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The distribution of stable isotopes and heavy metals in Dreissena polymorpha (zebra mussel): Chemical tracers for environmental contamination in Lake St. Clair (Ontario, Michigan).

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THE DISTRIBUTION OF STABLE ISOTOPES AND HEAVY METALS IN *DREISSENA POLYMORPHA* (ZEBRA MUSSEL) - CHEMICAL TRACERS FOR ENVIRONMENTAL CONTAMINATION IN LAKE ST. CLAIR

BY
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ABSTRACT

The zebra mussel (*Dreissena polymorpha*) was employed to biomonitor heavy metal (Fe, Zn, and Mn) pollution and to evaluate the distribution of carbon and oxygen stable isotopes in the Lake St. Clair and Detroit River mouth aquatic system. Isotopic analysis of bulk *Dreissena polymorpha* shells within the study area revealed a $\delta^{13}C$ range from -4.23 ‰ to -1.07 ‰ VPDB, with an average of -2.98 ± 1.11‰ VPDB (n= 10) for shells within Lake St. Clair. The $\delta^{18}O$ (VPDB) values ranged from -8.41 ‰ to -6.08 ‰, with a Lake St. Clair average of -7.05 ± 0.69‰ (n=10). The shells were deposited close to isotopic equilibrium with the ambient water, with the $\delta^{13}C$ being depleted by 0.7 ‰ with respect to the equilibrium value in Lake St. Clair. The observed slight depletion could be due to the incorporation of metabolically derived carbon during shell formation. Shells taken from the Detroit River mouth displayed the most enriched $\delta^{13}C$ values, averaging -1.3 ± 0.2‰ VPDB (n = 3). This enriched value may reflect the discharge of chemicals that are enriched in $\delta^{13}C$ from the heavily industrialized shores of the Detroit River. The average concentrations of the heavy metals Fe, Zn, and Mn in the mussel shells were 149 ± 102, 9 ± 8, and 14 ± 7 ppm (n=15), respectively, exhibiting accumulation factors of 611, 130, and 2300, respectively, relative to metal concentrations in the water. There was no statistical difference in the mean concentrations of each of the studied metals between Lake St. Clair shells and those sampled from the Detroit

River mouth, implying that the heavy metal contamination level in Lake St. Clair is comparable to that at the Detroit River mouth.

Incremental analysis of *Dreissena polymorpha* shells revealed annual variations in the heavy metal concentrations and the isotopic composition of the shells. The heavy metal content seemed to be mainly influenced by the ambient environmental conditions, such as the temperature and the metal concentration of the water column, while the carbon and oxygen isotopic compositions were affected by a combination of environmental factors and intrinsic factors, such as the incorporation of metabolic carbon and kinetic fractionation resulting from the high growth rate displayed by the organism during its first year of growth. The latter factors were of more significance during the first year of growth, producing $\delta^{13}C$ and $\delta^{18}O$ values as depleted as -10 and -20 ‰.

DEDICATION

To my patient parents, my sister, Laura, and my brother, Basel.

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

Anthropogenic flux of heavy metals into the Great Lakes basin is seriously threatening the quality of its ecosystem. Studies assessing the bioavailability of heavy metals in this basin are therefore of utmost importance in order to better understand their effect on the aquatic biota. This study employs the zebra mussel *Dreissena polymorpha* as an indicator species to biomonitor heavy metal pollution and to evaluate the stable isotope distribution of carbon and oxygen in the Lake St. Clair and Detroit River aquatic system. Owing to its relatively low position in the food chain, *Dreissena polymorpha* provides a more direct reflection of the ambient environmental conditions than other organisms higher in the food chain.

1.1 Objectives of Study

The main objectives of this study are:

(1) To determine the concentrations of the heavy metals Fe, Mn, and Zn, in addition to major (Ca) and minor (Mg) elements, in the water of Lake St. Clair and the Detroit River mouth and to compare them with the accumulated concentrations of the same metals in the shells of *Dreissena polymorpha* samples within the study area.

(2) To determine and compare the carbon and oxygen isotopic composition of *Dreissena polymorpha* shells from different areas within Lake St. Clair and the mouth of the Detroit River, and consequently decide whether the shell material was formed in isotopic

equilibrium with the ambient water. Such information allows the evaluation of factors governing the isotopic fractionation of carbon and oxygen in the biogenic carbonate. A state of isotopic equilibrium implies that the $\delta^{18}O$ and the $\delta^{13}C$ (D.I.C.) composition of the ambient water are the primary factors governing the $\delta^{18}O$ and $\delta^{13}C$ of the *Dreissena polymorpha* shell. A state of isotopic disequilibrium, however, implies that kinetic fractionation of isotopes and vital effects (metabolic processes) within the mussel play a significant role in determining the isotopic composition of the shell.

(3) To determine and compare the carbon isotopic composition of dissolved inorganic carbon (D.I.C.) and the oxygen isotopic composition of water from different areas within Lake St. Clair and the mouth of the Detroit River. Depletion and enrichment of water $\delta^{18}O$ and $\delta^{13}C_{DIC}$ can reflect the level of biologic productivity, organic matter oxidation, anthropogenic input of contaminants, and the prevailing ambient environmental conditions at each site within the study area.

(4) To develop ontogenic records of carbon and oxygen isotopes in addition to heavy metals (Fe, Mn, Zn) by the sequential sampling of growth rings within individual shells taken from different locations within the study area. Ultimately, the objective is to explain the observed variations, if any, which can be attributed to external environmental factors or metabolic processes within the organism.

1.2 Previous Studies

1.2.1 Heavy Metals

A growing concern about the extent of contamination in the Great Lakes has led to the emergence of many studies that assessed the level of pollution in the water and sediment of the area (Goldberg et al. 1981; Hoff 1994; Wong et al. 1995). The primary objective of such studies was to quantify the amount of heavy metal loading to the system and to investigate the sources and pathways of metal loading (Hoff 1994; Shaw et al. 1990). Contamination of Lake St. Clair and Detroit River sediments was investigated by Rossman and Borres (1988) and Thomas et al.(1975), who concluded that the sediments contained high concentrations of heavy metals, which poses a serious risk to the quality of the Great Lakes ecosystem.

Studies by Shwetz (1998) and MacFarlane (1998) went further to develop a sequential extraction procedure that determined the level of heavy metal contamination in different fractions of the sediment. Such extractions can reveal more details about the speciation and the bioavailability of heavy metals; such information is of utmost importance when considering the effect of heavy metals on aquatic and ultimately human life.

Other studies employed molluscs as biomonitors to investigate pollution trends of heavy metals in industrial and urban areas (Al-Aasm et al. 1998; Elder and Collins 1991). Such filter-feeding organisms can bioaccumulate heavy metals in their tissues and biomagnify existing levels in the ambient aquatic environment (Amiard et al. 1986; Broman et al. 1991; Coleman et al. 1986; Sadiq & Alam 1992). Recent research has also dealt with heavy metal concentrations in mussels and the associated sediments. Many significant relationships were found between the heavy metal concentrations of the

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sediments and that of the associated mussels, where an increase in the metal content of the sediment was accompanied by an increase in the metal content of the mussel tissues (De Gregori 1996; McConchie and Lawrence 1991; Stoeppler 1992).

Moreover, other research focused on heavy metal uptake and depuration rates with the aid of heavy metal artificial isotopes such as ^{110}Ag and ^{58}Co (Mersch et al. 1992). Ingestion rates, absorption efficiencies, in addition to efflux rates were used to calculate depuration and influx rate constants for a variety of heavy metals in an attempt to develop bioaccumulation models (Wang and Fisher 1996). Other laboratory experiments shed light on the chronic ecotoxicity of mixtures of essential metals (Cu, Zn) and non-essential metals (Cd, Pb). Such experiments showed a 50% decrease in filtration rate and an increase in the mortality of mussels exposed to equitoxic mixtures of the above metals (Kraak et al. 1992). Experiments were also conducted to compare the accumulation of metals by mussels from food and water. It was concluded that metals obtained from food sources were mostly associated with the soft part tissues of the mussel, while metals from the dissolved phase (water) were associated with the shells (Fisher et al. 1996).

As opposed to bulk analysis of mussel shells for heavy metal content, a study by Al-Aasm et al. (1998) undertook the analysis of individual shell increments (growth rings) of the bivalve *Dreissena polymorpha*. The study revealed annual variations in the concentration of Pb, Cu, Mn, Cd, and other heavy metals. The growth rings exhibited intervals of increased uptake of heavy metals that coincided with isotopic enrichment, which probably corresponded to periods of warmer temperatures.

1.2.2 Stable Isotopes

In addition to heavy metal studies, research dealing with environmental stable isotopes has also been extensively undertaken in the past few years. The carbon and oxygen isotopic composition of mollusc shells has been utilized in numerous paleoenvironmental studies (Mitchell et al. 1994; Stuvier 1970; Veinott and Cornett 1998; Wang & Peng 1990). The fact that freshwater molluscs deposit their shells close to isotopic equilibrium with the ambient water makes it possible to determine current and previous $\delta^{18}O$ of the water and $\delta^{13}C$ of dissolved inorganic carbon (Turner et al. 1983).

Isotopic equilibrium equations for oxygen, developed by Craig (1953) and Grossman and Ku (1986), made it possible to determine water paleotemperatures, based on the assumption that the shell was actually formed in isotopic equilibrium with the lake or ocean water. A classical study by Fritz and Poplawski (1974) showed that laboratory grown freshwater molluscs do actually precipitate their shells in isotopic equilibrium with the water, and that the carbon isotopic composition of the shells was mainly controlled by the $\delta^{13}C$ of aqueous carbonate species. Vital effects and ingested food were thought to have a minor influence on the shells.

Studies by Fritz and Poplawski (1974) and Turner et al. (1983) examined the isotopic composition of whole shells rather than sequential increments. However, more recently researchers have adopted the increment sequential sampling method which led them to discover significant variations in the isotopic composition of shell increments, some of which were in isotopic disequilibrium with the water (Al-Aasm et al. 1998;

Abell and Williams 1989; Dettman and Lohmann 1993). Such detailed work allowed a better understanding of the variables that control the isotopic composition of the shell, whether it be annual fluctuations in temperature, changes in the isotopic composition of the water, or the incorporation of light, metabolic CO_2.

1.3 Iron, zinc, and manganese

The shell and water samples were analyzed for a variety of metals, including some highly toxic agents such as Cd, Cu, As, and Pb; however, the only three heavy metals that were present above the detection limit were Fe, Zn, and Mn. Although iron, zinc, and manganese are essential for the proper functioning of organisms when found in the appropriate concentrations, these metals can be harmful at higher concentrations.

In order to understand the level at which these three metals are toxic, they should be compared to the allowable concentrations specified by government agencies. The Environmental Protection Agency listed the maximum allowable concentrations of Fe, Zn, and Mn in drinking water as 0.05, 0.05, and 5.0 mg/L. The average chemical composition of streams for Fe, Zn, and Mn is 40, 30, and 8 ppb (Drever 1982).

CHAPTER 2

STUDY AREA

2.1 Geographic Setting and Physiography

2.1.1 Lake St. Clair

Lake St. Clair is located between the St. Clair River and the Detroit River, within the Lake Huron - Lake Erie corridor (Fig.2.1). The St. Clair River supplies 98% of its water, while the remaining 2% is supplied from the Clinton, Sydenham, and Thames Rivers. Outflow from the lake leaves through the Detroit River into Lake Erie. The largest delta within the Great Lakes system is located at the north-eastern part of Lake St. Clair; however, it is the smallest lake within that system. The total area of Lake St. Clair is 1,114 km^2 while the area of its drainage basin amounts to 12,430 km^2. It has a maximum length of 43 km and a maximum width of 40 km. The average depth of the lake is only 3m, with the maximum natural depth reaching 6.4 m. However, the maximum depth reaches 8 m along a dredged shipping channel which bisects the lake, running in a northeast-southwest direction between the St. Clair River Delta and the head of the Detroit River (Bolsenga and Herdendorf 1993). Due to the small size and shallow nature of the lake, water residence in the lake averages 9.2 days (Herdendorf et al. 1986). From a biological point of view the St. Clair Lake is especially important because its wetlands and delta provide the appropriate habitats for animal (e.g. waterfowl) resting, feeding, and breeding.

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2.1.2 Detroit River

The Detroit River flows from Lake St. Clair in a southwesterly direction and drains into Lake Erie. The average flow of the river is 5,300 m³ / sec. The upper portion of the 50 km long Detroit River has a width of 1 km and is characterized by steep banks. Depth in this part of the river reaches 15 m. The two islands of Belle Isle and Peach Island are present at the head of the river. Gentle sloping banks characterize the lower portion of the river, which has a width of 6 km at the mouth (Bolsenga and Herdendorf 1993). The mouth of the river has an average depth of 3 m, except in the shipping channel, and is characterized by the presence of many islands, among which is Grosse Ile, which serves as a disposal site for byproducts from the manufacturing of soda ash.

2.1.3 Current Patterns of Lake St. Clair

The primary causes for water movement include the water being higher at one point than another, which implies that the water will move towards the lower point under the effect of gravity. Other causes are the friction that occurs between surface wind and the water, and differences in the density of water masses (Bolsenga and Herdendorf 1993).

As shown in Fig (2.2), the most dominant trend of current flow is from the St. Clair River towards the Detroit River. This figure illustrates the surface currents of Lake St. Clair under the effect of various wind directions. The development of these

Figure 2.1: Map of the Great Lakes showing the location of the study area.

circulation patterns was based on a mathematical model, but there is currently no actual data that supports it (Bolsenga and Herdendorf 1993). Surface and bottom water flow patterns are very similar, implying that they are controlled by the same factor, with the highest speed of current flow found near the rivers.

2.1.4 Water Temperature of Lake St. Clair

Some of the variables that control the water temperature of Lake St. Clair include its depth, characteristic hydraulic retention time, and the rate of water inflow. Due to the shallow nature of Lake St. Clair (maximum depth of 6.5 m), thermal stratification is not observed. This results in the water being isothermal from surface to bottom. Moreover, Lake St. Clair has a short hydraulic retention time (9.2 days) and a high rate of water inflow from Lake Huron, thus making the temperature of Lake Huron an important factor that can significantly affect the water temperature of Lake St. Clair. The water has the highest temperatures in August with an average of 22.5 °C. In Anchor Bay, temperatures are usually 2-4 °C lower because of the large amount of inflow from the St. Clair River. On the other hand, temperatures may be 5 °C higher in the coastal wetlands (Herdenhorf et al. 1986). According to Herdendorf et al. (1986), since Lake St. Clair is shallow and because thermal stratification is not observed , dissolved oxygen levels are close to saturation. This agrees with results from previous research conducted by Mudroch and Capobianco (1978) who studied the well-mixed coastal wetland waters and found that all oxygen saturation levels were above 75%.
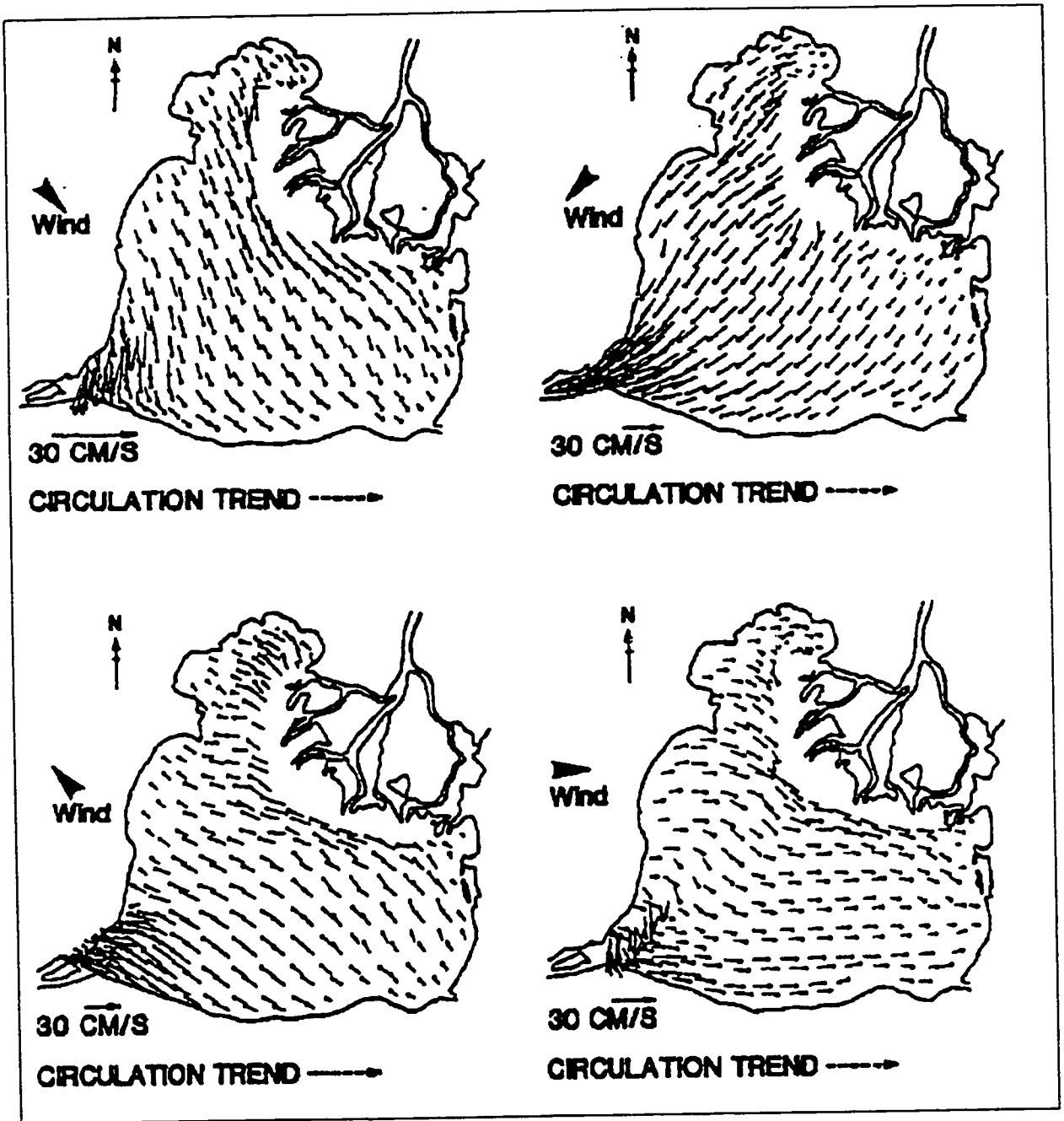
Figure 2.2 : Surface current flow in Lake St. Clair under the effect of various wind directions (after Bolsenga and Herdendorf 1993).

2.2 Pollution within the Study Area

2.2.1 Lake St. Clair

The upper part of the St. Clair River is heavily industrialized and utilized primarily by Ontario's "chemical valley" in the Sarnia area. Point source discharges of heavy metals and organic contaminants occur through numerous industrial facilities such as the Sarnia Refinary of Esso Petroleum Canada and Esso Chemical Canada, which undertake the processing of crude oil into gasolines, petrochemical feedstocks, and waxes. Other facilities include Polysar Limited, which specializes in the manufacture of synthetic rubber and other organic compounds such as ethylbenzene and styrene. The Dow Chemical Canada Inc., which is involved in the production of styrene, chlorinated solvents, and polyethylene, is also a major contributor of heavy metal (Cr, Cd, Pb, Mn) and organic waste discharges into the St. Clair River (Environment Canada 1986). The level of mercury in the sediment and fish of Lake St. Clair created a serious environmental problem in the early seventies. High mercury concentrations in fish tissues and Lake St. Clair sediments were attributed to the accidental release of mercury, which was released from the Dow Chemical Corporation as a byproduct from the manufacture of chlorine gas by the electrolysis of brine (Walters et al. 1974). Years after the chlor-alkali plant diminished operation, the mean concentration of mercury in surface sediments fell from 3.8 ppm (Walters et al. 1974) to background levels of 0.6 ppm

(Wilson and Walters 1978). The Dow Chemical experienced a major spill in 1985 that caused the discharge of 11,000 L of perchloroethylene, which is a toxic dry cleaning solvent, into the St. Clair River (Environment Canada 1986). In Michigan, industrialization of the river shoreline is centered at Port Huron. While the Canadian shoreline of Lake St. Clair is dominated by wetlands and agricultural activities, the American lake shoreline is mostly urbanized.

