0	11	12	68	17
Lead	6	7	2	3	1	0	10	13	19	24
Nickel	42	0	5	0	9	0	18	6	74	6
Zinc	14	9	4	1	2	0	17	11	37	21

*total number of stations.

Shwetz (1998) analyzed sediment 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 (1999) studied zebra mussels to determine heavy metals (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±7ppm (part per million), respectively. Other studies, carried out in Lake Erie and other Great Lakes, employed molluscs as biomoniters to investigate pollution trends of heavy metals in industrial and urban areas (Al-Aasem et al., 1998). Such organism can accumulate heavy metals in their tissues and biomagnify existing levels in the aquatic environment (Al-Aasem et al., 1998).

Recent studies have also dealt with trace metals concentrations in mussels and the associated sediments. A significant relationship was found between trace metal concentrations of the sediment and that of associated mussels, where an increase in the metal content of the sediment was accompanied by increase in the metal content of the mussel tissues (De Gregori et al., 1996). Din (1999) collected and analyzed sediment from Lake St. Clair to determine the amounts of Li, Se, As, Sr, Ba, Sb, Th, Pb, Ti and Cs. His study showed limited dispersion in values.

While human impacts to the Lake St. Clair watershed have been immense, efforts over the past three decades to mitigate those impacts have also been substantial. A wide array of laws, regulations and pollution prevention activities has dramatically reduced the impact of human activities on water quality. Other programs have safeguarded public water supplies and protected public health. The impact of large industrial and municipal discharges in the watershed is well studied and for the most part well regulated. The combined impact of many smaller, less regulated sources has been known for many years but is only now coming into focus within federal, state and local programs. For years, these smaller sources were not considered as high a priority as larger sources. However, as the entire system becomes better understood, it was recognized that control of these sources is important in order to control water quality degradation (USACE, 2004).

In Michigan, the Part 201 generic clean-up criteria are not used for evaluating sediment quality. Rather, the Department of Environmental Quality (DEQ) conducts site-specific remedial investigations, in collaboration with potentially responsible parties, to evaluate potential impacts to aquatic life from sediments. As a first step, sediments are sampled and the analytical results are compared to various screening levels, including the "Threshold Effect Concentration" (TEC) and the "Probable Effects Concentration" (PEC) (Table 3) (http://www.michigan.gov/deq).

The assessment of sediment quality was based on evidence from chemical analysis of sediment, sediment bioassays, and assessment of native biotic communities, termed the "sediment quality triad". These sediment quality parameters have been recommended based on studies from both freshwater and marine sediments (Chapman, 1986, Besser et al. 1996).

Table 3. Michigan's sediment quality guideline values for trace metals (Adapted from DEQ, 2013).

Contaminant	Threshold Effects Concentration (TEC)	Probable Effects Concentration (PEC)
Metals (mg kg^{-1} DW)*		
Arsenic	9.79	33.0
Cadmium	0.99	4.98
Chromium	43.4	111
Copper	31.6	149
Lead	35.8	128
Mercury	0.18	1.06
Nickel	22.7	48.6
Zinc	121	459

DW=dry weight basis

The Federal channel improvements have impacted Lake St. Clair by altering flow regimes and replacing productive shoal-water habitat with less productive channel habitat. In addition, scientists believe that dredging the navigation channel has affected water levels, permanently lowering the levels of lakes Huron and Michigan by almost one foot (0.3 meters). While the public generally recognizes the need for commercial navigation and maintenance dredging to support waterborne commerce, people are also concerned about the siting of dredged material disposal sites, whether the sediments are clean or contaminated.

Prior to 1970, sediments removed from the Lake St. Clair navigation channel during maintenance dredging operations were routinely placed in the open water. In 1970, this disposal practice was suspended due to high mercury levels in the sediments (USACE, 2004). Subsequently, a confined disposal facility (CDF) was designed and constructed to contain the dredged sediments from Lake St. Clair and portions of the St. Clair River navigation channels. The CDF was cited on a high pre-modern delta deposits on Dickinson Island adjacent to the St.

Clair Delta's North Channel. This new disposal practice addressed the growing federal interest in pollution abatement and water quality restoration. To date, more than 500,000 cubic yards (CY) of contaminated sediments have been placed in the CDF and removed from the Lake St. Clair system as a result of maintenance dredging of the federal project. In addition, more than 700,000 CY of dredged material removed from the St. Clair River project has been placed in the CDF (USACE, 2004).

The removal of contaminated sediments for the specific purpose of restoration is usually termed environmental dredging. Environmental dredging was identified as an issue of concern in the St. Clair River. Environmental dredging is being conducted to remove sediments that were contaminated by historical point source loadings along the upper reaches of the Canadian St. Clair River shoreline. While the contaminated site is outside of the shipping channel, there is the possibility that commercial and recreational use of the river, as well as weather related events could disturb the sediments (USACE, 2004).

1.8 Previous Geochemical Monitoring at Lake St. Clair and St. Clair River

Contamination of Lake St. Clair sediment was studied by several investigators. Thomas et al. (1975), Murdoch (1983), and Rossman and Borres (1988) found that the sediments contained high concentrations of trace metals.

Thomas et al., (1975), sampled four sites in the Detroit River/Lake Erie western basin which were evaluated for their toxicity. A sequence of decreasing contamination was determined from the chemical composition based on the elutriation released of metals such as Zn, Mn, Cd, Ni, and Co. A direct relationship between the water-soluble metal fraction and toxicity was observed.

From 1980 through 1985, Rossman and Borres (1988) collected water samples from the Great Lakes and were tested the water samples for dissolved particulate, and total trace elements. Major sampling occurred in 1980 for Lake Huron, in 1981 for Lake Erie and Michigan, in 1983 for Lake Superior, and in 1985 for Lake Ontario. Element concentrations were highest in Lake Erie and Michigan and lowest in Lakes Huron and Lake Superior. All five Great Lakes had more than 50% of their total iron, aluminum, and manganese associated with particulate matter.

Mudroch (1983) collected sediment cores from Lake St. Clair and in the St. Clair River 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 from 7 ug g^{-1} to 1 ug g^{-1}.

Din (1999) in his study collected water sampling 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 (Din, 1999). The following conclusions were made from this study:

- Results revealed that Li, Se, As, Sr, Y, Ba, Sb, Th, Pb, T1 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.
- Average concentrations obtained for Al, Ni, Mo, As, Se, Pb and T1 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.

Toms (1999) conducted a study to determine the level of mercury contamination in the sediment of Lake St. Clair. Sediment core samples were collected from various sites in the lake and the delta in the summer or 1997. His data indicate that the Hg contamination in this lake appears to be solely due to recent anthropogenic factors, as opposed to any long-term natural sources such that mercury would be found to permeate the sediments more extensively. Sites tested for methyl mercury have a fairly uniform methyl mercury concentration, with only a few exceptions.

Shwetz (2004) collected sediments from the Detroit River - Lake Erie waterway and subjected to a sequential extraction procedure in order to evaluate the precision of the procedure and determine metal partitioning and concentrations of Pb, Zn, Ni, Cu and Cr. The metal concentrations and distribution among three sediment fractions were scrutinized in the context of other sediment characteristics including grain-size, total carbon and total major element data. The highest metal concentration of Pb, Cu, Zn and Cr were found in Lake St. Clair sediment at site L S I7, adjacent to the shipping channels and in the deeper part of the Lake. Ni, Cu and Zn recorded higher concentrations than released in previous reports. Lower metal levels were recorded in Detroit River sediment but Detroit River sediment recorded higher proportions of the more labile metal forms (Shwetz, 2004).

The U.S. Army Corps of Engineers presented Comprehensive Management Plan for Lake St. Clair and St. Clair River in 2004. This plan was developed to address the following:

- Identifies the causes and sources of environmental degradation to Lake St. Clair and the St. Clair River;
- Addresses continuous monitoring of organic, biological, metallic and chemical contamination levels;
- Provides for the timely dissemination of information of contamination levels to public authorities, other interested parties and the public; and
- Include recommendations for potential restoration measures.

Further studies of this nature should be carried out to determine seasonal changes in concentrations of the lake and also to conduct detailed mapping for concentrations of trace metals. In this thesis, sediment samples were analyzed to assess the concentrations of trace metals distribution in the river system, and compared with previous studies on St. Clair River and Lake St. Clair sediments as well as Michigan's sediment quality guideline values for trace metals. Evaluated concentration levels of trace metals in sediments can be used as an indicator of the health of the St. Clair River and Lake St. Clair. In addition, this thesis will determine the pollution levels of the sediment prior to dredging and use of dredged sediment for other use.

CHAPTER II - MATERIAL AND METHODS

2.1 Site Description

Lake St. Clair and the St. Clair River form a significant portion of the connecting channel from the upper to the lower Great Lakes. Together with the Detroit River, they provide an outlet of waters from Lake Huron into Lake Erie. The St. Clair River is the natural outlet from Lake Huron and flows 64 km in a southerly direction from Lake Huron to Lake St. Clair (Figure 1) and forms part of the international boundary between Canada and the United States (USACE, 2004).

The St. Clair River, with its high flow rate, averaging about 5000 m^3/s, inhibits the deposition of fine-grained material on its bottom; the fast-flowing river is incising downward into hard consolidated glacial clays and finer-grained silt clays (Rukavina, 1986). Firm, hard, glacial lacustrine clays were found to exist in some areas of the river channel (Sly et al., 1972). Sediment transported along the St. Clair River substrate consists of these eroding glacial clays and medium to coarse sands and gravels (Mudroch and Hill, 1975). The river drops almost 1.5 m from the elevation of Lake Huron to that of Lake St. Clair. The river is a relatively straight channel with artificial structures, such as riprap and retaining walls, some narrow beaches, and vegetated cliffs. Both sides of the river have highly urbanized portions (Wightman, 1961; Liu et al., 2012). The river is a significant component in the Great Lakes Waterway, with shipping channels permitting cargo vessels to travel between the upper and lower Great Lakes (USACE, 2004). Much of the shoreline on both sides of the St. Clair River is urbanized and heavily industrialized. Intensive development has occurred in and near the adjacent cities of Port Huron, Michigan and Sarnia, Ontario, at the northern end of the river. The heaviest concentration of industry (including a large petrochemical complex) lies along the Ontario shore south of Sarnia

(USACE, 2004). Several communities along the St. Clair rely on the river as their primary source of drinking water. About one-third to one-half of the residents of Michigan receives their water from the St. Clair/Detroit River waterway (USACE, 2004). The St. Clair delta on the other hand is part of the Huron-Erie Corridor which extends from the mouth of the St. Clair River through Lake St. Clair to the outlet of Detroit River (Figure 5). This is the largest delta in the Laurentian Great Lakes. It extends 18 km from the open waters of Lake St. Clair to the river and consists of massive sedimentary deposit formed by a series of radial distributaries in various stages of activity. The delta has a surface area of approximately 80 km^2 in newly emergent wetland habitat. The delta characteristics and distributaries are presented in Figure 5.

Lake St. Clair is a shallow, sub-circular lake located within the Lake Huron-Lake Erie corridor, with a surface area covering 1190 km^2. 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. 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.

The deltaic islands of the St. Clair Delta wedge outward onto 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 sediment transported by the St. Clair River branching into three distributary channels referred to as the North, Middle and South channels (Herdendorf and Raphael, 1986). The hydrogeology of the watershed is controlled by glacial deposits, with moraines and outwash plains found predominantly in the western portion and related lacustrine deposits laid down in Pleistocene Lake Maumee, in the eastern portion of the Clinton River basin (Farrand, 1988; Francis and Haas, 2005). The Marshall Sandstone aquifer and Coldwater Shale formations, found in the western and northern portion of the watershed, are part of the Michigan geological basin and contain elevated As concentrations because they are arsenian pyrite-rich (Kim et al., 2002).

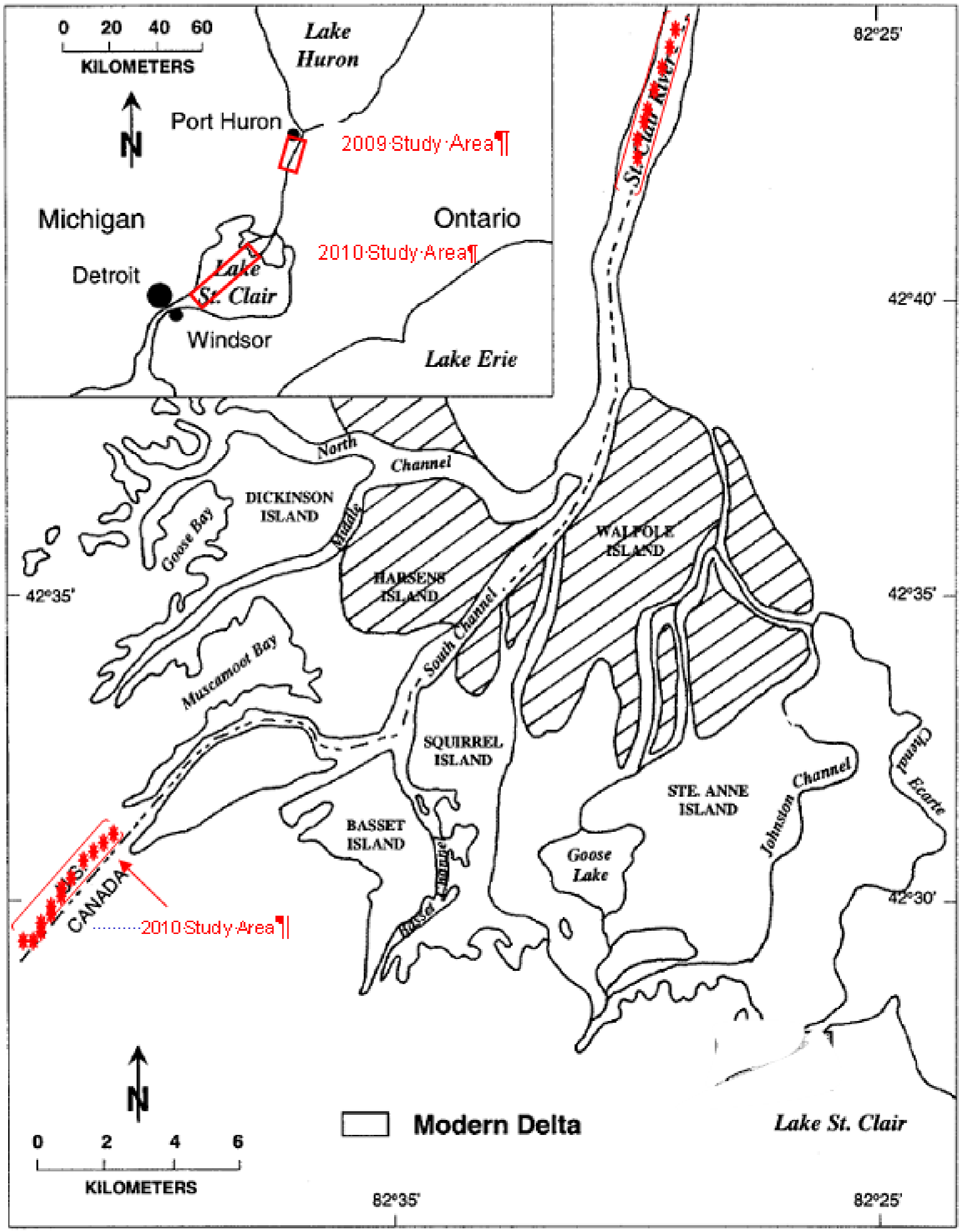


Figure 5. The St. Clair River delta showing the pre-modern and modern surface and the delta distributaries (Adapted from Ralph and Jaworski, 1982) and showing approximate sampling sites in 2009. (SC-09-01, SC-09-02, SC-09-03 SC-09-04, SC-09-05, SC-09-06, and SC-09-07) and 2010 (LC-10-01, LC-10-02, LC-10-03, LC-10-04 LC-10-05, LC-10-06, LC-10-07, LC-10-08 LC-10-09, LC-10-10, LC-10-11, LC-10-12 LC-10-13, LC-10-14, LC-10-15, LC-10-16, LC-10-17, LC-10-18, and LC-10-19).

2.2 Sampling locations

The St. Clair River sampling locations are located near the underground railroad tunnel along St. Clair River between Port Huron, Michigan and Sarnia, Ontario (Figure 5), while Lake St. Clair sampling locations are located near St. Clair Delta to the mouth of Detroit River (Figure 5). The 2009 and 2010 sediment samples were selected to cover the upper portion of St. Clair River and the entire navigation channel from Lake St. Clair to Lake Huron, since the incoming waters from Lake Huron passes through St. Clair River to Lake St. Clair. Seven river sampling locations were selected in 2009 from St. Clair River (Sites SC-09-01, SC-09-02, SC-09-03, SC-09-04, SC-09-04, SC-09-05, SC-09-06, and SC-09-07) and 19 sampling locations in 2010 from Lake St. Clair (Sites LC-10-01, LC-10-02, LC-10-03, LC-10-04, LC-10-05, LC-10-06, LC-10-07, LC-10-08, LC-10-09, LC-10-10, LC-10-11, LC-10-12, LC-10-13, LC-10-14, LC-10-15, LC-10-16, LC-10-17, LC-10-18, and LC-10-19) (Figure 5)

Sample locations of St. Clair River and Lake St. Clair were determined based on the bathometric survey conducted by the USACE in 2009 and 2010. Therefore, sediment samples were collected from shoaled locations in the federal navigation channel where the dredging activity was proposed. The distance between the 2009 sample locations were approximately 91.44 m, while the distance between the 2010 sample locations were approximately 804.67m.

While the physico-chemical characteristics of the sediments in St. Clair River and Lake St. Clair had been characterized previously (Rossmann, 1988), but the microbial properties of the sediments have not yet been characterized. Thus, additional sediment samples were collected from three sites from the shores of St. Clair River and three sites from Lake St. Clair in spring (April 18, 2015), summer (June 20, 2015), fall (August 16, 2015) and winter (November 26, 2015). Sediments were collected to determine the metabolic activities of heterotrophic microorganisms in sediments at different seasons (Figure 6).

Figure 6. Sediment sample location map for the 2015 sampling. This map shows the St. Clair River, Lake St. Clair, and surrounding rivers and cities.

2.3 Sampling

Three sampling events were conducted of St. Clair River and Lake St. Clair in 2009, 2010 and 2015, respectively. Prior to collecting the sediment samples, the sample coordinates were determined using a GPS (Garmin GPSMAP 276C) unit with one to three-meter accuracy. The GPS accuracy was verified daily prior to sampling activities at site bench marks. The water depth was measured by using a weighted scale tape. Reference water levels (in feet) were obtained from the NOAA/NOS Web site as "Preliminary Water Level Data, Great Lakes Stations" (http://www.coops.nos.noaa.gov/data_res.html), and were used to calculate the amount of sediment needed to obtain project depth. The nearest NOAA water level reference station for Lake St. Clair is the St. Clair Shores, Michigan Station (#9034052) which is located approximately 9.7 km west of the navigation channel. One sample was collected for each of the seven locations in St. Clair River, MI in 2009 (Table 4), with the exception of SC-09-05 which was split into two sub samples (SC-09-05A and SC-09-05B) due to changes in sediment components (stratigraphy). Similarly, one sediment sample was collected from each of the 19 sample locations (Table 5).

The 2009 sampling was performed on Tuesday, June 16, 2009, while 2010 sampling event was performed for three days as follow: Seven samples (LC-10-09 to LC-10-16) were collected on June 25, 2010; two samples (LC-10-07 and LC-10-08) were collected July 1, 2010; and nine samples (LC-10-01 through LC-10-06, and LC-10-17 through LC-10-19) were collected on July 7, 2010. Samples locations for the 2009 and 2010 sampling were preselected based on the bathometry survey conducted by the USACE. These samples were collected from the shoaling area in the navigation channel of St. Clair River and Lake St. Clair to determine the impact of disturbing the sediment during the dredging activities.

In 2015, a total 24 sediment samples were collected from the shore of Lake St. Clair and three St. Clair River (Figure 6). One sample was taken from each of the six locations (Table 6 and Figure 6) of the four sampling events (spring, summer, fall and winter). Site SC-15-01 is located upstream where the water from Lake Huron drains into Lake St Clair; site SC-15-02 is close to the City of Marysville Wastewater Treatment Plant, City Public Park and public boat launch; and site SC-15-03 is situated at the mouth of Pine River, which empties into the St. Clair River. Site LC-15-01 is located downstream of St. Clair River where it empties its water into Lake St. Clair and is close to the residential private boating docks; site LC-15-02 is close to the Veterans Memorial Park located south of Clinton River; and site LC-15-03 is situated downstream where Lake St. Clair empties its water into Detroit River at the City of Gross Point park.

The river and lake sites are situated in the vicinity of known point sources (e.g. City of St. Clair permitted wastewater discharges, marina, major river follow, and public parks) to adequately represent source areas upstream and downstream.

Table 4. St. Clair River 2009 sampling locations and thickness of sediment core retrieved*.

Station ID#	Thickness of core retrieved (cm)	GPS coordinates
SC-09-01	76.2	N 42° 57.971'; W 82° 25.262'
SC-09-03	125.4	N 42° 58.121'; W 82° 25.201'
SC-09-04	124.9	N 42° 58.160'; W 82° 25.189'
SC-09-05	182.9	N 42° 58.224'; W 82° 25.164'
SC-09-06	76.2	N 42° 58.282'; W 82° 25.146'
SC-09-07	88.4	N 42° 58.328'; W 82° 25.140'
SC-09-08	91.5	N 42° 58.404'; W 82° 25.103'

*Two samples were collected from site SC-09-05 and were referred to in this thesis as: SC-09-05A and SC-09-05B.

Table 5. Lake St. Clair 2010 sampling locations and thickness of sediment core retrieved.

Station ID#	Thickness of core retrieved (cm)	GPS Coordinates
LC-10-01	100.6	N 42° 30.851'; W 82° 41.761'
LC-10-02	103.6	N 42° 30.7251'; W 82° 41.53'
LC-10-03	70.1	N 42° 30.543'; W 82° 42.102'
LC-10-04	54.9	N 42° 30.075'; W 82° 42.431'
LC-10-05	88.4	N 42° 29.764'; W 82° 42.789'
LC-10-06	88.4	N 42° 29.5321'; W 82° 43.08'
LC-10-07	106.7	N 42° 28.873'; W 82° 43.850'
LC-10-08	112.8	N 42° 28.061'; W 82° 44.806'
LC-10-09	121.9	N 42° 27.769'; W 82° 45.180'
LC-10-10	106.7	N 42° 27.120'; W 82° 46.213'
LC-10-11	106.7	N 42° 27.059'; W 82° 46.213'
LC-10-12	106.7	N 42° 26.732'; W 82° 46.945'
LC-10-13	106.7	N 42° 25.945'; W 82° 47.869'
LC-10-14	106.7	N 42° 25.749'; W 82° 48.405'
LC-10-15	106.7	N 42° 25.317'; W 82° 48.807'
LC-10-16	106.7	N 42° 24.975'; W 82° 49.561'
LC-10-17	103.6	N 42° 24.581'; W 82° 49.902'
LC-10-18	100.6	N 42° 24.315'; W 82° 50.541'
LC-10-19	106.7	N 42° 23.683'; W 82° 51.498'

Table 6. St. Clair River (SC) and Lake St. Clair (LC) sediment samples field data – 2015*.

Station ID#	Thickness of core retrieved (cm)	GPS coordinates
SC-15-01	30.5	N 42° 58.393'; W 82° 25.141'
SC-15-02	30.5	N 42° 54.323'; W 82° 28.036'
SC-15-03	30.5	N 42° 49.219'; W 82° 29.220'
LC-15-01	30.5	N 42° 37.878'; W 82° 30.970'
LC-15-02	30.5	N 42° 31.630'; W 82° 52.268'
LC-15-03	30.5	N 42° 21.560'; W 82° 55.547'

*Three samples were collected from each location.

Vibracore sediment sampler mounted on Pontoon Boat was used to recover representative, undisturbed sub-bottom sediment samples in 2009 and 2015. Sediment samples were collected using clean polyethylene tube attached to the Vibracore sampler (Figures 7A and 7B). The Vibracore sediment sampler was lowered to top of sediment and driven into the sediment to the point of refusal.

A ponar grab sampler was also used to collected additional sediment samples from the bank of St. Clair River and Lake St. Clair in 2015 for EcoBiolog test (Figure 7C). Manually, the Ponar was lowered slowly to the bottom sediment to reduce the disturbance of the upper layer of sediment. Upon retrieval, the Ponar was slowly opened, releasing the collected sediments into a stainless-steel pan, the sample was then thoroughly mixed with stainless steel spoon.

