#### **Carbon Loading to Lake Michigan Sediments**

BY

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#### THESIS

Submitted as partial fulfillment of the requirements for the degree of Doctor of Philosophy in Civil Engineering in the Graduate College of the University of Illinois at Chicago, 2016

Chicago, Illinois

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### **Dedication**

I dedicate my dissertation thesis to my family and many friends all around the world. A special feeling of gratitude to my loving parents and brother for their unconditional support and words of encouragement Although far away, yet very close to me, I am eternally thankful to have not being never alone throughout my all PhD journey.

#### Acknowledgements

The present thesis is made possible thanks to the help of a number of people whose knowledge, patience, advice and skill helped to make this work possible. I have included a few names but if I have missed anyone; I sincerely apologize, and please note that any omission was not deliberate.

My thesis research is the final result and an expression of the excellence of the entire scientific community with which I worked at the University of Illinois at Chicago (UIC), including the Department of Civil and Materials Engineering (CME), the School of Public Health (SPH) and the Earth and Environmental Sciences (EaES) Department, and the U.S. Environmental Protection Agency (U.S. EPA), which partially funded my research project, and for whom I have been working as intern since February 2013.

- From the formative stages of my PhD journey to the final defense of my research, I owe an immense debt of gratitude to my advisor, Dr. Karl J. Rockne, whose depth of knowledge and skill must first be thanked. His enthusiasm for science has been contagious, and his energy unparalleled. Dr. Rockne taught me about environmental engineering, and answered innumerable questions. His sound advice, and careful guidance were the key to ensure the quality of my work.
- I would like to thank my PhD defense committee members: Drs. An Li, Neil C. Sturchio, Amid P. Khodadoust, Ben L. O'Connor, and again Karl J. Rockne, committee chair. I am grateful to all of them for sharing their high expertise, valuable experience, skills and advice. They all helped make my time at UIC an experience I will never forget. Many thanks from the bottom of my heart.

- I want to thank all the other staff, students, and post-docs, who have helped me on my graduate school journey by inspiring, teaching, and supporting me. First of all, my Great Lakes Sediment Surveillance Program GLSSP-mates, Dr. Garry Coding for his constructive comments, inputs and reviews, Meg Corcoran, and Jeihong Guo, who have been with me from the very start. Also, my heartfelt thanks go to my lab-mates, Kelly Granberg, Priscilla Viana Zuconi, Soheil Hosseini, Raja S. Kaliappan, Azivy C. Aziz, Asha Rani, Itzel Godinez, etc., who have now become life-long friends.
- This thesis involved many opportunities to travel and to collect samples from all over the Great Lakes (GL). This, however, would not have been possible without the help of people during those sampling campaigns, and the support of locals based at these locations. In particular, I would like to thank Captain Bob Christensen and the entire crew of the *R.V. Lake Guardian*, U.S. EPA's vessel. I must also thank Todd Nettesheim, project manager of U.S. EPA at the Great Lakes National Program Office (GLNPO) who successfully managed the whole GLSSP project.
- And last but not least, I would like to thank immensely Oak Ridge Institute for Science and Education (ORISE) for having selected me as U.S. EPA intern via GLNPO at the Chicago Regional Laboratory for Region 5 (CRL R-5). I am deeply grateful to all the scientists and staff at the U.S. EPA for sharing their extensive and well-known knowledge, for their help in accessing laboratory resources, safety and quality training. I am so lucky and honored to have been welcomed aboard the U.S. EPA team and treated as part of a unique scientific family since the day I started my 3-year internship. In particular, I would also like to acknowledge Danielle Kleinmair, my mentor with her outstanding organizational skills, Mark Loomis, my "high-quality"co-mentor at GLNPO,

Lawrence Zintek (ORISE Program Officer), Troy Strock (dedicated Chemist), Wayne Wapple (high expertise Analyst), Angela Ockrassa (Quality Manager at CRL), Louis Blume (Quality Manager at GLNPO), George Schupp (CRL Deputy Director), Dennis Wesolowski (Laboratory Director at CRL), who have fueled my passion for science and research, and appreciate my enthusiastic work efforts. Their gentle manners, patience, tireless guidance and unique encouragement have meant so much to me.

This work was mainly supported by GLNPO of the U.S. EPA grant number GL-00E00538 and by other resources and funds from the Applied Environmental Biotechnology Laboratory (AEBL).

This research was one of the most important and formative experiences in my life, my heartfelt thanks for making this a reality.

#### Solidea M.C Bonina

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## **List of Equations**

Equation 1: Autotrophy Condition
Equation 2: Heterotrophy Condition
Equation 3: Net Ecosystem Production
Equation 4: Net Primary Production
Equation 5: Net Community Production
Equation 6: Percent of Moisture
Equation 7: Percent Solids
Equation 8: Wet Bulk Density
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## **List of Abbreviations**

Acetanilide	<i>N</i> -Phenylacetamide
AEBL	Applied Environmental Biotechnology Laboratory
AOC	(Great Lakes) Area of Concern
APHA	American Public Health Association
ArcGIS	Geographic Information System (Software)
ASCE	American Society of Civil Engineers
ASE	Accelerated Solvent Extraction
ASTM	American Society for Testing and Materials (Standard Methods)
AWWA	American Water Works Association
В	Bias
BBOT	2,5-Bis-2(5-Tert-Butyl-Benzoxalyl)Thiophene
BC	Black Carbon
С	Carbon
°C	Celsius
Са	Calcium
CaCO <sub>3</sub>	Calcite or Aragonite
Caffeine	1,3,7 Trimethylxanthine
CaMg(CO <sub>3</sub> ) <sub>2</sub>	Dolomite
Cd	Cadmium
CE	Cultural Eutrophication
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CH <sub>4</sub>	Methane
CL	Confidence Level
CME	Civil and Materials Engineering Departments
$CO_2$	Carbon Dioxide
Cr	Chromium
CRL R-5	Chicago Regional Laboratory Region 5
Cu	Copper
CWA	Clean Water Act
DIW	Deionized Water
DL	Detection Limit
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
Е	East
EA	Elemental Analyzer
EaES	Earth and Environmental Sciences (Department)
EC	Ekman dredge Core
EIGL	Environmental Isotope Geochemistry Laboratory
Eq.	Equation
EPA	United States Environmental Protection Agency
ER	Ecosystem Respiration
F	Fahrenheit
FF	Focus or Focusing (or normalization) Factor
FAO	Food and Agriculture Organization (of the United Nations)

Fe	Iron		
GC	Gas Chromatography		
GC-MS	Gas Chromatography – Mass Spectrometry		
GC-MSMS	Gas Chromatography-Tandem Mass Spectrometry		
GIS	Geographic Information System		
GL	(Laurentian) Great Lakes		
GLEON	Global Lake Ecological Observatory Network		
GLNPO	Great Lakes National Program Office		
GLLA	Great Lakes Legacy Act		
GLRI	Great Lakes Restoration Initiative		
GLWQA	Great Lakes Water Quality Act		
GLSSP	Great Lakes Sediment Surveillance Program		
GPP	Gross Primary Production		
Н	Hydrogen		
HAPs	Hazardous Air Pollutants		
HCl	Hydrochloric Acid		
Hg	Mercury		
HOCs	Hydrophobic Organic Contaminants		
Hr	Hour		
H <sub>2</sub> O	Water		
H <sub>2</sub> O <sub>2</sub>	Hydrogen Peroxide		
H <sub>3</sub> PO <sub>4</sub>	Phosphoric Acid		
H <sub>2</sub> SO <sub>3</sub>	Sulfurous Acid		
IAGLR	International Association for Great Lakes Research		
IC	Inorganic Carbon		
IDW	Inverse Distance Weighting		
IGERT	Integrative Graduate Education Research and Training		
IA	Iowa		
IL	Illinois		
IN	Indiana		
ISGS	Illinois State Geological Survey		
ISTC	Illinois Sustainable Technology Center		
ISWS	Illinois State Water Survey		
IUPAC	International Union of Pure and Applied Chemistry		
K	Potassium		
K <sub>OA</sub>	Octanol Air Partition Coefficient		
K <sub>Ow</sub>	Octanol Water Partition Coefficient		
LEAP	Landscape, Ecological, and Anthropogenic Processes		
LIMS	Laboratory Information Management System		
LM	Lake Michigan		
LOMD	Labile Organic Matter Degradation		
MC	Multi-Core		
MDL	Method Detection Limit		
Mg	Milligrams		
MI	Michigan		
MLE	Mono-Layer Equivalent		
Mn	Manganese		
MS	Mass Spectrometry		
mt	Metric tons		

Ν	Nitrogen
NB	Northern Basin
NCP	Net Community Production
NE	Northeast
NIST	National Institute of Standards and Technology
NPP	Net Primary Production
NW	Northwest
0	Oxygen
OC	Organic Carbon
OM	Organic Matter
ORAU	Oak Ridge Associated Universities
ORISE	Oak Ridge Institute for Science and Education
ORP	Oxidation-Reduction Potential
P	Phosphorus
PAHs	Polycyclic Aromatic Hydrocarbons
Ph	Lead
PBDEs	Polybrominated Diphenyl Ethers
PRTs	Persistent Bio-accumulative Toxic Compounds
PCBs	Polychlorinated Binbenyls
PG	Popar Grahs
PM	Particulate Matter
PM.	Particulate Matter, constituted by small particles (size less than 2.5 µm)
POC	Particulate Matter, constituted by small particles (size less than 2.5 µm)
	Particulate Organic Caldon Dereistant Organic Dollutants
	Primary Production
	Dertiale Size Distribution
	Quality Assurance/Quality Control
$\frac{QA}{QC}$	Quality Assurance/Quality Control
$R_A(OFR_a)$	Respiration by Autotrophs
$K_{\rm H}$ (or $K_{\rm h}$ )	Respiration by Heterotrophs
RL DCD	Reporting Limit
RSD	Relative standard deviation
<u>S</u>	Sultur
SA	Surface Area
SB	Southern Basin
<u>SC</u>	Soot Carbon
<u>SE</u>	Southeast
Si	Silica
SIA	Stable Isotopic Analysis
SOP	Standard Operating Procedure
SPE	Solid Phase Extraction
SPH	School of Public Health
SSA	Specific Surface Area
STD	Standard Deviation
SVOA	Semi-Volatile Organic Compound
SW	Southwest
SWE	Society of Woman Engineers
SYSTAT	System Statistics (Software)
ТС	Total Carbon
TCLP	Toxicity Characteristic Leaching Procedure

TDS	Total Dissolved Solids
Ti	Titanium
TN	Total Nitrogen
TOC	(Total) Organic Carbon
UIC	University of Illinois at Chicago
UNEP	United Nations Environment Programme
UNESCO	United Nations Educational Scientific and Cultural Organization
USA	United States of America
USEPA	United States Environmental Protection Agency
USGS	United States Geologic Survey
U <sub>95</sub>	Overall Uncertainty
Vs.	Versus
W	West
WEF	Water Environment Federation
WHO	World Health Organization
WI	Wisconsin
Wt.	Weight
XRF	X-Ray Fluorescence (Spectroscopy)
Yr	Year
Zn	Zinc

#### **Chapter 1. Introduction**

#### "Carbon Loading to Lake Michigan Sediments"

#### **1.1 Research Description and Rationale**

My research project is part of a five-year investigation of the spatial and temporal trends of persistent, bio-accumulative, toxic compounds (PBTs) and emerging contaminants in sediments of the five Laurentian Great Lakes called the Great Lakes Sediment Surveillance Program (GLSSP). My research study described here grew out of my participation in GLSSP. The GLSSP is one of the monitoring programs funded by the United States Environmental Protection Agency (USEPA), Region 5 Great Lakes National Program Office (GLNPO). Region 5 includes Illinois, Indiana, Michigan, Minnesota, Ohio, Wisconsin and 35 tribes. These sediment data, as well as the data from the air and fish surveillance programs, provide USEPA with needed information to protect the Great Lakes ecosystem and to support decision making with regard to pollution control and resource management. The GLSSP program is part of Great Lakes Restoration Initiative (GLRI) and involves four different laboratories working on multiple interdisciplinary analyses on one lake per year. Laboratory analysis includes chemical analysis via gas chromatography-mass spectrometry by the environmental organic chemistry laboratory at the Environmental and Occupational Health Sciences - School of Public Health at UIC), gamma spectroscopy for core radio-dating by the environmental isotope geochemistry laboratory (EIGL) at Earth and Environmental Sciences (EaES) at UIC, perfluorochemical analysis by environmental toxicology laboratory at Veterinary Biomedical sciences department at the University of Saskatchewan, (Canada), and physical and chemical analysis by the applied environmental biotechnology laboratory (AEBL) in the Civil and Materials Engineering at UIC

where I worked to conduct my PhD research project. Research scientists from the four groups work closely sampling on a yearly basis, sharing findings and integrating results.

Sediment is one of the largest depository matrices of pollutants in aquatic systems (Li et al., 2011). Sediment often acts as the final reservoir for hydrophobic contaminants, particularly for the class of emerging contaminants designed by the USEPA as persistent, bio-accumulative and toxic pollutants (PBTs). PBT-polluted sediments are an important issue in the lake basin, caused by decades of municipal and industrial discharges, sewer overflows, and agricultural and urban non-point source runoff. Sediment samples can provide information valuable to the effective management and remediation of the contaminated water bodies.

The GLSSP study started in 2010 with the sampling of Lake Michigan, an important freshwater system, and one of the largest freshwater lakes in the world. Lake Michigan is an irreplaceable resource for drinking water, food, recreation, employment and transportation. Given its large surface area (57,780 Km<sup>2</sup>) to depth (85 m on average) ratio, long retention time, and small drainage basin relative to lake area, Lake Michigan is susceptible to contamination via atmospheric exchange and deposition. In contrast, smaller water bodies typically receive contaminants from riverine inputs. The atmospheric influence is especially apparent near urban/industrial areas, as studies have shown in the Chicago (e.g. Hornbuckle et al. (2006) and many other). Christensen and Arora (2007) identified traffic, coke oven, and wood burning signatures in the sediment of central Lake Michigan by factor analysis of pollutant data in sediment cores and observed that the coke oven signature in particular may be linked to metropolitan Chicago and its imprint on the lake. Even though Lake Michigan has been one of the most investigated large freshwater systems, the number of region-wide studies on both legacy and emerging chemical pollutants in the sediment is still limited. There is a research need for a

better understanding of the transport and transformation of PBT chemicals deposited in the sediments demands detailed characterization of the sediments and the over laying water column.

For the GLSSP project, samples have been taken from multiple sites throughout the Lake during 2010 and 2011 sampling cruises, including 30 surface grabs and 10 sediment cores, which were sliced into 20 sections of 0.5 cm to 2 cm thickness and analyzed for numerous analyses. For my work, Lake Michigan sediment samples were characterized for solids and water content, bulk density, porosity, particle and sediment density and particle size distribution (physical characteristics); the chemical parameters: total nitrogen, total organic carbon (OC), organic matter (OM), inorganic carbon (IC) and black carbon (BC). Carbon can be present in elemental, inorganic, or organic forms. Carbon is usually derived from weathering of the parent material/geology, the decomposition of plant and animal matter, or by addition through anthropogenic activities.

OC refers to the amount of carbon comprised in the organic matter (derived from plants or animals, contain carbon and hydrogen along) preserved within the sediment. OM (which includes OC) consists of carbon and other nutrient elements in the form of carbohydrates, proteins, fats and nucleic acids. The inorganic carbon forms are derived from carbonate minerals. Total nitrogen (N) (which is included in OM) is an important sediment nutrient element along with phosphorous (P), and has inorganic as well as part of organic sources. The amount of OM found in sediment is a function of the amount of various sources reaching the sediment surface and the rates at which different types of OM are degraded by microbial processes in the water column and sediment. BC is a soot-like form of organic carbon that is produced by incomplete combustion of plant material and fossil fuels in sediments (Schmidt and Noack, 2000). The determination of OC is an essential part of any site characterization or ecological assessment because its presence or absence can markedly influence how hydrophobic chemicals will react in the soil or sediment. For example, the level of carbon forms can significantly influence the physical, chemical, and biologically mediated behavior of contaminants. For this reason, the determination of OC has been an essential part of my research and has been accomplished through the development of a comprehensive and accurate analytical procedure. It was a fundamental method development stage needed in order to pursue my overall research plans.

#### **1.2 Objective, Hypotheses and Hypothesis Testing**

#### **1.2.1 Research Aim**

The GLSSP aims to investigate the presence of PBT chemicals, and reveal their spatial distribution and temporal trend in the Great Lakes sedimentary record. This record is of particular interest when studying contaminants deposited in the lake over the past 150 years, the time of greatest human impact.

My research questions can been classified into immediate or short-term questions and more long-term questions. My primary research goal is to measure the physical and chemical characteristics of the sediments in Lake Michigan that play an important role in the investigation of PBT contaminants. The first immediate goal is to identify the sources and loading of OM to Lake Michigan sediments. The second goal is to investigate how OM from these different sources was preserved in recent time in Lake Michigan sediments. I can distinguish the sedimentary carbon sources and their relative degradation/preservation in sediments by the technique of isotope analysis of <sup>13</sup>C, and <sup>15</sup>N analysis. My long-term research goal is to formulate and investigate research questions in support of the overall project itself.

#### **1.2.2 Research Objective**

The overall objectives of this research are to quantify the net loadings of OM, OC and important nutrient elements in Lake Michigan since European settlement and the industrial revolution. A specific research aim to support this objective is to develop rapid and accurate methodologies for sediment characterization. This specific research aim was achieved through testing and development of standardized procedures for bulk sediment physical and chemical characterization and analytical methods for use throughout the five-lake GLSSP study. For this purpose, I developed and tested a new physical and chemical method to obtain accurate measurements of OC and BC in sediments using an expanded form of procedures used in the literature (Verardo et al., 1990; Buckley et al., 2004), applying modifications suggested by Lukasewycz and Burkhard (2005). Physical and chemical characterization dominated the laboratory effort over the past years of my research. Physical-chemical results from this study have been combined with radio-dating data to determine the sedimentation rate and reconstruct the depositional history of all project analytes. These data allow the quantification of past and current depositional fluxes to the sediment, estimation of sediment chemical inventories and in situ sediment transport modeling. It is part of my research to compare OM, OC, BC fluxes and loadings from other Lake Michigan studies to better understand the source of PBTs to and from Lake Michigan sediment, and to identify if there have been significant changes in OM, OC, BC loadings and fluxes since the earlier studies were conducted.

#### **1.2.3 Research Hypotheses and Hypotheses testing**

The following specific hypotheses have been investigated for this research objective:

# Hypothesis 1: Recent enrichment of OM, OC, BC in Lake Michigan sedimentary record is due to Cultural Eutrophication.

In the scientific literature, the enrichment of OM, OC, BC in recent times has been explained by two competing theories. The "cultural eutrophication hypothesis" (CE) promulgated by Meyers (1994) argues that increasing organic loading since ~1700's are due to the impacts of increased populations resulting in increasing nutrient loadings and subsequent increased in-lake primary production. This hypothesis was investigated by looking at deep cores going back hundreds to thousands of years. The "labile OM degradation hypothesis" by Buckley et al. (2004), also Mayer (1995) and Keil et al. (1994) states that TC, OC, OM decreases down-core going back in time due to degradation of labile OM (LOMD). According to this latter hypothesis OM (which includes OC and N) levels in sediments would be relatively constant downcore, approaching the monolayer equivalent (referred to as MLE; approximately 1 mg  $C/m^2$  surface area). These hypotheses have been partially tested by measuring OC coverage and stable <sup>13</sup>C isotope analysis to identify carbon sources in Lake Michigan. In addition, this hypothesis will be investigated by comparing OC loading to sediment surface area relative to the MLE. It would be expected that much greater coverage (even downcore) relative to the MLE if CE and not LOMD were responsible for the observed profile of OC in the sediment column.

*Hypothesis* 2: *In Lake vs. terrestrial loading has changed since industrialization.* I aim to investigate how OM from these different sources was preserved in recent time (pre 1900's to the

present) in Lake Michigan sediments. Previous research in deep Lake Michigan sites indicates that >90% of algal OC is oxidized in the water column before it settles on the bottom (Meyers and Eadie, 1993). This cited research suggests that terrigenous OM would be more dominant in deeper sites, because autochthonous OM is known to dominate in shallower depths, whereas allochthonous OM is more important in near-bottom depths. OC concentrations would thus decrease with depth as a result of re-mineralization of organic matter by microbial activity and dilution by resuspended bottom sediments. Autochthonous carbon is primarily derived from photosynthesis by algae/cyanobacteria, and secondarily through cycling within the lake by zooplankton, plankitvorous fish and piscivorous fish. Conversely, allochthonous sources of carbon and or nutrients come from outside the lake sources such as plants and soil material, and those sources can be also distinguished into anthropogenic (such as BC and trace pollutants) and terrestrial such as dissolved organic carbon (DOC) and particulate organic carbon (POC) through runoff. Autochthonous sources dominate in large lakes and the ocean, while allochthonous sources of carbon are dominant in streams and small lakes (Eby, 2004).

Testing *hypothesis 2* consists of identifying Lake Michigan sediment carbon sources as autochthonous or allochthonous. In terms of sources, OM is preserved differently in recent sediments over the last 100-150 years. In particular, I hypothesize that OM was primarily autochthonous (lacustrine) source in the past, while more recently it is derived from more allochthonous (terrestrial) sources. It is possible to distinguish the sedimentary OM sources and their relative degradation/preservation in sediments by a variety of techniques like using atomic/isotopic ratios such as C/N, <sup>13</sup>C, <sup>15</sup>N analysis, and characterization of BC and pollutants (PCBs, PBDEs, etc.). To test *hypothesis 2* I investigated these ratios versus time to characterize the OC sources and evaluate OC coverage from particle size distribution data.

*Hypothesis* 3: *BC loading to LM sediment has increased significantly from pre-1900's due to increased industrial activity started.* Griffin and Goldberg (1983) argue that the BC sedimentary record is the result of combustion intensity of fossil fuels during industrial activity. From these data one may also determine the signal of developed controls, e.g. pollution controls on power plants and industrial facilities. This agrees with Buckley et al. (2004), where a strong correlation was found between BC loading and its spatial proximity to important pollution sources. They shown the highest BC loading occurred at Lake Michigan sediment samples nearest to urban/metropolitan area of Chicago.

Testing *hypothesis 3* consists of understanding BC loading in Lake Michigan sediment core samples as function of time relative to known population and industrial outputs. It is possible to distinguish the BC sources and their relative degradation/preservation in sediments by a variety of techniques like looking at BC concentrations and more importantly fluxes. Also, to test *hypothesis 3* I mapped BC loading using geographic information system (GIS) spatial distribution data and analysis for a better visualization of the data and quantification of whole-lake loading via advanced krieging methods within the ARCHVIEW GIS software.

 Table 1.1. Research driven hypotheses, selected techniques and tools to individually test each hypothesis.

HYPOTHESIS	TECHNIQUES & TOOLS TO TEST				
Hyp.1: "Recent enrichment/ increase of OM, OC, BC due to Cultural Eutrophication (CE)"	OM, OC, BC Fluxes as $f$ (Time)	Correlate w/ existing nutrient data from the literature	OC/TN and NBOC/TN ratios vs. Time	OC coverage from PSD	Loading as $f$ (Time)
Hyp.2: "In Lake vs. terrestrial loading has changed since industrialization"	Ratios as $f$ (Time)	SIA <sup>15</sup> N & <sup>13</sup> C	OC coverage as f (Surface area) from PSD		
Hyp.3: "BC loading increased with industrialization"	Conc's and more importantly fluxes	GIS Maps	BC Fluxes as <i>f</i> (Time)	Loading as $f$ (Time)	Population & Industrial Output vs. Time

#### **Chapter 2. Literature Review**

A literature review in support of my research study is presented in this chapter. This research is focused on organic carbon form, production rates, and loadings to Lake Michigan sediment from in-lake (autochthonous) and outside the lake (allochthonous) processes including riverine transport and atmospheric deposition from industrial sources and related activity. The objective of this document is to develop a thorough understanding of the scientific literature, identification of knowledge gaps, and development of experimental methodology to better understand carbon deposition in Lake Michigan.

The present section of this thesis comprises an introduction and a literature review of pollutant loading within lake sediments and factors affecting their fate in the sediment environment. This section includes an analysis of the carbon cycle in the lacustrine environment at a level necessary to understand the origins and sources of organic carbon and organic matter within the lake ecosystem. Next, I investigate the tools and methodology for the purpose of my study, and also consider factors affecting analytical performance and validation. Finally, I present the results of previous studies performed in Lake Michigan to identify research gaps for development of my research work.

#### 2.1 Sediments as a physical and chemical pollutant

Sediment is a mix of inorganic and/or organic material suspended and subsequently settled in water by force of gravity that accumulates in the bottom of lakes, rivers and oceans. Based on terrestrial environments and climate, the lake sediment contains different types of materials that may be used to reconstruct changes in the lake itself. The depth of sediment provides useful information about historical lake activities further back in time. In addition, atmospheric levels of many pollutants maybe reconstructed in the chronological record within lake sediments (Astle et al., 1987).

As stated by the Natural Resources Management and Food and Agriculture Organization of the United Nations (FAO), sediment pollution has two major dimensions; a physical dimension and a chemical dimension (Ongley, 1996). Based on the physical dimension, top soil loss and land degradation by runoff and erosion lead to excessive levels of turbidity in receiving waters, and off-site ecological and physical impacts from deposition in the lakebed. The fines fraction of sediment is comprised of a silt (2-63µm) and clay fraction (<2 µm fraction) that is the primary carrier of adsorbed chemicals like phosphorus, chlorinated pesticides and other organic pollutants, and most metals. The role of sediment in chemical pollution depends on the particle size of sediment as well as the amount of particulate organic carbon in the sediment. The particle size is important due to the large specific surface area of smaller particles, as they provide ionic exchange and sorptive more sites that are related to clay particles.

In polluted waters, pollutants are mainly adsorbed onto particles and bound to organic materials (Chapman et al., 1992). In Lakes, most persistent, bio-accumulative and toxic organic pollutants (PBTs) are strongly associated with sediment and especially with organic carbon transported as part of the sediment loading (Ongley, 1996). Accurate measurements of sediment concentrations and flow rates are important to compute total contaminant loadings to the water system. Changes in environmental conditions alter the phases of pollutants found on particulates, which can cause the pollutants to be released into the water. Various forms of organic matter, such as detritus and organic coatings on mineral particles, can be degraded, releasing bound pollutants (Chapman et al., 1992). As a result of changing environmental conditions, there is an internal recycling of pollutants in the aquatic environment.

#### 2.2 Importance and significance of Carbon Forms in the Carbon Cycle

Carbon is essential to life and all organic forms of life include it. The carbon cycle has two main components, the geologic, which includes both inorganic carbonates and organic carboncontaining compounds eroding from the land, washing into the sea, entering the earth's mantle layer and being expelled through erosion and volcanic activity, and the biologic so-called "biosphere", which includes plants, microbes and animals; all during complex but natural and continuous photosynthetic processes converting carbon dioxide and water into sugars with the release of oxygen gas. This is one small part of the cycle.

The carbon cycle is the exchange of carbon between the main carbon cycle reservoirs: the atmosphere, terrestrial biosphere, oceans and lakes, and soil and sediment. Each of these global reservoirs may be subdivided into smaller pools, ranging in size from individual communities or ecosystems to the total of all living organisms (Figure 2.1). A carbon sink, such as forest or ocean, is a carbon reservoir that stores more carbon than it releases. On the other hand, a carbon source is a reservoir that releases more carbon than it absorbs.



Figure 2.1. Simplified schematic of the global carbon cycle showing pool sizes of C (in blue; given in petagrams) and fluxes (in red; defined as mass/area x time =Pg. per year). Source: Adapted by NASA Earth Science Enterprise; www.globe,gov/projects/carbon.

Note:  $Pg=10^{15}$  grams-force  $=10^9$  metric tons (mt) of carbon.

In environmental science studies, lake sediments are well recognized as carbon sinks, and have large impact on the distribution, transport, and fate of contaminants. Hence, sediments and their role in lake environment functioning have been studied and documented extensively (Lindeman, 1942; Staehr et al., 2012). Lake sediments receive organic carbon (OC) from both in-lake (autochthonous) primary production or from external sources (allochthonous) in the surrounding basin (Figure 2.2a).

The primary OC sources are terrestrial in boreal lake sediments (von Wachenfeldt and Tranvik, 2008). The OC that reaches the lake sediment surface will typically be partially mineralized to carbon dioxide ( $CO_2$ ) or methane ( $CH_4$ ) by heterotrophic microorganisms, incorporated into microbial biomass. When OC fluxes to the sediment exceed the biological capacity to mineralize to OC, it becomes buried in the sediments (Figures 2.2 a-b).



Figures 2.2. (a) OC sequestration in lake sediments and carbon dioxide (CO<sub>2</sub>) from the atmosphere through geological timescales. Source: Chart modified from Sobek (2009); (b) OC cycling in lakes and different carbon isotopes in nature. Chart created by S. Bonina, 2015.

The rate of sequestration of OC in lake sediments (Mulholland and Elwood, 1982; Stallard, 1998; Einsele et al., 2001; Cole et al., 2007; Downing et al., 2008; Sobek et al., 2009), is similar to or even greater than in soils (Schlesinger, 1990; Harden et al., 1992; Trumbore and Harden, 1997; Rapalee et al., 1998) or in marine sediments (Cole et al., 2007). This is particular the case for boreal lake sediments (Kortelainen et al., 2004; Benoy et al., 2007). The balance between OC input and long-term storage of OC is controlled by the rate of microbial mineralization (Gudasz, 2011). Thus, the constraints on the microbial mineralization of sediment OC such as availability of electron acceptors like oxygen or nitrate is the key-factor in carbon biogeochemistry.

## **2.3 Organic and Inorganic Carbon, Organic Matter, Black Carbon in the Environment and in Lacustrine**

The first basic classification of carbon divides carbon as either organic or inorganic form. Organic carbon refers to the fact that the carbon forms are biologically derived compounds as complex substances produced primarily by living organisms; and inorganic carbon indicates mineral compounds that can be formed in absence of biological activity. Chemically, organic carbon has a C-H bond, whereas inorganic carbon does not. Halogen substitution of hydrogen can occur on many organic hydrocarbons, while not changing its organic status (e.g. Cl for H in CCl<sub>4</sub>). Three physical forms of carbon (C) are typically defined in soils and sediments, elemental C, organic C (OC), and inorganic C (IC). Elemental C includes charcoal, soot, graphite, and coal. The primary sources of elemental C are incomplete combustion of organic matter, from petrogenic geologic sources such as asphaltenes, graphite and coal or dispersion of these carbon forms during mining, processing, or combustion of these original materials.

OC derives from the decomposition of plants and animals. A wide variety of organic carbon forms such as freshly deposited leaves, twigs, branches or highly decomposed ones like humus are present in soils and sediments. In addition to these natural sources, there are sources that derive as a result of contamination through anthropogenic activities. Release of contaminants into the environment, which can be transported to the lacustrine environment, increases the total carbon content present in sediment.

The forms of IC are derived from geologic sources and in-lake precipitation and are present typically as carbonates within sediments. With respect to lake sediments, carbonate minerals represent a significant fraction of a great number of lakes. The two most common carbonate minerals found in lake sediments are calcite (CaCO<sub>3</sub>) and dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>), and other forms may be present (e.g., siderite, FeCO<sub>3</sub>) depending on where the soils were formed or where the sediment source was located (Table 2.1). Carbonate minerals form a significant fraction of the C pool in numerous lake sediments and can be derived in significant amount from three different processes: "allogenic" (derived from external sources transported to the lake), "endogenic" (originated internally), and "authigenic" (formed by precipitation or recrystallization during sedimentation) (Jones and Bowser, 1978).

 Table 2.1. Select list of minerals reported in freshwater lake sediments. Source: Adapted from Jones and Bowser (1978).

MINERAL	TYPE OF SOURCE			
	Allogenic	Endogenic	Authigenic	
Clays				
Illite	Х			
Smectite	X		37	
Chlorite	X		Х	
Kaolinite				
Nontronite	Λ			
Carbonates				
Calcite-CaCO <sub>3</sub>	Х	Х	Х	
Dolomite-CaMg(CO <sub>3</sub> ) <sub>2</sub>	Х		?	
Aragonite-CaCO <sub>3</sub>	Х	X		
Mg-Calcite-intermediate		Х	37	
Rhodochrosite-MnCO <sub>3</sub>			X	
Monohydrocalcite		v	А 2	
Siderite-FeCO <sub>3</sub>	?	Λ	?	
Fe-Mn Oxides				
Goethite-FeOOH	Х	Х	Х	
Magnetite-Fe <sub>3</sub> O <sub>4</sub>	Х			
Ilmenite-FeTiO <sub>3</sub>	Х			
Phosphates				
Apatite	Х			
Vivianite			X	
Iudlamite			Х	
Sulfides				
Pyrite-FeS <sub>2</sub>	X		Х	
Griegite-Fe <sub>3</sub> S <sub>4</sub>			Х	
Sphalerite-ZnS		Х		
Fluorides				
Fluorite-CaF <sub>2</sub>			Х	

Note: Illite and smectite formulas are taken from Perry (1971); nontronite formula is derived from Weaver and Pollard (1973).

The relative roles of organic and inorganic processes in determining the source and nature of lake carbonate mineralogy have not yet been completely explained in the literature(Jones and Bowser, 1978; Brezonik and Arnold, 2011). For example, "inorganic" carbonates like calcite can form biologically in an endogenic and/or authigenic manner due to the influence of algae or bacterial activity in the water column or sediment. Carbonate mineral distribution is highly variable in Great Lakes sediments (Jones and Bowser, 1978). Rossmann (1975), (2004) reported
that Lake Michigan sediments are rich in carbonates, for instance 12.6% of calcite (CaCO<sub>3</sub>) as well as dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>), reaching as highest 43.5 % of Aragonite (CaCO<sub>3</sub>) in the southeast of the Lake (Eadie and Robbins, 2005). The presence of IC in the Lake Michigan sediments has been a challenging part of the method development for determination of organic carbon in my overall research, overcoming the earlier study of Buckley et al. (2004) in which improperly the sediment was considered to be lacking of inorganic carbonates and thus total carbon measurements was comprised only of organic carbon. In their Great Lakes study, they characterized sediment for OC and BC via indirect acidification (acid vapor) to remove carbonate forms. Based upon the mineralogy of the Great Lakes region, the soil and bedrock are characterized by limestone whereas lake waters are almost saturated by calcium carbonate (Meyers, 2003; Eadie and Robbins, 2005). As described in details in the methodology and analysis section two of this report, choosing the adequate level of acidification to apply to the sediments prior analysis is a critical and significant step to achieve a complete removal of any possible carbonate, inorganic forms present within the sediment.

Organic matter (OM) is present in all continental and aquatic environments, and extensively distributed on earth's surface (Schnitzer, 1978). In sediments OM consists of many different types of organic materials including sugars and carbohydrates, proteins, nucleotides, fats, waxes, and also complex humic, and fulvic acids, lignins and humins (Meyers and Teranes, 2001). Chemically, OM has not been characterized and there is no unique structure, because it is heterogeneous and very complex. Characterizing physicochemical, and thermodynamic properties of the matter using analytical techniques is the best and common method to define OM (Senesi et al., 2009). In terms of weight, OM typically includes 45-55% carbon, 35-45% oxygen, 3-5% hydrogen, and 1-4% nitrogen; about 10-35% of the C present in OM creates

stable aromatic rings, difficult to break down and sensitive to electron donors or acceptors to polymerize and build larger and complex particles of OM (Cabaniss et al., 2004).

OM has very important characteristics such as the ability to form water-soluble and waterinsoluble complexes with metal ions and hydrous oxides, interact with clay minerals and bind particles together, sorb and desorb naturally-occurring as well as anthropogenically-introduced organic compounds, absorb and release plant nutrients, and hold water in its environment. The determination of the total organic carbon (OC) is frequently used as a measure of the OM content in the sediment (Schumacher, 2002). Sediment OC determinations are typically integrated with specific contaminant analyses as fundamental aspect of any site characterization and any overall ecological risk assessment of the ecosystem. Alternatively, OM can be determined gravimetrically based on low temperature oxidation (375°C) to oxidize the OM to CO<sub>2</sub>, while leaving behind the heat stable elemental carbon.

Several aquatic environmental studies (Gustafsson et al., 1996; Jonker and Koelmans, 2001; Rockne et al., 2002; Gobas and MacLean, 2003) have shown that OM in sediment affects the fate and accumulation of pollutants, such as hydrophobic organic contaminants (HOCs). The structure and degree of diagenetic alteration of sediment OM strongly affects its HOC sorption capacity. In general, the more extensive the aging, the stronger the sorption capacity (Huang and Weber, 1997; Næs et al., 1998; Gobas and MacLean, 2003). In addition, the transport of some HOCs to the sediments in the systems such as the Laurentian Great Lakes has been controlled by OM sedimentation processes (Pearson et al., 1997; Skoglund and Swackhamer, 1999; Buckley et al., 2004; Madigan and Martink, 2005). Thus, knowledge of not only the OM concentration but also the composition and rate of diagenetic alteration of the OM is helpful in understanding the fate of HOCs in sediments.

Black Carbon (BC) is a component of the elemental pyrogenic C that results from pyrolized carbon produced by incomplete combustion. BC occurs ubiquitously in soils and sediments. A review by Schmidt and Noack (2000) emphasizes the ubiquity of BC, which is defined as "a continuum from partly charred materials to highly graphitized soot particles, with no general agreement on clear-cut boundaries of definition" (Schmidt et al., 2001). BC is also sometimes referred to as charcoal, elemental carbon, and soot found in air, soils, sediments, and water. Although there are many environmental sources of BC, BC formation can occur basically in two different ways, through partial combustion of vegetation (likely plants and wood), or fuels, and as a coke production by-product of industrial processes. Both forms of BC are quite environmentally inert and are distributed universally by water via fluvial and atmospheric transport. Factors affecting the chemical and physical properties of BC in the environment include the composition of the materials being combusted, the method of combustion (oxygen to carbon ratio), and the transport mechanism from the site of their formation (Buckley et al., 2004). The determination of the source of BC and the distance traveled has been fully investigated using surface morphologies, size distributions and chemical structure (Goldberg, 1985). Rockne et al. (2000) argued that BC particles in the atmosphere have the ability to adsorb gas phase HOCs from the air because of their high surface area, high organic carbon contents, and adsorption characteristics. Therefore, BC is considered a likely key vector for transport in the atmosphere.

## 2.4 Significance of OM in Lake Sediment

Research studies conducted by Meyers and Ishiwatari (1995) present an overview of the origins and digenesis (mineralogy change and consolidation of sediments into rocks) of organic compounds in Great Lakes sediment. Based on these studies, OM content is a minor but important fraction of lake sediments, and is considered a key record of source (with elemental, isotopic and molecular composition). This is because OM provides paleo-environmental information of earlier physical and geochemical environments in the lake, paleo-liminological records preserved within sediments, impacts of humans on the ecosystems, and the history of climate change (Meyers and Ishiwatari, 1995).

In the related study of OM degradation in near-surface Laurentian Great Lakes sediments conducted by Li et al. (2006b), the settling rate of organic-rich particles is the dominant factor controlling the redox potential and terminal electron accepting process in the sediment. High concentrations of OM are found in sediments where either high rates of preservation, high rates of production, or both occur. The main factor affecting the rate of OM preservation is the presence or absence of oxic conditions. In an anoxic environment, the rate of organic matter degradation is typically much slower than by oxygen respiring heterotrophic bacteria, thus fully aerobic sediments result in maximal rates of OM degradation (Meyers and Ishiwatari, 1995). In the absence of sediment mixing due to bioturbation or physical processes, gradients in dated sediment profiles can be used to ascertain past rates of deposition and in situ rates of biodegradative change. This information can often be more predictive of long-term primary production rates than short-term measurements obtained through water column samples.

Only a minor portion of organic particles produced within the euphotic zone of lakes reaches the lake bottom layer, with the rest being remineralized within the water column. The fraction that is ultimately buried in the sediments depends on the water depth, i.e. the residence time in the water column, and redox conditions, as I stated above. Microbial decomposition (and biosynthesis) can progressively modify the bulk composition of the organic matter because different OM fractions have a different susceptibility to microbial degradation. All these aspects are not only important for a general understanding of the controlling factors, affecting the OM breakdown processes, they are also relevant for assessing the integrity of sedimentary archives as recorder paleo-environmental information.

## 2.5 Source of Organic Matter in Lake Sediments and its alteration during deposition

Depending on the primary sources of carbon, a lake can be considered either "autotrophic", where a lake creates enough reduced C through primary production *in situ*, or "heterotrophic", where the lake requires transfer of OC from outside the lake (Kratz, 2009; Staehr et al., 2012). Autotrophy and heterotrophy occur given the following conditions:

## **Equation 1: Autotrophy Condition**

Autotrophy: **GPP** > **ER**  $\rightarrow$  lake makes sufficient reduced carbon *in situ*.

## **Equation 2: Heterotrophy Condition**

Heterotrophy: **GPP** < **ER**  $\rightarrow$  lake requires transfer of organic carbon from outside of lake.

Where GPP stands for Gross Primary Production  $(g/m^2/yr)$  and ER Ecosystem Respiration  $(g/m^2/yr)$ , I will define those two parameters in the following.

The Net Ecosystem Production (NEP) is defined as function of GPP and ER:

### **Equation 3: Net Ecosystem Production**

$$NPE = GPP - ER$$



Figure 2.3. Chart shown the aquatic ecosystem productivity in the case of lacustrine environment. Chart created by S. Bonina, 2015.

In terms of lake productivity, organic matter production is reported as the formation rate, the creation of new organic matter, per unit area of earth, per unit of time (g /m<sup>2</sup>/year). The Primary Production (PP) is production of new organic matter by autotrophs. Over time, PP results in the addition of new plant biomass to the lake system. The Gross Primary Production (GPP) consist of all CO<sub>2</sub> fixed by the plant in photosynthesis. Known respiration is CO<sub>2</sub> lost from metabolic activity, the Respiration by Autotrophs (R<sub>a</sub>) like plants represents how much energy or carbon is used for plant metabolism, whereas the Respiration by heterotrophs (R<sub>h</sub>) indicates how much energy or carbon is used for heterotrophic metabolism.

Net Primary Production (NPP) is defined as following:

## **Equation 4: Net Primary Production**

$$NPP = GPP - Ra$$

Net Community Production (NCP) indicates how much of GPP produced is not lost to respiration and is defined as

#### **Equation 5: Net Community Production**

NCP = NPP - Rh = GPP - Ra - Rh

The autotrophic-heterotrophic lake balance is a function of nutrient and dissolved organic carbon concentrations. In addition, based on studies of the biological, chemical and physical limnology, autochthonous sources of carbon are generally via growth of algae, cyanobacteria and the microbial breakdown of particulate organic carbon. The carbon in-lake source can be primary (photosynthesis by algae or cyanobacteria) and secondary such as its cycling in the lake by zooplankton, plankitvorous fish and piscivorous fish (Rockne and Mittal, 2012). Conversely, allochthonous sources of carbon and nutrients are plants and soil material. These allochthonous sources can be also categorized as anthropogenic (e.g. black carbon, trace pollutants) and terrestrial (e.g. dissolved organic carbon and particulate organic carbon). Oceans and large lakes are typically controlled by autochthonous sources of carbon (Eby, 2004).



Figure 2.4. Representation of the carbon dynamics in lakes, presented by Kratz (2009), Center for Limnology - the Global Lake Ecological Observatory Network (GLEON) Conference.

The primary source of OM to lake sediments is from primary production within the lake or on the land around it. The vast majority of OM derives from plants, which can be non vascular such as algae and vascular such as grasses, bushes and trees; less than 10% originates from animals (Meyers and Ishiwatari, 1995). Lake morphology, watershed topography, and the specific abundance of the two geochemically different types of plants influence significantly the contribution of these two plant species. Furthermore, microorganisms and other bacteria in the sediment and in the water of lakes continuously change and degrade aquatic and land-derived OM. Even though some bacteria are able to live chemotropically, lake environments generally contain sufficient quantities of OM, and because of it, the lake microbiome is thought to be dominated by heterotrophic decomposers organic detritus. Bacteria have a primary role as OM producers in stratified lakes. Generally, lacustrine ecosystems have different levels of productivity in terms of the amount of nutrients availability and growth. Defining trophic nutrient or growth level of a lake consists of classifying it based on of its productivity. Lake Michigan has been classified as a large oligotrophic freshwater lake (Lehman, 1988; Dean and Gorham, 1998). The total OC amount of about 90% is from the algal production in Lake Michigan water, the other 5% comes from the rivers and the other 5% is transported in with atmospheric particles and natural precipitation (Andren and Strand, 1981). These contributions of OM are subject to selective degradation as they fall to the lake bottom, and so the original source percentages might not be preserved in the sediment record.

A sediment trap study of Eadie et al. (1984) indicates that only 6% of the OC formed sinks to the sediment surface of Southern Lake Michigan (Table 2.2); approximately 85 % of the OC is oxidized in the epilimnion upper layer of the water column (~ 115g  $C_{org}/m^2/yr$ ). Due to the continuous oxidative alteration and degradation in the bottom of the lake, the resuspension of sedimented OM can be considerable (75 g  $C_{org}/m^2/year$  of OC Flux at 100 m depth) or approximately ten times the annual OC flux at the lake bottom layer (Eadie et al., 1984; Meyers et al., 1984; Meyers and Eadie, 1993).

Element of	Flux
C Cycle	$(gC_{org}/m^2/yr)$
Primary Production	139
Oxidation the In epilimnion	-115
Sinking into the hypolimnion	24
Oxidation in the hypolimnion	-16
Sinking to the sediment surface	8
Resuspension into the hypolimnion	75

Table 2.2. OC Flux estimates in Lake Michigan lacustrine system.

Data are from sediment trap studies described by Eadie et al. (1984) and assume a 100 m-deep water column.

Thus, it is expected that shallow-water lakes would be richer in OM within their sediment, compared to the OM concentrations/ loadings in deep lakes as the Great Lakes and this is confirmed by experiment (Eadie et al., 1984; Cooke et al., 2001). Bioturbation or mixing of surface, biological mixing, seasonal or permanent anoxic bottom-water conditions and other processes all can change the original sedimented OM. During recycling residues of modified OM are mixed with the new incoming OM, which can subsequently be either preserved or degraded.