2.2.2 Detroit River

Sediments of the Detroit River exhibit one of the highest concentrations of heavy metals and polychlorinated biphenyls within the Upper Great Lakes connecting channels (Hamdy and Post 1985).The upper portion of the river is highly urbanized and borders many municipal and industrial facilities. The lower portion of the river is also highly industrialized and lined by numerous petrochemical plants, steel mills, petroleum refineries, and producers of rubber, automotive parts, and plastics. More than fifty major industrial facilities along the Michigan shore, and eleven along the Canadian shore hold discharge permits for industrial wastes including polychlorinated biphenyls, polycyclic aromatic hydrocarbons, cyanide, phenols, and heavy metals such as Hg, Cd, Pb, Fe, Zn, Cu, and Mn (Manny et al. 1988).

2.3 Regional Bedrock Geology

2.3.1 Precambrian Era

The cratonic Precambrian basement is composed of dense and crystalline metamorphosed sedimentary and igneous suites that are overlain by the assemblages of the Paleozoic. The oldest rocks in the Great Lakes region are the Keewatin rocks, which consist of metamorphosed thick lava flows and sedimentary deposits that are surrounded by the Laurentian granites, which cut through and across them (LaBerge 1994).

Overlying the Keewatin rocks are the Timiskaming and Huronian rocks, consisting of sandstones, shales, and limestones deposited over the smoothed surfaces of the Laurentian granites. Deposition of conglomerates and sandstones commenced early in the Keweenawan and was later followed by the outpouring of lavas from fissures close to the current centre of Lake Superior. The Keweenawan lavas extend thousands of square metres around Lake Superior and reach a thickness of 20,000 metres in northern Wisconsin and Michigan, constituting the central area of the keweenaw Peninsula (LaBerge 1994).

The craton's surface was smoothed by extensive erosion during the 400 million year period between the Grenville Orogeny and the initial deposition of the Paleozoic sediments (Carter et al. 1993). It was reduced to a surface of low relief referred to as a peneplain. Marking the end of the Precambrian is a granitic intrusion and severe structural deformation of the Keweenawan rocks from southern Lake Superior till the northeastern part of Lake Huron.

2.3.2 Paleozoic Era

Figure (2.3) illustrates the Paleozoic geology of southern Ontario. The Paleozoic witnessed the tendency of certain areas of the region to sink down. This phenomenon was most clearly noted in the Michigan structural basin and the Appalachian geosyncline. It was in these basins that the 185 to 520 million years old sedimentary rocks of the Paleozoic were mainly deposited, attaining a thickness of around 3,000 metres. Initial sediment deposition occurred during the marine invasion of the Lower, Middle, and Upper Cambrian seas, which spread through the United States and covered southern Ontario. The marine invasion was also repeated during the Ordovician and Silurian. The period between the Devonian and the Permian was characterized by alternate flooding and draining (LaBerge 1994).

Early deposition of Paleozoic rocks occurred in the Cambrian, which is mainly characterized by sandstones attaining maximum thicknesses of 165 metres. The ordovician deposits consisted primarily of shale, limestone, and dolomite, which amounted to a thickness of approximately 900 metres. The marine invasion of the Silurian resulted primarily in the deposition of dolomite, shale, rock salt, and gypsum. During the Devonian, carbonates and black shales were extensively deposited, followed by the deposition of shales, siltstones, and sandstones during the Mississippian (LaBerge 1994) . There is, however, no trace of Permian deposits in the Great Lakes which indicates that the period of erosion and emergence which continues to the present time commenced during the late Paleozoic.
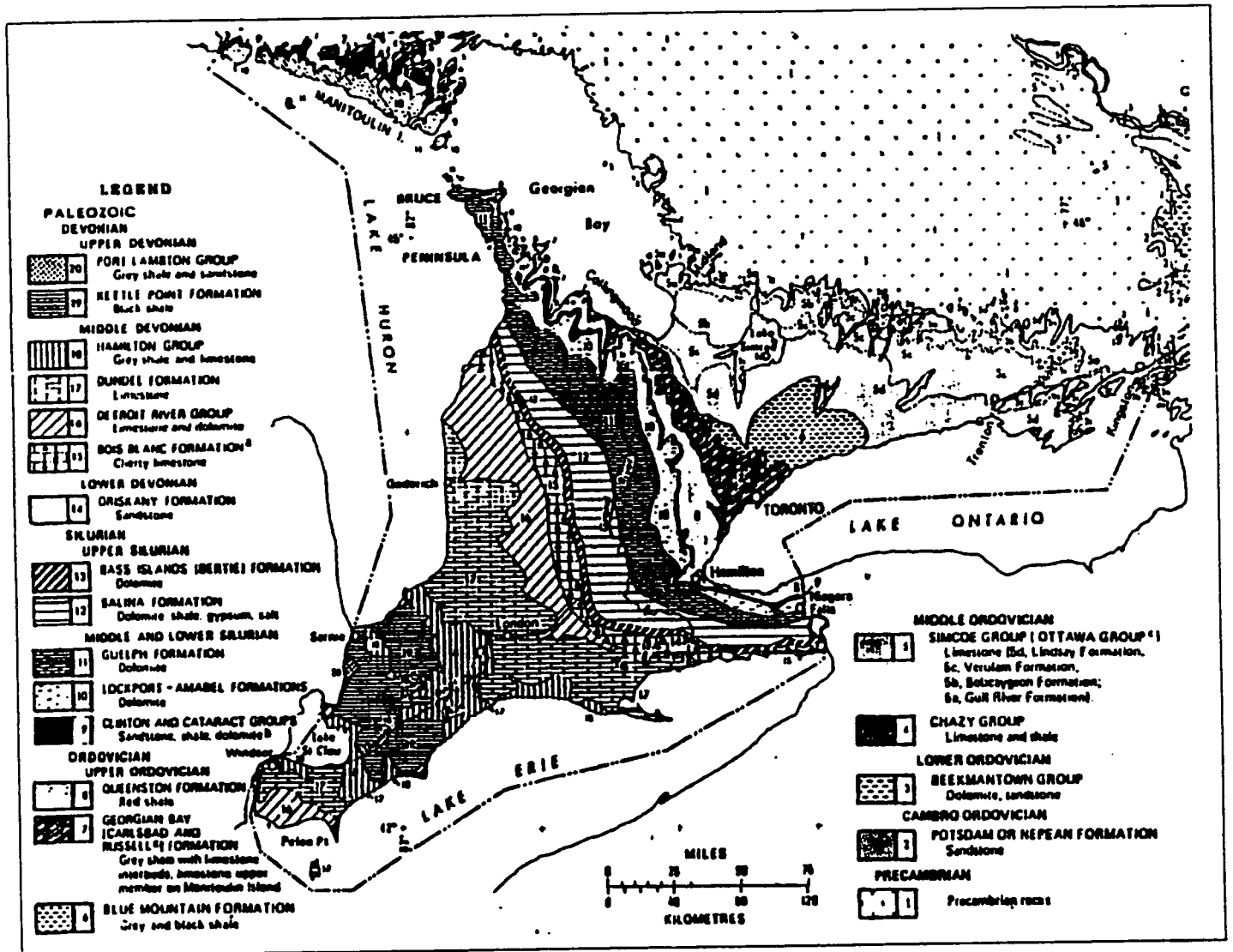
Figure 2.3: Paleozoic geology of southern Ontario (after Mazur et al. 1981)

2.3.3 Post-Paleozoic Time

During the end of the Paleozoic Era the sea withdrew from the Great Lakes Region. Throughout the last 200 million years (Mesozoic and Cenozoic) the Great Lakes stayed above sea level, and the most important process affecting the area ever since has been erosion.

2.3.4 Glacial History of the Great Lakes

The Pleistocene epoch, which extended approximately two million years, witnessed four glacial stages with the following ages (LaBerge 1994):

(1) Wisconsin	(10,000-50,000 years ago)
(2) Illinoian	(300,000 years ago)
(3) Kansan	(700,000 years ago)
(4) Nebraskan	(1,000,000 years ago)

Each glacial stage lasted around 50,000 years, whereas the interglacial stages lasted for a much longer time.

Glacial erosion and deposition caused marked changes in the landscape of the region, deepening valleys and filling others, and ultimately altering the existing drainage patterns. During the Pleistocene, most of the weathered rock that had accumulated in the northern Great Lakes during the Paleozoic was transported southward and deposited in lower Michigan, Illinois, and Wisconsin. Depending on the susceptibility of the rock to

erosion, thickness of the removed material varied from a few metres to hundreds of metres. Rocks that are susceptible to erosion such as shales and weathered areas along faults were heavily excavated by the advancing ice sheets. This type of glacial erosion was the precursor for the creation of many lake basins in Ontario, Michigan, Minnesota, and Wisconsin. The lakes actually developed after the thinning of the Laurentide ice sheet and the ice-marginal retreat into Lake Erie and Lake Michigan basins around 14,500 B.P. (Mickelson et al. 1983).

2.4 Geology of Lake St. Clair and the Detroit River

Underlying the Lake St. Clair-Detroit River system are Middle and Upper Devonian and lower Mississippian rocks. The limestone of the Dundee Formation , near the mouth of the Detroit River, in addition to the dolomites of the Detroit River Formations constitute the oldest rocks in the system (Bolsenga and Herdendorf 1993). Moving in a northwesterly direction from the mouth of the Detroit River, the rocks get gradually younger. Traveling in a northerly direction, the type of bedrock will change from carbonates to black shale (Antrim and Kettle Point formations) and then to sandstones (Marshall and Port Lambton formations). The bedrock surface in Lake St. Clair lies at about 137 m above sea level, while the lake itself lies at an elevation of about 175 m and has a depth that is less than 8 m. This explains why the bedrock which is buried by 30 m of glacial till and lacustrine deposits is not visible near the waterways. A much thinner layer of lacustrine deposits covers the bedrock under the mouth of the Detroit River; the bedrock in this case lies at 168 m above sea level.

During the glacial lake stages, there was a strait that connected the waters in Lake Huron and Lake Erie and occupied the area that is presently occupied by the St. Clair-Detroir River valley. This strait had a wide and flat floor with a few characteristic low ridges. The ridges, which remain nearly unaltered, were left behind as the glaciers that scoured the valley gradually retreated. With this gradual retreat of the glaciers, water levels fell, the strait became narrower, and the St. Clair and Detroit Rivers were formed with Lake St. Clair as a pool between them (Bolsenga and Herdendorf 1993).

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CHAPTER 3

SAMPLING AND ANALYTICAL PROCEDURES

3.1 Sample Collection

A ponar grab sampler was used to collect live *Dreissena polymorpha* samples. Sampling locations are shown in Figure (3.1). The precise sample locations were determined using a Global Positioning System unit (G.P.S.). In addition to Lake St. Clair, samples were collected from the Detroit River mouth in order to detect any differences in metal or isotopic composition caused by the extensive presence of industrial facilities along the western Detroit River shore. Some samples were collected from Mitchell's Bay to detect the impact of river water (e.g. Wallaceburg River) that flows into the area. Samples from the Colchester site were part of an attempt to collect more samples from the western basin of Lake Erie in order to understand what geochemical changes occur as the distance from the river mouth increases. The samples were transferred to plastic bags and kept cold in a cooler before being frozen until the time of isotopic ($\delta^{13}C$ and $\delta^{18}O$) and trace metal analysis.

Water samples were taken using a Van Dorn water sampler at each site where zebra mussel samples were collected. Two water samples were taken from each site at approximately 0.5 m above the bottom of the lake. One sample was taken for $\delta^{13}C$ and $\delta^{18}O$ analysis, and the other was taken for heavy metal analysis. The samples were transferred to acid-cleaned, 100 mL polyethylene bottles and kept cold in a cooler filled with ice before being refrigerated at 4 °C until the time of analysis. Bottles intended for
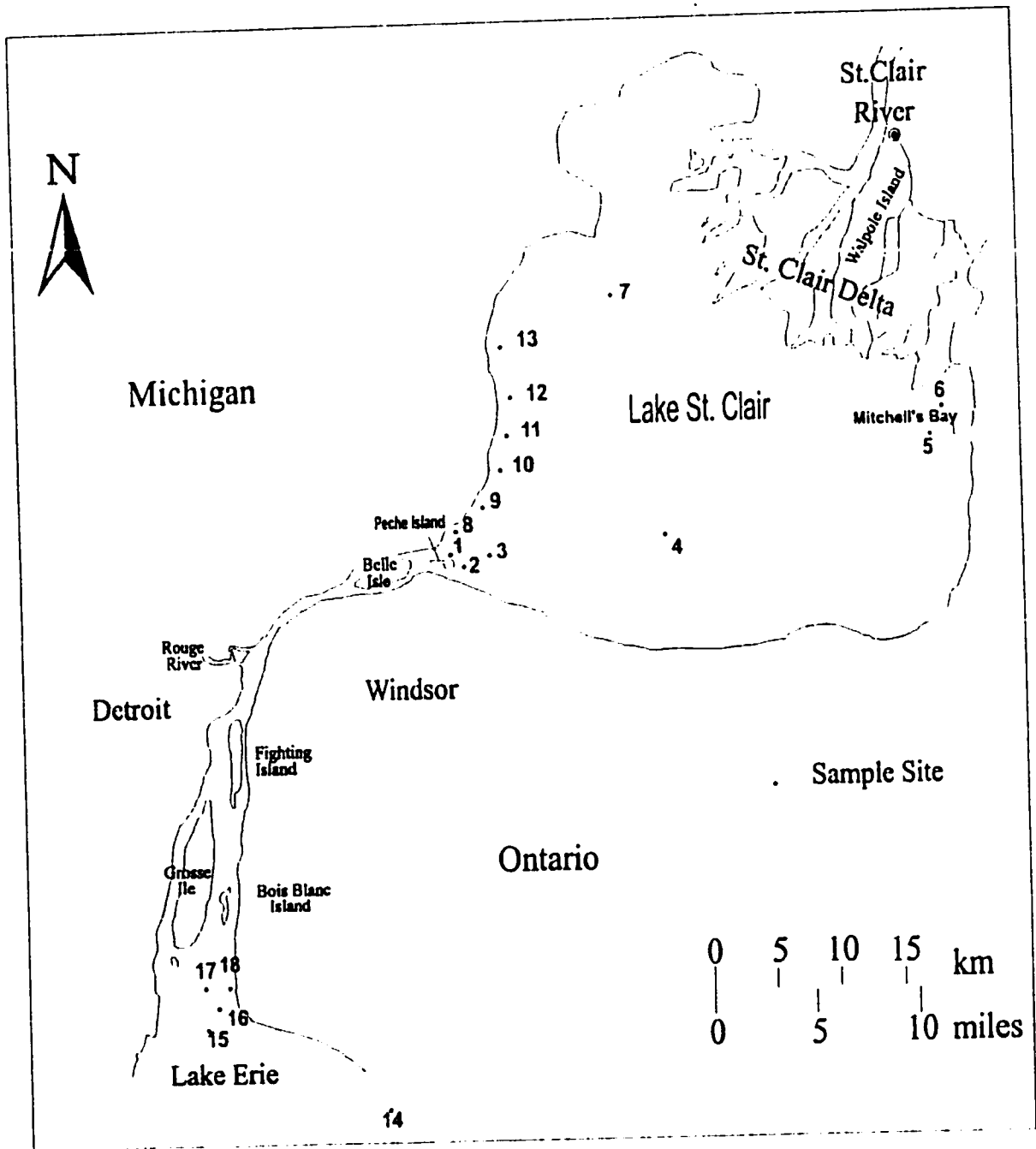
Figure 3.1: Map of the study area showing water and *Dreissena polymorpha* shells sample locations.

isotopic analysis were completely filled with water and properly sealed to prevent CO_2 exchange with the atmosphere. Two drops of mercuric chloride solution were added to each bottle to prevent bacterial growth. Water samples intended for heavy metal analysis were acidified to 1% HNO_3 (ACS grade). At each site the temperature, dissolved oxygen, pH, and conductivity were determined in situ using a portable hydrolab. All samples were collected between June 10 and June 25 of 1997 in order to minimize temporal variations.

3.2 Analytical Procedures

3.2.1 Isotopic Analysis

The *Dreissena polymorpha* samples were thawed at room temperature, the right and left valves were separated, and the soft bodies were scraped out using a plastic knife. A micrometer was used to measure the width and length of each valve with an accuracy of 0.25 mm. The left valve of each shell was then treated with 30% hydrogen peroxide for 12 hours to remove the organic matter. The organic matter-free shells were then cleaned in an ultrasonic bath, lightly scrubbed with a nylon brush, and washed with ultra pure water (conductivity = 0.05 μS/cm, at 25°C).

Samples intended for whole shell analysis (also referred to as bulk shell analysis throughtout the thesis) were powdered using a mortar and pestle. An individual shell was taken to represent one sample, and when more than one sample was taken from a site, the individual shells were analyzed separately (not pooled). A microscope mounted 0.5 mm drill was used to obtain samples from growth rings within individual valves, commencing at the umbo and proceeding outwards. Each growth ring represents one year of growth (e.g. the presence of growth ring #7 implies the shell is 7 years old).

The carbonate samples were then reacted with 100% ACS grade phosphoric acid for 4 hours at 25°C in a water bath (c.f. McCrea 1950). CO_2 gas was then extracted and sent to the Ottawa/Carlton Geoscience Centre Stable Isotope Laboratory to determine the oxygen and the carbon isotopic composition of the gas using a SIRA-12 mass spectrometer. Water samples were also analyzed for their oxygen isotopic composition and the carbon isotopic composition of dissolved inorganic carbon by equilibrating 3 mL samples with carbon dioxide gas for 12 hours at 25"C (c.f. Graber and Aharon 1991). Precision of analysis at the Ottawa/Carlton Geoscience Centre Stable Isotope Laboratory was 0.1‰ for carbon and oxygen, in water and carbonate samples.

3.2.2 Major, Minor, and Trace Element Analysis

All labware (plastic/ teflon) was washed with ultrapure water. It was then submerged into a 13% ACS grade HNO_3 bath for one hour, before being transferred into an ultrapure water bath, and finally rinsed with ultrapure water and left to dry. After the bulk shell samples were accurately weighed into polyethylene bottles, 10 mL of 10% HNO_3 (ACS grade) were slowly added to each sample. The samples were heated for four hours until dryness. Four mL of concentrated HNO_3 (ACS grade) was added and later heated to dryness. The samples were again dissolved with 10% nitric acid and transferred into 60 mL bottles and made up to a volume of 30 mL with ultrapure water. The sequential growth ring sampling was performed using plastic tweezers and care was taken to avoid parts of the growth rings that were in contact with the drill by first breaking off the drilled parts, in order to prevent contamination. Carbonate samples from

the growth rings were accurately weighed before being digested with acid and were subsequently treated in the same manner as the bulk shell samples. The 1% HNO₃ acidified water samples were not filtered before analysis. This implies that the metal concentration values reflect both dissolved ions and ions that are adsorbed to particles in the water. Analysis of the water and the digested carbonate samples for their content of Fe, Mn, Zn, Ca, and Mg was performed using Inductively Coupled Plasma-Optical Emission Spectroscopy at the Great Lakes Institute for Environmental Research Metals Laboratory.

The instrument detection limits for Fe, Mn, Zn, Ca, and Mg in water samples and the acid- digested carbonate solutions are listed in Table (3.1). The solid detection limit of an element (μg/g) is defined as the product of the instrument detection limit (μg/L) and the digested carbonate solution volume (L), divided by the weight of the carbonate sample (g). Since the solution volume is always constant (30 mL), the only variable in this case is the weight of the carbonate sample.