The sampling depth for all sampling sites was 152.4 cm of navigation depth below low water datum (LWD). A minimum sediment depth of 60 cm was used. Each core was about 142.4 cm and at the least 60 cm, so multiple cores were required to reach the project dredging depth. The sediment cores were opened with power saw. After the cores were cut along both sides of the barrel and the sediments exposed (Figure 7), a thin metal spoon was used to halve the core transferring some of the sample to a stainless-steel pan, photographed, and thoroughly mixed with stainless steel spoon. The core was photo-logged and the sediment described in accordance with the Unified Soil Classification System (USCS). Full length sediment sample cores retrieved were placed in a 118 ml and one 473 ml borosilicate glass containers with Teflon linings and shipped to the laboratory for trace metals and grain size analysis.

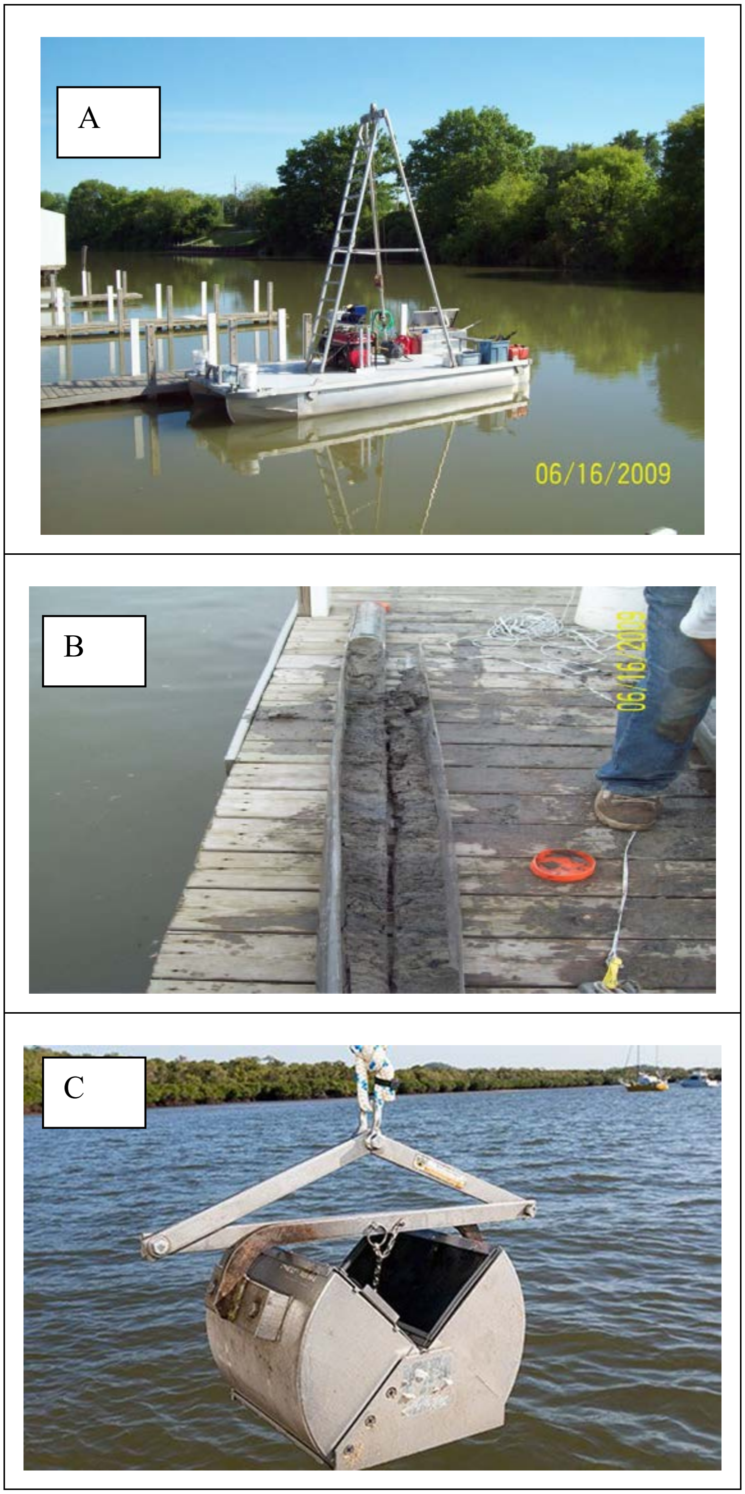


Figure 7. (A) Vibracore sediment sampler mounted on Pontoon Boat; (B) sediment sample in polyethylene tube; (C) Ponar sediment sampler.

Field conditions, activities, and field data were documented in a field logbook. Information recorded in the logbook included: (1) station identification number; (2) sample collection date;

(3) depth at each sampling location (4) thickness of each core retrieved; (5) description, measurement and identification of the material of each core retrieved according to ASTM D 2488-69 and EPA 2004, “Description of Soils (Visual Manual Procedure)”; (6) type of sampling equipment used; and (7) latitude and longitude of station locations.

Sampling equipment was decontaminated after each sample was processed. The decontamination procedure included rinsing the sampling pans and spoons with site water and using new sampling tube and gloves for each sample location. Work started at 8:00 am and concluded at 6:00 pm during the three sampling events. Prior to leaving the site, the crew cleaned the sample preparation area on the boat launch and properly disposed of all used sample tubes and unused sample material.

2.4 Sample Containers and Sample Preservation

The 2009 and 2010 samples were stored in pre-cleaned borosilicate glass containers with Teflon linings supplied by the laboratory, while the samples collected in 2015 were stored in one galloon zip lock bag. The samples were placed in bubble wrap to prevent breakage and stored in a cooler. Based on the proposed analysis parameters, none of the samples required additional chemical or physical preservation other than ice for temperature control. Samples collected in 2009 and 2010 were delivered to the accredited laboratory for analysis, while the 2015 samples were delivered to the University of Michigan, Dearborn laboratory for analysis.

Sampling equipment was decontaminated after each sample was processed. The decontamination procedure included rinsing the sampling pans and spoons with site water and using new sampling zip lock bags and gloves for each sample location.

2.5 Sample Custody

Chain-of-custody over samples was maintained at all times. Procedures for sample packaging, shipping, and chain-of-custody explicitly followed the guidelines as listed in the U.S Army Corps of Engineers Sample Handling Protocol for Low, Medium and High Concentration Samples of Hazardous Waste, dated October, 1986. Samples for this study were considered to be low level/environmental samples for safety, packaging and shipping purposes. Sample containers were carefully packed and wrapped with bubble wrap and placed in leak-proof sturdy coolers with ice. The ice was packed in zip lock bags and the coolers were then sealed. The sealed coolers were delivered to RTI laboratory for analysis. Signed chains-of-custody (s) were stored in zip lock bag attached to one of the cooler's lids.

2.6 Analytical Procedure

2.6.1 Field Analysis

Sediment pH and temperature were measured using Horiba's U-10 Water Quality Checker in the field or Multiparameter PT Testr 35, pH and TDS Meter. Water depth and turbidity were measured by using a Secchi disk. The Secchi disk is a plain white circular disk 30 cm in diameter used to measure water transparency in bodies of water. The disc contains alternating black and white quadrants and is mounted on a pole or line, and lowered slowly down in the water. This pole or line was used to lower the disk into a body of water with the purpose of measuring the clarity of the water. The depth at which the disk can no longer be seen is called the Secchi depth and is the measurement recorded. The Secchi depth is reached when the reflectance equals the intensity of light backscattered from the water. This depth in meters divided into 1.7 yields an attenuation coefficient (also called an extinction coefficient), for the available light averaged over the Secchi disk depth. While used as a variable, the extinction coefficient is also used as a variable for turbidity.

Weather history (air temperature, moisture precipitation, sea level pressure and wind) as well as reference water depth and water elevation were obtained from the NOAA/NOS Web site (http://www.coops.nos.noaa.gov/data_res.html). Reference water levels from the from the NOAA/NOS Web site were used to calculate the amount of sediment obtained. The nearest NOAA water level reference station for Lake St. Clair is the St. Clair Shores, Michigan Station (# 9034052) which is located approximately 9.7 km west of the Navigation Channel. The Low Water Datum (LWD) of Lake St. Clair is listed as 174.44 m from the International Great Lakes Datum 1985 (IGLD 1985).

2.6.2 Physico-Chemical Analysis

Other physico-chemical properties such as moisture content, pH, total organic carbon, total suspended solids, specific gravity, density, chemical oxygen demand and grain (particle) size analysis were characterized in accordance with the USCS. Standard test method for dry preparation of soil samples for particles size analysis and determination of soil contestant were analyzed according to ASTM-D421

2.6.3 Determination of Trace Metal Contents in Sediments

The sediment samples were analyzed at RTI Laboratories, Inc of Livonia, MI. The EPA 6020B analytical method were followed (Figure 8) using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)- Perkin Elmer (ELAN 6000) to obtain the concentration of the trace metals. The method is applicable to the determination of sub-µg/L concentrations for all elements listed in Table 12 & 18 as well as numerous other elements (www.epa.gov/method 6020A).

The method describes multi-elemental determinations by ICP-MS, measuring ions produced by a radio-frequency ICP. Samples were nebulized and the resulting aerosol was transported to the plasma torch and ionized. The ions were introduced into the mass spectrometer where they were sorted according to their mass-to-charge ratios and quantified. The ICP-MS lower detection limit for elements analyzed were 0.039mg/kg (As), 0.046 mg/kg (Ba), 0.034 mg/kg (Cd), 0.076 mg/kg (Cr), 0.05 mg/kg(Cu), 13.98 mg/kg (Fe), 0.03 mg/kg (Pb), 0.207 mg/kg (Mn), 0.133 mg/kg (Ni), 0.146 mg/kg (Se), 0.192 mg/kg (Zn), 0.024 mg/kg (Ag), and 0.002 mg/kg (Hg).

2.6.3.1 Apparatus and materials

The following apparatus and materials were required for the sediment digestion process:

- Digestion Vessels – 250 mL
- Vapor recovery device (e.g. ribbed watch glasses, appropriate refluxing device, appropriate solvent handling system).
- Drying ovens - able to maintain 30°C ± 4°C.
- Temperature measurement device capable of measuring to at least 125°C with suitable precision and accuracy (e.g., thermometer, IR sensor, thermocouple, thermistor, etc.
- Filter paper - Whatman No. 41 or equivalent.
- Centrifuge and centrifuge tubes.
- Analytical balance - capable of accurate weighing to 0.0001 g.

- Heating source - Adjustable and able to maintain a temperature of 90-95°C. (e.g., hot plate, block digestor, microwave, etc.)
- Funnel or equivalent.
- Graduated cylinder or equivalent volume measuring device.
- Volumetric Flasks - 100-mL.

2.6.3.2 Reagents

All reagents conformed to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Ultra-high purity-grade chemicals, must be used in all tests.

- Deionized water was used as a solvent to be interference free.
- Nitric acid ((TraceMetal™ Grade), Fisher Chemical, 67 to 70% (HNO_3, w/w)), HNO_3.
- Hydrochloric acid ((TraceMetal™ Grade), Fisher Chemical), HCl.
- Hydrogen peroxide (30%, Fisher Chemical), H_2O_2.

2.6.3.3 Sample preservation

- All sample containers were demonstrated to be free of contamination at or below the reporting limit (www.epa.gov/method 3050). Plastic and glass containers are both suitable.
- Nonaqueous (sediment) samples were refrigerated upon delivered to the laboratory and analyzed within 7 days.
- All representative samples with wet or damp materials were dried, crushed, and grounded to reduce subsample variability as long as drying does not affect the extraction of the analytes of interest in the sample.

2.6.3.4 Digestion Procedure

Prior to analysis, samples which require total ("acid-leachable") values were digested with nitric acid and hydrofluoric acid (www.epa.gov/method 3050). A representative sample was weighed and well-mixed to the nearest 0.001g as follow:

- Sample was mixed thoroughly to achieve homogeneity and sieve, using a USS #10 sieve.
- 10 mL of 1:1 HNO_3 was added to the sample, mixed the slurry, and covered with a watch glass or vapor recovery device. The sample was heated to 5°C ± 5°C and refluxed for 10 to

15 minutes without boiling. The sample was left to cool, added 5 mL of concentrated HNO_3, replaced the cover, and refluxed for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO_3, steps were repeated (addition of 5 mL of concentrated HNO_3) over and over until no brown fumes were given off by the sample indicating the complete reaction with HNO_3. A ribbed watch glass or vapor recovery system was used to allow the solution to evaporate to approximately 5 mL without boiling or heat at 95°C ± 5°C without boiling for two hours. A covering of solution over the bottom of the vessel was maintained at all times.

- After the sample has cooled, 2 mL of water and 3 mL of 30% H_2O_2 was added. The vessel was covered with a watch glass or vapor recovery device and return the covered vessel to the heat source for warming and to started the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the vessel. Do not add more than a total of 10 mL 30% H_2O_2
- The sample was covered with a ribbed watch glass or vapor recovery device and continued heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL or heated at 95°C ± 5°C without boiling for two hours. A covering of solution over the bottom of the vessel was maintained at all times.
- After cooling, diluted to 100 mL with water. Particulates in the digestate then removed by filtration, by centrifugation (at 2,000-3,000 rpm for 10 minutes), or by allowing the sample to settle. The samples at this stage were ready for analysis by ICP-MS.

The concentrations determined were reported on the basis of the actual weight of the sample (www.epa.gov/method 3050).

All laboratory glassware was decontaminated with deionized water, then placed into 13% ACS grade HNO_3 bath for one hour, rinsed with deionized water, and then placed it in oven under 100C° to dry.

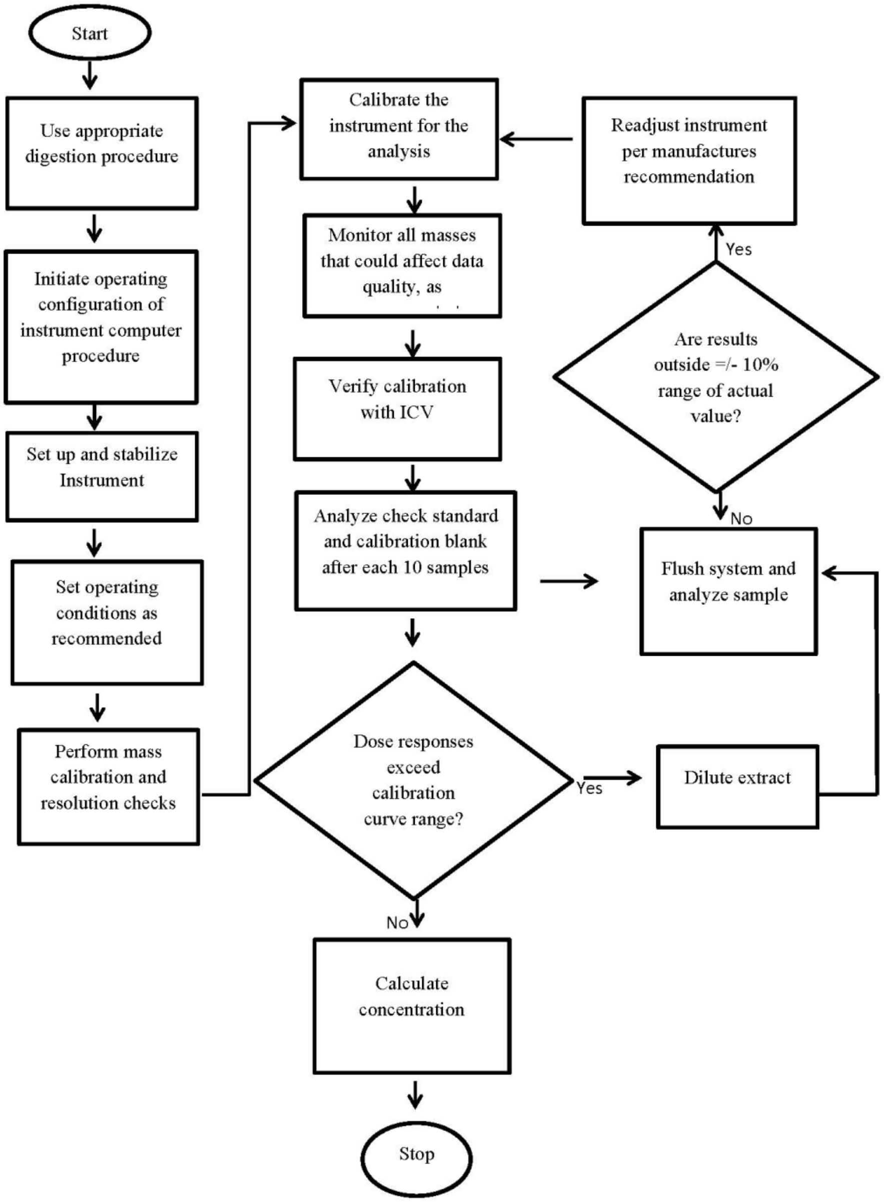


Figure 8. EPA Method 6020B, Steps ICP-MS Analysis for the Trace Metals

2.6.3.5 Reporting Limits for Trace Metals

The reporting limit (RL) for an individual analyte is dependent on the concentration of the lowest non-zero standard in the initial calibration or the low-level calibration verification (LLCV), analyzed under identical conditions as the sample, with adjustments made for the sample size, preparation factors, percent solids, dilution factors, etc., as required. The CAM RLs for target analytes are 0.05 - 0.5 mg/kg for all target analytes (Table 12 and Table 18).

Reporting limits lower than the above-referenced CAM RLs for target analytes may be required to satisfy project requirements. The RL (based on the concentration of the lowest calibration standard or the LLCV) for each target metal must be less than or equal to the MCP standards or criteria that the contaminant concentrations are being compared to (e.g., Method 1 Standards, benchmark values, background, etc.).

2.6.3.6 QC Requirements

- Matrix spike (MS) recovery were collected at a frequency of one per 20 samples per matrix to document the accuracy and precision of the method for that specific sample.
- Duplicate sample were collected at a frequency of one per 10 samples per site location to validate the accuracy and precision of the method for that specific sample.
- RLs, sensitivity, and the optimum and linear concentration ranges of the analytes can vary with the mass spectrometer, matrix, and operating conditions.
- An appropriate internal standard was required for each analyte determined by ICP-MS. Recommended internal standards are ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, and ^{209}Bi; however, experienced analysts should choose an IS based on mass for the metals of interest. Preparation of the recommended internal standard stock solutions is described in Section 7.4 of Method 6020 (www.epa.gov/method 6020).

2.6.4 Determination Total Organic Carbon (TOC)

The Organic Carbon content of a water governs the adsorption of organic compounds to the sediment, and is directly related to the mobility and retardation of organic contaminants in water moving through sediment. Organic Carbon content (TOC) can be used to predict the partitioning and bioavailability of organic contaminants when they interact with a soil or sediment. Method SW9060 was used for sample preparation and analysis for the TOC, content was expressed as a decimal fraction (e.g. 1.0%). Sediment samples were analyzed Schimadzu and OI analyzer, the linear range was up to 50000 mg/Kg, detection limit was 350 mg/Kg, and Limit of Quantification (LOQ) was 2000 mg/Kg.

A small sub-sample of a dried, ground soil sample was mixed with catalyst or accelerators and heated to high temperature (generally ≥ 1000°C) within a resistance or induction

furnace in a stream of oxygen to convert all forms of Carbon into CO2. Evolved CO2 is most commonly detected and quantified using infrared or thermal conductivity detection.
Total Organic Carbon was determined from the difference of Total Carbon minus Total Inorganic Carbon.

$$\text{TOC} = \text{Total Carbon (TC)} - \text{Inorganic Carbon (IC)}$$

Precision of the analyses were below 10%, therefore the quality of the data analyses was considered to be good.

2.6.5 Determination of Sediment Microbial Properties using Eco Biolog

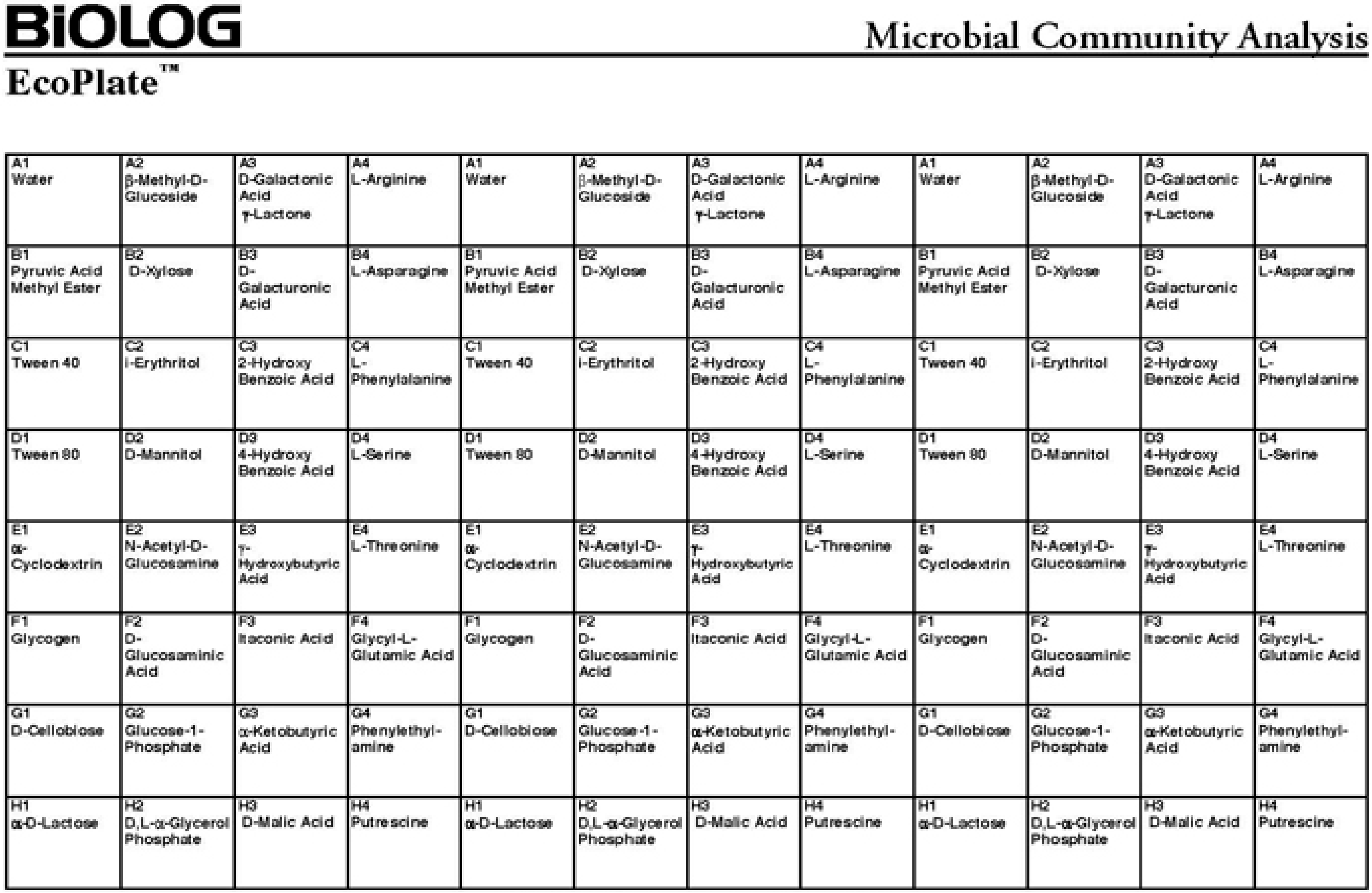
The St. Clair River and Lake St. Clair act as an important link for the Great Lakes, and is not only an important ecological water system, but also an important recreational system for the solutions that surround it. Because of this, several studies have been done to look at the pollution within the river, and potentially harmful bacteria within the water. (Fogarty, 2007; Tiquia et al., 20108; Tiquia et al., 2010). However, no study has been done that examines the bacterial contents of the sediments, nor has any study been done to search for metal remediating bacteria. This is an especially important aspect to look at considering that several major cities are located on the shores of the lake and river, and metals such as lead have been found in the two water systems (Healy, 2007). In order to study the microbial properties of the sediment, six samples were taken, three from the lake, and three from the river, samples were collected in every season over the course of 2015 (Figure 6).