# **2.6 Pollution caused by Natural or Cultural Eutrophication**

Eutrophication is the natural process by which the lake water gradually becomes extremely high productive, rich in plants such as algae due to excess input of nutrients to the lake. Eutrophication may happen naturally, but it often is accelerated by anthropogenic pollution. The sources and the leading contributions to eutrophication are municipal and industrial wastewater effluents from chemical industries; also agricultural activities, and urbanization; which all provide large nutrient quantities adsorbed to initiate the eutrophication process (Thomas et al., 1996). This phenomenon generally takes thousands of years to progress; however humans have greatly speeded up the process in numerous lakes around the world. This "cultural eutrophication" caused by humans has dramatically altered the Laurentian Great Lakes over the last 100-200 years (Meyers and Eadie, 1993; Meyers and Ishiwatari, 1993b). Due to agriculture and residential or industrial expansions, the natural habitat is transformed and phosphorus is no longer held in the soil but is washed into lakes. Nutrients from run-off, accompanied by the discharge of effluent from industrial, agricultural and polluted sources change the nutrient high levels of a lake into a eutrophic lake. The nutrient loading changes based on to the types and amounts of human activity occurring in each watershed (Smith and Schindler, 2009). Combining these conditions causes rapid growth of algae and other biomass as it no-longer is

nutrient limited, together with a significant reduction in the concentration of dissolved oxygen, impairing lake ecosystems.

The mass of nutrients with the Lake available for growth determines the final biomass attained. The primary key nutrients, nitrogen (N) and phosphorus (P), are utilized until growth is complete, and the exhaustion of the pool of either one of these nutrients places a final limit on phytoplankton growth. Therefore, the nutrient, which is exhausted, is defined as the limiting nutrient in the lake system. According on Meybeck et al. (1990), the N/P ratio greater than 7 to 10 indicates that the lake water is P-limited, whereas N is limiting with a N/P ratio lower than 7.



Figure 2.5. Trophic lake classification, ranging from very low to very high productivity: Lakes range from oligotrophic to hypereutrophic, based on the primary source of carbon. Source: Adapted from Hakanson and Jansson (1983).

The process of eutrophication, shown in the chart of figure 2.5, is one of the most significant processes affecting lake management. The highlighting concept is related to the loading of OM, which is fundamental as food for all other organisms. OM can be internally produced via photosynthesis and known as autotrophic production, or external from the watershed (known as allotropy), which generates dystrophic lakes rich in OM. In these lakes where majority of OM is

derived from the surrounding watershed, the internal carbon production is generally low (Figure. 2.4). There is a continuous range of nutrient concentrations connected to biomass production. Eutrophic and hypertrophic lakes tend to be shallow and suffer from high rates of nutrient loadings from point and non-point sources. In regions of rich soils, lake bottom sediments are comprised of nutrient-enriched soil particles eroded from nearby soils. The association of P with sediment is a serious problem in the restoration of shallow, OM-enriched lakes. P-enriched particles settle to the bottom of the lake and form a large pool of nutrient in the bottom sediments that is freely available to rooted plants and which is released from bottom sediments under conditions of anoxia into the overlying water column and which is quickly utilized by algae. This P-pool, which represents an internal load of P, can greatly balance any actions taken by ecosystem basin managers to regulate lake eutrophication by control of external P sources from agriculture and point sources.

Table 2.3. Modified table of nutrient levels, biomass and productivity of lakes for each trophic lake type. Sources: Hakanson (1980); Hakanson and Jansson (1983); Meybeck et al. (1990).

Trophic Lake category (OM production)	Mean total Phosphorus (mg m <sup>-3</sup> )	Annual mean Chlorophyll (mg m <sup>-3</sup> )	Chlorophyll maxima (mg m <sup>-3</sup> )	Minimum Oxygen (%sat <sup>n</sup> )	Dominant Fish
Ultra- oligotrophic (Very low OM)	4.0	1.0	2.5	<90	Trout, Whitefish
Oligotrophic (Low)	10.0	2.5	8.0	<80	Trout, Whitefish
Mesotrophic (Medium)	10-35	2.5-8	8-25	.40-89	Whitefish, Perch
Eutrophic (High)	35-100	8-25	25-75	40-0	Perch, Roach
Hypereutrophic (High OM)	100	25	75	10-0	Roach, Bream

The change in trophic status over the natural lake condition is the common cause of the problems held by eutrophication. Efficient utilization of nutrients depends on the interplay of a

number of factors, which together define the growth conditions, and thus the final total biomass production at the primary producer level (Figure 2.7). Foraging of phytoplankton by zooplankton (secondary producers) and predation of zooplankton by fish (tertiary consumers) as well constitutes the trophic transfer system of carbon in the lake (Rockne and Mittal, 2012). As shown in the conceptual schematic of trophic levels (figure 2.6), in nature each inter-trophic mass transfer may represent multiple rate-limiting processes.



Figure 2.6. Simplified pyramid of trophic levels in aquatic food web showing bounded trophic levels and inter-trophic transfer processes. Source: Adapted from Mittal (2006).

The efficiency of the system depends on two factors: first, the quantity of biomass created at the primary producer level and, then the species composition that determines the efficiency of grazing, the quality and quantity of the fish which settle the inside food chain. With death, organisms decay, resulting in the recycling of nutrients to the lake system. The effects of eutrophication can be highly harmful to lake water quality and severely limit the usages for which the water is suitable. Among some already discussed effects, the increase in biomass results transform in impaired water use of the lake.



Figure 2.7. Schematic illustration of the eutrophication process, showing its causes and effects (Thomas et al., 1996).

Lake Michigan, together with Lakes Erie and Ontario, underwent dramatic eutrophication events over the last100 year, this stimulated the institution of the federal *Great Lakes Water Quality Act* (GLWQA) and the Clean Water Act (CWA) in 1972 (Sweeney, 1993; Schelske and Hodell, 1995). The excessive growth of algae stimulated by phosphates changed water quality, particularly in Lake Erie and also in the other Great Lakes. Algal blooms and subsequent mineralization of decaying algal biomass led to oxygen depletion and resultant fish kills. Many native fish species disappeared, to be replaced by species more resilient to the new ecoconditions. Throughout the 1960's, rapid cultural eutrophication occurred initially in Lake Erie, following by Lake Michigan; and considerable concern was voiced in Canada and USA. Sewage was a major source of phosphorus to these lakes when detergents contained large amounts of phosphates (which acted as water softeners to improve the cleaning action) but they also stimulated drastically the algal growth when flushed into the lakes.



Figure 2.8. Magnitude and direction of processes (kg/yr) that move phosphorus (P) into and out of Lake Michigan annually (Miller et al., 2000). Consequent Eutrophication occurred. Source: http://www.epa.gov/med/grosseile\_site/LMMBP/eutrophication.html

The USEPA (2005a) mass balance study on eutrophication offers an estimation of the sources, sinks, and inventory of total P in Lake Michigan. Internal recycle (such as settling of 7 x  $10^{6}$  kg/yr and sediment recycle 4 x  $10^{6}$  kg/yr) accounts mainly for the bulk of P flux occurring in Lake Michigan (figure 2.7). A significant mass of P settles to the Lake bottom layer, although a large percentage (approximately 60%) is recycled back to the water column. The tributaries (with a loading monitored of 1.83 x  $10^{6}$  kg/yr) represent the principal external total P-sources to the

lake, while atmospheric loading is a relatively minor source (0.29 x  $10^6$  kg/yr). The P export at the Chicago diversion (13,000 kg/yr) is a small amount of the total P export.

The best estimate using the 1994-1995 average loading is that Lake Michigan is experiencing a 5% annual reduction in P loading, which implies that there is a steady reduction in P lake concentration. Overall, P is the primary limiting nutrient for phytoplankton in Lake Michigan, while silica may limit diatoms growth.

Table 2.4. Comparison of water-column silica, chrophyll a and phosphorous concentrations (Schelske et al., 1983). The silica data from the early 1960's are based on average chemical characteristics (Beeton and Chandler, 1968). Note: N.D.= No Data.

LAKE	LA	SILICA (mg m <sup>-3</sup> ) TE 1970's	EARLY	Avg. Chrophyll a	Avg. Winter	Reference	
	Summer Minimum	Winter Maximum	1960's Avg.	(mg m <sup>-3</sup> )	Phosphorous (mg m <sup>-3</sup> )		
L. Ontario	0.1 x10 <sup>-3</sup>	0.4 x10 <sup>-3</sup>	0.3 x10 <sup>-3</sup>	4.8	25	Dobson et al. (1974)	
L. Erie (Eastern)	<0.1 x10 <sup>-3</sup>	0.3 x10 <sup>-3</sup>	N.D.	4.3	25	Dobson et al. (1974)	
L. Erie (Central)	<0.1 x10 <sup>-3</sup>	0.4 x10 <sup>-3</sup>	N.D.	5.5	29	Dobson et al. (1974)	
L. Erie	N.D.	N.D.	1.5 x10 <sup>-3</sup>	N.D.	N.D.	Dobson et al. (1974)	
Lake Michigan	0.1 x10 <sup>-3</sup>	1.5 x10 <sup>-3</sup>	3.1 x10 <sup>-3</sup>	2.2	8	Schelske et al. (1980)	
L. Huron	1.1 x10 <sup>-3</sup>	$1.9 \text{ x} 10^{-3}$	2.3 x10 <sup>-3</sup>	1.8	5	Dobson et al. (1974)	
L. Superior	2.3 x10 <sup>-3</sup>	2.4 x10 <sup>-3</sup>	2.1 x10 <sup>-3</sup>	0.9	4	Dobson et al. (1974)	

Schelske et al. (1983) hypothesized that eutrophication in the lower Great Lakes, particularly in Lake Michigan in the early 1960's resulted from nutrient enrichment associated with initial watershed settlement and forest clearance. This hypothesis was supported by the pattern of biogenic silica in the sediments, correlated with P-loading and the silica-depletion sequence. The silica depletion process with increased P loading results from diatom production and silica demand increasing until diatom demand production reduced silica supplies to limiting levels, causing a change in phytoplankton from diatoms to algae (which do not require silica). Indeed in Lakes Erie and Ontario the most probable cause of diatom production and silica limitation is

high nutrient loading resulting from settlement during 1800's while in Lake Michigan these events occurred in mid-1900's (Table 2.4).

### 2.7 Tools and Methodology: procedures and relevant examples in the literature

Sedimentary OM sources and their degradation and products in sediments can be distinguished by a variety of techniques. These include atomic and isotopic ratios such as C/N, C/H, <sup>13</sup>C, <sup>15</sup>N, chemical characterization of black carbon, pollutants (e.g. Polycyclic Aromatic Hydrocarbons (PAHs), Polychlorinated Biphenyls (PCBs), Polybrominated Diphenyl Ethers (PBDEs, etc.), alkanes, alkanoic acids, sterols, lignin derivatives, other chemical characterizations, and more advanced techniques. After creating a temporally (sediment cores) and spatially (surface grabs) sediment data set for Lake Michigan, one of my primary interest of this study is to analyze the production and decomposition processes within the LM lacustrine ecosystem utilizing a variety of characterization techniques.

Biogeochemical research has shown predictive relationships between elemental mass ratios and carbon isotopic composition of living organic matter and both the physical and biochemical processes associated with carbon assimilation (Meyers and Ishiwatari, 1993b). Processes including biosynthesis and degradation in the photic zone and bacterial growth in both the water column and the sediment affect these ratios. Meyers and Ishiwatari (1993b) found that C/N ratios of sediments are influenced by the presence or absence of cellulosic sources of OM. OM elemental ratio analysis not only acts as an indicator of past environmental changes, but such techniques may also be useful in understanding mechanisms controlling primary productivity and seasonal lake behavior. Stable isotope analysis (determination of <sup>13</sup>C and <sup>15</sup>N), is a relatively new quantitative method for identifying sources of carbonaceous contaminants (Schmidt et al., 2004). This technique exploits the differential rates at which heavier natural isotopes pass across membranes, resulting in different fractionation ratios of heavier to lighter isotopes (Madigan and Martink, 2005).

For many elements there are several isotopes, which differ in the number of neutrons present. Certain isotopes are unstable and break down as a result of radioactive decay; while others, the stable isotopic ones, are not radioactive but are metabolized differentially by microorganisms. Consequently, stable isotopes are used to study various microbial transformations in nature. The most useful stable isotopes in microbial ecology are carbon, particularly carbon dioxide (CO<sub>2</sub>) as well as N, and oxygen (O). Carbon exists in nature primarily as <sup>12</sup>C but a small amount (about 5% exists as <sup>13</sup>C). The relative abundance of these isotopes changes when organisms metabolize the element because biochemical reactions favor the lighter isotope. Therefore, the heavier isotope is discriminated against relative to the lighter isotope when enzymes metabolize the compounds. For example, the cellular carbon in oligotrophic CO<sub>2</sub> fixation becomes enriched in <sup>12</sup>C and depleted in <sup>13</sup>C, relative to CO<sub>2</sub> source (Figure 2.9). This biological isotopic fractionation can be used as an assay for whether a particular transformation is biologically mediated.



Figure 2.9. Mechanism of isotopic transformation using carbon (Madigan and Martink, 2005).

Stable Isotopic Analysis (SIA) consists of a fraction by biotic processes, typically due by mass transfer in membranes and enzymes. SIA identifies the distribution of certain stable isotopes and chemical elements within chemical compounds. Carbon isotopes assist in determining the primary production source responsible for the energy flow in an ecosystem. The transfer of <sup>13</sup>C through trophic levels remains relatively the same, except for a small increase (an enrichment < 1 ‰). Because  $\delta^{13}$ C indicates the original source of primary producers, the isotopes can also help to determine shifts in diets, both short-term, long term or permanent. Nitrogen isotopes indicate the trophic level position of various marine organisms. There is a larger enrichment component with  $\delta^{15}$ N because its retention is higher than that of <sup>14</sup>N. In addition to trophic positioning of organisms,  $\delta^{13}$ C and  $\delta^{15}$ N values have become commonly used in distinguishing between land derived and natural sources of nutrients. Besides, the isotopic composition of any sample contains a record of its past biological activity.

Plant material and petroleum, derived from plant material, have similar isotopic compositions (Figure 2.10a). Carbon from both sources is isotopically lighter than a non-biological standard because it was fixed as a  $CO_2$  by a pathway that discriminated against <sup>13</sup>C. Moreover, methane of microbiological origin is isotopically light, indicating that methanogenic Achaea discriminate against <sup>13</sup>C. By contrast, marine carbonates are of geological origin. Because of the differences in the proportion of <sup>12</sup>C and <sup>13</sup>C in carbon of biological and geological origin, the isotopic ratio <sup>13</sup>C/<sup>12</sup>C (measured using mass spectrometry) of geological strata has been used to detect the presence of once living material in sediments.



Figure 2.10. (a) Chart represents carbon isotopic compositions of various substances (Madigan and Martink, 2005). (b) Distinctive source combinations of atomic C/N ratios and organic  $\delta^{13}$ C. Their value ranges of marine algae, lacustrine algae, C3 land plants and C4 lands (Meyers, 1994).

Nitrogen also undergoes isotopic enrichment during biological uptake and metabolism using C and N isotopic data, atomic C/N ratios and organic  $\delta^{13}$ C values (Figure 2.10b). Marine algae can be discriminated from lacustrine algae and terrestrial plants. Lands plants are grouped into C3

land plants, barley, potatoes and sugar beet, and C4 plants, which include corn, sugar cane, and food crops.

# 2.8 Lake Michigan and the Laurentian Great Lakes

Lakes can be both fresh and saline. The total surface of area of freshwater lakes is estimated to be approximately 855,000 km<sup>2</sup>, which represents less than 1% of the ice free continental surface; while the total volume of freshwater lakes is about 125 000 km<sup>3</sup>. The total volume of freshwater lakes is dominated by a few large water bodies listed below in Table 2.5.

FRESHWATER LAKES by WATER SURFACE AREA					FRESHWATER I	AKES by WAT	ER VOLUME
#	Lake Name	Surface Area	Country	#	Lake Name	Volume	Country
1	Caspian Sea*	371,000 km <sup>2</sup> 1/3 000 Miles <sup>2</sup>	Kazakhstan/ Iran Russia/Turkmeni	1	Caspian Sea *	78,200 km <sup>3</sup> 18 800	Kazakhstan/Iran Russia/Turkmenist
		143,000 Miles	stan/Azerbaijan/			Miles <sup>3</sup>	an/Azerbaijan/
2	L. Superior	82,100 km <sup>2</sup> 31,700 Miles <sup>2</sup>	USA/Canada	2	L. Baikal	23,600 km <sup>3</sup> 5,700 Miles <sup>3</sup>	Russia
3	L. Victoria	69,485 km <sup>2</sup> 29,828 Miles <sup>2</sup>	Africa	3	L. Tanganyika	18,900 km <sup>3</sup> 4,500 Miles <sup>3</sup>	Tanzania/Congo/ Burundi/Zambia
4	L. Huron	59,600 km <sup>2</sup> 23,000 Miles <sup>2</sup>	USA/Canada	4	L. Superior	12,100 km <sup>3</sup> 2,900 Miles <sup>3</sup>	USA/Canada
5	L. MICHIGAN	57,800 km <sup>2</sup> 22,300 Miles <sup>2</sup>	USA	5	L. Malawi	7,725 km <sup>3</sup> 1,853 Miles <sup>3</sup>	Malawi/Mozambiq ue/Tanzania
6	L. Tanganyika	32,900 km <sup>2</sup> 12,700 Miles <sup>2</sup>	Tanzania/Congo/ Burundi/Zambia	6	L. Vostok	$5,400\pm1,600$ ~1 300Miles <sup>3</sup>	Antarctica
7	L. Baikal	31,722 km <sup>2</sup> 12,248 Miles <sup>2</sup>	Russia	7	L. MICHIGAN	4920 km <sup>3</sup> 1180 Miles <sup>3</sup>	USA
8	Great Bear L.	31,153 km <sup>2</sup> 12,028 Miles <sup>2</sup>	Canada	8	L. Huron	3540 km <sup>3</sup> 850 Miles <sup>3</sup>	USA/Canada
9	L. Malawi	29,600 km <sup>2</sup> 11,400 Miles <sup>2</sup>	Malawi/Mozambi que/Tanzania	9	L. Victoria	2,700 km <sup>3</sup> 650 Miles <sup>3</sup>	Tanzania/Uganda/ Kenya
10	Great Slave L.	27,200 km <sup>2</sup> 10,500 Miles <sup>2</sup>	Canada	10	Great Bear L.	2,236 km <sup>3</sup> 536 Miles <sup>3</sup>	Canada

Table 2.5. Fresh water lakes ranked by surface area and volume from Herdendorf (1982), USEPA and Canada (1995), and USEPA Website Database.

\* Note: Although the Caspian Sea is commonly considered to be as the world's largest lake, it is geologically considered an ocean.

Lake Michigan together with Lakes Superior, Huron, Erie and Ontario constitute the five Laurentian Great Lakes (GL). The GL comprise large parts of USA and Canada, covering more than 1,200 kilometers (750 miles) from west to east, including eight US states of the USA and two provinces of Canada. The GL are the largest surface freshwater system on Earth (Table 2.5).

The GL are a dominant part of the physical and cultural assets of North America, and have supplied water for consumption, transportation, power, recreation and a many other usages for over three centuries. They cover approximately 84 percent of the surface fresh water in the North America and approximately 21 percent of the supply on a global scale. The GL have a very large surface area, but depth is shallow. Also, the GL watersheds are small compared with their surface area. The lakes have been affected by a wide range of pollutants and environmental issues, which include toxic and nutrient pollution, the presence of invasive species and habitat degradation. The runoff of soils and farm chemicals from agricultural lands, waste from cities, discharges from industrial areas and leachate from disposal sites are among the primary sources of GL pollution. The great surface area to the volume ratio of the GL (nearly two orders of magnitude higher than that of the oceans) makes them to be particularly sensitive to atmospheric pollutants via rain, snow, or dust. Moreover, outflows from the GL are relatively small (less than 1 percent per year), resulting in a long hydraulic residence time. Therefore, contaminants that enter the lakes are held in the lake system and can become more concentrated with time. With respect to volume, Lake Superior is the largest, deepest, and coldest of the five Lakes. Within GL, Lake Superior has the longest retention time of 191 years due to its large size. Lake Huron with an intensively farmed basin and productive fishery, is the third largest of the lakes by volume. Lake Erie has an intensively farmed basin because of fertile soils surrounding the lake

and the highest population, is the smallest of the Lakes in volume and is exposed to the greatest effects from urbanization and agriculture. It is the shallowest of the five lakes, in particular in the western basin with an average depth of 7.4 meters (24 feet). Therefore, Lake Erie has warm temperature over in spring and only summer, and frequently frozen during winter. Consequently, it has the shortest retention time of the all GL, 2.6 years. Lake Ontario is the smallest by area (slightly smaller than Lake Erie), but its depth (average depth of 86 meters, 283 feet) results in retention time of about 6 years.

Table 2.6. Physical and hydraulic features of the Great Lakes.

Sources: Quinn (1992), Meyers (2003), USEPA Website Database (http://www.epa.gov/greatlakes/lakestats.html), and NOAA-GLERL Website Database (http://www.glerl.noaa.gov/pr/ourlakes/lakes.html).

<u>GREAT</u> <u>LAKES</u>	Surface	e Area	Water V	Volume	Avg. I	Depth	Max.	Depth	Draina	ge Area	Shor Len	eline gth	Ret. Time	Popul USA – Can	ation ada (2000)
	Km <sup>2</sup>	Mile <sup>2</sup>	Km <sup>3</sup>	Miles <sup>3</sup>	Meter	Feet	Meter	Feet	Km <sup>2</sup>	Mile <sup>2</sup>	Km	Miles	Years	US	Canada
L. Superior	82,100	31,700	12,100	2,900	147	483	406	1,332	127,700	49,300	4,385	2,726	191	444,000	229,000
L. Michigan	57,800	22,300	4,920	1,180	85	279	283	925	118,000	45,600	2,633	1,638	99	12,052,743	N/A
L. Huron	59,600	23,000	3,540	850	59	195	229	750	134,100	51,700	6,157	3,827	22	1,500,000	1,500,000
L. Erie	25,700	9,910	484	116	19	62	64	210	78,000	30,140	1,402	871	2.6	10,500,000	1,900,000
L. Ontario	18,960	7,340	1,640	393	86	283	244	802	64,030	24,720	1,146	712	6	2,800,000	2,800,000
Total	244,160	94,250	22,684	5,439	-	-	-	-	521,830	201,460	17,017	10,210	-	27,296,743	6,429,000

Lake Michigan (LM) has a surface area of 57,780 km<sup>2</sup> (22300 miles<sup>2</sup>) with an average depth of 85m (279 feet). LM is second largest of the GL by volume; and is the only Great Lake entirely within the United States. The northern part is in the colder, less developed upper Great Lakes region. It is sparsely populated, except for the Fox River Valley, which drains into Green Bay. This bay has one of the most productive Great Lakes fisheries but receives the wastes from the world's largest concentration of pulp and paper mills. The more temperate southern basin of Lake Michigan is among the most urbanized areas in the Great Lakes system. It contains the two important metropolitan areas of Milwaukee and Chicago, whit a population of almost 8 million, approximately one-fifth of the total population of the GL basin. LM retention time is quite long, for instance, it flows into Lake Huron through the straits of Mackinac at a rate equal to a complete change of water about every 100 years.

Addressing the problems of the whole GL ecosystem is a complex task given the fact that the whole GL basin is shared, regulated and managed between the USA and Canada. The first major agreement between the two countries was the *Great Lakes Water Quality Act* (GLWQA). The GLWQA was completed in 1972, and amended periodically since then, reviewed in 1978 ("the 1978 Agreement"), confirmed in 1983 and amended again in 1987, and most recently updated in 2012, provides a vital framework for bi-national consultation and cooperative action to restore, protect and enhance the water quality of the GL to promote the ecological health of the Great Lakes basin. Under the GLWQA, the USA and Canada agreed "to restore and maintain the chemical, physical and biological integrity of the waters of the Great Lakes Basin Ecosystem". The agreement provides the basis for international efforts to manage the GL as shared resource. The USEPA is primarily responsible in the US through its Great Lakes National Program Office (GLNPO); in addition nine other federal agencies together administer more than 140 different federal programs, also 8 U.S. states, nearly 40 tribal nations, more than half a dozen main metropolitan areas, and numerous county and local governments all help with funding and implementation of environmental restoration and management activities in the GL basin. The Great Lakes five-Year Strategy, built on the institution of the GLWQA and developed together with U. S. EPA and its multi-state, multi-agency partners offers the agenda for GL ecosystem management, and its lakewide management plans have been established for each single lake.

## 2.9 Historical Concentrations, Fluxes, and Loadings of C in Lake Michigan

There have been numerous studies of short-term changes in OM and OC loading and sources in LM (Meyers et al., 1980; Eadie et al., 1984; Meyers et al., 1984; Meyers and Ishiwatari, 1993a; Meyers, 1994; Meyers and Lallier-Vergès, 1999). Most of these studies were small in scope, comprising less than a dozen sampling sites; there are relatively few major scale works. Among more recent multi-site studies within the last 10 years, I have focus on a five-lake study of twenty-two sediment cores in 2001 and 2002, conducted by Li, Rockne and Sturchio. The major findings of this study are presented in a set of four journal papers (Li et al., 2004; Li et al., 2005a; Li et al., 2005b; Li et al., 2006a).

Li et al. investigated the spatial distribution and temporal trends of polybrominated diphenyl ether (PBDE) deposition as recorded in the sediments. They found that year of deposition, latitude, and the OM content of the sediments are the main influencing factors for PBDEs in the Great Lakes sediments. In particular, Lake Michigan PBDE concentrations as function of sediment depth (Table 2.7) mirror the increasing production and usage of the commercial PBDE products in recent times. The highest concentrations appear in the top layers of sediments, which implies the risk of PBDEs is increasing with time. The chemical inventory of  $\Sigma_0$ BDEs were highest in the Southern LM Basin > Central Open Lake > Northern LM Basin. They calculated a total load of  $\Sigma_0$ BDEs in the sediments of Lake Michigan would be in the range of 760 to 2,400 kg, and the total load of PBDEs is estimated to range from 29,000 to 50,000 kg, including BDE209, the most abundant. Buckley et al. (2004) reported the sediment OC and BC concentrations (where BC was referred to as soot C in this study) as a function of time, showing great variability between and within the Great Lakes. In all three Lake Michigan sample sites, the BC profile was very similar in shape and the BC concentration was not significantly (95% CL) different for the past 50 years, after peaking near 1950. Prior to 1950, BC decreased significantly (95% CL) to approximately 1900, and then was relatively constant to the bottom of the core. These trends are consistent with literature reports of PAH deposition trends at the same locations (Simcik et al., 1996; Pearson et al., 1997). The constant trend and variance in magnitude among the locations may be explained through sediment mixing and focusing. The closest site to the Chicago metropolitan area had the highest surface BC concentrations, while the northern basin sites had fairly similar surface concentrations of BC; approximately half that of the southern basin site. BC and OC in Lake Michigan were much higher (three times) than Lake Superior. At the sediment-water interface, southern basin OC was higher than down-core depths corresponding to 1950. At deeper core depths, the OC decreased, which was purported to be the result of degradation of the OC downcore with time. This diagenetic alteration proceeded with a relatively linear temporal decrease in concentration to the mid-1800s (i.e. it followed a first order kinetic rate). Other studies have

correlated fuel consumption in the region with BC and polycyclic aromatic hydrocarbons (PAHs) loadings in Lakes Erie (Kralovec et al., 2002) and Michigan (Simcik et al., 1996). Previous characterization of BC (Rockne et al., 2000), together with an expression defining partitioning of HOCs to aerosols (Harner and Shoeib, 2002), was used to predict that soot could be a major vector for long range (allowing equilibrium) PAH and PBDE transport, whereas PCBs and organo-chlorine pesticides (OCPs) were not as likely to partition to soot in the atmosphere. The finding that higher BC levels occurred in locations close to large metropolitan areas was well correlated to a recent report on PAH deposition to Lake Michigan and is consistent with the other studies that BC and PAHs co-occur in the environment. Buckley et al. (2004)'s data quantitatively reveal the importance of large industrial/metropolitan areas on the BC flux to the lakes. It has already well known that BC and PAH deposition in southern Lake Michigan were highly correlated. Several studies, Gustafsson et al. (1996), Gustafsson and Gschwend (1998), Ghosh et al. (2000), Rockne et al. (2000), Jonker and Koelmans (2001), Jonker and Koelmans (2002), Rockne et al. (2002), Fernández et al. (2003), Ribes et al. (2003), Rockne et al. (2003a), and Rockne et al. (2004) indicate that BC contains high levels of PAHs and may influence the distribution and bioavailability of PAHs in sediments. Although they did not measure BC levels in the sediment, Simcik et al. (1996) proposed that BC from coal combustion was the main source of PAHs to Lake Michigan sediments, considering historical coal usage and/or combustion data available. They showed a correlation between historic records of coal usage and their measured PAH accumulation rates, and also higher input rate of PAHs in the southern basin relative to the northern basin of the lake have been reported. Using Lake Michigan sample data from the same southern Lake Michigan sampling location in 2001 and 2003 from Buckley et al. (2004), reported sediment accumulation data for 28 PAHs (Simcik et al., 2003) supports the

proposed source pathway. The following summary findings of this study were strong and highly significant correlations found between BC and PAH accumulation rate; the least highly significant correlation was seen for the PAHs with the lowest octanol air partition coefficient  $(K_{OA})$  values; strong correlations (and their relative pattern) are highly suggestive of a connection between BC and PAH deposition at this Lake Michigan site.

McCarty et al. (2004) reported average sediment PCB concentrations of 40-70 ng/g and open waters of the Great Lakes (as well as more isolated water bodies) are dominated by atmospheric input (Hornbuckle et al., 2006). In 2005 the USEPA carried out an inventory of the mass balance of nutrients, metals and toxic compounds found in Lake Michigan, identifying relative loading rates of specific pollutants coming into the Lake from air, tributaries, and sediments (figure 2.11 a, b and c.), to understand the environmental process controlling the fate of the pollutants, and to predict the environmental benefits of specific load decreases over time needed to accomplish beneficial impacts.



Figure 2.11. Annual magnitude and direction of processes (kg/yr) that move (a) PCBs. Data from USEPA (2005a), Rossmann (2006), Hornbuckle et al. (2006); (b) Mercury (Vette et al., 2002), (c) Atrazine in Lake Michigan (Miller et al., 2000).

Mass balance of PCBs, mercury and atrazine in Lake Michigan are shown in figure 2.11a, highlighting the importance of atmospheric exchange as PCB loss and gain mechanisms and its current role as a net source to the region (USEPA, 2005a; Hornbuckle et al., 2006). On smaller

temporal and spatial scales processes are more dynamic. For example over days near Chicago the net total PCB gas exchange with southern Lake Michigan changes direction given variations in wind direction, temperature, and atmospheric PCB concentrations (Hornbuckle et al., 2001).

Also, Lesht and Rockwell (1987) conducted a modeling study of phosphorus in the water column of Lake Michigan based on the measured nutrient concentrations in the water (Lesht et al., 1991). According to their study, the rate of phytoplankton growth and nutrient uptake was lower in the Northern Basin of Lake Michigan than the Southern in 1984, and the Northern basin had lower biomass (chorophyll-a) than the Southern, but higher rate of nutrient (silica and nitrogen) uptake. Also, their study reported that the surface concentration of TP measured in the open water was  $4.8 \pm 0.7 \mu g/l$  in the Southern Basin, and  $5.6 \pm 1.7 \mu g/l$  in the Northern basin. The TP concentrations measured in the 1980s have been quite stable since the late 70s. In 1985 during the spring time the nitrate + nitrite nitrogen concentrations were marginally higher in the Northern basin (297  $\mu g/l$ ) than the Southern basin (283  $\mu g/l$ ). Due to epilimnetic depilation of nitrate + nitrite nitrogen concentrations, there was a significant decrease in both Northern and Southern basins in 1985. TP is higher in the North of Lake Michigan, even though fluxes are higher in the South. This might be explained by different geographic conditions: there is more sunlight and high temperature in the south than the north.

More recent Guo et al. (part of the GLSSP research project) has shown that concentrations of atrazine are significantly higher in southern basin than in the north; approximately 3.4 tonnes atrazine, 1.4 tonnes of simazine, 0.17 tonnes of alachlor, 1.9 tonnes of desethyl-atrazine (DEA), and 2.9 tonnes desisopropylatrazine (DIA). For instance, the ratio of DEA to atrazine increases with latitude and depth (Guo et al. (in review)). The estimated concentrations in pore water are much higher than those reported for the bulk water of Lake Michigan, suggesting that the sediments may be a significant source of the overlying water column.



Figure 2.12. Atrazine inputs are increasing exponentially and continuously in the sediment samples were collected from Lake Michigan in 2010 and 2011(Guo et al., in review).

A summary of selected Lake Michigan studies is provided in table 2.7.

Table 2.7. Summary of research studies showing element, compound concentration, flux and/or loading to Lake Michigan sediments.

Compound/Element	Matrix/Test Method	Conc.s	Flux	Loading Rate	Citation/ Reference	Note
тос	LM Sediment Trap (15m) LM Sediment Trap (35m) LM Sediment Trap (80m) LM Sediment Trap (120m) LM Sediment Trap (140m) LM Sediment Trap (11m) LM Sediment Trap (31m) LM Sediment Trap (91m) LM Sediment Trap (146m) LM Sediment Trap (166m)	$16.0 \% \\ 14.2 \% \\ 6.4 \% \\ 4.8 \% \\ 8.8 \% \\ 38.1 \% \\ 45.8 \% \\ 10.9 \% \\ 4.8 \% \\ 5.7 \% \\ $	64 mg/m²/day 70 mg/m²/day 62 mg/m²/day 93 mg/m²/day 329 mg/m²/day 27 mg/m²/day 119 mg/m²/day 45 mg/m²/day 27 mg/m²/day 66 mg/m²/day	- - - - - - - - - - - - - - - - - - -	Meyers and Ishiwatari (1995) & Book Physics and Chemistry of Lakes (Ed.2) Meyers and Eadie (1993)	Two locations: Station 4- South LM Station 11- North LM
OC	LM Sediment Trap in Unstratified collection period LM Sediment Trap in Stratified collection period	-	259mg/m²/day 63 mg/m²/day	-	Eadie et al. (1984)	Measured 0.012(mg/m <sup>2</sup> /yr) <sup>2</sup> annual Measured 23(mg/m <sup>2</sup> /yr) <sup>2</sup> annual
BC	LM Sediment	0.37 % (Avg.)	-	-	Lim and Cachier (1996) Griffin and Goldberg (1983)	Method: H <sub>2</sub> O <sub>2</sub> /Infrared Spectroscopy

Compound/Element	Matrix/Test Method	Conc.s	Flux	Loading Rate	Citation/ Reference	Note
δ <sup>13</sup> C	LM Surface Sediment LM Settling Sediment LM Mixed Plankton LM Sediment Trap (15m) LM Sediment Trap (35m) LM Sediment Trap (80m) LM Sediment Trap (120m) LM Sediment Trap (140m) LM Sediment Trap (140m) LM Sediment Trap (31m) LM Sediment Trap (91m) LM Sediment Trap (146m) LM Sediment Trap (166m)	$\begin{array}{c} -26.3 \ \%_0 \\ -27.5 \pm 0.9 \ \%_0 \\ -26.8 \pm 1.4 \ \%_0 \\ \hline \\ -28.8 \ \%_0 \\ -26.8 \ \%_0 \\ -26.2 \ \%_0 \\ -26.6 \ \%_0 \\ \hline \\ -29.2 \ \%_0 \\ -28.1 \ \%_0 \\ -27.5 \ \%_0 \\ -27.4 \ \%_0 \\ -27.8 \ \%_0 \end{array}$	- - - - - - - - - - - - - - - - - - -	- - - - - - - - - - - - - - - - - - -	Rea et al. (1980) Meyers and Eadie (1993) Meyers (Unpubl.)	(N=6) Lacustrine Sed. (N=7) Lacustrine Plants Station 4- South LM Station 11-North LM
δ <sup>15</sup> N	LM Sinking particulate Sed. (near surface) LM Sinking particulate Sed. (near bottom) LM Sediment Trap (15m) LM Sediment Trap (35m) LM Sediment Trap (80m) LM Sediment Trap (120m) LM Sediment Trap (140m) LM Sediment Trap (140m) LM Sediment Trap (31m) LM Sediment Trap (91m) LM Sediment Trap (146m) LM Sediment Trap (166m)	-1‰ -2‰ ND 3.6‰ 4.3‰ ND ND ND ND ND 3.3‰ 3.3‰		- - - - - - - - - -	Meyers and Eadie (1993) Meyers and Ishiwatari (1995) & Book Physics and Chemistry of Lakes (Ed.2)	(N=6) Lacustrine Sed. (N=7) Lacustrine Plants Station 4- South LM Station 11-North LM

Compound/Element	Matrix/Test Method	Conc.s	Flux	Loading Rate	Citation/ Reference	Note
Atomic C/N ratio	LM Settling Sediment LM Resuspended Sediment	9 8	- -	- -	Meyers et al. (1984a)	Lacustrine Sed. Lacustrine Sed.
	LM Sediment Trap (15m) LM Sediment Trap (35m) LM Sediment Trap (80m) LM Sediment Trap (120m) LM Sediment Trap (140m) LM Sediment Trap (11m) LM Sediment Trap (31m) LM Sediment Trap (91m) LM Sediment Trap (146m) LM Sediment Trap (166m) LM Lacutrine plants Plankton	19.8 22.5 8.7 10.7 21.2 13.1 20.9 16.5 8.1 13.3 7			Meyers and Ishiwatari (1995) & Book Physics and Chemistry of Lakes (Ed.2) Meyers (1994)	Station 4- South LM Station 11- NorthLM
Deep chlorophyll maxima (DCM): Chrysosphaerella spp. Dinobryon divergens Imhof Planktonema lauterborni Schm. Cryptomonas erosa Ehr. Mallomonas spp. Peridinium spp. Gomphosphaeria lacustris Chod. Cryptomonas phaseolus Skuja Dinobryon bavaricum Imhof Cryptomonas marssonii Skuja Dinobryon sociale var. americanum (Brunnth.) Bachm. Cryptomonas spp.	LM Water Column Profile	-16.28% -9.21% -7.43% -4.57% -3.59% -3.50% -2.38% -1.72% -1.33% -1.15% -1.07% -0.73%	- - - - - - - - - - - - -			Average percent decrease in species biomass in the DCM compared to the epilimnion.

Compound/Element	Matrix/Test Method	Conc.s	Flux	Loading Rate	Citation/ Reference	Note
Metals:	LM Core (115) Sediment				Frye and	
Si		25.4	-		Shimp (1973)	
Al		2.75	-			
Fe		1.48	-			
Ca		10.8	-			
Mg		4.08	-			
Na		0.27	-			
K		1.19	-			
Mn		0.08	-			
P		0.13	-			
		0.08	-			
SI/AI		9.24			Simcik et	
PAHs		-	-	-	al. (1996) Christensen and Arora (2007)	PAHs source as proxy info
PCBs	LM Surface Sediments	-	-	$\Sigma_{9}PCBs:$ Load = 11.83 $\pm$ 3.38 tons; Loading Rate = 0.151 $\pm$ 0.101 tons/yr	Li et al. (2006b)	The sum of PCBs 8, 18, 28, 52, 44, 66, 153, 187, 180, 195, and 206; around 2002 year.
PBDEs	LM Superficial Sediments	$\Sigma_9 PBDEs = 1.7 - 4$ ng g <sup>-1</sup>	-	-	Li et al. (2006a)	The sum of BDEs 28, 47, 66, 85, 99.
		BDE209 = 96%	-	-		100, 153, 154, and 183; around 2002 year.
	LM Surface Sediments	-	-	$\Sigma_9$ BDEs: Load = 1.48 ± 0.83 tons;	Li et al. (2006b)	Around 2002 year.
Compound/Element	Matrix/Test Method	Conc.s	Flux	Loading Rate	Citation/ Reference	Note
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PBDEs	LM Surface Sediments	-	-	Loading Rate = $0.036$ $\pm 0.023$ tons/yr BDE 209: Load = $38.8 \pm$ 10.3 tons; Loading Rate = $0.75 \pm 0.41$ tons/yr		

# Chapter 3. Analysis of Organic Carbon, Inorganic Carbon, Black Carbon and Bulk Physical Properties of Lake Michigan Sediments

#### **3.1 Introduction**

The most common constituents of lacustrine sediments are sands, silts, clays (by size) and carbonates (both biogenic and abiotic) and organic matter, detrital material, biogenic silica (from diatoms) and elemental "black carbon" (by chemical structure/activity). The importance of each constituent changes over the course of lake development on the order of hundred to tens of thousands of years (Dean and Fouch, 1983). The total carbon (TC) content of sediment samples is composed of an organic carbon (OC) component, an inorganic carbon (IC) component, and the black carbon (BC) component. In sediments, these components are commonly measured by a sequential fractionation and/or alteration of the sediment fractions followed by carbon measurement (Jones and Bowser, 1978; Accardi-Dey and Gschwend, 2003).

The depositional setting, climate, water chemistry, and biological activities in the lake affects the mineralogical composition of sedimented carbonates (Kelts and Hsü, 1978). In carbonate-saturated waters like those found in parts of Lake Michigan, carbonates can be a significant fraction of the dry sediment mass. Therefore, accurate analysis of TC, OC, IC, and BC necessitates the development of a procedure for the complete removal of IC prior to elemental analysis. This is particularly true in carbonate-rich sediments such as those found in Lake Michigan, due to the presence of slowly dissolving carbonate forms that may be resistant to removal (Lukasewycz and Burkhard, 2005). Complete separation and/or removal of IC is also important for isotopic composition studies due to the great difference in  $\delta^{13}$ C for carbonates and organic matter (OM) (Komada et al., 2008).

IC is typically removed by acidifying the sediment, either through direct acidification with aqueous phase acids or via acid vapor treatment. This assumes that sediment IC is in the form of carbonate minerals, and that these carbonates react rapidly with the acid to form gaseous CO<sub>2</sub> which evolves out of the sample (Bisutti et al., 2004). Reviews of current methodologies for the determination of OC in solid samples in environmental studies were carried out by Bisutti et al. (2004); and Komada et al. (2008) discussing the advantages and disadvantages of each method. Four main techniques have been identified for sample acidification: HF demineralization, acid rinsing, endpoint titration, or gas phase acid vapor methods. Details of these methods are summarized in Table 3.1.

ACIDIFICATION Description For IC separation		Advantages	Disadvantages	Reference
Demineralization Method	<ol> <li>HF dissolution of mineral phase</li> <li>C analysis on the remaining organic components</li> </ol>	Concentrated sample allows further characterization of the OC	Dangerous chemicals; time consuming reaction and procedure	Hedges and Keil (1995) Gélinas et al. (2001b) Gélinas et al. (2001a) Simpson and Hatcher (2004)
Acid Rinse Method	<ol> <li>Acidification and degassing by acid rinse</li> <li>Rinsed with H<sub>2</sub>O</li> <li>Drying and C analysis on the remaining material</li> </ol>	For high carbonates samples	OC loss into the dissolved phase	Roberts et al. (1973) Froelich et al. (1980) McNichol et al. (1994) Batista et al. (2004) Galy et al. (2007)
Acid Endpoint Titration Method	<ol> <li>Sample pre-weighed</li> <li>Endpoint titration and degasing</li> <li>Drying and C analysis on the remaining material</li> </ol>	Free from dissolved OC	Labor intense; Risk of sample spill; Ambiguous titration endpoint	Verardo et al. (1990) Lohse et al. (2000) Ingalls et al. (2004) Lukasewycz and Burkhard (2005) Brodie et al. (2011)
Acid Vapor Method	<ol> <li>Sample pre-weighted</li> <li>Exposure to acid vapors in desiccator</li> <li>Drying and C analysis on the remaining material</li> </ol>	Free from dissolved OC; Least labor intense	May not thoroughly remove slowly dissolving carbonates	Yamamuro and Kayanne (1995) Schubert and Nielsen (2000) Harris et al. (2001) Ryba and Burgess (2002) Komada et al. (2008)

Table 3.1. Summary of four different methods by which acidification can be carried out.

While demineralization has been used in many studies, acidification with either hydrochloric (HCl), sulfurous (H<sub>2</sub>SO<sub>3</sub>), or phosphoric (H<sub>3</sub>PO<sub>4</sub>) acid is more prevalent in the literature; with HCl the most commonly used acid for this procedure. The lack of consensus on the most appropriate and efficient treatment method for acidification stems in part from the fact that differences in sediment mineralogy and grain size may favor one technique over the other (Caughey and Barcelona, 1994). For example, HCl reacts readily with the most common sodium and calcium carbonates in sediments (e.g. calcite and aragonite), but less rapidly with dolomite and, only poorly with siderite.

In previous Great Lakes mineralogy studies, Meyers (2003) and Eadie and Robbins (2005) reported that the bedrocks and soils of Great Lakes area are rich in limestone, the waters of the Great Lakes (though not in Lake Michigan) are likely saturated with calcium carbonate, and during Summer period there are usually whiting events that caused the formation of calcium carbonate precipitate as a result of changes in the freshwater water temperature or from increased photosynthesis. Lake Michigan in particular was found to contain high levels of carbonate minerals in sediment samples at 5 sites (Lukasewycz and Burkhard, 2005), sediment rich carbonate minerals throughout the whole Lake (Rossmann, 1975), predominantly high levels in southeast Lake Michigan where carbonate levels of 43.5% and dolomite levels of 12.6% along with calcite have been reported (Eadie and Robbins, 2005), and manganese carbonate with ferromanganese deposited in northwest Lake Michigan in Green Bay (Callender et al., 1973). The mineralogy and reported carbonate content of Lake Michigan helps to choose the level of acidification needed to fully decarbonate the sediments.

The correct determination of OC including the method of IC removal by different pretreatments is an important topic and the main focus of the present method development study. The overall goal of the research described in this chapter was to test and develop an effective and robust procedure for the fractionation of sediment for physical and chemical characterization. The first objective to achieve this goal was to optimize a method for complete removal of IC from Lake Michigan sediments for accurate determination of OC and  $\delta$  <sup>13</sup>C. A secondary objective was to develop a method for the complete removal OM from Lake Michigan sediments for particle grain size characterization. For the first objective, systematic comparisons of acid treatment methods for IC removal were performed to Lake Michigan sediment samples to investigate method variability on elemental analysis. These results were further compared to those from a previous study by Buckley et al. (2004) that used an acid vapor IC removal procedure on Lake Michigan samples taken from several of the same sampling locations as in the present study. For the second objective, three methods of OM removal were applied and compared the resulting particle size distributions to those of the untreated sediment agglomerates.