Table 3.1: Elemental Instrument Detection Limits in Water and Acid Digested Carbonate Solutions.

Element Analyzed (ICP-OES)	I.D.L. (μg/L) Water Samples	I.D.L. (μg/L) Acid Digested Carbonate
Fe	5	5
Mn	0.5	0.5
Zn	1	5
Ca	10	100
Mg	10	10

3.3 Precision and Accuracy of Metal Analysis

Precision for the results of heavy metal and major element concentration determinations in water samples are listed in Table (3.2). Reproducibility of element concentrations in water was determined by the duplicate analysis of sample number 1 (two water samples were analyzed from the same site). Precision was excellent for all elements as indicated by the very low relative standard deviations (RSD), which were <1% for each element analyzed. Accuracy of the results was also excellent The experimentally determined values for the certified reference material (W-SLRS3) either coincided or were within 15 % of the published CRM values.

Table 3.2 : Precision and accuracy results of element concentrations in water determined using Inductively Coupled Plasma- optical emission spectroscopy. Mean (μg/L), standard deviation (μg/L), and relative standard deviations (%) are listed for each element.

Element analyzed by ICP-OES	Real Sample Duplication (sample #1)	Pubished Value of CRM (W-SLRS3)	Determined Value of CRM (W-SLRS3)
Fe	218 ± 2, <1% (RSD)	100±2	97
Mn	4.90 ± 0.03, <1% (RSD)	3.9±0.3	3.6
Zn	47.0 ± 0.3, <1% (RSD)	1.04±0.09	1.3
Ca	28500 ± 200, <1% (RSD)	6000±400	5600
Mg	8130 ± 20, <1%(RSD)	1600±200	1620

Precision results of element concentrations in the shells are given in Table (3.3).

Precision data was determined by the duplicate analysis of the certified reference

material (R-MRG). Relative standard deviation values of all elements were <10%.

Laboratory determined values for Mn and Zn concentrations in the certified reference

material (S-Mess2) either coincided with or were within 15% of the published values.

Table 3.3: Precision and accuracy results for element concentrations in the aragonitic shells of *Dreissena polymorpha*. Mean (μg/g), standard deviation (μg/g), and relative standard deviation values (%) are given for each element.

Element	Duplication of CRM (R-MRG)		Published Value of CRM (S-Mess2)	Determined Value of CRM (S-Mess2)
Fe	56700±4000,	7% (RSD)		38700
Mn	511±12,	2% (RSD)	365±21	356
Zn	138±8,	6% (RSD)	172±16	146
Ca	24900±700,	3% (RSD)		15700
Mg	35200±400,	1% (RSD)		14100

CHAPTER 4

BIOLOGY OF *DREISSENA POLYMORPHA*

4.1 History, external morphology, and habitat

Dreissena polymorpha (Pallas 1771) is a small shellfish that was first introduced to the Great Lakes in 1986 through the discharge of ballast water from cargo ships in the St. Clair River. Within two years of its discovery in Lake St.Clair, the mussel had spread downstream to Lake Erie and Lake Ontario through the transport of its veliger larvae by water currents (Griffiths et al., 1991). High densities of zebra mussels can be currently found in the Mohawk/Hudson River systems of western New York, the Ohio River, and the lower Mississippi River as far as Baton Rouge (New York Sea Grant 1993). This endemic, freshwater, bivalve mollusc originated in the northern Black Sea and has been known in the euxinian basin since the Kimmerian. Its life span is in the range of 3 - 5 years, surviving more than 10 years in some cases (Stanczykowska 1977). This organism has been used as an indicator of aquatic pollution and in eco-toxicological projects involving new chemicals (Neumann and Jenner 1992). The mussel is considered a useful freshwater indicator species because of its: (1) body size; (2) availability throughout the year; (3) high fecundity; (4) passive dispersion in the planktonic veliger stage; (5) wide geographic distribution; (6) firm attachment by byssal threads; and (7) its ability to tolerate a relatively high level of chemical pollution.

Dreissena polymorpha is a small mollusc usually less than three centimetres in length. The species name, *polymorpha*, reflects the tremendous variety in the pattern of

the stripes observed on the shell. Some shells are pure black, brown, or even albino in specific cases. The dark stripes are the result of an overlap in the deposition of aragonite at the beginning of each active growth season (Chamberlain 1980). Growth in *Dreissena polymorpha* is rapid during the summer, during which most of the aragonitic shell is precipitated, and slow in the winter.

This bivalve prefers shallow, low energy environments with a salinity range of 0.2 to 3.0 parts per thousand. While the organism can tolerate chemical pollution to a certain degree, it adapts poorly to deficits in oxygen (Neumann and Jenner 1992). Under anoxic conditions, the organism shows impaired ionic and osmotic regulation within 24 hours at 20°C and, therefore, it is restricted to the littoral zone in eutrophic lakes. The optimum temperature for the successful development of *Dreissena polymorpha* embryos is 18°C, while the optimum pH is estimated at 8.5. It is essential that calcium ions be present at a concentration higher than 60 mg per litre; lower concentrations will eventually result in the crumbling of the embryo into separate cells (Sprung 1987).

Although the mussels are known for their preferential invasion of rocks and other hard substances within a water shed, high mussel densities were observed colonizing sand and mud sediments across hundreds of square Kilometres in Lake Erie (Berkman et al. 1998). Densities of zebra mussels ranged from 1,500 to 32,500 individuals per square metre. Such density values are also similar to those determined by Coakley et al. (1997), who observed colonization levels of up to 20,000 mussels per m^2 in soft sediments of the western basin of Lake Erie. These densities are an order of magnitude higher than previously observed densities in sedimentary habitats from the European continent. This

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phenomenon implies that zebra mussels possess the ability to directly colonize sand and bind the sediment into conglomerates using their byssal threads.

4.2 Anatomy

The shell of *Dreissena polymorpha* has a heteromyarian form with a reduced anterior end and an inflated posterior end. The ventral shell margin is sinusoidal and forms a byssal gape (Fig.4.1A). According to Taylor et al. (1973), shell microstructure shows the presence of an outer crossed-lamellar layer and an inner crossed-lamellar layer. The shell has a septum that occupies the umbonal region of each valve and to which the anterior adductor and anterior byssal retractor muscles are attached. The posterior adductor and posterior byssal and pedal retractor muscles are attached posterdorsally to the pallial line (Fig.4.1A).

The organism has a posteriorly elongate ligament which is called the primary ligament. A secondary ligament of periostracum covers the primary ligament and is divided into inner and outer components by a tongue of mantle which secretes it. The zebra mussel has an inhalant siphon with a large opening surrounded by tentacles and an exhalant siphon with a smaller posterdorsally directed opening (Fig.4.1B). The siphons are the result of fused inner folds of the mantle (Yonge 1982).

The mouth lies between the bases of the anterior byssal retractor muscles and is connected to the esophagus. The esophagus is directed upwards from the mouth and leads to the stomach which lies beneath the ligament, near the surface of the visceral mass (Morton 1993). The midgut leaves the wall of the stomach and passes

posteroventrally, traversing the visceral mass, then turns anterodorsally as the hindgut into the pericardium (Fig.4.1B). The rectum pervades the heart ventricle and passes between the posterior byssal retractor muscles, ultimately terminating in an anal papilla. The pericardium contains many organs including the heart, kidney, genital aperture, and the excretory aperture.

4.3 Life Cycle

Zebra mussels are either male or female with the ratio of females to males being 3 : 2 in Lake St. Clair (Makie 1990). One female produces an average of 30, 000 eggs, nevertheless less than one per cent of the larvae will grow to adulthood given the dangers posed by predators and parasites. Eggs from the female, each having a size of approximately 70 μm (Sprung 1993), are released into the water during the end of May. After the eggs have been shed, they start to sink to the bottom. Successful fertilization occurs above 10°C. Within a temperature range of 12-24°C, the eggs are externally fertilized by the sperm 2.5 - 4.75 hours after their release. Then the veliger stage begins. At this stage, the young larvae can swim by means of a velum and can be easily distinguished by their straight - hinged shells. As it enters the planktonic stage, the larva has a shell size of 100 μm and weighs 0.12 μg.

The post-veliger stage is associated with an increase in the weight of the shell, thus reducing the ability of the larvae to swim. By the end of this stage, the larva has a shell length of 200 μm and weighs around 1.27 μg. As the larva grows, its tolerance limit for a variety of environmental conditions increases. For example, a *Dreissena* larva
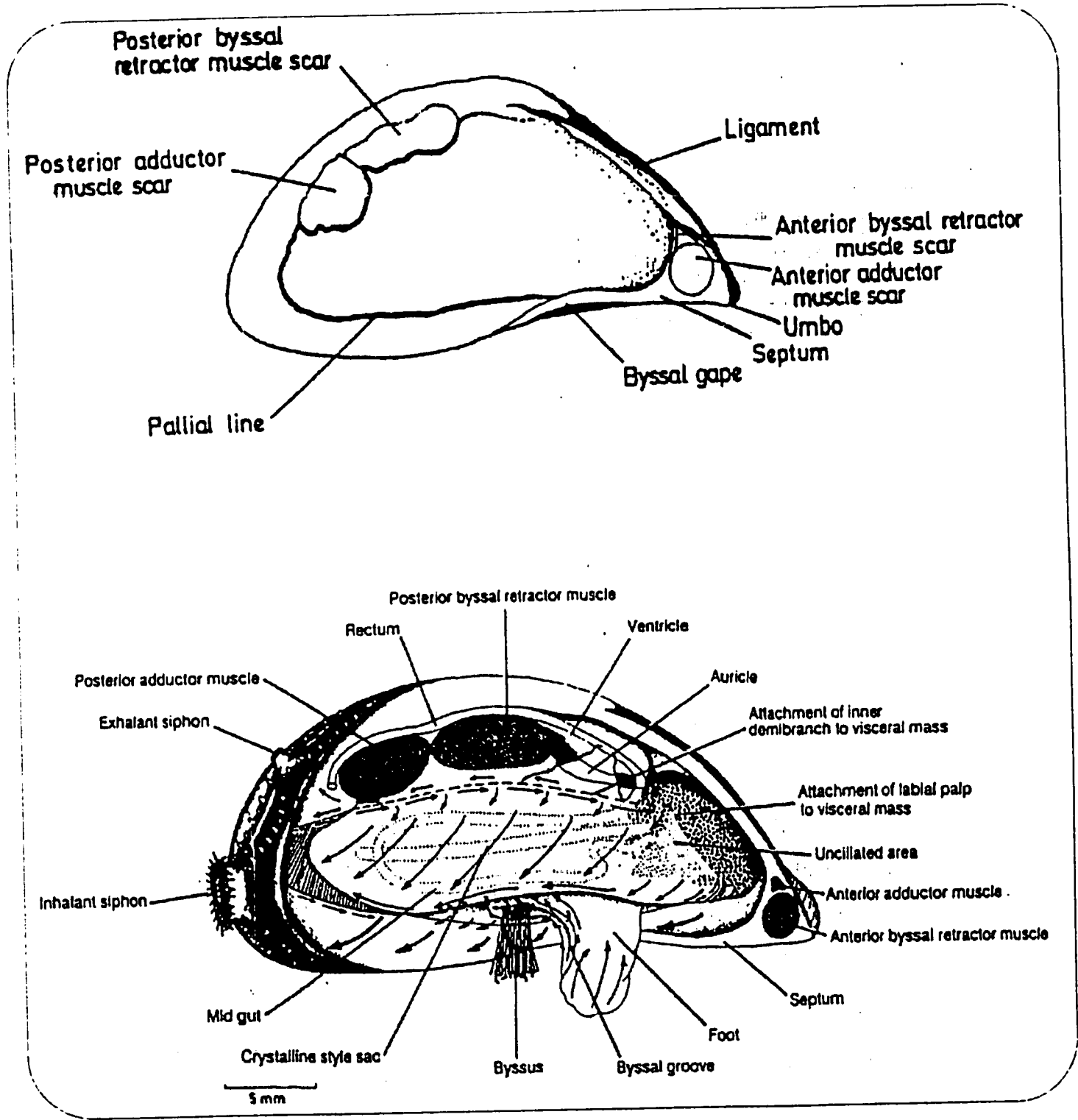
Figure 4.1: (A) Shell morphology of *Dreissena polymorpha*.
(B) Alimentary system of *Dreissena polymorpha*.

will tolerate a temperature range between 0 and 30°C. Other changes include the reorientation of organs in the cavity of the mantle and the disappearance of the velum. The larvae will spend around a month moving around before they settle down in their desired habitat and enter the adult or benthic stage (Sprung 1993). As adults the Zebra mussels secrete their byssal threads, attaching themselves to solid objects and other animals too. Within the first year of their adult stage, the mussels can relocate themselves from one site to another and secrete new byssal threads to reattach themselves.

4.4 Environmental Impacts of *Dreissena polymorpha*

Dreissena polymorpha is an efficient filter feeder that was shown to have 100% retention of particles greater than 1 μm (Reeders and Bij de Vaate 1990). The bivalve prefers consuming particles between 15 and 40 μm, but has been known to ingest particles up to 750 μm in size. This filtering action is responsible for the removal of phytoplankton and consequently increasing water transparency in many North American and European lakes (Ludyanskiy et al. 1993; Leach et al. 1992). A study by Griffiths (1992) showed that Secchi disk transparency in Lake St. Clair increased from 0.5 - 1.5 m, before zebra mussels were introduced to the lake in 1986, to 1.8 - 2.8 m in the year 1990. Griffiths (1992) also predicted that the current process of oligotrophication of Lake St. Clair will not cease unless there is a decrease in the zebra mussel population.

Filter feeding by zebra mussels contributes to the removal of excessive amounts of algae and microzooplankton, and can therefore help in the restoration of lakes. They have already been used as biomanipulation tools for water quality management: in the Netherlands zebra mussels were intentionally introduced to lakes in an attempt to improve water quality. Zebra mussels bear an impact on nutrient pathways by ingesting phosphorus, dissolved nutrients, and calcium carbonate. Since they can significantly reduce phosphorus and other nutrient levels, zebra mussels are currently being considered for controlling eutrophication in lakes (Reeders and Bij de Vaate 1992). *Dreissena polymorpha* has also been shown to be capable of accelerating the conversion of certain toxic nitrogenous wastes, such as ammonia and nitrite, to non-toxic compounds that are safe to be consumed by other benthic organisms (Mackie et al. 1989).

Since zebra mussels are responsible for removing nutrients by filter-feeding, they will eventually cause a decrease in the primary productivity of lakes. Mackie (1991) predicted that the zebra mussels' continuous biodeposition of nutrients on Lake St. Clair's floor will reduce the energy available to pelagic food webs and result in the increased development of benthic organisms. This will cause a reduction in zooplankton and fish populations in Lake St. Clair and eventually negatively impact commercial and sports fisheries.

Moreover, zebra mussels are able to remove contaminants from the water column and biodeposit them on lake shores and floors. Dobson and Makie (1998) observed that the biodeposition rate of polychlorinated biphenyls (PCBs) and cadmium by zebra mussels was 8-10 times greater than natural sedimentation values for the same contaminants in westen Lake Erie. De Kock and Bowmer (1993) also observed the

transfer of cadmium and organochlorines from zebra mussels to the tufted duck and ultimately to duck eggs, causing serious damage to duck populations.

The invasion of *Dreissena polymorpha* has also affected the diversity of many benthic species. Makie (1993) documented the negative effects of zebra mussels on unionid communities in Lake St. Clair and Lake Erie. High densities of zebra mussels were found to settle over unionid communities, interfering with the opening and closing of their valves. The growing population of zebra mussels caused the extinction of many unionid species and consequently is contributing to the reduction of the diversity of benthic organisms.

The negative impacts of zebra mussels on the dissolved oxygen resources of invaded aquatic environments were investigated by Effler and Siegfried (1994). They studied the effects of a recent invasion of the Seneca River, New York, by zebra mussels. In this study, *Dreissena polymorpha* densities of 33,000 - 61,000 individuals per m^2 were regarded as the cause of an observed average depletion of 1.7 mg L^{-1} across the river. The introduction of a new sink for oxygen , such as zebra mussels in this example, can have serious environmental impacts, especially in systems with poor reaeration capacity. The demand for oxygen by zebra mussels at the bottom of the Seneca River in this study was estimated at 35 g m^{-2} d^{-1}, which is much greater than the sediment oxygen demand of organically enriched sediments (SOD = 5.0 g m^{-2} d^{-1}). A reduction in oxygen resources implies a loss of waste assimilative capacity in the river, which means that waste discharge permits issued by the state of New York have to be modified in order to protect the depleted oxygen resources of the Seneca River.

4.5 Shell Formation

A mollusc's shell is formed by the deposition of calcium carbonate crystals on an organic matrix of protein called conchiolin. The specific tissue that undertakes the formation of the shell is called the mantle, which is usually seen covering the internal surface of the shell. The mantle area is therefore the variable that controls the increase in the shell's area. The thickness of the shell, however, is controlled by the rate of secretion of calcium carbonate and the organic matrix. The deposition of calcium carbonate occurs in one of the following three forms: calcite, aragonite, and vaterite. These three forms are identical in their chemical composition but show distinct differences in their crystal lattice structure. The three primary crystal arrangements of the shell are: (1) prismatic structure with columnar arrangement of the crystals, which are surrounded by the matrix; (2) laminar arrangement in which layers are parallel and one crystal in thickness; (3) crossed lamellar arrangement with small lamellae joining large lamellae at angles to each other (Wilbur 1964).

The amount of calcium in the shell is dependent on the concentration of calcium in the immediate vicinity of the organism. Calcium may either enter the mantle directly or through other parts, ultimately getting transferred into the mantle by the blood. It can then move across the mantle in both directions. This bidirectional movement can be quantified by measuring the calcium turnover rate, which in turn can provide an estimate of the capacity of the mantle to move the calcium across the epithelium to the site of deposition. It was noted that equilibrium between medium and tissue calcium is achieved faster in marine organisms than in freshwater organisms. This difference is due

to a higher tissue calcium content and a slower calcium turnover rate in freshwater organisms (Wilbur 1964).

The formation of the shell takes place within a layer of fluid called the extrapallial fluid, which occurs between the mantle and the inner surface of the shell. The source of the shell carbonate is the CO_2-bicarbonate pool within the mantle. This pool has three main sources: (1) from the surrounding environment; (2) from urea through the activity of urease in some species; (3) and from the decarboxylation of Krebs cycle intermediates. One example of the latter source is oxaloacetate which can be a source of CO_2 when it undergoes decarboxylation by oxaloacetic decarboxylase which can be found in the mantle. Carbonate formation is dependent on the rate of conversion of CO_2 to bicarbonate and carbonate. The following equations illustrate the relationship between these compounds:

$$+HO^-$$

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \longleftrightarrow HCO_3^- + H^+ \longleftrightarrow CO_3^{-2} + H_2O$$

$$\updownarrow \qquad -OH^-$$

$$CO_3^{-2} + CO_2 + H_2O$$
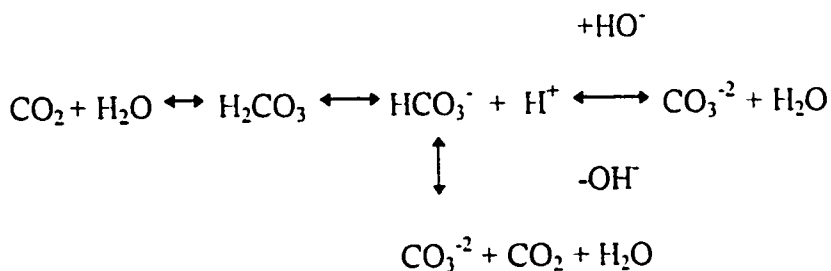
This implies that the carbonate can be formed via bicarbonate in the presence of hydroxyl ions or through decarboxylation. The following reactions are catalysed by carbonic anhydrase:

$$CO_2 + H_2O \longrightarrow H_2CO_3 \quad \text{and} \quad CO_2 + OH^- \longrightarrow HCO_3^-$$
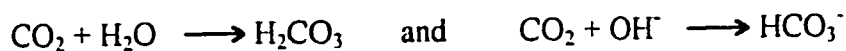
Carbonic anhydrase is found in the mantle of many species and it plays an important role in the control of the rate of calcification. This fact was noted when the addition of inhibitors to carbonic anhydrase, such as sulfonamide compounds, also inhibited the

calcification process (Freeman 1960). When the concentration of bicarbonate is high, the rate of calcification becomes dependent on the rate of conversion of bicarbonate to carbonate. This conversion occurs by CO_2 removal and its consequent fixation in the mantle.