In this experiment Biolog EcoPlate^{TM} (Biolog, Inc., Hayward, CA) was used to determine the "metabolic fingerprint" of heterotrophic microorganisms present in the sediment samples based on the carbon source they utilize. Biolog EcoPlates^{TM} composed of 31 different carbon compounds and a control (Figure 9). It contains three replicates of the carbon source and control wells. A redox dye (tetrazolium violet) was added in each well, which turns purple when the carbon source is used by the microbial communities present in the sample. As a particular carbon source is used, the color of the well changes. To determine metabolic diversity, the absorbance of the wells is measured in a spectrophotometer or plate reader (Stephanowicz, 2006). The Biolog EcoPlates assay has been used in the past to determine the metabolic diversity of the groundwater and river water from the Rouge River system (Tiquia et al. 2008; Tiquia, 2010).

For this assay, 1:10 sediment extracts were prepared by transferring 5g of sediment samples in a Falcon tubes containing 45 ml of 0.9% saline (NaCl) solution. The samples were then placed in a shaking incubator at room temperature set at 250 rpm in order to extract the bacteria from the sediments. After an hour of incubation, the samples put through a funnel with filter paper to filter out any particulates that may hinder the assay.

The water extracts (1:10 w/v; sediment: saline solution) were inoculated into each well of the Biolog EcoPlates within one day of sample collection. Each well of EcoPlates plates were inoculated with 125 µl of this suspension incubated at room temperature. Color development in the microplate wells were measured at 590 nm using an automated Sunrise microplate reader (Tecan, Research Triangle Park, NC). Biolog Ecoplates from the spring, summer, fall and winter sampling were read at 0, 24, 48 and 72 h, in order to generate relationship between average well color development and time.

Because the samples were cloudy even after filtration, a background correction had to be done, meaning the measurements done at the time 24, 48, and 72 hours had to be subtracted from the initial measurements, giving corrected absorbencies. From these corrected absorbencies. The average well color development, or AWCD, could be taken. The AWCD is the average of the OD595 of all the wells at a particular time. The closer to 0.75 the AWCD the better, as 0.75 is regarded to be the best solution because at this value the response of a microbial community can be seen in most wells and the wells with the most active microbial communities reach the asymptote of color development" (Stefanowicz, 2006). Each time for each sample was measured, and those which were closest to 0.75 were used in statistical analysis. Thus, relative abundance of the different substrates was determined based on the amount (AWCD value) of substrate were utilized relative to the total amount of substrates (sum of AWCD values of each plate) used by the microbial community, tested based on the measured densities of reduced tetrazolium dye in wells.



BIOLOG

Microbial Community Analysis

EcoPlate™

A1 Water	A2 β-Methyl-D-Glucoside	A3 D-Galactonic Acid γ-Lactone	A4 L-Arginine	A1 Water	A2 β-Methyl-D-Glucoside	A3 D-Galactonic Acid γ-Lactone	A4 L-Arginine	A1 Water	A2 β-Methyl-D-Glucoside	A3 D-Galactonic Acid γ-Lactone	A4 L-Arginine
B1 Pyruvic Acid Methyl Ester	B2 D-Xylose	B3 D-Galacturonic Acid	B4 L-Asparagine	B1 Pyruvic Acid Methyl Ester	B2 D-Xylose	B3 D-Galacturonic Acid	B4 L-Asparagine	B1 Pyruvic Acid Methyl Ester	B2 D-Xylose	B3 D-Galacturonic Acid	B4 L-Asparagine
C1 Tween 40	C2 i-Erythritol	C3 2-Hydroxy Benzoic Acid	C4 L-Phenylalanine	C1 Tween 40	C2 i-Erythritol	C3 2-Hydroxy Benzoic Acid	C4 L-Phenylalanine	C1 Tween 40	C2 i-Erythritol	C3 2-Hydroxy Benzoic Acid	C4 L-Phenylalanine
D1 Tween 80	D2 D-Mannitol	D3 4-Hydroxy Benzoic Acid	D4 L-Serine	D1 Tween 80	D2 D-Mannitol	D3 4-Hydroxy Benzoic Acid	D4 L-Serine	D1 Tween 80	D2 D-Mannitol	D3 4-Hydroxy Benzoic Acid	D4 L-Serine
E1 α-Cyclodextrin	E2 N-Acetyl-D-Glucosamine	E3 γ-Hydroxybutyric Acid	E4 L-Threonine	E1 α-Cyclodextrin	E2 N-Acetyl-D-Glucosamine	E3 γ-Hydroxybutyric Acid	E4 L-Threonine	E1 α-Cyclodextrin	E2 N-Acetyl-D-Glucosamine	E3 γ-Hydroxybutyric Acid	E4 L-Threonine
F1 Glycogen	F2 D-Glucosaminic Acid	F3 Itaconic Acid	F4 Glycyl-L-Glutamic Acid	F1 Glycogen	F2 D-Glucosaminic Acid	F3 Itaconic Acid	F4 Glycyl-L-Glutamic Acid	F1 Glycogen	F2 D-Glucosaminic Acid	F3 Itaconic Acid	F4 Glycyl-L-Glutamic Acid
G1 D-Cellobiose	G2 Glucose-1-Phosphate	G3 α-Ketobutyric Acid	G4 Phenylethyl-amine	G1 D-Cellobiose	G2 Glucose-1-Phosphate	G3 α-Ketobutyric Acid	G4 Phenylethyl-amine	G1 D-Cellobiose	G2 Glucose-1-Phosphate	G3 α-Ketobutyric Acid	G4 Phenylethyl-amine
H1 α-D-Lactose	H2 D,L-α-Glycerol Phosphate	H3 D-Malic Acid	H4 Putrescine	H1 α-D-Lactose	H2 D,L-α-Glycerol Phosphate	H3 D-Malic Acid	H4 Putrescine	H1 α-D-Lactose	H2 D,L-α-Glycerol Phosphate	H3 D-Malic Acid	H4 Putrescine

Figure 9. The lay-out of the Biolog Ecoplate showing the locations of the different carbon sources.

2.7 Statistical Analyses

Several statistical analyses were performed with the data. The first was an unpaired 2 sample *t*-test that compared the river and the lake sediments. Analysis of variance (ANOVA) tests were used to compare among three lake sites (LC-15-01, LC-15-02 and LC-15-03) and three river sites (SC-15-01, SC-15-02 and SC-15-03). A separate ANOVA test was also carried out to compare the carbon utilization patterns of the microbial communities at different seasons (spring, summer, fall and winter) for the lake and river sediments. When ANOVA showed significant difference between sites or between seasons ($P \leq 0.05$), means were separated using Tukey's honest significant test. The statistical analyses were executed Minitab 17 Statistical software (Minitab Inc., State College, PA).

There was also the pattern of utilization which was calculated using the average of the absorbencies of a particular carbon source and dividing it over the sum of all the absorbencies:

$$\frac{\frac{A_1 + A_2 + A_3}{3}}{\sum OD_{595}} \times 100 = \textit{Pattern of Utilization}\ (\%)$$

CHAPTER III - ANALYTICAL RESULTS

3.1 Analytical Results of St. Clair River Sediment

3.1.1 Field Conditions at St. Clair River

Table 7 presents the field conditions during the 2009 sampling event. The average air temperature during the sampling activities on June 16, 2009 was an average of 18°C. Sky condition was dominantly clear and sunny. Water clarity was typically very clear, 1.5 m or more as a result of the water low turbidity. The average wind speed was 8 km/h. Average humidity was 55%. Dew point was 10°C. Precipitation was 0 mm. Sea level pressure was 772.16 mmHg. Visibility 16 km (Table 7).

Table 7. Weather condition of sampling activities on June 16, 2009.

Temperature	
Mean temperature	18°C
Maximum temperature	25°C
Min temperature	13°C
Moisture	
Dew point	10°C
Average humidity	55%
Maximum humidity	84%
Minimum humidity	31%
Precipitation	0 mm
Sea level pressure	772.16 mmHg
Wind	
Wind speed	8 kph
Minimum wind speed	19 kph
Maximum wind speed	0 kph
Visibility	16 km

Field data for the 2009 sampling are presented in Table 8. The water level remained stable (167 m to 167.2 m). The thickness of core sample retrieved ranged from 0.76m to 1.83m based on the sediment thickness at each sample location (Table 8). The pH value ranged from 7.0 to 8.3. The highest pH value was 8.3 downstream at sample SC-09-01 and SC-09-03, while the lowest value was 8 upstream at sample SC-09-08 (Table 8). Water clarity data varied between sites. The highest water clarity was downstream at sample SC-09-03, and SC-09-04, while the lowest water clarity data was upstream at sample SC-09-06, and SC-09-07 (Table 8). Water temperature ranged from 10 °C to 12°C. The highest temperature was recorded at sites SC-09-08, SC-09-07, and SC-09-06, while the lowest temperature was recorded at sites SC-09-01 and SC-09-05 (Table 8). Core depth was ranged from 0.76 m to 1.8 m. Core depth was based on the sediment shoaling at each sample location. The highest core depth was from site SC-09-05 and lowest core depth was from site SC-09-01 (Table 8). Core sample SC-09-05 was split into two subsamples (SC-09-05A and SC-09-05B) due to the higher depth at this location and sediment change.

Table 8. St. Clair River 2009 field data of the seven sampling locations.

Sample ID#	Water depth (m.)	Water elevation (m.)	Sediment elevation (m.)	Core thickness (m.)	Water temperature (◦C)	Water clarity (m)	Sediment pH
SC-09-01	8.4	176.0	167.6	0.76	10	2.0	8.3
SC-09-03	8.2	176.2	168.0	1.52	11	2.0	8.3
SC-09-04	8.2	176.0	168.0	1.25	11	2.0	7.9
SC-09-05	7.6	176.0	168.4	1.80	10	1.5	8.2
SC-09-06	7.8	176.2	168.4	0.76	12	1.5	7.5
SC-09-07	8.2	176.2	168.0	0.88	12	1.5	8.2
SC-09-08	8.7	176.2	167.5	0.9	12	1.7	7.0

We have also observed an increase in both quantity of water and bedload. As we tracked the river downstream, the bedload became much smaller and smoother. In the lower course bedload can only really be found in the form of fine sediments and muds, known as alluvium. Therefore, sediment collected was mostly brown silty sand, and with some clay at some sample locations (Table 9). No organic odor was observed.

Table 9. Lithology of the 2009 sediments samples collected from St. Clair River.

Sample ID#	Lithology
SC-09-01	0.46 m brown silty sand with some black lenses of clay
SC-09-03	Brown fine sand with lenses of black clay
SC-09-04	Brown sand with silty clay
SC-09-05A	Interbedded brown to gray sand and brown to dark gray silty clayey sand
SC-09-05B	Brown to gray sand to dark gray silty clayey
SC-09-06	0.6m Brown to dark sand
SC-09-07	Brown sand
SC-09-08	Interbedded brown sand (SP) with dark brown silty sand

3.1.2 Physico-Chemical Properties of St. Clair River Sediment

Selected physico-chemical characteristics were determined for each of the sediment samples. Results for solids, specific gravity, density, chemical oxygen demand, volatile solids and total organic carbon are presented in Table 10. Moisture and grain size analysis results are presented in Table 11.

Table 10. Physico-chemical properties of St. Clair River sediment samples.

Sample ID	SC-09-01	SC-09-03	SC-09-04	SC-09-05A	SC-09-05B	SC-09-06	SC-09-07	SC-09-08
% Solids	70	67	70	73	73	76	73	68
S.G. (g/cc)	2.16	1.93	2.15	2.01	1.87	1.86	1.96	1.91
Density	2.16	1.93	2.14	2.00	1.87	1.86	1.97	1.91
COD (mg/kg)	180,000	230,000	160,000	180,000	220,000	130,000	150,000	170,000
V. S. (%)	1.3	1.8	1.9	2.2	2.4	1.4	1.4	1.6
TOC (%)	0.46	0.43	0.91	0.33	0.74	0.5	0.41	0.58

The analytical results for percentage solids presented in Table 10 show that the values for all samples were distributed uniformly (between 68 and 76%). Specific gravity and density results were similar and ranged between 1.87 and 2.16 g/cc. The highest value was 2.16 g/cc found in sample SC-09-01, and the lowest value was 1.86 g/cc in sample SC-09-06 for the samples collected at depth from zero to one meter from the top sediment surface. Specific gravity for sample SC-09-05B (sample collected at depth below one meter from top sediment) was 1.87 g/cc. The chemical oxygen demand values for all sample locations varied between 130, 000 and 230, 000 mg/kg. Sample SC-09-03 and SC-09-05B showed the highest chemical oxygen demand of 230,000 mg/kg and 220,000 mg/kg, respectively. While the lowest value is 130,000 mg/kg in sample SC-09-06. Volatile solids were generally highest 2.4 % in sample SC-09-05B (deeper sediment) and gradually decreased to 2.2 % towards samples collected at shallower area (SC-09-05A). The lowest volatile solids value is 1.3% found in sample SC-09-01 (Table 10). Highest value for total organic carbon (TOC) concentration is 0.91 % was recorded in sample SC-09-04 and lowest value is 0.33 % was recorded in sample SC-09-05A for the sample collected at depth from zero to one meter from top sediment surface (Table 10). The comparatively high concentration value of TOC is 0.74% in sample SC-09-05B collected at depth below one meter from the top sediment surface (Table 10).

3.1.3 Particle Size Distribution

Sediment moisture content was relatively consistent; the lowest value was 24% (sample SC-09-06). Among the eight samples, highest moisture content (33%) was observed in sample SC-09-01 (Table 11). For the majority of all samples collected during June of 2009 in high river-flow event, more than 80% of the sediment was composed of fine-grained particles (less than 0.062 mm) collected from sample locations SC-09-01, SC-09-03, SC-09-04, SC-09-05A, SC-09-07, and SC-09-08. Sample SC-09-05B collected from depth more than one meter from top sediment surface had the highest percentage of silt and clay sediment (Table 11). Highest coarse sand percentage (2%) was found in sample SC-09-08, while the lowest percentage (0 %) was found in samples SC-09-01, SC-09-03, SC-09-05B and SC-09-07. The medium sand ranged between 2 and 8% with the highest being in samples SC-09-01 and SC-09-08, and the lowest in samples SC-09-07 and SC-09-05B. Fine sand was highest (79%) in sample SC-09-08, and the lowest (64%) in sample SC-09-05B. The highest percentage of silt – clay content (25%) was found in sample SC-09-06, while the lowest (4%) in sample SC-09-07 (Table 11).

Table 11. St. Clair River sediment grain size analysis.

Sample ID	% Moisture	% Coarse Sand	% Medium Sand	% Fine Sand	%Silt – Clay %
SC-09-01	30%	1.0	8.0	83.0	8.0
SC-09-03	33%	0.0	4.0	79.0	17.0
SC-09-04	30%	1.0	5.0	80.0	14.0
SC-09-05A	27%	1.0	4.0	83.0	12.0
SC-09-05B	27%	0.0	2.0	64.0	34.0
SC-09-06	24%	1.0	5.0	69.0	25.0
SC-09-07	27%	0.0	2.0	94.0	4.0
SC-09-08	32%	2.0	8.0	79.0	11.0

3.1.4 Trace Analysis of Sediments from St. Clair River

The concentrations of trace metals from eight sediment cores retrieved from the seven sites are compiled in Table 12 and illustrated in Figure 10. The arsenic, barium, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver and zinc concentrations between the sites range from 2.0-5.1 mg/kg, 9-25 mg/kg, 0.23-0.54 mg/kg, 4.7-10 mg/kg, 14-25 mg/kg, 4500-11, 000 mg/kg, 5-115 mg/kg, 87-260 mg/kg, 5-9.5 mg/kg, and 33-55 mg/kg, respectively (Table 12; Figure 10). Elevated concentrations for all metals except for mercury, selenium, and silver were found at sample location SC-09-05B, which was collected at depth below one meter of the top sediment surface. The concentration of metals increased with sediment depth. Deeper sediments (SC-09-05B) had higher metal concentrations that the shallower sediments (SC-09-01, SC-09-03, SC-09-04, SC-09-05A, SC-09-06, SC-09-07, and SC-09-08) (Table 12).

Table 12. Trace metals analytical results (mg/kg dry weight) of sediments from St. Clair River.

Sample ID	SC-09-01	SC-09-03	SC-09-04	SC-09-05A	SC-09-05B	SC-09-06	SC-09-07	SC-09-08	Mean
Arsenic	**3.1**	**3.7**	**3.5**	**3.0**	**5.1**	**2.7**	**2.0**	**3.9**	3.38
Barium	**13**	**20**	**19**	**25**	**29**	**11**	**9**	**17**	17.86
Cadmium	**0.27**	**0.34**	**0.32**	**0.28**	**0.54**	**0.2**	<0.23	**0.4**	0.32
Chromium	**5.8**	**7.3**	**7.2**	**5.6**	**10.0**	**4.7**	**4.7**	**6.8**	6.51
Copper	**16**	**17**	**17**	**16**	**25**	**8**	**18**	**14**	16.35
Iron	**7,000**	**8,400**	**7,500**	**6,000**	**11,000**	**4,500**	**4,600**	**8,000**	7125.00
Lead	**7**	**8**	**7**	**9**	**11**	**5**	**7**	**11**	8.10
Manganese	**180**	**210**	**190**	**150**	**260**	**87**	**95**	**260**	179.00
Mercury	<0.044	<0.044	<0.042	<0.040	<0.038	<0.039	<0.043	<0.044	<0.04
Nickel	**7.1**	**9.5**	**8.9**	**6.5**	**12.0**	**5.2**	**5.0**	**9.3**	7.94
Selenium	<0.47	<0.51	<0.46	<0.49	<0.58	<0.50	<0.57	<0.63	<0.53
Silver	<0.048	<0.043	<0.042	<0.056	<0.052	<0.057	<0.064	<0.054	<0.05
Zinc	**40**	**45**	**43**	**44**	**72**	**33**	**36**	**55**	46.00

Numbers in bold are metal concentrations above the equipment's detection limit. Numbers of "< "denote metal concentrations below the detection limit.

The distribution of the metals concentration in the river sediment is not uniform (Table 12 and Figure 10). The lowest arsenic concentration value (2.0 mg/kg) was found in sample SC-09-07, while the highest concentration value (3.9 mg/kg) was found in sample SC-09-08, which is located upstream of the river. Arsenic concentrations in downstream sites (SC-09-01, SC-09-03 and SC-09-04) varied between 3.1 and 3.7 mg/kg. The concentration in upstream sites (SC-09-05A, SC-09-06 and SC-09-07) were generally lower (2-3 mg/kg), with the exception of sample SC-09-08 in which the concentration (3.7 mg/kg) is comparable to the upstream sites. A comparatively high concentration value of arsenic (5.1 mg/kg) was found in deeper sediments (SC-09-05B) (Table 12 and Figure 10).

The highest barium concentration was 25 mg/kg (SC-09-05A) and the lowest concentration value was 9 mg/kg (SC-09-07). Barium concentration values were higher in sites located downstream of the river: 13 mg/kg, 20 mg/kg, 19 mg/kg, 25 mg/kg in sample SC-09-01, SC-09-03, SC-09-04, SC-09-05A, respectively. The barium concentration in upstream sites (SC-09-06, SC-09-07, and SC-09-08) were lower (9-11 mg/kg) than the upstream sites. The deeper sediments (SC-09-05B) had higher 29 mg/kg barium concentrations than the shallower sediments (Table 12 and Figure 10).

The cadmium highest concentration was found in the upstream sample SC-09-08 (0.4 mg/kg), while the lowest concentration (<0.23 mg/kg), which is below the detection limit was found in sample SC-09-07. Cadmium concentrations in the upstream sites (SC-09-01, SC-09-03, SC-09-04) ranged from 0.27 to 34 mg/Kg. Comparatively, high cadmium concentration (0.54 mg/kg) was found in SC-09-05B (deeper sediments) (Table 12 and Figure 10).

The chromium concentrations of sediment samples collected between 0-1 meter varied from 5.6 to 7.3 mg/kg with the highest value found in sample SC-09-03 and the lowest in sample SC-09-05A. Chromium concentration of sediment sample retrieved below 1 meter (SC-09-05B) was 10 mg/kg (Table 12 and Figure 10).

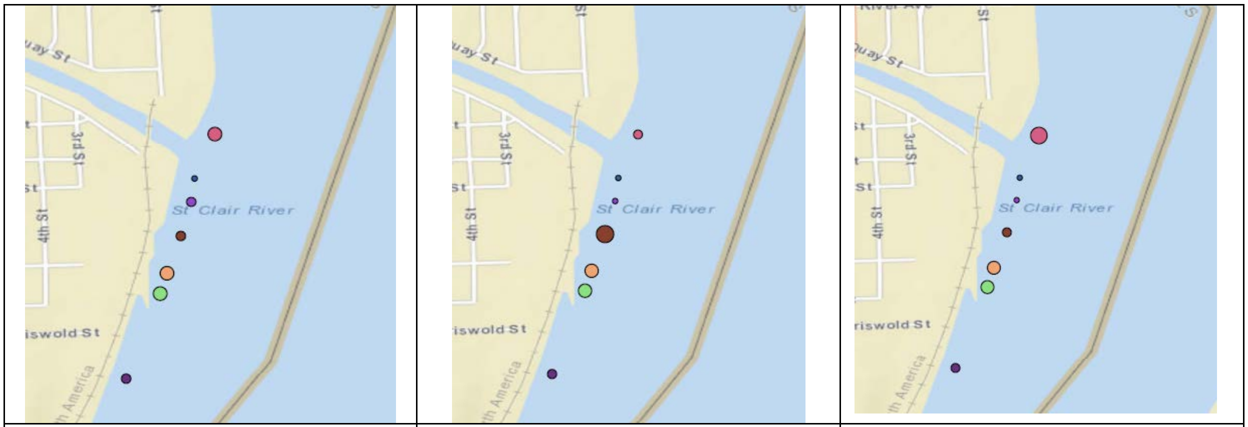
Copper concentrations in the sediments collected within 0-1 meter were varied between 4.7 mg/kg (SC-09-06 and SC-09-07) to 17 mg/kg (SC-09-03 and SC-09-04). Sample SC-09-05B (deeper sediments) had similar concentration as the most of the shallower sediments (Table 12 and Figure 10).

Iron concentration concentrations (Table 12) were the highest value among all other 12 metals analyzed in this study. The highest concentration value is 8,400 mg/kg, while the lowest concentration value is 4,500 mg/kg found in sample SC-09-03 and SC-09-006, respectively. These concentrations were lower than that of the deeper sediment (SC-09-05B; 11, 000 mg/kg).

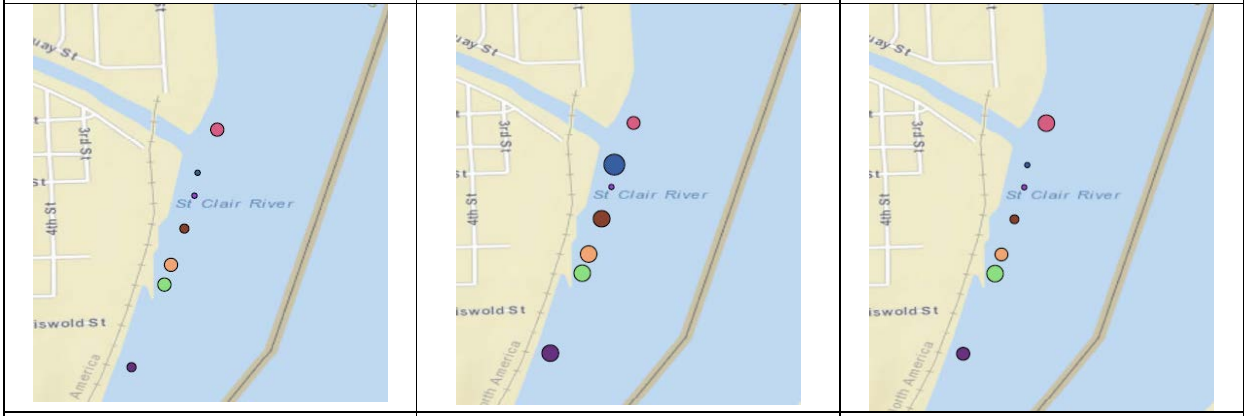
Sediment samples collected from zero to one meter depth from the top surface sediment showed Pb concentrations ranging from 5 to 11 mg/kg, the highest concentration being from sample SC-09-08 and the lowest from sample SC-09-06. Sample SC-09-05B had similar Pb concentration as SC-09-08 (Table 12 and Figure 10).