### **3.2 Materials and methods**

### **3.2.1** Sediment sampling, collection and storage

### Sampling Sites

Sediment and water sampling in Lake Michigan was conducted onboard the USEPA *R/V* Lake Guardian September of 2010 and May of 2011. Site selection focused on depositional sites because these locations would have the greatest sedimentation rates, deep water for less-risks (e.g. storm events, dredging and fishing) of sediment disturbance, and existing USEPA sampling stations were used for possible comparisons between the present research and previous sediment studies.

The selected locations included the southern, central and northern basins of Lake Michigan. A total of 30 locations were sampled during the two campaigns. Ten core samples were collected (8 in 2010 and 2 in 2011) at each site a ponar sample taken at the same time along with 20 additional sites for just ponar grab (Figure 3.2a, Table 3.2). In addition, 34 water samples and 12 field and trip blanks were obtained for QA/QC.



Figure 3.1. (a) Map of sampling locations in Lake Michigan. GIS Map created by S. Bonina, 2015. (b) UIC scientific Lake Michigan sampling crew 2011 onboard of the USEPA *R/V* Lake Guardian Vessel.

Note: Stars represent locations where both ponar grab and core were taken, while black circles indicate ponar samples only.

Location	Sample	Latitude N <sup>(1)</sup>	Longitude W <sup>(1)</sup>	Depth <sup>(2)</sup> (m)	Grab	Core Segments
M010	PG	42.066168	87.379170	51	1	0
M020	PG	42.366502	87.667172	46	1	0
M030	PG	42.660002	87.738172	18.4	1	0
M044	PG	42.952833	87.315498	92	1	0
M024	BC, PG	43.483003	87.488167	150	1	20
M032	BC, PG	44.371502	86.933337	257	1	20
M088	PG	44.718670	87.174005	95	1	0
M050	BC, PG	45.116500	87.416503	33	1	19
M113	PG	45.326668	87.009002	37	1	0
M120	PG	45.528835	86.170835	140	1	0
M047	BC, PG	45.178333	86.374503	200	1	20
M103	PG	45.062333	86.491833	207	1	0
M093a	PG	44.962168	86.055172	100	1	0
M093b	PG	44.771170	86.116835	60	1	0
M093c	PG	44.856168	86.243002	129	1	0
M041	PG*MC	44.736667	86.721505	272	1+1	0
M083	PG	44.473667	86.706000	270	1	0
M028	PG*MC	43.800333	86.799833	137	1+1	0
M061	PG	43.474168	86.784670	137	1	0
M048	PG	43.058503	86.663005	107	1	0
M019	PG*	42.733502	86.583337	93	1	0
M018	EC, PG	42.733833	86.999500	165	1	20
M011	EC, PG	42.528333	86.922005	164	1	20
M009	EC, PG	42.385002	86.591498	62	1	20
M008	EC, PG	41.984168	87.014172	66	1	20
M002	PG	41.789668	87.292167	20.3	1	0
Total (in 2010)					26	159
M028	MC, PG	43.8000	86.8005	133.3	1	17
M041	MC, PG	44.7367	86.7213	265.6	1	20
M116	PG	45.4008	85.4995	36.0	1	0
M125	PG	45.7225	85.3317	16.4	1	0
Total (in 2011)					4	37

Table 3.2. Sampling locations and conditions during LM sampling 2010 and 2011. Grab sample counts for and core segments.

\* Originally planned coring station, aborted due to equipment issue in 2010.

(1) Latitude and Longitude data were obtained directly from the R/V Lake Guardian ship log at the moment the box core or surface grab was deployed. Due to drift of ship and coring devise from GPS location, the horizontal positioning error was estimated to be 450 m for the spatial location of a sample. Distances between sampling locations are subject to the error of both locations and so will have an error of 900 m unless otherwise stated.

(2) Adjusted depth is (Measured Depth  $\times$  0.973), according to Captain's instructions.

#### Sampling Procedures - Field collecting Methods

Sediment Surface Grabs: Surface grab samples (Figure 3.2b) were collected using the ponar sampler (Figure 3.2a) at each location. Upon retrieving the sampler onto the deck, the overlaying water was collected for water chemistry analysis. After draining excess surface the water, the sediment was collected in a bucket, and homogenized using a drill-driven stainless steel mixer. The homogenized ponar grab (PG) sample was sub-sampled into appropriate containers for different specific analyses (i.e. plastic or glass with different caps dependent on the analysis), and stored appropriately at either 4 °C (in the refrigerator) or at -20 °C (freezer).



Figure 3.2. Samplers used (a) ponar sediment grab sampler, (b) ponar/surface sediment grab.

Sediment Cores: At coring locations, either the box corer (BC; Figure 3.3a) (model BX-750, Ocean Instruments, San Diego CA), the multi-corer sampler (MC; Figure 3.3b) (model MC-400 Spyder Instruments, San Diego, CA) or the Ekman dredge (EC; Figure 3.3c) (custom built, c. 1990) was deployed to collect a bulk sediment with undisturbed sediment-water interface (Figure 3.1a and table 3.2).



Figure 3.3. Samplers used box corer (a), spider sampler (b), samples, and Ekman dredge (c), to collect sediment core samples.

All three coring devices used the same collection tubes (MC-400-4 (P), 10 cm x 60 cm polycarbonate, Ocean Instruments, San Diego, CA). For use in the BC and the EC the tubes were 45 cm lengths. The BC collected a 30 cm by 30 cm by 90 cm tall section of sediment up to with the water sediment interface undisturbed. The last four sites in 2010 were collected using the EC device, which collected a 38 cm by 38 cm by 50 cm deep section of sediment with the water sediment interface undisturbed. For both these core sampler when the device returned to the ship deck four tubes were manually pushed into the collected sediment. The tubes were pulled upwards with an L-shaped metal puller (custom made in the UIC machine shop); and their bottom ends were closed by hand inserting a polyethylene puck with double O-rings, before the ends were exposed to air, until sectioning could be done. For the four intact tubes or sub-corers of sediment could not be obtained using the box corer or Ekman dredge, the device was redeployed.

For the MC, 4 tubes, spaced 32.5 cm apart were deployed, directly into the sediment of the lake. Spring loaded plates closed the base of the tubes, keeping the sediment intact in the

tubes. Once the MC returned to the ship deck the tubes were removed from it and the bottoms were sealed with a polyethylene "puck" with double Viton O-rings and a cap on top preventing contamination. Tubes were stored vertically. For each site the MC was deployed twice to collect a minimum of five intact sediment tubes with similar stratification. Some cores were omitted due to height variance, loss of sub-cores, air bubbles or vacuum losses.

Tubes were extruded and sectioned in the wet laboratory of the *R/V* Lake Guardian, using hydraulic extruders (Figure 3.4c) (customized design, Cambron Engineering, Bay City, MI). Sectioning was performed at 1.0 cm thickness intervals for the first 10 cm, then in 2 cm increments for the remainder of the core. The outer approximately 1 mm-thick circumference of each section was trimmed to eliminate smearing effects (Golden et al., 1993; Crusius and Kenna, 2007). The trimming technique (Figure 3.4d) was performed by eyes in 2010 but using a customized "cookie cutter" in 2011 sampling campaign. Most core sites generated ~20 segments, with the exception of core 2010-M050 BC (which had 19 segments) and 2011-M028-MC (17 segments). The same sediment segments at corresponding depth were combined and homogenized with stainless steel spoons in glass bowls (Figure 3.4e). These were distributed into appropriate containers for future laboratory analyses, and stored the same as ponar samples, (Figure 3.4d). Transport to University of Illinois in Chicago was done in cool boxes with cool packs taking approximately 3 hours and were stored at the UIC in appropriate locations for the ideal preservation.



Figure 3.4. Selected photos of (a, b) sediment cores, (c) sediment cores extrusion and core sectioning, (d) core outer edge trimming, (e) Pyrex® glass bowl homogenizing vessels, and (f) mixed sediment samples distributed into proper containers, labeled and checked for multiple laboratory analyses.

#### 3.2.2 Laboratory sediment measurements and methods

Lake Michigan core sediment samples were characterized for physical and chemical characteristics including solid content, bulk density, porosity, OM, OC, and BC according to standard methods, ASTM (1998a) and (1998b), and the modified and extended methodology from previous Great Lakes Restoration Initiative (GLRI) sediment related projects.

Physical-Chemical Measurements and Analysis Methods: There are several methods for the identification and quantitation of TOC. These methods can be qualitative, semi- quantitative, or quantitative depending upon the technique. Quantitative methods generally involve some form of sample preparation to remove water and/or inorganic carbonates. After sample preparation is complete, either wet chemistry digestion or combustion techniques are used to convert the OM in the sample to carbon dioxide  $(CO_2)$ , which is then quantified. Quantitation techniques range from simple gravimetric determinations through volumetric and manometric measurements, through the more complex spectrophotometric and chromatographic methods. Lake Michigan sediments have all been characterized for the physical parameters such as bulk density via gravimetric analysis, % water and solid content, porosity via drying, gravimetric analysis, and particle size distribution via automated laser-settling analysis. Furthermore, all Lake Michigan samples were characterized for chemical parameters such as TC via automated elemental analysis of dried samples, OM via gravimetric analysis following high temperature oxidation, OC and BC via automated elemental analysis following high temperature oxidation on pretreated sediment samples. In addition, further analyses such as stable isotope  $\delta^{13}C$  and  $\delta^{15}N$ analysis, were performed on selected core samples.

Laboratory Analysis for Physical Characterization: Bulk density is defined as the mass/volume ratio of the fresh sediment sample. It is measured gravimetrically for each core segment after extrusion and ponar sample. After homogenization a known volume of sediment is introduced to a 3 mL syringe of known mass with cut tip. For triplicate measurements were made of each sample to assess sample variability in measurement. Syringe volume was calibrated by measuring the mass of the syringe filled with 3 ml deionized water (DIW) having first equilibrated the water to room temperature and offsetting mass for temperature variance in water density. The syringe was filled with the homogenized sediment, weighed, then extruded into a labeled tared aluminum weighing boat.

The mass was taken accurate to  $\pm 10 \ \mu g$  with the balance routinely calibrated with traceable mass standards. Wet bulk density was calculated as the ratio of the wet mass to the known sediment volume and the sample then dried in an oven at 105°C for 48 hours to constant mass. Water content (% moisture), and porosity was calculated from the dry mass, as detailed in (Rockne et al., 2003b). One of the 3 samples was further combusted at 375 °C, and its mass loss upon low temperature combustion normalized to the original dry mass was operationally defined as the OM content using the method of Rockne et al. (2002).

## NEW SOP - Physical Characterization: Drying, Combustion, and Acidification Method Sample train for physical characterization processes



Figure 3.5. The sample process and analytical scheme for physical characterization, including mass measurements, drying, combustion, acidification and elemental analysis. Chart created by S. Bonina, 2013.

The following formulae were used to calculate dry mass, water content, bulk density, OM, and

porosity:

#### **Equation 6: Percent of Moisture**

Percent moisture (%) = 
$$\left(\frac{\text{Sample wet mass } (g) - \text{Sample dry mass } (g)}{\text{Sample wet mass } (g)}\right) \times 100\%$$

The moisture as a percentage (%) in a sample can be calculated using equation 6, while the solid content,

as % can then be derived from the following Eq. 7:

## **Equation 7: Percent Solids**

Percent solids 
$$(\%) = 100\%$$
 – Percent moisture  $(\%)$ 

The wet bulk density (g cm<sup>-3</sup>) is extrapolated from the following Eq. 8:

**Equation 8: Wet Bulk Density** 

Wet bulk density 
$$\left(\frac{g}{cm^3}\right) = \frac{Sample \ wet \ mass \ (g)}{Sample \ volume \ (cm^3)}$$

**Equation 9: Dry Bulk Density** 

Dry bulk density 
$$\left(\frac{g}{cm^3}\right) = \frac{Sample \, dry \, mass \, (g)}{Sample \, volume \, (cm^3)}$$

**Equation 10: Organic Matter (OM)** 

$$OM~(\%) = \left(\frac{Sample~dry~mass~(g) - Sample~combusted~mass~(g)}{Sample~dry~mass~(g)}\right) \times 100\%$$

Equation 11: Ratio OM to Ash Mass F

Ratio organic matter to ash mass, 
$$F = \frac{\frac{OM(\%)}{100(\%)}}{1 - \frac{OM(\%)}{100(\%)}}$$

**Equation 12: Dry Particle Density** 

Dry particle density 
$$\left(\frac{g}{cm^3}\right) = \frac{1+F}{\frac{F}{1.55} + \frac{1}{2.65}}$$

Where 1.55 g/cm<sup>3</sup> is the approximate particle density for the OM fraction and 2.65 g/cm<sup>3</sup> is the approximate particle density for the mineral (ash) fraction. (Source: Soil Sampling and methods of Analysis (SS&MA), edited by Carter (2007)).

**Equation 13: Porosity** 

$$POROSITY(\%) = \left(\frac{Dry \ Particle \ Density\left(\frac{g}{cm^3}\right) - Dry \ Bulk \ Density\left(\frac{g}{cm^3}\right)}{Dry \ Particle \ Density\left(\frac{g}{cm^3}\right)}\right) \ge 100\%$$

(Source: Equation from SS&MA, 2007)

A more detailed account of sample preparations for each calculated parameter is available in the applied environmental biotechnology laboratory (AEBL) standard operational procedure (SOP) manual developed from this research.

*Chemical Characterization (OC, BC, IC, Nitrogen (N), and Sulfur (S))*: Chemical characterization was the primary focus of this study. After the method validation, a new SOP was developed for quantitative determination of sediment physical and chemical parameters. This SOP for OC and BC accurate determination consists of multi-step method, beginning with measuring mass and volume of the sample. Then drying all samples at 105 °C for 48 hours, combusting 1 sample at 375 °C for 24 hours and then acidifying the dried samples for OC and the combusted for BC samples with hydrochloric acid (HCl) for the complete removal of inorganic carbonates in each sample before instrumental analysis of carbon using an Elemental Analyzer (EA) (Figure 3.5 and 3.6 and Table 3.3 a-b).



Figure 3.6. The Flash EA1112 inside instrument structure.

Tables 3.3. EA Components: (a) for the NC configuration for NC, NC-Filters, NC-Soils and NC-Sediments; (b) for NCS configuration.

Component	NC Description	Component	NCS Description
EV1 - EV2		EV1 - EV2	
EV3 - EV4	They constitute the EFC module.	EV3 - EV4	They constitute the EFC module.
EVP1 - EVP2		EVP1 - EVP2	
S1 - S2		S1 - S2	
AS	Autosampler	AS	Autosampler
R1	Reactor	R1	Oxidation Reactor
F1	Adsorption Filter	R2	Reduction Reactor
CC1	Cas chromatographic column	F1	Adsorption Filter for carbon dioxide
		F2	Adsorption Filter for water
TCD	TCD Thermal conductivity detector	CC	Gas chromatographic column
	·	TCD	TCD Thermal conductivity detector
(a)	(b)	CEP	Pressure stabilizing cylinder

Inorganic Carbon Removal: Organic carbon is measured by the combustion of OM and creation of CO<sub>2</sub>. None of the methods available for the determination of OC are capable of distinguishing between inorganic of OM or organic of OM derived CO<sub>2</sub>. Therefore, the removal of the interfering inorganic carbonates is an imperative that requires a titration with acid in order to provide and ensure straightforward methodologies and removal of interferences. The most common method for IC removal is the addition of an acid or a combination of acids. Two acids are commonly quoted for carbonate removal, specifically, hydrochloric acid (HCl) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). Two disadvantages with the use of HCl are that the HCl might also remove some organic carbon compounds leading to a carbon loss prior to sample quantitation and Cl<sup>-</sup> is interference for the wet oxidation methods. Alternatively, a combination of H<sub>2</sub>SO<sub>4</sub> and ferric sulphate or iron-II sulphate (FeSO<sub>4</sub>) may be used; Nelson and Sommers (1996), Allison (1960) give detailed specification about quantity and proportion of the acidification method. Removal of carbonates for samples that undergo dry combustion quantitation may be more problematic than for those undergoing wet chemistry techniques (Nelson and Sommers, 1996). HCl was used in a

manner similar to that used for the wet sediment chemistry but the samples must be at least airdried prior to analysis and there was the concern about the loss of organic matter due to its decomposition by the HCI. Experiments have been conducted to overcome any side procedure problems. The Isotope Analysis Laboratory of University of California Saint Cruz is one of the trusted resources for its IC removal experimental procedure and a modified AEBL procedure based in part on their work and methods was introduced (see table 3.4 for a summary of the methods and pros and cons of each).

Table 3.4. Summary of experimental IC removal methodologies compared in the present study.

PRE –TREATMENT Description		Advantages	Disadvantages	Reference	
For IC REMOVAL					
1. No pre-treatment	Drying in the oven at	Least labor	No remove IC at all,	Schubert and Calvert	
(Drying only - No Fuming)	105 C for 48 hours (prior elemental	intense	assuming no carbonate in the samples:	Sampei and Matsumoto (2008)	
	analysis)	Useful for	No reliable results of		
X7 A • 1• /• .•		method	TC, OC compromised:		
No Actalfication		comparison	erroneous nign OC		
2. Acid-Fuming with HCl	Fuming with	Method	No thoroughly remove	Yamamuro and Kayanna (1905)	
	HCl for 48 hours	routinely	IC;	Schubert and Nielsen	
		applied in	Results of TC, OC	(2000) Harris et al. (2001)	
Vanon Indinast Asid Mathad		marine and	compromised:	Ryba and Burgess	
vapor inaireci Acia Meinoa		sediments	maccurate, amoi-	(2002) Buckley et al. (2004)	
		seuments.	guous ingli OC	Komada et al. (2008)	
3. Acidification with	1. Sample pre-weighted,	Free from	Very labor intense;	Verardo et al. (1990) Lobse et al. (2000)	
Concentrated HCl	2. Acidification with	dissolved	Risk of Sample spill;	Bisutti et al. (2004)	
(e.g.6 N HCl)	concentrated or diluted	OC.	Ambiguous Titration	Ingalls et al. (2004)	
	HCl,	Reliable	endpoint.	Burkhard (2005)	
4. Acidification with Diluted	3. Rinse with $H_2O$ ,	measure-		Brodie et al. (2011)	
HCl	4. Centrifugation,	ments with			
(e.g.10% v/v with 6 N HCl)	5. Neutralization,	different			
	6. Drying.	level of acid.			
Aqueous Direct Acid Methods					

Sediment preparation prior Elemental Analysis: The primary interference in the determination of TOC or simply OC is the presence of inorganic carbonates in sediments. An acidification step for inorganic carbon removal is therefore critical for accurate determination of OC. The protocol of physical-chemical characterization described here is an improved and optimized variation of previous researches of Verardo et al. (1990) and Buckley et al. (2004). In a fumehood, 50 µL of DIW was added to each dried sample this prevents violent bubbling from the reaction of HCL with carbonate. A 10% HCl solution (1:1 dilution of 6 N HCl into DIW) is introduced in 50-100 µl aliquots up to the calculated volume (target 8-10 µl HCl/mg dry sediment mass; e.g. I used 50 mg dry sediment that needed 500 µl of HCl). Additional care to avoid any scraping of the epi-tubes used to prevent carbon contamination. Once any reaction subsides, each sample in epi-tube is closed tightly, and vortexed for 20s to homogenize and shaken for 24 hours to ensure complete reaction. After 24 hours, samples were centrifuged (5 min at 10,000 RPM at 20 °C) and the supernatant pipetted off. An additional 1 ml DIW, was introduced to the sediment epi-tube, followed by vortexing for 20s. The centrifugation step and decanting of the supernatant was repeated and the DIW rinse was repeated 3 times and more until sample was neutralized (tested with pH paper). After inorganic removal, sediment sample in the open epi-tube was placed in an oven at 40 °C for 48 hr.

Due to the mineralogy of Lake Michigan sediment that is rich in carbonates (e.g. 12.6% of calcite (CaCO<sub>3</sub>), dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>) and up to 43.5 % of Aragonite (CaCO<sub>3</sub>) in the southeast of the Lake (Rossmann et al., 2004; Eadie and Robbins, 2005), inefficient removal of IC would potentially result in more than 50% variability in accurate determination. *Carbon measurement by Elemental Analyzer*: Two sub-samples were used for OC measurement, out of the three prepared for each sample. OC (mg g<sup>-1</sup>) was obtained from total carbon (TC; mg g<sup>-1</sup>) measurement after complete acidification. The following formula was used to calculate the sample OC concentration, (Eq.14):

#### **Equation 14: Organic Carbon (OC)**

$$OC\left(\frac{mg}{g}\right) = TC_{acid}\left(\frac{mg}{g}\right)$$

*Black Carbon Measurement by Elemental Analyzer:* BC was determined from the TC content of acidified samples combusted at 375 °C for 24 hr. This step results in the oxidation of labile organic matter (by heating) and removal of inorganic carbonate (by acidification), leaving behind BC. All carbon measurements, OC and BC, were obtained using the modified form of the procedures developed for lake sediments, which include the direct acidification step described earlier. The TC in acidified samples calculated as following (Eq.15)

#### **Equation 15: Total Carbon (TC)**

$$TCacid\left(\frac{mg}{g}\right) = NBOC\left(\frac{mg}{g}\right) + BC\left(\frac{mg}{g}\right)$$

The TC measured in acidified ( $TC_{acid}$ ) samples was subtracted from the TC measured in unacidified ( $TC_{unacid}$ ) samples to calculate IC (Eq.16):

#### **Equation 16: Inorganic Carbon (IC)**

$$IC\left(\frac{mg}{g}\right) = TCunacid\left(\frac{mg}{g}\right) - TCacid\left(\frac{mg}{g}\right)$$

TC of samples was analyzed using the Carlo Erba elemental analyzer (EA; Flash EA1112, ThermoQuest/CE Elantech, Lakewood, NJ, USA). Samples prepared as described above were

pulverized and placed in combustion boats supplied by the manufacturer (CE Elantech, NJ). The reported TC concentration ( $TC_{acid+comb}$ ) is the BC normalized to the combusted mass, not the original dry mass. This BC must be normalized to the original dry mass by correcting for the mass loss upon combustion using the following formulae to calculate the sample BC and NBOC concentrations (Eq.17):

## **Equation 17: Black Carbon**

BC 
$$\left(\frac{\text{mg}}{\text{g}}\right) = \left(\text{TC}_{\text{acid}} + \text{comb}\left(\frac{\text{mg}}{\text{g comb}}\right)\right) x \left(1 - \frac{\text{OM}(\%)}{100}\right)$$

Where OM is from Eq. 10.

#### **Equation 18: Non-Black Organic Carbon**

$$NBOC \left(\frac{mg}{g}\right) = OC\left(\frac{mg}{g}\right) - BC \left(\frac{mg}{g}\right)$$

Where OC is from 13 and BC from Eq.17.

Instrumental Operating Conditions: Elemental C analysis was conducted using automated combustion at 900°C followed by molecular sieve gas chromatography and thermal conductivity detection system at 60°C. Integrated peak areas for C were compared to six points of the 2,5-Bis-2(5-Tert-Butyl-Benzoxalyl)Thiophene standard (BBOT) using Eager 300 v2.4 chromatography software. Size integration was performed on the Eager v5.0. New BBOT standard curve calibrations for C, N and S was validated from standard which is 72.56% C, 6.5% N, 7.44% S. For every run, a calibration curve was run to check instrument stability and reproducibility, ( $R^2 \ge 0.99$ ). The Eager 300 v2.4 calculates the C, N, and S normalized to dry mass of the sample based on the calibration curve and the mass input. Samples, ran as unknown, with any samples outside the linear range of the calibration curve re-analyzed using a modified BBOT standard.



С	Н	Ν	0	S
26	26	2	2	1
12	1	14	16	32
312	26	28	32	32
72.56%	6.05%	6.51%	7.44%	7.44%

Figure 3.7. BBOT FW: 430 Daltons; Molecular formula:  $C_{26}H_{26}N_2O_2S - 2,5$ -Bis-2(5-Tert-Butyl-Benzoxalyl)Thiophene.

For quality control, at least one in ten sediment samples and BBOT were analyzed as unknowns to determine the accuracy and precision according to Standard Methods (APHA; AWWA; WEF (2005)). Relative standard deviation (RSD) is defined as the absolute difference between duplicates divided by their average. Overall precision is defined as the square root of the mean of all RSD<sup>2</sup> values. Overall accuracy is defined as the square root of the mean of the squared bias ( $B^2$ ), where B is the variability of deviation of analytical results from the mean value caused by systematic variation within the system. The overall uncertainty (U<sub>95</sub>) was calculated by the following Eq.19:

## **Equation 19: Overall Uncertainty**

$$U_{95} = \sqrt{2RSD^2 + B^2}$$

B, RSD and U<sub>95</sub> for OC varied for all core measurements, for example, at M08 B was -1.33%, RSD 2.96%, and U<sub>95</sub> 4.39%, while for BC at the same site B was -0.44%, RSD 3.22%, and U<sub>95</sub> 4.57%. The averaged overall U<sub>95</sub> for all OC measurements was 4.78%, whereas U<sub>95</sub> for BC 4.16%. The QA/QC and statistical results from laboratory analyses have been summarized in the appendix D.1.

*Total Carbon, and Total Nitrogen by Elemental Analysis.* TC, TN contents were determined from elemental analysis of unacidified samples. Due to potential losses of N during the acidification procedure, analysis has to be done on non-acidified material. TC and TN elemental analysis was performed, as described in the instrumental operating conditions section for OC and BC, using the Carlo Erba EA.

*Fluxes:* Depositional fluxes for TC, OC, BC, and IC were calculated for each site by combing concentration data and radionuclide information (e.g. sedimentation rate and focus factor Pb-210) supplied by environmental isotope geochemistry laboratory (EIGL) from Earth and Environmental Sciences (EaES) department at UIC (Corcoran (2013); and updated in 2015). Flux changes with time can then be extrapolated from the dated core samples. The flux of any chemical or parameter into sediment was calculated by dividing the product of the concentration and the sedimentation rate by the focusing factor.

## **Equation 20: Flux Calculation**

$$Flux\left(\frac{mg/cm^2}{yr}\right) = \frac{Concentration\left(\frac{mg}{g}\right) x Sedimentation Rate\left(\frac{g}{(cm^2x yr)}\right)}{Focus Factor}$$

**3.2.3.** *Experiments and Additional Analyses:* A more in-depth approach on the structure of the OM in Lake Michigan sediment was undertaken to better understand the variability within the lake system and to identify the source of OM. Analyses included particle size distribution (PSD), stable isotopic analysis (SIA) of carbon (<sup>13</sup>C) and nitrogen (<sup>15</sup>N) isotopes, and, X-ray fluorescence (XRF) spectroscopy.

Particle Size Distribution by grain size analysis: The particle size distribution (PSD) of a material is important in understanding its physical and chemical properties. There are to date many definition of PSD based on the way that the distribution is calculated and the interpretation of the findings. PSD is most often described in two ways it can be considered the size distribution of *in situ* sediment aggregates or the size of the mineral structure (without OM). In the first case, sediment particles are "glued" together with OM to produce larger aggregates through biological activity (for example fecal pellets and organic exudates); in the other case the OM-free sediment mineral phase does not really characterize what exists in situ. The literature has some conflicting results and both views have their merits depending on the hypothesis you are trying to answer. Some researchers are highly critical of this complex OM included PSD because it is less reproducible than OM-free PSD. To address this issue, a variety of technologies were investigated and applied using a variety of treatments. Laser diffraction on the mastersizer instrument using four different treated sediments: wet (homogenized but otherwise untreated sediment) and three pre-treated sediment sample typed (dried, combusted, and hydrogen peroxide H<sub>2</sub>O<sub>2</sub> treated).

Samples, pretreated with hydrogen peroxide  $H_2O_2$  were suspended and homogenize in 1 L beaker of DIW until the rarefaction index reading was stable. It is recognized that this method does not measure in-situ particle size; particle measurement reflects agglomerate nature of sediment due to particle-to-particle attraction. In this study, PSD measurement is used primarily as validation of other analyses using the surface area to provide additional understanding of insitu sediment condition.

Laser diffraction on the Mastersizer instrument (Malvern Instrument, Worchestershire, UK) through the suspension measures the size of particles by measuring the intensity of light scattering as a beam passes through a dispersed particulate sample. The angle of diffraction increases as particle size decreases, so that this method is particularly good for measuring sizes between 0.1 and 3,000  $\mu$ m. The results were then analyzed to calculate the grain size of the particles that created the scattering pattern using Mastersizer-2000 software.

The PSD analysis equipment used was made up of three main elements: the optical bench, the sample dispersion units and Mastersizer-2000 Instrument software. Dispersed sample passed through the measurement area of the optical bench, where a laser beam illuminated the particles.



Figure 3.8. The Mastersizer-2000 instrument for PSD.

A series of detectors then precisely measured the intensity of light scattered by the particles within the sample over a wide range of angles. A range of wet and dry dispersion units, which ensured that the particles were delivered to the measurement area of the optical bench at the correct concentration and in a suitable stable state of dispersion, controls sample dispersion. At the end, the Mastersizer-2000 software controlled the whole system during the measurement process and analyzed the scattering data to calculate the sample actual particle size distribution.

*Carbon and Nitrogen Isotope Analysis* (<sup>13</sup>C and <sup>15</sup>N): For the purpose of the determination of OC isotopic signatures, carbon and nitrogen stable isotope analysis (<sup>13</sup>C and <sup>15</sup>N via SIA) was performed on selected core sediments to investigate and quantify the OC sources in the Lake, i.e. if they were autochthonous (in lake) and/or allochthonous (terrogenic) in origin. Sediment core samples from six depths (surface 1 cm, 5 cm, 10 cm, 13 cm, 15 cm and 20 cm) at each site were analyzed for carbon and nitrogen isotopes using continuous flow isotope ratio mass spectrometry (EA-IRMS for determination of %N, %C,  $\delta^{15}$ N,  $\delta^{13}$ C), following the procedures already established by the research team at Environmental Isotope Geochemistry Laboratory (EIGL), where I performed this additional analysis.



Figure 3.9. Isotope-Ratio Mass Spectrometer: continuous flow ThermoFinnigan Delta Plus XL equipped with Conflo III, Gas Bench II and Elemental Analyzer (Costech Analytical, ECS 4010, zero blank autosampler).

The SIA instrument utilized (Figure 3.9) was made up of multiple components: Costech ECS4010 Elemental Combustion System (CHNSO), Thermo-Finnigan ConFlo III, Thermo-Finnigan DeltaPlus XL Isotope Ratio Mass Spectrometer and Software EAS Clarity ISODat 2.0 The samples were analyzed using an elemental analyzer coupled to an isotope ratio mass spectrometer through an open split interface. During this process, the weighed sample was combusted at 1050 °C  $Cr_2O_3$ , pushed along by a helium carrier stream enriched with  $O_2$ .

Under these conditions, the tin capsule ignited, raising the sample temperature to 1800 °C, forming H<sub>2</sub>O, CO<sub>2</sub> and N<sub>2</sub>. Any halogens or sulfur was chemically removed and the remaining combustion products were sent into a 650 °C reducing Cu<sup>+</sup> reactor, where incomplete combustion products (NO<sub>x</sub>, CO, etc.) were reduced and excess O<sub>2</sub> was removed. Water was then chemically scrubbed from the helium. The final product gases (N<sub>2</sub>, CO<sub>2</sub>) were separated on a 3-meter packed gas chromatography column (80 mL min<sup>-1</sup>, 40 °C) before entering the IRMS. Ultra high purity (UHP) reference gases were used to stabilize for instrument drift during the run.

X-Ray Fluorescence (XRF) Spectroscopy Analysis Carbonates are a significant fraction of Lake Michigan TC. Characterizing the IC composition for more detailed elemental analysis is valuable to understand the source. X-ray fluorescence (XRF) was used to screen, characterize and quantify range of elements in samples (Figure 3.10a-c). XRF consists of a three-step process of fluorescence used to identify what atoms are present and in which concentrations within the sediment sample. The first step is when the atom is struck by a high-energy photon (x-ray or  $\gamma$ ray) from a radioactive source, which depends on what elements are tested and eventually measured. In the second step, the electrons absorb the high-energy photon and are knocked out of the atom to a different level energy. The third step of XRF consists of filling by a more outer shell electron. During the whole fluorescence test, different metals present in the sample are fluorescing. Therefore, XRF spectrometry is a combination of an x-ray detector, which responds differently to various and distinct frequencies of x-rays; connected to electronics, which use this differing response to determine the frequency of every x-ray that enters the detector. Because all elemental atoms have unique, specific x-ray emission frequencies, the XRF analyzer determines what element emitted the specific x-ray. By determining the total x-rays number at a particular

frequency during a fixed time, the XRF spectrometer can determine the concentration of that precise element identified in the sample.



Figure 3.10. Selected photos of (a) Thermo-Scientific Niton XL3 Instrumental Kit used for X-ray fluorescence (XRF) analysis, (b) XRF experimental set-up, and (c) measurements and readings obtained by XRF spectrometer/analyzer.

Lake Michigan samples analyzed by XRF include sediment from six core segments (surface 1 cm, 5 cm, 10 13 cm, 15 cm and 20 cm depths) at each of the 10 coring sites and at all the 30 ponar grab sites. Analyses were performed using Thermo-Scientific Niton XL3 spectrometer (figure 3.10a-c), using the method of Sackett and Martin (1998), according to USEPA Method 6200 by USEPA (2007), and applying specific manufacturer protocols. All core segment and ponar grab sediment samples, dried and untreated, were analyzed for the selected elements: iron (Fe), potassium (K), manganese (Mn), calcium (Ca), zinc (Zn), titanium (Ti), chromium (Cr). A complete data set was produced, including triplicates of each core sediment segment (BCs and MCs) depth, triplicates of surface (PGs) sediment samples, and quality control samples.

#### **3.3 Results and discussion**

*Carbonate Removal:* Previous Lake Michigan sediment reports had suggested low carbonate content that may be the cause of inconsistent results of OC and BC (Buckley et al. (2004). Carbonate removal has received significant attention and since the 2004 publication robust and a comparable Lukasewycz and Burkhard (2005) The complete removal of carbonates for reliable measurements of OC and BC by Lukasewycz and Burkhard (2005) recommended a titration step increasing levels of acidification. By considering mineralogy of the site and reported carbonate levels, as well as requiring independent verification with acid aqueous direct method for sediment samples to prove that the measured OC and BC between the two techniques are comparable when the acid vapor indirect method is used. The recommendations from Lukasewycz and Burkhard (2005) have been fully tested and integrated into the present method development study.

*Comparison of TC, OC, BC and IC:* The unacidified sediment results representing the total carbon, ranging from approximately 5% and 6% in the upper 5 cm, of sites on average with a decrease with the depth of sediment (Figure 3.11, top left). Two core sites M50 and M28 are outliers when compared to the other locations: M50 from the Green Bay had significantly greater TC, almost 10% in the upper sediment and decreasing with depth to 6 %, and M28 representing a ridge and low deposition, showing less TC in the sediment (2% in the upper sediment to 4 % at depth). TC with OC had being approximately 50% TC (Figure 3.11, top right). This factor while known previously is useful in that future studies as it may be possible to use the one measurement rather than both. It is also useful in a validation of methods as TC and OC should be comparable. BC represents a small fraction of TC, varying constantly below 0.5% for all 10 coring sites (Figure 3.11, bottom left). As BC is generally considered to be atmospherically

derived its concentration may be governed by a range of variables that are independent of those for other carbon sources. In full agreement with the review of Lukasewycz and Burkhard (2005), OC and IC concentrations include the main fraction of TC in Lake Michigan, indicate that OC and IC are nearly 50% of the TC for each site (Figure 3.11, top and bottom right). These results proved that the acid-fuming technique for IC elimination was not sufficient or efficient for any site, including the low IC content ones such as M50 where the BC was unacidified. Therefore, the potential incomplete removal of IC in Lake Michigan sediment would significantly compromise the carbon contents and loadings, and consequently mislead in data interpretation.



Figure 3.11. A) Carbon measurements: TC, OC, BC and IC concentrations with sediment depth in all Lake Michigan coring sites.



Figure 3.11. B) Carbon measurements: TC, OC, BC and IC concentrations with time in all Lake Michigan coring sites.

Comparison of BC and OC fluxes from Buckley et al. (2004) with the present study demonstrated that the same pre-treated acid-fumed sediment samples had the same temporal trend and comparable findings (Figure 3.12A-B). However, when directly acidified there was greater variability from that of Buckley (Figure 3.12C). For example, when comparing the fluxes for BC, and OC and BC/OC ratio (%) at three sites (M47, M41, M18) of Lake Michigan sediments (Table 3.5) treated with two different approaches, only acid-fuming from the earlier study of Buckley et al. (2004) and again only acid fuming or direct acidification were comparable with the present study.

Table 3.5. Location, sediment accumulation rates, mixing depths and focusing factor of sediment core compared between previous studies and this study.

LAKE MICHIGAN							
SITE	Sedimentation Rate	Mixing Depth	Focusing Factor	Latitude	Longitude	Sampling Date	
	$(g cm^2 yr^{-1})$	(cm)					
Reported V	Reported Values from <b>Buckley et al. (2004)</b> (and from earlier <b>Pearson et al. (1997</b> ))						
LM-47	0.028	<1	1.27	45°10.7'	87°22.5'	2002 (1997)	
LM-41	0.035, 0.016 *	<1	1.5	44°44.2'	86°4.3.3'	2002 (1997)	
LM-18	0.039, 0.018 **	4	2.43	42°43.9'	86°00'	2002 (1997)	
Measured and used values for sites in this study N W							
LM-47	0.0311	3	2.64	45.1783	86.3745	2010	
LM-41	0.0221	-	2.11	44.7366	86.7215	2011	
LM-18	0.0183	-	1.52	42.7338	86.9995	2010	

\*Sedimentation rate below 11 cm. \*\*Sedimentation rate below 12 cm.

Note: Buckley et al. (2004) has 12 total segment depths (sectioning 1 cm for the first ten top layers and the remaining 2 bottom layers 5 cm thick). The present study has a total of 20 segment depths with the first 10 top layers 1 cm thick and the remaining 10 bottom layers 2 cm thick. Thus, dating is slightly shifted.

Comparing results from the present study to similar sampling locations reported by Pearson et al. (1997) and Buckley et al. (2004), previously BC made up more than 40% of the TC in sediment of southern Lakes Michigan while this study found almost identical BC results when sediment was acid-fumed but that BC makes up only ~20% when directly acidified. In Lake Michigan sediment, BC measured after acid-fuming treatment was much greater (between 8 and 10 times)

than the BC measured after direct acidification treatment; similarly OC measured after acidfuming treatment was greater (2 times) than the OC measured after direct acidification treatment, which removed approximately another 50% fraction of IC.



Figures 3.12. Black carbon (BC), organic carbon (OC) and BC/OC ratio in Lake Michigan at three sites (M47, M41, M18) from (A) the earlier study of Buckley et al. (2004) (B) this present study with only acid-fuming, and (C) this present study with direct acidification applied.

Note: Locations are given in figure 3.1a and table 3.2. Coordinates and additional information such as sediment accumulation rates, mixing depths and focusing factor of sediment are given in table 3.5.

In all three comparable sample sites, the BC profile was generally similar, but when sediment samples were only acid-fumed the BC concentration was not significantly (95% CL) different in

the upper sediment with the last 50-60 years, after reaching a peak near 1940-50, then diminished significantly (95% CL) until nearly 1900, and after which was quite constant to the deepest section of the sediment samples (~1750). The results of BC after acidification were less but with the same temporal trend. As BC is associated with industry and the burning of fossil fuel it is not surprising that BC levels were greatest in locations close to large metropolitan areas. BC is often associated with PAHs and may sorb compounds from the atmosphere and be a significant source of contaminants to the environment. These patterns are consistent with studies of PAH depositional patterns at the same locations. The persistent pattern and variance in magnitude among the 3 locations may be justified through sediment mixing and focusing. Sediment accumulation rates, mixing depths and focusing factors of sediment cores at these locations are reported in Table 3.5.

The most significant finding is clearly that the same trend of the BC, and OC from acid fuming are found in the current study as was found by Buckley et al. (2004) (Figure 3.12:  $A \approx B \neq C$ ). The consequent implication is that in the new protocol to remove IC via direct acidification a significant different BC, OC result was identified and that this provides a more reliable understanding of all types of carbon in the Lake.

From the development of the inorganic carbon removal method using SIA, the  $\delta^{13}$ C SIA in acid fumed sediment from cores M50 and M08 (reported here) revealed  $\delta^{13}$ C ratios of approximately -5 to -15 range (Figure 3.13, "w/acid fume" data points); a result lower than any possible organic matter endpoint. This reliably confirmed the presence of inorganic carbon ( $\delta^{13}$ C=0) in the sediment samples despite the use of HCl acid fuming using a method routinely applied in marine and estuarine sediments. Based on a review of the literature, this IC was likely in the form of slowly dissolving carbonate minerals such as dolomite, which reportedly has a dissolution rate 100 times slower than carbonate (Rossmann, 1975; Rossmann et al., 2004; Lukasewycz and Burkhard, 2005). This discovery necessitated the improvement of a new inorganic carbonate removal protocol developed in consultation with the scientific literature and the protocol employed by "Stable isotope laboratory of University of California Santa Cruz" 2012). Afterwards the new methodology protocol was developed, validation through titration of numerous sample sediments from Lake Michigan as suggested by Lukasewycz and Burkhard (2005), introducing levels of verification and quality control in all the multiple steps for determination of OC, BC, IC in the whole scheme of analysis. The re-analysis of OC, BC, in Lake Michigan samples using the new procedure with IC acidification removal, is an important step of the validation of the method development. As discussed at the outset, the new protocol did not affect the results of all physical parameters (such as bulk density, water and solids content, density, porosity, organic matter, grain size) and the re-analysis of the remaining project analytes was unnecessary as they were unaffected by the presence of slowly dissolving carbonate. In addition, the previous outcomes have suggested a new research avenue for exploration. Knowing the great impact of inorganic carbonate mineral forms have had on driving the new method, quantifying the total inorganic carbon (IC) in all samples is a secondary benefit of the new step-wise technique.

To assess the effects of various acidification pre-treatments on  $\delta^{13}$ C and  $\delta^{15}$ N ratios and compare to the non-treatment (dried only) case a series of experiments were performed. In this case study results are shown for site M08 (Figure 3.13). Little difference in  $\delta^{13}$ C was observed in untreated samples and those treated with the acid-fuming protocol previously developed for estuarine systems. In contrast, acidification with concentrated HCl in excess of all IC, as well as acidification with diluted HCl resulted in nearly identical  $\delta^{13}$ C. Sediment samples from M08 had
$\delta^{13}$ C changing from a high of -6‰ to -26‰, consistent with typical  $\delta^{13}$ C ratios for organic matter from either terrestrial or aquatic sources.



Figure 3.13. Comparison of  $\delta^{13}$ C and  $\delta^{15}$ N stable isotope ratios M08 sediment samples in untreated (green triangles) and as a function of various sediment pre-treatments.



Figure 3.14. Comparison of the effects of 4 different treatments (no acid fuming, acid fuming, diluted acidification, concentrated acidification) on <sup>13</sup>C and <sup>15</sup>N at M08 core site at five selective segments (surface 1 cm, 5 cm, 10 13 cm, and 15 cm depth) of Lake Michigan sediment cores.

Small changes in  $\delta^{15}$ N were observed between the excess acidification and the diluted HCl acidification procedures. However, all sample pre-treatments resulted in significant changes in  $\delta^{15}$ N compared to the un-treated samples, generally decreasing from 0.5 to as much low as 1.5‰. This observation is consistent with other research by Lukasewycz and Burkhard (2005) that indicates acidification affects  $\delta^{15}$ N and that no sample pre-treatment should be performed prior to  $\delta^{15}$ N SIA. For this reason, the new protocol measured TC (inorganic and organic C) and TN (as well as  $\delta^{15}$ N) only on un-treated, dried samples. A second sample with acidification by diluted HCl was analyzed for OC and BC only. Sediments were prepared according the new SOP employing direct acidification (10% v/v with 6 N HCl), to remove the slowly-dissolving IC, neutralization, and analysis as described before. Comparisons were made between dried with no acidification with 10% 6 N HCl to determine the effects of the various treatments on OC, OM structure.

The results demonstrated that acidification treatment decreased  $\delta^{13}$ C by approximately 15 ‰ to within values consistent with typical OC endmembers, while  $\delta^{15}$ N did not change substantially. In addition, there was no discernible difference between the excess acidification and the 10% acidification, demonstrating that complete removal of carbonates from sediments was achieved. It should also be noted that effervescence was not observed following either procedure, a commonly-used metric of IC removal that has been critiqued by Lukasewycz and Burkhard (2005). Thus SIA allowed confirmation of the successful removal of IC from the Lake Michigan samples using the 10% direct acidification step. The new acidification procedure was used in all subsequent analyses of the project. It is interesting to highlight the impacts of the new acidification protocol on OC and BC results and related parameters.

*OC Coverage relative to the monolayer equivalent:* OC coverage of samples without acidification (only with acid-fuming treatment) was much greater than the monolayer equivalent that would be expected for sediments with OM biodegradation rates greater than OM deposition rates (Figure 3.15a). It should be noted that OC/SA ratios exceed 50 mg/m<sup>2</sup> at site M50 and all depositional sites exceed 10 mg/m<sup>2</sup> (Figure 3.15 a-b). Site M28 at the mid-lake sill had the lowest OC coverage of all sites at 7.4 mg/m<sup>2</sup> in contrast, oligotrophic continental shelf sediment typically are found with OC/SA ratios near the "mono-layer equivalent" of 1 mg/m<sup>2</sup>. These preliminary results indicate that recent sediments in Lake Michigan are organic rich, particularly in Green Bay.



Figure 3.15. Effects of the new acidification protocol on the OC coverage normalized to surface area in Lake Michigan sediments. (a) C unacidified before IC removal (TC), (b) OC acidified using the new IC removal protocol.

The re-analysis of  $OC_{acid}$  yields greatly decreased OC concentrations, with corresponding decreases in the OC/SA ratios (Figure 3.15b). In spite of this, recent sediment in Lake Michigan remain organic rich. Furthermore, all data shift downwards on the y-axis as the IC mass is

removed from the TC result. These resulting values are more in line with expectations of MLE.

The OC coverage results (Figure 3.15b) of this re-analysis according to the IC removal protocol affected previous high OC coverage results found without any direct acid treatment (Figure 3.15a). Comparing results (figure 3.15a and b), this combined data clearly show that OC without acidification (which more properly to indicate as TC), and OC with acidification are both significantly higher than the MLE of 1mg/m<sup>2</sup>. This outcome supports the cultural eutrophication (CE) hypothesis.