In summary, the rate of calcification is controlled by the following factors: (1) the supply of calcium available to the mantle; (2) the rate of conversion of bicarbonate to carbonate; (3) the rate of the synthesis of the organic matrix; (4) the rate of secretion of calcium by the mantle; (5) the required alkaline pH of the extrapallial fluid for the deposition of $CaCO_3$.

CHAPTER 5

CARBON AND OXYGEN STABLE ISOTOPES

5.1 Theoretical Background

Isotopes are atoms that contain the same number of protons but a different number of neutrons. They are either radioactive or stable. Radioactive isotopes decay into radiogenic daughter isotopes as a function of time. The decay is accompanied by the release of radiation, which can be divided into alpha, beta, gamma, and electron capture radiation. Stable isotopes exist for all elements having an atomic number within the range 1 to 83, except for 5 and 8.

Differences in the atomic masses of isotopes create some differences in their physicochemical properties (Hoefs 1987). Mass differences between isotopes affect the strength of the bonds between them and ultimately their readiness to participate in chemical reactions. Heavy isotopes form stronger bonds, which are harder to break, and this causes them to react less readily than lighter isotopes which form the weaker bonds.

Variations in the abundance of stable isotopes can be produced by a process called isotope fractionation. Fractionation is caused by the aforementioned differences in the physicochemical properties of isotopes and is defined as the partitioning of isotopes between two substances having different isotope ratios. Isotope fractionation occurs via kinetic processes, which are controlled by the reaction rates of different isotopes, and

isotope exchange processes, which are characterized by an isotope exchange between different phases or chemical substances (Hoefs 1987).

The ratio of two isotopes in a certain chemical substance A divided by the same ratio in another substance B is called the fractionation factor α, which is expressed by the following equation (Faure 1986):

$$\alpha_{A-B} = R_A / R_B$$

The fractionation factor is related to the equilibrium constant K by the following equation (Faure 1986), assuming a random distribution of isotopes in substances A and B:

$$\alpha = K^{1/n} \ ,$$

where n is the number of atoms exchanged. Studies have also shown that the fractionation factor α is linearly related to $1/T^2$, where T is the temperature in degrees Kelvin.

5.2 Fractionation of Carbon Isotopes

Although it is an abundant element in the universe, carbon occurs in the earth only in trace amounts. Carbon has two stable isotopes:

$^{12}C = 98.89\ \%$

$^{13}C = 1.11\ \%$

The isotopic composition of carbon can be expressed as a per mil deviation from a standard. Although currently exhausted, the most commonly referred to standard is a Cretaceous belemnite from the Pee Dee formation (PDB). An artificial (synthesized) standard called the Vienna PDB (VPDB), which is identical to PDB in its isotopic composition, is currently used in many laboratories. The following equation is used to express the isotopic composition of carbon:

$$\delta^{13}C = [\{(^{13}C/^{12}C) \text{ sample}/(^{13}C/^{12}C) \text{ standard}\} - 1] * 1000$$

Figure (5.1) shows the $\delta^{13}C$ (PDB) values of some important carbon compounds. The isotope composition of carbon is highly variable; it reaches values of +20 per mil in heavy carbonates and values as low as - 90 per mil in light methane (Hoefs 1987). This variability in isotopic composition is due to the partitioning of isotopes between two substances possessing different isotope ratios; a phenomenon called fractionation. Fractionation of carbon isotopes leads to two isotopically distinctive reservoirs : organic matter and sedimentary carbonates. The fractionation event can occur either through a kinetic effect which depends on differences of reaction rates of isotopes or a chemical exchange effect.

5.2.1 Kinetic Fractionation of Carbon

The first mechanism of fractionation occurs during photosynthesis where there is a preferential intake of light CO_2 by plants. This process of CO_2 fixation will alter the

ratio of $^{13}C/^{12}C$ between plant material and dissolved CO_2 (Gillon 1998). This photosynthetic discrimination occurs in three main steps:

1. The preferential incorporation of $^{12}CO_2$ across the cell wall and dissolution in the cytoplasm.

2. The preferential conversion of $^{12}CO_2$ in the cytoplasm into phosphoglyceric acid.

3. The synthesis of organic compounds from phosphoglyceric acid (Faure 1986)

The factor that controls the extent of discrimination depends primarily upon the rate of supply of CO_2. When CO_2 is not a limiting factor, the discrimination will be controlled by the carboxylation enzymes (Gillon 1998). In C_3 plants, the main carboxylation enzyme is ribulose-1, 5-biphosphate carboxylase/ oxygenase (RUBISCO). In order to estimate the amount of fractionation caused by RUBISCO, the first product of the carboxylation reaction, 3-phosphoglycerate, was combusted and yielded estimates of fractionation that ranged from 20 per mil to 40 per mil (Deleens et al., 1974; Wong 1979). In C_4 plants, the main carboxylation enzyme is phosphoenolpyruvate carboxylase (PEPC). This pathway involves the fixation of CO_2 into C_4 acids in the mesophyll cells, whereby CO2 is dissolved and hydrated into an HCO_3^- ion before carboxylation. The latter pathway produces fractionation values around -5.9 per mil (Whelan 1973).

5.2.2 Equilibrium Fractionation of Carbon

The second mechanism of fractionation is a chemical exchange of atoms that occurs within an equilibrium established between atmospheric CO_2 and dissolved bicarbonate. The end result is an enrichment of ^{13}C in the bicarbonate (Hoefs 1987). In this process, there is only a redistribution of isotopes between different chemical substances or phases. Fractionation that occurs between carbon dioxide gas and the dissolved carbonate species has been studied by Emrich et al. (1970). This system of carbonate equilibria can be represented as follows:

$$CO_2(g) \ <=> \ CO_2(aq) \tag{1}$$

$$CO_2(aq) + H_2O \ <=> \ H^+ + HCO_3^-(aq) \tag{2}$$

$$\underline{CaCO_3(s) + H^+ \ <=> \ Ca^{+2} + HCO_3^-(aq)} \tag{3}$$

$$CO_2(g) + H_2O + CaCO_3(s) \ <=> \ Ca^{+2}(aq) + 2HCO_3^-(aq) \tag{4}$$
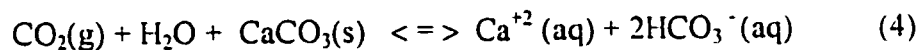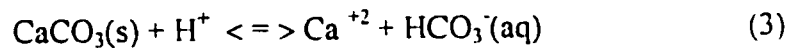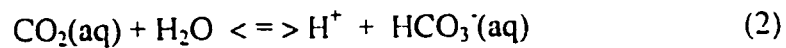
According to Emrich et al. (1970), the fractionation factors associated with this equilibria at 20 °C are:

1. Calcium carbonate-bicarbonate: 1.00185

2. Bicarbonate - carbon dioxide gas: 1.00838

3. Calcium carbonate-carbon dioxide gas: 1.01017

These fractionation factors vary with temperature and can be used to calculate $\delta^{13}C$ values of calcium carbonate precipitated in equilibrium with CO_2 of known $\delta^{13}C$ value. Such calculation can be performed using the following equation (Faure 1986):

$$\alpha_{AB} = \delta_A + 1000 / \ \delta_B + 1000$$

Using the above equation, it can be shown that calcium carbonate that is precipitated in isotopic equilibrium with carbon dioxide gas is richer in ^{13}C by 10 ‰ with respect to the carbon dioxide gas.

5.3 Fractionation of Oxygen Isotopes

Oxygen is the most abundant element on earth, and it has three stable isotopes:

1. ^{16}O = 99.736%

2. ^{17}O = 0.0375%

3. ^{18}O = 0.1995%

The isotopic composition of oxygen is expressed as a per mil deviation from a standard using the following equation:

$$\delta^{18}O = [\{(^{18}O/^{16}O)sample-(^{18}O/^{16}O) \text{ standard}\} - 1] * 1000$$

Craig (1961) introduced a standard which was called the Standard Mean Ocean Water (SMOW). The Vienna Standard Mean Ocean Water (VSMOW), which is a synthesized standard, is isotopically identical to SMOW and is commonly used in many laboratories. Another standard introduced for paleotemperature determinations is a Cretaceous belemnite from the Pee Dee formation (PDB). In order to compare values from different types of samples, the following equation is used to convert PDB values into SMOW values :

$$\delta \text{ SMOW} = 1.03086 \ \delta \text{ PDB} + 30.86 \text{ per mil}$$

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As is the case with carbon, fractionation of oxygen isotopes occurs through two main mechanisms: kinetic and equilibrium processes. Such fractionation mechanisms cause the tremendous variations in the ratio $^{18}O/^{16}O$ which varies by 100 per mil in nature (Hoefs 1987). Figure (5.1) shows the $\delta^{18}O$ (SMOW) values of some important oxygen-containing compounds.

5.3.1 Kinetic Fractionation of Oxygen

Fractionation of a kinetic nature occurs during the processes of photosynthesis and respiration. During respiration, there is a preferential uptake of ^{16}O which causes isotopic fractionation leading to the enrichment of atmospheric oxygen in ^{18}O with respect to the hydrosphere. Oxygen isotope enrichment during respiration varies from 7 per mil to 25 per mil (Gillon 1998). This phenomenon of atmospheric oxygen enrichment is called the Dole effect (Dole 1954). It is known that oxygen produced during photosynthesis is a result of the splitting of H_2O molecules. The liberated oxygen is enriched in ^{18}O by 5 per mil compared to the source water (Faure 1986). This 5 per mil enrichment is very close to the 6 per mil enrichment of atmospheric oxygen relative to water calculated by Urey (1947) to represent equilibrium between the hydrosphere and the atmosphere. However, equilibrium does not exist and, therefore, photosynthesis cannot account for the Dole effect.
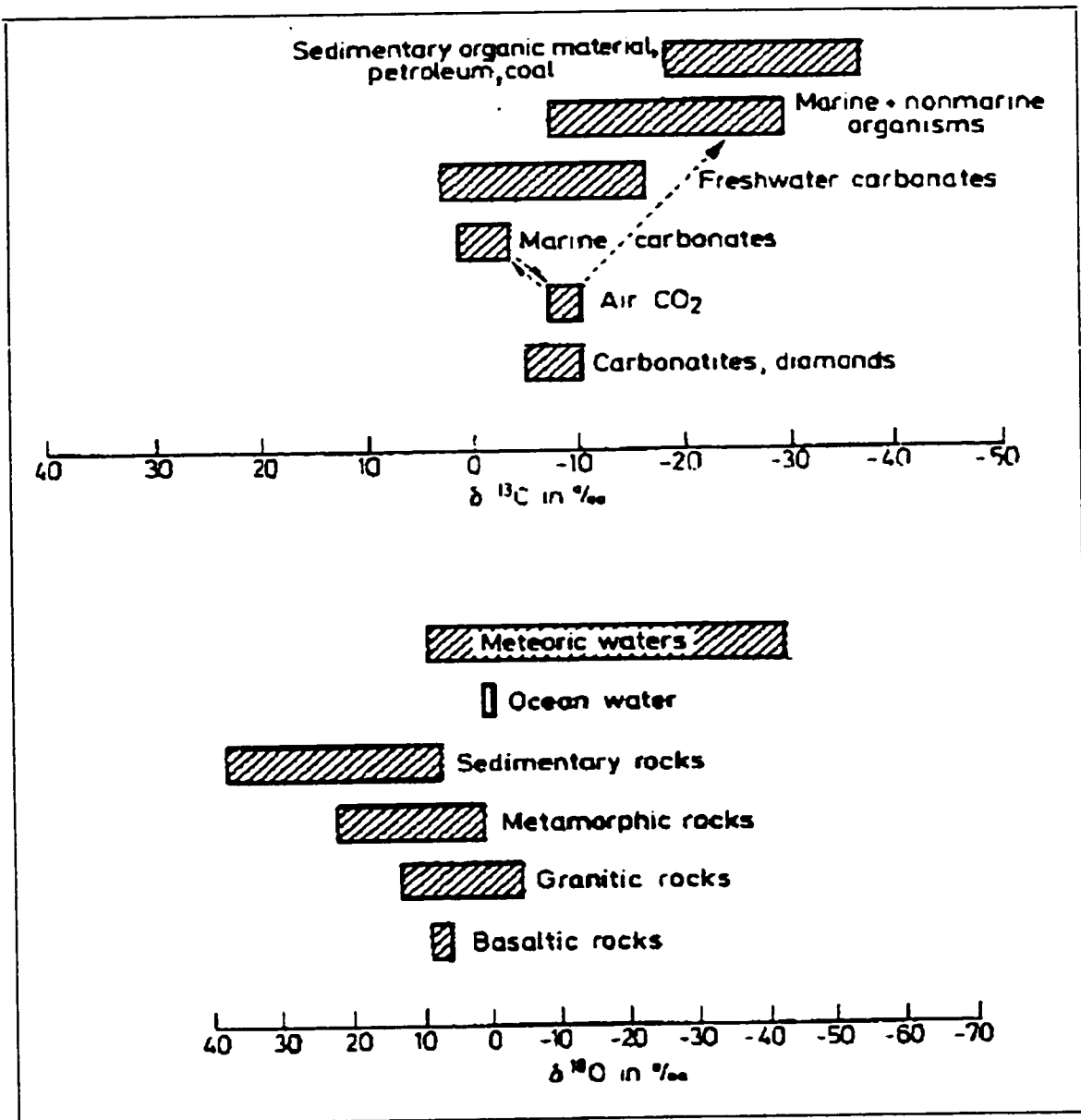
Figure 5.1: $\delta^{13}C$ (PDB) and $\delta^{18}O$ (SMOW) of some important carbon and oxygen-containing compounds (After Hoefs 1987)

5.3.2 Equilibrium Fractionation of Oxygen

Equilibrium exchange reactions are primarily due to differences in bond strengths. Minerals such as silicates are rich in ^{18}O and have oxygen strongly bonded to cations of high ionic potential. Other minerals where weaker and longer Al-O bonds dominate have lower $^{18}O/^{16}O$ ratios.

Other factors that play a role in oxygen isotope fractionation include vapor pressure differences and hydration processes (Rayleigh 1896). Water molecules containing the lighter oxygen isotopes have a higher vapor pressure than water molecules with heavier oxygen isotopes and tend to evaporate first, leaving behind the heavy isotopes in the liquid phase. The opposite happens in the process of condensation during which the heavier oxygen isotopes leave the vapor phase first. Fractionation also occurs during the hydration of ions; this is especially important for highly evaporated water bodies.

5.4 Isotopic Composition of Lake Water

5.4.1 Oxygen Isotopic Composition

The isotopic composition of oxygen in water is influenced by the ^{18}O content of inflowing water and precipitation as well as evaporation and exchange reactions with the atmosphere (Yang et al. 1996). Other factors such as the surface area and the depth of the lake should also be considered. Shallow lakes show considerable seasonal variations

in their oxygen isotopic composition, displaying the highest ^{18}O contents during the summer. Large and deep lakes, however, show a more or less stable ^{18}O content which could change to reflect long term climatic changes (Fritz & Poplawski 1974).

In the cold northern climates, the lakes are covered with ice during the winter and are affected by the inflowing surface and groundwater which tend to decrease their ^{18}O content. During the summer, there is an enrichment in the ^{18}O content which is caused by extensive evaporation and the preferential loss of light water ($H_2^{16}O$). Major climatic changes could also change the amount of precipitation occurring, which will affect the ^{18}O composition of inflowing waters.

5.4.2 Carbon Isotopic Composition

According to Yang et al. (1996), the major sources of DIC in natural waters are atmospheric CO_2 and CO_2 from plant respiration, the decay of organic material, and the dissolution of carbonate minerals. There are many factors that govern the $\delta^{13}C_{DIC}$ content of lake water. These factors include isotopic exchanges with inflowing groundwater, atmospheric carbon dioxide, and carbon dioxide that results from the decay of organic matter. Another important process is photosynthesis by aquatic plants. During this process there is a preferential intake of light carbon ^{12}C resulting in an enrichment in $^{13}C_{DIC}$ as seen in the Danube (Pawellek and Veizer 1995). Theoretically, the dissolution of carbonates can also produce an enrichment in ^{13}C. The latter factor, however, has been shown to play a minimal role in changing the isotopic composition of

DIC as demonstrated by the depleted ^{13}C values (-11 to -8 ‰) observed in the Grand and Thames rivers which drain carbonate basins (Yang et al. 1996).

As a result of the interplay of these factors, a ^{13}C stratification can be observed. The surface waters are more enriched in ^{13}C than the deep waters with $\delta^{13}C$ values between -5 and -9 per mil. Deeper waters are affected by biological activities such as the aerobic decomposition of organic matter which produce CO_2 with $\delta^{13}C$ lower than -20 per mil. Under anaerobic conditions methane is generated along with CO_2 which becomes enriched in ^{13}C, resulting in DIC with $\delta^{13}C$ values between -10 and -20 ‰ (Fritz & Poplawski 1974).

Values of the $\delta^{13}C$ and $\delta^{18}O$ content of several lakes that were collected at different times during the year show that there is a clear positive correlation between the abundance of the two isotopes. This can be logically accounted for in shallow and stagnant lakes which are naturally enriched in ^{18}O and characterized by high biological activity. This higher biological activity implies higher rates of anaerobic decomposition of organic matter and more extensive photosynthetic activity, which would cause an enrichment in ^{13}C of carbon dioxide (Fritz and Poplawski 1974).

5.5 Isotopic Equilibrium

5.5.1 Oxygen Isotopic Equilibrium

When isotopic equilibrium between ^{18}O of the ambient water and ^{18}O of the precipitated carbonate exists, it is possible to determine paleotemperatures of oceans and

lakes. This was first suggested by H. C. Urey (1947), known best for his studies on the fractionation of stable isotopes. In 1950, McCrea was the first to actually introduce a paleotemperature scale, which was modified by Epstein et al. (1953) and Craig (1965) into the following relationship:

$$T (°C) = 16.9 - 4.2 (\delta^{18}O \text{ carbonate } -\delta^{18}O \text{ water}) + 0.13 (\delta^{18}O \text{ carbonate } -\delta^{18}O \text{water})^2$$

The isotopic composition of oxygen of the precipitating carbonate is different than that of the water from which it precipitated, thus making the construction of a paleotemperature scale essential. The difference in the isotopic composition is due to the occurrence of fractionation events that include isotopic exchange between the calcium carbonate and the water as illustrated by the following equation (Faure 1986):

$$CaCO_3^{16} + 3H_2O^{18} = CaCO_3^{18} + 3H_2O^{16}$$
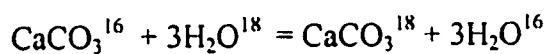
However, there are three factors that complicate the interpretation of the calculated paleotemperatures (Hoefs 1987):

1. the unknown oxygen isotopic composition of ancient oceans: it has to be assumed that the isotopic composition of ancient ocean waters did not significantly change over time, although secular trends in the $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios of marine carbonates have been previously observed (Veizer 1976).

2. metabolic effects on isotopic composition: some species, including many molluscs, do deposit their shells in isotopic equilibrium with the ambient water; however, other species (echinoderms, asteriodea, and crinoidea) do not (Weber 1968). This diequilibrium results from isotopic exchanges between respiratory CO_2 and HCO_3 close to the site of shell deposition.

3. preservation of the primary isotopic composition of oxygen: the original oxygen isotopic composition of the shell will be preserved unless the shell carbonate underwent dissolution or recrystallization (Al-Aasm and Veizer 1984).