Highest manganese, nickel and zinc concentrations were found in SC-09-08 (260 mg/kg, 9.3 mg/kg, and 55 mg/kg, respectively) and lowest in SC-09-06 (87 mg/kg, 5,2 mg/kg, and 33 mg/kg, respectively). The deeper sediments (SC-09-05B) had higher Mn, Ni and Zn concentrations than the shallower sediments (Table 8 and Figure 10). Mercury, selenium and silver were below detection limit in all sediment samples analyzed (Table 12 and Figure 10).

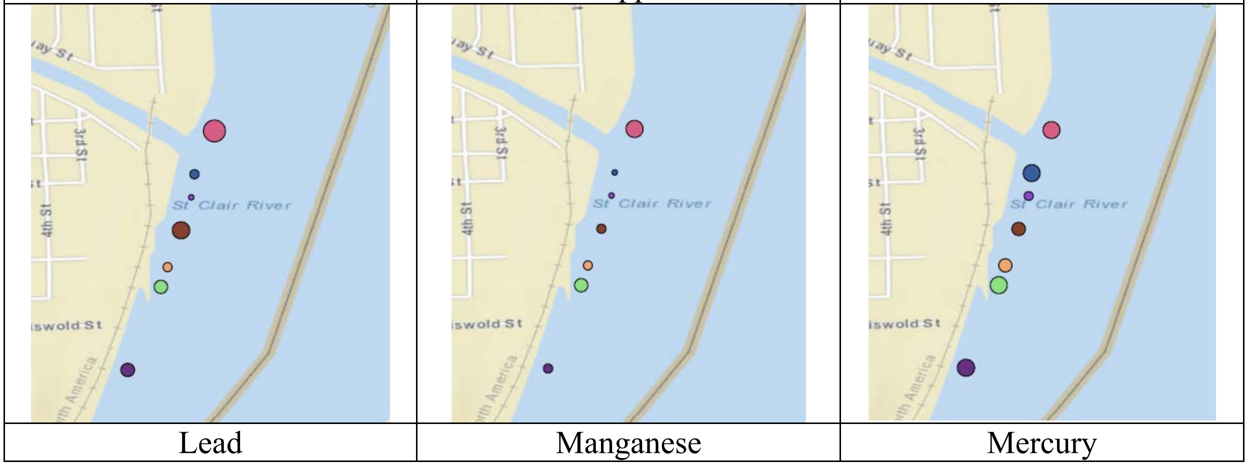
Geographic Resources Analysis Support System (GRASS), Micro station and ESRI ArcMap 10.0 were employed to map the sample location and assess trace metals concentration at the St. Clair River (Figure 10). The size of the circle reflects the relative concentration of the trace metal. The larger is the circle at the site, the higher is the trace metal concentration.



Arsenic | Barium | Cadmium

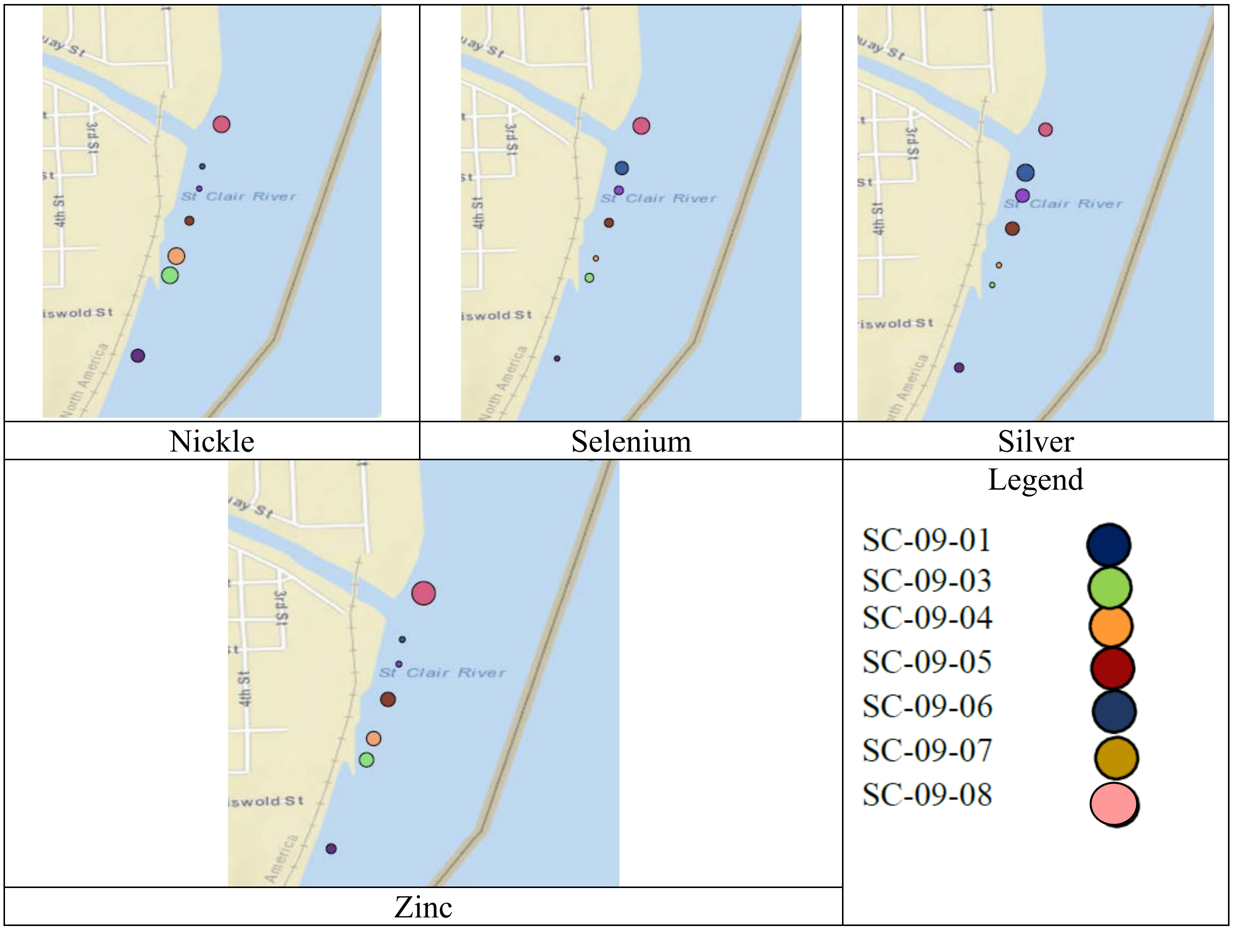


Chromium | Copper | Iron



Lead | Manganese | Mercury

Figure 10. Map showing the trace metal concentrations of the sediments at each sampling site at St. Clair River (Size of circles indicate metal concentration level).



Nickle

Selenium

Silver

Zinc

Figure 10. Map showing the trace metal concentrations of the sediments at each sampling site at St. Clair River (Size of circles indicate metal concentration level). (Continued)

The highest concentration value of all metals (Figure 10) were observed at depth below one meter from the top sediment surface in sample SC-09-05B, suggesting that the sediment type and sediment at deeper are encapsulated by the top one meter of upper sediment lead to low connection with water is the reason of high concentration values. Sample SC-09-03 located downstream and sample SC-09-08 located upstream had the highest concentration value for all metals compering to other sediment samples collected at depth zero to one meter of top sediment (Figure 10).

3.2 Analytical Results Lake St. Clair Sediment

3.2.1 Field Conditions at Lake St. Clair

The air temperature during field activities on June 25, 2010 averaged 22 °C with mostly sunny conditions, average humidity was 51%, visibility was 15km, sea level pressure was 1017 mmHg, and wind speed was 16 Km/h during the sampling hours. On July 1, 2010, the air temperature averaged 18°C with mostly sunny conditions, average humidity was 53%, visibility was 16km, sea level pressure was 1027 mmHg, and wind speed was 16 Km/h during the sampling hours. On July 7, 2010, the air temperature averaged 30°C with mostly sunny conditions, average humidity was 54%, visibility was 16km, sea level pressure was 1018 mm Hg, and wind speed was less than 12 Km/h during the sampling hours (Table 13).

Table 13. Weather condition during the sampling activities in Lake St. Clair in 2010.

Temperature	June 25, 2010	July 1, 2010	July 7, 2010
Mean temperature	22 ºC	18 ºC	29 ºC
Maximum temperature	28 ºC	25 ºC	35 ºC
Min temperature	17 ºC	13 ºC	24 ºC
Moisture			
Dew point	11 ºC	8 ºC	19 ºC
Average humidity	51%	53%	54%
Maximum humidity	75%	77%	71%
Minimum humidity	31%	32%	44%
Precipitation	0 mm	0 mm	0 mm
Sea level pressure	1017 mmHg	1027 mmHg	1018 mmHg
Wind			
Wind speed	6 (WNW)	8 (NNE)	10 (SW)
Minimum wind speed	6 kph	8 kph	10 kph
Maximum wind speed	21 kph	21 kph	19 kph
Visibility	15 km	16 km	16 km

Field data for the 2010 sampling are presented in Table 14. The water level remained stable (175.0 m to 175.1 m). The water depth ranged from 7.7 to 8.5 m. The highest water depth was at sample LC-10-04 and LC-10-06 (8.5m), while the lowest water depth was at sample LC-10-19 (7.7m). The thickness of core sample retrieved ranged from 0.55m to 1.20m (Table 14). The pH of the lake sediments ranged from 7.4 to 8.1. The highest pH values (8.0 to 8.1) recorded were from samples LC-10-01, LC-10-04, LC-10-05, LC-10-09, LC-10-11, LC-10-12, LC-10-17, LC-10-18, and LC-10-19, while the lowest values (7.4 to 7.9) were from samples LC-10-02, LC-10-3, LC-10-06, LC-10-07, LC-10-08, LC-10-13, LC-10-14, LC-10-15 and LC-10-16 (Table 14). Water clarity data were very close among sites. The highest water clarity (between 3.0m and 3.1m) was found in samples LC-10-01, LC-10-02, LC-10-05, LC-10-07, LC-10-09, LC-10-10, LC-10-11, LC-10-12, LC-10-13, LC-10-16, LC-10-,17, LC-10-18 and LC-10-19, while the lowest water clarity data (between 2.8m and 2.9 m) was found in samples LC-10-03, LC-10-,4, LC-10-06, LC-10-08, LC-10-14 and LC-10-15 (Table 14). Water temperature ranged from 19 °C to 24°C. The highest temperature was recorded at sites LC-10-04, while the lowest temperature was recorded at sites LC-10-07, LC-10-08 and LC-10-010 (Table 14).

The sampling area is covered with alluvium, consisting of clay and slit (Table 15). The lithology of samples collected showed no major changes with the sediment types of the samples collected from upstream (LC-10-01 to LC-10-09) compared with the samples collected downstream (LC-10-10 to LC-10-19). Sediments collected from sites LC-10-01, LC-10-02, LC-10-03, LC-10-04, LC-10-05, LC-10-06, LC-10-07, and LC-10-08 consisted of gray silty clay, slight organic odor (vegetative) with sand, and very similar to sediments from site LC-10-15 except that LC-10-15 had a soft and wet consistency. Sediments collected from LC-10-09, LC-10-10, LC-10-11, LC-10-12, LC-10-13 and LC-10-14 composed of dark gray clay, soft, wet, slight organic odor (vegetative). Sediments collected from sites LC-10-16, LC-10-17, LC-10-18, LC-10-19 were made up of gray silty clay, soft, wet, slight organic odor (vegetative) characteristics (Table 15).

Table 14. Lake St. Clair 2010 field data of the seven sampling locations

Sample ID#	Water depth (m.)	Water elevation (m.)	Sediment elevation (m.)	Core thickness retrieved (m.)	Water temperature (°C)	Turbidity (m)	pH
LC-10-01	8.00	175.0	167.0	1.00	23	3.0	8.0
LC-10-02	8.10	175.1	175.2	1.00	23	3.0	7.8
LC-10-03	8.40	175.0	166.6	0.70	23	2.9	7.5
LC-10-04	8.50	175.0	166.6	0.55	24	2.9	8.1
LC-10-05	8.20	175.0	166.9	0.89	22	3.0	8.1
LC-10-06	8.50	175.0	166.5	0.89	22	2.9	7.9
LC-10-07	8.20	175.0	166.9	1.07	19	3.0	7.6
LC-10-08	8.05	175.0	167.0	1.13	19	2.8	7.6
LC-10-09	8.14	175.0	166.9	1.20	20	3.0	8.0
LC-10-10	8.20	175.0	166.9	1.07	19	3.0	8.0
LC-10-11	8.23	175.0	166.9	1.07	21	3.0	8.0
LC-10-12	8.40	175.1	166.7	1.07	21	3.0	8.0
LC-10-13	8.17	175.1	166.9	1.07	21	3.0	7.4
LC-10-14	8.17	175.1	166.9	1.07	22	2.8	7.6
LC-10-15	8.13	175.1	167.0	1.07	21	2.9	7.8
LC-10-16	7.96	175.1	167.1	1.07	20	3.0	7.9
LC-10-17	7.96	175.0	166.9	1.04	22	3.0	8.0
LC-10-18	8.00	175.0	167.0	1.00	20	3.1	8.1
LC-10-19	7.70	175.0	167.0	1.07	21	3.1	8.0

Table 15. Lithology of the 2010 sediment samples collected from Lake St. Clair.

Sample ID#	Lithology
LC-10-01	Gray silty clay, slight organic odor (vegetative) with sand
LC-10-02	Gray silty clay, slight organic odor (vegetative) with sand
LC-10-03	Gray silty clay, slight organic odor (vegetative) with sand
LC-10-04	Gray silty clay, slight organic odor (vegetative) with sand
LC-10-05	Gray silty clay, slight organic odor (vegetative) with sand
LC-10-06	Gray silty clay, slight organic odor (vegetative) with sand
LC-10-07	Gray silty clay, slight organic odor (vegetative) with sand
LC-10-08	Gray silty clay, slight organic odor (vegetative)
LC-10-09	Dark gray clay, soft, wet, slight organic odor (vegetative)
LC-10-10	Dark gray clay, soft, wet, slight organic odor (vegetative)
LC-10-11	Dark gray clay, soft, wet, slight organic odor (vegetative)
LC-10-12	Dark gray clay, soft, wet, slight organic odor (vegetative)
LC-10-13	Dark gray clay, soft, wet, slight organic odor (vegetative)
LC-10-14	Dark gray clay, soft, wet, slight organic odor (vegetative)
LC-10-15	Gray silty clay sand, soft, wet, slight organic odor (vegetative)
LC-10-16	Gray silty clay, soft, wet, slight organic odor (vegetative)
LC-10-17	Gray silty clay, soft, wet, slight organic odor (vegetative)
LC-10-18	Gray silty clay, soft, wet, slight organic odor (vegetative)
LC-10-19	Gray silty clay, soft, wet, slight organic odor (vegetative)

3.2.2 Physico-Chemical Properties of Lake St. Clair Sediment

Selected physico-chemical characteristics were determined for each of the sediment samples. Results for solids, specific gravity, density, chemical oxygen demand, volatile solids and total organic carbon are presented in Table 16. Moisture and grain size analysis results are presented in Table 16.

Solid percentage of the sediments ranged from 47% (LC-10-18) to 74% (LC-10-03); specific gravity value ranged from 1.51 g/cc (LC-10-12) to 2.24 g/cc (LC-10-05); density ranged from 14.2 g/cc (LC-10-11) to 18.7 g/cc (LC-10-05); and volatile solids ranged from 2.1% (LC-10-04) to 4.9 % (LC-10-09) (Table 16).

COD value ranged from 29,000 mg/kg dry (LC-10-01) to 110,000 mg/kg dry (LC-10-05). The high values indicate the greater amount of oxidizable organic material in the sample, which reduce dissolved oxygen (DO) levels. A reduction in DO can lead to anaerobic conditions, which is deleterious to higher aquatic life forms (Table 16).

In addition to the COD, TOC was also show high values ranged from <1.3 % by wt (LC-10-04) to 3.1 % by wt (LC-10-09). The overall pattern of TOC value in relation to COD was consistent. The higher TOC levels for these samples mostly in deep area in the navigation channel. A variety of anthropogenic factors could contribute to such variability and potential misclassification as well (Table 16).

Table 16. Physico-chemical properties of Lake St. Clair sediments.

Sample ID	LC-10-01	LC-10-02	LC-10-03	LC-10-04	LC-10-05	LC-10-06	LC-10-07	LC-10-08	LC-10-09	LC-10-10
% Solids	60	68	74	69	66	53	69	58	58	57
Specific Gravity (g/cc)	2.02	1.81	2.14	2.07	2.24	2.12	1.8	1.81	2.23	2.19
Density	16.8	15.1	17.9	17.2	18.7	17.7	15	15.1	18.6	18.3
Chemical oxygen demand (mg/kg)	29,000	46,000	33,000	72,000	110,000	65,000	100,000	53,000	75,000	58,000
Volatile Solids (%)	3.5	3.4	3.6	2.1	3.4	4.3	3.3	3.7	4.9	4.7
Total organic Carbon (%)	2.2	2.0	2.0	<1.3	1.4	2.0	1.8	3.0	3.1	1.9

Sample ID	LC-10-11	LC-10-12	LC-10-13	LC-10-14	LC-10-15	LC-10-16	LC-10-17	LC-10-18	LC-10-19
% Solids	61	50	62	65	58	60	56	47	54
Specific gravity (g/cc)	1.71	1.51	2.01	1.94	1.81	2.12	2.21	1.99	1.99
Density	14.2	12.6	16.7	16.1	15.1	17.7	18.5	16.6	16.6
Chemical oxygen demand (mg/kg)	61,000	65,000	43,000	49,000	57,000	50,000	65,000	90,000	77,000
Volatile solids (%)	4.2	4.5	3.7	4.3	4.6	4.8	3.8	4.8	4.6
Total organic Carbon (%)	2.5	3.0	2.6	2.9	2.4	2.2	1.6	<2.1	2.3

3.2.3 Particle-Size Distribution

Sediment moisture content ranged from 26% to 53%; the lowest value (26%) was found in sample LC-10-03, while the highest moisture content (53%) was observed in sample LC-10-18 (Table 17). To evaluate the changes in the process and energy of sediment transport and its relation to transport the trace metals sediment samples were analyzed for grain size analysis (Table 17). For the majority of all samples collected in summer of 2010, high water-flow event was expected thus, the sediments from the 19 sample locations were composed of an average of 84.2% fine-grained particles (less than 0.062 mm). The highest percentage of fine particles were found in sample LC-10-02 (97.8%) and the lowest fine particles (53.9%) was found in sample LC-10-01 (Table 17). Fine gravel (4.3%) was found only in sample LC-10-01. The highest coarse sand percentage (1.9 %) was found in sample LC-10-07, while the lowest (0 %) was found in samples LC-10-03, LC-10-11, LC-10-15, LC-10-17, LC-10-18 and LC-10-19. The medium sand ranged from 0% (LC-10-02) to the highest value of 4.7% (LC-10-01) (Table 17).

Table 17. Lake St. Clair sediment grain size analysis.

Sample ID	% Moisture	% Fine Gravel	% Coarse Sand	% Medium Sand	% Fine Sand	% Silt - Clay
LC-10-01	38.0%	4.3	0.8	4.7	37.2	53.9
LC-10-02	31.0%	0.0	0.1	0.0	2.1	97.8
LC-10-03	26.0%	0.0	0.0	0.9	4.0	95.1
LC-10-04	32.0%	0.0	0.1	0.9	51.8	47.2
LC-10-05	35.0%	0.0	0.2	0.6	31.0	68.2
LC-10-06	48.0%	0.0	0.4	2.1	25.9	71.6
LC-10-07	37.0%	0.0	1.9	2.2	22.0	73.9
LC-10-08	42.0%	0.0	0.9	1.1	6.5	91.5
LC-10-09	42.0%	0.0	1.7	0.7	5.1	92.5
LC-10-10	43.0%	0.0	0.2	1.8	6.5	91.5
LC-10-11	39%	0.0	0.0	1.0	8.3	90.7
LC-10-12	50%	0.0	1.4	0.7	1.5	96.4
LC-10-13	38%	0.0	1.0	0.3	11.1	87.6
LC-10-14	35%	0.0	0.2	1.4	1.7	96.7
LC-10-15	42%	0.0	0.0	0.1	23.5	76.4
LC-10-16	40%	0.0	0.1	0.1	6.2	93.6
LC-10-17	42%	0.0	0.0	0.2	5.7	94.1
LC-10-18	53%	0.0	0.0	0.2	3.6	96.2
LC-10-19	48%	0.0	0.0	0.8	8.1	91.1

Grain size analysis revealed that sediments of Lake St. Clair are finer grained (Table 17) than the sediments collected from St. Clair River. Sediments in Lake St. Clair were primarily silty sand with some clay, with 53.9 % to 97.8% fines. An overall, grain size sorting for sediment collected from Lake St. Clair ranged from moderate to extremely poorly sorted.

3.2.4 Trace Analysis Concentration in Lake St. Clair Sediments

The concentration of Trace Metals analysis of 19 sediment cores from 19 sample locations are compiled in Table 18 and illustrated in Figure 11.

The average As, Ba, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Se, Ag, and Zn concentrations in the sediments were 6.1 mg/kg, 44 mg/kg, 0.63 mg/kg, 17 mg/kg, 21 mg/kg, 16000 mg/kg, 16 mg/kg, 440 mg/kg, 0.22 mg/kg, 21 mg/kg, 0.69 mg/kg, 0.088 mg/kg, and 74 mg/kg, respectively (Table 18). Concentrations below the instrument's solid detection limits are reported (<). The concentration of arsenic, barium, cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc were detected in all sediment sampling location except cadmium at sample location LC-10-03 and LC-10-13 (<0.27 mg/kg and <0.51mg/kg , respectively); mercury in sample location LC-10-02 and LC-10-03 (<0.034 mg/kg and <0.033 mg/kg, respectively); silver in sample locations LC-10-04, LC-10-09, LC-10-10 & LC-10-12 (<0.039 mg/kg, <0.073 mg/kg, <0.074 mg/kg, and <0.087 mg/kg, respectively). Selenium was not detected in all samples expect at sample locations LC-10-12 (0.84 mg/kg), LC-10-14 (0.71 mg/kg) and LC-10-15 (0.69 mg/kg) and LC-10-16 (0.7 mg/kg) (Table 18).

Sampling locations covered in this study were divided in two groups: upstream group and downstream group. The upstream group consisted of sites LC-10-01 to LC-10-09, while the downstream group consisted of sites LC-10-10 to LC-10-19.

Arsenic concentrations upstream were 5.4 mg/kg (LC-10-01), 6.8 mg/kg (LC-10-02), 6.5, mg/kg (LC-10-03), 3.7 mg/kg (LC-10-04), 5.1 mg/kg (LC-10-05), 5.9 mg/kg (LC-10-06), 7.4 mg/kg (LC-10-07), 6.9 mg/kg (LC-10-08), and 6.6 mg/kg (LC-10-09). The highest concentration was found in sample LC-10-07 (7.4 mg/kg), the lowest concentration was found in sample LC-10-04 (3.7 mg/kg) (Table 18). Arsenic concentrations were downstream were 6.8 mg/kg (LC-10-10), 6.3 mg/kg (LC-10-11), 6.2 mg/kg (LC-10-12), 5 mg/kg (LC-10-13), 4.7 mg/kg (LC-10-14), 5.3 mg/kg (LC-10-15), 6.1 mg/kg (LC-10-16), 4.5 mg/kg (LC-10-17), 6.7 mg/kg (LC-10-18, and

5.6 mg/kg (LC-10-19).The highest concentration was found in sample LC-10-10 (6.8 mg/kg), while the lowest concentration was found in sample LC-10-17 (4.5 mg/kg) (Table 18).

Table 18. Trace metal concentrations (mg/kg dry weight) of sediments from Lake St. Clair.