*PSD is affected in sediments of Lake Michigan:* Three experiments were performed to assess the effects of various acidification pre-treatments on PSD. The first experiment is a comparison of the grain size with and without OM removal at three selected core depths, to understanding how PSD is a function of OM removal (Figure 3.14). The second experiment consists of measuring the % of each size fraction (Figures 3.15) when  $H_2O_2$  treated, 375 °C combusted, and dried sediment and were then compared to wet sediment PSD (Figures 3.16 and 3.17). The third experiment is a comparison of grain size with treated sediment at differing depths at two sites where huge variability was seen to assess the range of distribution these were: Green Bay (M50) and mid-lake (M28), and, north basin site (M47) and south basin site (M11).

Cumulative frequency curves for M024 (north basin) at three different segment depths (1-10-18cm going from the sediment surface; Figure 3.16). This comparison indicates that PSD is function of OM removal and that  $H_2O_2$  treatment for OM removal results in a shift in PSD to smaller average particle sizes. This effect is observed consistently throughout the core depth.

In addition, the effect of four pre-treatments ( $H_2O_2$  chemical treatment, 375 °C combustion, 105 °C drying and wet sediment) on sediment surface area from PSD, shows that  $H_2O_2$  treatment

results in a large, uniform shift to higher surface area compared to those determined in wet sediment, while combustion and drying resulted in similar to lower surface areas compared to the wet sediment (Figure 3.17).



Figure 3.16. Comparison of the PSD with and without OM removal at surface (5 cm, top), mid-core (10 cm, middle), and down core (18 cm, bottom) sediment depths for site M24 in the north basin of Lake Michigan.



Figure 3.17. Effect of sediment pre-treatment on sediment surface area as measured by laser velocimetry. Comparison of the sediment surface area calculated from the PSD data in H<sub>2</sub>O<sub>2</sub> treated, 375 °C combusted, and dried sediment compared to wet sediment surface area.

Another test conducted to identify the effect of pre-treatment on clay (<2  $\mu$ m), silt (2-63  $\mu$ m), and sand (>63  $\mu$ m) content as measured by laser velocimetry (Figure 3.18). Based on the comparison of the PSD data in H<sub>2</sub>O<sub>2</sub> treated, 375 °C combusted, and dried sediment compared to wet sediment PSD, H<sub>2</sub>O<sub>2</sub> treatment to remove OM results in a uniform decrease in particle size, particularly decreasing sand and increasing clay, due to particle aggregation by OM. In particular, the H<sub>2</sub>O<sub>2</sub> treatment uniformly increases the surface area by a factor of around 3. In contrast, combustion and drying resulted in a non-uniform change in PSD, likely due to concretion of sediment particles during heating. It has been demonstrated with these findings that combustion affects the PSD and the less destructive peroxide technique is necessary for accurate determination of grain size in Lake Michigan sediments.



Figure 3.18. Effect of pre-treatment on clay (<2  $\mu$ m), silt (2-63  $\mu$ m), and sand (>63  $\mu$ m) content as measured by laser velocimetry. Shown are comparison of the PSD data in (upper) H<sub>2</sub>O<sub>2</sub> treated, (middle) 375 °C combusted, and (lower) dried sediment compared to wet sediment PSD.

Further comparisons of grain size with  $H_2O_2$  treated sediment depth were made at a total of 4 sites in Lake Michigan; Green Bay (M50) and mid-lake (M28) and north basin site (M47) and in south basin site (M11) (Figure 3.19 and Figure 3.20). There is a relative similarity of PSD with depth (1, 5, 10, 13, 15, 17/18, and 20 cm) for site M50 (Green Bay) compared to the large differences in PSD with  $H_2O_2$  treated sediment depth at site M28 (mid-lake sill), whereas for both the north basin site M47 (upper) and the south basin site M11 (lower). In general, most depositional sites (all except M28) had relatively homogeneous well-graded PSDs similar to those shown here.



Figure 3.19. Variation in PSD with location and depth for sites M50 (Green Bay) and M28 mid- Lake Michigan.



Figure 3.20. Variation in PSD by sediment basin and sediment depth for site M47 in the north basin and M11 in the south basin of Lake Michigan.

The XRF results showed two distinct clusters within the sediments data, one group with a 2:1 Ca/IC ratio prevalent in the south basin of Lake Michigan, and the other with a 1:2 Ca/IC ratio in the north. I speculate that the Ca mineral form in the north may include Ca hydroxides, while carbonates are dominant in the south (e.g. calcite (CaCO<sub>3</sub>) dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>), Aragonite (CaCO<sub>3</sub>)), consistent with literature reports of chemistry, composition and accumulation of sediments in the Lake (Rossmann et al., 2004; Eadie and Robbins, 2005).



Figure 3.21. Calcium (Ca) vs. Inorganic Carbon (IC) of Lake Michigan sediments. For comparison, pure calcite CaCO<sub>3</sub>: 40:12 = 3.33; magnesium substituted calcite depends on substitution but dolomite has a structure of CaMg(CO<sub>3</sub>)<sub>2</sub> 40:24 = 1.67.

# **3.4 Recommendations**

It is clear from the work presented here and supported by previous studies that direct acidification in lacustrine sediment is needed to remove IC (Rossmann et al., 2004; Eadie and Robbins, 2005; Lukasewycz and Burkhard, 2005). For accurate determination of TC, OC, BC, <sup>13</sup>C, and removal of the whole IC present in the sediments, aqueous direct acidification with HCl is highly recommended over the other testing methods. The labor costs are increased but greater accuracy and precision of the results is found and in reality this should be the primary goal of any investigation of this nature. Determination of TN and <sup>15</sup>N does not require acidification; therefore those parameters can and should be measured on unacidified sediment samples. Nonetheless, caution must be paid when HCl reacts with the different type of carbonate minerals present because it may impact OM content and release CO<sub>2</sub>, under particular condition of heat, trying to accelerate the entire removal process. Incomplete removal of IC and loss of OC during

acidification are the two common procedural issues that need to be carefully addressed prior instrumental analysis. The accuracy of OC will be obtained with uncompromised OC values only if IC is removed completely, quantitatively, and with no loss of OC. This concept is fundamental to the whole principle of OC quantification.

# **3.5 Conclusion**

Based on the recommendations stated above together with the scheme of analysis developed in the present research investigation, the overall results of all the numerous experiments have been performed to optimize the technique, and to understand and properly interpret the effect of each different treatment on the measured TC, OC and BC. Considering the importance of carbonate mineral removal to the correct analysis of OC and/or BC in lake sediments, direct acidification is necessary and essential. Whenever sediment samples are prepared for carbon measurements, applying a direct acidification method that includes the dissolution of carbonates with 10% HCl and further treatment with several rinses with deionized water and drying before measuring is suggested. However, this might lead to small deviations of the carbon isotopic values; using this method, therefore, is dependent on the precision needed for the analyses and interpretation of the results. In addition, the labor-reduced methodology of acid-fuming the samples in a desiccator is not a useful or straightforward IC removal technique for lake sediments and should be absolutely avoided, unless proved differently. In any case, and this should be obvious for any treatment user, vacuum silicone grease usage on the seal of the desiccator must be prevented at any time (Schubert and Nielsen, 2000).

# Chapter 4. Terrigenous and in-lake sources to Organic Matter in Lake Michigan since industrialization

# **4.1 Introduction**

Organic matter (OM) is widely distributed throughout the ecosystem, and is a particularly dynamic constituent of the food, geochemical and microbial cycle in lacustrine system (Meyers and Eadie, 1993). In sediment OM, which chemically has a heterogeneous, complex structure, consists of many different types of organic compounds including sugars, carbohydrates, proteins, nucleotides, fats, waxes, humins, lignins and complex humic, and fulvic acids (Meyers and Teranes, 2001).

OM has very important characteristics such as the ability to form water-soluble and insoluble complexes with metal ions and hydrous oxides. It can interact with clay minerals and bind particles together, sorb and desorb natural and anthropogenic organic compounds, plant nutrients, and hold water. The determination of the total organic carbon (TOC or simply OC) is frequently used as a measure of the OM content in the sediment (Schumacher, 2002).

Previous studies present a broad overview of the sources and diagenesis (mineralogy change and consolidation of sediment into rocks) of organic compounds in Great Lakes sediments (Meyers et al., 1980; Eadie et al., 1984; Meyers et al., 1984; Meyers and Eadie, 1993; Meyers and Ishiwatari, 1995). Based on these studies, OM content is minor in terms of mass, but an important fraction of lake sediments, and is considered a key record of source (with elemental, isotopic and molecular composition). OM provides paleo-environmental information of earlier physical and geochemical environments in the lake. Paleo-liminological records can indicate the

impact of man on the ecosystems, and natural changes within lake dynamics (Meyers and Ishiwatari, 1995; Tse et al., 2014).

The formation, degradation and/or preservation of OM is a dynamic process due to several factors such as nutrients, aquatic temperature, mixing and the biota living in the waterbody and sediment. OM has two possible origins, firstly, from aquatic biota in the photic zone, where only a small fraction (<10%) of this OM is deposited and incorporated in the lacustrine sediment (Dean, 1981, Eadie et al., 1984, Meyers and Eadie, 1993). Secondly, anthropogenic and biological origins on land, when transported directly to the lake impact the sedimentary OM loadings and alter the aquatic OC processing cycle (Meyers et al., 1984).

The principal factor affecting the rate of OM preservation in sediment is the presence or absence of oxic conditions. In an anoxic environment, the rate of OM degradation is typically much slower than by oxygen respiring heterotrophic bacteria (Meyers and Ishiwatari, 1995). OM is the dominant factor in the redox potential and terminal electron accepting process in near-surface Great Lakes sediments (Li et al., 2006b). Alterations in the redox potential will change the oxygen content of the surrounding environment and hence change the OM deposition.

In the absence of sediment mixing due to bioturbation or physical processes, gradients in dated sediment profiles can be used to ascertain past rates of deposition and in situ rates of biodegradative change. This information can often be more predictive of long-term primary production rates than short-term measurements obtained through water column samples. The fraction of OM that is buried in the sediments depends upon numerous factors mainly water depth, residence time in the water column, and redox conditions. Microbial decomposition (and biosynthesis) can progressively modify the bulk composition of the OM. All these aspects are

not only important for a general understanding of the controlling factors, affecting the OM breakdown, they are also relevant for assessing the integrity of sedimentary paleo-environmental archives. Hence, knowledge of not only the OM concentration but also the composition and rate of diagenetic alteration of the OM is helpful in understanding the fate of pollutants (e.g. hydrophobic organic contaminants (HOCs)).

Lake Michigan sediment and water column studies of OM dynamics have shown that complex interactions of different organic sources, combined with re-mineralization, oxidation in the water column, and resuspension of bottom sediment in the hypolimnion influence the OM concentrations (Meyers et al., 1980; Eadie et al., 1984; Meyers et al., 1984; Meyers and Eadie, 1993; Meyers and Ishiwatari, 1995; Meyers, 2003). The major source of OM to lake sediments is from primary production (photosynthesis by algae or cyanobacteria) within the lake or on the land around it. The vast majority of OM derives from plants, which can be non-vascular such as algae and vascular such as grasses, bushes and trees; less than 10% originates from animals (Meyers and Ishiwatari, 1995). Of the total OC within the aquatic system of Lake Michigan, 90% is from aquatic algal production within Lake Michigan, 5% from fluvial sources such as the rivers and the remaining 5% from atmospheric deposition and natural precipitation has eolian source (Andren and Strand, 1981). Lake morphology, watershed topography, and the specific abundance of geochemically different types of plants influence significantly the contribution to OM. Microorganisms and other bacteria in the sediment and in the water column of lakes change and degrade aquatic and land-derived OM. Even though some bacteria are able to live chemotrophically, lacustrine environment generally contains sufficient quantities of OM. Because of its OM richness, lake microbiome is typically dominated by heterotrophic decomposers of organic detritus.

The recent increase of OM, OC, and black carbon (BC) in the Great Lakes has been explained by two competing theories. First, the "cultural eutrophication hypothesis" (CE) promulgated by Meyers (1994) argues that increasing organic loading since ~1700's are due to the impact of increased population resulting in increased nutrient loading and subsequent increasing in-lake primary production. This idea was investigated by looking at deep cores going back 100s to 1000s of years. Second, the "labile OM degradation hypothesis" (LOMD) supported by Buckley et al. (2004), also Mayer (1995) and Keil et al. (1994) states that TC, OM, and OC decrease down-core going back in time due to degradation of labile OM.

Due to agricultural, residential and/or industrial expansions, this "CE" caused by man has dramatically altered the Great Lakes over the last 100-200 years (Meyers and Eadie, 1993; Meyers and Ishiwatari, 1993b). Natural or cultural eutrophication lake water gradually becomes extremely productive, rich in plants such as algae due to excess nutrients. Eutrophication may happen naturally, but it is often accelerated by anthropogenic activities. Nutrient enrichment and/or loadings have been already recognized as a serious environmental issue during particularly rapid growth of population, agriculture and industrial production (Smith, 2003; Hecker et al., 2012). Combining these conditions causes rapid growth of algae and other biomass as it no-longer is nutrient limited, together with a significant reduction in the concentration of dissolved oxygen, impairing lake ecosystems. In Lake Erie and also to a lesser extent in the other Great Lakes, the excessive growth of algae stimulated by phosphates caused algal blooms that destroyed the local ecosystem in the 1950s-60s. Concern was voiced in USA and Canada and the eutrophication event stimulated the institution of the Federal *Great Lakes Water Quality Act* (GLWQA) and The *Clean Water Act* (CWA) in 1972.

Because of the focus on the Great Lakes and the concerns over contamination and changes quantifying the historical and current OM, OC, BC and important nutrients within the lake deposits both temporally and spatially will go a long way towards understanding of the changes that have and may be occurring within the region.

#### **4.2 Materials and methods**

*4.2.1 Study Area:* Lake Michigan together with Lakes Superior, Huron, Erie and Ontario constitute the five Laurentian Great Lakes, which represent the largest surface freshwater system on Earth (Tables 2.5 and 2.6). Lake Michigan has a surface area of 57,780 km<sup>2</sup> (22,300 miles<sup>2</sup>) with an average depth of 85m (279 feet); it is the second largest of the Great Lakes by volume of 4,920 km<sup>3</sup> (1,180 mile<sup>3</sup>).

The project was conducted to cover the entire area of Lake Michigan (Figure 4.1 and Table 3.2). Within the Lake, sampling was conducted in five main regions extending from north to south. According to the National Oceanic and Atmospheric Administration (NOAA) bathymetry map of Lake Michigan (realized by Great Lakes Environmental Research Laboratory), these five study areas are the *straits and islands area* (topographically irregular area with small ridges, valleys, and islands in the northeast), *Green Bay* (a long, narrow, shallow estuary off the northwest corner with a mean water depth of around 20 m), *Chippewa Basin* (a steep northern basin with a maximum water depth of 281 m), a *Mid-lake Plateau* (a central open-lake area, going from 125 m deep to shallow areas less than 40 m deep covered in thin or missing sedimentation, perhaps because of heavy currents), and *South Chippewa Basin* (a southern basin, large depositional area particularly in southeastern area, with a smoother bottom of a maximum water

depth of 163 m, and close to the major metropolitan and industrial areas of Lake Michigan). The whole basin is diverse in the quantity and type of OM that may be deposited.



Figure 4.1. Bathymetry map of five main regions of Lake Michigan, shown core (star) and surface ponar grab (solid circle) sampling locations. Source: National Oceanic and Atmospheric Administration (NOAA) bathymetry map realized by Great Lakes Environmental Research Laboratory. GIS Map created by S. Bonina, 2015.

The northern region of the Lake is colder, mainly surrounded by forests, less developed and sparsely populated compared to the south. Green Bay has one of the most productive Great Lakes fisheries but receives discharge from the world's largest concentration of pulp and paper mills. Also, two important Rivers, the Fox and the Menominee, drain one third of Lake Michigan drainage basin into Green Bay (Christensen and Chien, 1981). The more temperate southern basin of Lake Michigan is among the most urbanized areas of the Great Lakes system. It contains the two large conurbations Milwaukee and Chicago, with a combined population of almost 8 million, approximately one-fifth of the total population of the Great Lakes basin, and many farms surround these cities. Water retention time within the Lake is approximately 100 years for a complete change of water into Lake Huron through the Straits of Mackinac. Although Lake Michigan has been considered as a large oligotrophic freshwater lake (Lehman, 1988; Dean and Gorham, 1998), its southern area has greater levels of productivity that may be due to the anthropogenic input surrounding the basin (Meyers and Eadie, 1993).

Lacustrine sediments do not accumulate uniformly crosswise the whole bottom layer. Deposition of sediments is not uniform across the lake. Lake bottom topography current circulation patterns establish areas in the lake that are depositional. So to identify a valid chronological record a location must be continuously depositional (Corcoran, 2013). Based on the Illinois State Geological Survey (ISGS, (1975)) map of the depositional areas of Lake Michigan, the deepest locations of the Lake are not all depositional areas. Also, there is a large depositional area in the in the southeast of the South Chippewa Basin due to sediment arriving from the watershed (Cahill, 1981; Waples et al., 2005; Eadie et al., 2008). The volume of sediment transported depends on the intensity, current and path of waves and wind. Not all deposition is uniform a single storm event occurrence in 1999, for example, caused a transfer of sediment from the

western near shore region into the southeastern depositional region in an equivalent volume to 20% of the annual estimated deposition to the whole Lake (Waples et al., 2005; Eadie et al., 2008).

Lake Michigan sediment sources comprise fluvial input, aerosol input, bluff erosion, and lakebottom erosion associated with the bluff. Colman and Foster (1994) report that in the South Chippewa Basin 88.5% (by weight) of imported sediment comes from bluff erosion, another 5.5% is from aerosol deposition, and the remaining 6.0% input from watercourses such as rivers, streams. In addition to that, Eadie et al. (2008) study indicates that biogenic silica, organic matter, and carbonates have autochthonous sources, since they are produced inside the lake itself.

In terms of contamination sources, the runoff from soils, farm agrochemicals, waste from metropolitan areas, discharges from industrial areas and leachate from disposal sites are among the primary sources of Lake Michigan contamination. The surface area to the volume ratio of the Lake makes it to be particularly sensitive to atmospheric pollutants via wet and dry deposition. Moreover, outflows from the Lake are relatively small resulting in a long hydraulic residence time. Therefore, contaminants that enter the Lake are held in its lacustrine system and can accumulate with time.

4.2.2 Sampling and processing: Lake Michigan sediment sampling was conducted in September 2010 and May 2011 as part of the USEPA-funded Great Lakes Sediment Surveillance Program (GLSSP), onboard the US Environmental Protection Agency's (USEPA's) *R/V Lake Guardian*. Site selection focused on depositional sites because these locations would have the highest sedimentation rates, and existing USEPA sampling stations were used for possible comparisons between the present and previous studies. The selected locations included the southern, central and northern basins of Lake Michigan. A total of 30 locations were sampled during the two campaigns.

Among these locations, ten were sediment core sites (Figure 4.1) distributed throughout the whole lake: four sites in the northern basin, M47 (Island and straits), M41 and M32 (Chippewa Basin) and M50 (Green Bay), two sites, M28 and M24 in the central open-lake area (Mid-Lake Plateau), and in the southern basin the remaining four coring sites, M18, M11, M09 (all southeast of South Chippewa Basin) and M08 (southwest). The other twenty locations were sampled for grab surface sediment only (Figure 4.1 and 3.1a). At every location, a surface grab sample was collected using the ponar sampler (Figure 3.2a). Box corer (BC; model BX-750, Ocean Instruments, San Diego CA; Figure 3.3a, from 2010 sampling activity), or Ekman dredge (EC; custom made in 1990; Figure 3.3c), or multicorer (MC; model MC-400 "Spyder" corer Instruments, San Diego, CA; Figure 3.3b, from 2011) was deployed to collect sediment core samples at pre-selected locations. All coring devices used the same collection tubes (MC-400-4(P), 10 cm x 60 cm polycarbonate, Ocean Instruments, San Diego, CA). For use in the BC and the ED the tubes were 45 cm long, while for MC tubes were 60 cm. Sectioning was performed at 1 cm thickness intervals from the surface sediment for the first 10 cm, then in 2 cm increments for the remainder of the core in the general field laboratory of the R/V Lake Guardian. For most coring sites, 20 segments were obtained, with the exception of core M050 (which had 19 segments) and M028 (which had 17 segments). A summary of the Lake Michigan sampling is provided in table 3.2. All detailed information about sampling, sectioning, field procedures and laboratories analyses conducted for this study are reported and discussed in chapter 3.

# 4.2.3. Laboratory Analyses

*Concentration of OM, TC, OC, BC, and Total Nitrogen (TN):* Sediment samples were characterized for physical and chemical properties including solids content, bulk density, porosity, and OM, OC, and BC according to standard methods (ASTM, 1998a, 1998b), and the modified and extended methodology from Great Lakes Restoration Initiative (GLRI) projects (Rockne et al., 2000; Buckley et al., 2004; Li et al., 2006b). Comprehensive and descriptive information about methodology and laboratories analyses conducted for this work are discussed in the methodology chapter 3 of this thesis. The OM, OC, TN, and BC data were essential to determine sedimentation rate, focus factor (FF), chemical inventory, depositional fluxes, loadings and annual input rate.

OC is obtained from TC measurement after complete acidification. BC is obtained from the TC in completely acidified samples following low temperature combustion. IC content is the TC in acidified samples subtracted from the TC measured in unacidified samples. To find this 3 mL sediment samples were volumetrically tested from mixed and homogenized core sections (Buckley et al., 2004). For quality control purposes, triplicate measurements were made for each sample. Each sample was weighed on a labeled tared aluminum tray and dried in an oven at 105°C for 48 hours to constant mass. The mass was read to a minimum of three to four decimal places (down to  $\pm 10 \ \mu$ g) on an analytical balance calibrated with traceable mass standards. As the ratio of the wet weight (w/wt.) to volume, a wet bulk density was determined. Samples were re-weighed after drying, and the dry sediment mass, moisture (%) and solids (%) were determined as described in the method chapter (chapter 3). Following drying, one of the three samples was placed in a muffle furnace and further combusted at 375 °C for 24 hours. OM was operationally defined as the mass loss upon this low temperature combustion normalized to the

original dry mass using the method of Rockne et al. (2002). Samples were ground using a clean mortar and pestle. A multistage acidification procedure, using a solution of 10% HCl, 1:1 dilution of 6 N HCl into DIW, was used to remove inorganic carbonate in samples for OC and BC determination. Analyses for carbon used an Elemental Analyzer (EA).

For determination of the elemental values of TC, OC, BC, and N, the EA was run in triplicate for each sample for different carbon types. Ten to twenty milligrams (mg) of sample were placed in pre-tared tin combustion boats (CE Elantech Inc., Lakewood, NJ, USA), sealed and weighed. Elemental analysis was conducted using automated combustion/reduction (900 °C for carbon (C) and nitrogen (N)) followed by molecular sieve gas chromatography and thermal conductivity detection at 60 °C using a Carlo Erba Flash EA1112 (ThermoQuest/CE Elantech, Lakewood, NJ, USA).

Peak areas for C, and N were compared to six points of the 2,5-Bis-2(5-Tert-Butyl-Benzoxalyl)Thiophene standard (BBOT) and integrated using Eager v.5.0 peak integration chromatography software. New BBOT standard curve calibrations for C, and N were obtained from the BBOT standard which is 72.56% C, and 6.5% N. The calibration curve was re-ran for every sample set to ensure instrument stability,  $R^2$  value of  $\geq$ 0.99 were required for acceptable runs and intensity was checked against previous runs. For QA/QC, sediment sample duplicates and BBOT were analyzed every ten sediment to determine accuracy and precision according to Standard Methods (APHA; AWWA; WEF (2005)). Where samples were outside the range of the standard calibration curve samples were reran with additional BBOT standards to ensure concentrations remained within the curve.

*4.2.4 Additional Analysis:* Production and decomposition processes within the Lake Michigan lacustrine ecosystem were characterized utilizing a variety of techniques. It is possible to distinguish the sedimentary OM sources and their relative degradation/preservation in sediments, by atomic/isotopic ratios such as carbon-nitrogen (C/N) ratio, <sup>13</sup>C, <sup>15</sup>N analysis, and characterization of BC and pollutants (e.g.: Polycyclic Aromatic Hydrocarbons (PAHs), Polychlorinated Biphenyls (PCBs), Polybrominated Diphenyl Ethers (PBDEs), etc.).

Table 4.1. Selected parameters of this study as proxy measures for limnological processes.

Measured Parameter	Proxy Information	Reference	Note
Core Sediment Concentration of OC (also referred as TOC)	Temporal OM abundance in sediment	Meyers (2003).	
Surface Grab Sediment Concentration of OC (or TOC)	Spatial OM abundance in sediment		
C/N	Identification of proportion of algal and land-plant OM	Meyers (1994); Kaushal and Binford (1999); Meyers (2003).	C must be the Organic Carbon and N the Total Nitrogen
$\delta^{13}C$	Proportion of C3 and C4 plants, enriched algal productivity	Talbot and Johannessen (1992); Meyers (2003).	
δ <sup>15</sup> N	Identification of proportion of algal and land-plant OM, evidence of N fixation, increased algal productivity	Hodell and Schelske (1998); Brenner et al. (1999); Teranes and Bernasconi (2000); Meyers (2003).	
Sedimentation Rate of OC	OM delivery rate	Hodell and Schelske (1998); Meyers (2003).	

Biogeochemical research has shown predictive relationships between elemental mass ratios and carbon isotopic composition of living organic matter and both the physical and biochemical processes associated with carbon assimilation (Meyers and Ishiwatari (1993b). Processes including biosynthesis and degradation in the photic zone and bacterial growth in both the water column and the sediment affect these ratios. Meyers and Ishiwatari (1993b) found that C/N ratios

of sediments are influenced by the presence or absence of cellulosic sources of OM. OM elemental ratio analysis not only acts as an indicator of past environmental change, but such techniques may also be useful in understanding mechanisms controlling primary productivity and seasonal lake behavior. In addition to that, stable isotope analysis (for determination of <sup>13</sup>C and <sup>15</sup>N), can identify sources of carbonaceous contaminants (Schmidt et al., 2004). This technique exploits the differential rates at which heavier natural isotopes pass across membranes, resulting in different fractionation ratios of heavier to lighter isotopes (Madigan and Martink, 2005). Therefore, stable isotopes are used to study various microbial transformations in nature. Biodegradation (e.g. oxidation, reduction, addiction, etc.) is typically a multiple stage and/or multiple step mineralization process of organic materials achieved by microbial organisms such as algae, protozoa, bacteria, etc. (Christensen and Li, 2014). Typically, biological isotopic fractionation can be used as an assay for whether particular transformation is biologically mediated.

*Organic matter C/N ratios:* Ratios such as C/N, <sup>13</sup>C, and <sup>15</sup>N against depositional time can characterize the C sources and evaluate OC coverage from grain size (or particle size distribution data).

The C/N ratio is an informative proxy of OM sources and reliable indicator of the proportions of algae and land-plants as OM sources. Within the atomic C/N ratio, the C represents organic carbon while the N is the total nitrogen, both concentrations measured during physical and chemical characterization by elemental analysis. However, C must be accurately calculated after acidification and consequent carbonate removal while total N prior such removal, otherwise the C/N ratio might lead to an erroneous OM origins (Meyers, 2003). The atomic C<sub>organic</sub>/N<sub>total</sub> ratios have often been used to distinguish between algal and land-plant origins of sedimentary organic

matter (Meyers (1994), and reference therein, e.g., Prahl et al. (1980)). Typically, lacustrine algae, rich in protein and poor in cellulose, create OM that has atomic C/N ratios between 4 and 10, whereas vascular land plants, rich in cellulose and poor in protein, have OM with high C/N values of  $\geq$ 20 (Meyers, 1994, 2003). These distinctions in OM composition mostly persist the sinking/settlement and sedimentation processes and consequently can be clearly seen in their distinctive atomic C/N values. For instance, Meyers (1994) from his unpublished work found that mixed plankton as OM source with a C/N ratio of 7 (and  $\delta^{13}$ C of 26.8 %<sub>0</sub> vs. PDB) in Lake Michigan. Another example of sediment trap results on organic suspended and setting particulate matter in Lake Michigan by Meyers et al. (1984) indicated an abundant contribution of aquatic OM with C/N values within the range of 7 and 10. This proportion was greater near the deep bottom layer traps, but indicated largely terrigenous OM sources in the open-lake.

*Carbon and Nitrogen stable isotopic composition:* Carbon (C) and nitrogen (N) stable isotope analysis (SIA) of selected box-core and multi-core sediment samples from Lake Michigan were investigated. SIA may be used to identify not only the difference between organic and inorganic carbon but may also be used to identify changes in a food chains, both spatially and temporally. The transfer of <sup>13</sup>C through trophic levels remains relatively constant, except for a small increase (an enrichment < 1 ‰). Because of the differences in the proportion of <sup>12</sup>C and <sup>13</sup>C in carbon of biological and geological origin, the isotopic ratio <sup>13</sup>C/<sup>12</sup>C (measured using mass spectrometry) of geological strata has been used to detect the presence of once living material in sediments. These may be short-term alterations or long-term depending on the extent in the sediment record. The input of nitrogen isotopes may also indicate the tropic level of organisms or their OM reaching the sediment and the ratios of  $\delta^{13}$ C and  $\delta^{15}$ N have been used to determine the autochthonous and allochthonous sources. Furthermore, the isotopic composition of any sample contains a record of its past biological activity. Lake Michigan sediment core samples from six core segments at each site: surface 1 cm, 5 cm, 10 13 cm, 15 cm and 20 cm depths were analyzed for determination of %N, %C,  $\delta^{15}N$  (N<sub>total</sub>),  $\delta^{13}C$  (C<sub>organic</sub>) using an Elemental Analyzer (EA; Costech Analytical, ECS 4010 Elemental Combustion System (CHNSO), with zero blank autosampler) coupled to an Isotope Ratio Mass-Spectrometry (IRMS, ThermoFinnigan Delta Plus XL equipped with Conflo III, Gas Bench II) through an open split interface, following the procedures established by the research team at Environmental Isotope Geochemistry Laboratory (EIGL), where I performed this additional analysis. In brief during the instrumental analytical process, the weighed sample (1-3 mg) is dropped into a 1050 °C Cr<sub>2</sub>O<sub>3</sub> combustion reactor, transported by a helium carrier stream that has been enriched with O<sub>2</sub>. Under these conditions, the capsule combusts, raising the sample temperature to 1800 °C, forming H<sub>2</sub>O, CO<sub>2</sub> and N<sub>2</sub>. Any gas formed which contains halogens or sulfur is chemically removed and the remaining combustion products are sent into a 650 °C Cu<sup>+</sup> reducing reactor, where incomplete combustion products (NO<sub>x</sub>, CO, etc.) are reduced and excess  $O_2$  is removed. Water is then chemically scrubbed from the helium. The final product gases (N<sub>2</sub>, CO<sub>2</sub>) are separated on a 3meter packed gas chromatography column (80 mL min<sup>-1</sup>, 40 °C) before entering the IRMS. According to the instrument method configuration, pure reference gases such as UHP grade  $N_2$ and CO<sub>2</sub> enter the mass spectrometer at specified times to ensure proper mass calibration. Peak areas for C, and N were compared to six points of the standard Acetanilide, equally called N-Phenylacetamide, and integrated using the software EAS Clarity ISODat 2.0.

Acetanilide standard curve calibrations for C, and N were obtained from the acetanilide standard which is 71.09% C, and 10.36% N (also checking delta  ${}^{15}N/{}^{14}N = 0.00921$  per mil and delta  ${}^{13}C/{}^{12}C= -30.054$  per mil). In addition to the acetanilide standard, a second source standard,

caffeine (3,7 Trimethylxanthine: 49.48 % of C and 28.85 % of N) was calibrated and checked against the primary standard material (acetanilide as secondary reference material to ensure correct instrument operation and no sample contamination or carry-over. For every run, six acetanilide standards were run to ensure accuracy. The calibration curve must meet the criteria of an  $R^2$  value of 0.99 or greater. For quality control, acetanilide and laboratory sediment sample duplicate at least one of ten sediment samples were run as unknowns to determine the accuracy and precision according to standard methods. Exclusive samples, analyzed as unknown, with peaks within the standard curve were used for the analysis, whereas with exceptionally high or low peak areas outside the range of standards were re-analyzed using a modified six point acetanilide standard.

*Particle Size Distribution by grain size analysis:* The particle size distribution (PSD) of granular material (e.g. sediment) is important in understanding and characterizing its physical and chemical properties. Laser diffraction on the mastersizer instrument (Malvern Instrument, Worchestershire, UK) was used to determine the agglomerate particle size distribution of Lake Michigan sediment. Sediment samples, pretreated with  $\frac{1}{2}$  vorgen peroxide H<sub>2</sub>O<sub>2</sub> were suspended and homogenize in 1 L beaker of DI water until the rarefraction index reading was stable.

Laser diffraction through the suspension measures the size of particles by measuring the intensity of light scattering as a beam passes through a dispersed particulate sample. The angle of diffraction increases as particle size decreases, so that this method is particularly good for measuring sizes between 0.1 and 3,000  $\mu$ m. The results were then analyzed to calculate the grain size of the particles that created the scattering pattern using Mastersizer-2000 software.

This method is limited in that it does not measure in-situ particle size; particle measurement reflects agglomerate nature of sediment due to particle-to-particle attraction. PSD measurement is used primarily as validation of surface area (SA) to provide additional understanding of in-situ sediment condition.

*Dating (sedimentation rate and focus factor):* As a part of the GLSSP framework core dating was performed using measurements of <sup>210</sup>Pb measurement based on alpha spectrometry of <sup>210</sup>Po (Song et al., 2004; Ford, 2005). Lake Michigan sediments were evaluated in greater detail for the activity of <sup>210</sup>Pb, <sup>226</sup>Ra, <sup>7</sup>Be, and <sup>137</sup>Cs by gamma ray spectroscopy and has been discussed in detail in other publications (Corcoran, 2013; Smalley, 2013).

The sedimentation rate was calculated from the slope of the regressions of corrected <sup>210</sup>Pb concentration versus the cumulative mass of the sediments at each depth. The focus or focusing or normalization factor (FF), calculated and used for each site in Lake Michigan, is a ratio that describes the accumulation or focusing (how much) of sediment within a specific region. The FF was determined by dividing the concentration of a compound by the atmospheric deposition rate, knowing <sup>210</sup>Pb and <sup>137</sup>Cs. This is only possible for any compounds where the atmospheric input is known such as <sup>210</sup>Pb and <sup>137</sup>Cs (Eadie et al., 2008). A FF of one indicates all the expected atmospheric deposition is found in the sediment. If the FF value is below one, this would indicate that not all of the target compound is in the sediment; if the FF is above one, then there is some accumulation above the atmospheric background input at this site.

In effect the FF can be used to describe if a site has a net loss or gain of sediment compared to the expected mean, assuming that the uptake is uniform (Hermanson and Christensen, 1991). Great care was taken in the GLSSP to accurately date cores and variations in expected ratios and

transport of sediment caused some uncertainty in the analysis.

*Fluxes and Loadings:* Fluxes and loadings are calculated for each site by combing concentration data and radionuclide data. The depositional flux of each component was calculated from sediment concentration, sediment deposition rate and focus factor as describe in the following. The flux of any chemical or parameter into a sediment segment is calculated by dividing the product of the concentration and the sedimentation rate by the focusing factor.

# **Equation 20: Flux Calculation**

$$Flux\left(\frac{mg/cm^2}{yr}\right) = \frac{Concentration\left(\frac{mg}{g}\right) x Sedimentation Rate\left(\frac{g}{(cm^2x yr)}\right)}{Focus Factor}$$

The loading, measured in tons or metric tons per year (tons/year or mt/year), is calculated using the surface integration of the flux over the whole lake through the Inverse Distance Weighting (IDW), method for multivariate interpolation with a known scattered set of points.

# **Equation 21: Loading Calculation**

$$Loading\left(\frac{tons}{yr}\right) = \oint F\widehat{n} \, dA$$

At the end, Lake-wise calculated loadings and fluxes are reconstructed against the sediment depositional year, respectively plotted and mapped using the ArcMap component of the software geographic information system (GIS, called extensively ArcGIS) version v.10.3, supplied by the environmental systems research institute (Esri from Redlands in California, USA). Complete raw data of fluxes and loadings for all Lake Michigan studied parameters, which have been used for plotting charts and interpolation before mapping, are reported in the appendix A and B, correspondingly.

# 4.3 Results and discussion

Chemical Characteristics: C loading forms results. In general, C concentration results are divided for sites grouped by Northern Chippewa Basin (including sites M47, 41, 32, and 24), Green Bay and the mid-lake sill Plateau (sites M50 and M28, respectively), and Southern Chippewa Basin (sites M18, 11, 09, and 08). Based on the OC sediment profile data (Figure 4.2b, top right) OC loading is less in the open lake than in Green Bay (M50), and an enrichment of TC and IC relative to OC has occurred in recent times, specifically the last 4 decades (Figure 4.3 a-c). Although sedimentation rates vary among sample sites, similar concentration trends are evident with sediment depth (Figure 4.2) and time (Figure 4.3). Both figures show a pronounced increase from north to south for C coverage, with greatest levels of OC nearest Chicago (in the Southern Chippewa Basin). Sediments from M24, M18, M32, M41, M47 sites are similar. The OC percentage is between 2 and almost 4% of the sediment (dry mass) in the upper 5 cm of all locations, with a decrease at greater sediment depth into the more distant past. OC concentrations at depths >5cm are approximately equal in the open lake. This would appear to indicate an enrichment of C-loading during the last two or three decades depending on sedimentation rates. Sites M24, M32, M41, and M47 have similar trends with depth and time, as these are all within the same basin (north) it would appear that sources and deposition in this region comes from the same or similar sources. Two outliers are M50 Green Bay sediment and M28 ridge samples between the north and south basin (Figures 4.1). M50 site has higher OC in the sediment (almost 8% in the upper sediment in recent years and decreasing to around 6%). This likely results from a much more productive basin (in terms of algal and photosynthesis); there is also greater sedimentation and outfall from the two major drainage rivers. M28 site (ridge samples) presents lower OC in the sediment (less than 1% (0.5 %)) at the surface increasing with depth to

approximately ~1.5 %. This might result from the sediment being dense clay that limited the porosity and thus had low OM content. Additionally, based on the bathymetry of Lake Michigan (Figure 4.1) site M028 is located on the edge of a deep channel, within an area of quite higher currents than other locations. High-energy currents able to entrain heavy particles may not allow finer and lighter particles to deposit in contrast to slower currents. Because of the limited radionuclide record in this core, it cannot be dated (Corcoran, 2013), and is thus not shown in Figure 4.3.



Figure 4.2. Carbon measurements: (a) TC, (b) OC, (c) OM, and (d) IC concentrations with sediment depth in all Lake Michigan coring sites.



Figure 4.3. Carbon measurements: (a) TC, (b) OC, (c) OM, and (d) IC concentrations versus time in all Lake Michigan coring sites.

In the South Basin, sites M18-M9-M11 and M8 are more heterogeneous, and may also be influenced by their proximity to the more antropogenically impacted southern shoreline. M08 and M09 sites differ from M11 and M18: all have greater OC concentrations at the surface layers. M09 has a shallow gradient with depth indicating a more uniform deposition of OC while M08 has lower concentrations at the surface and peaks at 9 and 15 cm (Figure 4.2). At M11 and M18 a steep decline in OC occurs at 9 cm and at 7 cm for these locations respectively. The sedimentation rate at site M11 is very high compared to M18, thus the decrease may occur at the same time period (Figure 4.3). It is interesting to note that M08 (no GLSSP dating available) is considered an edge depositional zone by Cahill (1981), and M09 with the highest sedimentation rate of 0.0653 g/cm<sup>2</sup>/yr represent a scour process area in the lake where sediment circulation occurs. Thus, these sites may not be continuously depositional, explaining their unique and particularly high C concentrations compared to the rest of the lake. The high scour would also explain why dating at M08 and M28 (high porosities and the low bulk densities) was not possible. Sediments in these locations were susceptible to movement by physical processes, hence both excluded from figure 4.3.

Mixing within the water column may also occur (as in 4 sites, M11, M24, M47, M50, Figure 4.3) as a result of physical lake processes, resulting in large-scale resuspension of sediments from depositional areas and temporary repositories on the lake margins (Corcoran, 2013). Examples are annual lake turnover and destratification, storm events, and upwelling (Bell and Eadie, 1983; Eadie et al., 1990; Plattner et al., 2006; Eadie et al., 2008).

Table 4.2. Tabulated core radio-dating results (mixing depth, if present, sedimentation rate and focus factor Pb-210) via GLSSP by environmental isotope geochemistry laboratory at Earth and Environmental Sciences (EaES) at UIC. Source: Corcoran (2013); used data reviewed on September 2015.

LAKE MICHIGAN SITES			Radio-dating Analysis Results			
SITE ID	LOCATION in LAKE	Water DEPTH (m)	Mixing Depth (cm)	Mixing Depth (g/cm²)	Sedimentation Rate (g/cm²/yr)	Focus Factor: Pb-210
M008 *	Southern Edge of Lake, near shore	66	NOT DATABLE	NOT DATABLE	NOT DATABLE	0.49
M009	South Chippewa Basin, near shore	62	-	-	0.0653	2.20
M011	South Chippewa Basin	164	3	0.527	0.0406	2.99
M018	South Chippewa Basin	165	-	-	0.0183	1.52
M024	Mid-Lake Plateau	150	2	0.277	0.0192	1.98
M032	Chippewa Basin	257	-	-	0.0184	2.09
M047	North End Chippewa Basin	200	3	0.470	0.0311	2.64
M050	Green Bay	33	3	0.198	0.0314 - 0.0221	2.85
M028 *	Mid-Lake Plateau, near shore	137	NOT DATABLE	NOT DATABLE	NOT DATABLE	0.30
M041	Chippewa Basin	272	-	-	0.0221	2.11

The calculated <sup>210</sup>Pb FF was in the range between 1.52 (M18) and 2.99 (M11). As the FF was above one for all sites in Lake Michigan, it would indicate that more <sup>210</sup>Pb was found in the sampled sediment than is deposited on the surface of the lake from atmospheric deposition alone.

Particle size distribution by grain size may go some way towards explaining the C results. In Lake Michigan most sediment was dominated by silt-sized particles with the only exception of M28. The two predominant size fractions were silt and clay (Figure 4.4) indicating with the exception of M28 a relatively similar distribution of material, with fine particles predominating the surface area to volume ratio for the sorption of contaminates in Lake Michigan is high. The largest silt fraction was found at sites M50 (62%) and M09 (61%), while the largest clay fraction was at M24 (49%). Beside M28 with a significant fraction of sand up to 31%, M50 had a 5% of sand; also M08 and M09 had a measurable fraction of sand, which were 12% and 3%, respectively.



Figure 4.4. Grain Size shown bulk sediment fractions such as clay (<2  $\mu$ m), silt (2-63  $\mu$ m), and sand (>63  $\mu$ m) for all coring sites in Lake Michigan.

These data show that most sediment are very fine in Lake Michigan. All the sampling location were in deep water and it is assumed not affected and disturbed by shoreline processes with the exception of extreme storm events that may introduce terrigenous material over a wide area.

In lake sediments the concentration of OC is an important proxy for describing the abundance of OM: OM generally includes ~50 % carbon, so OM concentration can be estimated. In Lake Michigan sediment OM profiles (Figure 4.2c) confirmed the OC pattern and validated the hypothesis that OC is equal to ~1/2 OM. IC profile (Figure 4.2 d) indicated that IC is  $\geq$  50% of the TC for each sites (with the exception of M50), consequently OC profile (Figure 4.2 b) has shown that OC makes up ~50% of TC with the same loading pattern. This would indicate the sources of TC and OC may be similar. Combusted BC was a very small fraction of the OM environmental sources, this may reflect the different distribution mechanism via fluvial and
atmospheric transport, as discussed in detail in the following chapter.

In agreement with Meyers and Eadie (1993), it was found that throughout Lake Michigan the OM concentrations (as well as the OC concentrations) generally show greater increased concentrations at surface layers in the sediment and decrease with sediment depth starting between 5 and 10 cm. In literature, this enrichment of OM in the recent sediment has been explained differently by the two competing theories, "CE" or "LOMD". In the present study, the recent OM increase has been partially tested by measuring OC coverage and stable <sup>13</sup>C isotope analysis to identify carbon sources in Lake Michigan, and identified as possible consequent of the occurred CE phenomena in the Lake.

 ${}^{13}C/{}^{15}N$  results: Data from SIA suggests that algae are the dominant source of OM to Lake Michigan sediment. All sediment  $\delta^{13}C$  values (of -25 to -27‰) lie within the range of lacustrine algae "endmembers" (Figure 4.5 a-b). This finding is supported by the C/N ratios, which are typically <10 (typical for photo-synthetically-derived OM (Meyers, 1994). Manly all 8 organic matter C/N values are between 6 and 10 in the range of the lacustrine algae. A few sediment sites may have a mixture of lacustrine algae and C3 plant sources, as suggested by C/N ratios greater than this value, but still much lower than C4 plants (Figure 4.5 a-b). Southern Chippewa Basin sites, M09 and M08, ratios exceed 10 and suggest that some C4 OM in the sediment and though land-derived OM makes a small contribution to particulate material at those locations.

The majority of plants in the Lake Michigan watershed are wheat, barley, potatoes and sugar beet, which are grouped into C3 land plants typical of temperate climate zones, while C4 plants include corn, sugar cane, and food crops, abundant in the agricultural area of Illinois and Indiana.

However, C4 plants do not appear to be significant sources of OM to Lake Michigan sediments, as OM from these sources would have much lower  $\delta^{13}$ C values of -10 to -15‰. Most of the "corn belt" lies outside the Lake Michigan watershed to the south and west.



Figure 4.5. Shown are (a)  $\delta^{13}$ C versus C/N ratios in Lake Michigan sediments, and (b) distinctive source combinations of atomic C/N ratios and organic  $\delta^{13}$ C ratios in authentic samples from Meyers (1994).

N also undergoes isotopic enrichment during biological uptake and metabolism using C and N isotopic data, atomic C/N ratios and organic  $\delta^{13}$ C values. Overall, this study found that OM was primarily autochthonous (lacustrine) source in the past, while more recently it is derived from

more allochthonous (terrestrial) sources from outside the Lake.

Further support of predominantly algal-derived OM comes from  $\delta^{15}$ N analysis. Sediment OM  $\delta^{15}$ N and  $\delta^{13}$ C fall between lacustrine algae and C3 plant endmembers, but closer to the former (Figure 4.6).



Figure 4.6. SIA of  $\delta$  <sup>13</sup>C vs.  $\delta$  <sup>15</sup>N for Lake Michigan sediment samples.