An important factor that should be considered when discussing the relationship between $\delta^{18}O$ of the carbonate shell and temperature is the mineralogy of the carbonate. Horibe and Oba (1972) cultured two pelecypod species with differing shell mineralogy and demonstrated that the $\delta^{18}O$-temperature relationship is different for each mineral. Based on the species *Andara broughtoni*, with the aragonitic shell, the empirical relationship is as follows:

$$T(^\circ C) = 13.85 - 4.54(\delta^{18}O_{aragonite} - \delta^{18}O_{water}) + 0.04(\delta^{18}O_{aragonite} - \delta^{18}O_{water})^2$$

Based on the species *Patinopecten yessoensis*, with the calcitic shell, the empirical relationship is as follows (Horibe and Oba 1972):

$$T(^\circ C) = 17.04 - 4.34(\delta^{18}O_{calcite} - \delta^{18}O_{water}) + 0.16(\delta^{18}O_{calcite} - \delta^{18}O_{water})^2$$

Grossman and Ku (1981) modified the Horibe and Oba (1972) paleotemperature equation into the following relationship:

$$T(^\circ C) = 19.00 - 3.52(\delta^{18}O_{aragonite} - \delta^{18}O_{water}) + 0.03(\delta^{18}O_{aragonite} - \delta^{18}O_{water})^2$$

Finally, Grossman and Ku (1986) developed the following equation based on a series of coeval mollusc samples:

$$\delta^{18}O_{aragonite} - \delta^{18}O_{water} = 4.65 - 0.213(T^\circ C)$$

5.5.2 Carbon Isotopic Composition

When shells are formed in isotopic equilibrium with lake water, $\delta^{13}C$ values of DIC can be calculated using equilibrium fractionation equations. Shells, however, can be precipitated out of isotopic equilibrium with the ambient water. Such disequilibrium with respect to ^{13}C can be due to many factors including the incorporation of metabolic carbon and kinetic fractionation that can occur during shell growth (Erez 1978; Vincent and Berger 1981).

Many equations exist for equilibrium fractionation of ^{13}C in biogenic aragonite, and they include the following:

(1) $\delta^{13}C(\text{aragonite}) = \delta^{13}C(\text{DIC}) + 1.85 + 0.035(T - 25°C)$ (Rubinson and Clayton 1969);

(2) $\delta^{13}C(\text{aragonite}) - \delta^{13}C(\text{DIC}) = 12.40 - [2980/ (T°K)]$ (Grossman 1984), based on *H. elegans*;

(3) $\delta^{13}C(\text{aragonite}) - \delta^{13}C(\text{DIC}) = 2.40 - 0.108(T°C)$ (Grossman and Ku 1986), also based on *H. elegans*; and

(4) $\delta^{13}C(\text{aragonite}) - \delta^{13}C(\text{DIC}) = 2.66 - 0.131(T°C)$ (Grossman and Ku 1986), based on coeval mollusc samples.

CHAPTER 6

HEAVY METALS

6.1 Theoretical Background

The heavy metals (Fe, Mn, and Zn) investigated in this study are first row transition metals. The term "heavy" is applied to them since they have densities in excess of 5.0 g/cm^3 (Forstner and Wittmann 1983). Those metals are classified as essential since their presence in trace amounts (<0.01% of the organism's mass) is necessary for the proper growth of an organism and the completion of its life cycle. However, the same heavy metals can be toxic when their concentration levels are higher than those required for a correct nutritional response. For example, overconsumption of zinc may cause impaired functioning of the heart and the respiratory system, and it may cause stomach distress and diarrhea. Toxic mixtures of zinc and other essential metals have also been shown to significantly increase the mortality and decrease the filtration rate of zebra mussels by 50% (Kraak et al. 1992).

Iron is the most abundant transition element. It participates actively in biologic systems by attaching to the globin protein, forming hemoglobin which carries oxygen in the blood. Manganese is the second most abundant metal. Due to its chemical similarity to Mg^{2+}, Mn^{2+} can readily substitute for Mg^{2+} in biologic systems, thus activating important enzymes that are involved in glucose utilization. Zinc, as well, is one of the most abundant essential metals as it acts as a cofactor for the proper functioning of many enzymes (Forstner and Wittmann 1983).

6.2 Metal Pollution Sources

The five major sources of metal inputs into freshwater systems are: (1) geologic weathering, (2) mining effluents, (3) industrial effluents, (4) domestic effluents, and (5) inputs from rural areas. These sources are regarded either as point or nonpoint sources. Metal pollution is classified as point source pollution when its origin is attributed to one specific area, factory, or industrial practice. Nonpoint sources of metal pollution result from large regional areas and not from a single distinguishable origin or practice.

Geologic weathering is the source of background levels of metal concentrations. Waters and sediments of areas that are rich in metal bearing formations will in turn have high concentrations of those metals. An example of that is the high mercury content of water and aquatic organisms in the La Grande River that is thought to be a result of the geologic weathering of the mercury rich rocks in that area (Boyle and Jonasson 1973). However, since such metal bearing formations are usually exploited by humans, not too many cases of natural weathering can be observed that are entirely devoid of human contribution.

Mining effluents can have a severe impact on the quality of lake and river water and consequently on the organisms living there. The dispersal of toxic metals from lead, arsenic, and zinc mines has caused a dramatic reduction in fish populations in many lakes and rivers (Lewin et al. 1977). Mines are not the only source of such harmful effluents; they can also originate from waste rock dumps and tailings areas. Such areas are rich in metal sulphides, including iron sulphide (pyrite) which can readily undergo weathering

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reactions that result in the introduction of acid and free Fe^{2+} cations that are ultimately

oxidized to Fe^{3+} cations. Effluents seeping from gold / uranium slimes dams are also

high in metal concentrations. The concentrations of manganese, cobalt, and nickel in

such effluents are usually 10,000 times the concentrations in normal surface water, while

the concentrations of iron and zinc are increased about a thousand fold. The high zinc

concentrations are a result of the cyanidation process used in the process of gold

recovery, while the high manganese concentrations result from the oxidation of uraninite

by pyrolusite in the presence of sulfuric acid (Wittmann and Forstner 1976).

Industrial effluents are another major source of metal pollution. Some of the

many industries that contribute to metal pollution are the pulp, papermills, petroleum

refining, organic chemicals, steel and fertilizer production industries. Some industries,

such as the fertilizer production industry, involve the release of a variety of heavy metals

in their effluents (Cd, Cr, Cu ,Fe, Hg, Mn, Pb, Ni, and Zn) while others involve the use of

a single heavy metal, such as the use of chromium in the tanning industry. Numerous

industries use organic compounds that are rich in metal additives. Examples of such

organic compounds include gasoline and heavy duty oil, which contain tetraethyl lead,

and synthetic rubber, which contains Zn, Sn, Pb, and Cd.

An interesting study by Von Gunten et al. (1997) examined the concentration of

calcium, manganese, iron, copper, zinc, cadmium, lead, and mercury in dated sediment

cores (^{210}Pb) from Lake Zurich, Switzerland. The study covered a time span of the last

200 years. Metal concentrations in pre-anthropogenic sediments did not vary

significantly and represented the geochemical background concentrations of these

elements. As industries began to develop and expand in the beginning of the 19th

century, concentrations of copper, zinc, and cadmium increased until the 1960's, afterwhich there were sharp decreases in metal concentrations. The decrease in sediment heavy metal concentrations reflects the growing public awareness towards the conservation of the environment.

Domestic effluents consist of untreated wastewaters, substances passing through the filters of biologic treatment plants, and/or waste substances passing over sewage outfalls. An example of the occurrence of such incidences can be taken from Germany in the early seventies. Official figures show that only 38% of 7 billion m^3 of domestic effluents received complete biologic treatments that involve oxygen replenishment; 52% was released after receiving only the primary mechanical treatment. This caused a high concentration of heavy metals in the effluents since metals are only removed if the wastewater undergoes tertiary treatment.

Nearly 97% of the land area of the United States is considered to be rural (McElroy et al. 1975). The agricultural practices in such areas make it one of the main contributors of nonpoint sources of pollution. Phosphatic fertilizers used in such areas contain high concentrations of trace elements, one of which is toxic cadmium. In addition to fertilizers, animal waste and the use of pesticides and arsenicals as herbicides introduces a variety of heavy metals to the soil. Eventually, agricultural runoff that is enriched in heavy metals will find its way to aquatic systems.

6.3 Bioaccumulation and Metal Speciation

Chemicals in general tend to bioaccumulate in aquatic organisms and reach higher concentrations than in the ambient water (Wang et al. 1997). This phenomenon of increasing concentration of chemicals persists throughout the food web, resulting in the biomagnification of those chemicals up to a million times their initial concentration in water. Therefore the top predators can bioaccumulate high concentrations of certain toxic chemicals that can be the underlying cause of major deformities and even death in some cases. Being at the top of many food chains, humans can be seriously affected by this biomagnification process, depending on the level of consumption of contaminated items that are lower in the food chain.

Accumulation of persistent organic compounds, such as PCB's is related to the compound's hydrophobicity and stereochemistry, whereby certain PCB's are preferentially more accumulated than others (Colombo et al. 1997). PCB's have a tendency to bioaccumulate in a fashion where the highest trophic levels coincide with the highest concentrations of the chemical. Although heavy metal bioaccumulation is in fact observed in aquatic systems, this does not imply that organisms higher in the food web will display a higher concentration of heavy metals than those organisms that are from lower trophic levels. A study by Enk and Mathis (1977) revealed the following heavy metal biomagnification pattern:

water< fish< sediments< benthic invertebrates

Due to the fact that sediments generally have a higher heavy metal concentration than water, benthic organisms will consequently possess higher heavy metal concentrations than the other organisms.

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

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

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

(3) weak complexes: e.g. Cu-fulvic acid

(4) adsorbed on colloidal particles: e.g. $Cu-Fe(OH)^3$-humic acid

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

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

(7) particulate: adsorbed onto clay particles

In a study by Wang et al. (1997), the assimilation efficiencies of Cr^{3+} and Cr^{4+} from ingested food and from the dissolved phase were determined in the mussel *Mytilus edulis*. The study showed that 13-38% of Cr in mussels was from the dissolved Cr^{4+}, while the rest of the Cr was from ingested Cr^{3+}. The dissolved Cr^{3+} and the ingested Cr^{4+} seemed to have no significant contribution to Cr accumulation in mussels, simply because these specific chemical forms were not bioavailable for the organism. Other metals, such as copper, behave in a similar fashion. Copper can form complexes with a number of inorganic ligands including OH^-, HCO_3^-, NH_3, and Cl^-, and it is also capable of

binding to organic ligands such as glycine (Pankow 1991). However, it was demonstrated that only copper present as a free ion or in inorganic complexes is bioavailable. The binding of copper to suspended particles or to dissolved organic matter renders it nonbioavailable (Herbert and Hansen 1996).

It is not only the concentration of a metal in an aquatic environment that determines its bioavailability and toxicity but also its chemical behavior in specific surroundings. This behavior is, to a large extent, dependent on the metal's chemical speciation and the reactions involved with the transformation of species. Therefore, studies dealing with metal speciation are essential to ensure the proper management of heavy metals in the aquatic environment.

6.4 Transport of Metals in Freshwater

The two primary mechanisms involved in the transport of heavy metals within freshwater systems are water discharge, which operates mainly in rivers, and biologic productivity, which is of more significance in lakes.

Hellmann (1970) studied the relationship between metal concentration (Zn) and discharge in the River Rhine. He observed that an increase in discharge will cause a decrease in the filtrable (dissolved) fraction of the metal load by dilution and an increase of the nonfiltrable (solid) fraction due to the resuspension of particles from the river bed. It was also found that the amount of cations sorbed by undissolved materials decreased with increasing discharge which can be explained by dilution and by the lower exchange capacities of coarse materials that increase with increasing discharge. A study by

Schleichert (1975) carried out on the Rhine River also showed that every discharge maximum is associated with a concentration minimum and that high concentration peaks that are independent of discharge are very rare. A model developed by Howdeshell and Hites (1994) illustrates the significant role that resuspension events, caused by river discharges, play in the transport of pollutants. They suggested that 2% of the Detroit River sediment-bound pollutants is transported to Lake Ontario annually

Large quantities of heavy metals can be taken up by sediment - associated organisms, such as tubificid worms (Aston 1973). In this case the worms feed on contaminated bacterial cells in the sediment and thus accumulate high heavy metal concentrations. These heavy metals can later be released from the sediment into the water during the excretion of faeces. Other benthic organisms, such as zebra mussels, associated with polluted sediments can serve as a nutrient source for other organisms in higher trophic levels, which in turn can release some of the heavy metals they accumulated into the water column. Moreover, experiments support the possibility that zebra mussels play a key role in alternating the movement of many contaminants by biodeposition of organic matter and heavy metals (Dobson and Mackie 1998). Biodeposition rates of Cd and PCB's by zebra mussels were 8 times greater than natural sedimentation values, which emphasizes the efficiency of these filter-feeders in decreasing contaminant loads in the water column.

6.5 Shell Incorporation of Trace Elements

As is the case with other carbonates, minor and trace elements can be incorporated into the aragonitic shell of *Dreissena polymorpha* in one or more of the following ways (McIntire 1963; Zemann 1969):

(1) substitution for Ca^{2+} in the $CaCO_3$ lattice

(2) presence between lattice planes

(3) occupation of free positions resulting from structural defects

(4) adsorption due to surface ionic charges

The process of incorporation of trace elements, via all of the aforementioned methods, is controlled by the distribution coefficient D, according to the following equation (McIntire 1963; Kinsman 1969):

$$[^mMe/^mCa]_s = D\ [^mMe/^mCa]_w$$

where m stands for the molar concentration, Me stands for the trace element, and s and w indicate the solid phase ($CaCO_3$) and water, respectively. The system studied has to be at equilibrium for this equation to be valid. This implies that neither of the phases involved should exhibit any concentration gradients with respect to the trace elements during precipitation. The equilibrium condition usually exists in systems where the amount of the solid phase is much smaller than the volume of the water.

According to this equation, when D>1 this implies that the solid phase contains a higher trace element concentration, relative to Ca, than the water from which it precipitated. The opposite is also true for trace elements having D<1. Compared to the smaller rhombohedral cell of calcite, which favors the incorporation of small cations

(Mg, Fe, Mn, Zn, Cu, and Cd), the orthorhombic aragonite cell is larger and prefers the incorporation of cations that are larger than Ca (Sr, Na, Ba, and U). However, Fe and Mn are also incorporated into the aragonitic lattice in their reduced divalent state (Tucker et al. 1990).

Published values for the distribution coefficient, D, can vary with temperature. This is why published distribution coefficients for different elements should be regarded as order of magnitude estimates only. Since in many situations it is only needed to get crude estimates of the water composition, the order of magnitude and the sign of the distribution coefficient should be enough to accomplish the task.

CHAPTER 7

RESULTS

7.1 Physiochemical Parameters of Lake St. Clair and Detroit River Water

Field observations that were recorded at each water and *Dreissena polymorpha* sample site are listed in Table (7.1). Included in this table are the G.P.S. locations and the water depth at each sample site. Other parameters that were measured utilizing a portable hydrolab meter include water temperature, pH, dissolved oxygen percent, and conductivity.

Values of dissolved oxygen percent, (D.O.%) ranged from 13.5 % to 58.7 % with an average of 36.3 %. The highest D.O.% values were observed at the head of the Detroit River, averaging around 56 %. Conductivity values were relatively uniform throughout the study area and averaged 0.25 mS/cm. Water pH averaged 8.1, which is identical to the pH value determined by Yang et al.(1996) for Lake St. Clair, and was the lowest at the Colchester site (6.84).

7.2 Isotopic Analysis of *Dreissena polymorpha* Shells

Results of the isotopic analysis of the bulk shells are shown in Figures 7.1 and 7.2. The $\delta^{13}C$ (VPDB) values ranged from a minimum of -4.23 ‰ for shell 6 (Mitchell's Bay) to a maximum of -1.07 ‰ for shell 17 B (mouth of the Detroit River), with an

Table 7.1: Field measurements for water samples taken from Lake St. Clair and the mouth of the Detroit River.

Site	G.P.S. Location	Temperature (°C)	pH	Conductivity (mS/cm)	Water Depth (m)
1	N 42° 21' 03" W 82° 55' 67"	16.3	8.30	0.23	3.3
2	N 42° 20' 76" W 82° 55' 12"	16.4	8.17	0.23	2.5
3	N 42° 20' 94" W 82° 53' 56"	16.2	7.91	0.23	6.1
4	N 42° 22' 42" W 82° 41' 70"	14.8	8.13	0.22	5.9
5	N 42° 27' 28" W 82° 27' 01"	18.0	8.38	0.30	3.3
6	N 42° 27' 80" W 82° 46' 55"	19.1	8.32	0.32	2.0
7	N 42° 31' 55" W 82° 46' 55"	14.8	8.35	0.22	4.5
8	N 42° 22' 50" W 82° 54' 80"	18.3	8.29	0.24	1.9
9	N 42° 23' 50" W 82° 53' 50"	18.5	8.11	0.25	2.5
10	N 42° 25' 30" W 82° 52' 60"	18.8	8.12	0.25	4.0
11	N 42° 26' 90" W 82° 51' 90"	19.0	8.19	0.26	3.0
12	N 42° 28' 38" W 82° 52' 43"	19.3	8.10	0.30	4.0
13	N 42° 29' 41" W 82° 52' 55"	19.0	8.29	0.27	3.0
14	N 42° 58' 72" W 82° 56' 49"	20.9	6.84	0.23	2.4
15	N 42° 02' 12" W 82° 07' 89"	22.4	8.23	0.24	5.0
16	N 42° 04' 39" W 83° 07' 36"	22.5	8.23	0.23	5.5
17	N 42° 05' 12" W 83° 07' 56"	22.5	8.33	0.23	5.0
18	N 42° 04' 79" W 83° 07' 18"	22.3	8.30	0.23	5.5

average $\delta^{13}C$ of -2.49 ± 1.16‰ (n=14) in the study area as a whole. The $\delta^{18}O$ (VPDB) values ranged from -8.41 ‰ for shell 12 (Lake St. Clair west shore) to -6.08 ‰ for shell 5 B (Mitchell's Bay), with an average $\delta^{18}O$ of -6.94 ± 0.69‰ (n=14) in the study area as a whole.

As shown in Table (7.2), the average $\delta^{13}C$ values at the Detroit River mouth were noticeably more enriched compared to those from Lake St. Clair. The size of shell samples chosen was relatively constant; shell length data is listed in Appendix (1). Table (7.3) shows values of $\delta^{13}C$ and $\delta^{18}O$ for large and small shells sampled from the same location. The smaller shells were depleted in their $\delta^{18}O$ values (about 2 ‰) with respect to larger shells from the same location.

Figures (7.5), (7.7), (7.9), and (7.11) show the results of the incremental isotopic analysis of shells 5 (Mitchell's Bay), 8 (Grosse Pointe), 13 (St. Clair Shores), and 17 (mouth of Detroit River). Such a technique of sampling provides an ontogenetic history of the isotopic composition of the growth rings, starting at the umbo and moving sequentially to the outer rings of the shell. Shells 5, 8, and 13 show a remarkable depletion in $\delta^{13}C$ and $\delta^{18}O$ during their first year of growth, displaying values as low as -10‰ and -20‰, respectively (shell 8). The isotopic composition of both oxygen and carbon tends to become more enriched during the second year of growth. Incremental isotopic analysis also revealed a general enrichment in $\delta^{13}C$ and $\delta^{18}O$ during the third and fourth years of growth (3rd and 4th rings away from the umbo).

7.3 Isotopic Analysis of Water from Lake St. Clair and the Detroit River

The $\delta^{13}C_{DIC}$ and $\delta^{18}O(VSMOW)$ of water were determined in order to know

whether the aragonite shells were in fact formed in isotopic equilibrium with the ambient

water. Results of the isotopic analysis of water samples are shown in Figures (7.3) and

(7.4). Values of $\delta^{18}O(VSMOW)$ ranged from -8.01 ‰ for sample 11 (Lake St. Clair

west shore) to -6.94 ‰ for sample 16 (mouth of the Detroit River). The average

$\delta^{18}O(VSMOW)$ was -7.52 ± 0.22‰ (n=18), which is close to the -7.1 ‰ value

determined by Yang et al. (1996) for Lake St. Clair.