Sample ID	**LC-10-01**	**LC-10-02**	**LC-10-03**	**LC-10-04**	**LC-10-05**	**LC-10-06**	**LC-10-07**	**LC-10-08**	**LC-10-09**	**LC-10-10**
Arsenic	**5.4**	**6.8**	**6.5**	**3.7**	**5.1**	**5.9**	**7.4**	**6.9**	**6.6**	**6.8**
Barium	**22**	**75**	**67**	**15**	**23**	**28**	**49**	**40**	**44**	**48**
Cadmium	**0.46**	**0.27**	<0.27	**0.39**	**0.45**	**0.52**	**0.92**	**1**	**0.67**	**0.66**
Chromium	**10**	**21**	**20**	**8.3**	**11**	**12**	**20**	**16**	**16**	**17**
Copper	**14**	**17**	**16**	**11**	**16**	**19**	**30**	**24**	**25**	**25**
Iron	**9,800**	**28,000**	**22,000**	**7,900**	**9,700**	**11,000**	**15,000**	**16,000**	**17,000**	**17,000**
Lead	**9**	**10**	**10**	**7.8**	**10**	**11**	**29**	**17**	**16**	**17**
Manganese	**270**	**570**	**520**	**230**	**280**	**320**	**390**	**450**	**460**	**440**
Mercury	**0.13**	<0.034	<0.033	**0.22**	**0.18**	**0.22**	**2.6**	**0.21**	**0.25**	**0.19**
Nickel	**15**	**28**	**28**	**12**	**15**	**17**	**21**	**21**	**22**	**21**
Selenium	<0.74	<0.66	<0.68	<0.64	<0.70	<0.88	<1.2	<1.4	<0.66	<0.66
Silver	**0.062**	**0.094**	**0.053**	<0.039	**0.049**	**0.049**	**0.17**	**0.2**	<0.073	<0.075
Zinc	**50**	**52**	**48**	**44**	**50**	**54**	**94**	**74**	**75**	**75**

Numbers in bold are metal concentrations above the equipment's detection limit. Numbers of "< " denote metal concentrations below the detection limit.

Table 18. Trace metal concentrations of sediments from Lake St. Clair (mg/kg dry weight). (Continued)

Sample ID	LC-10-11	LC-10-12	LC-10-13	LC-10-14	LC-10-15	LC-10-16	LC-10-17	LC-10-18	LC-10-19	Mean
Arsenic	**6.3**	**6.2**	**5**	**4.7**	**5.3**	**6.1**	**4.5**	**6.7**	**5.6**	5.87
Barium	**41**	**56**	**150**	**38**	**39**	**47**	**41**	**51**	**45**	48.37
Cadmium	**0.63**	**0.71**	<0.51	**0.54**	**0.57**	**0.64**	**0.57**	**0.7**	**0.71**	0.61
Chromium	**16**	**19**	**29**	**14**	**15**	**18**	**17**	**21**	**23**	17.02
Copper	**22**	**25**	**19**	**18**	**19**	**23**	**21**	**27**	**27**	20.95
Iron	**16,000**	**19,000**	**27,000**	**14,000**	**15,000**	**17,000**	**15,000**	**20,000**	**17,000**	16494.74
Lead	**16**	**18**	**13**	**14**	**16**	**21**	**17**	**25**	**53**	17.36
Manganese	**450**	**490**	**530**	**380**	**410**	**460**	**410**	**510**	**400**	419.47
Mercury	**0.2**	**0.099**	**0.037**	**0.37**	**0.3**	**0.25**	**0.2**	**0.22**	**0.29**	0.35
Nickel	**21**	**26**	**34**	**19**	**19**	**23**	**22**	**28**	**26**	22.00
Selenium	<0.63	**0.84**	<0.51	**0.71**	**0.69**	**0.7**	<0.81	<0.99	<0.85	0.70
Silver	**0.089**	<0.087	**0.08**	**0.07**	**0.085**	**0.099**	**0.088**	**0.098**	**0.12**	0.09
Zinc	**74**	**85**	**74**	**64**	**67**	**76**	**65**	**81**	**80**	67.47

Numbers in bold are metal concentrations above the equipment's detection limit. Numbers of "< " denote metal concentrations below the detection limit.

Barium concentrations ranged from 15 mg/kg to 75 mg/kg in upstream sites (LC-10-01, LC-10-02, LC-10-03, LC-10-04, LC-10-05, LC-10-06, LC-10-07, LC-10-08, and LC-10-09) and 38 mg/kg to 150mg/kg in downstream sites (LC-10-10, LC-10-11, LC-10-12, LC-10-13, LC-10-14, LC-10-15, LC-10-16, LC-10-17, LC-10-18, and LC-10-19). The highest concentration was found in sample LC-10-13 (150 mg/kg), while the lowest concentration was found in sample LC-10-04 (15 mg/kg) (Table 18).

Cadmium concentrations varied between <0.27 mg/kg and 1 mg/kg. The highest concentration was found in sample LC-10-08 (1 mg/kg), the lowest concentration was found in sample LC-10-03 (<0.27 mg/kg) (Table 18).

Chromium concentrations in upstream sites were 10 mg/kg (LC-10-01), 21 mg/kg (LC-10-02), 20 mg/kg (LC-10-03), 8.3 mg/kg (LC-10-04), 11 mg/kg (LC-10-05), 12 mg/kg (LC-10-06), 20 mg/kg (LC-10-07), 16 mg/kg (LC-10-08), and 16 mg/kg (LC-10-09). Chromium concentrations in the downstream sites were 17 mg/kg (LC-10-10), 16 mg/kg (LC-10-11), 19 mg/kg (LC-10-12), 29 mg/kg (LC-10-13), 14 mg/kg (LC-10-14), 15 mg/kg (LC-10-15), 18 mg/kg (LC-10-16), 17 mg/kg (LC-10-17), 21 mg/kg (LC-10-18), and 23 mg/kg (LC-10-19). The highest concentration was found in sample LC-10-13 (29 mg/kg), while the lowest concentration was found in sample LC-10-01 (10mg/kg) (Table 18).

Copper concentrations in upstream sites ranged from 11 mg/kg to 30 mg/kg, while that of the downstream sites ranged from 18 to 27 mg/kg. The highest concentration was found in sample LC-10-07 (30 mg/kg), while the lowest concentration was found in sample LC-10-04 (11mg/kg) (Table 18).

Iron concentrations were varied in between 7,900 mg/kg and 28,000 mg/kg in all 19 sites with the highest found in LC-10-02 (28,000mg/kg) and lowest sample LC-10-04 (7,900 mg/kg) (Table 18)

Lead concentrations were higher in the downstream sites (13 mg/kg to 53 mg/kg) than the upstream sites (7.8 mg/kg to 29 mg/kg). The highest concentration was found in sample LC-10-19 (53 mg/kg), while the lowest concentration was found in sample LC-10-04 (7.8 mg/kg) (Table 18).

Manganese, mercury nickel, selenium, silver and zinc concentrations were also higher in the upstream sites than the downstream sites (Table 18). The highest manganese concentration was found in sample LC-10-02 (570 mg/kg), while the lowest concentration was found in sample LC-10-04 (230 mg/kg) (Table 18).

Highest mercury concentration was found in sample LC-10-07 (2.6 mg/kg), while the lowest concentration was found in sample LC-10-02 (<0.034 mg/kg) and LC-10-03 (<0.033 mg/kg) (Table 18).

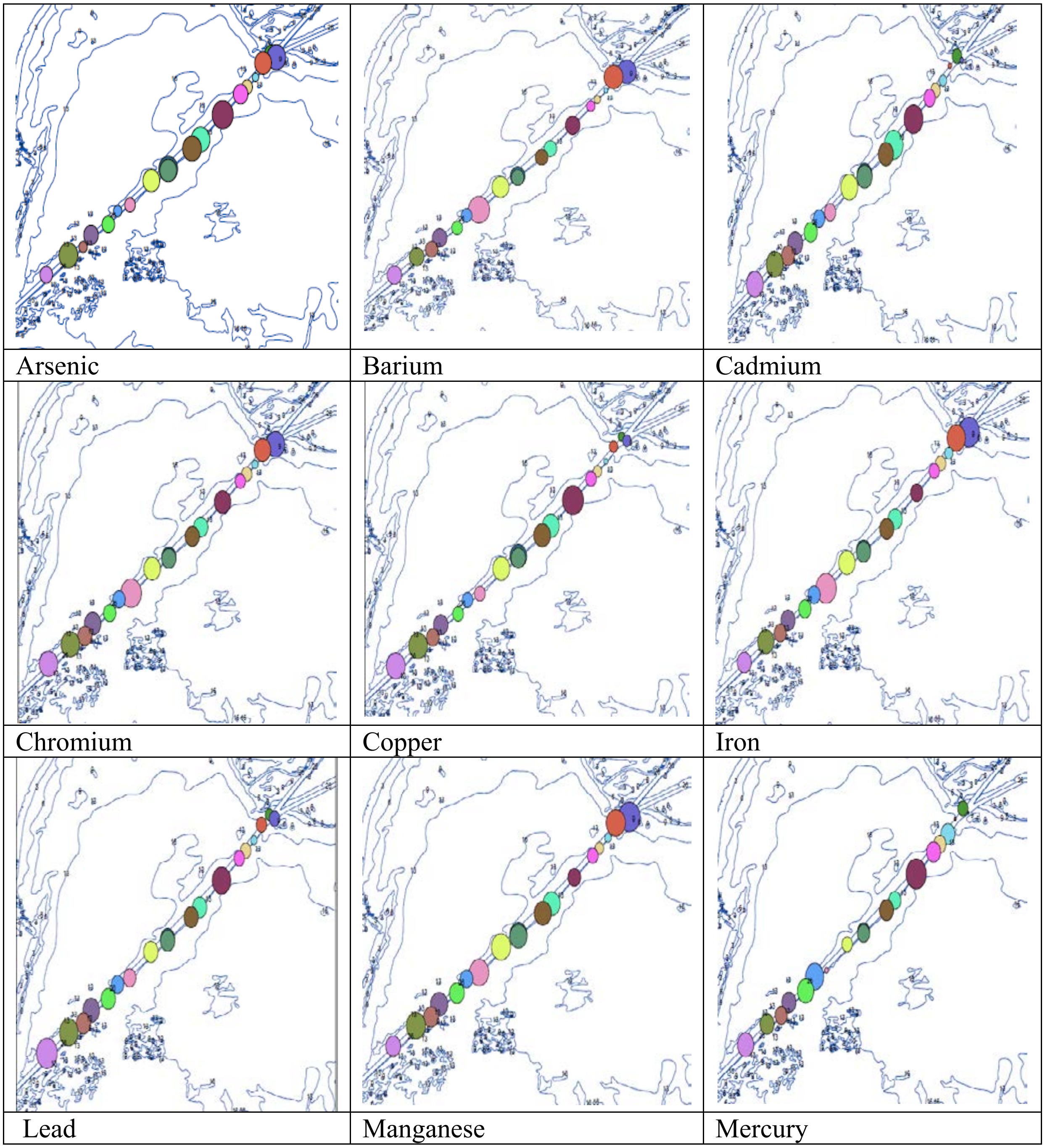
The highest nickel concentration was found in sample LC-10-13 (34 mg/kg), while the lowest concentration was found in sample LC-10-14 (19 mg/kg) (Table 18). The highest nickel concentration was found in sample LC-10-03 and LC-10-02 (22mg/kg), while the lowest concentration was found in sample LC-10-04 (12 mg/kg) (Table 18).

Selenium concentration was found below the detection limit for all the samples collected upstream. The higher concentration was found downstream in sample LC-10-12 (0.84 mg/kg), while the lowest concentration was found in sample LC-10-14, LC-10-15, and LC-10-16 (0.7 mg/kg), all other samples collected downstream were below the detection limit (Table 18).

Sliver highest concentration was found upstream in sample LC-10-08 (0.2 mg/kg), and downstream in sample LC-10-19 (0.12 mg/kg) (Table 18).

Zinc highest concentration was found upstream in sample LC-10-07 (94 mg/kg), while the lowest concentration was found in sample LC-10-04 (44 mg/kg) (Table 18). The highest nickel concentration was found downstream in sample LC-10-12 (85 mg/kg), while the lowest concentration was found in sample LC-10-12 (64 mg/kg) (Table 18).

The distribution of the contaminated sediment may depend on the topography of the lake bottom, and/or the velocity of the sediment particles. The highest metal concentrations were for the elements iron, manganese and zinc in all samples locations as compared to other elements concentration (Figure 11). In addition, the trace metals concentration presented in Table 18 shows the concentration fluctuated with few increasing along the study gradient from upstream at sample location LC-10-01 moving downstream toward sample location LC-10-19. The highest concentration was found upstream in sample LC-10-07 and downstream in sample LC-10-13, LC-10-18, and LC-10-19 for most trace metals analyzed. The lowest concentration was found upstream in sample LC-10-04 and downstream in sample LC-10-14 for most trace metals analyzed.



Arsenic

Barium

Cadmium

Chromium

Copper

Iron

Lead

Manganese

Mercury

Figure 11. Map showing the concentrations of the trace metals in the sediments at each sample location at Lake St. Clair (Size of circles indicate metal concentration level).

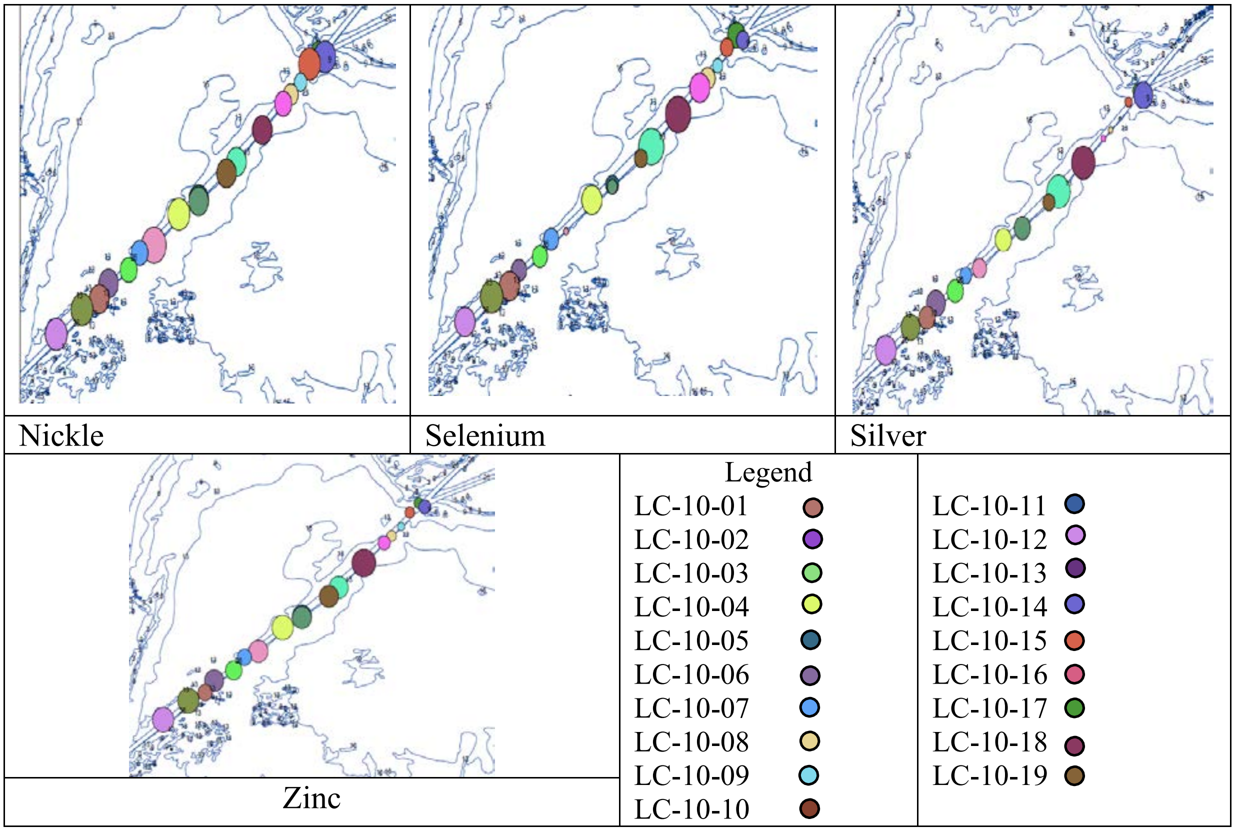


Figure 11. Map showing the concentrations of the trace metals in the sediments at each sample location at Lake St. Clair (Size of circles indicate metal concentration level). (Continued)

3.3 Trace Metals Statistical Analysis Results

The statistical *t*-test was used by White and Tittlebaum (1984) in their analysis of lake and river sediment evaluates the null hypothesis, i.e., that the mean of one data set is equal to the mean of another set of data (Murray, 1996). Fundamental to this procedure is the incorporation of variances of each set of data. Murray (1996) used the statistical *t*-test to determine the existence of any significant concentration and /or ratio differences ($P<0.05$) between each sample location and the background samples in the Rouge River, Michigan.

A *t*-test was used to determine if there is significant difference in trace metal contents between the lake and river sediments (Table 19). *t*-test results showed significant difference between the two sediment samples. Results from the *t*-tests can be found in Table 19.

Comparison of the mean concentrations for trace metals between the Lake St. Clair and St. Clair River revealed significant differences between lake and river sediments (Table 15). The lake sediments had significantly higher As, Ba, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Se, Silver and Zn ($P < 0.05$) than the river sediments (Table 19).

3.4 Microbial Activities in St. Clair River and Lake St. Clair Sediments

3.4.1 Weather History and Field Data

The highest mean air temperature was in fall (22°C), and the lowest was in winter (10 °C). The highest mean humidity was in the summer, and the lowest was in spring. None of the sampling days had any precipitation. Pressure was highest in the winter (771 mmHg) and lowest in the summer (760 mmHg). Visibility was lowest in the fall at 11.27km, and while in summer and winter, visibility was at its highest at 16.09km (Table 20).

The average water temperature for spring was 12°C, summer was 19°C, fall was 25°C, and winter was 7°C (Table 20). Water depth remained fairly consistent throughout the year, with the shallowest in site LC-15-02 in every season (0.31m to 0.76 m) and the deepest in site SC-15-01 (2.31 m to 3.05 m). Sediment height elevation varied between 172 and 174 m above the sea level. The turbidity data was measured in the summer, fall and winter (Table 20). Turbidity readings were higher in sites SC-15-02 (1.19 m to 1.49 m) and LC-15-03 (1.22 m) than that of sites SC-15-01 (0.31 m), SC-15-03 (0.31 m), LC-15-01 (0.76 m to 0.91 m) and LC-15-02 (0.61 m). Water turbidities remained consistent at each site at different seasons. The pH of the water was relatively consistent across all seasons (Table 20), with the lowest pH being 7.1 (LC-15-02 summer) and the highest being 8.9 (SC-15-02 summer) (Table 20).

Table 19. Comparison of total mean concentrations of trace metals (mg/kg dry) of the Lake St. Clair and St. Clair River (mean is mean value; CV is coefficient of variation (%).

Element	Lake St. Clair (2010)			St. Clair River (2009)				
	Mean	SD±	CV	Mean	SD±	CV	*P* value	Significance
Arsenic	5.868	0.972	16.56%	3.375	0.921	27.29%	<0.0001	***
Barium	48.4	28.6	59.09%	17.88	6.88	38.48%	<0.0001	***
Cadmium	0.589	0.187	31.75%	0.336	0.110	32.74%	<0.0001	***
Chromium	17.02	4.93	28.97%	6.51	1.74	26.73%	<0.0001	***
Copper	20.95	5.01	23.91%	16.38	4.69	28.63%	0.040	*
Iron	16495	5276	31.99%	7125	2141	30.05%	<0.0001	***
Lead	17.4	10.2	58.62%	8.13	2.10	25.83%	0.001	***
Manganese	419.5	92.6	22.07%	179.0	66.1	36.93%	<0.0001	***
Mercury	0.318	0.560	176.10%	0.04175	0.00243	5.82%	0.046	*
Nickel	22.00	5.43	24.68%	7.94	2.41	30.35%	<0.0001	***
Selenium	0.787	0.213	27.06%	0.5263	0.0602	11.44%	<0.0001	***
Silver	0.0884	0.0399	45.14%	0.05200	0.00743	14.29%	0.001	***
Zinc	67.5	14.2	21.04%	46.0	12.4	26.96%	0.001	***

CV=coefficient of variation; P≤ 0.05, *; P ≤0.01,**; P≤0.001, ***; P≥ 0.5, “ns” = not significant.

Table 20. Water temperature, water depth, turbidity and sediment pH- 2015 sediment samples.

Sites	Water temperature (°C)	Water depth (m)	Sediment elevation (m)	Turbidity (m)	Sediment pH
Spring					
St. Clair River					
SC-15-01	11.5	3.05	172.2	nd	8.7
SC-15-02	10.2	091	174.3	nd	8.2
SC-15-03	12.9	1.22	170.0	nd	7.9
Lake St. Clair					
LC-15-01	12.4	1.07	174.2	nd	7.9
LC-15-02	15.5	0.76	174.2	nd	7.9
LC-15-03	12.3	0.52	174.2	nd	8.0
Summer					
St. Clair River					
SC-15-01	22.9	3.05	172.2	031	7.9
SC-15-02	21.3	1.19	172.2	1.19	8.9
SC3-15-0	20.6	1.31	172.2	0.31	8.2
Lake St. Clair					
LC-15-01	20.6	0.76	174.8	0.76	7.3
LC-15-02	15.6	0.61	174.9	0.61	7.1
LC-15-03	12.3	1.31	174.2	1.22	8.0
Fall					
St. Clair River					
SC-15-01	25.0	2.35	173.2	0.31	7.7
SC-15-02	23.9	1.49	174.0	1.49	8.7
SC-15-03	22.2	1.41	173.1	0.31	7.7
Lake St. Clair					
LC-15-01	22.8	0.91	174.6	0.91	8.7
LC-15-02	25.6	0.31	175.2	1.19	8.7
LC-15-03	28.9	1.80	173.7	0.31	8.8
Winter					
St. Clair River					
SC-15-01	5.00	2.68	172.4	0.31	8.6
SC-15-02	6.67	0.91	174.2	1.19	8.1
SC-15-03	8.89	1.95	173.1	0.31	7.9
Lake St. Clair					
LC-15-01	7.22	0.91	174.2	0.76	8.0
LC-15-02	7.78	0.61	174.5	0.61	7.7
LC-15-03	7.22	1.37	173.7	1.22	7.8

3.4.2 Physico-Chemical Properties of St. Clair Sediments

Sediment samples collected from St. Clair River had relatively higher moisture contents than those from Lake St. Clair (19 to 68%), particularly those from sites SC-15-01 (72 to 102%) and SC-15-03 (48 to 95%) (Table 4). Moisture contents of the sediments from the lake sites (LC-15-01, LC-15-02 and LC-15-03) were stable in the spring (22 to 68%), summer (31 to 56%) and fall (38 to 45%) but dropped significantly during the winter sampling (19 to 20%). Moisture contents of the sediments from the river sites were highest in the spring, with site SC-15-01 reaching as high as 102%. Summer and winter moisture content ranges for the three sites (SC-15-01, SC-15-02, and SC-15-03) were similar (24 to 72% and 19 to 78%, respectively). The moisture contents between the lake sites (19 to 68%) and the river sites (22 to 102%) also varied considerably. It should also be noted that these variabilities are due to differences in the sediments' texture. For instance, sediment samples with high clay contents (SC-15-01, SC-15-02, and LC-15-03) would hold more water and thus, had higher moisture contents than sediment samples with higher sand contents (SC-15-01, LC-15-02 and LC-15-03) (Table 21).

The pH ranges of the sediment extracts (1:10 sediment-water ratio) from the river and lake sites were very similar (6.29-7.32 for river sites; 6.52-7.23 for lake sites), and varied little between seasons. The average pH of all sites for spring, summer, fall and winter was 6.77, 7.00, 6.99 and 6.81, respectively (Table 21). These pH values were lower than the water pH of the sites at the time of sampling (Table 20). The seasonal averages for all sites were 8.10 in spring; 7.90 in summer; 8.26 in fall; and 8.01 winter (Table 20). Regardless of the lower sediment pH values, the extracts had similar pH between the seasons.

The electrical conductivity of the extracts (1:10 sediment-water ratio) varied significantly between sites (Table 4). The electrical conductivity reading of the extracts from the river sites varied between 20 and 258 µS cm-1, while that of the lake sites fluctuated between 25 and 225 µS cm-1. The highest electrical conductivity reading (258 µS cm-1), was from sediment extracts in the summer at site SC-15-01, while the lowest (20 µS cm-1) was in the winter at site SC-15-02. The average conductivity for spring across all sites was 152 µS cm-1; 119 µS cm-1 for summer; 131 µS cm-1 for fall; and 89 µS cm-1 for winter (Table 21).