Some general spatial patterns are observed in stable isotope ratios. Sites M08, M09 and M41 are different from other sites on the C/N versus  $\delta^{13}$ C graph with greater C/N values (Figure 4.5), suggesting that terrigenous OM is more of an influence in these regions. The lower  $\delta^{15}$ N values at sites M41 and M47 in the Northern Chippewa Basin (Figure 4.7 A) and at sites M09 and M08 in the Southern Chippewa Basin (Figure 4.7 B), represent the four deepest and most central locations within their respective basins, and the results are consistent with greater terrigenous input at these locations. In contrast, the SIA results at site M11, M18, M24 and M32 suggest almost exclusively algal OM source. In Robbins and Edgington (1975) study of Lake Michigan

it has been suggested that the central deep regions of the two basins may be sinks of sediment due to gyre action and this may corroborate the greater land based input. It may also be that these deeper sites have less oxygen and the ability of aquatic bacteria to degrade land-based OM is less, so there is accumulation.

General temporal patterns are observed in stable isotope ratios as well, as determined from variation in stable isotope ratios with depth in a particular core. Typically,  $\delta^{13}$ C,  $\delta^{15}$ N and C/N ratio increase with increasing sediment depth (Figure 4.7 A-B).



Figure 4.7. Variation in  $\delta^{13}$ C versus  $\delta^{15}$ N in A) the north basin and B) the south basin of Lake Michigan.

Note: Samples include sediment from six selected core segments at each site: surface 1 cm, 5 cm, 10 cm, 13 cm, 15 cm and 20 cm depths.

It is not clearly defined what accounts for these observations. In first place, preferential degradation of labile algal derived OM has been suggested by sediment trap experiments in Lake Michigan (Eadie et al., 1984) and also supported by Meyers and Lallier-Vergès (1999). This would result in  $\delta^{15}N$  and  $\delta^{13}C$  increasing, while the C/N ratio would decrease. Conversely, preferential degradation of C3 OM would be expected to have the opposite effect: decreasing  $\delta^{13}C$  and  $\delta^{15}N$ , with concomitant increasing C/N ratios. Neither is consistent with findings of this study, and further investigation both with field observations and laboratory experiments using OM derived from algae, C3, and C4 sources may be needed to rectify this inconsistency. But this may go towards explain why terrigenous OM can cause a greater impact than lacustrine sources.

*Cultural Eutrophication (CE) as a source:* To complete and interpreter my research results, the CE hypothesis has been investigated by comparing OC loading to sediment surface area relative to the "monolayer equivalent" (MLE).



Figure 4.8. OC vs. SA showing OC coverage relative to the MLE for all sediment core sites.

In this study, OC was significantly greater than the MLE of 1 mg/m<sup>2</sup> (Figure 4.8). The OC/SA ratios exceeded 10 mg/m<sup>2</sup> for all depositional sites and 50 mg/m<sup>2</sup> at site M50 (Figure 4.8). Only site M28 at the mid-lake, where OC was lowest and had results similar to the MLE found in oligotrophic continental shelf sediments. These results confirm that recent sediments in Lake Michigan were organic rich (particularly in Green Bay) supporting the CE hypothesis. Consequently, OM and OC levels decrease in deeper sediment with time, when lake nutrient input was lower. Another finding in support the CE is that in Lake Michigan there has been the shift in pollen from forest to farm land over time indicating a change from a forested region to open farms with concomitant increased run off resulting in a potentially large shift in OM input.

In agreement with this, the sites with high OM loading including M50, M09 and M08 have corresponding high ratios of OC:OM approaching 1:2; similar to what would be expected in new OM (Figure 4.9a). Conversely, the other sites have OC:OM ratios between 1:2 and 1:5, with sites like M24, M28 and M32 having the lowest ratios. M28 is also the site with the lowest OC and is the only site with a coverage of OC/SA approaching the MLE (Figure 4.8), as underlined previously.

A similar trend of decreasing OC relative to other components of the sediment OM can be observed in figure 4.9b. High OM sites, M09 and M08, have the highest OC:TN ratios (10:1 to 20:1), whereas most other have ratios of 2:1 to 10:1.

Therefore, I would conclude that OC is progressively mineralized in OM like N as the sediment ages.



Figure 4.9. Chart (a) Organic Carbon (OC) vs. Organic Matter (OM), and (b) OC vs. Total Nitrogen (TN) of Lake Michigan sediments.

A sediment trap study of Eadie et al. (1984) indicated that only about 6% of the pelagic OC formed in-lake reached the sediment surface of Southern Lake Michigan in 1978 (Table 4.3); approximately 85 % of the OC was oxidized in the epilimnion upper layer of the water column (~  $115g C_{org}/m^2/yr$ ).

Table 4.3. OC Flux Estimation in Lake Michigan and illustration of OM recycling within lacustrine system. Source: Data from Eadie et al. (1984) and table adapted from Meyers and Ishiwatari (1995).

Element of	Flux
C Cycle	<b>Eadie et al. (1984)</b>
	$(g C_{org}/m^2/yr)$
Primary Production (GPP)	139
Oxidation In the epilimnion (Ra+Rh)	-115
Sinking into the hypolimnion (NPP)	24
Oxidation in the hypolimnion	-16
Sinking to the sediment surface (NCP)	8
Resuspension into the hypolimnion	75



Figure 4.10. Organic carbon budget in southern Lake Michigan (Eadie et al., 1984). Boxes include  $C_{org}$  concentration (in g of C), while arrows represent fluxes (g of  $C_{org}/m^2/year$ ). Chart created by S. Bonina, 2015.

Due to the continuous oxidative alteration and degradation in the bottom of the lake, the resuspension of sedimented OM was considerable (75 g  $C_{org}/m^2/year$  of OC Flux at 100 m depth), approximately ten times the annual OC flux at the lake bottom layer (Eadie et al., 1984; Meyers et al., 1984; Meyers and Eadie, 1993). During winter season, when temperature is significantly lower, the resuspension went to 75 g  $C_{org}/m^2$ . To place resuspension in perspective, data from sediment trap studies described by Eadie et al. (1984) assumed a 100 m-deep water column in the Southern of Lake Michigan (Table 4.3 and Figure 4.10). The large quantity of resuspension is indicative of a mechanism of intimate coupling of recent sediments and the water column (Eadie et al., 1984).

In this present sediment core study, I have measured the net C sinking to the sediment surface, which represents the NPP. NPP was about 8 g  $C_{org}/m^2/yr$  in the Eadie et al. (1984) study, and this indicated that only approximately 5.7 % of NPP burried in the sediment, as OM (Figure 4.10).

A later more detailed study by Meyers and Eadie (1993) found nhanced results (Eadie et al., 1984). Based on OC cycling and relative budget, the OC loading decreased approximately 15-20% per decade in the whole lake. Later research (Meyers and Eadie, 1993) found higher results than the numbers from Eadie et al. (1984) and this study (Table 4.4). Assuming that the net OC flux limit in the upper layer was 22.6 g/m<sup>2</sup>/year in Eadie's and 3.75 g/m<sup>2</sup>/year in the present study at the two similar sites sampled in the Southern Basin, while the OC Flux was 9.9 and 3.5 g/m<sup>2</sup>/year in the two sites from the Northern Basin. This suggested that there was continuous degradation in the hypolimnion. Thus, it is difficult to estimate the net sedimentation flux of the OC in the southern basin from the available data because the high sediment resuspension rate obfuscates hypolimnion. In contrast, in the northern basin there was less resuspension. However, if it is assumed a similar 67 % hypolimnionic oxidation of OC (comparing 24 g  $C_{org}/m^2/yr$  to 8 g

 $C_{org}/m^2/yr$ , table 4.3) as in Eadie et al. (1984), we would expect a NPP of 7 g/m<sup>2</sup>/yr in the southern basin and 3.3 g/m<sup>2</sup>/yr in the northern basin.

LAKE MICHIGAN									
SITE Location/Depth	TOC	Atomic C/N	δ <sup>13</sup> C	$\delta^{15}N$	TOC Flux	Sampling/ Depositional Date			
LM /(m)/ Seg. Depth	(%)	(cm)	$(\%_{0)}$	$(\%_0)$	(g/m²/year)	(year)			
Reported literature values from water column sediment trap study of Meyers and Eadie (1993)									
SITE 4 (South Basin)									
15 m	16.0	19.8	-27.7	5.2	23.4	1980			
35 m	14.2	22.5	-28.8	ND	25.6	1980			
80 m	6.4	8.7	-26.8	3.6	22.6	1980			
120 m	4.8	10.7	-26.2	4.3	33.9	1980			
140 m	8.8	21.2	-26.6	ND	120	1980			
SITE 11 (North Basin)									
11 m	38.1	13.1	-29.2	ND	9.9	1980			
31 m	45.8	20.9	-28.1	ND	43.4	1980			
91 m	10.9	16.5	-27.5	ND	16.4	1980			
146 m	4.8	8.1	-27.4	3.3	9.9	1980			
166 m	5.7	13.3	-27.8	3.3	24.1	1980			
Measured values for s	ites in this sed	iment core study	y						
SITE 11 (South Basin)	)								
LM-11-01	2.76	6.05	-25.4	7.2	3.75	2009			
LM-11-05	2.68	7.08	-25.4	6.5	3.64	1990			
LM-11-07	2.63	7.33	-25.3	6.3	3.57	1978			
SITE 47 (North Basin)									
LM-47-01	2.97	6.31	-25.6	6.2	3.50	2009			
LM-47-05	2.60	7.38	-25.5	5.8	3.07	1986			
LM-47-07	2.36	7.05	-25.4	5.5	2.78	1972			

<b>Table 4.4.</b>	Comparison of OC deposition from	n water column s	ediment trap	study by
Meyers an	d Eadie (1993) and the present sed	iment core study.		

NB: TOC (or simply OC) = Total organic carbon (organic carbon).

Thus, it is expected that shallow-water lake sediment would be richer in OM, compared to the OM concentrations/loadings in deep lakes such as the Great Lakes and this is confirmed through experiment (Eadie et al., 1984; Cooke et al., 2001). Bioturbation or mixing of surface, biological mixing, seasonal or permanent anoxic bottom-water conditions and other processes all can

change the original sedimented OM. During recycling residues of modified OM are mixed with the new incoming OM, which can subsequently be either preserved or degraded. It is also expected that shallow water lake locations would have greater levels of disturbance.

Comparison of the organic  $\delta^{13}$ C values from sediment trap results and this study at similar locations of the southern and northern basins of Lake Michigan (Table 4.4) shows a pattern of isotopic changes consisting of a significant decrease in OM (from primary production) lost during sinking through the water column. The initial and final  $\delta^{13}$ C values were – 26 to -27 %<sub>0</sub>, similar to those determined in this study, and decrease to -29 %<sub>0</sub> in the upper water column where the OC losses are greater. This is to be expected in the photic zone, where primary productivity is greatest. According to Meyers and Eadie (1993), these outcomes of OM isotopic composition are in line with observed changes in biomarker compositions that reveal selective losses of algal components in the epilimnion water column. Isotopic variations obviously reflect progressive diagenetic reductions of algal OM and final survival of the most resilient OM fractions. There was no significant digenetic  $\delta^{13}$ C changes with depth (constant at -26 % with time and OC concentrations varied between 1 and 3%) in core sediments of Lake Michigan where the hypolimnion OM is not dominated by algae (Rea et al., 1980).

Comparing OM results in the present study to published phosphorous (P) water column and P depositional data from previous studies suggests a correlation between total phosphorus (TP) and P loading to any aquatic environment, which has long been known to stimulate primary production (Hecker et al., 2012). In lakes where P is the limiting nutrient for algal growth, the addition of P results in the stimulation of eutrophication and can cause massive algal blooms while depleting dissolved oxygen levels when the algal cells die.



Figure 4.11. Phosphorus budget in southern Lake Michigan (Eadie et al., 1984). Boxes as reservoirs include P concentration in mass (g) of P, while arrows represent fluxes (g of  $P/m^2/year$ ). Chart created by S. Bonina, 2015.

Lesht and Rockwell (1987) and Lesht et al. (1991) constructed a model of P in the water column of Lake Michigan based on the measured nutrient concentrations in the water. According to their study, the rate of phytoplankton growth and nutrient uptake was less in the northern basin of Lake Michigan than the southern in 1984, and the northern basin had less biomass (based on chorophyll-a) than the southern, but higher rate of nutrient (silica and nitrogen) uptake. They reported that the surface concentration of TP in the open water was  $4.8 \pm 0.7 \mu g/l$  in the southern basin, and  $5.6 \pm 1.7 \mu g/l$  in the northern basin. The TP concentrations measured in the 1980s reflected those from the 70s. In 1985 during the spring the nitrate (NO<sub>3</sub>) and nitrite (NO<sub>2</sub>)

nitrogen concentrations were marginally greater in the northern basin (297  $\mu$ g/l) than in the southern basin (283  $\mu$ g/l). Due to epilimnetic depletion of nitrate and nitrite nitrogen concentrations, there was a significant decrease in both northern and southern basins in 1985. TP is greater in the north of Lake Michigan, even though fluxes are higher in the south. This might be explained by different geographic conditions, i.e. there is more sunlight and higher mean temperature in the south than the north.

The USEPA mass balance modeling study on eutrophication offers an estimation of the sources, sinks, and inventory of total P in Lake Michigan (USEPA, 2005a). Internal recycling (such as settling of 7 x  $10^6$  kg/yr and sediment recycling 4 x  $10^6$  kg/yr) accounts for the bulk of P flux occurring in the Lake Michigan (figure 2.8 of the literature review chapter). A significant mass of P settles to the lake bottom, although ~60% is is recycled to the water column. The tributaries (with a loading monitored of  $1.83 \times 10^6$  kg/yr) represent the principal external total P-sources to the lake, while atmospheric loading is a relatively minor source (0.29 x  $10^6$  kg/yr). The P export at the Chicago diversion (13,000 kg/yr) is a small amount of the total P export. The best estimate using the 1994-1995 average loading is that Lake Michigan is experiencing a 5% annual reduction in P loading, which implies that there is a steady reduction in P lake concentration. Overall, P is the primary limiting nutrient for phytoplankton in Lake Michigan, while silica may limit diatoms growth.

Schelske et al. (1983) hypothesized that eutrophication in the lower Great Lakes, particularly in Lake Michigan in the early 1960's resulted from nutrient enrichment associated with initial watershed settlement and forest clearance. This hypothesis was supported by the pattern of biogenic silica in the sediments, correlated with P-loading and the silica-depletion sequence.

The silica depletion process with increased P loading results from diatom production and silica demand increasing until diatom demand production reduced silica supplies to limiting levels, causing a change in phytoplankton from diatoms to algae (which do not require silica). Indeed in Lakes Erie and Ontario the most probable cause of diatom production and silica limitation was high nutrient loading resulting from settlement during 1800's while in Lake Michigan these events occurred in mid-1900s. Further research avenue on P budget and silica depilation would be encouraged to better explain the characterization of C loadings and sources (including CE) to Lake Michigan sediment.

To validate the initial hypothesis of enrichment of OM and OC in recent time in the upper 5cm of sediment, fluxes in mg/cm<sup>2</sup>/year were calculated (via equation 20) for all measured parameters for each site by combing concentration data and radionuclide data plotted against the sediment deposition year.



Figure 4.12. OM Flux as function of sediment deposition year for each core site in Lake Michigan.

Based on Lake Michigan sediment dating and OM and OC deposition history for the last 150 years, contemporary C deposition fluxes to Lake Michigan sediment have been produced and evaluated. Recent increases of OM flux is abundantly clear (Figure 4.12). Sediment C fluxes at most sites in the Northern Chippewa Basin (M47, M41, and M32) and Mid-Lake Plateau (M24) had similar OM fluxes, although some Southern Chippewa Basin sites also had similar flux distribution (M11, M18). OC flux had a similar relationship. Site M32 had one of the highest OC fluxes (especially in 2010) compared to one the lowest OM fluxes. Given the relative similarity in OC and OM fluxes, this suggests that the OM is primarily reduced OC. Being at the southern end of the northern basin gyre, this site could be influenced by complex current and water flow patterns. To explain this further study around this location would be needed to assess if the findings were due to a localized phenomenon i.e. something may have settled on the sediment in the region causing abnormal findings or if it is connected with the position geographically.

The Green Bay site M50 was distinct in having relatively high fluxes that increased greatly since 1990. Site M09 in the south basin was significantly higher than the others for both OC and OM in years prior to 1990 and 1970 respectively. The 1980's OC flux data in M050 indicated that a change occurred. In 1977 the army core of engineers built Renards island (Kidney Island) in the Fox River. This man made Isle, which was designed to be used to dump contaminated sediment, dredged from the Fox River and other locations. In 1993 this reached its capacity; it may be that this island has caused some changes along with the dredging of the contaminated sediment.



Figure 4.13. Flux as function of sediment deposition year for each core site in Lake Michigan: (a) OC flux, (b) IC flux, (c) TN flux, and (d) BC flux.

Total loading (tons/years) of OM, OC, IC, BC, and TN to the sediment were calculated (via equation 21) by using the surface integration of the flux over the whole lake through IDW then plotted against the sediment deposition year (Figures 4.14- 4.18). Supportive raw data of loadings and other plots are reported in the appendix section (B.1 and B.2). The increase of total loading for OM (Figure 4.14) in the recent sediment is evident with 635,000 metric tons/year (= $635 \times 10^6 \text{ Kg/yr}$ ) around 2000 increasing to 690,000 mt/year (= $690 \times 10^6 \text{ Kg/yr}$ ) after 10 years in 2010. A similar trend of total OC loading is shown in figure 4.14; from 400,000 mt OM/yr (= $400 \times 10^6 \text{ Kg/yr}$ ) in 1850 to 690,000 mt OM/yr (= $690 \times 10^6 \text{ Kg/yr}$ ) in 2010. A steady increase is shown in OM and OC deposition since the 1850's, respectively: From 400,000 mt OM/yr to >685,000 mt OM/yr in Lake Michigan, and from 150,000 mt OC/yr to >335,000 mt OC/yr in Lake Michigan.



Figure 4.14. Lake Michigan Organic Matter (OM) Annual Net Loading (metric tons/year).

With respect to total OC loading (Figure 4.15), its continuous increase has shown, going from 150,000 mt OC/yr (= $150 \times 10^6 \text{ Kg/yr}$ ) in 1850, increasing constantly every decade until reaching

340,000 mt OC/yr (=340x10<sup>6</sup> Kg/yr) in 2010. Total loading and sedimentation of IC (Figure 4.16) throughout Lake Michigan was almost constant at 200,000 mt/yr (= $200x10^{6}$  Kg/yr) ± 20,000 mt/yr (= $20x10^{6}$  Kg/yr).



Figure 4.15. Lake Michigan Organic Carbon (OC) Annual Net Loading (metric tons/year).



Figure 4.16. Lake Michigan Inorganic Carbon (IC) Annual Net Loading (metric tons/year).

The column chart of BC loadings in Lake Michigan (Figure 4.17) consists of a smooth symmetric peak, showing an increase from the early industrial revolution in the mid 1800's to the 1940's, then followed by a decrease from 1950 to the present. The highest BC loading was in the 1930's and 1940's, likely as a result of war-time, fuel driven production, manufacture and shipping. The significant decrease of BC loading might be related to a decreasing production and the federal regulation of the GLWQA put in place in 1972. Due to the public concern on the water quality of all the Great Lakes, the pollution prevention policy of GLWQA likely contributed to continued decreases over time. This is a benefit to the health of Great Lakes ecosystem because BC is considered as a vector of contaminants.



Figure 4.17. Lake Michigan Black Carbon (BC) Annual Net Loading (metric tons/year).

The plot of the TN loading (Figure 4.18) has shown similar trends to the OM and OC loading in Lake Michigan. Particularly, there was an almost constant increase of TN loading with time starting from the 1850's and almost doubling by 2010.



Figure 4.18. Lake Michigan Total Nitrogen (TN) Annual Net Loading (metric tons/year).

From both a spatial and temporal view OM flux increased every decade consistently across the lake (Figure 4.19-4.21). From the 1850's (early years of industrialization) until 2010, there was an increase of OM flux to Lake Michigan sediment. Site M09 had the highest OM flux in the south basin, and M50 in the north basin. Open-lake and the remaining north basin are uniformly lower than other sites, even though OM flux in the north basin increased from 1940 site M32 was the lowest OM flux of the whole lake for the following decades. In case of additional consultation and interest, appendix C.1 includes all the GIS maps produced for this study, e.g. for each parameter (TC, TN, BC, IC) from 1850 with 10 year increment until 2010.



Figure 4.19. OM fluxes to Lake Michigan sediment over decadal increments from 1850 to 1910.



Figure 4.20. OM fluxes to Lake Michigan sediment over decadal increments from 1920 to 1980.



Figure 4.21. OM Fluxes to Lake Michigan sediment over decadal increments from 1990 to 2010.

## **4.4 Conclusion**

Overall, the results of this study demonstrate that:

- Depositional OM and OC in Lake Michigan was primarily autochthonous (lacustrine) in the past, while more recently it is derived from more allochthonous (terrestrial) sources. Particularly, the outcomes from the present study are as follows:
- Sediment samples indicate an enrichment of OC in recent surface sediment as compared to deeper samples (<15 cm). This is correlated with recent increases in PP, and is consistent with the CE hypothesis.
- OC levels are lower in the open lake compared to the Green Bay. These trends are consistent with those observed for OM and N levels (Data reported in the appendix section), and are indicative of the hypothesized effects of the enclosed region and water sources.
- 4. LM sediments have C/N ratios that are greater then or equal to the lacustrine algae endmember (C/N ratios are much lower than C3 or C4 plants). Further,  $\delta^{13}$ C is in the range of lacustrine algae and C3 land plant endmembers. This is in keeping with expected farming practices in the surrounding region.
- Together, these data suggest that algae are the dominant source of OM to Lake Michigan sediments, while possible terrigenous sources to the Southern Chippewa Basin sites M08, M09 (and M41 to the Northern Chippewa Basin).

In addition the summary of this sedimentation study on OM, OC and IC found that:

- 6. A steady increase in OM and OC deposition has occurred since the 1850's, further confirming the CE hypothesis. IC sedimentation has been relatively constant in Lake Michigan (~200,000 mt/yr = 200x10<sup>6</sup> Kg/yr) since at least the 1850's.
- Sediment OM/OC ratios 2.1±2.4 and OC/N ratios 6.4±1.6 are consistent with algal Redfield ratio for OM;
- 8. It is unclear from these data alone whether recent increases in OM and OC deposition are a signal of more rapid mineralization in recent sediments or increased OM loading.

This overview of the OM primary production and OM sources in Lake Michigan since industrialization provides a large dataset that helps better our understanding of the changes that may be occurring within the Lake. The CE hypothesis and LOMD theory cannot be fully justified within this study, though much evidence supports the CE. To gain further confirmation, the same study would be needed after a significant time frame (e.g. 20 years) to assess if the OM measured in this study has remained stable with subsequent sedimentation. Another option may be to perform laboratory observations on degradation, though these would be equally time consuming.

### **Chapter 5. Black Carbon fluxes and industrial impacts in Lake Michigan**

# **5.1 Introduction**

Black Carbon (BC) is a component of the elemental pyrogenic carbon (C) that results from pyrolized carbon produced by incomplete combustion of fossil fuels (e.g. coal, oil, and diesel), biofuels (e.g. wood, plants, forest, animal waste fires and wildfires), and biomass (e.g. agricultural wastes, cookstoves) (Hammes et al., 2007). It is ubiquitous in soil and sediment and maybe be best defined in as "a continuum from partly charred materials to highly graphitized soot particles, with no general agreement on clear boundaries of definition" (Schmidt et al., 2001). When first characterized, BC was considered composed of heterogeneous poly-aromatic carbon, but today it has been known BC includes a range of carbon components (Goldberg, 1985; Schmidt and Noack, 2000; Masiello and Druffel, 2003; Elmquist et al., 2006). Past studies have also described it as charcoal, elemental carbon, and soot but current terminology is to refer to all of these as BC. Historically BC has been released from anthropogenic activities such as cooking but with the industrial revolution concentrations have increased significantly (Wik and Natkanski, 1990). In the atmosphere, soot comprises the significant fraction of the atmospheric particulates (up to 97%), and nearly all of the carbon may be classified as soot (Nielsen, 1996; Kasparian et al., 1998; Allen et al., 1999; Rockne et al., 2000).

BC is considered a solid component of particulate matter (PM), emitted directly into the atmosphere in the form of small particles (>2.5 micrometer ( $\mu$ m) particles (PM<sub>2.5</sub>), which significantly absorbs solar energy in both infrared and visible wavelengths (Bohren and Huffman, 1983).

It is the major form and the most effective light-absorbing PM, by mass, at adsorbing light (unit of mass in the atmosphere), while other types of particles such as organic carbon (OC), sulfate (S), and nitrate usually reflect solar radiations. In comparison to carbon dioxide ( $CO_2$ ), BC is estimated to be 1 million times more effective at absorbing solar radiation (Sasser et al., 2012).



Figure 5.1. BC cycle, primary sources, emissions, aerosol processes, distribution, and importance in the climate system. Source: Adapted from Bond et al. (2013).

The absorption of solar energy by BC warms surrounding air and can alter the albedo, if deposited on ice or snow it hastens glacier melting. In the atmosphere it changes the properties (reflectivity and lifetime) of clouds and may act a nucleus for formation of ice and rain (Hansen

and Nazarenko, 2004; Andreae et al., 2005; Flanner et al., 2007). Because of all these factors, BC may alter the radioactive heat balance of the Earth both locally and globally (Kirkevåg et al., 1999; Jacobson, 2001; Menon et al., 2002; Dickens et al., 2004; Andreae et al., 2005).

There has been growing attention to BC emissions with concerns over its health effects and contaminants it may transport along with its effects on Earth system processes (Goldberg, 1985; Druffel, 2004; Shrestha et al., 2010).

BC particles are present everywhere in the atmosphere, water, snow, ice, soil, and sediment. BC is persistent and has been found in soils (Goldberg, 1985; Skjemstad et al., 1996), lacustrine and aquatic sediments (Goldberg, 1985; Wik and Renberg, 1991; Rose, 1995; Gustafsson and Gschwend, 1997) and ice (Goldberg, 1985; Chylek et al., 1992). Where deposition occurs such as in sediment and glacier ice BC can reconstruct historical input from various sources (Cass et al., 1982; Hansen et al., 1989). Under preserving conditions BC storage in sediment could be into the millions of years and its deposition may be an additional carbon store though there is still limited understanding of the process (Masiello and Druffel, 2003; Dickens et al., 2004; Lohmann et al., 2009; Huang et al., 2015). Often our understanding of environmental changes is limited and identifying deposition sites such as sediment may allow past climate and environmental changes to be identified (Cong et al., 2013).

It has been estimated that anthropogenic activates such as agriculture and cooking fires may triple pyrogenic carbon in a region (Thevenon et al., 2010). With any colonization event such as the settling of the American West a notable increase in vegetation fires are noted (Pyne and Goldammer, 1997). Because most anthropogenic fires use wet fuel while natural fires result most often from dry fuel the variation in BC type can identify anthropogenic/natural variation (Saamak, 2001).

BC is subject to atmospheric transport and may be deposited hundreds to thousands of kilometers (Km) from source. However deposition of BC is typically subject to diffusion gradient from source regions with particulate mass also subject to gradients with larger mass particles typically diffusing closer to source (Masiello and Druffel, 2003; Lohmann et al., 2009).

Aquatic transport processes may also move BC globally (Jones et al., 1997). There is a significant correlation between BC and  $CO_2$  indicating that they often are products of the same combustion processes (Hopper et al., 1994).

The chemical and physical properties of BC in the environment is subject to the material combusted, the form of combustion (oxygen to carbon ratio), and the environmental transport mechanism (Buckley et al., 2004). Determination of the source of BC and the long range transport has been investigated using surface morphologies, size distributions and chemical structure (Goldberg, 1985; Rockne et al., 2000). The great surface area to volume ratio, organic matter content and adsorption characteristics give BC the potential to adsorb semi-volatile organic compounds from the atmosphere (Rockne et al., 2000). Therefore, though the mass of BC may be less than the total carbon material in sediment it is considered likely key vector for atmospherically transported contaminants.

Globally Asia, Africa, and South America are the continents that emit the greatest amounts of BC. The primary sources of BC is from mobile sources (19%) biomass burning (35%) residential heating, and cooking (25%) and industry (19%). In 2005 the United States was the 7<sup>th</sup> largest global emitter of BC emitting approximately 5.5 million tons of PM<sub>2.5</sub> of which

~0.64 million tons (12%) was BC and about 1.7 million tons (30%) was OC. The domestic emissions represent ~8% of the global BC emissions (Lamarque et al., 2010). In developing countries the BC sources differ with 52% from mobile sources (especially diesel engines and vehicles).

Diesel engines are the greatest mobile source contributing some 93% of all mobile source emissions in 2005. Recent studies have indicated a decrease in BC emissions largely due to improved diesel engines and industrial regulations. However emerging industrial nations and population growth in less developed regions may overshadow reduction.

Studies in Lakes Michigan (Simcik et al., 1996) and Erie (Kralovec et al., 2002) have correlated fuel consumption with BC and polycyclic aromatic hydrocarbons (PAHs) loading. Previous characterization of BC, together with partitioning of HOCs to aerosols, was used to predict that BC could be a primary vector for long-range transport of PAH and PBDEs, whereas PCBs and organo-chlorine pesticides (OCPs) were more likely to remain in the gas phase (Gustafsson et al., 1996; Gustafsson and Gschwend, 1998; Ghosh et al., 2000; Rockne et al., 2000; Jonker and Koelmans, 2001; Harner and Shoeib, 2002; Jonker and Koelmans, 2002; Rockne et al., 2002; Fernández et al., 2003; Ribes et al., 2003; Rockne et al., 2003a; Rockne et al., 2004). Given that BC can be found as a range of carbon types and PAHs with the lowest octanol air partition coefficient ( $K_{OA}$ ) do not partition strongly to BC this may add additional complexity to environmental source and fate of such chemical classes. BC concentrations are greatest in locations close to large conurbations and correlated to PAH deposition in Lake Michigan. This is consistent with the hypothesis that BC may sorb PAHs thus BC may be a sink of PAHs but also concentrate PAHs from the gas phase and deposit these to the aquatic and terrestrial environment (Buckley et al., 2004). Correlation between PAHs and coal usage

indicated that coal combustion may be a primary source to Lake Michigan sediment ((Simcik et al., 1996).

Further investigation on Lake Michigan show a variation in PAH concentration and compound between the highly urbanised southern region and the more forested northern supporting the source pathway (Buckley et al. (2004), (Simcik et al., 2003). Because of the significant impact that BC may have on the sorption of particle phase SVOCs like PAHs understanding the concentration and flux within the sediment is a key to explaining the fate and transport of many harmful compounds while also giving an understanding of the historical input from industrialization around the lake (Goldberg, 1985; Karls and Christensen, 1998).

## **5.2 Materials and methods**

#### 5.2.1. Study Area:

As one of the largest lakes in the world, Lake Michigan was once considered too large for anthropogenic activity to impact, but today we know that there is widespread contamination and the implications to human and environmental health could be significant. Given its long water retention time (99 years), large surface area (52,800 km<sup>2</sup>) to depth (avg. 85 m) ratio, and small drainage basin to lake area, many Lake Michigan contaminants arrive by atmospheric exchange and deposition rather than by riverine inputs as it typically occurs with smaller water bodies. The atmospheric influence is especially apparent near urban/industrial areas, as studies have shown in the Chicago area (Hornbuckle et al., 2006). Christensen and Arora (2007) identified traffic, coke oven, and wood burning signatures in the sediment of central Lake Michigan by factor analysis of pollutant data in sediment cores and observed that the coke oven signature in particular may be linked to metropolitan Chicago and its imprint on the lake.

According to historical economic data on industrial productivity, particularly in the manufacturing sector, there have been identified industrial cities and areas (Figure 5.2) which impacted Lake Michigan ecosystem: Green Bay (WI, West-North of Lake Michigan), Grand Rapids (MI, East-Middle), Milwaukee (West-Middle), Chicago (IL, South-West), and Gary (North IN, South-East).



Figure 5.2. Industrial cities and metropolitan areas impacting Lake Michigan: Green Bay (WI, West-North of Lake Michigan), Grand Rapids (MI, East), Milwaukee (West), Chicago (IL, South-West), and Gary (IN, South). Source: Map adapted from Industrial City Initiative (ICI), Federal Reserve Bank of Chicago website.

The report of the Federal Reserve Bank of Chicago shown how the 20th century manufacturing and industries strongly influenced the environment of those cities, areas, and surrounding population. Simcik et al. (1996) reported steel industries of Chicago, IL and Gary, IN as the main causes of Lake Michigan pollution; Karls and Christensen (1998) and Christensen and Arora (2007) considered coal as a contribution to contamination as well; additionally wood and oil components have been recognized to heavily impact the entire area. Based on the amount of BC produced of various sources (coal, wood, transportation, petroleum, steel industry etc.) in the Lake Michigan area since ~1800s, historically coal was one of the key fuels in the southern Lake Michigan steel industry (Goldberg et al., 1981; Karls and Christensen, 1998; Doskey, 2001).

## 5.2.2. Sampling:

Sediment samples were collected at ten core locations around Lake Michigan in 2010 and 2011 as part of the USEPA-funded Great GLSSP, onboard the USEPA's *R/V Lake Guardian*. Details about these locations and sampling methods are presented elsewhere in specific sections (3.2 and 4.2) of chapter 3 and 4. Analytical methods and complete elemental analysis are described elsewhere (as above); the following paragraphs briefly report basic and supportive dating information and elemental analysis details for determination of BC.

### 5.2.3. Dating:

As a part of the GLSSP framework core dating was performed using measurements of <sup>210</sup>Pb measurement (Song et al., 2004; Ford, 2005). Lake Michigan sediments were evaluated in greater detail for the activity of <sup>210</sup>Pb, <sup>226</sup>Ra, <sup>7</sup>Be, and <sup>137</sup>Cs by gamma ray spectroscopy and has been discussed in detail in other publications (Corcoran, 2013; Smalley, 2013) and elsewhere in specific section (4.2) of chapter 4 of this thesis. Great care was taken in the GLSSP project to accurately date cores and variations in expected ratios and transport of sediment caused some

uncertainty in the analysis.

#### 5.2.3. Elemental analysis for BC:

Sediment samples were characterized for physicochemical properties including the solid content, bulk density, in-situ density, solid density, porosity, and the contents of organic matter (OM), organic carbon (OC), and BC, all according to the standard methods ASTM (1998a) and (1998b), and the procedures established previously (Rockne et al., 2002; Buckley et al., 2004; Li et al., 2006b), were validated, improved and developed as reported in earlier chapters. This information was needed to determine sedimentation rate, focus factor, chemical inventory, depositional fluxes and annual input rate from radionuclide data. Using an open-ended 3 cc syringe, sediment samples were volumetrically tested from mixed core sections (Buckley et al., 2004). Each sample was weighed on tared aluminum trays and dried to constant weight (105° C, 48 hr). Samples were re-weighed after drying, and the dry sediment mass, percent moisture, percent solids and OM were calculated as described in the following references (Rockne et al., 2002; Buckley et al., 2004) and in previous materials and methods sections (3.2 and 4.2). Following drying, sub-sets of the samples for OM analysis were placed in a muffle furnace and combusted (375 °C, 24 hr). Combusted samples were homogenized using a clean mortar and pestle. Using a multistage direct acidification procedure, as per developed method described in chapter 3, the inorganic carbonate (IC) in all of the sediment samples was removed for measurements of OC and BC. Particularly, BC is obtained from the TC in completely acidified samples following low temperature combustion. In acidification stage, pulverized sediment samples from all Lake Michigan were exposed to HCl solution of 10%, 6 normal (1:1 dilution of 6 N HCl into DIW) for 48 hours to remove inorganic carbonates from the OC measurement.

Measurement of BC, which operationally defined as the organic carbon remaining after low temperature oxidation, was made and the non-black carbon fraction of total organic carbon was determined from the difference. This was done to separate the highly complex BC fraction from biologically-derived OC in the sediments, named non black organic carbon (NBOC).

For determination of the elemental value of BC, 7-10 milligrams (mg) of samples were placed in pre-tared tin combustion boats (CE Elantech Inc., Lakewood, NJ, USA), sealed and weighed, then together with lab blanks, duplicates were run via automated combustion/reduction (950 °C for C and N) followed by molecular sieve gas chromatography and thermal conductivity detection using elemental analyzer (EA) Carlo Erba Flash EA1112 (ThermoQuest/CE Elantech, Lakewood, NJ, USA). Integration was conducted using area for C compared to desiccated BBOT reference standard and integrated using EAGER v5 peak integration software.

### **5.3 Results and discussion**

The acidified combusted surface ponar sediment samples (PGs) collected in 30 locations throughout Lake Michigan reported low BC concentrations (Figure 5.3), ranging from about 0.2 mg/g (M10, M20, M30 sites) in the west region of South Chippewa Basin near Chicago to circa 5mg/g (M09, M08, M11 sites) in the east of South Chippewa Basin closer to the Grand Rapids. The North Basin, which includes sites in Green Bay, Islands and Straits and Chippewa Basin, reported lower BC levels in sediment surface than the Mid-lake Plateau and east of South Chippewa Basin. Thus, the BC levels have been lower in sediment surface, in the north basin compared to the south basin of the Lake.

However, BC represents a small fraction of the total carbon, varying constantly below 0.5% for all ponar grab sites (Figure 5.3 and 5.4). As BC is generally considered to be atmospherically derived, its concentration may be governed by a range of variables that are independent of those

for other carbon sources. In full agreement with the review of Lukasewycz and Burkhard (2005), the elemental analysis indicated that OC concentrations (combined with IC concentrations as well) was the main fraction of the total carbon in Lake Michigan.



Figure 5.3. BC concentrations (mg/g) in surface sediment across Lake Michigan. Map created by S. Bonina, 2015.
Based on the elemental analysis data of Lake Michigan combusted, acidified, sediment samples, BC predominantly made up ~20%. The EA results of BC vs. OC showed three distinct clusters within the sediment, one large group with a 20:1 BC/OC ratio (prevalent in the South Chippewa Basin of Lake Michigan), the second small group below, and a group with a 10:1 BC/OC ratio and higher.



Figure 5.4. OC vs. BC in sediment surface (PGs) samples of Lake Michigan.

Comparing core sediment results for BC (Figure 5.5), South Chippewa Basin BC concentrations have been confirmed to be relatively higher compared to the rest of the Lake, in particular, M08 in the upper 8 cm of core sediment and M09 between 10 and 13 cm of core sediment. M11 and M18 (with the exception of a large peak around 7cm segment depth) are closer in value to the mean lake value. In the North Basin (Chippewa and Green Bay), all sediments appear similar and consistently lower than the South Basin. The southern basin may be impacted more heavily from urban and industrial emissions due to the proximity of numerous metropolitan and industrial areas. Most sediment samples exhibit higher BC levels in deeper

sediment, indicative of greater emissions in the past that is consistent with changes in industrial and domestic BC production, with the exclusion of M08 and M28 sites, which could not be dated.



**Figure 5.5. Black Carbon measurements: (a) BC concentrations with sediment depth and (b) BC concentrations with sediment depositional date in all Lake Michigan coring sites.** Note: M08 and M28 were not datable, thus they are not included in the lower figure 5.5b.

Based on Lake Michigan sediment dating and historical BC production estimates over the last 150 years, contemporary BC deposition fluxes to Lake Michigan sediment have been determined. Sediment BC fluxes (Figure 5.6) at most sites in the Northern Chippewa Basin (M47, M41, and M32) and Mid-Lake Plateau (M24) had similar BC fluxes, although some Southern Chippewa Basin sites also had similar flux distribution (M11, M18). A large peak of BC flux at site M18 around the 1930s may be due to a localized event in the area or it may be related to its geographical position. While it had elevated OC values, it has relatively low BC values and is not impacted by similar sources to the South Basin.



Figure 5.6. BC flux as function of sediment depositional date for each core site in Lake Michigan.

Note: M08 and M28 were not datable, thus they are not included in the figure 5.6 above.

Further sampling around these locations combined with historical information would be needed to make this determination. Investigations have already hypothesized that Southern Chippewa Basin is influenced by complex current and water flow patterns (Cahill, 1981; Eadie et al., 2008; Corcoran, 2013). Furthermore, the site M09, located in the South Chippewa Basin, was distinct in having significantly higher BC flux than the other sampled sites, with fluxes over 0.1  $mg/cm^2/yr$  from 1890 to 1970.

Sediment samples from M050 in Green Bay were similar to the North Basin and Mid-Lake Plateau in terms of BC levels. The 1940's BC flux peak in M050 indicated that a significant change occurred.

Because of different sedimentation rate at each site, BC concentrations with sediment depth (Figure 5.5a) are slightly different when compared with time (Figure 5.5.b). For instance, the large peak of site M18 around 7cm from sediment surface occurred around 1900s.

Comparison of BC fluxes from Buckley et al. (2004) with the present study has demonstrated that there was large variability between the two sediment sample sets (Figure 5.7 a and b), due to the different analysis methodology. For example, comparing the fluxes for BC, at three sites (M47, M41, M18) of Lake Michigan sediments (Table 3.5) treated with two different approaches, only acid-fuming from the earlier study of Buckley et al. (2004) were different from the direct acidification applied from this present study.

Comparing results from the present study to similar sampling locations reported by Pearson et al. (1997) and Buckley et al. (2004), in Lake Michigan sediment, BC measured after acid-fuming treatment was 8x - 10x higher than the BC measured after direct acidification treatment.



Figures 5.7. Black carbon (BC) in Lake Michigan sediment at three sites (M47, M41, M18) from (a) the earlier study of Buckley et al. (2004), (b) this present study with direct acidification applied.

Note: Locations are given in figures 5.3 or 3.1 and table 3.2. Coordinates and additional information such as sediment accumulation rates, mixing depths and focusing factor of sediment are given in table 3.5.

In all three comparable sample sites, the BC profile was generally similar, but when sediment samples were only acid-fumed the BC concentration was not significantly (95% CL) different in the upper sediment with the last 50-60 years, after reaching a peak near the 1940-50s, then diminished significantly (95% CL) until nearly 1900, and after which was quite constant to the deepest section of the sediment samples (~1750). The results of BC after acidification were less but with similar temporal trend (expect for site M18). The comparable pattern and variance in magnitude among the 3 locations may be justified through sediment mixing and focusing. Additionally, as BC is associated with industry and the burning of fossil fuel it is not surprising that BC levels were greatest in locations closer to metropolitan areas.

These patterns are consistent with studies of PAH depositional patterns at the similar locations (Doskey, 2001).

According to the more accurate methodology for IC removal applied in this study, the finding is clearly that the BC concentrations are different between the current study and those from Buckley et al. (2004) (Figure 5.7: a  $\neq$ b). The consequent implication is that, in the new protocol to remove IC via direct acidification, a significant different BC results were identified and this provides a more reliable and comprehensive understanding of all types of carbon in the Lake.



Figure 5.8. Lake Michigan Black Carbon (BC) Annual Net Loading (metric tons/year).

The column chart of BC loadings in Lake Michigan (Figure 5.8) consists of a smooth symmetric peak in the 1930's and 1940's, showing an increase from the end of the industrial revolution in the mid-1800s to a peak, then a steady decrease from 1950 to the present. The highest BC loading was in the 1930's and 1940s, possibly related to war-driven and fuel-intensive production, manufacturing and shipping. The significant decrease in BC loading might be related to decreasing production as well as the federal regulation known as Clean Water Act (CWA) put in place in 1972. Due to the public concern on the water quality of all the Great

Lakes, this pollution prevention policy of the CWA likely contributed to a constant decrease over time. The reduction in BC is a benefit to the heath of Great Lakes ecosystem because BC is a strong geosorbent and may be a vector for contaminants.

Lake Michigan BC fluxes (Figures 5.9 - 5.11) indicate that BC flux was higher (M09) in the South Basin than the other areas of Lake approximately around the 1850s, decreased during the following 30 years, increased again from 1890 until 1940s, then started significantly decreasing from the 1970s to 2010. The southern tip of Lake Michigan is clearly a BC hot-spot. While significantly lower in the North Basin, BC trends also show a general increase through the 40s then a similar steady decrease to recent times. For instance, wood percentage was high, and there was a decrease starting from mid 1960s; oil production increased from 1905 to 1995 until 2 decades ago, and many other industrial events related to air pollution occurred and impacted the health of Lake Michigan. Based on U.S. energy consumption, the BC results most closely mimic and reflect historical signals of the whole area. From historical 1850 information 1825 was the official opening of Erie Canal, this opened the Lakes to colonization and rapid expansion adding access to metals and other minerals (Finch, 1925). Lake Michigan along with the other lakes were settled during this expansion period and the clearing of the forest, occurred in the South Basin may be the cause of the peak seen in 1850. Ideally this hypothesis may be tested by analysis of PAH and pollen in the sediment as there would be evidence of wood burning and changes in pollen type, however this is not the purpose of this study.



Figure 5.9. BC fluxes to Lake Michigan sediment over decadal increments from 1850 to 1910.



Figure 5.10. BC fluxes to Lake Michigan sediment over decadal increments from 1920 to 1980.



Figure 5.11. BC fluxes to Lake Michigan sediment over decadal increments from 1990 to 2010.

### **5.4 Conclusion**

BC represents a small fraction of the total carbon, had low concentration varying across Lake Michigan. However, BC levels were greater in the south basin than the other areas of the Lake. BC concentration was similar and constant in the upper sediment with the last 50-60 years, after reaching a peak near the 1940-50s. Prior to the 1940s BC decreased significantly until 1850. As BC is generally considered to be atmospherically derived, its concentration may be governed by a range of variables that are independent of those for other carbon sources.

BC analysis for Lake Michigan adds greater understanding to complete the overview of carbon (C) concentrations and loadings to the sediment, even though a great deal of fluctuations in the amount, type, and size of C particles in this whole area may be influenced by regional, geographical and natural events.

This dataset of BC results represent an additional information set for further work on BC as a vector for SVOC deposition (PCBs vs. PBDEs) within Lake Michigan or the all five Laurentian Great Lakes; it also allows us to hypothesize the changes in anthropogenic carbon use around the Lakes.

## **Chapter 6. Heavy Metals in Lake Michigan Sediment**

#### **6.1 Introduction**

Heavy metals are defined as a subclass of the group of chemical elements of atomic number 21 or higher and with an incomplete d-shell with metallic properties and specific gravity greater than 5 mg m<sup>-3</sup>, belonging to the d-block in the periodic table (So and Lal, 2002; Chesworth, 2008). They include the transition metals, some metalloids (a mixtures of metals, and nonmetals such as arsenic (As)), lanthanides (atomic number 57 through 71) and actinides (atomic number 89 through 103). In soil and sediment, the predominant metallic elements include cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn). The heavy metals group is commonly associated with the "trace elements" (present in the lithosphere in concentrations less than  $0.1\% = 100 \text{ mg Kg}^{-1}$ ) that are specifically distinct as those elements occurring in the environment (e.g. sediment and soil) at concentrations less than 100 mg Kg<sup>-1</sup>, this categorization does not include several heavy metals such as Cr, Fe, and Mn (McLaughlin, 2002).