A wider range was exhibited by $\delta^{13}C_{DIC}$, where the most depleted value was as

low as -9.74 ‰ (Mitchell's Bay) and the most enriched value was found to be -1.39 ‰

(mouth of Detroit River). The average $\delta13C_{DIC}$ within the study area was determined as

-3.43 ± 1.86‰ (n=17). As shown in Table 7.2, average $\delta^{13}C_{DIC}$ values from the mouth of

the Detroit River were noticeably more enriched than values from Lake St. Clair.

7.4 Heavy Metals in Water of Lake St. Clair and the Detroit River

Heavy metal concentrations in water samples from the study area are shown in

Figure (7.13). The average concentration of iron in water within the study area was 228

± 117 ppb (n=18). High iron concentrations were found in the Mitchell's Bay area and at

the mouth of the Detroit River, with an average of 373 and 332 ppb, respectively. Similarly, the highest manganese concentrations were also found in the Mitchell's Bay area and at the mouth of the Detroit River with an average concentration of 8 ppb at each area, compared to an average of 6 ± 2 ppb (n=18) for the study area as a whole. Zinc concentrations were the highest at the mouth of the Detroit River with an average concentration of 112 ± 61 ppb (n=4), which is higher than the average value of 76 ± 52 ppb (n=18) for the study area as a whole.

7.5 Heavy Metals in *Driessena polymorpha* Shells

Results of heavy metal concentrations in *Dreissena polymorpha* shells are illustrated in Figure (7.14) . The average iron concentration in the shell was 149 ± 102 ppm (n=15) for the study area as a whole. The highest concentration of iron was 392 ppm for shell 5 (Mitchell's Bay), the same site where the highest iron concentration in water was found. Manganese and zinc concentrations averaged 14 ± 7 and 9 ± 8 ppm (n=15), respectively, for the study area as a whole. However, the anomalous zinc concentration of 382 ppm at site 6 was not included in determining the average zinc concentration. Site 6 is the closest site to the Thames River, which might be a source of high level of heavy metal input into Lake St. Clair.

Average iron, manganese, and zinc concentrations were 162 ± 107, 16 ± 6, and 11 ± 7 ppm (n= 11) in Lake St. Clair shells compared to 139 ± 96, 10 ± 5, and 6 ± 1 ppm (n=3) in shells from the Detroit River mouth, respectively. Figure (7.15) shows the

difference in metal concentrations between large and small shells. The smaller shells displayed a significantly lower metal content than the larger ones. Results of incremental heavy metal analysis for shells 5,8,13, and 17 are shown in Figures 7.6, 7.8, 7.10, and 7.12. Iron exhibited high concentrations in the first growth rings of the analyzed shells, followed by a depletion in concentration in the third and fourth rings, only to be followed by a significant increase in concentration in the later years of the organism's life, except for shell 5 from Mitchell's Bay which did not display the latest increase in Fe concentration. Manganese and zinc showed some significant variations in concentration within the growth rings of each shell, but showed no uniform trend in the way they varied.

7.6 Calcium and Magnesium in Water and *Dreissena polymorpha* Shells

Table (7.4) shows the results of calcium and magnesium concentrations in water samples and *Dreissena polymorpha* shells within the study area. The average concentrations of calcium and magnesium in water were 30800 and 8600 ppb, respectively. The average calcium and magnesium concentrations in the aragonitic shell were 35.5% and 77 ppm, respectively.

N

St. Clair
River

St. Clair Delta

Walpole Island

-1.11

-3.89

Michigan

-4.18

Lake St. Clair

-4.23

Mitchell's Bay

-3.52

-3.60

-3.20

Peche Island

-2.47

-1.99

Belle
Isle

-1.61

Rouge
River

Windsor

Detroit

Fighting
Island

. Sample Site

Ontario

Grosse
Ile

Bois Blanc
Island

0   5   10   15   km

-1.09   -1.41

0   5   10   miles

-1.50

Lake Erie

-2.39 .
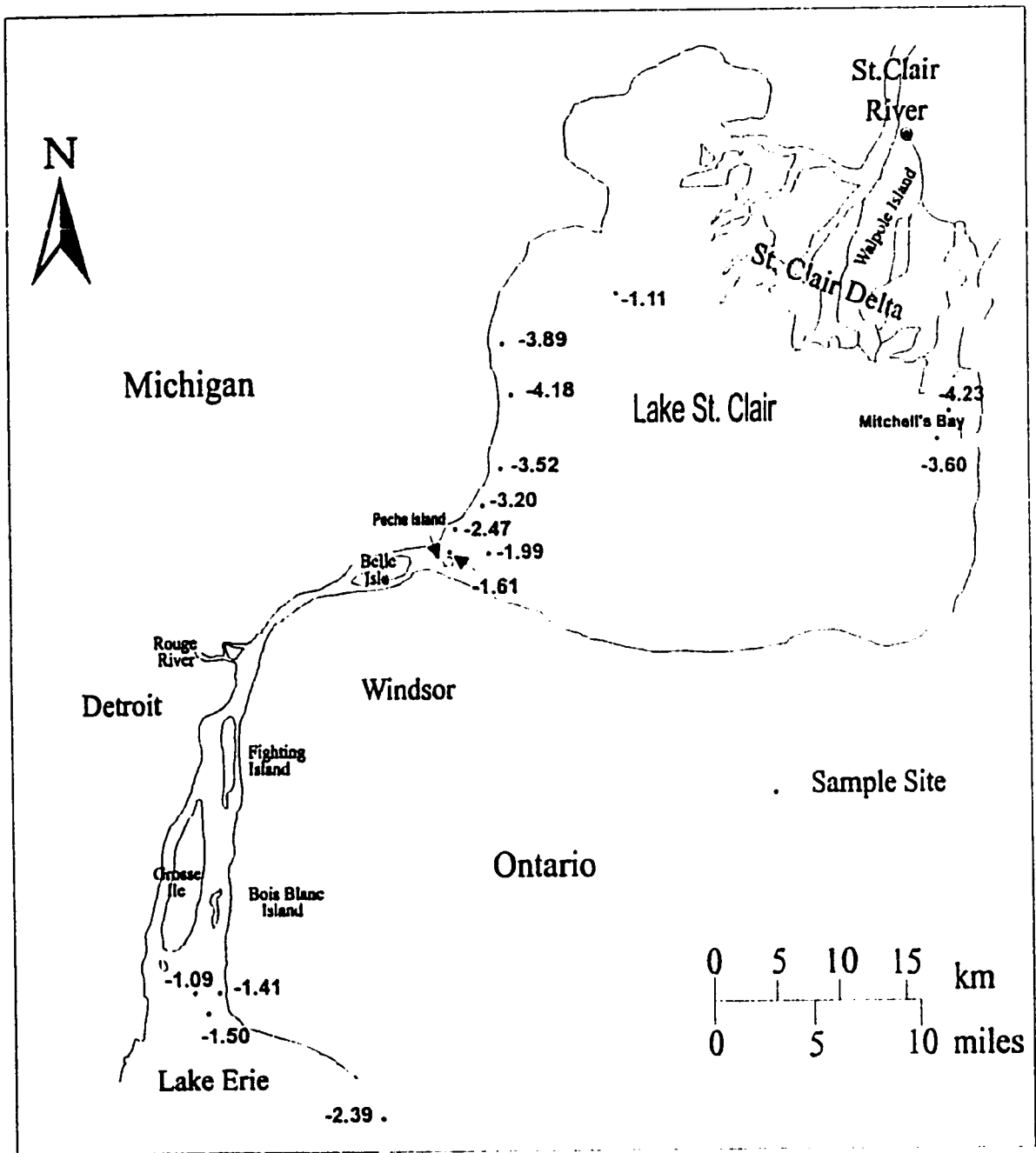
Figure 7.1: Map of the study area showing the $\delta^{13}C$ (VPDB) ‰ distribution in *Dreissena polymorpha* shells.

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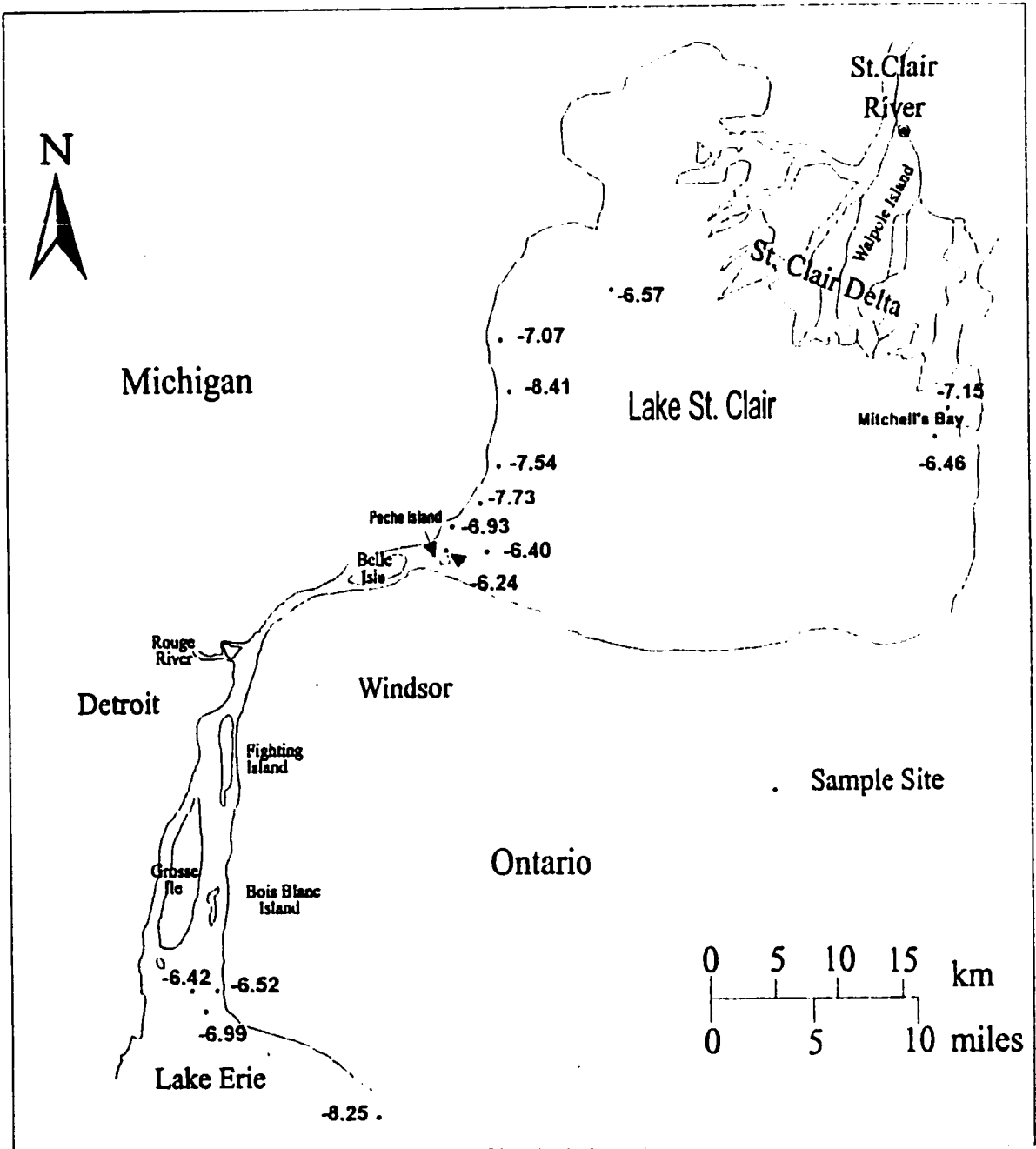
Figure 7.2: Map of the study area showing the δ¹⁸O (VPDB) ‰ distribution in *Dreissena polymorpha* shells.

Table 7.2: Comparison between average $\delta^{13}C$ and $\delta^{18}O$ values of water and *Driessena polymorpha* samples from Lake St. Clair and the mouth of the Detroit River.

	Lake St. Clair	Mouth of Detroit River
$\delta^{13}C$ (shells) ‰ VPDB	-2.9±1.1, n=10	-1.3±0.2, n=3
$\delta^{18}O$ (shells) ‰ VPDB	-7.1±0.7, n=10	-6.6±0.3, n=3
$\delta^{13}C$ (water) ‰ VPDB	-3.8±1.9, n=13	-1.7±0.2, n=3
$\delta^{18}O$ (water) ‰ VSMOW	-7.5±0.2, n=13	-7.1±0.2, n=4

Table 7.3: Results of $\delta^{18}O$ (VPDB) and $\delta^{13}C$ (VPDB) for large versus small *Dreissena polymorpha* shells.

Site	1 (Large)	1 (Small)	3 (Large)	3 (Small)	7 (Large)	7 (Small)	16 (Large)	16 (Small)
Shell Length (mm)	19.50	7.00	20.00	7.50	19.75	6.75	18.75	7.75
$\delta^{18}O$ ‰	-6.40	-8.55	-6.24	-8.79	-6.57	-8.73	-6.99	-6.94
$\delta^{13}C$ ‰	-1.61	-1.83	-1.99	-2.23	-1.11	-1.60	-1.50	-1.26
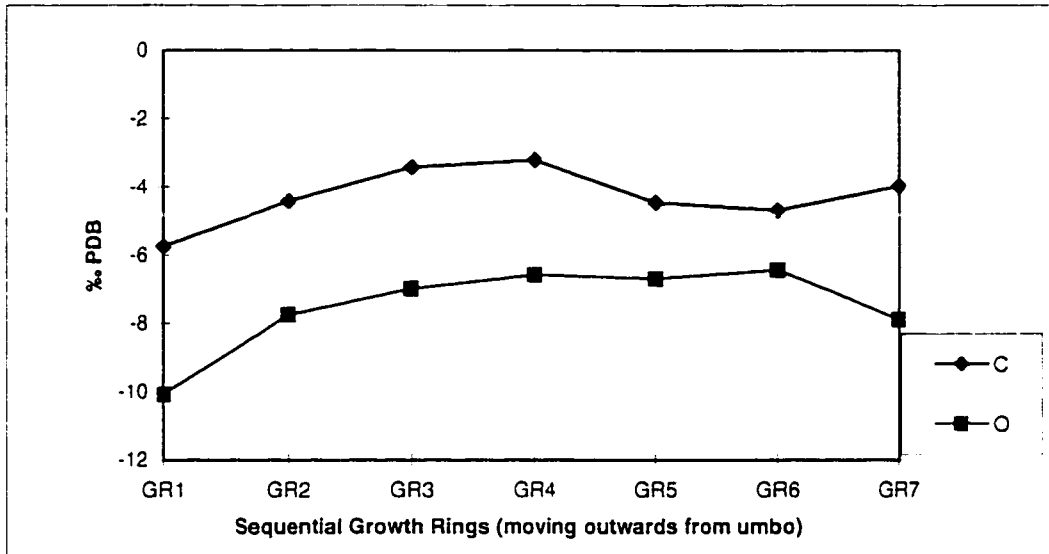
Figure 7.5: Distribution of $\delta^{13}C$ and $\delta^{18}O$ in growth rings of shell 5 (Mitchell's Bay)
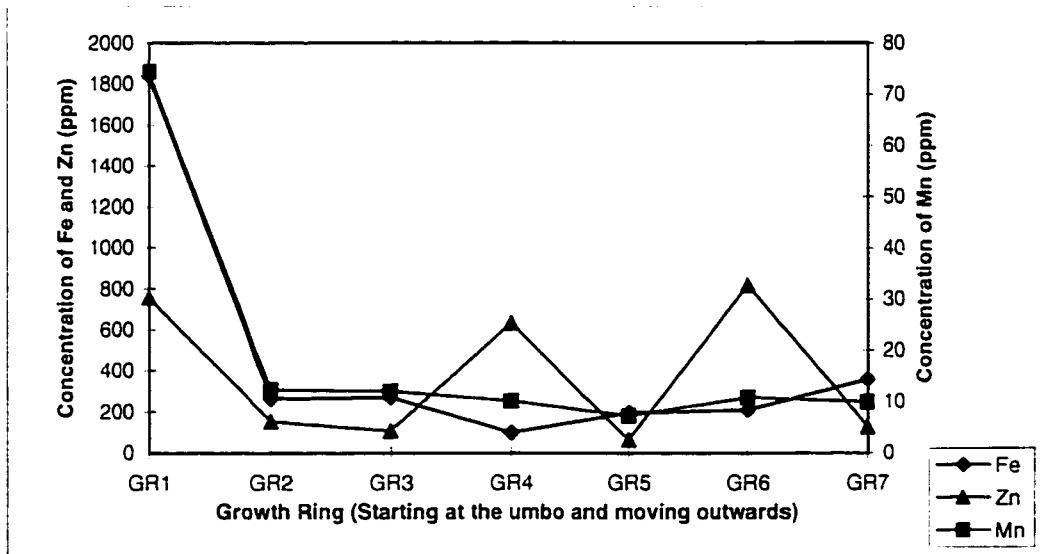
Figure 7.6: Heavy metal distribution in growth rings of shell 5 (Mitchell's Bay)
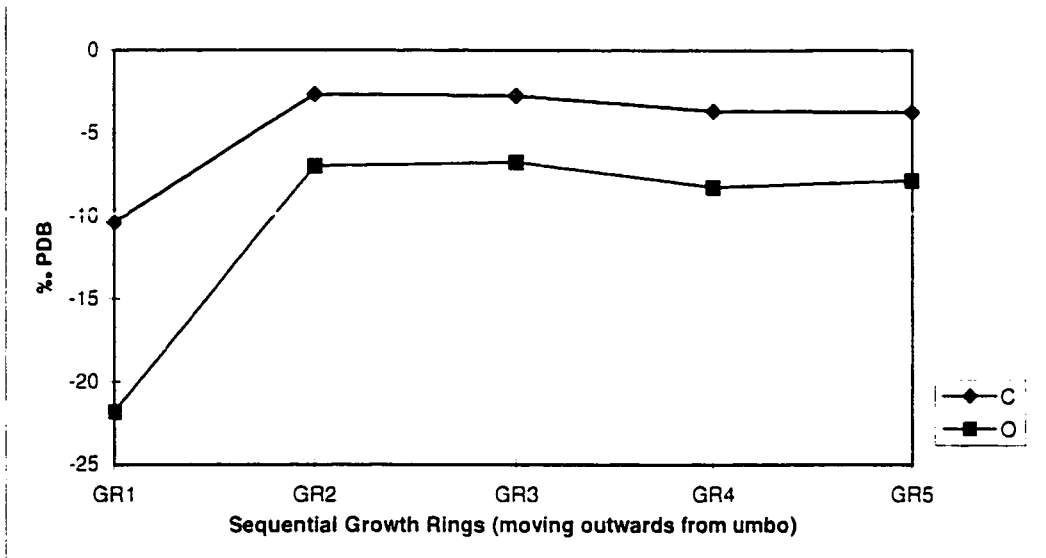
Figure 7.7: Distribution of $\delta^{13}C$ and $\delta^{18}O$ in growth rings of shell 8 (Grosse Pointe)
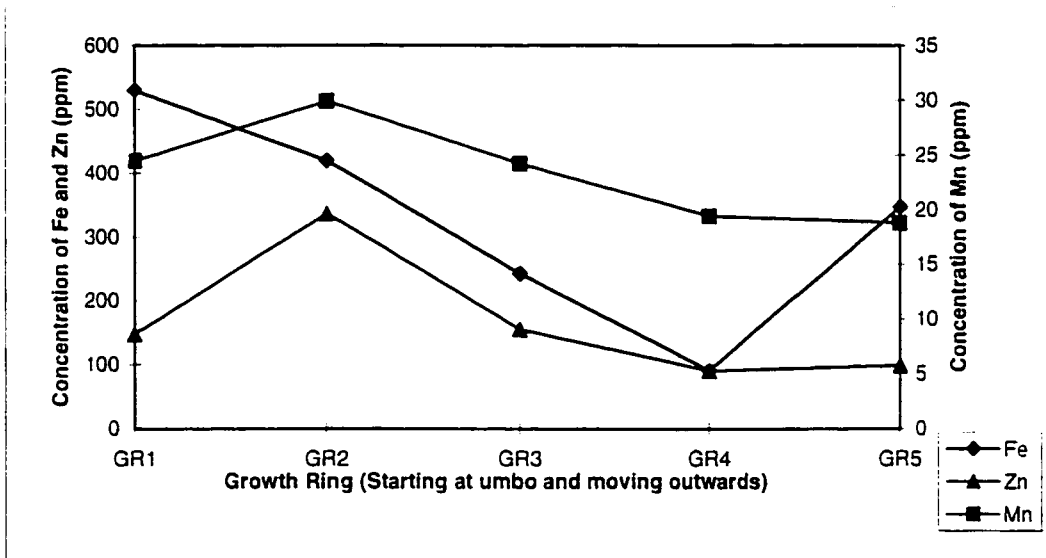
Figure 7.8: Heavy metal distribution in growth rings of shell 8 (Grosse Pointe)