The total organic carbon (TOC) and ash content are inversely proportional (Table 4). The sediments from the river sites tended to have much higher TOC contents than the lake sites, particularly sites SC-15-01 and SC-15-03, which ranged in TOC from 4.94% to 67.5%. The lake had far lower TOC contents (0.64% to 21.35%). The total organic carbon contents were highest in the spring, especially in the sediment samples from sites SC-15-01 (40.5%), SC-15-03 (67.5%) and LC-15-03 (24.63%). As the seasons went on, the TOC contents of the sediments declined in all sites from an average reading of 31.59% in spring 2.68% by winter sampling. As the TOC contents of the sediments decreased over time, the ash contents increased reaching their peaks in the winter. Sediment samples from sites SC-15-02, LC-15-01 and LC-15-02 had particularly higher ash contents than the other river and lake sites. These are the same sites that have much higher sand contents, which suggest that the sand may be poorer at holding organic carbon than the soils with higher clay contents (Table 21).

Table 21. Physico-chemical properties of 2015 sediments samples

Sites	Moisture content (%)	pH (1:10 water extract)	Electrical conductivity (µS cm^{-1})	Ash content (%)	TOC (%)
Spring					
St. Clair River					
SC-15-01	102 ± 16.3	6.64 ± 0.02	228 ± 17.1	36.67 ± 40.57	64.33 ± 40.46
SC-15-02	22 ± 2.2	6.29 ± 0.14	33 ± 5.0	86.40 ± 16.84	13.60 ± 16.84
SC-15-03	95 ± 15.0	6.88 ± 0.07	255 ±20.8	32.54 ± 11.17	67.50 ± 11.17
Lake St. Clair					
LC-15-01	26 ± 0.3	6.53 ± 0.35	90 ± 11.6	96.95 ± 1.568	3.052 ± 1.568
LC-15-02	32 ± 6.2	7.08 ± 0.20	80 ± 0.0	78.65 ± 37.12	21.35 ± 37.12
LC-15-03	68 ± 16.1	7.17 ± 0.29	225 ± 5.8	80.28 ± 24.63	19.72 ± 24.63
Summer					
St. Clair River					
SC-15-01	72 ± 81.46	6.67 ± 0.02	258 ± 17.1	67.37 ± 32.58	32.63 ± 32.58
SC-15-02	24 ± 6.50	7.13 ± 0.13	45 ±5.8	99.05 ± 0.36	0.95 ± 0.36
SC-15-03	48 ± 5.80	7.32 ± 0.01	168 ± 5.0	95.21 ± 0.88	4.79 ± 0.88
Lake St. Clair					
LC-15-01	31 ± 0.90	6.68 ± 0.21	73 ± 20.6	98.26 ± 0.99	1.75 ± 0.98
LC-15-02	28 ± 0.54	6.96 ± 0.15	55 ±5.8	98.34 ± 0.10	1.66 ± 0.10
LC-15-03	56 ± 7.41	7.23 ± 0.05	115 ± 5.8	92.46 ± 0.67	7.54 ± 0.67
Fall					
St. Clair River					
SC-15-01	81 ± 22.50	6.80 ± 0.05	193 ± 9.6	91.34 ± 1.80	8.66 ± 1.80
SC-15-02	37 ± 7.96	7.10 ± 0.10	63 ± 5.0	98.16 ± 0.09	1.84 ± 0.09
SC-15-03	81 ± 27.34	6.86 ± 0.03	150 ± 0.0	90.89 ± 0.91	9.11 ± 0.91
Lake St. Clair					
LC-15-01	38 ± 10.06	6.78 ± 0.12	160 ± 58.8	97.18 ± 0.80	2.82 ± 0.80
LC-15-02	42 ± 15.89	7.18 ± 0.04	113 ± 9.6	98.27 ± 0.97	1.74 ± 0.97
LC-15-03	45 ± 14.50	7.24 ± 0.10	105 ± 5.8	95.76 ± 1.16	4.24 ± 1.16
Winter					
St. Clair River					
SC-15-01	74 ± 23.93	6.70 ± 0.43	185 ± 12.9	95.06 ± 2.05	4.94 ± 2.05
SC-15-02	19 ± 0.84	6.75 ± 0.14	20 ± 0.0	98.81 ± 0.38	1.19 ± 0.38
SC-15-03	78 ± 5.38	6.73 ± 0.06	165 ± 17.3	92.82 ± 1.42	7.18 ± 1.42
Lake St. Clair					
LC-15-01	21 ± 1.85	6.75 ± 0.04	33 ± 5.0	99.36 ± 0.31	0.87 ± 0.29
LC-15-02	19 ± 0.86	7.17 ± 0.27	103 ± 59.67	98.76 ± 0.33	1.24 ± 0.33
LC-15-03	20 ± 1.28	6.77 ± 0.10	25 ± 5.8	99.13 ±0.27	0.64 ± 0.32

3.4.3 Metabolic diversity profile

Inoculum density was a major issue on interpreting the Biolog Ecoplate data. It was noted the color development was correlated with the cell density (Figure 12).

Figure 12. Color change in the Biolog plate.

The microbial numbers were low across all samples and the variations between samples were relatively small (≤ one order of magnitude) (Figure 12).

AWCD varied between Lake St. Clair sediment samples and St. Clair River sediment samples collected at different season are shown in Table 22, AWCD demonstrated a sigmoid pattern for the different treatments as incubation time increased, the overall utilization of all carbon sources was greater during the period from summer to fall season, but it dropped rapidly in winter.

Table 22. AWCD values of Lake St. Clair versus St. Clair River sediment at different seasons.

Spring (ID & Time in hours)	AW CD	Summer (ID &Time in hours)	AW CD	Fall (ID & Time in hours)	AW CD	Winter ID & Time in hours)	AW CD
LC-15-01 72	0.106	LC-15-01 48	1.042	LC-15-01 72	0.193	LC-15-01 72	0.093
LC-15-02 72	0.147	LC-15-02 24	0.711	LC-15-02 24	0.847	LC-15-02 72	0.691
LC-15-03 72	0.304	LC-15-03 72	0.721	LC-15-03 72	0.707	LC-15-03 72	0
SC-15-01 48	0.661	SC-15-01 72	0.295	SC-15-01 72	0.604	SC-15-01 72	0.305
SC-15-02 72	0.146	SC-15-02 48	1.063	SC-15-02 48	0.807	SC-15-02 72	0.056
SC-15-03 72	0.708	SC-15-03 72	0.702	SC-15-03 72	0.796	SC-15-03 72	0.293

3.4.3.1 Community-level physiological profiles (CLPP)

In this study, the 31 carbon sources were grouped to sum utilization responses to all substrates within these six functional classes. These include 2 amines, 6 amino acids, 10 carbohydrates, 7 carboxylic acids, 4 polymers, and 2 phenolic compounds. A complete list of the substrate with class is noted in Figure 13. The community-level physiological profiles (CLPP) from different sediments showed that the measured utilization typically differed among substrates, and revealed differences and similarities among type of sediment sample, ecosystems, seasons, and sites. About 5 to 31 substrates were used by the microbial communities at each site (Figure 13) and the relative abundance based on AWCD for each substrate was different. Substrates that produced consistently low relative responses were probably poorly degraded by the microbial communities studied here. However, most substrates apparently supported at least some bacterial activity. In this study, we considered 3-4% absorbance of the total absorbance per plate as the threshold for substrate utilization.

3.4.3.2 Analysis of substrate utilization data from Lake St. Clair and St. Clair River Sediments

Inspection of the CLPPs suggests that some differences in sediments between two ecosystems (Figure 13). In general, similar numbers of substrates were used in the lake sediment samples (2 to 29) and the river sediment samples (5 to 31). The lake sediments samples varied considerably with regard to the number of utilized substrates, with highest number in the summer (23 to 28) and lowest in the spring (8 to 15). The river sediment samples showed higher utilization in all seasons (16 to 29), with only the winter samples showing very low signals, particularly in site SC-15-02 (Figure 13). *T*-test results showed no significant difference between the two sediment samples (Table 23), with the exception of phenylethylamine, L-threonine, D-xylose, and D-malic acid. The river sediment samples were characterized by significantly higher (≤ 0.05) phenylethylamine (amine), L-threonine (amino acid), D-xylose (carbohydrate), and D-malic acid (carboxylic acid) utilization than the lake sediments (Table 23). Another key difference included the higher utilization of amines, amino acids, carbohydrates, carboxylic acids, and polymers in the lake sediments (Figure 13). Interestingly, α-ketobutyric acid was not utilized by the microbial communities in lake sediments (Figure 13).

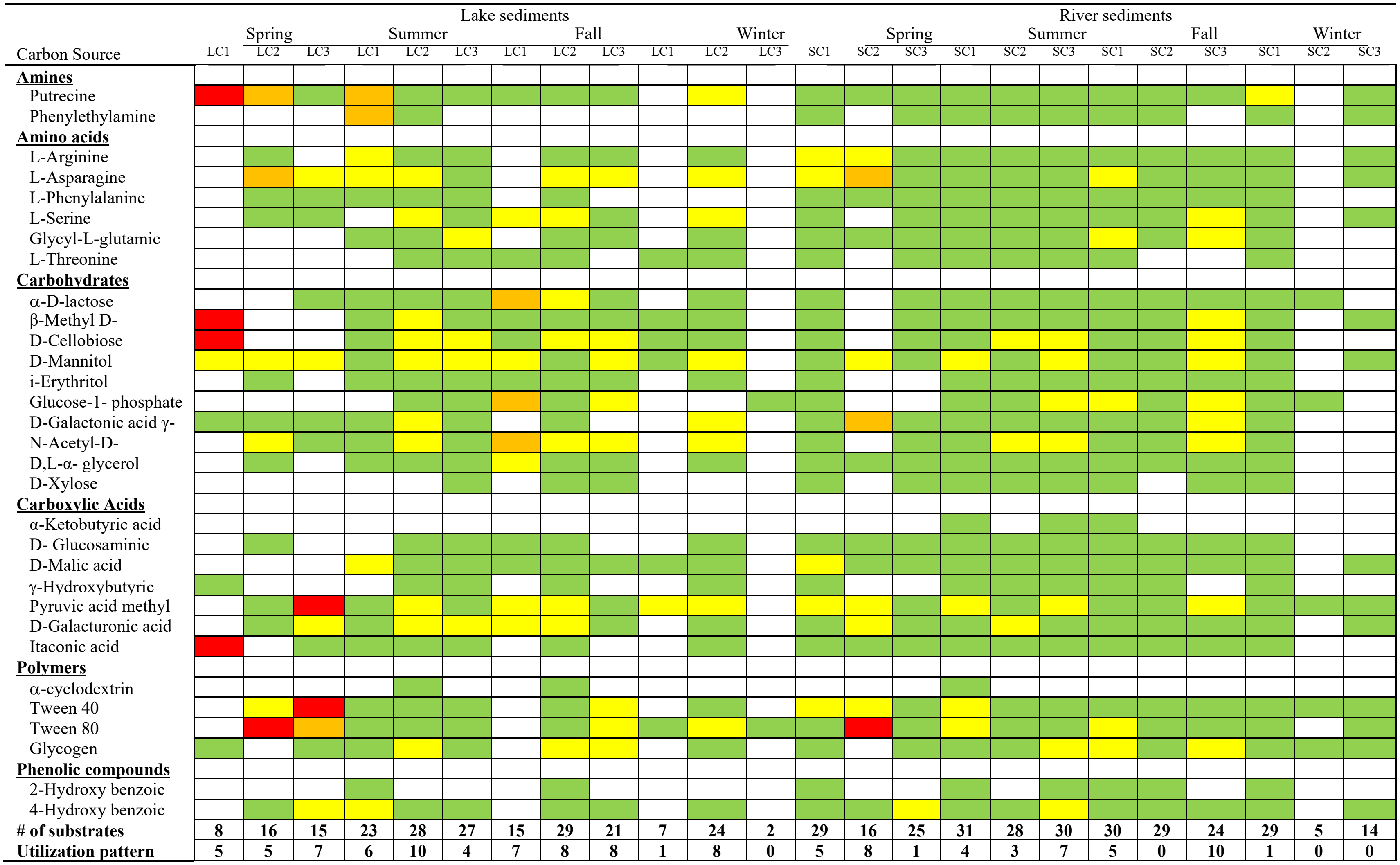
3.4.3.3 Comparison of substrate utilization data at different sites

The breakdown of the percent utilization of the carbon sources into six substrate guilds showed very similar use among lake sites (LC-15-01, LC-15-02 and LC-15-03) (Figure 13). Results of the ANOVA demonstrated no significant differences for the 31 carbon sources exception of 8 carbon substrates: L-asparagine, D-galactonic acid γ-lactone, N-acetyl-D-glucosamine, γ-hydrobutyric acid, α-cyclodextrin, tween 40, tween 80 and glycogen (Table 24). Sediments in site LC-15-02 showed highest carbon utilization compared to sediments in sites LC-15-01 and LC-15-03 (Figure 13). It had significantly higher utilization of one amino acid (L-asparagine), two carbohydrates (D-galactonic acid γ-lactone and N-acetyl-D-glucosamine), one carboxylic acud (γ-hydrobutyric acid) and two polymers (α-cyclodextrin and glycogen) (Table 24). Site LC-15-02 also had higher utilization of amino acids and carbohydrates, while sites LC-15-01 and LC-15-03 had higher utilization of amines and polymers, respectively (Figure 13). Phenylethylamine and 2 hydroxy benzoic acid were not utilized in site LC-15-03. No utilization was observed for D, L α glycerol phosphate, D-xylose, and α-cyclodextrin in site LC-15-01 (Figure 13).

Utilization patterns of all carbon sources in the sediments from the river sites (SC-15-01, SC-15-02 and SC-15-03) were similar from each other except for 11 carbon substrates: phenylalanine, L-arginine, L-threonine, D-galactonic acid γ-lactone, D-xylose, α-ketobutyric acid, D-malic acid, itaconic acid, α-cyclodextrin, 2-hydroxy benzoic acid and 4-hydroxy benzoic acid (Table 25). The analysis of variance (ANOVA) indicated significant difference in the utilization of these carbon sources was significantly lower in sediments from site SC-15-02 than in sites SC-15-01 and SC-15-03 and the utilization in sites SC-15-01 and SC-15-03 were similar (Table 25). Site SC-15-02 had higher utilization of carbohydrates and carboxylic acids, while sites SC-15-01 and SC-15-03 had higher utilization of polymers and phenolic compounds, respectively (Figure 13). Suprisingly, α-ketoglutaric acid and 2-hydroxy benzoic acid were not utilized in site SC-15-02. No utilization was observed for α-cyclodextrin sites SC-15-02 and SC-15-03 (Figure 13).

3.4.3.4 Seasonal patterns of substrate utilization

The pattern of carbon utilization of the heterotrophic communities in sediments varied with season (Figure 13). The number of carbon substrates utilized was less in spring (8-16 for lake sediments; 16 to 29 for river sediments) than in summer (23 to 28 for lake sediments; 25 to 31 for river sediments) and fall (15 to 29 for lake sediments; 24 to 30 for river sediments) seasons. The winter season had the least number of carbon utilized (2 to 24 for lake sediments; 5 to 29 for river sediments). ANOVA results indicated significant seasonal trends for all 31 carbon sources with the exception of 10 carbon sources: putrecine, phenylethylamine, L-arginine, L-asparagine, L-threonine, D-xlose, D-glucosaminic acid, D-malic acid, itaconic acid, tween 40, tween 80 and 4-hydroxybenzoic acid (Table 26). Carbon utilization of these 10 carbon sources are significantly higher in the summer and fall than in spring and winter. Higher utilization of amino acids, carbohydrates and polymers were observed in the fall; and amines, carboxylic acids, and phenolic compounds in the spring and summer (Figure 13). Notably, neither α-cyclodextrin nor α-ketoglutaric acid were utilized in in spring (Figure 13).



	Lake sediments												River sediments											
	Spring			Summer			Fall			Winter			Spring			Summer			Fall			Winter		
Carbon Source	LC1	LC2	LC3	LC1	LC2	LC3	LC1	LC2	LC3	LC1	LC2	LC3	SC1	SC2	SC3	SC1	SC2	SC3	SC1	SC2	SC3	SC1	SC2	SC3
Amines																								
Putrecine	🟥	🟧	🟩	🟧	🟩	🟩	🟩	🟩	🟩	⬜	🟨	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟨	⬜	🟩
Phenylethylamine	⬜	⬜	⬜	🟧	🟩	⬜	⬜	⬜	⬜	⬜	⬜	⬜	🟩	⬜	🟩	🟩	🟩	🟩	🟩	🟩	⬜	🟩	⬜	🟩
Amino acids																								
L-Arginine	⬜	🟩	⬜	🟨	🟩	🟩	⬜	🟩	🟩	⬜	🟩	⬜	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	⬜	🟩
L-Asparagine	⬜	🟧	🟨	🟨	🟨	🟩	⬜	🟨	🟨	⬜	🟨	⬜	🟨	🟧	🟩	🟩	🟩	🟩	🟨	🟩	🟩	🟩	⬜	🟩
L-Phenylalanine	⬜	🟩	🟩	🟩	🟩	🟩	⬜	🟩	⬜	⬜	⬜	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	⬜	⬜
L-Serine	⬜	🟩	🟩	⬜	🟨	🟩	🟨	🟨	🟩	⬜	🟨	⬜	🟩	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟨	🟩	⬜	🟩
Glycyl-L-glutamic	⬜	⬜	⬜	🟩	🟩	🟨	⬜	🟩	🟩	⬜	🟩	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟨	🟩	🟨	🟩	⬜	⬜
L-Threonine	⬜	⬜	⬜	⬜	🟩	🟩	🟩	🟩	⬜	🟩	🟩	⬜	🟩	⬜	🟩	🟩	🟩	🟩	🟩	⬜	⬜	🟩	⬜	⬜
Carbohydrates																								
α-D-lactose	⬜	⬜	🟩	🟩	🟩	🟩	🟧	🟨	🟩	⬜	🟩	⬜	🟩	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	⬜
β-Methyl D-	🟥	⬜	⬜	🟩	🟨	🟩	🟩	🟩	🟩	🟩	🟩	⬜	🟩	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟨	🟩	⬜	🟩
D-Cellobiose	🟥	⬜	⬜	🟩	🟨	🟨	🟩	🟨	🟨	🟩	🟩	⬜	🟩	⬜	🟩	🟩	🟨	🟨	🟩	🟩	🟨	🟩	⬜	⬜
D-Mannitol	🟨	🟨	🟨	🟩	🟨	🟨	🟨	🟩	🟨	🟩	🟨	⬜	🟩	🟨	🟩	🟨	🟩	🟨	🟩	🟩	🟨	🟩	⬜	🟩
i-Erythritol	⬜	🟩	⬜	🟩	🟩	🟩	🟩	🟩	🟩	⬜	🟩	⬜	🟩	⬜	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	⬜	⬜
Glucose-1- phosphate	⬜	⬜	⬜	⬜	🟩	🟩	🟧	🟩	🟨	⬜	⬜	🟩	🟩	⬜	⬜	🟩	🟩	🟨	🟨	🟩	🟨	🟩	🟩	⬜
D-Galactonic acid γ-	🟩	🟩	🟩	🟩	🟨	🟩	⬜	🟩	⬜	⬜	🟨	⬜	🟩	🟧	🟩	🟩	🟩	🟩	🟩	🟩	🟨	🟩	⬜	⬜
N-Acetyl-D-	⬜	🟨	🟩	🟩	🟨	🟩	🟧	🟨	🟨	⬜	🟨	⬜	🟩	⬜	🟩	🟩	🟨	🟨	🟩	🟩	🟨	🟩	⬜	⬜
D,L-α- glycerol	⬜	🟩	⬜	🟩	🟩	🟩	🟨	🟩	🟩	⬜	🟩	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	⬜	⬜
D-Xylose	⬜	⬜	⬜	⬜	⬜	🟩	⬜	🟩	🟩	⬜	⬜	⬜	🟩	⬜	🟩	🟩	🟩	🟩	🟩	⬜	🟩	🟩	⬜	⬜
Carboxylic Acids																								
α-Ketobutyric acid	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	🟩	⬜	🟩	🟩	⬜	⬜	⬜	⬜	⬜
D- Glucosaminic	⬜	🟩	⬜	⬜	🟩	🟩	🟩	🟩	⬜	⬜	🟩	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	⬜	⬜
D-Malic acid	⬜	⬜	⬜	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	⬜	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	⬜	🟩
γ-Hydroxybutyric	🟩	⬜	⬜	⬜	🟩	🟩	⬜	🟩	⬜	⬜	🟩	⬜	🟩	⬜	⬜	🟩	🟩	🟩	🟩	🟩	⬜	🟩	⬜	⬜
Pyruvic acid methyl	⬜	🟩	🟥	🟩	🟨	🟩	🟨	🟨	🟩	🟨	🟨	⬜	🟨	🟨	🟩	🟨	🟩	🟨	🟩	🟩	🟨	🟩	🟩	🟩
D-Galacturonic acid	⬜	🟩	🟨	🟩	🟨	🟨	🟨	🟨	🟩	⬜	🟩	⬜	🟩	🟨	🟩	🟩	🟨	🟩	🟩	🟩	🟩	🟩	⬜	🟩
Itaconic acid	🟥	⬜	🟩	🟩	🟩	🟩	⬜	🟩	⬜	⬜	🟩	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	⬜	⬜
Polymers																								
α-cyclodextrin	⬜	⬜	⬜	⬜	🟩	⬜	⬜	🟩	⬜	⬜	⬜	⬜	⬜	⬜	⬜	🟩	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜
Tween 40	⬜	🟨	🟥	🟩	🟩	🟩	⬜	🟩	🟨	⬜	🟩	⬜	🟨	🟨	🟩	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Tween 80	⬜	🟥	🟧	🟩	🟩	🟩	⬜	🟩	🟨	🟩	🟨	🟩	🟩	🟥	🟩	🟨	🟩	🟩	🟨	🟩	🟩	🟩	⬜	🟩
Glycogen	🟩	⬜	🟩	🟩	🟨	🟩	⬜	🟨	🟨	⬜	🟩	⬜	🟩	⬜	🟩	🟩	🟩	🟨	🟨	🟩	🟨	🟩	🟩	🟩
Phenolic compounds																								
2-Hydroxy benzoic	⬜	⬜	⬜	🟩	⬜	⬜	⬜	🟩	⬜	⬜	⬜	⬜	🟩	⬜	⬜	🟩	⬜	🟩	🟩	🟩	⬜	🟩	⬜	⬜
4-Hydroxy benzoic	⬜	🟩	🟨	🟨	🟩	🟩	⬜	🟩	🟩	⬜	🟩	⬜	🟩	🟩	🟨	🟩	🟩	🟨	🟩	🟩	🟩	🟩	⬜	🟩
# of substrates	**8**	**16**	**15**	**23**	**28**	**27**	**15**	**29**	**21**	**7**	**24**	**2**	**29**	**16**	**25**	**31**	**28**	**30**	**30**	**29**	**24**	**29**	**5**	**14**
Utilization pattern	**5**	**5**	**7**	**6**	**10**	**4**	**7**	**8**	**8**	**1**	**8**	**0**	**5**	**8**	**1**	**4**	**3**	**7**	**5**	**0**	**10**	**1**	**0**	**0**

Figure 13. Pattern of utilization (based on mean AWCD) of the 31 carbon substrates for the lake and river sediments across sites and seasons. Shading in the boxes indicates the range of percentage absorbance of the total absorbance of the plate. Values are as follows: White, <0.1%; green, 0.1-2%; yellow, 3-4%; orange, 5-6%; red, >6%. The number of substrates with >4% absorbance for each sampling site is indicated below each column.

Table 23. T-test Utilization comparison of St. Clair River and Lake St. Clair.