Heavy metal elements are grouped into three sub-classes: alkaline earth metals (such as Calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K)), lower metals (such as Mn, Fe etc.) and "trace" metals, which are quite relevant from an environmental viewpoint as often these trace elements are toxic at relatively low concentrations, therefore they have greater environmental contamination relevance.

Some heavy metals (e.g. Cr, Cu, Fe, Mn, Ni, and Zn) are necessary for metabolic function, for example they are essential micronutrients for plants and animals, whereas others (e.g. Hg and Pb) are not essential and harmful at low concentration (McLaughlin, 2002).

Limitations on a single element may affect the whole ecosystem; for example, it is estimated that Fe concentrations restrict the growth of algae in the southern oceans. In an enclosed system such as a lake changes in metals may have widespread implications.

In sediments and soils, concentrations of heavy metals can be significantly increased by human activities (McLaughlin, 2002). Fergusson (1990) identified a number of primary and secondary sources in sediment and soil (Table 6.1).

 Table 6.1. Heavy metal primary and secondary sources to soils and sediments. Source:

 Adapted from Barry and Rayment (1997)

Main Heavy Metals	Primary Source	Secondary Source
Cd	Fertilizers, Irrigation water, manures and composts, sewage biosolids (sludges)	Mine waste and effluents, nonferrous smelter waste, paint dispersal, tire wear, and waste combustion.
Cr	Manures and composts, sludges.	
Cu	Fertilizers, manures and composts, pesticides, sludges, soil amendments (lime, gypsum, etc.).	Mine waste and effluents, nonferrous smelter waste.
Fe	Irrigation water, manures and composts, sludges.	Mine waste and effluents.
Нg	Manures and composts, pesticides, sludges.	Mine waste and effluents, nonferrous smelter waste.
Mn	Manures and composts, sludges, soil amendments.	Mine waste and effluents, nonferrous smelter waste.
Ni	Manures and composts, sludges.	Mine waste and effluents, nonferrous smelter waste.
Pb	Fertilizers, manures and composts, pesticides, sludges, soil amendments.	Automobile aerosols, coal combustion, mine waste and effluents, nonferrous smelter waste, paint dispersal, waste combustion.
Zn	Fertilizers, manures and composts, pesticides, sludges, soil amendments.	Mine waste and effluents, nonferrous smelter waste, tire wear.

Acute and chronic exposure criteria protective to sensitive organisms have been established by the United States Environmental Protection Agency (USEPA, 2006). The USEPA introduced the criterion for maximum concentration (CMC) and the criterion for continuous concentration (CCC) for metals in freshwater and saltwater (Table 6.2). In terms of exposure to contaminants, the CMC is defined as the "highest concentration of a compound in surface water to which an aquatic community can be exposed briefly without resulting in a deleterious effect", thus representing an acute criterion. The CCC is considered an estimate of the "highest concentration of a compound in surface water" and that no observable effect concentration (NOEC) is found in

an aquatic community chronically exposed to a compound (USEPA, 2006).

Pollutant	Fresh	water	Salt	water			
	CMC (µg l <sup>-1</sup> )	CCC (µg l <sup>-1</sup> )	CMC (µg l <sup>-1</sup> )	CCC (µg l <sup>-1</sup> )			
Cd	2.0	0.25	40	8.8			
Cr (III)	570	74					
Cr (VI)	16	11	1,100	50			
Pb	65	2.5	210	8.1			
Ag	3.2		1.9				
As	340	150	69	36			
Hg	1.4	0.77	1.8	0.94			
CH <sub>3</sub> Hg *	1.4	0.77	1.8	0.94			
CN	22	5.2	1	1			
*According to USEPA, if a substantial portion of the mercury (Hg) in the water column is methyl mercury, this criterion will probably be under protective.							

 Table 6.2. USEPA CMC and CCC for metals in freshwater and saltwater. Source: Adapted from USEPA (2006).

In an aquatic system sediment acts as a reservoir for the majority of metals as they tend to sorb to particles, with the notable exceptions of mercury (Hg). The sediment can be a dynamic system, and affect the bioavailability of elements and compounds, that can be metals, metalloids and/or organic substances.

The Great Lakes sediment represents the endpoint for suspended solids in the watershed, and thus may serve as a record of human activities. Due to their toxicity and their typically low environmental concentration, the heavy metals in lake sediment are of concern as many human activities may concentrate and elevate these compounds above the natural levels.

There are two main concerns of sediment contamination for non-essential heavy metals. Preliminary changes from input may alter the chemical keep biological function of the natural lake habitat. Secondly, the accumulation and transformation of heavy metals within the sediment may result in them being made more bioavailable either through direct sediment uptake by bivalves or through equilibrium partitioning to the water column; either of which could allow compounds to enter the food chain. These elements or their transformation products may be toxic at environmentally relevant concentrations and thus are of concern if determined in sediment.

As anthropogenic pollutants of primarily industrial origins, heavy metals are often linked with other contaminants including POPs, PAHs and ionic species such as nitrites, nitrates, phosphates, ammonium, chlorides, fluorides and sulfates (Sauer and Tyler, 1996). Many guidelines focus on total metal concentration but this might be not sufficient to evaluate the impact of metals on the environment and organisms; as it is well known that metal speciation plays a key role on activity (Stumm and Morgan, 1996). Toxic equivalent units (TEQs) such as those for PCBs would be a more useful way of assessing the risks of metals. However measuring the true metal speciation in situ for analysis has some practical difficulties (e.g. sample preservation during sampling and analysis, particularly in the case of redox-sensitive metals, and the presence of extremely low concentrations of different metal species), and complex matrices (USEPA, 2005b). It is important to note that assuming metal speciation is invariant with time may lead to incorrect assessment of risk because metal species concentrations can change rapidly due to changing environmental conditions. In some studies it has been suggested that the pore water may be used a better factor in understanding the bioavailability of metals (Ankley et al., 1996).

Metal speciation is influenced by many factors. The main parameters that affect the chemical form of the metal in water are pH, oxidation potential, organic matter (especially dissolved organic matter (DOM)), presence of solid precipitating phases, other catalysts of heterogeneous reactivity (like iron and manganese-oxides and sulfur), acid volatile sulfides (AVS) and salinity.

Under acidic environments (pH <7) metals are more likely in the ionic form thus increasing their solubility. As a consequence ionic metal species more readily bioavailable and thus more likely to enter the food chain and be of greater toxicological relevance. Under more alkaline metals due to the form oxides and hydroxides, which precipitate with a consequential strong decrease in their digestibility. Knowledge of pH change is one the fundamental pieces needed to study water chemistry, and from there water quality and usage management (Li and Christensen, 2014).

Lake Michigan has shown to have a great buffering capacity possibly due to the bedrock being limestone but even prior to the Great Lakes Water Quality Agreement when high concentrations of acidic and basic waste material entered the lake the capacity to buffer such input was not exceeded.

The rate at which the solid phases present in sediments adsorb heavy metals can be summarized as follows:  $MnO_2 > humic acids > iron oxides > clay$ . In clay sediment such as found across the majority of Lake Michigan (Figure 6.12) the pH plays a fundamental role in the processes of adsorption of the metals on the clays, since the ion  $H_3O^+$  competes with the cations of trace elements with consequent partial release of the latter. Groups such -SiOH-, -Al (OH) 2-, -AlOH- (found in clays) and other hydroxyl groups, carboxylic and phenolic compounds, present in organic compounds are mainly responsible for the process adsorption: among these humic acids have an exchange capacity of quite high.

The content of organic substances and their decomposition products in aquatic systems is of great importance with regard to the fate of trace metals (Lietz and Galling, 1998). Organic substances and their derivatives alter the equilibrium phase partitioning of metals in solution by the reaction of complexation, with the consequent multiple effects such as increased solubility of

metals, alteration of their distribution between oxidized and reduced forms, alteration in bioavailability and therefore their toxicity, influence on the adsorption of metals on the suspended material, and influence on the stability of the metal-containing compounds.

In natural aquatic environments, the amount of dissolved organic substances depends on the balance between the production of biomass and biodegradation. The influence of organic compounds on the toxicity and accumulation of heavy metals plays a key role in eutrophic lakes or where there are organic pollutants of anthropogenic origin (with copper (Cu) being a notable exception).

The redox potential is another factor that influences the release of metals in solution by sediment (Gotoh and Patrick, 1972, 1974; Holmes et al., 1974; Millward and Moore, 1982; Gambrell et al., 1991; Patrick and Verloo, 1998; Van Ryssen et al., 1998; Soares et al., 1999; Peng et al., 2009; Brezonik and Arnold, 2011). Solubility and complex formation depend on the state of oxidation of the metal. The type of oxidizing or reducing environment alters the form in which the metal is present.

The metals most affected by redox potential changes are those characterized by having a greater number of oxidation states such as Fe, Cu, Cr and Mn; these metals participate in redox reactions that occur in the sediments, regulated by the relative stability of the oxidized or reduced species that take part in the reaction. The insoluble sulfides of many heavy metals, which were formed under conditions reduced, can then be oxidized when conditions become aerobic, prior to elemental sulfur and then to sulfate, releasing soluble ion of the metal. Therefore at low pH and under oxidising conditions, the free ions are present in greater quantities and so are usually more bioavailable. Under reducing conditions, the metals are present mainly as insoluble sulfides and are less bioavailable (Burton, 1992).

Salinity affects, directly and indirectly, the release of heavy metals from sediments overlying waters (Salomons and Förstner, 2012). With metals released in saline systems being complex chloride ions and other ligands making it less likely their adsorption on suspended particles. Within the sediment itself the oxides and hydroxides of Fe and Mn may be present in amorphous form, crystalline or microcrystalline, such as coatings of minerals or finely dispersed. The influence of salinity is negligible in marine environments where it remains relatively constant, but is important in estuarine and transitional environments where there is mixing of fresh water with saline (Salomons and Förstner, 1980). Though not a primary concern at present the Saginaw River that flows into Lake Michigan had the greatest salinity of any Great Lakes regions (1/10<sup>th</sup> that of seawater), but there are concerns that use of rock salt on roads and in industry for example has started a trend in increasing the salinity that may ultimately alter the equilibrium partitioning of metals as well as changing the whole ecosystem of the lake as a whole.

The oxidation state of the iron and manganese depends on the oxygen concentration and pH. In anoxic water these Mn and Fe are in their reduced forms such as  $Mn^{2+}$  and  $Fe^{2+}$ , while in in the presence of oxygen the oxidized forms insoluble, as  $Fe_2O_3$  (H<sub>2</sub>O) x MnO<sub>x</sub> are present (pH >7 is also needed) (Manahan, 1994). Other factors influence the state of oxidation of Fe and Mn such as the presence of inorganic ions like bicarbonates, sulfates and phosphates and the presence of organic substances containing hydroxyl or carboxyl groups, which can reduce the Fe<sup>3+</sup> and MnO. There is a complex process within the sediment that governs the bioavailability of metals to organisms and hence the potential toxicity. A single particle of sediment is complex if we imagine it on a macro scale it has craters, cave like interstices, an organic layer and a thin water film. Once a compound has been sorbed to a particle over time it may move to regions where it is less easily bioavailable. Therefore desorption with respect to changes in equilibrium partitioning between the sediment and water phase may not occur as readily. Different particles behave differently typically the finer sediments will have a greater surface area to volume ration so uptake may be greater but desorption may also be faster while carbon materials tend to have a more complex structure increasing the sorption capacity (Lebo et al., 2003).

Given the complexities within a system there are many co-factors that must be considered and this can make any conclusions difficult to justify fully. Thus, the primary metric of effectiveness used in this work will be the total metal concentration. That being said, the importance of speciation on toxicity and mobility are additional steps that should be considered and perhaps using the wider understanding of the physical and chemical properties that we have generated during this study; additional models of metal speciation may be created to estimate the type and risk that these compounds may pose to Lake Michigan ecosystem within the all Laurentian Great Lakes.

The focus of this chapter is on selected elements: Ca, Cr, Fe, K, Mn, titanium (Ti), and Zn, measured via X-ray fluorescence (XRF) on dried and untreated sediment core segment and ponar grab sediment samples, due to their importance as sediment contaminants, and described with their chemical characteristics in the table 6.3.

# Table 6.3. Chemical properties of selected heavy metals. Sources: Science Education Jefferson Lab, Website Database http://education.jlab.org/itselemental/

METALS (Symbol)	Atomic Number	Atomic Weight	Element Classification	Period Number	Group - Name	Group Usage and history
Iron (Fe)	26	55.85	Metal	4	8 - Alkali Metal	Humans have been using iron for at least 5000 years. Fe is the cheapest, one of the most abundant of all metals(5.6% of earth's crust); is primarily obtained from the minerals hematite and magnetite. Minerals taconite, limonite and siderite are other important sources. Fe as steel is used to make paper clips, skyscrapers, and so on. It helps keep plants and animals alive (e.g. chlorophyll in plants and is an essential part of hemoglobin, the substance that carries O <sub>2</sub> ).
Potassium (K)	19	39.10	Metal	4	1	Although K 8 <sup>th</sup> most abundant element on earth (2.1% of earth's crust), it is a very reactive element and is never found free in nature. K can be obtained from the minerals (e.g. sylvite, carnallite langbeinite, and polyhalite), which are often found in ancient lake and sea-beds. Caustic potash is another K source (primarily mined in Germany, New Mexico, California and Utah).
Manganese (Mn)	25	54.94	Metal	4	7	In 1774, Mn was discovered by heating the mineral pyrolusite in the presence of charcoal. Today Mn is still obtained from pyrolusite, although it is usually burned in a furnace with powdered Al or is treated with sulfuric acid to form manganese sulfate, which is then electrolyzed.
Zinc (Zn)	30	65.38	Metal	4	12	Zn compounds used for at least 2,500 yr in brass production; zinc wasn't considered as a distinct element until much later. Initially used to make coins, decorations, today, musical instruments, screws and other hardware. Zn must resist corrosion. Zn + lead for electrical components, pipes and metallic items.
Titanium (Ti)	22	47.87	Metal	4	4	Ti the 9 <sup>th</sup> most abundant element in the earth crust (0.57%)and is primarily found in the minerals rutile and sphene. Ti as strong, light metal, and Ti alloys are used in airplanes, missiles and rockets strength, due to low weight and resistance to high temperatures properties.
Chromium (Cr)	24	52.00	Metal	4	6	Cr discovered as metallic chromium by simply heating chromium oxide in a charcoal oven. Today, Cr is primarily obtained by heating the mineral chromite in the presence of Al or silicon. It is hard and very corrosion resistant.
Calcium (Ca)	20	40.08	Metal	4	2 - Alkaline Earth Metal	Ca is the 5th most abundant element in the earth's crust, but it is never found free in nature since it easily forms compounds by reacting with $O_2$ and $H_2O$ .

The specific objective was to determine the distribution of the selected heavy metals throughout Lake Michigan, and to assess the historical and current state of the lake sediment to metals and establish the current trend in heavy metal contamination (with respect to past input and if there is cause for concern at current levels).

### **6.2 Materials and methods**

Sediment samples were collected at 10 core locations around Lake Michigan. Details about these locations and sampling methods are presented elsewhere in specific sections (3.2 and 4.2) of chapter 3 and 4. Analytical methods, particularly analysis of X-Ray Fluorescence (XRF) spectroscopy, are described elsewhere in previous chapters.

### 6.3 Results and discussion

Concentrations of heavy metals in surface sediment samples and core sediment samples are summarized in Table 6.4 and Figure 6.1 for surface samples and Tables 6.5-6.7 and Figures 6.3-6.5 for cores. Greater levels were observed in the South Chippewa Basin than the other areas of the Lake. Ca concentrations were greatest at sites M11, M08 and M09 in the South Chippewa Basin almost double that compared with the North Basin. All sites in the South Chippewa behave quite constantly and suggest that the deposition of Ca in currently was most likely due to eutrophication processes.

Table 6.4. Levels of Fe, K, Ca, Zn, Ti, Cr (mg/g) in all ponar surface sediment samples (PGs) in the Green Bay, Islands and Straits, Chippewa Basin, Mid-Lake Plateau and South Chippewa Basin sections of Lake Michigan.

PG SITES	Lake Michigan Area	Fe (mg g)	K (mg/g)	Mn (mg/g)	Ca (mg/g)	Zn (mg/g)	Ti (mg/g)	Cr (mg/g)
M010	South Chippewa Basin	7.22	14.8	2.36	27.53	0.10	1.06	0.03
M020	South Chippewa Basin	8.80	17.5	1.97	41.44	0.10	1.48	0.05
M030	South Chippewa Basin	11.98	10.7	0.39	34.68	0.09	2.04	0.05
M044	Mid-Lake Plateau	18.79	31.6	0.40	105.02	0.28	2.26	0.09
M024	Mid-Lake Plateau	27.63	37.6	0.53	28.83	0.31	4.32	0.13
M032	Chippewa Basin	23.67	36.2	0.66	16.22	0.20	3.61	0.11
M088	Chippewa Basin	12.50	27.6	0.56	34.01	0.13	2.38	0.06
M050	Green Bay	16.89	25.9	1.59	19.34	0.13	3.30	0.08
M113	Green Bay	7.35	22.6	0.27	88.77	0.06	1.58	-
M120	Islands and Straits	7.10	8.75	0.17	24.74	0.04	1.27	-
M047	Chippewa Basin	11.12	24.4	0.35	16.84	0.10	2.32	0.06
M103	Chippewa Basin	21.16	30.7	0.66	21.38	0.27	3.03	0.08
M083	Chippewa Basin	25.51	38.1	0.46	15.29	0.15	3.62	0.10
M061	Mid-Lake Plateau	26.76	35.6	0.97	49.04	0.33	4.03	0.14
M048	Mid-Lake Plateau	16.08	31.7	0.28	33.32	0.09	3.22	0.06
M019	South Chippewa Basin	18.74	28.4	0.41	25.46	0.14	3.22	0.09
M018	South Chippewa Basin	20.28	30.5	0.45	26.37	0.15	3.32	0.08
M011	South Chippewa Basin	20.78	32.5	0.89	67.15	0.28	3.30	0.09
M009	South Chippewa Basin	27.52	33.3	0.61	77.95	0.28	3.91	0.11
M008	South Chippewa Basin	12.72	26.1	0.29	61.54	0.08	2.83	0.06
M002	South Chippewa Basin	18.84	8.85	0.87	56.53	0.06	0.60	0.05
M125	Islands and Straits	2.17	6.90	-	32.56	0.03	0.48	0.04
M116	Islands and Straits	4.06	17.6	0.19	19.64	0.06	0.67	-
M028	Mid-Lake Plateau	7.89	13.0	0.28	3.11	0.09	1.13	0.06
M041	Chippewa Basin	17.41	28.6	0.47	13.86	0.15	2.89	0.09

The geographical distribution of heavy metals concentration patterns is exemplified for the selected elements, Ca, Cr, Fe, K, Mn, Ca, Ti, and Zn for all surface sediments across the Lake. Figure 6.1 shows that the concentrations of the elements Ca, Fe and K are overwhelmingly greater than the other elements Ti, Zn, Cr, and Mn.



Figure 6.1. Map of Fe, Ca, K, Ti, Cr, Mn, Zn concentrations (mg/g) in Lake Michigan sediment surface samples.

Particularly, Ca results, consistent with previous findings on chemistry, composition and accumulation of Lake Michigan sediments, as discussed earlier in this thesis, are greater in the southern basin than the sites in the northern basin (with the only exception at site M113, north of Green Bay), whereas Fe and K concentrations are relatively constant across the whole lake. Fe concentrations (ranging from 25 mg/g in the upper to 11 mg/g in the bottom layers) have slight change with the time (as it appears in the chars on the left and middle of Figures 6.2 a-b), as well

as K concentrations (from 40 mg/g to 25 mg/g) around the all Lake. Given that the predominant rock strata in Lake Michigan within the Great Lake basin is limestone (CaCO<sub>3</sub>) it is not surprising to identify Ca as the primary metal.

Fe is one of the main soil particle components, which may be derived from atmospheric dust particles from the exposed soil in the southern agricultural region or agricultural run-off. It may also result from industrial activities (steel manufacturing and cement production) that dominate the southern lake (Gatz, 1975; Eisenreich, 1980; Hurley et al., 1996).

Table 6.5. Average of the concentrations (mg/g) of Ca, Cr, Fe, K, Mn, Ti, and Zn for all sediment core samples in Lake Michigan.

Lake Michigan Area	Site	Avg. Ca	Avg. Cr	Avg. Fe	Avg. K	Avg. Mn	Avg. Ti	Avg. Zn
					$(mg g^{-1})$			
Chippewa	M32	16.39	0.09	20.11	35.71	0.92	3.54	0.15
Basin	M41	22.98	0.10	16.28	38.88	0.64	3.85	0.12
	M47	32.22	0.10	17.53	39.93	0.69	4.39	0.13
Green Bay	M50	18.87	0.08	23.19	26.66	1.74	3.46	0.15
Mid-Lake Plateau	M24	24.98	0.11	24.38	37.38	0.77	4.22	0.14
	M28	29.20	0.06	14.49	30.00	0.40	2.58	0.06
South Chippewa	M08	63.02	0.10	13.36	33.73	0.36	3.71	0.08
Basin	M09	70.32	0.10	15.03	31.89	0.44	3.64	0.12
	M11	57.50	0.11	18.64	39.36	0.83	3.99	0.11
	M18	30.81	0.08	23.07	37.58	1.03	3.89	0.14

The present results indicate that among these measured heavy metals in sediment across Lake Michigan most of them were concentrated in upper layers (Tables 6.4 - 6.7). Thus increased metal concentrations might indicate emerging contamination, however it is difficult to distinguish among atmospheric, stream water, and /or groundwater inputs.

Increased Ca can be explained by water change chemistry in Lake Michigan, in particular pH change. When pH increases in the water, decreasing oxidation will form compounds that are less likely to be sorbed to the sediment. The lithophile element, Ca, indicated conservative behavior

in Lake Michigan and does not likely have relevant atmospheric contributions. Conversely, several studies (Edgington and Robbins, 1976; Cahill, 1981) have already demonstrated that anthropogenic activities had increased the flux of metals, trace elements to Lake Michigan as proved by enrichment of metals level in surface sediments. Thus, trace elements such Mn and Zn had 100% atmospheric source contribution, accumulating in the Lake from increased emissions in surrounding industrial and metropolitan areas (Southern Lake Michigan, specifically Milwaukee, Chicago, and northwest Indiana urban regions as described in figure 5.2 in the early chapter 5). The majority of trace elements within surface sediments can be attributed to atmospheric loading, much of which is anthropogenic in nature (Eisenreich, 1980).

Mn is the second most abundant heavy metal in the earth's crust. However its low reactivity and solubility limit its bioavailability. In deeper sediment, (1850s to the 1970s), Mn remains fairly constant followed by an increase in more recent years (Figure 6.2 a and b). Based on Mn physical and chemical properties, its behavior in the aquatic environment, and its sedimentary cycling (assuming that the pH in Lake Michigan is around 7-8) suggest that Mn would be present as MnO in the water column (Brezonik and Arnold, 2011). The increase noted in the sediment would indicate some changes either a pH change driving repartitioning from the water to sediment or a secondary input.

# Table 6.6. Ca, Cr, Fe, K, Mn, Ti, Zn concentrations (mg/g) at six segment depths for all coring sediment samples across Lake Michigan.

Note: Besides metal concentration, table includes site, area info and specific depositional year.

Lake Michigan	Site	Seg.	Depositional	Ca	Cr	Fe	K	Mn	Ti	Zn
Area		Depth	Year							
		(cm)		1			(mg g <sup>-1</sup> )			
Chinnewa	M32	1	2008	24.64	0.10	17.81	33.80	1.10	3.38	0.24
Dagin	11102	4	1985	22.66	0.10	20.44	32.69	1.74	3.22	0.22
Dasin		10	1923	14.28	0.08	18.80	33.43	0.76	3.49	0.16
		15	1852	12.96	0.08	19.22	39.19	0.53	3.90	0.08
		20	1796	12.89	0.09	23.07	39.30	0.68	3.75	0.10
	N/41	30	1644	11.61	0.09	20.38	37.76	0.41	3.66	0.09
	M41	5	1979	35.84	0.12	15.02	36.95	0.96	3.57	0.18
		10	1931	16.18	0.08	14.04	31.51	0.57	3.33	0.11
		15	1870	16.12	0.09	15.98	40.93	0.40	3.95	0.07
		20	1822	17.85	0.14	20.60	46.07	0.48	4.61	0.08
		30	1699	13.72	0.09	17.43	43.12	0.41	4.24	0.06
	M47	1	2009	39.91	-	15.34	37.46	1.93	5.94	0.15
		5	1986	38.59	0.12	16.63	37.29	0.05	3.94	0.19
		10	1948	30.78	0.07	14.89	35.61	0.54	3.92	0.14
		15	1901	29.18	0.12	18.75	45.47	0.58	4.51	0.09
		20	1861	26.17	0.09	19.75	43.22	0.47	4.43	0.08
		30	1763	27.78	0.10	20.62	43.27	0.05	4.30	0.07
Green Bay	M50	3	2005	24.43	0.08	22.35	27.63	2.42	3.86	0.16
		8	1985	20.12	0.08	24.74	26.98	2.01	3.72	0.16
		9	1980	19.63	0.07	23.08	25.76	1.70	3.44	0.16
		17	1920	13.93	0.08	23.49	23.90	1.28	2.86	0.16
		23	1875	14.24	0.08	26.55	29.45	1.34	3.29	0.09
		27	1841	17.21	-	16.79	27.37	0.89	3.47	0.10
Mid-Lake	M24	2	2000	27.31	0.10	30.93	33.29	2.06	3.90	0.23
Plateau		5	1972	30.01	0.15	24.77	35.17	0.80	4.28	0.23
		10	1914	27.63	0.11	26.59	39.85	0.58	4.49	0.14
		15	1839	21.44	0.11	20.82	38.04 20.07	0.40	4.00	0.07
		20	1/85	20.02	0.11	20.09	20.07 20.25	0.44	4.50	0.09
~ 1	1.600	30	1033	20.46	0.07	21.05	20.07	0.55	4.12	0.08
South	M09	l c	2009	63./5	0.11	18.55	38.97	1.4/	4.40	0.10
Chippewa		5	1991	04.15	0.07	11.49	27.03	0.25	3.20 2.27	0.10
Basin		10	1905	79.87 60.16	0.11	10.02	22.62	0.29	3.57	0.10
		13	1928	72 54	0.14	19.95	32.02 25.12	0.36	2.99	0.20
		20	1901	60.40	0.12	11.09	30.40	0.30	3.99	0.15
	M11	1	2009	58 47	0.07	17.63	36.03	1.35	3.04	0.05
		5	1990	70 54	0.11	20.23	37 79	1.33	4 00	0.10
		10	1959	93.16	0.08	16 39	35 36	0.58	3 30	0.12
		15	1922	58.63	0.00	16.08	39.88	0.56	3.81	0.13
		20	1895	26.43	0.11	19.51	43.37	0.59	4.37	0.07
		30	1825	24.89	0.11	21.18	43.96	0.55	4.64	0.07
	M19	1	2007	50.89	0.08	17.52	34.34	1.67	3.60	0.16
	1110	5	1965	65.93	0.09	21.84	32.80	2.27	3.26	0.25
		10	1888	19.58	0.08	29.99	40.32	0.71	4.24	0.12
		15	1803	13.76	0.09	24.02	40.73	0.35	4.37	0.09
		20	1743	12.04	0.08	22.38	40.45	0.39	4.19	0.09
		30	1591	12.47	0.07	20.32	37.81	0.40	3.90	0.10

Table 6.7. Ca, Cr, Fe, K, Mn, Ti, Zn concentrations (mg/g) at six segment depths of the two coring sediment samples in Lake Michigan, where radio-dating analysis was not successful. Note: Besides metal concentration, site, area info, thus table does not specific depositional year.

Lake Michigan Area	Site	Seg. Depth	Depositional Year	Ca	Cr	Fe	K	Mn	Ti	Zn
		(cm)	(date)				(mg g <sup>-1</sup> )			
Mid-Lake	M28	1	NOT DATABLE	19.62	0.06	9.17	22.36	0.47	2.17	0.64
Plateau		5		6.67	0.06	13.11	31.86	0.36	2.77	0.05
1 micun		10		9.36	0.06	14.31	30.36	0.42	2.84	0.06
		15		57.33	0.09	17.34	32.05	0.38	2.60	0.07
		20		65.27	0.06	17.78	30.64	0.41	2.22	0.06
		23		70.64	0.06	18.79	31.95	0.39	2.48	0.06
South Chippewa	M08	1	NOT DATABLE	45.40	0.10	13.97	30.13	1.16	3.28	0.11
Rasin		5		60.86	0.12	15.89	36.71	0.39	4.21	0.13
Dusin		10		74.94	0.09	13.53	35.81	0.23	3.73	0.08
		15		76.14	0.10	12.97	35.77	0.21	3.72	0.05
		20		68.94	0.12	12.74	34.75	0.18	4.10	0.05
		30		47.21	0.07	9.86	26.62	0.16	2.81	0.05

The South Chippewa Basin (at sites M11, M09, and M18; Figure 6.4) had approximately doubled the Ca concentrations; particularly sites M011 and M18 have increased in the 1900's to be similar to the other sites of the lake southern basin. This might indicate that cyanobacteria precipitation occurred (Merz, 1992) and if this is the case, the effect on Ca deposition was limited to the South Chippewa Basin. There has been concern that many inland lakes are becoming eutrophic and increases in the Ca deposition would be indicative of a greater abundance of carbonate using bacterial species. Given that the southern basin had a greater increase and the surrounding farmland that may be an input of nutrients compared to the more forested north the findings of Ca may substantiate an increase in algal species.

Schelske and Stoermer (1971) Schelske et al. (1983) advanced the hypothesis of accelerated eutrophication stimulated by pollution inputs in the lower Great Lakes, especially in Lake Michigan in the early 1960's resulted from nutrient enrichment associated with initial watershed settlement and forest clearance.

This was supported by the pattern of biogenic silica in the sediments, correlated with P-loading and the silica-depletion sequence. The silica decline and its depletion process with increased P loading were results from diatom production and silica demand increasing until diatom demand production reduced silica supplies to limiting levels, causing a change in phytoplankton from diatoms to algae (which do not require silica). In the Great Lakes, particularly in Lakes Erie and Ontario the most probable cause of diatom production and silica limitation is high nutrient loading resulting from settlement during 1800's whereas in Lake Michigan these changes occurred in a later time in mid-1900's (Schelske et al., 1983).



Figure 6.2. Fe, K, and Mn concentration as function of (a) depth and (b) time.



Figure 6.3. Zn, Ti, and Cr concentration as function of (a) depth and (b) time.



**Figure 6.4. Ca concentration as function of (a) depth and (b) time.** Note: M08 and M28 were not datable, that is because they are not included in the lower figure.

*Heavy Metals Fluxes:* Particular attention has been given to the fluxes of Fe, Zn and Cr compared to black carbon (BC; Figure 5.6). These metals can be related to coal combustion as contaminants. For example, Fe is prevalent in coal ash from high temperature pyrite combustion and/or combustion related Zn and Cr are heavy metals from industrial origins. Industrial output in the south Lake Michigan basin was initially driven with coal fired power generators so increases together with combustion and BC emissions could be correlated.

From both a spatial and temporal view, heavy metal fluxes (Figure 6.5-6.7) were quite similar every decade across Lake Michigan. From the 1850's (early years of industrialization) until 2010, in the South Chippewa Basin site M09 had the highest value of Fe flux, for example, compared to the other sites in the whole Lake. The entire northern basin and the open-lake were uniformly lower than other sites in the south basin from 1850 until 2010. Similar patterns were observed for Zn and Cr with lower levels.





Note: M08 and M28 were not datable, thus they are not included in the figure above.



Figure 6.6. Zn Flux as function of sediment depositional time for each core site in Lake Michigan.

Note: M08 and M28 were not datable, thus they are not included in the figure above.



Figure 6.7. Cr Flux as function of sediment depositional time for each core site in Lake Michigan.

Note: M08 and M28 were not datable, thus they are not included in the figure above.

*Heavy Metal Loading to Lake Michigan:* The measured fluxes were used to estimate the loading to Lake Michigan. Total loadings (metric tons/years) of the heavy metals Fe, Zn, and Cr were calculated (via equation 21) by using the surface integration of the flux over the whole lake through the modeling method of Inverse Distance Weighting (IDW). These results were then plotted against the sediment deposition year (Figures 6.8- 6.10). Neither Fe nor Zn had large changes in loading since 1850. This could indicate that anthropogenic input has not occurred, but more likely these results demonstrate that Fe is the most abundant heavy metal that any man made loadings cannot be extracted from the background input.

Total loading and sedimentation/accumulation of Fe (Figure 6.8) within sediment throughout Lake Michigan was almost constant at circa 140,000 mt/yr (= $140 \times 10^6 \text{ Kg/yr}$ ) ± 5,000 mt/yr (= $5 \times 10^6 \text{ Kg/yr}$ ).



Figure 6.8. Lake Michigan Fe Annual Net Loading (metric tons/year).

With respect to total Zn loading (Figure 6.9), its continuous increase has shown with time, going from 590 mt Zn/yr (= $590 \times 10^3$  Kg/yr) in 1850, increasing constantly until reaching 1,350 mt Zn/yr (= $1,350 \times 10^3$  Kg/yr) in the early 1970's, following by a slow decrease until 2010. The

primary use of zinc has been as a galvanizing metal in the car industry. Given the decrease observed and the period this may reflect the changes in waste discharge or potential alterations in the industrial manufacturing near the lake.



Figure 6.9. Lake Michigan Zn Annual Net Loading (metric tons/year).



Figure 6.10. Lake Michigan Cr Annual Net Loading (metric tons/year).

The major industrial use of chromium is in leather and steel plating the results here indicates that any potential anthropic input is negligible compared to natural loading. The plot of the total Cr loading (Figure 6.10) has shown a similar lack of temporal trend to those observed for the total Fe loading in Lake Michigan. There was a relatively steady loading in the range of 700 ton/yr  $(=700 \times 10^3 \text{ Kg/yr})$  from 1850's (early years of industrialization) until 2010.

Additional GIS maps have been produced for this study, e.g. for heavy metals (Ca, Cr, Fe, K, Mn, Ti, Zn) concentrations, and Fe, Zn and Cr fluxes from 1850 with 10 year increment until 2010, and are placed in the supplementary information (Appendix C.2).

There is a great degree of uncertainty in the analysis of lake sediment, by studying core sections based upon depth values i.e. 1-2cm sections individual time periods are not designated and variability from seasonal or other events may be largely averaged out (Corcoran, 2013). However strong currents (such as those in the mid-lake plateau) that result in the movement of water between the Chippewa and South Chippewa basins may alter the particle size and point of deposition (Lineback et al., 1974; Eadie et al., 1990). Shallow water and subsurface flow can resuspend sediment, as can destratification of the water column, storm events, and upwelling (Bell and Eadie, 1983; Eadie et al., 2008; Eadie et al., 1990; Plattner et al., 2006). After the breakdown of the thermocline a large amount of material from the water-sediment interface at depth less than 100 m is suspended and mixed uniformly throughout the water column (Eadie et al., 1990; Edgington and Robbins, 1990; Hawley and Lee, 1999).

Lake Michigan dry deposition loading from Chicago based on a transport and particle size was modeled and integrated using macro and micro-meteorological data and other measurements (Sievering et al., 1979). This work demonstrated that the total mass transported to the Lake by dry deposition (1-2%) was equal to or greater than wet deposition (e.g. scavenging by precipitation), as dry deposition was a continuous process, while wet deposition was sporadic. Heavy metals transport/transfer to the Lake was greater (2-20%) when the particle size
dependency on dry deposition velocity is considered.

Large concentrations in bulk deposition of those studied heavy metals indicated an influence/impact of anthropogenic activities around the perimeter of southern Lake Michigan. Since the concentrations of those heavy metals in urban air particulates were high and heavy metals had anthropogenic sources (fossil fuel, smelting, and so on), which could be associated with small size particles, their concentration would be expected to be higher near the emission source, which, in this case, it is the southern basin of Lake Michigan (Eisenreich, 1980).

Comparison of grain size fluxes in the present study has demonstrated that there was a clear consistency between clay and sand, two major constituents of Lake Michigan sediments (Figure 6.11a and b). For example, comparing the fluxes for the sediment clay particles at all sites of Lake Michigan sediments (Figure 6.11a), the results were constant from a temporal and spatial standpoint. Clay fluxes varied from ~2.6 mg/cm<sup>2</sup>/yr to ~6.8 mg/cm<sup>2</sup>/yr at all core sediment locations, with one exception being a value of 11.06 mg/cm<sup>2</sup>/yr, in the 1930s, as expected at site M09 in the eastern of South Chippewa Basin. The reason for this 1930-40 variation is not clear, storms have caused massive point loading and may simply be a cause of a storm event. Similarly, the silt fluxes (Figure 6.11b) had the same patterns of the finer clay fluxes in all the Lake (except at site M09) as above, and ranging between ~3.8 mg/cm<sup>2</sup>/yr to ~7.9 mg/cm<sup>2</sup>/yr and reaching a peak of ~18.5 mg/cm<sup>2</sup>/yr at location M09 in the 1970s.

Sand fluxes had lower values, approximately 10x lower than clay and silt fluxes, and ranging from ~0.03 mg/cm<sup>2</sup>/yr to 1.5 mg/cm<sup>2</sup>/yr (at M50 recent time). Site M09 had constantly greatest sand fluxes of the rest of Lake sites from the early industrialization in 1850 on until 1990.



Figure 6.11. Sediment flux by grain size fraction: (a) clay (<2  $\mu$ m), (b) silt (2-63  $\mu$ m), and (c) sand (>63  $\mu$ m) as function of sediment depositional year for each core site in Lake Michigan.

Note: Sand flux plot (c) has different scale from the others (a) and (b).

#### **6.4 Conclusion**

The concentrations for all heavy metals analyzed were significantly greater in the southern basin than in the northern basin. Bulk deposition of heavy metals indicated an influence of anthropogenic activities around the southern lake perimeter. The present results of heavy metals in Lake Michigan are consistent with those in past studies, which demonstrate that flux of heavy metals to Lake Michigan were primarily through enhanced atmospheric deposition with the consequent effect of increased emissions in the most industrial and urban regions surrounding southern Lake Michigan.

USEPA criteria and NOAA guidelines are to date focused on single hazards and the findings of metals here could be combined to findings of other organic contaminants such as Pb and Hg, PCBs and PAHs, for a greater understanding of the state of the lake both now and over the last century. Further characterization of Lake Michigan sediments with some modeling of the physical chemical properties could be integrated to identify the potential metal species present and thus their bioavailability and toxicity.

### **Chapter 7. Conclusions**

This thesis represents an in-depth study of organic matter (OM), total carbon (TC), organic carbon (OC), inorganic carbon (IC), and black carbon (BC) concentrations in surface and core sediments of Lake Michigan. By combining with radio-dating from the UIC department of Earth and Environment Sciences, this work was able to quantify not just spatial but temporal changes in sediment loading within the lake.

In comparison to previous studies, this work identified potential inaccuracies in early investigations and developed methods to correct these issues. The results support alternate hypotheses that could not have been validated at the time given the smaller sample sizes.

Sediment is a very complex matrix and past studies have made wide-ranging statements on a lake based upon just 1 or 2 core samples. This project has instead been to date one of the most comprehensive investigations of a single lake with samples that span the entire region of the deep water (>30m). There will always be a degree of uncertainty associated with sediment studies when a 1 cm section may depending upon the rate of sedimentation represent many decades but it is hoped that by using multiple cores homogenized at each site and sampling across a wide area we have to some degree mitigated some of this. What is presented is an environmental snapshot of the major industrialization and settlement of Lake Michigan from the perspective of carbon and metal to its sediment. Unlike other lakes in Europe or Asia for example the impacts of large scale human activity can be narrowed to a century and a half, give or take, and as such we can in a 30cm sediment core see some of these changes.

The accurate determination of OC including the method of IC removal by different pretreatments is an important topic and the focus of the method development part of this thesis prior analysis. The present research tested and developed an effective and robust standardized operating procedure for the fractionation of sediment for physical and chemical characterization. To optimize a method for complete removal of IC from Lake Michigan sediments for accurate determination of OC and  $\delta$  <sup>13</sup>C, systematic comparisons of acid treatment methods for IC removal were performed to Lake Michigan sediment samples. These results were further compared to those from a previous study by Buckley et al. (2004), that had in the past been used as a benchmark for Lake Michigan sediment carbon information. Furthermore, a method for the complete removal OM from Lake Michigan sediment for particle grain size characterization was validated, taking three existing methods of OM removal and comparing the resulting particle size distributions to those of the untreated sediment agglomerates.

From the work presented and supported by previous studies that direct acidification in lacustrine sediment is needed to remove IC. For accurate determination of TC, OC, BC, <sup>13</sup>C, and removal of the whole IC present in the sediments, aqueous direct acidification with HCl is highly recommended over the other testing methodologies used in other studies. The labor costs is increased but greater accuracy and precision of the results being the paramount goal. Determination of TN and <sup>15</sup>N does not require acidification; therefore those parameters can and should be measured on unacidified sediment samples. It must be noted that the use of HCl may cause reactions with the different type of carbonate minerals present releasing CO<sub>2</sub>, and consequently a loss of carbon may occur. Incomplete removal of IC and loss of OC during acidification are the two common procedural issues that need to be carefully addressed prior to instrumental analysis. The accurate uncompromised OC determination was possible in the case that IC was removed completely, quantitatively, and with no loss of OC. This concept is

fundamental to the whole principle of OC quantification. Applying a direct acidification method that includes the dissolution of carbonates with 10% HCl and further treatment with several rinses with deionized water and drying before measuring from this development appears to be the ideal method. However as there is some risk of loss of C from acidic reactions choice of method should be dependent on the precision required and whether OC or IC is the most important C type in that study.

In the Lake Michigan sample themselves, an enrichment of OC in recent surface sediment was identified an enrichment of OC in recent surface sediment as compared to deeper samples (<15 cm). This is correlated with recent increased primary production (PP), and is consistent with the argument that cultural eutrophication (CE) occurred. OC concentrations are less in the open lake than Green Bay. These trends are consistent with those observed for OM and N levels, and are indicative of the hypothesized effects of the enclosed region and water sources within Green Bay. Lake Michigan sediments have C/N ratios that are > lacustrine algae endmember (C/N ratios are much lower than C3 or C4 plants). Further,  $\delta^{13}$ C is in the range of lacustrine algae and C3 land plant endmembers. This is in keeping with reported farming practices in the surrounding region and suggests that some of the OM deposited to the sediment comes from the watershed. However algae are the dominant source of OM to Lake Michigan sediments, while possible terrigenous sources to the Southern Chippewa Basin (sites M08, M09; and M41 to the Northern Chippewa Basin), this is in keeping with surrounding land use. In addition the summary of this sedimentation study on OM, OC and IC found a steady increase in OM and OC deposition since the 1850's, further confirming the CE hypothesis. IC sedimentation is constant in Lake Michigan (~200,000 mt/yr =  $200 \times 10^6$  Kg/yr).

The OM primary production and OM sources in Lake Michigan since industrialization, part of this thesis, represents the most in depth of its type to date and goes a long way towards bettering our understanding of the changes that may be occurring within the Lake. The CE hypothesis and Labile Organic Matter Degradation (LOMD) theory cannot be fully justified within the scope of this study though much evidence has gone towards the CE. To gain further credence the same study would be needed after a significant time frame (e.g. 20 years) to assess if the OM measured today has remained stable with subsequent sedimentation. Another option may be to perform laboratory observations on degradation, though these would be equally time consuming.

BC it represents a small fraction of the total carbon, with low concentration varying across Lake Michigan. However, BC concentrations were greater in the South Basin. BC concentration was similar and constant in the upper sediment with the last 50-60 years, after reaching a peak near the 1940-50s. Prior to the 1940s BC decreased significantly until 1850. As BC is generally considered to be atmospherically derived, its concentration may be governed by a range of variables that are independent of those for other carbon sources.

BC analysis for Lake Michigan added greater understanding to complete the overview of C concentrations and loadings to the sediment, even though a great deal of fluctuations in the amount, type, and size of C particles in this whole area may be influenced by regional, geographical and natural events. The study of BC and the information presented here can give an overview of the changing activities around the lake and act as a proxy for historical changes over the last 150 yr.

Based upon the method development and comparison to previous studies it may be that the BC loading had in the past been over estimated. What this may imply as it has been seen as a primary vector for many semi-volatile organic compounds (SVOCs) for the removal of

compounds from the atmosphere to soil and sediments is important. If this overestimation of the mass of BC is correct then it would imply that BC is even more efficient at removal than previously estimated.

Heavy metal distribution concentrations were greatest in the southern basin. The bulk deposition of heavy metals potentially identified an influence of anthropogenic activity around the southern lake. These findings are comparable to previous though less detailed studies, which demonstrated that flux of heavy metals to the whole of Lake Michigan were evidence of atmospheric aerosol concentrations, and enhanced atmospheric deposition with the consequent effect of increased emissions in the most industrial and urban regions surrounding southern Lake Michigan.

Though metals were identified in this study further work would be needed to estimate speciation of metals and thus their potential bioavailability. Regulations such as USEPA criterion and NOAA guidelines typically focus on single hazards and the findings of metals here could be combined to findings of other organic contaminants such as lead (Pb) and mercury (Hg), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), for a greater understanding of the state of the lake both now and over the last century. Further characterization of Lake Michigan sediments with some modeling of the physical chemical properties could be integrated to identify the potential metal species present and thus their bioavailability and toxicity. This study would not be complete if it did not include cautious annotations and few comments that should be taken as future research avenue.