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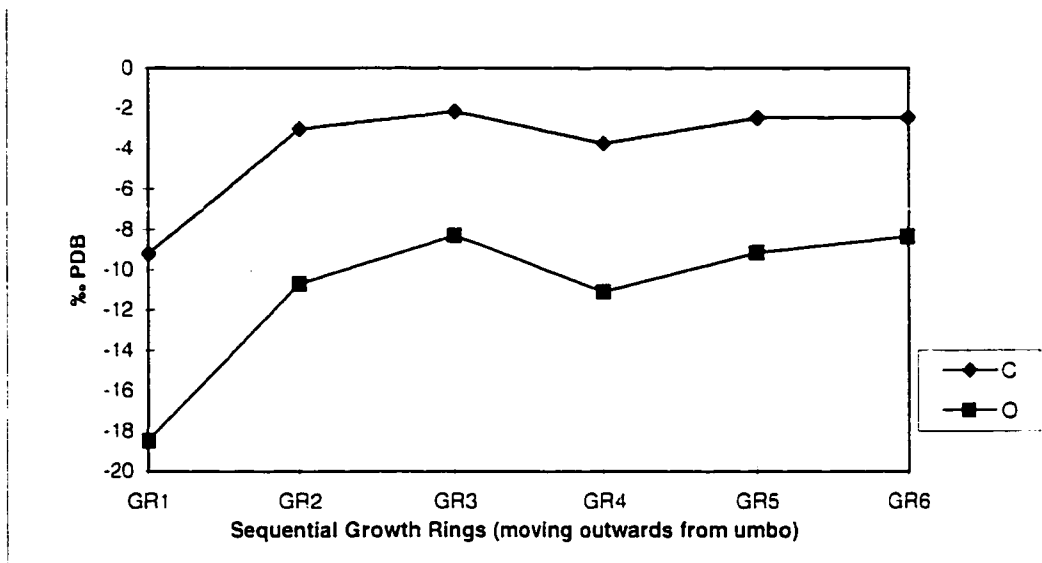
Figure 7.9: Distrbution of $\delta^{13}C$ and $\delta^{18}O$ in growth rings of shell 13 (St. Clair Shores)
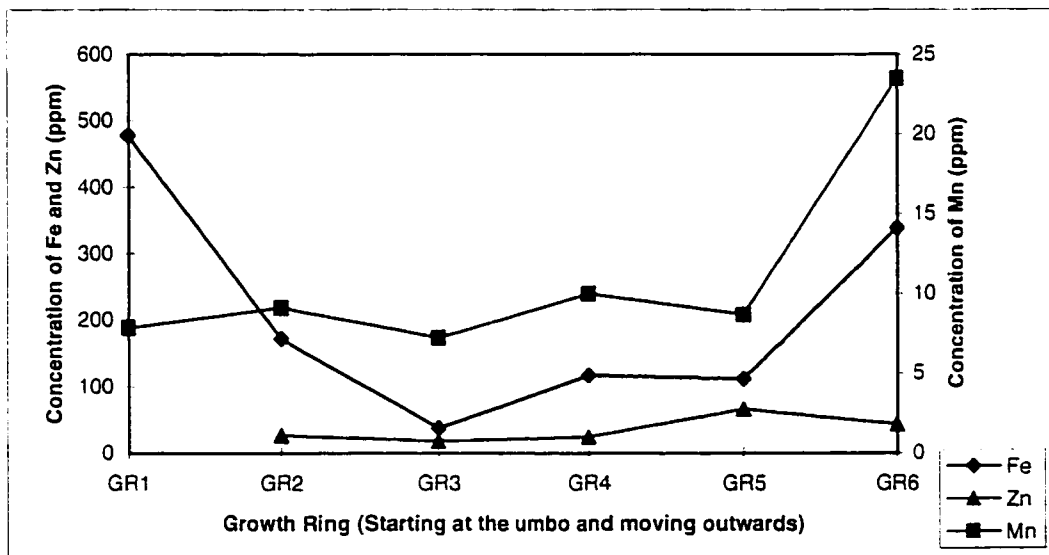
Figure 7.10: Heavy metal distribution in growth rings of shell 13 (St. Clair Shores)
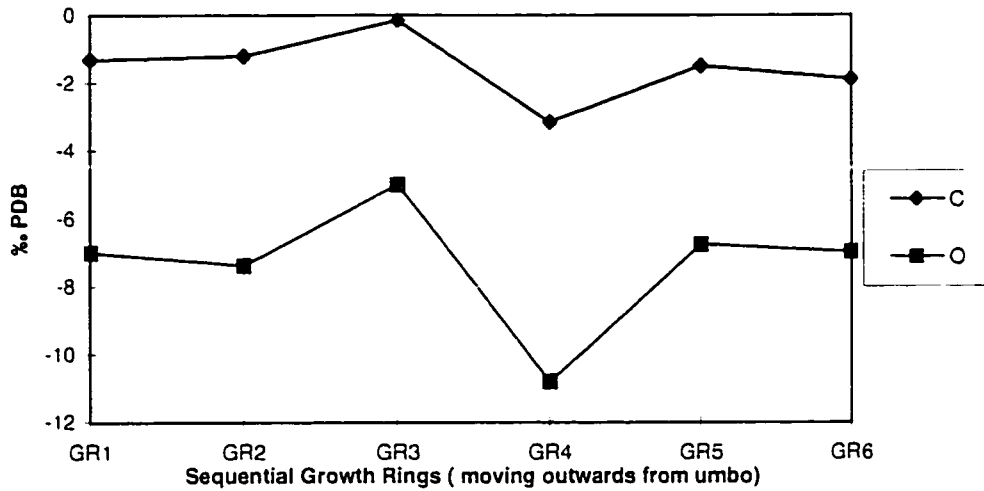
Figure7.11: Distribution of $\delta^{13}C$ and $\delta^{18}O$ in growth rings of shell 17 (Detroit River Mouth).
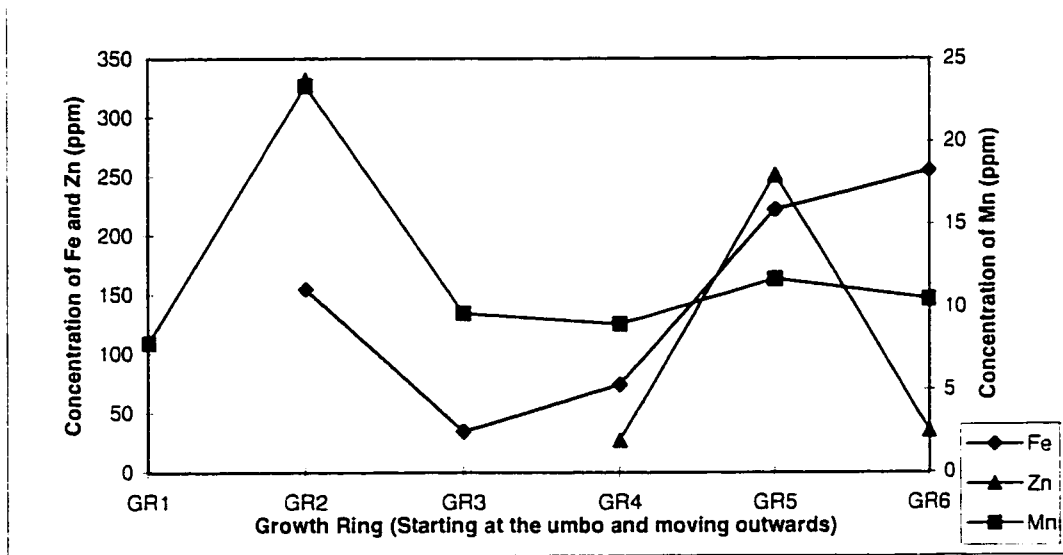
Figure 7.12: Heavy metal distribution in growth rings of shell 17 (Detroit River Mouth)
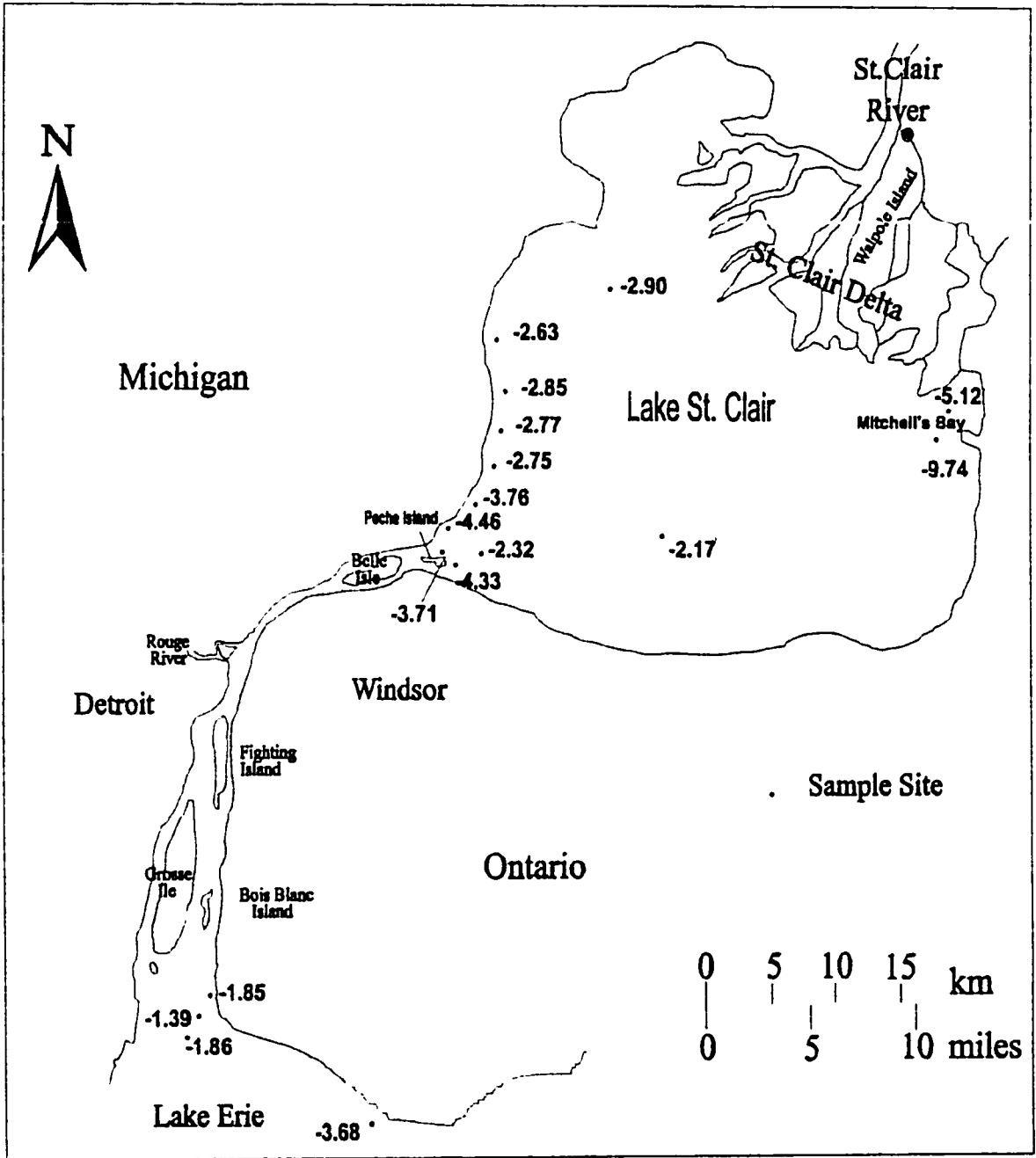
Figure 7.3: Map of the study area showing the $\delta^{13}C$ DIC (VPDB) ‰ distribution in water samples.
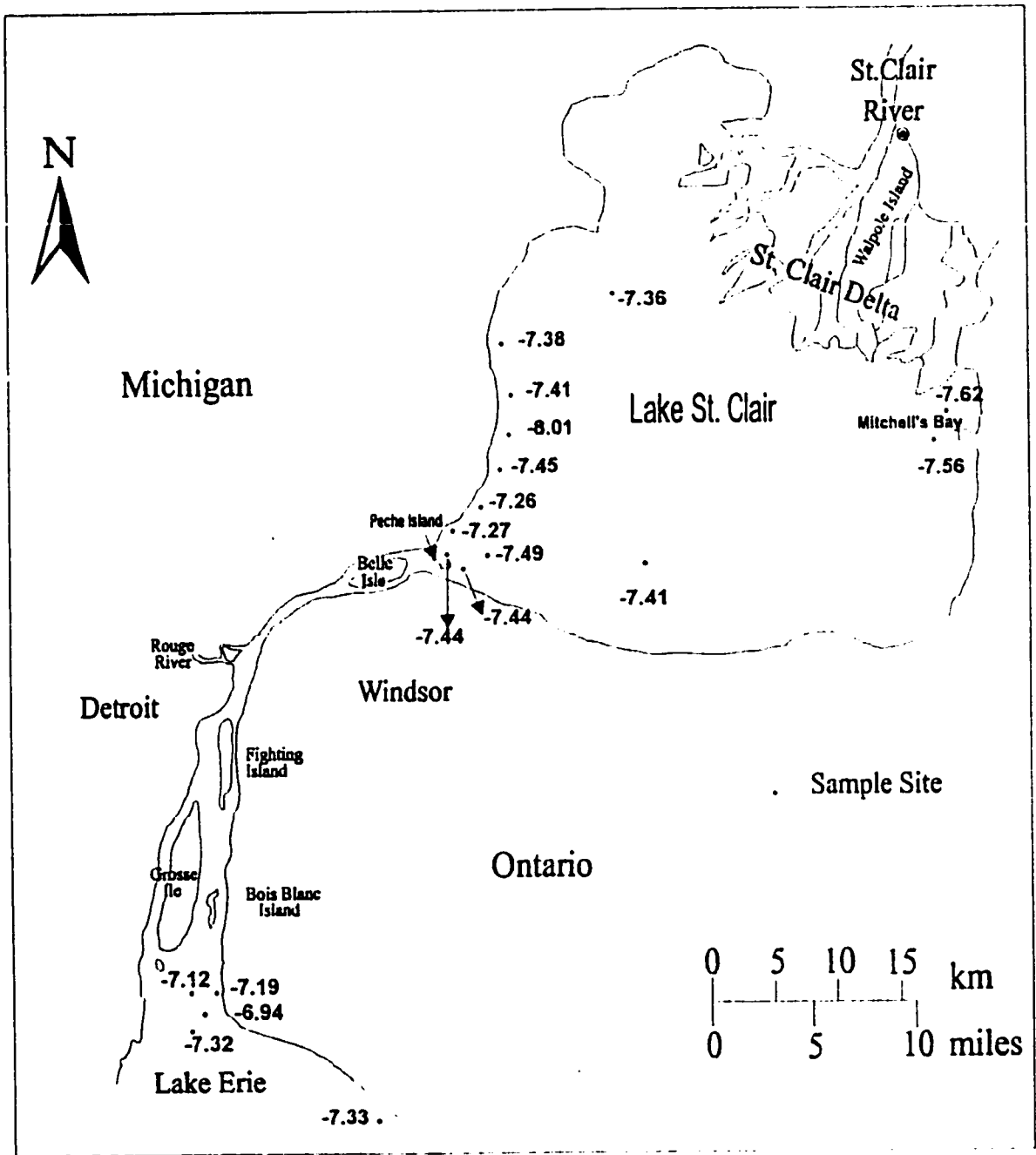
Figure 7.4: Map of the study area showing the $\delta^{18}O$ (VSMOW) ‰ distribution in water samples.
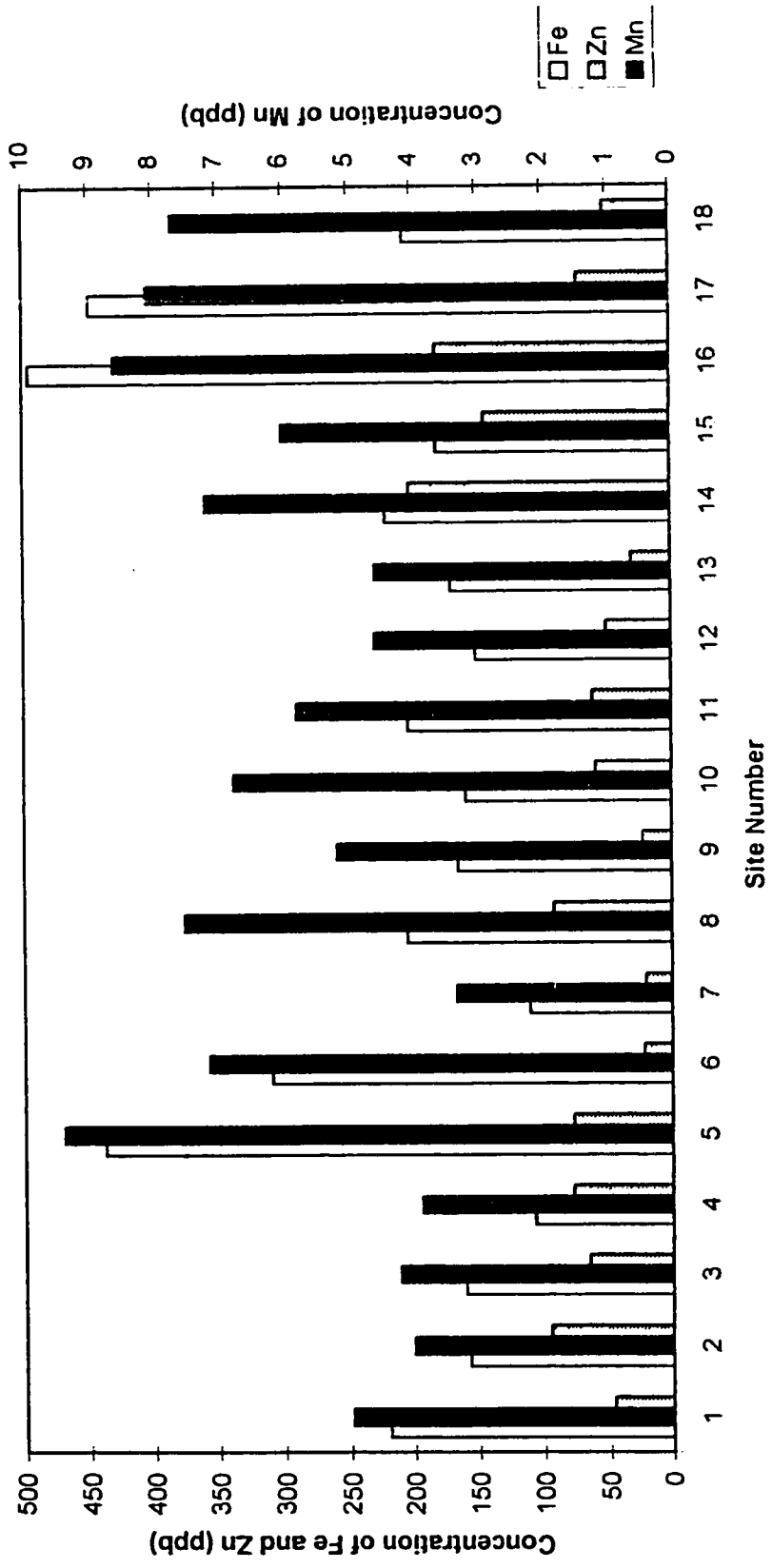
Figure 7.13 : Heavy Metals Distribution in Water of Lake St. Clair and Mouth of the
Detroit River.
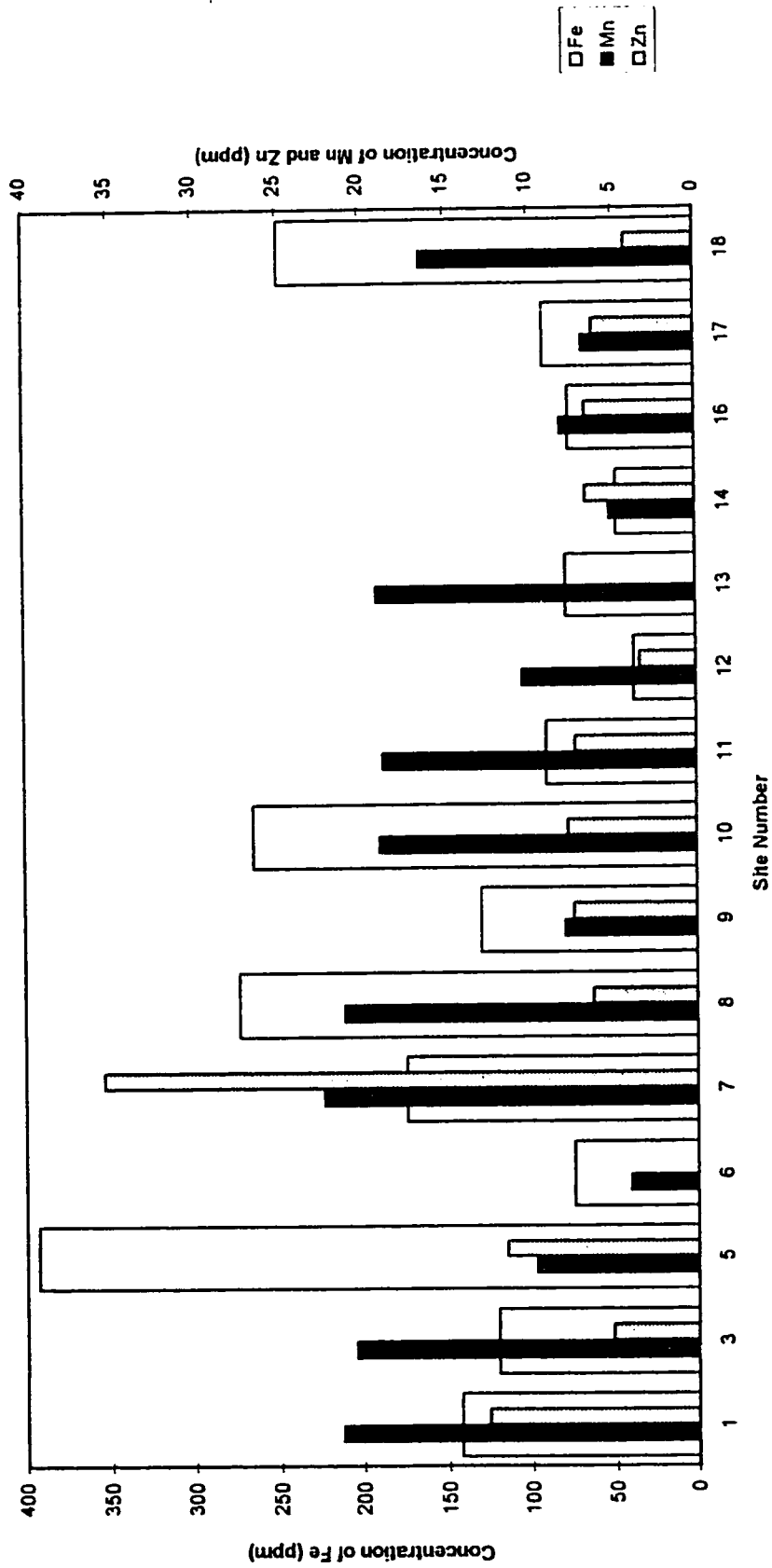
Figure 7.14: Heavy Metals Distribution in *Dreissena polymorpha* Shells from Lake St. Clair and the Mouth of the Detroit River
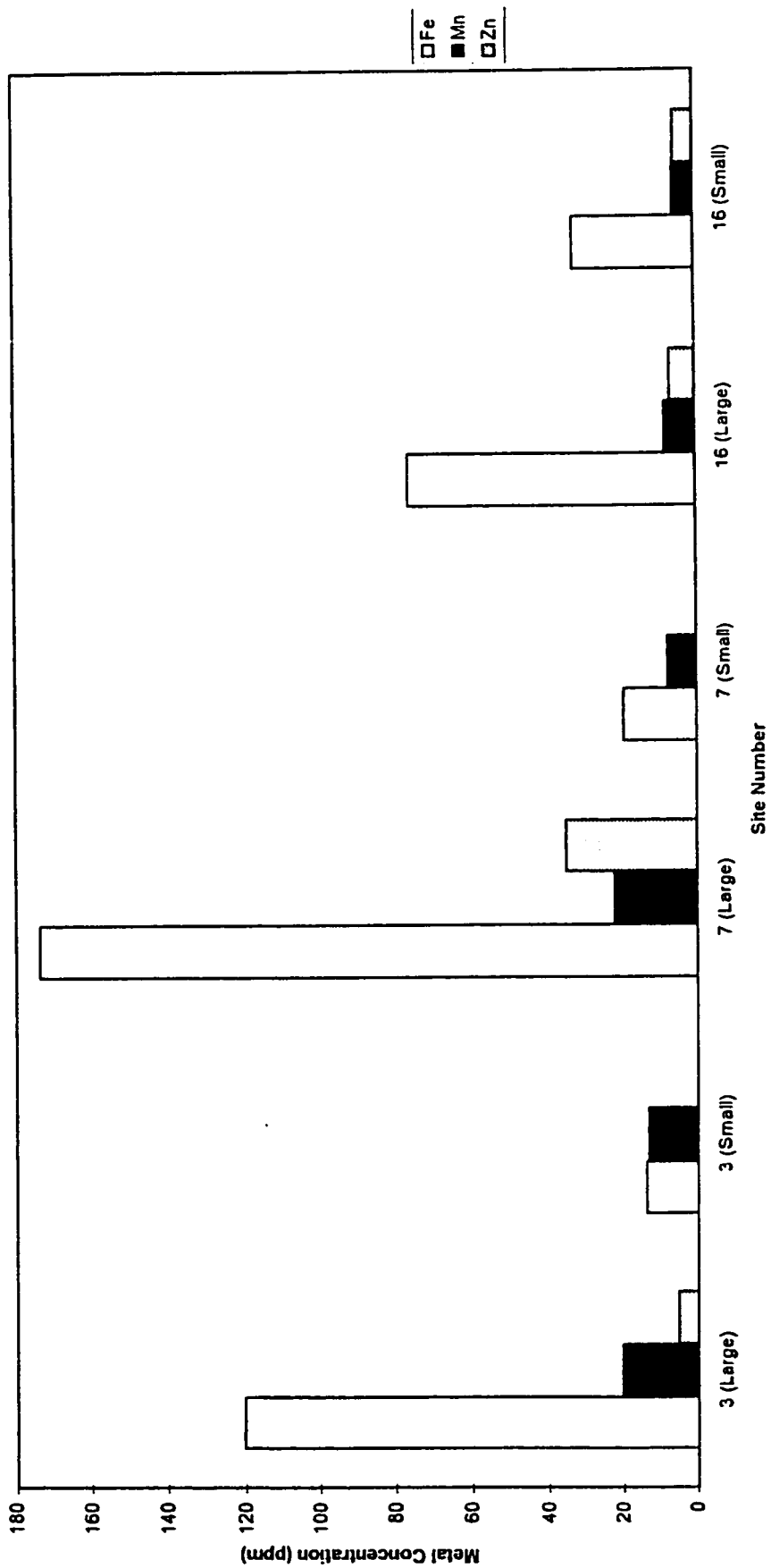
Figure 7.15: Heavy metal concentration in large versus small *Dreissena polymorpha* shells