Carbon Source	Lake (Mean ± SEM)	River (Mean ± SEM)	*P*-value	Significance
Amines				
Putrecine	0.737 ± 0.120	0.794 ± 0.130	0.752	ns
Phenylethylamine	0.177 ± 0.095	0.456 ± 0.098	0.045	*
Amino acids				
L-Arginine	0.466 ± 0.110	0.742 ± 0.110	0.085	ns
L-Asparagine	0.930 ± 0.150	0.998 ± 0.110	0.718	ns
L-Phenylalanine	0.113 ± 0.033	0.200 ± 0.051	0.159	ns
L-Serine	0.843 ± 0.140	0.837 ± 0.120	0.974	ns
Glycyl-L-glutamic acid	0.297 ± 0.086	0.532 ± 0.120	0.118	ns
L-Threonine	0.063 ± 0.022	0.269 ± 0.073	0.01	*
Carbohydrates				
α-D-lactose	0.430 ± 0.120	0.372 ± 0.091	0.697	ns
β-Methyl D-glucoside	0.779 ± 0.130	0.695 ± 0.120	0.643	ns
D-Cellobiose	0.776 ± 0.140	0.773 ± 0.140	0.986	ns
D-Mannitol	1.039 ± 0.140	0.943 ± 0.110	0.599	ns
i-Erythritol	0.121± 0.030	0.175 ± 0.054	0.382	ns
Glucose-1- phosphate	0.420 ± 0.100	0.709 ± 0.130	0.087	ns
D-Galactonic acid γ-lactone	0.348 ± 0.100	0.430 ± 0.094	0.553	ns
N-Acetyl-D-glucosamine	0.992 ± 0.150	0.849 ± 0.130	0.712	ns
D,L-α- glycerol phosphate	0.305 ± 0.054	0.331 ± 0.050	0.724	ns
D-Xylose	0.074 ± 0.047	0.324 ± 0.088	0.015	*
Carboxylic Acids				
α-Ketobutyric acid	0.009 ± 0.006	0.009 ± 0.021	0.32	ns
D- Glucosaminic acid	0.159 ± 0.058	0.282 ± 0.066	0.168	ns
D-Malic acid	0.323 ± 0.100	0.650 ± 0.120	0.042	*
γ-Hydroxybutyric acid	0.071 ± 0.022	0.115 ± 0.026	0.199	ns
Pyruvic acid methyl ester	1.116 ± 0.130	1.059 ± 0.081	0.704	ns
D-Galacturonic acid	0.735 ± 0.140	0.764 ± 0.130	0.88	ns
Itaconic acid	0.295 ± 0.100	0.364 ± 0.086	0.603	ns
Polymers				
α-cyclodextrin	0.035 ± 0.019	0.023 ± 0.030	0.200	ns
Tween 40	0.744 ± 0.130	0.941 ± 0.098	0.238	ns
Tween 80	0.823 ± 0.110	0.789 ± 0.076	0.796	ns
Glycogen	0.766 ± 0.140	0.884 ± 0.110	0.518	ns
Phenolic compounds				
2-Hydroxy benzoic acid	0.027 ± 0.018	0.070 ± 0.023	0.151	ns
4-Hydroxy benzoic acid	0.663 ± 0.140	0.582 ± 0.100	0.769	ns

Note: *P*> 0.05, not significant (ns); P ≤ 0.05, *; P≤0.01, **; P≤ 0.001, ***

Table 24. ANOVA for the three lake sites.

Carbon Source	LC-15-01 (Mean ± STD DEV) τ	LC-15-02 (Mean ± STD DEV) τ	LC-15-03 (Mean ± STD DEV) τ	F-value	*P*-Value	Significance
Amines						
Putrecine	0.833 ± 0.944 ^{a}	0.918 ± 0.554 ^{a}	0.461 ± 0.648 ^{a}	1.32	0.282	ns
Phenylethylamine	0.496 ± 0.928 ^{a}	0.0273 ± 0.0404 ^{a}	0.0085 ± 0.0404 ^{a}	3.16	0.055	ns
Amino acids						
L-Arginine	0.541 ± 0.976 ^{a}	0.635 ± 0.534 ^{a}	0.2225 ± 0.3101 ^{a}	1.26	0.297	ns
L-Asparagine	0.567 ± 0.247 ^{a}	1.425 ± 0.590 ^{b}	0.796 ± 0.181 ^{a}	3.2	0.044	*
L-Phenylalanine	0.056 ± 0.104 ^{a}	0.1890 ± 0.2734 ^{a}	0.0952 ± 0.1744 ^{a}	1.45	0.249	ns
L-Serine	0.689 ± 1.074 ^{a}	1.254 ± 0.762 ^{a}	0.585 ± 0.607 ^{a}	2.22	0.125	ns
Glycyl-L-glutamic acid	0.054 ± 0.161 ^{a}	0.313 ± 0.376 ^{a}	0.526 ± 0.741 ^{a}	2.81	0.075	ns
L-Threonine	0.074 ± 0.183 ^{a}	0.0820 ± 0.0794 ^{a}	0.0343 ± 0.1162 ^{a}	0.44	0.648	ns
Carbohydrates						
α-D-lactose	0.348 ± 0.543 ^{a}	1.744 ± 0.924 ^{a}	0.173 ± 0.473 ^{a}	2.46	0.101	ns
β-Methyl D-glucoside	0.657 ± 0.887 ^{a}	1.109 ± 0.731 ^{a}	0.571 ± 0.687 ^{a}	1.68	0.203	ns
D-Cellobiose	0.565 ± 0.803 ^{a}	0.919 ± 0.800 ^{a}	0.845 ± 0.943 ^{a}	0.58	0.566	ns
D-Mannitol	0.692 ± 0.784 ^{a}	1.332 ± 0.694 ^{a}	1.091 ± 0.970 ^{a}	1.85	0.174	ns
i-Erythritol	0.063 ± 0.115 ^{a}	0.1781 ± 0.1692 ^{a}	0.121 ± 0.238 ^{a}	1.22	0.309	ns
Glucose-1- phosphate	0.226 ± 0.540 ^{a}	0.308 ± 0.391 ^{a}	0.724± 0.756 ^{a}	2.53	0.095	ns
D-Galactonic acid γ-lactone	0.126 ± 0.398 ^{a}	0.756 ± 0.779 ^{b}	0.162 ± 0.349 ^{a}	5.09	0.012	*
N-Acetyl-D-glucosamine	0.769 ± 0.127 ^{a}	1.396 ± 0.690 ^{b}	0.610 ± 0.175 ^{a}	2.99	0.034	*
D,L-α- glycerol phosphate	0.265 ± 0.387 ^{a}	0.3748± 0.2603 ^{a}	0.276± 0.324 ^{a}	0.41	0.667	ns
D-Xylose	<0.001 ± 0.007 ^{a}	0.0566 ± 0.1684 ^{a}	0.167 ± 0.457 ^{a}	1.11	0.342	ns

Table 24. ANOVA for the three lake sites. (Continue)

Carbon Source	LC-15-01 (Mean ± STD DEV) τ	LC-15-02 (Mean ± STD DEV) τ	LC-15-03 (Mean ± STD DEV) τ	F-value	P-Value	Significance
Carboxylic Acids						
α-Ketobutyric acid	-0.019 ± 0.0348 ^{a}	-0.012 ± 0.025 ^{a}	-0.004 ± 0.047 ^{a}	0.84	0.440	ns
D- Glucosaminic acid	0.0128 ± 0.0230 ^{a}	0.323 ± 0.486 ^{a}	0.143 ± 0.306 ^{a}	2.64	0.086	ns
D-Malic acid	0.524 ± 0.930 ^{a}	0.135 ± 0.151 ^{a}	0.311 ± 0.519 ^{a}	1.18	0.320	ns
γ-Hydroxybutyric acid	0.0065 ± 0.046 ^{b}	0.164 ± 0.166 ^{a}	0.044 ± 0.106 ^{b}	5.93	0.006	**
Pyruvic acid methyl ester	0.985 ± 0.808 ^{b}	1.315 ± 0.671 ^{a}	1.049 ± 0.795 ^{a}	0.63	0.537	ns
D-Galacturonic acid	0.421 ± 0.745 ^{b}	1.757 ± 0.072 ^{a}	0.359 ± 0.902 ^{a}	1.02	0.372	ns
Itaconic acid	0.416 ± 0.916 ^{b}	0.346 ± 0.379 ^{a}	0.124 ± 0.331 ^{a}	0.77	0.473	ns
Polymers						
α-cyclodextrin	-0.0115 ± 0.044 ^{a}	0.1306± 0.1565 ^{b}	-0.015 ± 0.023 ^{a}	9.22	0.001	**
Tween 40	0.357± 0.726 ^{b}	0.659 ± 0.372 ^{ab}	1.214 ± 0.979 ^{b}	4.19	0.024	*
Tween 80	0.328 ± 0.456 ^{a}	0.943 ± 0.382 ^{b}	1.197 ± 0.704 ^{b}	8.46	0.001	***
Glycogen	0.426 ± 0.260 ^{a}	1.170 ± 0.855 ^{b}	0.702 ± 0.248 ^{ab}	2.51	0.046	*
Phenolic compounds						
2-Hydroxy benzoic acid	0.052 ± 0.137 ^{b}	0.028 ± 0.133 ^{a}	0.001 ± 0.023 ^{a}	0.62	0.543	ns
4-Hydroxy benzoic acid	0.603 ± 1.086 ^{b}	0.548 ± 0.594 ^{a}	0.749 ± 0.862 ^{a}	0.17	0.844	ns

*, $P \leq 0.05$; **, $P \leq 0.01$; $P \leq 0.001$; ns, not significant; τValues are means and standard deviation from triplicate wells. Means in a row followed by different letters are significantly different (ANOVA followed by Tukey's honest significant test, $P \leq 0.05$).

Table 25. ANOVA for the three river sites.

Carbon Source	SC-15-01 (Mean ± STD DEV) τ	SC-15-02 (Mean ± STD DEV) τ	SC-15-03 (Mean ± STD DEV) τ	F-value	*P*-Value	Significance
Amines						
Putrecine	0.719 ± 0.835 ^{a}	0.533 ± 0.757 ^{a}	0.786 ± 0.437 ^{a}	0.42	0.660	ns
Phenylethylamine	0.342 ± 0.239 ^{b}	0.033 ± 0.054 ^{a}	0.685 ± 0.249 ^{b}	9.63	0.001	**
Amino acids						
L-Arginine	0.945 ± 0.261 ^{b}	0.311 ± 0.345 ^{a}	0.913 ± 0.271 ^{b}	4.24	0.023	*
L-Asparagine	1.097 ± 0.803 ^{a}	0.745 ± 0.711 ^{a}	1.121 ± 0.237 ^{a}	1.32	0.281	ns
L-Phenylalanine	0.200 ± 0.085 ^{a}	0.130± 0.186 ^{a}	0.317 ± 0.494 ^{a}	1.12	0.337	ns
L-Serine	0.543 ± 0.680 ^{a}	0.784 ± 0.877 ^{a}	1.117 ± 0.185 ^{a}	2.36	0.110	ns
Glycyl-L-glutamic acid	0.423 ± 0.549 ^{a}	0.557 ± 0.752 ^{a}	0.327 ± 0.468 ^{a}	0.44	0.647	ns
L-Threonine	0.477 ± 0.575 ^{b}	0.032± 0.0583 ^{a}	0.344 ± 0.193 ^{b}	3.66	0.037	*
Carbohydrates						
α-D-lactose	0.264 ± 0.265 ^{a}	0.257 ± 0.496 ^{a}	0.393 ± 0.671 ^{a}	0.28	0.761	ns
β-Methyl D-glucoside	0.480± 0.591 ^{a}	0.848 ± 0.884 ^{a}	0.710 ± 0.604 ^{a}	0.83	0.443	ns
D-Cellobiose	0.359 ± 0.375 ^{a}	0.855 ± 0.931 ^{a}	0.954 ± 0.761 ^{a}	2.31	0.115	ns
D-Mannitol	0.652 ± 0.553 ^{a}	0.954 ± 0.888 ^{a}	1.220 ± 0.440 ^{a}	2.25	0.121	ns
i-Erythritol	0.208 ± 0.114 ^{a}	0.116 ± 0.128 ^{a}	0.213 ± 0.539 ^{a}	0.34	0.717	ns
Glucose-1- phosphate	0.517 ± 0.523 ^{a}	0.645± 0.758 ^{a}	0.688 ± 0.975 ^{a}	0.16	0.854	ns
D-Galactonic acid γ-lactone	0.262 ± 0.148 ^{b}	0.966 ± 0.873 ^{a}	0.312 ± 0.427 ^{b}	5.74	0.007	**
N-Acetyl-D-glucosamine	0.629 ± 0.601 ^{a}	0.894 ± 0.939 ^{a}	0.956 ± 0.698 ^{a}	0.63	0.540	ns
D,L-α- glycerol phosphate	0.308 ± 0.216 ^{a}	0.294 ± 0.333 ^{a}	0.302 ± 0.238 ^{a}	0.01	0.992	ns
D-Xylose	0.294 ± 0.082 ^{b}	-0.004 ± 0.013 ^{a}	0.340 ± 0.410 ^{a}	6.15	0.005	**

Table 25. ANOVA for the three river sites. (Continue)

Carbon Source	SC-15-01 (Mean ± STD DEV) τ	SC-15-02 (Mean ± STD DEV) τ	SC-15-03 (Mean ± STD DEV) τ	F-value	*P*-Value	Significance
Carboxylic Acids						
α-Ketobutyric acid	0.194 ± 0.075 ^{b}	0.001 ± 0.028 ^{a}	0.159 ± 0.171 ^{b}	6.05	0.006	**
D- Glucosaminic acid	0.297 ± 0.228 ^{a}	0.091 ± 0.134 ^{a}	0.434 ± 0.609 ^{a}	2.43	0.103	ns
D-Malic acid	0.589 ± 0.725 ^{ab}	0.104 ± 0.158 ^{a}	0.906 ± 0.578 ^{b}	6.65	0.004	**
γ-Hydroxybutyric acid	0.204 ± 0.052 ^{a}	0.022 ± 0.133 ^{b}	0.131 ± 0.201 ^{ab}	4.97	0.013	ns
Pyruvic acid methyl ester	1.095 ± 0.345 ^{a}	1.040 ± 0.697 ^{a}	1.086 ± 0.398 ^{a}	0.04	0.960	ns
D-Galacturonic acid	0.588 ± 0.621 ^{a}	0.781 ± 0.879 ^{a}	0.783 ± 0.592 ^{a}	0.30	0.744	ns
Itaconic acid	0.320± 0.337 ^{ab}	0.119 ± 0.205 ^{a}	0.602 ± 0.667 ^{b}	3.54	0.040	*
Polymers						
α-cyclodextrin	-0.054 ± 0.216 ^{ab}	0.060 ± 0.148 ^{a}	-0.194 ± 0.191 ^{b}	5.55	0.008	**
Tween 40	0.941 ± 0.705 ^{a}	0.646 ± 0.642 ^{a}	1.140 ± 0.241 ^{a}	2.30	0.116	ns
Tween 80	0.777 ± 0.547 ^{ab}	0.557 ± 0.416 ^{b}	0.988 ± 0.288 ^{a}	3.01	0.063	ns
Glycogen	0.584 ± 0.489 ^{b}	1.001± 0.889 ^{a}	1.068 ± 0.548 ^{a}	1.86	0.171	ns
Phenolic compounds						
2-Hydroxy benzoic acid	0.170 ± 0.066 ^{b}	0.014 ± 0.025 ^{a}	0.151 ± 0.019 ^{b}	7.36	0.002	**
4-Hydroxy benzoic acid	0.998 ± 0.121 ^{b}	0.137 ± 0.161 ^{a}	1.058 ± 0.556 ^{b}	10.76	<0.0001	***

*, $P \leq 0.05$; **, $P \leq 0.01$; $P \leq 0.001$; ns, not significant; τValues are means and standard deviation from triplicate wells. Means in a row followed by different letters are significantly different (ANOVA followed by Tukey's honest significant test, P ≤ 0.05).

Table 26. ANOVA for the four seasons.

Carbon Source	Spring (Mean ± STD DEV) τ	Summer (Mean ± STD DEV) τ	Fall (Mean ± STD DEV) τ	Winter (Mean ± STD DEV) τ	F-value	*P*-Value	Significance
Amines							
Putrecine	0.724 ± 0.602 ^{a}	0.701 ± 0.782 ^{a}	0.748 ± 0.680 ^{a}	0.661 ± 0.815 ^{a}	0.05	0.987	ns
Phenylethylamine	0.280 ± 0.535 ^{a}	0.423 ± 0.745 ^{a}	0.257 ± 0.415 ^{a}	0.102 ± 0.202 ^{a}	1.18	0.324	ns
Amino acids							
L-Arginine	0.602 ± 0.731 ^{a}	0.690 ± 0.713 ^{a}	0.615 ± 0.593 ^{a}	0.471 ± 0.678 ^{a}	0.32	0.811	ns
L-Asparagine	0.864 ± 0.798 ^{a}	1.199 ± 0.724^{a}	1.134 ± 0.653 ^{a}	0.637 ± 0.873 ^{a}	2.06	0.114	ns
L-Phenylalanine	0.178 ± 0.298 ^{ab}	0.274 ± 0.184 ^{b}	0.204 ± 0.322 ^{b}	0.001 ± 0.143 ^{b}	3.95	0.012	*
L-Serine	0.481 ± 0.646 ^{a}	1.267 ± 0.751 ^{b}	1.093 ± 0.682 ^{b}	0.474 ± 0.704 ^{a}	6.28	0.001	***
Glycyl-L-glutamic acid	0.085 ± 0.246 ^{a}	0.637 ± 0.563 ^{b}	0.693 ± 0.673 ^{b}	0.051 ± 0.274 ^{b}	9.47	<0.0001	***
L-Threonine	0.171 ± 0.380 ^{a}	0.184 ± 0.182 ^{a}	0.098 ± 0.119 ^{a}	0.176 ± 0.511 ^{a}	0.25	0.858	ns
Carbohydrates							
α-D-lactose	0.141 ± 0.384 ^{a}	0.582 ± 0.277 ^{b}	0.700 ± 0.692 ^{b}	0.246 ± 0.707 ^{a}	3.14	0.031	*
β-Methyl D-glucoside	0.313 ± 0.613 ^{a}	1.292± 0.638 ^{b}	1.032 ± 0.673 ^{b}	0.280 ± 0.490 ^{a}	12.74	<0.0001	***
D-Cellobiose	0.353 ± 0.615 ^{a}	1.233 ± 0.639 ^{b}	1.184 ± 0.790 ^{b}	0.227 ± 0.563 ^{a}	11.84	<0.0001	***
D-Mannitol	0.742 ± 0.103 ^{a}	1.586 ± 0.162 ^{b}	1.197 ± 0.137 ^{b}	0.437 ± 0.232 ^{a}	11.37	<0.0001	***
i-Erythritol	0.012 ± 0.116 ^{a}	0.227 ± 0.123 ^{b}	0.360 ± 0.112 ^{b}	0.001 ± 0.162 ^{a}	11.74	<0.0001	***
Glucose-1-phosphate	0.053 ± 0.215 ^{a}	0.991 ± 0.147 ^{b}	1.228 ± 0.439 ^{b}	0.101 ± 0.447 ^{a}	22.27	<0.0001	***
D-Galactonic acid γ-lactone	0.294 ± 0.155 ^{b}	0.748 ± 0.174 ^{b}	0.663 ± 0.161 ^{b}	0.018 ± 0.130 ^{a}	6.55	0.001	***
N-Acetyl-D-glucosamine	0.406 ± 0.272 ^{a}	1.344 ± 0.234 ^{b}	1.460 ± 0.254 ^{b}	0.285 ± 0.340 ^{a}	17.14	<0.0001	***
D,L-α- glycerol phosphate	0.096 ± 0.153 ^{a}	0.472 ± 0.211 ^{b}	0.583 ± 0.232 ^{b}	0.062 ± 0.103 ^{a}	37.78	<0.0001	***
D-Xylose	0.143 ± 0.280 ^{a}	0.158 ± 0.365 ^{a}	0.200 ± 0.299 ^{ab}	0.002 ± 0.080 ^{a}	1.74	0.167	ns

Table 26. ANOVA for the four seasons. (Continue)

Carbon Source	Spring (Mean ± STD DEV) τ	Summer (Mean ± STD DEV) τ	Fall (Mean ± STD DEV) τ	Winter (Mean ± STD DEV) τ	F-value	*P*-Value	Significance
Carboxylic Acids							
α-Ketobutyric acid	-0.060 ± 0.019 ^{a}	0.052 ± 0.074 ^{a}	0.033 ± 0.006 ^{b}	-0.025 ± 0.061 ^{a}	7.39	<0.0001	***
D- Glucosaminic acid	0.378 ± 0.477 ^{a}	0.246 ± 0.253 ^{a}	0.141 ± 0.255 ^{a}	0.102 ± 0.429 ^{a}	2.03	0.117	ns
D-Malic acid	0.361 ± 0.656 ^{a}	0.627 ± 0.781 ^{a}	0.486 ± 0.578 ^{a}	0.239 ± 0.435 ^{a}	1.28	0.288	ns
γ-Hydroxybutyric acid	0.029 ± 0.096 ^{b}	0.198 ± 0.014 ^{b}	0.113 ± 0.018 ^{b}	0.041 ± 0.094 ^{a}	6.19	0.001	***
Pyruvic acid methyl ester	0.812 ± 0.701 ^{a}	1.540 ± 0.129 ^{b}	1.162 ± 0.176 ^{b}	0.866 ± 0.138 ^{a}	6.13	0.001	***
D-Galacturonic acid	0.567 ± 0.194 ^{a}	1.118 ± 0.202 ^{b}	0.984 ± 0.287 ^{b}	0.236 ± 0.208 ^{a}	5.82	0.001	***
Itaconic acid	0.476 ± 0.733 ^{a}	0.437 ± 0.560 ^{a}	0.309 ± 0.407 ^{a}	0.0629 ± 0.295 ^{a}	2.27	0.088	ns
Polymers							
α-cyclodextrin	-0.147 ± 0.204 ^{a}	0.124 ± 0.014 ^{a}	0.0063 ± 0.01293 ^{b}	-0.039 ± 0.100 ^{b}	10.36	<0.0001	***
Tween 40	0.845 ± 0.752 ^{ab}	1.005 ± 0.626 ^{b}	1.062 ± 0.731 ^{b}	0.394 ± 0.526 ^{a}	3.73	0.015	ns
Tween 80	0.885 ± 0.533 ^{a}	0.721 ± 0.446 ^{a}	1.003 ± 0.617 ^{a}	0.584 ± 0.536 ^{a}	2.11	0.107	ns
Glycogen	0.249 ± 0.400 ^{a}	1.422 ± 0.636 ^{b}	1.234 ± 0.653 ^{b}	0.397 ± 0.627 ^{a}	18.01	<0.0001	***
Phenolic compounds							
2-Hydroxy benzoic acid	0.001 ± 0.092 ^{a}	0.102 ± 0.013 ^{b}	0.108 ± 0.015 ^{b}	-0.020 ± 0.085 ^{a}	6.07	0.001	***
4-Hydroxy benzoic acid	0.625 ± 0.776 ^{a}	0.759 ± 0.892 ^{a}	0.582 ± 0.607 ^{a}	0.429 ± 0.661 ^{a}	0.60	0.616	ns

*, $P \leq 0.05$; **, $P \leq 0.01$; $P \leq 0.001$; ns, not significant; τValues are means and standard deviation from triplicate wells. Means in a row followed by different letters are significantly different (ANOVA followed by Tukey's honest significant test, $P \leq 0.05$).

CHAPTER IV - DISCUSSION

This chapter discusses and interprets the data presented in Chapter 3. The results include the field and laboratory testing of physical, chemical and microbiological properties of the sediment samples collected from St. Clair River and Lake St. Clair in Michigan in 2009, 2010 and 2015. Chapter 3 reported the distribution and concentration surveys of 13 different metals (As, Ba, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Se, Ag and Zn) in the sediments, as well as the metabolic diversity of the microorganisms inhabiting these sediments. A comparison of the metals concentrations reported in this study with previous studies from common sample locations provides a measure of whether there have been any improvements due to recent efforts of various stakeholders (e.g., USEPA and USACE).

4.1 St. Clair River

Sediment assessments in the St. Clair River have been conducted for decades and have documented the extent of the contamination along with the recovery (SLEA, 2008). In 2009, the USACE-Detroit District planned to dredge sediment material in the Federal Navigation Channel of the St. Clair River, Michigan, therefore, the current study was designed to characterize sediment for the purpose of estimating environmental impacts of disposal of the dredged material. The concentrations of the major metals in sediments of St. Clair River in this study were generally higher than the metal concentrations from the study conducted by Szalinska et al. in 2007 (Table 27). In comparison with the USEPA Great Lake Sediment-Quality Guidelines developed by MacDonald et al. in 2000, the concentrations of most of these metals including, As, Cd, Cr, Cu, Pb, Hg, Ni and Zn were lower in the sediments conducted in this study. Although the metal concentrations in the current study were higher than that conducted two years earlier, the levels were lower than the allowable concentration limit imposed by USEPA. Therefore, the data presented in Table 27 indicates that the sediment of St. Clair River is not concern with respect to sediment quality.