#### **References**

#### (Alphabetically ordered)

- Accardi-Dey, A., and Gschwend, P. M. (2003). Reinterpreting literature sorption data considering both absorption into organic carbon and adsorption onto black carbon. *Environmental Science & Technology*, *37*(1), 99-106.
- Allen, G. A., Lawrence, J., and Koutrakis, P. (1999). Field validation of a semi-continuous method for aerosol black carbon (aethalometer) and temporal patterns of summertime hourly black carbon measurements in southwestern PA. *Atmospheric Environment*, 33(5), 817-823.
- Allison, L. E. (1960). Wet-combustion apparatus and procedure for organic and inorganic carbon in soil. *Soil Science Society of America Journal*, 24(1), 36-40.
- Andreae, M. O., Jones, C. D., and Cox, P. M. (2005). Strong present-day aerosol cooling implies a hot future. *Nature*, 435(7046), 1187-1190.
- Andren, A. W., and Strand, J. W. (1981). Atmospheric deposition of particulate organic matter and polyaromatic hydrocarbons in Lake Michigan. In J. (Ed.), *Atmospheric Pollutants in Natural Waters* Ann Arbor Science, Ann Arbor.
- APHA, AWWA, and WEF. (2005). Standard Methods for the Analysis of Water and Wastewater. 21Ed. . Washington, DC.
- Astle, J. W., Gobas, F. A. P. C., Shiu, W. Y., and Mackay, D. (1987). Lake sediments as historic records of atmospheric contamination by organic chemicals.
- ASTM. (1998a). American Society for Testing and Materials. Standard test method for laboratory determination of water (moisture) content of soil and rock, ASTM D2216-92. Philadelphia, PA.
- ASTM. (1998b). American Society for Testing and Materials. Standard test method for specific gravity of soils, ASTM D854-92. Philadelphia, PA.
- Barry, G., and Rayment, G. (1997). Heavy metals and nutrients in soils and sediments of Raine Island, Great Barrier Reef. *Land Contamination & Reclamation*, 5(4), 281-286.
- Batista, F. C., McNichol, A. P., and Gerlach, D. S. (2004). The effect of different acid treatments on the radiocarbon age of sedimentary organic matter. *Abstract: OS41A-09. Eos, Transactions, American Geophysical Union*.
- Beeton, A. M., and Chandler, D. C. (1968). Limnology in North America, D.G. Frey, Ed. (Univ. of Wisconsin. Press. Madison., pp. 535-558.
- Bell, G. L., and Eadie, B. J. (1983). Variations in the distribution of suspended particles during an upwelling event in Lake Michigan in 1980. *Journal of Great Lakes Research*, 9(4), 559-567.
- Benoy, G., Cash, K., McCauley, E., and Wrona, F. (2007). Carbon dynamics in lakes of the boreal forest under a changing climate. *Environmental Reviews*, *15*(NA), 175-189.
- Bisutti, I., Hilke, I., and Raessler, M. (2004). Determination of total organic carbon–an overview of current methods. *TrAC Trends in Analytical Chemistry*, 23(10), 716-726.

- Bohren, C. F., and Huffman, D. R. (1983). Absorption and scattering by a sphere. *Absorption and Scattering of Light by Small Particles*, 82-129.
- Bond, T. C., Doherty, S. J., Fahey, D., Forster, P., Berntsen, T., DeAngelo, B., Flanner, M., Ghan, S., Kärcher, B., and Koch, D. (2013). Bounding the role of black carbon in the climate system: A scientific assessment. *Journal of Geophysical Research: Atmospheres*, 118(11), 5380-5552.
- Brenner, M., Whitmore, T. J., Curtis, J. H., Hodell, D. A., and Schelske, C. L. (1999). Stable isotope (δ13C and δ15N) signatures of sedimented organic matter as indicators of historic lake trophic state. *Journal of Paleolimnology*, 22(2), 205-221.
- Brezonik, P., and Arnold, W. (2011). *Water chemistry: an introduction to the chemistry of natural and engineered aquatic systems:* Oxford University Press.
- Brodie, C. R., Leng, M. J., Casford, J. S., Kendrick, C. P., Lloyd, J. M., Yongqiang, Z., and Bird, M. I. (2011). Evidence for bias in C and N concentrations and  $\delta$  13 C composition of terrestrial and aquatic organic materials due to pre-analysis acid preparation methods. *Chemical Geology*, 282(3), 67-83.
- Buckley, Rockne, K. J., Li, A., and Mills, W. J. (2004). Soot deposition in the Great Lakes: Implications for semi-volatile hydrophobic organic pollutant deposition. *Environmental Science & Technology*, 38(6), 1732-1739.
- Burton, G. A. (1992). Sediment collection and processing: factors affecting realism. *IN: Sediment Toxicity* Assessment. Lewis Publishers, Boca Raton, Florida. 1992. p 37-66. 1 fig, 1 tab, 203 ref.
- Cabaniss, S., Madey, G., Maurice, P., Zhou, Y., Leff, L., Wetzel, B., Leenheer, J., and Wershaw, B. (2004). Stochastic Synthesis of Natural Organic Matter. Savannah, GA.
- Cahill, R. A. (1981). Geochemistry of recent Lake Michigan sediments. Circular no. 517.
- Callender, E., Bowser, C., and Rossmann, R. (1973). *Geochemestry of Ferromanganese and Manganese carbonate crusts from Green Bay, Lake Michigan.* Paper presented at the Transactions American Geophysical Union
- Carter, M. R. (2007). Soil Sampling and Methods of Analysis (Carter Ed.): Canadian Society of Soil Science.
- Cass, G. R., Boone, P., and Macias, E. (1982). Emissions and air quality relationships for atmospheric carbon particles in Los Angeles *Particulate Carbon* (pp. 207-243): Springer.
- Caughey, M. E., and Barcelona, M. J. (1994). Improved Quantitation of Organic and Inorganic Carbon in Soils and Aquifer Materials. WMRC Reports. Waste Management and Research Center: Authority of the State of Illinois.
- Chapman, D. V., World Health, O., and Press, C. R. C. (1992). Water quality assessments: a guide to the use of biota, sediments and water in environmental monitoring.
- Chesworth, W. (2008). Encyclopedia of soil science: Springer Science & Business Media.
- Christensen, E. R., and Arora, S. (2007). Source apportionment of PAHs in sediments using factor analysis by time records: application to Lake Michigan, USA. *Water research*, *41*(1), 168-176.

- Christensen, E. R., and Chien, N.-K. (1981). Fluxes of arsenic, lead, zinc, and cadmium to Green Bay and Lake Michigan sediments. *Environmental Science & Technology*, *15*(5), 553-558.
- Christensen, E. R., and Li, A. (2014). *Physical and Chemical Processes in the Aquatic Environment*: John Wiley & Sons.
- Chylek, P., Johnson, B., and Wu, H. (1992). Black carbon concentration in a Greenland Dye 3 Ice Core. *Geophysical research letters*, *19*(19), 1951-1953.
- Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., and Middelburg, J. J. (2007). Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems*, 10(1), 172-185.
- Colman, S. M., and Foster, D. S. (1994). A sediment budget for southern Lake Michigan: source and sink models for different time intervals. *Journal of Great Lakes Research*, 20(1), 215-228.
- Cong, Z., Kang, S., Gao, S., Zhang, Y., Li, Q., and Kawamura, K. (2013). Historical trends of atmospheric black carbon on Tibetan Plateau as reconstructed from a 150-year lake sediment record. *Environmental science & technology*, 47(6), 2579-2586.
- Cooke, D., Lombardo, P., and Brant, C. (2001). Shallow and Deep Lake: Determining Succeful Management Options. *Lakeline*.
- Corcoran, M. B. (2013). Variations in sedimentation rate and sediment focusing in Lake Michigan using radionuclide profiles. (Master of Science Thesis), University of Illinois at Chicago.
- Crusius, J., and Kenna, T. C. (2007). Ensuring confidence in radionuclide-based sediment chronologies and bioturbation rates. *Estuarine, Coastal and Shelf Science*, 71(3), 537-544.
- Dean, W. E., and Fouch, T. (1983). Lacustrine environment *Carbonate Depositional Environments* (Scholle, PA; Bebout, DG; Moore, CH (pp. 97-130).
- Dean, W. E., and Gorham, E. (1998). Magnitude and significance of carbon burial in lakes, reservoirs, and peatlands. *Geology*, 26(6), 535-538.
- Dickens, A. F., Gélinas, Y., Masiello, C. A., Wakeham, S., and Hedges, J. I. (2004). Reburial of fossil organic carbon in marine sediments. *Nature*, 427(6972), 336-339.
- Dobson, H. F. H., Gilbertson, M., and Sly, P. G. (1974). A summary and comparison of nutrients and related water quality in Lakes Erie, Ontario, Huron, and Superior. *Journal of the Fisheries Board of Canada*, *31*(5), 731-738.
- Doskey, P. V. (2001). Spatial variations and chronologies of aliphatic hydrocarbons in Lake Michigan sediments. *Environmental Science & Technology*, 35(2), 247-254.
- Downing, J. A., Cole, J. J., Middelburg, J. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Prairie, Y. T., and Laube, K. A. (2008). Sediment organic carbon burial in agriculturally eutrophic impoundments over the last century. *Global biogeochemical cycles*, 22(1).
- Druffel, E. R. (2004). Comments on the importance of black carbon in the global carbon cycle. *Marine Chemistry*, 92(1), 197-200.

- Eadie, B. J., Chambers, R. L., Gardner, W. S., and Bell, G. L. (1984). Sediment trap studies in Lake Michigan: Resuspension and chemical fluxes in the southern basin. *Journal of Great Lakes Research*, 10(3), 307-321.
- Eadie, B. J., and Robbins, J. A. (2005). Composition and accumulation of recent sediments in Lake Michigan. State of Lake Michigan: Ecology, Health and Management, Ecovision World Monogr. Ser, 89-111.
- Eadie, B. J., Robbins, J. A., Klurnp, J. V., Schwab, D. J., and Edgington, D. N. (2008). Winter-spring storms and their influence on sediment resuspension, transport, and accumulation patterns in southern Lake Michigan. *Oceanography*, 21(4), 118-135.
- Eadie, B. J., Vanderploeg, H. A., Robbins, J. A., and Bell, G. L. (1990). Significance of sediment resuspension and particle settling *Large Lakes* (pp. 196-209): Springer.
- Eby, G. N. (2004). Principles of environmental geochemistry: Brooks/Cole.
- Edgington, D., and Robbins, J. (1990). Time scales of sediment focusing in large lakes as revealed by measurement of fallout Cs-137 *Large Lakes* (pp. 210-223): Springer.
- Edgington, D. N., and Robbins, J. A. (1976). Records of lead deposition in Lake Michigan sediments since 1800. *Environmental Science & Technology*, *10*(3), 266-274.
- Einsele, G., Yan, J., and Hinderer, M. (2001). Atmospheric carbon burial in modern lake basins and its significance for the global carbon budget. *Global and Planetary Change*, *30*(3), 167-195.
- Eisenreich, S. (1980). Atmospheric input of trace metals to Lake Michigan. *Water, air, and soil pollution,* 13(3), 287-301.
- Elmquist, M., Cornelissen, G., Kukulska, Z., and Gustafsson, Ö. (2006). Distinct oxidative stabilities of char versus soot black carbon: Implications for quantification and environmental recalcitrance. *Global biogeochemical cycles*, 20(2).
- Fergusson, J. E. (1990). Heavy elements: chemistry, environmental impact and health effects: Pergamon.
- Fernández, P., Carrera, G., Grimalt, J. O., Ventura, M., Camarero, L., Catalan, J., Nickus, U., Thies, H., and Psenner, R. (2003). Factors governing the atmospheric deposition of polycyclic aromatic hydrocarbons to remote areas. *Environmental Science & Technology*, 37(15), 3261-3267.
- Finch, R. G. (1925). *The story of the New York State canals: historical and commercial information*: JB Lyon Co., printers.
- Flanner, M. G., Zender, C. S., Randerson, J. T., and Rasch, P. J. (2007). Present day climate forcing and response from black carbon in snow. *Journal of Geophysical Research: Atmospheres (1984 2012), 112*(D11).
- Ford, J. (2005). Sedimentation in the Laurentian Great Lakes as Determined by Alpha Spectroscopy. MS Thesis. University of Illinois at Chicago. Fall.
- Froelich, P. N., Smart, P. L., Finlayson, B. L., and Rylands, W. D. (1980). Analysis of organic carbon in marine sediments'. *Limnol. Oceanogr*, 25(3), 564-572.

- Frye, J. C., and Shimp, N. F. (1973). *Major, minor, and trace elements in sediments of Late Pleistocene Lake Saline compared with those in Lake Michigan sediments*: Illinois State Geological Survey.
- Galy, V., Bouchez, J., and France Lanord, C. (2007). Determination of Total Organic Carbon Content and  $\delta$  13C in Carbonate - Rich Detrital Sediments. *Geostandards and Geoanalytical research*, 31(3), 199-207.
- Gambrell, R., Wiesepape, J., Patrick Jr, W., and Duff, M. (1991). The effects of pH, redox, and salinity on metal release from a contaminated sediment. *Water, air, and soil pollution*, 57(1), 359-367.
- Gatz, D. F. (1975). Pollutant aerosol deposition into southern Lake Michigan. *Water, air, and soil pollution, 5*(2), 239-251.
- Gélinas, Y., Baldock, J. A., and Hedges, J. I. (2001a). Demineralization of marine and freshwater sediments for CP/MAS 13 C NMR analysis. *Organic Geochemistry*, *32*(5), 677-693.
- Gélinas, Y., Prentice, K. M., Baldock, J. A., and Hedges, J. I. (2001b). An improved thermal oxidation method for the quantification of soot/graphitic black carbon in sediments and soils. *Environmental Science & Technology*, 35(17), 3519-3525.
- Ghosh, U., Gillette, J. S., Luthy, R. G., and Zare, R. N. (2000). Microscale location, characterization, and association of polycyclic aromatic hydrocarbons on harbor sediment particles. *Environmental Science & Technology*, 34(9), 1729-1736.
- Gobas, F. A. P. C., and MacLean, L. G. (2003). Sediment-water distribution of organic contaminants in aquatic ecosystems: The role of organic carbon mineralization. *Environmental Science & Technology*, 37(4), 735-741.
- Goldberg, E. D. (1985). Black carbon in the environment: properties and distribution. *Environmental* science and technology (USA).
- Goldberg, E. D., Hodge, V. F., Griffin, J. J., Koide, M., and Edgington, D. N. (1981). Impact of fossil fuel combustion on the sediments of Lake Michigan. *Environmental Science & Technology*, 15(4), 466-471.
- Golden, K. A., Wong, C. S., Jeremiason, J. D., Eisenreich, S. J., Sanders, G., Hallgren, J., Swackhamer, D. L., Engstrom, D. R., and Long, D. T. (1993). Accumulation and preliminary inventory of organochlorines in Great Lakes sediments. *Water Science & Technology*, 28(8-9), 19-31.
- Gotoh, S., and Patrick, W. (1972). Transformation of manganese in a waterlogged soil as affected by redox potential and pH. *Soil Science Society of America Journal*, *36*(5), 738-742.
- Gotoh, S., and Patrick, W. (1974). Transformation of iron in a waterlogged soil as influenced by redox potential and pH. *Soil Science Society of America Journal, 38*(1), 66-71.
- Griffin, J. J., and Goldberg, E. D. (1983). Impact of fossil fuel combustion on sediments of Lake Michigan: a reprise. *Environmental Science & Technology*, 17(4), 244-245.
- Gudasz, C. (2011). *Boreal lake sediments as sources and sinks of carbon*. (Doctorate of Philosophy Thesis), Uppsala Universitet.

- Guo, J., Bonina, S., Corcoran, M., Kaliappan, R., Yan, W., Chen, D., Sandy, A. L., Rockne, K. J., Sturchio, N. C., Giesy, J. P., and Li, A. (in review). Accumulation of Atrazine and Related Compounds in Sediments of Lake Michigan. *Environmental Science & Technology*.
- Gustafsson, O., and Gschwend, P. M. (1997). Soot as a strong partition medium for polycyclic aromatic hydrocarbons in aquatic systems. *Molecular markers in environmental geochemistry*, 671, 365-381.
- Gustafsson, Ö., and Gschwend, P. M. (1998). The flux of black carbon to surface sediments on the New England continental shelf. *Geochimica et Cosmochimica Acta*, 62(3), 465-472.
- Gustafsson, Ö., Haghseta, F., Chan, C., MacFarlane, J., and Gschwend, P. M. (1996). Quantification of the dilute sedimentary soot phase: implications for PAH speciation and bioavailability. *Environmental Science & Technology*, *31*(1), 203-209.
- Hakanson, L. (1980). An ecological risk index for aquatic pollution control. A sedimentological approach. *Water research*, *14*(8), 975-1001.
- Hakanson, L., and Jansson, M. (1983). Principles of Lake Sedimentology. Springer-Verlag, Berlin, Germany, 23, 243.
- Hammes, K., Schmidt, M. W., Smernik, R. J., Currie, L. A., Ball, W. P., Nguyen, T. H., Louchouarn, P., Houel, S., Gustafsson, Ö., and Elmquist, M. (2007). Comparison of quantification methods to measure fire - derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. *Global biogeochemical cycles*, 21(3).
- Hansen, A., Conway, T., Strele, L., Bodhaine, B., Thoning, K., Tans, P., and Novakov, T. (1989). Correlations among combustion effluent species at Barrow, Alaska: Aerosol black carbon, carbon dioxide, and methane. *Journal of Atmospheric Chemistry*, 9(1-3), 283-299.
- Hansen, J., and Nazarenko, L. (2004). Soot climate forcing via snow and ice albedos. *Proceedings of the National Academy of Sciences of the United States of America*, 101(2), 423-428.
- Harden, J. W., Mark, R. K., Sundquist, E. T., and Stallard, R. F. (1992). Dynamics of soil carbon during deglaciation of the Laurentide ice sheet. *Science*, 258(5090), 1921-1924.
- Harner, T., and Shoeib, M. (2002). Measurements of octanol-air partition coefficients (K OA) for polybrominated diphenyl ethers (PBDEs): Predicting partitioning in the environment. *Journal of Chemical & Engineering Data*, 47(2), 228-232.
- Harris, D., Horwáth, W. R., and van Kessel, C. (2001). Acid fumigation of soils to remove carbonates prior to total organic carbon or carbon-13 isotopic analysis. *Soil Science Society of America Journal*, 65(6), 1853-1856.
- Hawley, N., and Lee, C. H. (1999). Sediment resuspension and transport in Lake Michigan during the unstratified period. *Sedimentology*, *46*(5), 791-805.
- Hecker, M., Khim, J. S., Giesy, J. P., Li, S.-Q., and Ryu, J.-H. (2012). Seasonal dynamics of nutrient loading and chlorophyll A in a northern prairies reservoir, Saskatchewan, Canada. *Journal of Water Resource and Protection*, 4(04), 180.
- Hedges, J. I., and Keil, R. G. (1995). Sedimentary organic matter preservation: an assessment and speculative synthesis. *Marine Chemistry*, 49(2), 81-115.

Herdendorf, C. E. (1982). Large lakes of the world. Journal of Great Lakes Research, 8(3), 379-412.

- Hermanson, M. H., and Christensen, E. R. (1991). Recent sedimentation in Lake Michigan. *Journal of Great Lakes Research*, 17(1), 33-50.
- Hodell, D. A., and Schelske, C. L. (1998). Production, sedimentation, and isotopic composition of organic matter in Lake Ontario. *Limnology and Oceanography*, 43(2), 200-214.
- Holmes, C. W., Slade, E. A., and McLerran, C. (1974). Migration and redistribution of zinc and cadmium in marine estuarine system. *Environmental Science & Technology*, 8(3), 255-259.
- Hopper, J., Worthy, D., Barrie, L., and Trivett, N. (1994). Atmospheric observations of aerosol black carbon, carbon dioxide and methane in the high Arctic. *Atmospheric Environment*, 28(18), 3047-3054.
- Hornbuckle, K. C., Carlson, D. L., Swackhamer, D. L., Baker, J. E., and Eisenreich, S. J. (2006). Polychlorinated biphenyls in the Great Lakes *Persistent Organic Pollutants in the Great Lakes* (pp. 13-70): Springer.
- Hornbuckle, K. C., Green, M. L., Miller, S. M., and DePinto, J. V. (2001). Results from the Lake Michigan mass balance study: concentrations and fluxes of atmospheric polychlorinated biphenyls and trans-nonachlor. *Environmental Science & Technology*, 35(2), 278-285.
- Huang, L., Zhang, J., Wu, Y., and Wang, J. (2015). Distribution and preservation of black carbon in the East China Sea sediments: Perspectives on carbon cycling at continental margins. *Deep Sea Research Part II: Topical Studies in Oceanography*.
- Huang, W., and Weber, W. J. (1997). A distributed reactivity model for sorption by soils and sediments. 10. Relationships between desorption, hysteresis, and the chemical characteristics of organic domains. *Environmental Science & Technology*, 31(9), 2562-2569.
- Hurley, J. P., Shafer, M. M., Cowell, S. E., Overdier, J., Hughes, P. E., and Armstrong, D. E. (1996). Trace metal assessment of Lake Michigan tributaries using low-level techniques. *Environmental Science & Technology*, 30(6), 2093-2098.
- Ingalls, A. E., Aller, R. C., Lee, C., and Wakeham, S. G. (2004). Organic matter diagenesis in shallow water carbonate sediments. *Geochimica et Cosmochimica Acta*, 68(21), 4363-4379.
- Jacobson, M. Z. (2001). Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. *Nature*, 409(6821), 695-697.
- Jones, B. F., and Bowser, C. J. (1978). The mineralogy and related chemistry of lake sediments *Lakes* (pp. 179-235): Springer.
- Jones, T., Chaloner, W., and Kuhlbusch, T. (1997). Proposed bio-geological and chemical based terminology for fire-altered plant matter *Sediment records of biomass burning and global change* (pp. 9-22): Springer.
- Jonker, M. T. O., and Koelmans, A. A. (2001). Polyoxymethylene solid phase extraction as a partitioning method for hydrophobic organic chemicals in sediment and soot. *Environmental Science & Technology*, 35(18), 3742-3748.

- Jonker, M. T. O., and Koelmans, A. A. (2002). Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment: mechanistic considerations. *Environmental Science & Technology*, *36*(17), 3725-3734.
- Karls, J. F., and Christensen, E. R. (1998). Carbon particles in dated sediments from Lake Michigan, Green Bay, and tributaries. *Environmental Science & Technology*, 32(2), 225-231.
- Kasparian, J., Frejafon, E., Rambaldi, P., Yu, J., Vezin, B., Wolf, J., Ritter, P., and Viscardi, P. (1998). Characterization of urban aerosols using SEM-microscopy, X-ray analysis and Lidar measurements. *Atmospheric Environment*, 32(17), 2957-2967.
- Kaushal, S., and Binford, M. W. (1999). Relationship between C: N ratios of lake sediments, organic matter sources, and historical deforestation in Lake Pleasant, Massachusetts, USA. *Journal of Paleolimnology*, 22(4), 439-442.
- Keil, R. G., Tsamakis, E., Fuh, C. B., Giddings, J. C., and Hedges, J. I. (1994). Mineralogical and textural controls on the organic composition of coastal marine sediments: Hydrodynamic separation using SPLITT-fractionation. *Geochimica et Cosmochimica Acta*, 58(2), 879-893.
- Kelts, K., and Hsü, K. (1978). Freshwater carbonate sedimentation Lakes (pp. 295-323): Springer.
- Kirkevåg, A., Iversen, T., and Dahlback, A. (1999). On radiative effects of black carbon and sulphate aerosols. *Atmospheric Environment*, 33(17), 2621-2635.
- Komada, T., Anderson, M. R., and Dorfmeier, C. L. (2008). Carbonate removal from coastal sediments for the determination of organic carbon and its isotopic signatures,  $\delta 13C$  and  $\Delta 14C$ : comparison of fumigation and direct acidification by hydrochloric acid. *Limnology and Oceanography: Methods*, 6(6), 254-262.
- Kortelainen, P., Pajunen, H., Rantakari, M., and Saarnisto, M. (2004). A large carbon pool and small sink in boreal Holocene lake sediments. *Global Change Biology*, *10*(10), 1648-1653.
- Kralovec, A. C., Christensen, E. R., and Van Camp, R. P. (2002). Fossil fuel and wood combustion as recorded by carbon particles in Lake Erie sediments 1850-1998. *Environmental Science & Technology*, 36(7), 1405-1413.
- Kratz, T. (2009). Carbon Dinamics and Lakes *The Global Lake Ecological Observatory Network*. Center for Limnology.
- Lebo, J. A., Huckins, J. N., Petty, J. D., Cranor, W. L., and Ho, K. T. (2003). Comparisons of coarse and fine versions of two carbons for reducing the bioavailabilities of sediment-bound hydrophobic organic contaminants. *Chemosphere*, 50(10), 1309-1317.
- Lehman, J. T. (1988). Algal biomass unaltered by food-web changes in Lake Michigan.
- Lesht, B. M., Fontaine, T. D., and Dolan, D. M. (1991). Great Lakes total phosphorus model: post audit and regionalized sensitivity analysis. *Journal of Great Lakes Research*, 17(1), 3-17.
- Lesht, B. M., and Rockwell, D. C. (1987). The state of the middle Great Lakes: Results of the 1984 water quality survey of Lakes Erie, Huron, and Michigan: Argonne National Lab., IL (USA). Environmental Research Div.

- Li, A., Buckley, D. R., Ford, J. C., Mills, W. J., Rockne, K. J., and Song, W. (2004). Polybrominated diphenyl ethers in the sediments of the Great Lakes. 1. Lake Superior. *Environmental Science & Technology*, 38(12), 3286-3293.
- Li, A., Buckley, D. R., Ford, J. C., Mills, W. J., Rockne, K. J., Song, W., and Sturchio, N. C. (2005b). Polybrominated diphenyl ethers in the sediments of the Great Lakes. 2. Lakes Michigan and Huron. *Environmental Science & Technology*, *39*(10), 3474-3479.
- Li, A., and Christensen, E. R. (2014). *Physical and Chemical Processes in the Aquatic Environment*: Wiley.
- Li, A., Ford, J. C., Buckley, D. R., Mills, W. J., Rockne, K. J., Song, W., and Sturchio, N. C. (2005a). Polybrominated diphenyl ethers in the sediments of the Great Lakes. 3. Lakes Ontario and Erie. *Environmental Science & Technology*, 39(15), 5600-5605.
- Li, A., Giesy, J. P., Rockne, K. J., and Sturchio, N. (2011). Quality Management Plan for the Great Lakes Sediment Surveillance Program (GLSSP), submitted to U.S. EPA Great Lakes National Program Office (GLNPO). Quality Assurance Project Plan.
- Li, A., Rockne, K. J., Sturchio, N., Song, W., Ford, J. C., Buckley, D. R., and Mills, W. J. (2006a). Polybrominated diphenyl ethers in the sediments of the Great Lakes. 4. Influencing factors, trends, and implications. *Environmental Science & Technology*, 40(24), 7528-7534.
- Li, A., Rockne, K. J., Sturchio, N. C., Mills, W. J., Song, W., Ford, J. C., and Buckley, D. R. (2006b). Chronology of PBDE Air Deposition in the Great Lakes from Sedimentary (Division, Trans.) (Final Report ed.). Great Lake Atmospheric Deposition Program. USEPA Region V: University of Illinois at Chicago.
- Lietz, W., and Galling, G. (1998). Metals from sediments. Water research, 23(2), 247-252.
- Lim, B., and Cachier, H. (1996). Determination of black carbon by chemical oxidation and thermal treatment in recent marine and lake sediments and Cretaceous-Tertiary clays. *Chemical Geology*, *131*(1), 143-154.
- Lindeman, R. L. (1942). The trophic-dynamic aspect of ecology. *Ecology*, 23(4), 399-418.
- Lineback, J. A., Gross, D. L., and Meyer, R. P. (1974). Glacial tills under Lake Michigan. *Studies of Lake Michigan bottom sediments; no. 11.*
- Lohmann, R., Bollinger, K., Cantwell, M., Feichter, J., Fischer Bruns, I., and Zabel, M. (2009). Fluxes of soot black carbon to South Atlantic sediments. *Global biogeochemical cycles*, 23(1).
- Lohse, L., Kloosterhuis, R. T., de Stigter, H. C., Helder, W., van Raaphorst, W., and van Weering, T. C. (2000). Carbonate removal by acidification causes loss of nitrogenous compounds in continental margin sediments. *Marine Chemistry*, 69(3), 193-201.
- Lukasewycz, M. T., and Burkhard, L. P. (2005). Complete elimination of carbonates: A critical step in the accurate measurement of organic and black carbon in sediments. *Environmental toxicology and chemistry*, 24(9), 2218-2221.
- Madigan, M. T., and Martink, J. M. (2005). Methods in Microbial Ecology. Brock Biology of Microorganisms. (11th ed., pp. 593-612). Upper Saddle River, NJ07458: Pearson, Prentice Hall.

- Manahan, S. E. (1994). Environmental Chemistry, Publish by Lewis Publishers, Boca Raton. Ann Arbor, London, and Tokyo, 330.
- Masiello, C., and Druffel, E. (2003). Organic and black carbon 13C and 14C through the Santa Monica Basin sediment oxic - anoxic transition. *Geophysical research letters*, *30*(4).
- Mayer, L. M. (1995). Sedimentary organic matter preservation: an assessment and speculative synthesis—a comment. *Marine Chemistry*, 49(2), 123-126.
- McCarty, H. B., Schofield, J., Miller, K., Brent, R. N., Van Hoof, P., and Eadie, B. (2004). Results of the Lake Michigan mass balance study: polychlorinated biphenyls and trans-nonachlor data report. *USEPA*.
- McLaughlin, M. J. (2002). Heavy metals. *Encyclopedia of soil science*. *Marcel Dekker, New York*, 650-653.
- McNichol, A., Osborne, E., Gagnon, A., Fry, B., and Jones, G. (1994). TIC, TOC, DIC, DOC, PIC, POC—unique aspects in the preparation of oceanographic samples for 14 C-AMS. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 92(1), 162-165.
- Menon, S., Hansen, J., Nazarenko, L., and Luo, Y. (2002). Climate effects of black carbon aerosols in China and India. *Science*, 297(5590), 2250-2253.
- Merz, M. U. (1992). The biology of carbonate precipitation by cyanobacteria. Facies, 26(1), 81-101.
- Meybeck, M., Chapman, D. V., and Helmer, R. (1990). *Global freshwater quality; a first assessment, Global Environment Monitoring System*. Oxford: OMS.
- Meyers, P. A. (1994). Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chemical Geology*, *114*(3), 289-302.
- Meyers, P. A. (2003). Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. *Organic Geochemistry*, *34*(2), 261-289.
- Meyers, P. A., and Eadie, B. J. (1993). Sources, degradation and recycling of organic matter associated with sinking particles in Lake Michigan. *Organic Geochemistry*, 20(1), 47-56.
- Meyers, P. A., Edwards, S. J., and Eadie, B. (1980). Fatty acid and hydrocarbon content of settling sediments in Lake Michigan. *Journal of Great Lakes Research*, 6(4), 331-337.
- Meyers, P. A., and Ishiwatari, R. (1993a). The early diagenesis of organic matter in lacustrine sediments. *Organic Geochemistry* (pp. 185-209): Springer.
- Meyers, P. A., and Ishiwatari, R. (1993b). Lacustrine organic geochemistry—an overview of indicators of organic matter sources and diagenesis in lake sediments. *Organic Geochemistry*, 20(7), 867-900.
- Meyers, P. A., and Ishiwatari, R. (1995). Organic matter accumulation records in lake sediments. *Physics* and chemistry of lakes (pp. 279-328): Springer.
- Meyers, P. A., and Lallier-Vergès, E. (1999). Lacustrine sedimentary organic matter records of Late Quaternary paleoclimates. *Journal of Paleolimnology*, 21(3), 345-372.

- Meyers, P. A., Leenheer, M. J., Eaoie, B. J., and Maule, S. J. (1984). Organic geochemistry of suspended and settling particulate matter in Lake Michigan. *Geochimica et Cosmochimica Acta*, 48(3), 443-452.
- Meyers, P. A., and Teranes, J. L. (2001). Sediment organic matter *Tracking environmental change using lake sediments* (pp. 239-269): Springer.
- Miller, S. M., Sweet, C. W., DePinto, J. V., and Hornbuckle, K. C. (2000). Atrazine and nutrients in precipitation: results from the Lake Michigan mass balance study. *Environmental Science & Technology*, 34(1), 55-61.
- Millward, G., and Moore, R. (1982). The adsorption of Cu, Mn and Zn by iron oxyhydroxide in model estuarine solutions. *Water research*, *16*(6), 981-985.
- Mittal, M. (2006). *Dynamic models of multi-trophic interactions in microbial food webs*. (Doctor of Philosophy), University of Illinois at Chicago.
- Mulholland, P. J., and Elwood, J. W. (1982). The role of lake and reservoir sediments as sinks in the perturbed global carbon cycle. *Tellus*, *34*(5), 490-499.
- Næs, K., Axelman, J., Näf, C., and Broman, D. (1998). Role of soot carbon and other carbon matrices in the distribution of PAHs among particles, DOC, and the dissolved phase in the effluent and recipient waters of an aluminum reduction plant. *Environmental Science & Technology*, 32(12), 1786-1792.
- Nelson, D. W., and Sommers, L. E. (1996). Total carbon, organic carbon, and organic matter. *Methods of soil analysis. Part*, 3(3), 961-1010.
- Nielsen, T. (1996). Traffic contribution of polycyclic aromatic hydrocarbons in the center of a large city. *Atmospheric Environment, 30*(20), 3481-3490.
- Ongley, E. D. (1996). *Control of water pollution from agriculture*. Rome: Food and Agriculture Organization of the United Nations (FAO).
- Patrick, W., and Verloo, M. (1998). Distribution of soluble heavy metals between ionic and complexed forms in a saturated sediment as affected by pH and redox conditions. *Water Science and Technology*, 37(6), 165-171.
- Pearson, R. F., Swackhamer, D. L., Eisenreich, S. J., and Long, D. T. (1997). Concentrations, accumulations, and inventories of polychlorinated dibenzo-p-dioxins and dibenzofurans in sediments of the Great Lakes. *Environmental Science & Technology*, 31(10), 2903-2909.
- Peng, J.-f., Song, Y.-h., Yuan, P., Cui, X.-y., and Qiu, G.-l. (2009). The remediation of heavy metals contaminated sediment. *Journal of hazardous materials*, *161*(2), 633-640.
- Perry, E. A. (1971). *Silicate—sea water equilibria in the ocean system: a discussion*. Paper presented at the Deep Sea Research and Oceanographic Abstracts.
- Plattner, S., Mason, D. M., Leshkevich, G. A., Schwab, D. J., and Rutherford, E. S. (2006). Classifying and forecasting coastal upwellings in Lake Michigan using satellite derived temperature images and buoy data. *Journal of Great Lakes Research*, *32*(1), 63-76.

- Prahl, F. G., Bennett, J. T., and Carpenter, R. (1980). The early diagenesis of aliphatic hydrocarbons and organic matter in sedimentary particulates from Dabob Bay, Washington. *Geochimica et Cosmochimica Acta*, 44(12), 1967-1976.
- Pyne, S. J., and Goldammer, J. G. (1997). The culture of fire: an introduction to anthropogenic fire history Sediment Records of Biomass Burning and Global Change (pp. 71-114): Springer.
- Quinn, F. H. (1992). Hydraulic residence times for the Laurentian Great Lakes. *Journal of Great Lakes Research, 18*(1), 22-28.
- Rapalee, G., Trumbore, S. E., Davidson, E. A., Harden, J. W., and Veldhuis, H. (1998). Soil carbon stocks and their rates of accumulation and loss in a boreal forest landscape. *Global biogeochemical cycles*, 12(4), 687-701.
- Rea, D. K., Bourbonniere, R. A., and Meyers, P. A. (1980). Southern Lake Michigan sediments: Changes in accumulation rate, mineralogy, and organic content. *Journal of Great Lakes Research*, 6(4), 321-330.
- Ribes, S., Van Drooge, B., Dachs, J., Gustafsson, Ø., and Grimalt, J. O. (2003). Influence of soot carbon on the soil-air partitioning of polycyclic aromatic hydrocarbons. *Environmental Science & Technology*, *37*(12), 2675-2680.
- Robbins, J. A., and Edgington, D. N. (1975). Determination of recent sedimentation rates in Lake Michigan using Pb-210 and Cs-137. *Geochimica et Cosmochimica Acta*, 39(3), 285-304.
- Roberts, A. A., Palacas, J. G., and Frost, I. C. (1973). Determination of organic carbon in modern carbonate sediments. *Journal of Sedimentary Research*, 43(4).
- Rockne, K. J., and Mittal, M. (2012). Dynamic models of multi-trophic interactions in microbial food webs. *Journal of Environmental Science and Health, Part A*, 47(10), 1391-1406.
- Rockne, K. J., Shor, L. M., Kosson, D. S., Young, L. Y., and Taghon, G. L. (2004). Combined effects of contaminant desorption and toxicity on risk from PAH contaminated sediments. *Risk Analysis*, 24(5), 1109-1120.
- Rockne, K. J., Shor, L. M., Liang, W., Young, L. Y., Taghon, G. L., and Kosson, D. S. (2003a). Intraaggregate mass transport-limited bioavailability of polycyclic aromatic hydrocarbons to Mycobacterium strain PC01. *Environmental Science & Technology*, 37(8), 1545-1552.
- Rockne, K. J., Shor, L. M., Taghon, G. L., Young, L. Y., and Kosson, D. S. (2003b). Desorption kinetics for field-aged polycyclic aromatic hydrocarbons from sediments. *Environmental Science & Technology*, 37(8), 1535-1544.
- Rockne, K. J., Shor, L. M., Young, L., Taghon, G. L., and Kosson, D. S. (2002). Distributed sequestration and release of PAHs in weathered sediment: the role of sediment structure and organic carbon properties. *Environmental science & technology*, 36(12), 2636-2644.
- Rockne, K. J., Taghon, G. L., and Kosson, D. S. (2000). Pore structure of soot deposits from several combustion sources. *Chemosphere*, 41(8), 1125-1135.
- Rose, N. L. (1995). Carbonaceous particle record in lake sediments from the Arctic and other remote areas of the Northern Hemisphere. *Science of the Total Environment, 160*, 487-496.

- Rossmann, R. (1975). Chemistry of nearshore surficial sediments from southeastern Lake Michigan. *Special Report*(57), 45.
- Rossmann, R. (2006). Results of the Lake Michigan Mass Balance Project: Polychlorinated Biphenyls Modeling Report U.S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Mid-Continent Ecology Division-Duluth, Large Lakes and Rivers Forecasting Research Branch, Large Lakes Research Station, Grosse Ile, Michigan.
- Rossmann, R., Marvin, C., Painter, S., Williams, D., Richardson, V., and Van Hoof, P. (2004). Spatial and temporal trends in surface water and sediment contamination in the Laurentian Great Lakes. *Environmental Pollution*, *129*(1), 131-144.
- Ryba, S. A., and Burgess, R. M. (2002). Effects of sample preparation on the measurement of organic carbon, hydrogen, nitrogen, sulfur, and oxygen concentrations in marine sediments. *Chemosphere*, 48(1), 139-147.
- Saamak, C. F. (2001). A shift from natural to human-driven fire regime: implications for trace-gas emissions. *The Holocene*, *11*(3), 373-375.
- Sackett, D., and Martin, K. (1998). *EPA method 6200 and field portable X-ray fluorescence*. Paper presented at the A presentation developed for the EPA Technology Innovation Office and On-Site In-Sights Workshops for innovative field characterization technologies.
- Salomons, W., and Förstner, U. (1980). Trace metal analysis on polluted sediments: part II: evaluation of environmental impact. *Environmental Technology*, 1(11), 506-517.
- Salomons, W., and Förstner, U. (2012). Metals in the Hydrocycle: Springer Science & Business Media.
- Sampei, Y., and Matsumoto, E. (2008). C/N ratios in a sediment core from Nakaumi Lagoon, southwest Japan. Usefulness as an organic source indicator. *Geochemical Journal*, *35*(3), 189-205.
- Sasser, E., Hemby, J., Adlerm, K., Anenberg, S., Bailey, C., Brockman, L., Chappelli, L., DeAngelo, B., Damberg, R., Dawson, J., Neil, F., Geller, M., Hagler, G., Hemming, B., Jantarasami, L., Luben, T., Mitchell, J., Moss, J., V, R., Rice, J., Sarofim, M., Somers, J., Spells, C., Terry, S., and Witosky, M. (2012). Report to Congress on Black Carbon: Department of the Interior, Environment, and Related Agencies Appropriations Act, 2010. United States Environmental Protection Agency.
- Sauer, P., and Tyler, E. (1996). Heavy metal and volatile organic chemical removal and treatment in onsite wastewater systems. *Water, air, and soil pollution, 89*(3-4), 337-350.
- Schelske, C. L., Feldt, L. E., and Simmons, M. S. (1980). Phytoplankton and physical-chemical conditions in selected rivers and the coastal zone of Lake Michigan, 1972: Michigan Univ., Ann Arbor (USA). Great Lakes Research Div.
- Schelske, C. L., and Hodell, D. A. (1995). Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie. *Limnology and Oceanography*, 40(5), 918-929.
- Schelske, C. L., and Stoermer, E. F. (1971). Eutrophication, silica depletion, and predicted changes in algal quality in Lake Michigan. *Science*, *173*(3995), 423-424.

- Schelske, C. L., Stoermer, E. F., Conley, D. J., Robbins, J. A., and Glover, R. M. (1983). Early eutrophication in the lower Great Lakes : New Evidence from Biogenic Silica in Sediments. *Science*, 222(4621), 320-322.
- Schlesinger, W. H. (1990). Evidence from chronosequence studies for a low carbon-storage potential of soils.
- Schmidt, M. W. I., and Noack, A. G. (2000). Black carbon in soils and sediments: analysis, distribution, implications, and current challenges. *Global biogeochemical cycles*, *14*(3), 777-793.
- Schmidt, M. W. I., Skjemstad, J. O., Czimczik, C. I., Glaser, B., Prentice, K. M., Gelinas, Y., and Kuhlbusch, T. A. J. (2001). Comparative analysis of black carbon in soils. *Global biogeochemical cycles*, 15(1), 163-167.
- Schmidt, T. C., Zwank, L., Elsner, M., Berg, M., Meckenstock, R. U., and Haderlein, S. B. (2004). Compound-specific stable isotope analysis of organic contaminants in natural environments: a critical review of the state of the art, prospects, and future challenges. *Analytical and bioanalytical chemistry*, 378(2), 283-300.
- Schnitzer, M. (1978). Humic Substances: Chemistry and Reactions: in Soil Organic Matter (Ed.) Schnitzer y Khan. Soil Organic Matter (Ed. Elsevier Scientific Publishing Co., New York. p. 1-64. ed.): Elsevier, NY.
- Schubert, C. J., and Calvert, S. E. (2001). Nitrogen and carbon isotopic composition of marine and terrestrial organic matter in Arctic Ocean sediments:: implications for nutrient utilization and organic matter composition. *Deep Sea Research Part I: Oceanographic Research Papers*, 48(3), 789-810.
- Schubert, C. J., and Nielsen, B. (2000). Effects of decarbonation treatments on δ 13 C values in marine sediments. *Marine Chemistry*, 72(1), 55-59.
- Schumacher, B. A. (2002). Methods for the determination of total organic carbon (TOC) in soils and sediments. US Environmental Protection Agency: Washington DC: EPA/600/R-02/069 (NTIS PB2003-100822).
- Senesi, N., Xing, B., and Huang, P. M. (2009). Biophysico-chemical processes involving natural nonliving organic matter in environmental systems (Vol. 2): John Wiley & Sons.
- Shrestha, G., Traina, S. J., and Swanston, C. W. (2010). Black carbon's properties and role in the environment: A comprehensive review. *Sustainability*, 2(1), 294-320.
- Sievering, H., Dave, M., Dolske, D., Hughes, R., and McCoy, P. (1979). An experimental study of lake loading by aerosol transport and dry deposition in the southern Lake Michigan basin: Great Lakes national program office, US Environmental protection agency.
- Simcik, M. F., Eisenreich, S. J., Golden, K. A., Liu, S.-P., Lipiatou, E., Swackhamer, D. L., and Long, D. T. (1996). Atmospheric loading of polycyclic aromatic hydrocarbons to Lake Michigan as recorded in the sediments. *Environmental Science & Technology*, 30(10), 3039-3046.
- Simcik, M. F., Jeremiason, J. D., Lipiatou, E., and Eisenreich, S. J. (2003). Enhanced removal of hydrophobic organic contaminants by settling sediments in western Lake Superior. *Journal of Great Lakes Research*, 29(1), 41-53.

- Simpson, M. J., and Hatcher, P. G. (2004). Overestimates of black carbon in soils and sediments. *Naturwissenschaften*, *91*(9), 436-440.
- Skjemstad, J. O., Clarke, P., Taylor, J., Oades, J. M., and McClure, S. G. (1996). The chemistry and nature of protected carbon in soil. *Soil Research*, *34*(2), 251-271.
- Skoglund, R. S., and Swackhamer, D. L. (1999). Evidence for the use of organic carbon as the sorbing matrix in the modeling of PCB accumulation in phytoplankton. *Environmental Science & Technology*, 33(9), 1516-1519.
- Smalley, C. C. (2013). *Radioisotope Geochronology of Lake Superior Sediments*. University of Illinois at Chicago.
- Smith, V. H. (2003). Eutrophication of freshwater and coastal marine ecosystems a global problem. *Environmental Science and Pollution Research*, *10*(2), 126-139.
- Smith, V. H., and Schindler, D. W. (2009). Eutrophication science: where do we go from here? *Trends in Ecology & Evolution, 24*(4), 201-207.
- So, H. B., and Lal, R. (2002). Encyclopedia of Soil Science: Taylor & Francis.
- Soares, H., Boaventura, R., Machado, A., and Da Silva, J. E. (1999). Sediments as monitors of heavy metal contamination in the Ave river basin (Portugal): multivariate analysis of data. *Environmental Pollution*, *105*(3), 311-323.
- Sobek, S. (2009). Buried in lakes how carbon is stored in sediments. . Eawag News. , 10-12.
- Sobek, S., Durisch-Kaiser, E., Zurbrügg, R., Wongfun, N., Wessels, M., Pasche, N., and Wehrli, B. (2009). Organic carbon burial efficiency in lake sediments controlled by oxygen exposure time and sediment source. *Limnology and Oceanography*, 54(6), 2243-2254.
- Song, W., Ford, J. C., Li, A., Mills, W. J., Buckley, D. R., and Rockne, K. J. (2004). Polybrominated diphenyl ethers in the sediments of the Great Lakes. 1. Lake Superior. *Environmental science & technology*, 38(12), 3286-3293.
- Stable isotope laboratory of University of California Santa Cruz. (2012). *Methods of Inorganic Carbon removal from Soils and Sediments*. from <u>http://es.ucsc.edu/~silab/acidify\_seds.php</u>
- Staehr, P. A., Testa, J. M., Kemp, W. M., Cole, J. J., Sand-Jensen, K., and Smith, S. V. (2012). The metabolism of aquatic ecosystems: history, applications, and future challenges. *Aquatic Sciences*, 74(1), 15-29.
- Stallard, R. F. (1998). Terrestrial sedimentation and the carbon cycle: coupling weathering and erosion to carbon burial. *Global biogeochemical cycles*, *12*(2), 231-257.
- Stumm, W., and Morgan, J. J. (1996). *Aquatic chemistry, chemical equilibria and rates in natural waters* (3rd ed. ed.). New York, NY: John Wiley & Sons, Inc.
- Sweeney, R. A. (1993). "Dead" Sea of North America?—Lake Erie in the 1960s and 70s. *Journal of Great Lakes Research*, 19(2), 198-199.