Table 27. Comparison of total mean concentrations of major metals in sediments from this study and that Szalinska et al. (2007) study, along with and USEPA Great Lake Sediment-Quality Guidelines showing the allowable concentration limit for different metals.

Metals	St. Clair River sediments (2009)	St. Clair River sediments (2007)	USEPA Great Lake Sediment-Quality Guidelines	
	Mean (mg/kg)	Mean (mg/kg)	Threshold Effect Concentration (TEC) (mg/kg)	Probable Effect Concentration (PEC) (mg/kg)
Arsenic	3.38	2.51	9.79	33
Barium	17.88	ND	ND	ND
Cadmium	0.34	0. 49	0.99	4.98
Chromium	6.51	8.20	43.4	111
Copper	16.38	7.91	31.6	149
Iron	7125	1.04	ND	ND
Lead	8.13	4.98	35.8	128
Manganese	179.0	166	ND	ND
Mercury	<0.04	0. 36	0.18	1.06
Nickel	7.94	8.76	22.7	48.6
Selenium	<0.53	ND	ND	ND
Silver	<0.05	ND	ND	ND
Zinc	46.0	37.07	121	459

ND=no data available

"< "denotes metal concentrations below the detection limit.

The highest metal concentrations encountered in SC-09-08 can be characterized as originating from natural geogenic or anthropogenic sources. One possible reason for the high concentration is the sample location. It is located approximately 3.5 Km from the mouth of Port Huron and immediately at the mouth of Black River, where it drains its water in St. Clair River. Therefore, transport of contaminants from the upper part of the Huron Corridor through St. Clair River and from upper part of Black River can be expected. Hydrological conditions of the river, with the water level fluctuating from 1760-176.2 m (Table 8) in the upper reach to 175.35 m in the middle one and decreasing to 175.0-175.1 m (Table 14) in the lower reach where St. Clair River drains its water into Lake St. Clair River, show that hydrological sorting and deposition is one of the reasons for elevated concentrations in sample SC-09-08. In this area of the river, low water flow energy favors the settling of finer particles (< 0.075 mm). As a result, the fine silty sediments (Table 7) are readily scoured and relocated or transported site SC-09-08 and downstream in St. Clair River. The data also revealed that the metal concentrations increased with sediment depth. Deeper sediments (SC-09-05B) had higher metal concentrations that the shallower sediments (SC-09-01, SC-09-03, SC-09-04, SC-09-05A, SC-09-06, SC-09-07, and SC-09-08) (Table 12). The increased of trace metal in deeper sediments (SC-09-05B) was due to the fact that it is located closer to the native sediment (Huron-Erie clay formation). The Huron-Erie clay formation that was deposited under the study area by Pleistocene Lake Maumee (MDEQ, 2005). The lithology of sample SC-09-05B (Table 10) is brown to gray sand to dark gray silty clayey is relatively comparable to the lithology of Huron-Erie formation. Therefore, the elemental concentrations in SC-09-05B can be characterized as originating from natural geogenic.

Metal concentration levels were generally higher in upstream sites (SC-09-08, SC-09-07, SC-09-06 and SC-09-05A) and then decreased in the downstream sites (SC-09-01, SC-09-03 and SC-09-04), which implies that one of the source of metal contamination is the water from Port Huron and Black River entering the St. Clair River. In the study area, there are five municipal Wastewater Treatment Plants (WWTPs) including the Marine City, Marysville, Port Huron, St. Clair County-Algonac and St. Clair WWTPs. The discharge from these facilities are regulated (USACE, 2004). Despite of the discharge from these locations being regulated, it is still considered as a potential anthropogenic source of contamination in addition to the emissions may be resulted from ships or any spill accident. Data obtained from Michigan Department of Environmental Quality (MDEQ) revealed that there were more than more than 200 discharge events into the St. Clair River form combined sewer overflow (CSO) of WWTPs occurred in 2009 and 2010 during the study period. More than 62,667 MG of contaminated water entered into the St. Clair River due to combined sewer overflow, a retention treatment basin discharge, a bypass of treatment or blending of treated/partially treated effluent and/or a sanitary sewer overflow. These events occurred as a result of wet weather, snowmelt or both. Less frequently, these can be triggered by a mechanical or electrical failure in the sewer system, such as a loss of power at the wastewater treatment plant (http://www.deq.state.mi.us/csosso/index.shtml).

While the metal concentrations from this study are not strictly comparable with previous studies due to differences in collection and analytical procedures, the comparison of mean values and ranges for selected metals (Cd, Cr, Cu, Hg, Ni, Pb, and Zn) for the river (Table 12 and 27) suggests that the overall quality of the St. Clair River sediments has been improved since the early eighties. Based on the data presented in Table 12 (Chapter 3), the concentration of metals varied drastically within the same site (depending on the depth) as well as among different sites.

The distribution of the trace metal concentrations (Figure 10) corresponded well with the flow patterns from the upstream samples into downstream samples. It showed a zone of deposition for outflow of each element from different sample locations in St. Clair River that corresponded well with the spatial distribution of trace metal concentrations. However, the sediments had a wide range of grain size distribution associated with spatial heterogeneity. The wide range of trace element concentrations found in river sediment indicates that there is spatial heterogeneity in the watershed originating from natural geogenic or anthropogenic sources. Thus, spatial heterogeneity in partitioning could be attributed to differences in land use. Differences in partitioning between elements could also result from differences in element origin and subsequent behavior. While the metal concentrations in the sediments were lower than the USEPA imposed limits, the concentrations had increased within two years. Hence, it is apparent that a risk assessment model is needed to the extent of the existing risk at St. Clair River from the surrounding environment.

Table 28. Range of total metal concentrations (mg/kg) of surficial sediments from St. Clair River and other rivers in Michigan.

Location	As	Cd	Cu	Mn	Ni	Pb	Zn	Reference
St. Clair River	2-3.9	<0.23-0.4	8-25	87-260	5-12	5-11	33-72	This study
Clinton River	0.8-14	0-16	2-225	62-784	4-10-	3-317	13-935	Hess et al., 2010
Rouge River	0-25	<2-10	<5-144	101-1170	<15-156	<5-210	10-690	Smith et al., 1995
Rouge River	0.22	5.5	540	ND	134	9.9	4900	Murray et al., 1997
Detroit River	ND	0.5-7.4	4.6-193	ND	6.1-66.4	5.0-687	50-741	Szalinska et al.2006

ND=no data available

Elevated concentrations of metals were found in Clinton River, Rouge River and Detroit River compared well with the trace metals concentration of current study (Table 28). Metro-Detroit is a very heavily urbanized and industrialized area where anthropogenic elements could originate from a number of sources. The major source is the automotive industry for which Detroit is the Word Capital. The wide range of trace metals concentration found in the river sediment near to the St. Clair River indicates that there is spatial heterogeneity in the watershed (Table 28). This reflects that the wide range of land uses (agricultural, residential, mixed industrial) had significant impacts on sediment quality. One possible explanation for the downstream industrial zone high concentration could be that lake water moved upstream and mixed with river water during storms that have strong west winds (USGS, 2007). This mechanism is considered a strong explanation because high winds are frequent and the water current from the Lake Huron in the north and Lake St. Clair south and the sediment content of lake water is much lower than that of river water, so the dilution factor would be affective. As a result of ongoing efforts of the USACE and MDEQ to achieving the important environmental improvement of the St. Clair River, contaminated sediments are now limited to locations in the upper part of the St. Clair River adjacent to historical industrial discharge points. all these efforts resulted of continuous improvement of the sediment quality of St. Clair River compared to other close by rivers.

4.2 Lake St. Clair

The concentrations for major metals in Lake St. Clair sediments in this study were lower that the metal contents from a study conducted by Rossmann in 1985. This result marks an important improvement with respect to sediment quality (Table 29). In addition, the concentrations of most of these metals (As, Cd, Cr, Cu, Pb, Hg, Ni and Zn) were lower in the sediments conducted in this study than the USEPA metal concentration limits (Table 29).

Table 29. Comparison of metals concentrations of Lake St. Clair sediments from this study and from previous studies (Rossman, 1985), along with and USEPA Great Lake Sediment-Quality Guidelines showing the allowable concentration limit for different metals.

Metal	Lake St. Clair 2010 (This study)	Lake St. Clair Mud (Rossmann, 1985)	USEPA Great Lakes Sediment-Quality Guidelines	
	Mean (mg/kg)	Mean (mg/kg)	Threshold Effect Concentration (TEC) (mg/kg)	Probable Effect Concentration (PEC) (mg/kg)
Arsenic	5.87	ND	9.79	33
Barium	48.37	ND	ND	ND
Cadmium	0.61	0.372	0.99	4.98
Chromium	17.02	54.7	43.4	111
Copper	20.95	40.1	31.6	149
Iron	16494.74	ND	ND	ND
Lead	17.36	68.4	35.8	128
Manganese	419.47	ND	ND	ND
Mercury	0.35	ND	0.18	1.06
Nickel	22.00	30.1	22.7	48.6
Selenium	0.70	ND	ND	ND
Silver	0.09	ND	ND	ND
Zinc	67.47	146	121	459

The highest concentration of metals was found in sediments from the upstream sites (LC-10-01 to LC-10-09). The origin of high metal concentrations in the upstream zone can be explained from the following possible sources. First, the trace metals are St. Clair River drain in Lake St. Clair. Even if the contaminant concentrations were within the threshold effect concentration or lowest effect level, St. Clair River (in which the upstream sites are adjacent to) is in the main stem and mouth of the Clinton River, Big Beaver Creek, Red Run, and Paint Creek. These rivers were identified as an area of concern (AOC), however, because of the ongoing remediation, many of these reviews were delisted as AOC. Currently there are eleven major point source discharges in St. Clair River. Five of which were municipal wastewater treatment plants, and six were industrial sources, including Detroit Edison Co. plants at St. Clair, Marysville and Belle River; AZKO Salt, Inc. in St. Clair, James River KVP in Port Huron, and

E.B. Eddy in Port Huron. The eleven major sources are still operating; with the exception of the Detroit Edison Co. power plant in Marysville which ceased operations in 2001 and was decommissioned in 2011. A second possible source is the land uses that appeared to correlate with certain elements and element origins.

The origin of element concentration in the downstream sites (LC-10-09 to LC-10-19) located south of Clinton River can be one of the following possible sources. First possible source is the high concentration of the trace metals is Rouge River. The Rouge River is the primary drainage for the Detroit Metropolitan area and it drains in Detroit River. The Detroit River has been known to virtually stop and even reverse in direction for a few hours toward Lake St. Clair. It is listed by the International Joint Commission as one of 43 areas of concern within the Great Lakes region (Hartig and Zarull, 1991). The metals introduced into the rogue river as a result of surface runoff, discharges of contaminated groundwater, air fall deposition of particulate matter, and contribution from combined sewer overflow (Murray, et al., 1997).

The thicker layer of dark grey with sometime slightly organic odor originated maybe from the fuel used by planes, ships, trucks, etc from the Selfridge Air National Bases, however, the origin of these element still not identified. Second possible explanation is the spills contamination that occurs near the oil refiners or gasoline spills (Bosco et al., 2005). Third possible explanation is the atmospheric deposition of airborne pollutants directly to the AOC is negligible owing to the small surface area of its drainage basin. However, inputs to Lake Huron and its drainage basin are considerable due to its large surface area. Atmospheric contamination directly to Lake Huron flows into the St. Clair River than to Lake St. Clair (UGLCCS 1988).

Table 30. A comparison of metal concentrations (mg/kg) of sediments from Lake St. Clair, Lake Superior, Lake Michigan and Lake Eire.

Metal	Lake St. Clair (This study)	Ontonagon Harbor, 2010 (Lake Superior) (USACE, 2010)	Grand Haven, 2010 (Lake Michigan) (USACE, 2010)	Lake Erie (Elsayed, 2002)
Arsenic	5.87	0.7	4.0	35.1-54.3
Barium	48.37	13.4	70.4	ND
Cadmium	0.61	ND	0.8	2.9-5.0
Chromium	17.02	5.2	25.7	111-121.1
Copper	20.95	6.0	21.0	36.7-65.8
Iron	16494.74	4000.0	8672.2	ND
Lead	17.36	2.5	21.5	80.9-103.5
Manganese	419.47	69.7	400.2	ND
Mercury	0.35	ND	0.1	ND
Nickel	22.00	4.7	14.3	33.9-43.7
Selenium	0.70	ND	0.7	ND
Silver	0.09	0.1	0.3	ND
Zinc	67.47	8.8	71.4	179.0-250.6

ND= not Detected

The data revealed that the trace metal concentrations in the sediments (Table 30) of Lake St. Clair are higher than the concentration of the trace metals in Ontonagon Harbor (Lake Superior), while they are lower in Grand Haven (Lake Michigan) with exception of As (5.87mg/kg), Fe (16494.74 mg/kg) and Ni (22 mg/kg). The trace metal concentrations in Lake St. Clair are lower than the concentration of the trace metals in Lake Erie except for Ba (48.37 mg/kg), Fe (16494.74 mg/kg), Mn (419.47 mg/kg), Hg (0.35 mg/kg), Se (0.70 mg/kg), and Ag (0.09 mg/kg). Therefore, our results confirmed that the trace metal concentrations in the sediment of Lake St. Clair are comparable to those obtained from Ontonagon Harbor, Grand Haven (USACE, 2010), and Lake Erie (Elsayed, 2002) all of which are characterized by trace industrialization, urbanization and contamination (Table 30).

4.3 Comparison between St. Clair River and Lake St. Clair metal concentration

The results presented in Table 19 shows that the concentrations of the trace metals are higher in Lake St. Clair compared to St. Clair River. These results are due to the fact that rivers are lotic ecosystems characterized by rapidly moving freshwater, and therefore do not accumulate much of the metals in the sediments but transports the metals it to the lakes where they accumulate. The St. Clair River's water flow high velocity, and its capacity to transport contaminated sediment is one of the major reasons for the accumulation of metals in lake waters. Because lakes are lotic ecosystems (still-water habitats), much of the metals drained in the water column trickles down the bottom of the lake. Hence the accumulation of metals in the sediments.

St. Clair River- Lake St. Clair system behave as a hydrographic unit, which go undergo complex interactions. One such interaction pertains to the role of St. Clair River in the dispersal of trace elements carried into the Lake St. Clair and out of Lake Huron. The results suggest that Lake St. Clair act as a filter and contribute to the self-purification of water that flows through them. As a result, the concentration of most metals in Lake St. Clair sediment showed and increase upstream (inflow) and downstream (outflow) sections (Tables 12, 18 and Figures 10, 11).

Trace element concentrations in the St. Clair River and Lake St. Clair were both controlled by clay, oxide and organic matter contents. However, differences in sediment granulometry (Table 9 and Table 15) could explain the observed differences in element concentrations. Trace element contents in the sand- and silt-size sediment fractions are comparable (Table 19) but are much lower than in the clay fraction, thus, explaining why Lake St. Clair sediments have much higher element concentrations than St. Clair River sediments. Moreover, the clay fraction had Fe concentrations were higher than those in the sand and silt and could indicate that the clay-size fraction is composed of clay minerals capable of retaining higher trace element concentrations (Murray et al., 1999). This association further confirmed that Fe concentrations corresponded mostly with the clay content.

4.4 Microbial Activities in St. Clair River and Lake St. Clair Sediments

Functional diversity, understood in this study as the utilization of single carbon sources in Biolog plates, showed clear differences between the lake and river sediments. Generally, the river sediment samples were characterized by significantly higher (≤ 0.05) phenylethylamine (amine), L-threonine (amino acid), D-xylose (carbohydrate), and D-malic acid (carboxylic acid) utilization than the lake sediments (Table 23). Another key difference included the higher utilization of amines, amino acids, carbohydrates, carboxylic acids, and polymers in the lake sediments (Figure 13). The carbohydrates (N-acetyl-D-glucosamine and D-cellobiose) have been shown to be important sources of bacterial growth in aquatic systems (Riemann and Azan 2002, Sala and Gude, 2004, Tiquia, 2010).

There were two basic sediment types, one of which was a poorly sorted sand (LC-15-01, LC-15-02, SC-15-02), while the other was silty clay (LC-15-03, SC-15-01, SC-15-03). Both of these environments likely hold different heterotrophic populations, and this is even more likely when looking at the sandy samples patterns of utilization in the spring, all of which showed less growth than their clay counterparts. Another question that arose involves samples SC-15-02, LC-15-02 and LC-15-03, all of which saw massive spikes in growth from the spring to later seasons. The only factor that changed between these seasons was the weather, as the average temperature, humidity, and precipitation all increased. In winter, which showed lower temperatures, the populations within the sites decreased overall. It is worth noting that the river seems to recover quicker from the winter die off than the lake, as seen in the spring river samples showing a very rapid increase in population. Which likely is related to the flow of the river bringing more nutrients. It would be worthwhile to examine if this change is consistent over the course of multiple years. There are some questions that remain unanswered. One is what occurred to cause the drastic changes in the summer for samples LC-15-01 and SC-15-01. In all likelihood it was simply a result of random chance, that in the particular samples taken in summer, more or less organisms were present. Ideally, more samples could have been tested, but due to a lack of time and resources this was an impossibility. Higher concentrations of TOC were found in Lake St. Clair comparison to St. Clair River. This trend may be due to the amounts of specific surface area, grain size distributions, water elevation fluctuation, and organism distributions.

The bioaccumulation process is dependent upon the bioavailability of trace elements. Bioavailability, which is a quantitative measure of the incorporation of metals by organisms, is in turn linked to metals speciation. Trace elements are present in a variety of chemicals forms, in both particulate and dissolved phases. The possible forms in which they exist are (Morrison, 1989):

1- simple ionic species: e.g. $Zn\,(H_2O)_6^{+2}$

2- multiple valency states: e.g. Fe^{+2}, Fe^{+3}, As^{+3}, As^{+5}, Cr^{+3}, Cr^{+4}

3- weak complexes: e.g. Cu-fluvic acid

4- adsorbed on colloidal particles: e.g. Cu-$Fe(OH)_3$ -humic acid

5- lipid-soluble complexes: e.g. CH_3HgCl

6- organometallic species: e.g. $CH_3AsO(OH)_2$

7- particulate: adsorbed onto clay particles

Bioassays, could be related to the synergistic effects of dissolved metals. The Lake St. Clair sediments may have provided a simplistic situation, but one must not ignore the complexity of synergistic interactions occurring in nature, such as between nutrients/metals and metals/organic compounds. These interactions and complexes ultimately determine the bioavailability and toxicity of contaminants to natural bio-community.

The community level physiological profile has been found to be a good indicator of reflecting changes of metabolic activity and/or potential functional versatility of microbial communities exposed to stress conditions, e.g., trace metals (Kapanen et al., 2013). The AWCD reflects the oxidative ability of microorganisms developed in Biolog Ecoplates, and it may be used as an indicator of microbial activity. In this study, the river sediments (lower metal contents) had higher AWCD than the lake sediments (higher metal contents), which suggest that the Biolog Ecoplate assay may be used as an indicator of sediment quality.

CHAPTER V - CONCLUSIONS

This study revealed the following:

1. The source of the trace metals in the study area can be separated into 2 categories: anthropogenic (Ba, Cd, Cr, Cu, Ni, Pb, Hg, Se, Ag and Zn) and geogenic (As, Fe, and Mg) sources. Anthropogenic factors dominated the process regulating the metal distributions and mobilization within the St. Clair River and Lake St. Clair. For example, drainage of treated and untreated waste water in St. Clair River and Lake St. Clair can be one source of contamination. The depositional areas of The Black River, Pine River, and Belle River outflows into St. Clair River is likely the source of the higher metal concentrations of St. Clair River. On the other hand, the depositional areas of the St. Clair River, Clinton River and Rouge River/Detroit River outflows into the Lake St. Clair, is likely the source of the higher metal concentrations of Lake St. Clair.

2. The concentration of metals from St. Clair River and Lake St. Clair varied to some extent, depending on the location and were unevenly distributed on the lake and river bottoms. The distribution of the trace metals and trace metal concentrations corresponded well with the flow patterns from the upstream samples into downstream samples.

3. Metal concentrations in lake sediments were controlled by sediment particle size, and, thus, by deposition/sedimentation areas. The higher metal concentrations were found in the fine grain sediment compared to the coarse grain sediments. Therefore, clay or silt rich sediment contain high metal concentration. In this study, the data do not indicate how these metals moved from the source to deposition areas, but I speculate that metals were absorbed onto sediment particles and carried downstream by river currents, or sediment was disturbed by ship propeller which cause the sediment to transport downstream.

4. A comparison of metal concentrations data of the sediment collected from the St. Clair River and Lake St. Clair navigation channel revealed that the contaminant levels of the Lake St. Clair were significantly higher than that found in St. Clair River sediments. St. Clair River is a lotic ecosystem characterized by rapidly moving freshwater, and therefore do not accumulate much of the metals in the sediments but transports the metals it to the lakes where they accumulate. In the other hand, Lake St. Clair lake is also a lotic ecosystem (still-water habitats), but much of the metals drained in the water column trickles down the bottom of the lake. Hence the accumulation of metals in the sediments. Lake St. Clair act as a filter and contribute to the self-purification of water that flows through them. It is important to note that the concentrations of metals from both ecosystems were below USEPA - Great Lake Sediment-Quality Guidelines.

5. The trace metal concentrations in St. Clair River were found lower compared with Clinton River, Rouge River and Detroit River as a result of ongoing efforts of the USACE and MDEQ to achieving the important environmental improvement of the St. Clair River, contaminated sediments are now limited to locations in the upper part of the St. Clair River adjacent to historical industrial discharge points.

6. Improvements in sediment quality throughout the St. Clair River have largely been the result of natural recovery processes, recent sediment remediation projects and reductions in municipal and industrial discharges. Industrial and municipal point sources are well regulated and are no longer the largest threat to the St. Clair River and Lake St. Clair ecosystem. However, accidental as well as illegal industrial/municipal releases, including discharges of untreated sewage during major weather events due to system overload, still occur. Municipal storm water remains a large pollutant source that has been traditionally unregulated.

7. Total organic carbon concentration increase in clay size sediment in Lake St. Clair versus St. Clair River where the sediments are mostly sand. Fine grain particles are an indication of energy levels within the two ecosystems. Therefore, the Lake St. Clair might experience less sedimentation which would favor benthic organisms

8. Bioavailability of metals released from river and lake sediment is very complex and dependent on many interrelated chemical, biological, and environmental processes. These processes may vary over time and among micro-organisms, plants, and animals.
9. The community level physiological profile has been found to be a good indicator of reflecting changes of metabolic activity and/or potential functional versatility of microbial communities exposed to stress conditions, e.g., trace metals. Microbial activities experiment shows that between the St. Clair River and Lake St. Clair, the differences in growth are only slightly significant, and that between samples within the particular regions, differences are much more significant, and this is likely a result of the type of sediment, as well as the weather.

CHAPTER VI - FUTURE RESEARCH

1. Additional studies are needed to determine the specific spatial distribution of the contaminated sediments and to develop an annual monitoring program to alleviate any environmental impacts from potential contaminated sediments at St. Clair River and Lake St. Clair, to achieve that, the following studies may be conducted:
    - Study the wide spatial variations in boundary shear stress in response to varying flow in St. Clair River and Lake St. Clair in which have created large spatial variations in the grain sizes of surface and subsurface materials.
    - Understand the type, speciation and levels of the trace metals in the sediment and under what physico-chemical conditions the metals species can be released to an aqueous phase.

2. Additional water samples and sediments should be collected concurrently to evaluate seasonal changes in concentration of the St. Clair River and Lake St. Clair and conduct detailed mapping to determine if there will be any significant difference in the distribution of the metals between them. A special focus to collect water and sediment samples near the inlet of Port Huron, Near Black River, central are of St. Clair River, Clinton River, the central area of Lake St. Clair and with the Lake St. Clair Delta.

3. A biological approach for the detection of metal pollution and assessment of metal toxicity in sediments should also be performed. The inhibitive effects of trace metals and organic chemicals to microorganisms are key considerations in hazard management and control because microorganisms are ubiquitous in nature, and they are relevant for preserving the ecological balance. The ecotoxicity of the sediments can be assessed using the Microtox or Biolog approach.

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