- Talbot, M. R., and Johannessen, T. (1992). A high resolution palaeoclimatic record for the last 27,500 years in tropical West Africa from the carbon and nitrogen isotopic composition of lacustrine organic matter. *Earth and Planetary Science Letters*, *110*(1), 23-37.
- Teranes, J. L., and Bernasconi, S. M. (2000). The record of nitrate utilization and productivity limitation provided by δ15N values in lake organic matter—A study of sediment trap and core sediments from Baldeggersee, Switzerland. *Limnology and Oceanography*, 45(4), 801-813.
- Thevenon, F., Williamson, D., Bard, E., Anselmetti, F. S., Beaufort, L., and Cachier, H. (2010). Combining charcoal and elemental black carbon analysis in sedimentary archives: Implications for past fire regimes, the pyrogenic carbon cycle, and the human–climate interactions. *Global and Planetary Change*, 72(4), 381-389.
- Thomas, R., Meybeck, M., and Beim, A. (1996). Lakes. In Chapman (Ed.), *Water Quality Assessments-A Guide to Use of Biota, Sediments and Water in Environmental Monitoring-* (2 ed.): UNESCO/WHO/UNEP
- Trumbore, S. E., and Harden, J. W. (1997). Accumulation and turnover of carbon in organic and mineral soils of the BOREAS northern study area. *Journal of Geophysical Research: Atmospheres (1984–2012), 102*(D24), 28817-28830.
- Tse, T., Codling, G., Jones, P., Thoms, K., Liber, K., Giesy, J., Wheater, H., and Doig, L. (2014). Reconstructing long-term trends in municipal sewage discharge into a small lake in northern Manitoba, Canada. *Chemosphere*, 103, 299-305.
- USEPA. (2005a). Lake Michigan Mass Balance Study Loadings Report. Chicago: Great Lakes National Program Office (GLNPO). US Environmental Protection Agency.
- USEPA. (2005b). Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: Metal mixtures (Cadmium, Copper, Lead, Nickel, Silver and Zinc). Washington, DC: U. S. Environmental Protection Agency.
- USEPA. (2006). National recommended water quality criteria (pp. 25): U. S. Environmental Protection Agency
- USEPA. (2007). U.S. EPA Method 6200 "Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment".
- USEPA, and Canada. (1995). *The Great Lakes. An Environmental Atlas and Resource Book* (3th ed.): National Service Center for Environmental Publications (NSCEP).
- Van Ryssen, R., Alam, M., Goeyens, L., and Baeyens, W. (1998). The use of flux-corer experiments in the determination of heavy metal re-distribution in and of potential leaching from the sediments. *Water Science and Technology*, 37(6), 283-290.
- Verardo, D. J., Froelich, P. N., and McIntyre, A. (1990). Determination of organic carbon and nitrogen in marine sediments using the Carlo Erba NA-1500 Analyzer. *Deep Sea Research Part A. Oceanographic Research Papers*, 37(1), 157-165.
- Vette, A. F., Landis, M. S., and Keeler, G. J. (2002). Deposition and emission of gaseous mercury to and from Lake Michigan during the Lake Michigan Mass Balance Study (July, 1994-October, 1995). *Environmental Science & Technology*, 36(21), 4525-4532.

- von Wachenfeldt, E., and Tranvik, L. J. (2008). Sedimentation in boreal lakes—the role of flocculation of allochthonous dissolved organic matter in the water column. *Ecosystems*, 11(5), 803-814.
- Waples, J. T., Paddock, R., Janssen, J., Lovalvo, D., Schulze, B., Kaster, J., and Klump, J. V. (2005). High resolution bathymetry and lakebed characterization in the nearshore of western Lake Michigan. *Journal of Great Lakes Research*, 31, 64-74.
- Weaver, C. E., and Pollard, L. D. (1973). The chemistry of clay minerals. New York, NY: Elsevier.
- Wik, M., and Natkanski, J. (1990). British and Scandinavian lake sediment records of carbonaceous particles from fossil-fuel combustion. *Philosophical Transactions of the Royal Society of London*. *B, Biological Sciences*, 327(1240), 319-323.
- Wik, M., and Renberg, I. (1991). Recent atmospheric deposition in Sweden of carbonaceous particles from fossil-fuel combustion surveyed using lake sediments. *Ambio*, 289-292.
- Yamamuro, M., and Kayanne, H. (1995). Rapid direct determination of organic carbon and nitrogen in carbonate - bearing sediments with a Yanaco MT - 5 CHN analyzer. *Limnology and Oceanography*, 40(5), 1001-1005.

# Appendix A.1: Flux Raw Data

Depositional FLUX Results for all Parameters	for all sampled coring sites in Lake Michigan.
*2010M08BC : NOT DATABLE> NO FLUX	

2010-N	1009BC	FLUX (mg/cm <sup>2</sup> /yr)					
SITE	Average date of section	TC Flux	IC Flux	OC Flux	N Flux	BC Flux	OM Flux
SAMPLE ID	(Date)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)
M009BC-01	2009	1.705	0.856	0.839	0.074	0.031	1.735
M009BC-02	2006	1.665	0.898	0.750	0.072	0.036	1.602
M009BC-03	2001	1.642	0.899	0.732	0.069	0.046	1.575
M009BC-04	1997	1.761	0.905	0.830	0.070	0.063	1.552
M009BC-05	1991	1.470	0.514	0.956	0.046	0.096	1.495
M009BC-06	1986	1.659	0.865	0.852	0.059	0.087	1.465
M009BC-07	1980	1.881	1.035	0.853	0.065	0.086	1.531
M009BC-08	1974	1.799	1.062	0.808	0.066	0.080	1.572
M009BC-09	1968	1.923	1.080	0.849	0.068	0.105	1.622
M009BC-10	1963	1.941	0.803	1.126	0.061	0.120	1.675
M009BC-11	1953	1.865	0.719	1.150	0.074	0.135	1.669
M009BC-12	1941	1.912	0.990	0.961	0.052	0.164	1.637
M009BC-13	1928	1.866	0.740	1.056	0.061	0.129	1.772
M009BC-14	1915	1.874	0.726	1.117	0.038	0.109	1.641
M009BC-15	1901	1.940	1.118	0.866	0.044	0.121	1.459
M009BC-16	1888	1.919	0.917	0.937	0.046	0.100	1.487
M009BC-17	1874	1.801	0.912	0.866	0.038	0.074	1.307
M009BC-18	1860	1.714	0.973	0.707	0.033	0.056	1.219
M009BC-19	1845	1.631	1.063	0.588	0.039	0.133	1.101
M009BC-20	1830	1.629	0.907	0.726	0.031	0.070	1.172

2010-N	1011BC	FLUX (mg/cm²/yr)					
SITE	Average date of section	TC Flux	IC Flux	OC Flux	N Flux	BC Flux	OM Flux
SAMPLE ID	(Date)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)
M011BC-01	2009	0.837	0.471	0.375	0.062	0.030	1.292
M011BC-02	2005	0.829	0.472	0.360	0.061	0.018	1.235
M011BC-03	2000	0.827	0.508	0.317	0.058	0.020	1.193
M011BC-04	1995	0.820	0.510	0.315	0.055	0.018	1.168
M011BC-05	1990	0.833	0.460	0.364	0.050	0.018	1.149
M011BC-06	1984	0.839	0.440	0.392	0.048	0.030	1.007
M011BC-07	1978	0.879	0.530	0.357	0.050	0.037	0.994
M011BC-08	1972	0.877	0.495	0.382	0.048	0.042	1.054
M011BC-09	1966	0.880	0.512	0.363	0.045	0.044	0.956
M011BC-10	1959	0.871	0.457	0.422	0.041	0.031	0.907
M011BC-11	1949	0.848	0.548	0.300	0.042	0.036	0.915
M011BC-12	1935	0.816	0.505	0.322	0.045	0.035	0.931
M011BC-13	1922	0.791	0.447	0.309	0.044	0.026	0.941
M011BC-14	1909	0.652	0.387	0.267	0.043	0.021	0.926
M011BC-15	1895	1.215	0.997	0.217	0.066	0.020	0.891
M011BC-16	1882	0.557	0.305	0.247	0.044	0.023	0.781
M011BC-17	1868	0.555	0.327	0.228	0.046	0.023	0.806
M011BC-18	1854	0.566	0.337	0.247	0.048	0.025	0.811
M011BC-19	1839	0.547	0.321	0.226	0.044	0.028	0.804
M011BC-20	1825	0.565	0.320	0.253	0.046	0.033	0.845

2010-N	1018BC	FLUX (mg/cm²/yr)					
SITE	Average date of section	TC Flux	IC Flux	OC Flux	N Flux	BC Flux	OM Flux
SAMPLE ID	(Date)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)
M018BC-01	2007	0.733	0.370	0.349	0.065	0.008	1.094
M018BC-02	2000	0.713	0.364	0.337	0.066	0.011	1.110
M018BC-03	1990	0.672	0.352	0.295	0.054	0.009	1.041
M018BC-04	1978	0.693	0.363	0.305	0.054	0.010	1.049
M018BC-05	1965	0.633	0.308	0.307	0.047	0.006	0.909
M018BC-06	1950	0.624	0.371	0.254	0.045	0.008	0.716
M018BC-07	1935	0.744	0.410	0.328	0.051	0.090	0.765
M018BC-08	1919	0.660	0.336	0.306	0.051	0.068	0.735
M018BC-09	1903	0.507	0.320	0.194	0.049	0.030	0.727
M018BC-10	1888	0.406	0.263	0.148	0.048	0.018	0.643
M018BC-11	1865	0.368	0.236	0.126	0.040	0.012	0.606
M018BC-12	1834	0.406	0.300	0.107	0.050	0.009	0.671
M018BC-13	1803	0.422	0.249	0.173	0.032	0.009	0.875
M018BC-14	1773	0.419	0.269	0.152	0.031	0.011	0.671
M018BC-15	1743	0.419	0.271	0.147	0.029	0.019	0.661
M018BC-16	1712	0.407	0.232	0.171	0.034	0.020	0.661
M018BC-17	1682	0.437	0.279	0.159	0.034	0.024	0.736
M018BC-18	1653	0.374	0.229	0.146	0.029	0.017	0.695
M018BC-19	1622	0.391	0.226	0.160	0.031	0.014	0.672
M018BC-20	1591	0.408	0.238	0.161	0.033	0.014	0.700

Flux Raw D	ata (continu	ed)
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2010-N	1024BC	FLUX (mg/cm²/yr)					
SAMPLE ID	Average date of section	TC Flux	IC Flux	OC Flux	N Flux	BC Flux	OM Flux
SITE	(Date)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)
M024BC-01	2007	0.511	0.257	0.262	0.055	0.006	0.838
M024BC-02	2000	0.502	0.292	0.213	0.053	0.007	0.824
M024BC-03	1992	0.487	0.255	0.230	0.052	0.006	0.816
M024BC-04	1983	0.472	0.277	0.208	0.049	0.007	0.820
M024BC-05	1972	0.515	0.281	0.228	0.048	0.006	0.854
M024BC-06	1962	0.495	0.292	0.203	0.046	0.005	0.773
M024BC-07	1951	0.498	0.297	0.198	0.045	0.006	0.765
M024BC-08	1940	0.462	0.244	0.207	0.040	0.006	0.744
M024BC-09	1927	0.417	0.199	0.196	0.034	0.017	0.658
M024BC-10	1914	0.413	0.263	0.144	0.033	0.013	0.626
M024BC-11	1894	0.377	0.297	0.103	0.034	0.004	0.581
M024BC-12	1867	0.366	0.265	0.102	0.032	0.005	0.558
M024BC-13	1839	0.344	0.236	0.105	0.031	0.005	0.550
M024BC-14	1811	0.342	0.246	0.082	0.030	0.004	0.621
M024BC-15	1783	0.413	0.318	0.097	0.037	0.005	0.752
M024BC-16	1755	0.344	0.259	0.087	0.032	0.003	0.611
M024BC-17	1726	0.350	0.240	0.100	0.032	0.005	0.621
M024BC-18	1696	0.347	0.250	0.099	0.033	0.006	0.633
M024BC-19	1666	0.351	0.259	0.091	0.032	0.005	0.631
M024BC-20	1635	0.336	0.243	0.093	0.031	0.006	0.588

2010-N	1032BC	FLUX (mg/cm <sup>2</sup> /yr)					
SITE	Average date of section	TC Flux	IC Flux	OC Flux	N Flux	BC Flux	OM Flux
SAMPLE ID	(Date)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)
M032BC-01	2008	0.483	0.332	1.490	0.043	0.031	0.870
M032BC-02	2002	0.449	0.329	0.896	0.041	0.023	0.730
M032BC-03	1994	0.460	0.316	0.961	0.034	0.018	0.702
M032BC-04	1985	0.466	0.332	0.802	0.032	0.016	0.012
M032BC-05	1976	0.458	0.315	0.816	0.032	0.011	0.691
M032BC-06	1966	0.461	0.302	0.921	0.030	0.008	0.671
M032BC-07	1956	0.445	0.297	0.772	0.030	0.038	0.607
M032BC-08	1946	0.421	0.283	0.740	0.025	0.015	0.604
M032BC-09	1935	0.416	0.254	0.783	0.025	0.009	0.628
M032BC-10	1923	0.394	0.236	0.729	0.020	0.007	0.627
M032BC-11	1905	0.372	0.236	0.596	0.027	0.004	0.580
M032BC-12	1879	0.339	0.214	0.487	0.026	0.003	0.580
M032BC-13	1852	0.301	0.219	0.315	0.022	0.003	0.538
M032BC-14	1824	0.299	0.158	0.556	0.023	0.001	0.516
M032BC-15	1796	0.302	0.250	0.198	0.018	0.001	0.515
M032BC-16	1766	0.311	0.253	0.193	0.018	0.039	0.506
M032BC-17	1736	0.314	0.248	0.237	0.020	0.037	0.492
M032BC-18	1706	0.317	0.261	0.203	0.016	0.026	0.533
M032BC-19	1675	0.309	0.234	0.253	0.013	0.026	0.527
M032BC-20	1644	0.312	0.247	0.229	0.011	0.024	0.510

2010-N	1047BC	FLUX (mg/cm²/yr)					
SITE	Average date of section	TC Flux	IC Flux	OC Flux	N Flux	BC Flux	OM Flux
SAMPLE ID	(Date)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)
M047BC-01	2009	0.623	0.286	0.350	0.055	0.021	1.052
M047BC-02	2004	0.571	0.253	0.278	0.051	0.017	0.997
M047BC-03	1999	0.582	0.296	0.290	0.046	0.024	0.950
M047BC-04	1993	0.576	0.294	0.283	0.045	0.020	0.925
M047BC-05	1986	0.541	0.187	0.307	0.038	0.018	0.903
M047BC-06	1979	0.510	0.246	0.283	0.040	0.024	0.894
M047BC-07	1972	0.594	0.315	0.278	0.039	0.034	0.855
M047BC-08	1964	0.592	0.299	0.291	0.036	0.031	0.833
M047BC-09	1956	0.593	0.332	0.269	0.035	0.035	0.816
M047BC-10	1948	0.536	0.241	0.300	0.034	0.052	0.844
M047BC-11	1936	0.537	0.289	0.248	0.033	0.053	0.803
M047BC-12	1919	0.526	0.277	0.254	0.032	0.049	0.770
M047BC-13	1901	0.464	0.269	0.199	0.026	0.034	0.679
M047BC-14	1881	0.437	0.266	0.171	0.027	0.031	0.622
M047BC-15	1861	0.437	0.257	0.184	0.026	0.030	0.635
M047BC-16	1842	0.418	0.282	0.145	0.027	0.026	0.566
M047BC-17	1823	0.424	0.271	0.146	0.027	0.026	0.599
M047BC-18	1803	0.429	0.286	0.145	0.027	0.027	0.590
M047BC-19	1783	0.414	0.272	0.151	0.025	0.023	0.628
M047BC-20	1763	0.431	0.255	0.172	0.025	0.025	0.599

2010-N	1050BC	FLUX (mg/cm <sup>2</sup> /yr)					
SAMPLE ID	Average date of section	TC Flux	IC Flux	OC Flux	N Flux	BC Flux	OM Flux
SITE	(Date)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)
M050BC-01	2010	1.021	0.221	0.823	0.132	0.008	1.949
M050BC-02	2008	0.996	0.114	0.877	0.126	0.010	1.803
M050BC-03	2005	0.969	0.065	0.910	0.117	0.013	1.818
M050BC-04	2002	0.929	0.028	0.916	0.109	0.015	1.764
M050BC-05	1998	0.984	0.108	0.875	0.122	0.010	1.706
M050BC-06	1995	0.949	0.066	0.868	0.107	0.010	1.678
M050BC-07	1990	0.946	0.055	0.885	0.109	0.011	1.665
M050BC-08	1985	0.649	0.047	0.592	0.074	0.009	1.174
M050BC-09	1980	0.667	0.036	0.622	0.076	0.006	1.140
M050BC-10	1973	0.561	0.000	0.596	0.064	0.006	1.151
M050BC-11	1963	0.549	0.000	0.609	0.059	0.009	1.124
M050BC-12	1949	0.533	0.000	0.574	0.056	0.009	1.063
M050BC-13	1935	0.518	0.000	0.593	0.051	0.007	1.042
M050BC-14	1920	0.494	0.000	0.603	0.048	0.007	1.031
M050BC-15	1905	0.509	0.000	0.616	0.006	0.006	1.084
M050BC-16	1891	0.511	0.005	0.507	0.005	0.004	1.038
M050BC-17	1875	0.481	0.008	0.469	0.052	0.004	1.035
M050BC-18	1859	0.434	0.000	0.446	0.004	0.004	0.905
M050BC-19	1841	0.410	0.000	0.457	0.004	0.005	0.875
SHORT CORE							

#### Flux Raw Data (continued)

#### \*2011M28MC : NOT DATABLE --> NO FLUX

2011-M	041MC	FLUX (mg/cm²/yr)					
SITE	Average date of section	TC Flux	IC Flux	OC Flux	N Flux	BC Flux	OM Flux
SAMPLE ID	(Date)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)	(mg/cm²/yr)
M041MC-01	2009	0.597	0.247	0.346	0.054	0.010	1.037
M041MC-02	2003	0.628	0.282	0.305	0.051	0.009	0.989
M041MC-03	1996	0.597	0.273	0.319	0.047	0.009	0.943
M041MC-04	1988	0.587	0.292	0.298	0.039	0.010	0.876
M041MC-05	1979	0.577	0.274	0.309	0.043	0.011	0.859
M041MC-06	1971	0.535	0.184	0.320	0.035	0.036	0.787
M041MC-07	1961	0.522	0.203	0.309	0.034	0.037	0.758
M041MC-08	1952	0.513	0.188	0.319	0.034	0.038	0.731
M041MC-09	1942	0.556	0.241	0.288	0.036	0.040	0.720
M041MC-10	1931	0.558	0.313	0.262	0.033	0.035	0.691
M041MC-11	1915	0.474	0.206	0.268	0.033	0.030	0.648
M041MC-12	1893	0.427	0.198	0.234	0.028	0.030	0.625
M041MC-13	1870	0.414	0.199	0.213	0.027	0.024	0.587
M041MC-14	1846	0.397	0.177	0.217	0.027	0.025	0.540
M041MC-15	1822	0.395	0.173	0.212	0.027	0.026	0.552
M041MC-16	1798	0.384	0.160	0.211	0.026	0.026	0.575
M041MC-17	1773	0.408	0.215	0.201	0.027	0.023	0.567
M041MC-18	1748	0.434	0.227	0.208	0.031	0.027	0.580
M041MC-19	1724	0.380	0.174	0.203	0.026	0.021	0.595
M041MC-20	1699	0.344	0.148	0.201	0.025	0.027	0.563

# **Appendix A.2: Flux Charts**



Figure Appendix A.2.1. TC Flux as function of sediment deposition date for each core site in Lake Michigan.

# **Appendix B.1: Loading Raw Data**

Year	OM Flux (mg/cm²/year) MEAN	STD	Total OM Loading from IDW (tons/year)
2010	1.18313	0.19211	686,214
2000	1.09039	0.17210	632,427
1990	1.00040	0.19618	580,234
1980	0.93350	0.16966	541,428
1970	0.95436	0.15422	553,526
1960	0.90741	0.16012	526,295
1950	0.90258	0.15305	523,498
1940	0.87633	0.15878	508,269
1930	0.85073	0.17737	493,422
1920	0.85073	0.17737	493,422
1910	0.82373	0.16736	477,761
1900	0.78758	0.15758	456,799
1890	0.76973	0.15549	446,441
1880	0.74156	0.13981	430,106
1870	0.72308	0.12639	419,386
1860	0.70551	0.11846	409,196
1850	0.68711	0.11302	398,524

### Tables Appendix B.1. Total Loadings for all Parameters for all sampled coring sites.

Year	TC Flux (mg/cm <sup>2</sup> /year) STD MEAN		Total TC Loading from IDW (tons/year)
2010	0.7699	0.2051	446,530
2000	0.7471	0.2045	433,315
1990	0.7181	0.1820	416,485
1980	0.7231	0.2508	419,372
1970	0.7231	0.2523	419,407
1960	0.7164	0.2577	415,484
1950	0.7122	0.2514	413,099
1940	0.7032	0.2632	407,850
1930	0.6901	0.2598	400,253
1920	0.6662	0.2595	386,370
1910	0.6335	0.2553	367,423
1900	0.6521	0.2948	378,211
1890	0.6316	0.2868	366,303
1880	0.5673	0.2431	329,010
1870	0.5535	0.2318	321,015
1860	0.5398	0.2255	313,092
1850	0.5291	0.2197	306,860

Year	IC Flux MEAN STD (mg/cm <sup>2</sup> /year)		Total IC Loading from IDW (tons/year)
2010	0.3656	0.1173	212,030
2000	0.3680	0.1365	213,414
1990	0.3191	0.0934	185,098
1980	0.3640	0.1636	211,099
1970	0.3638	0.1690	210,983
1960	0.3341	0.1199	193,765
1950	0.3364	0.1395	195,106
1940	0.3555	0.1618	206,180
1930	0.3308	0.1265	191,878
1920	0.3078	0.1176	178,552
1910	0.3139	0.1348	182,043
1900	0.3786	0.2086	219,599
1890	0.3533	0.1808	204,909
1880	0.2958	0.1323	171,547
1870	0.2955	0.1359	171,390
1860	0.2983	0.1445	173,021
1850	0.3060	0.1552	177,500

Year	OC Flux MEAN (mg/cm <sup>2</sup> /year)	DC Flux MEAN STD mg/cm²/year)	
2010	0.5840	0.1989	338,739
2000	0.4761	0.1368	276,145
1990	0.4915	0.1412	285,083
1980	0.4481	0.1136	259,877
1970	0.4567	0.1180	264,884
1960	0.4774	0.1459	276,913
1950	0.4576	0.1290	265,424
1940	0.4361	0.1220	252,927
1930	0.4404	0.1334	255,436
1920	0.4323	0.1387	250,763
1910	0.3953	0.1329	229,294
1900	0.3458	0.1180	200,577
1890	0.3307	0.1210	191,825
1880	0.3167	0.1172	183,691
1870	0.2960	0.1046	171,708
1860	0.2758	0.0888	159,990
1850	0.2607	0.0805	151.209

#### Loading Raw Data (continued)

Year	TN Flux (mg/cm <sup>2</sup> /year) MEAN	STD	Total TN Loading from IDW (tons/year)	Year	BC Flux MEAN (mg/cm²/year)	STD	Total BC Loading from IDW (tons/year)
2010	0.0646	0.0122	37,471	2010	0.0178	0.0025	10.310
2000	0.0596	0.0107	34,554	2000	0.0187	0.0034	10.859
1990	0.0515	0.0103	29,887	1990	0.0211	0.0069	12,260
1980	0.0491	0.0070	28,451	1980	0.0211	0.0005	12,560
1970	0.0457	0.0069	26,527	1970	0.0217	0.0071	16.704
1960	0.0432	0.0063	25,042	1960	0.0325	0.0090	18.852
1950	0.0429	0.0071	24,870	1950	0.0374	0.0104	21,704
1940	0.0404	0.0058	23,424	1940	0.0440	0.0134	25.537
1930	0.0397	0.0073	23,054	1930	0.0426	0.0119	24.679
1920	0.0375	0.0060	21,751	1920	0.0378	0.0100	21.909
1910	0.0339	0.0065	19,656	1910	0.0325	0.0091	18,861
1900	0.0340	0.0103	19,725	1900	0.0286	0.0093	16,600
1890	0.0338	0.0106	19,630	1890	0.0258	0.0081	14,976
1880	0.0346	0.0056	20,066	1880	0.0231	0.0067	13,411
1870	0.0332	0.0052	19,272	1870	0.0207	0.0054	12,010
1860	0.0298	0.0075	17,302	1860	0.0193	0.0045	11,179
1850	0.0301	0.0086	17,438	1850	0.0243	0.0086	14,109

Note: All the loadings are calculated based on the total area of Lake Michigan which is about  $58,000*10^{6} \text{ m}^{2}$ .

# **Appendix B.2: Loading Charts**



Figure Appendix B.2.1. Lake Michigan Total Carbon (TC) Annual Net Loading (metric tons/year).

# Appendix C.1: GIS Maps of TC, OC, IC, TN Fluxes





















Figure Appendix C.1.1. TC fluxes to Lake Michigan sediment over decadal increments from 1850 to 2000.



Figure Appendix C.1.2. TC flux to Lake Michigan sediment in 2010.
















Lege	n	d				
OC FI	u	x				
(mg/c	m	2/	v	r)		
	0.	10	-	0	.1	з
	0.	14	-	0	.1	8
	ο.	17	-	0	.1	8
	0.	19	-	0	2	1
	0.	22	-	0	2	з
	0.	24	-	0	2	6
3	0.	27	-	0	2	9
	0.	30	-	0	.3	1
	0.	32	-	0	3	4
	0.	35	-	0	3	6
	0.	37	-	0	.3	9
	0.	40	-	0	4	2
	0.	43	-	0	.4	4
	0.	45	-	0	.4	7
	0.	48	-	0	.4	9
S	0.	50	-	0	.5	2
	0.	53	-	0	.5	5
	0.	56	-	0	.5	7
	0.	58	-	0	.6	0
	0.	61	-	0	.6	2



Figure Appendix C.1.3. OC fluxes to Lake Michigan sediment over decadal increments from 1850 to 2000.



Figure Appendix C.1.4. OC flux to Lake Michigan sediment in 2010.

















Lege	nd	
IC FI	x	
(mg/c	m2/yr)	
	0.002 - 0	0.054
	0.055 - 0	1.105
	0.106 - 0	157
	0.158 - 0	1.208
1	0.209 - 0	260
	0.261 - 0	1.311
	0.312 - 0	363
	0.364 - 0	1.415
	0.416 - 0	466
	0.467 - 0	1.518
1	0.519 - 0	.569
1	0.570 - 0	1.621
1	0.622 - 0	673
2	0.674 - 0	1.724
<u> </u>	0.725 - 0	1.776
£ 3	0.777 - 0	.827
8	0.828 - 0	1.879
8 3	0.880 - 0	.930
1	0.931 - 0	.982
	0.983 - 1	.034



Figure Appendix C.1.5. IC fluxes to Lake Michigan sediment over decadal increments from 1850 to 2000.



Figure Appendix C.1.6. IC flux to Lake Michigan sediment in 2010.

















Leg	gend
TN	Flux
(mg	/cm2/yr)
	0.004 - 0.006
	0.007 - 0.008
	0.009 - 0.010
	0.011 - 0.013
	0.014 - 0.015
	0.016 - 0.017
	0.018 - 0.019
	0.020 - 0.021
	0.022 - 0.023
	0.024 - 0.025
	0.026 - 0.027
	0.028 - 0.030
	0.031 - 0.032
	0.033 - 0.034
	0.035 - 0.038
	0.037 - 0.038
	0.039 - 0.040
	0.041 - 0.042
	0.043 - 0.044
	0.045 - 0.047



Figure Appendix C.1.7. TN fluxes to Lake Michigan sediment over decadal increments from 1850 to 2000.



Figure Appendix C.1.8. TN flux to Lake Michigan sediment in 2010.



# **Appendix C.2: GIS Maps of Heavy Metal Concentrations and Fluxes**

Figure Appendix C.2.1. Fe, K and Ca concentrations (mg/g) of Lake Michigan surface sediments.



Figure Appendix C.2.2. Ti, Mn, Zn and Cr concentrations (mg/g) of Lake Michigan surface sediments.



Figure Appendix C.2.3. Fe concentrations (mg/g) of Lake Michigan surface sediments.



Figure Appendix C.2.4. K concentrations (mg/g) of Lake Michigan surface sediments.



Figure Appendix C.2.5. Ca concentrations (mg/g) of Lake Michigan surface sediments.



Figure Appendix C.2.6. Ti concentrations (mg/g) of Lake Michigan surface sediments.



Figure Appendix C.2.7. Mn concentrations (mg/g) of Lake Michigan surface sediments.



Figure Appendix C.2.8. Zn concentrations (mg/g) of Lake Michigan surface sediments.



Figure Appendix C.2.9. Cr concentrations (mg/g) of Lake Michigan surface sediments.

















Lege	end
Fe F	lux
(mg/	cm2/yr)
	0.148 - 0.169
	0.170 - 0.191
	0.192 - 0.213
	0.214 - 0.235
	0.236 - 0.257
	0.258 - 0.278
	0.279 - 0.300
	0.301 - 0.322
	0.323 - 0.344
	0.345 - 0.366
	0.367 - 0.387
	0.388 - 0.409
	0.410 - 0.431
	0.432 - 0.453
	0.454 - 0.475
	0.476 - 0.497
	0.498 - 0.518
	0.519 - 0.540
	0.541 - 0.562
	0.563 - 0.584



Figure Appendix C.2.10. Fe fluxes to Lake Michigan sediment over decadal increments from 1850 to 2000.



Figure Appendix C.2.11. Fe flux to Lake Michigan sediment in 2010.

















Lege	end
Zn F	lux
(mg/	cm 2/yr)
	0.00115 - 0.00138
	0.00139 - 0.00162
	0.00163 - 0.00185
	0.00186 - 0.00209
E 3	0.00210 - 0.00232
	0.00233 - 0.00256
	0.00257 - 0.00280
	0.00281 - 0.00303
	0.00304 - 0.00327
	0.00328 - 0.00350
6	0.00351 - 0.00374
	0.00375 - 0.00397
	0.00398 - 0.00421
	0.00422 - 0.00444
	0.00445 - 0.00468
	0.00469 - 0.00491
	0.00492 - 0.00515
2	0.00516 - 0.00538
	0.00539 - 0.00562
	0.00.563 - 0.005.85



Figure Appendix C.2.12. Zn fluxes to Lake Michigan sediment over decadal increments from 1850 to 2000.



Figure Appendix C.2.13. Zn flux to Lake Michigan sediment in 2010.















1900	K	Or.
1	3	
	Carl Long	

Lege	en d
Cr Fl (mg/d	lux cm2/yr)
	0.00062 - 0.00080
	0.00081-0.00098
	0.00099 - 0.00116
	0.00117 - 0.00134
	0.00135 - 0.00152
	0.00153 - 0.00170
	0.00171-0.00188
	0.00189 - 0.00206
	0.00207 - 0.00225
	0.00226 - 0.00243
	0.00244 - 0.00261
	0.00262 - 0.00279
	0.00280 - 0.00297
	0.00298 - 0.00315
	0.00316 - 0.00333
	0.00334 - 0.00351
	0.00352 - 0.00389
	0.00370 - 0.00387
	0.00388 - 0.00405
	0.00406 - 0.00423



Figure Appendix C.2.14. Cr fluxes to Lake Michigan sediment over decadal increments from 1850 to 2000.



Figure Appendix C.2.15. Cr flux to Lake Michigan sediment in 2010.

# **Appendix D.1: QA/QC and Statistical Analysis Results**

Tables Appendix D.1.1. QA/QC and statistical results (Bias, RSD, and overall uncertainty) of each core site (a) for OC analysis, and (b) for BC analysis.

Lake		STATISTICS for OC Analysis			
SITE	Michigan Area	BIAS (%)	<b>RSD</b> (%)	U95 (%)	
M32	Chippewa	0.97	2.19	3.25	
M41	Basin	-0.10	1.45	2.05	
M47		-0.45	1.31	1.91	
M50	Green Bay	-5.89	2.59	6.94	
M24	Mid-Lake	-0.55	4.56	6.47	
M28	Plateau	-0.90	5.03	7.17	
M08	South	-1.33	2.96	4.39	
M09	Chippewa	-0.02	3.94	5.57	
M11	Basin	0.30	6.23	8.82	
M18		0.19	0.88	1.26	
			Avg. U <sub>95</sub>	4.78	

(a)

	Lake	STAT	ISTICS for BC An	alysis
SITE	Michigan Area	BIAS (%)	<b>RSD</b> (%)	U <sub>95</sub> (%)
M32	Chippewa	-1.10	0.79	1.57
M41	Basin	-1.73	2.38	3.78
M47		-1.73	0.11	1.74
M50	Green Bay	1.18	1.01	1.85
M24	Mid-Lake	-2.87	2.04	4.07
M28	Plateau	5.25	4.75	8.53
M08	South	-0.44	3.22	4.57
M09	Chippewa	-0.8	2.70	3.90
M11	Basin	-0.27	4.80	6.79
M18		-2.56	2.86	4.79
			Avg.U <sub>95</sub>	4.16

(b)

## **Curriculum Vitae**

#### "Resume of Solidea Maria Cristina Bonina"

#### **Contact Info**

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#### Education

2016	PhD in Civil/Environmental Engineering - University of Illinois - Chicago, Illinois, United States Faculty advisor: Dr. Karl J. Rockne
2007	Master of Science in Civil Hydraulic Engineering Politecnico of Bari -The first Faculty of Engineering, Italy Faculty advisor: Dr. Piero Masini
2006	Bachelor of Science in Civil Engineering Politecnico of Bari - The first Faculty of Engineering, Italy

#### **Professional Experience**

02/2013 – Present Intern with the United States Environmental Protection Agency's (U.S. EPA) in the Great Lakes National Program Office (GLNPO) at the Chicago Regional Laboratory for Region 5 (CRL-R5) in Chicago, Illinois.

High quality experiences on analytical methods, lab procedures and analysis, data generation, quality control and review, real-world remediation national environmental projects.

Method Development for determination of Polychlorinated Biphenyls congeners (PCBs) in soil/sediment by TSD Quantum QQQ GC and Tandem Mass Spectrometry (GC-MSMS); GLNPO Sediment Sampling in the field (SAPPI Project) on Mudpuppy in Muskegon Lake, MI and analysis of sediments for semi-volatile organic compounds (SVOA) including Polynuclear Aromatic

Hydrocarbons (PAHs) and metals, field sediment sample analysis for PCBs in Ashtabula River Sediment Ashtabula, OH; Technical Systems Audit (TSA) of Great Lakes Legacy Act (GLLA) remediation project (Lincoln Park Phase 2); QAAP Auditing Participation in field inspection for of Remedial Action Oversight East Branch Grand Calumet River, Reaches 4A and 4B, etc.

09/2010 – 02/2013 Research Assistant, University of Illinois at Chicago, Illinois, United States Research on Great Lakes Sediment Surveillance Program (GLSSP) founded by Untied States Environmental Protection Agency (U.S. EPA).

Water and sediment sampling activity onboard the EPA R/V Lake Guardian on the Great Lakes, variety of laboratory and field analysis of Great Lakes water and sediments: Michigan (2010), Michigan and Superior (2011), inland Siskiwit (Isle Royale, MI) and Forest Lake (WI) (2012), Huron and Georgeon Bay (2012)

09/2009 - 2014 Teaching Assistant of Senior Design (Fall 2014), Water Resource Engineering (Spring 2014) and Fluid Mechanics and Hydraulics (Fall2009, Spring 2010), Department of Civil and Materials Engineering (CME), University of Illinois at Chicago, United States.

Manage a hydraulic class and assist in teaching with instructional responsibilities: Conducting, leading weekly laboratory sessions, grading home-works and lab reports, leading holding office hours, leading field trips, generating course and class materials, writing and proctoring examinations.

09/2009 – 03/2013 Chemical and Hygiene Officer, Applied Environmental Biotechnology Laboratory (AEBL), University of Illinois at Chicago, United States.

Health and safety officer responsible for laboratory health and safety issues, University of Illinois – Chicago, Illinois, United States.

- 09/2007 09/2008 Scholarship Researcher sponsored by Regione Apulia and High Cultural Activity on Porus Media and Visualization of nanoparticles research topic at University of Illinois at Chicago, United States.
- 01/2006 2007 C.I.B. Engineering Restauro Costruzioni S.r.l., Bari, Italy (Italian Construction and Engineering Company).

Engineering Specialist: Prepare, develop and review engineering project plans and risk assessments; perform corporate quality and safety inspections and surveys, responsible project communications with corporate/client, sub-contractors.

07/2001 – 12/2005 S.L.B. Engineering Restauro Costruzioni S.r.l., Bari, Italy (Italian Construction and Engineering Company).

Civil Engineering Trainee (worked with high expertise engineers on design, construction, restructuring, restoration and maintenance projects).

08/2007

Scholarship granted by Regione Apulia Agency (Italian Governmental Istitution) Bari - Italy.

### Skills

	Accelerated Solvent Extraction (ASE); Solid Phase Extraction (SPE), Cleanups
	(Florisil, Cupper and Acid), Analysis of Organic Pollutants in sludge, sediment,
	soil, oil field samples, Gas Chromatography Mass Spectrometry (GC-MS), TSD
	Quantum GC and Tandem Mass Spectrometry (GC-MSMS), Elemental Analyzer
	(EA), Particle Size Distribution (PSD), Stable Isotopic Analysis (SIA), Toxicity
	characteristic leaching procedure (TCLP), System Statistics Software (SYSTAT),
	Surveying and Global Positioning System, Geographic Information System (GIS),
	ArcVIEW/ArcINFO/ArcGIS, AutoCAD, ArchiCAD, Eager chromatography
	software, Laboratory Information Management System (LIMS), Agilent
	ChemStation Software package for Liquid or Gas Chromatography, Thermo
	Scientific Xcalibur software for Mass Spectrometry.
ns	

### Certifications

07/2013-Present	USEPA Certification of 24 hr-Field Safety Training
05/2013-Present	USEPA Certification of Fundamental Laboratory Procedures Review
04/2013- Present	USEPA Certificates of Environmental Management System Awareness Training
04/2013- Present	(2013, 2014 & 2015) USEPA Certificates of COOP Mandatory FY13, FY14, and FY15
04/2013- Present	USEPA Certificates of Security Awareness and Training FY13, FY14 and FY15
04/2013- Present	USEPA Certificates of my Workplace Mandatory Training (2013, 2014 & 2015)
03 /2013- Present	USEPA Certificates of Health and Safety Training for Laboratory Operations (2013, 2014 & 2015)
12/07-10/2013	USEPA Training Course - Certificate of completion: Polychlorinated Biphenyls (PCBs) Comprehensive Course by Resource Training Institute, LLC (RTI). Seattle, WA – USEPA Region 10.
09/2009 - Present	Certificate of Continuing Education on Laboratory Safety and Chemical Waste, University of Illinois at Chicago, Illinois, United States
11/2009 - Present	Certificate of University Ethics Officer Ethics Training for University Employees, University of Illinois – Chicago, Illinois, United States
12/2010 & 12/2011	USEPA Training programs for Great Lakes National Program Office and Office of Water:
	- Field and Laboratory Auditing
	263

	<ul> <li>Quality Program Tracking, Inventory and Reporting</li> <li>Verification, Validation and Usability</li> </ul>
12/2007	State Examination for professional qualification of engineer, taken at Politecnico of Bari, Bari, Italy
08/2006	License of Corporate Quality System Manager (UNI EN-ISO 9001), Bureau Veritas Certification, Bari, Italy
02/2005	Technical Drawing Course AUTOCAD & ArchiCAD Programs at studies Levant Centre, Bari, Italy

#### **Affiliation & Memberships**

2015-Present	United Nations Educational, Scientific and Cultural Organization (UNESCO) Italian Scientific and Cultural Representative of UNESCO - Bisceglie District.
2010-Present	International Association for Great Lakes Research (IAGLR)- Member
2009-Present	American Society of Civil Engineers (ASCE) - Member
2007-Present	Society of Woman Engineers (SWE) - Member

#### Scientific and Technological Communications

Publications/ Presentations (presenter underlined)

- <u>Darnault, C.J.G.</u>, Bonina, S., Uyusur, B., Snee, P. (2008). Fate and Transport of Quantum Dot Nanomaterials in the Vadose Zone. Flow and Transport in Heterogeneous Subsurface Formations: Theory, Modelling & Applications. IAHR International Symposium. June 18-20, 2008, Istanbul, Turkey.
- 2. <u>Darnault, C.J.G., Bonina, S.,</u> Uyusur, B., Snee, P. (2008). Fate of Quantum Dot Nanomaterials in Unsaturated and Saturated Porous Media. International Environmental Nanotechnology Conference. October 7-9, 2008, Chicago, Illinois, USA.
- Darnault, C.J.G., Bonina, S., Uyusur, B., Snee, P. (2009). Visualization and Transport of Quantum Dot Nanomaterials in Porous Media. In Linkov, I., Steevens, J. (eds.) Nanotechnology: Risks and Benefits © 2016 Springer. Textbook printed in the Netherlands.
- <u>Karl J. Rockne</u>, S.M. C. Bonina, (2009) Polybrominated Diphenyl Ether (PBDE) Fate in Wastewater Digesterts. Research Symposium sponsored by Illinois Sustainable Technology Center ISTC. Division of the Institute of Natural Resource Sustainability- University of Illinois at Urbana - Champaign. September 9, 2009. Champaign, Illinois, USA.
- 5. <u>Bonina S.M.C.</u>, K.J. Rockne (2010). Different levels of PBDEs in soil samples from France and China" UIC STUDENT RESEARCH FORUM. April 20, 2010, Chicago, Illinois, USA.
- 6. <u>Bonina S.M.C.</u>, K. J. Rockne, Krishna R. Reddy. (2010). Superfund sites in Chicago Environmental Remediation Engineering Seminar, Department of Civil and Materials Engineering- University of Illinois at Chicago. May 6, 2010, Chicago, Illinois, USA.

- Bonina S.M.C., K.J. Rockne, A. Li, J.P. Giesy, N. Sturchio, J. Guo, M. B. Corcoran, G. Codling, A.L. Sandy (Civil and Materials Engineering, 2012). An Analysis of Competing Hypotheses for Organic Matter Loading to Lake Michigan Sediments UIC Water Research Forum. Tuesday, April 10, 2012, Chicago, Illinois, USA.
- <u>Bonina S.M.C.</u>, K.J. Rockne, A.Li, J.P. Giesy, N. Sturchio, J. Guo, M. B. Corcoran, G. Codling, A.L. Sandy (2012). Physical Chemical Characterization of Sediment Samples in Lake Michigan. UIC STUDENT RESEARCH FORUM- April 17, 2012, Chicago, Illinois, USA.
- Li A., K.J. Rockne, J.P. Giesy, N. Sturchio, J. Guo, S.M.C. Bonina, M. B. Corcoran, G. Codling, C. Smalley, Y. Wang, A. L. Sandy. Monitoring Legacy and Emerging Organic Pollutants: The Great Lakes Sediment Surveillance Program (GLSSP). 2013 ICCBES 2013 International Congress on Chemical, Biological and Environmental Sciences (2013 ICCBES) and 2013 International Congress on Natural Sciences and Engineering (2013 ICNSE). January 8-10, 2013, Taipei, Taiwan.
- <u>Corcoran M.B.</u>, N. Sturchio, A .Li, K.J.Rockne J.P. Giesy, J. Guo, S.MC. Bonina, G. Codling, A.L. Sandy Sedimentation Rates in Lake Michigan Using <sup>210</sup>Pb, <sup>137</sup>Cs, and <sup>241</sup>Am<sup>th</sup> Annual Conference on Great Lakes Research, June 5, 2013, West Lafayette, Indiana, USA.
- 11. Codling Garry, Anja Vogt, Paul D. Jones, Tieyu Wang, Pei Wang, Y.-L. Lu, Margaret Corcoran, Solidea Bonina, An Li, Neil C. Sturchio, Karl J. Rockne, Kyunghee Ji, Jong-Seong Khim, Jonathan E. Naile, John P. Giesy. Historical trends of inorganic and organic fluorine in sediments of Lake Michigan. Chemosphere, 114, 203-209. 2014.
- <u>Kleinmaier Danielle</u>, Solidea Bonina, Troy Strock, Wayne Whipple. Developed Method for Selected PCB Congeners in Soil and Sediment by GC/MS/MS. U.S. EPA Region 5 - Chicago Regional Laboratory. Laboratory Technical Information Group (LTIG). April 30<sup>th</sup>, 2014, Chicago, Illinois, USA.
- <u>Bonina Solidea M.C.</u>, Karl Rockne An Li, John Giesy, Neil Sturchio, Garry Codling, Meg Corcoran, Jiehong Guo. The Great Lakes Sediment Surveillance Program (GLSSP). 2014 Senior Design Seminar. UIC. Civil Materials Engineering, September 10, 2014. Chicago, Illinois, USA.
- Bonina Solidea M.C., Garry Codling, Meg Corcoran, Jiehong Guo, Soheil Hosseini, Zhuona Li, Colin Smalley, Anja Vogt, <u>Karl Rockne</u>, An Li, John Giesy, Neil Sturchio. The Great Lakes Sediment Surveillance Program (GLSSP). Eight International Conference on Remediation and Management of contaminated sediments. Batelle. The Business of Innovation. January 12-15, 2015. New Orleans, Louisiana, USA.
- Bonina Solidea M.C., B. Jones, M. Loomis, N. Jannelle, H.B. McCarty, T. Vonnahme, (2015).
   " Lincoln Park Project Phase II (LPP2) Technical System Audit". U.S.EPA/ Great Lakes Legacy Act. GLNPO - April 24, 2015, Chicago, Illinois USA.