Table 7.4: Calcium and magnesium concentrations in water (ppb) and *Dreissena polymorpha* shells (ppm).

Location	Ca (shell)	Ca (water)	Mg (shell)	Mg (water)
1	359600	28700	43	8150
2	N/A	28500	N/A	8110
3	344300	29000	106	8100
4	N/A	29300	N/A	8140
5	366400	39800	32	9830
6	391700	38700	80	9830
7	296500	28800	93	8000
8	342100	31000	78	8730
9	375100	29900	91	8270
10	316300	29700	63	8530
11	373100	30300	83	8860
12	322800	29200	47	8250
13	380100	30000	135	8640
14	349600	29500	43	8070
15	N/A	29400	N/A	8540
16	343400	30600	90	8820
17	387100	31600	104	8850
18	372900	30500	68	8470

CHAPTER 8

DISCUSSION

8.1 Isotopic Composition of DIC ($\delta^{13}C_{DIC}$) in Lake St. Clair and the Detroit River

Isotopic analysis of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) in Lake St. Clair and the

Detroit River water revealed an enrichment in ^{13}C at the mouth of the Detroit River (Fig.

7.3). The average $\delta^{13}C$ value at the river mouth is -1.70 ± 0.27 ‰ PDB (n=3), compared

to average values of -3.71 ‰ PDB at the head of the Detroit River, -2.95 ‰ PDB for the

west shore of Lake St. Clair, and an anomalous -7.43 ‰ PDB in the area of Mitchell's

Bay. Isotopic enrichment of ^{13}C could be a reflection of increased biologic productivity.

Excessive plant growth and the preferential uptake of ^{12}C during the process of

photosynthesis could be responsible for the production of the observed enrichment.

Other possibilities include a higher residence time of water, which consequently implies

an increased CO_2 exchange with the atmospheric reservoir, which is more enriched in ^{13}C

(Yang et al. 1996). The latter possibility might contribute to the observed difference

between the $\delta^{13}C$ at the river mouth and that at the river head, the latter having a shorter

water residence time. The infiltration of groundwater that is affected and isotopically

altered by the carbonate bedrock at the river mouth could also be a contributing factor for

the observed enrichment in $\delta^{13}C_{DIC}$ at the Detroit River mouth. Dumping of chemicals

that are enriched in ^{13}C from shore areas at the mouth of the river can significantly alter

the carbon isotopic composition of the area. The latter scenario is the most probable

given the fact that industrial waste is regularly discharged from petrochemical plants and steel mills along the shore of the Detroit River (Howdeshell and Hites 1994; Manny et al. 1988). Finally, another important factor that can explain the enrichment is turbulent mixing at the mouth of the Detroit River which can resuspend part of the carbonate sediments, causing carbonate dissolution which can ultimately lead to the enrichment of the $\delta^{13}C$ signature. Furthermore, a $\delta^{13}C$ enrichment in the bulk *Dreissena polymorpha* shell samples is also observed at the mouth of the Detroit River, which implies that the enriched $\delta^{13}C_{DIC}$ values found at the Detroit River mouth are not transient and existed during shell formation.

Depleted $\delta^{13}C$ values, as is the case in the Mitchell's Bay area, can be attributed to the presence of organic material that is enriched in ^{12}C, the decay of which will yield isotopically light CO_2 (Veinott and Cornett 1998; Oana and Deevey 1960). This depletion in ^{13}C is, nevertheless, not reflected in the carbon isotopic composition of the aragonitic shells, which do not display such depletion, and therefore the anomalous $\delta^{13}C$ values are transient and probably not representative of the DIC present during shell formation. Figure (8.1) illustrates the absence of correlation between $\delta^{13}C_{DIC}$ and $\delta^{13}C$ of the shell, the correlation coefficient value of 0.41 is lower than the critical (r).

8.2 Oxygen Isotopic Composition of Lake St. Clair and Detroit River Water

It is clear from Figure (7.4) that the $\delta^{18}O$ composition of Lake St. Clair water is relatively uniform. This could be due to the fact that Lake St. Clair is considered a shallow, well-mixed lake with a relatively unvarying depth. This more or less regular depth minimizes temperature differences, which otherwise could exert a strong influence on oxygen isotope fractionation.
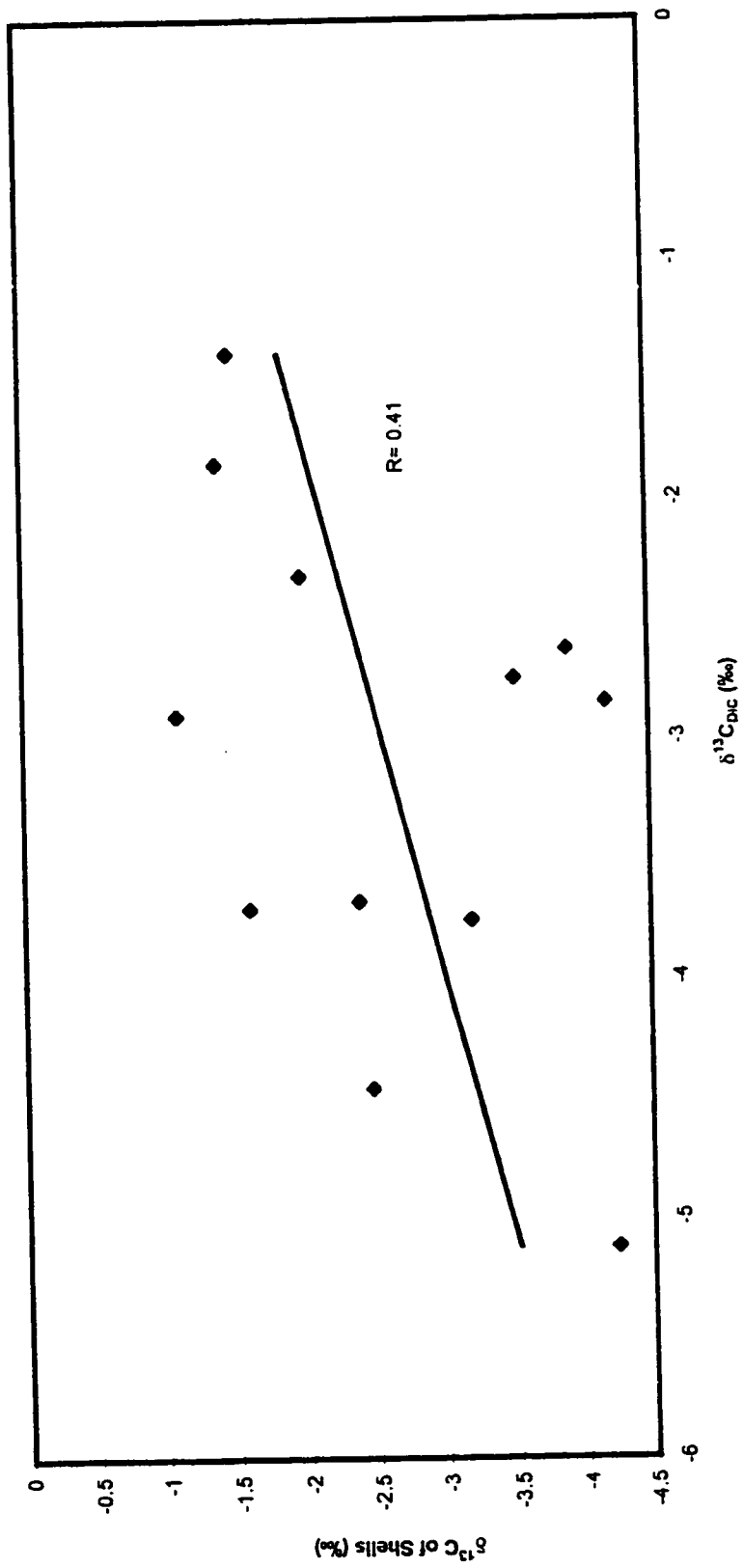
Figure 8.1: Scatter Plot of $\delta^{13}C$ (VPDB) of Lake Water DIC and *Dreissena polymorpha* Shells

Among the numerous variables that control the oxygen isotopic composition of water, evaporation exerts the greatest influence. The higher vapour pressure of $H_2^{16}O$ molecules leads to their preferential evaporation, leaving behind the heavier, lower vapour pressure $H_2^{18}O$ molecules (Faure 1986). Water's $\delta^{18}O$ composition is also affected by other processes including respiration, groundwater inflow, and the production of oxygen by plant photosynthesis. The contribution of these factors to the oxygen composition of water may vary from one aquatic environment to another, thus creating pronounced variations in the $\delta^{18}O$ composition of water.

8.3 Carbon Isotopic Composition of *Dreissena polymorpha* Shells

In order to determine whether the *Dreissena polymorpha* shells precipitated in isotopic equilibrium with the dissolved inorganic carbon (DIC) of the Lake, the following equation by Rubinson and Clayton (1969) was used:

$\delta^{13}C(aragonite) = \delta^{13}C(HCO_3^-) + 1.85 + 0.035\ (t-25^\circ C)$

The low temperature-dependent fractionation coefficient of 0.035 signifies the minor influence that temperature exerts on carbon fractionation. The fractionation that occurs between DIC and $CaCO_3$ is only 0.035 ‰ per degree Celsius (Emrich et al. 1970). Other scientists believe that temperature dependency does not exist at all, and that the aragonite-bicarbonate enrichment averages 2.7 ‰ (Romanek et al. 1992).

This equation was first applied to examine whether the shell samples from all different locations in Lake St. Clair were deposited in isotopic equilibrium. The average

$\delta^{13}C_{DIC}$ value for all locations within Lake St. Clair where shell samples were taken from was used in the equation. A temperature of 22.5 °C was used to represent the mean summer temperature (Bolsenga and Herdendorf 1993). If the aragonitic shells were precipitated in equilibrium with the ambient water of Lake St. Clair, the mean $\delta^{13}C$ (aragonite) value would be -2.26 ‰ (VPDB). The actual calculated mean for $\delta^{13}C$ of the shells is -2.98 ± 1.11‰ (n=10), implying that the aragonitic shells are depleted by 0.7‰ with respect to the equilibrium value. This slight depletion could be due to the incorporation of light, metabolically derived carbon.

The equation was applied again to examine whether *Dreissena polymorpha* shell samples from the western shore of Lake St. Clair were closer to the equilibrium value. In this case the mean $\delta^{13}C_{DIC}$ (-3.29‰) of the western shore was utilized. The mean $\delta^{13}C$ for the aragonitic shell samples was -3.45‰, which implies that it is depleted by 1.9‰ with respect to the equilibrium value. Similarly, when the mean $\delta^{13}C_{DIC}$ value (-1.7‰) at the Detroit River mouth is used in the aforementioned equation, there is an observed depletion by 1.3‰ in the $\delta^{13}C$ of the shells relative to the equilibrium value.

A GIS generated map displaying the distribution of $\delta^{13}C$ in *Dreissena polymorpha* shell samples from the western shore of Lake St. Clair is shown in Figure (8.2). The map shows a gradual enrichment in $\delta^{13}C$, moving south along the western shore of Lake St. Clair, with the most enriched $\delta^{13}C$ at the Detroit River head. This implies that there is a significant difference in the carbon isotopic composition of the ambient water within this area. One possibility is that the oxidation of organic matter at the river head has a less pronounced influence on the depletion of the $\delta^{13}C_{DIC}$ values due to the higher depth at

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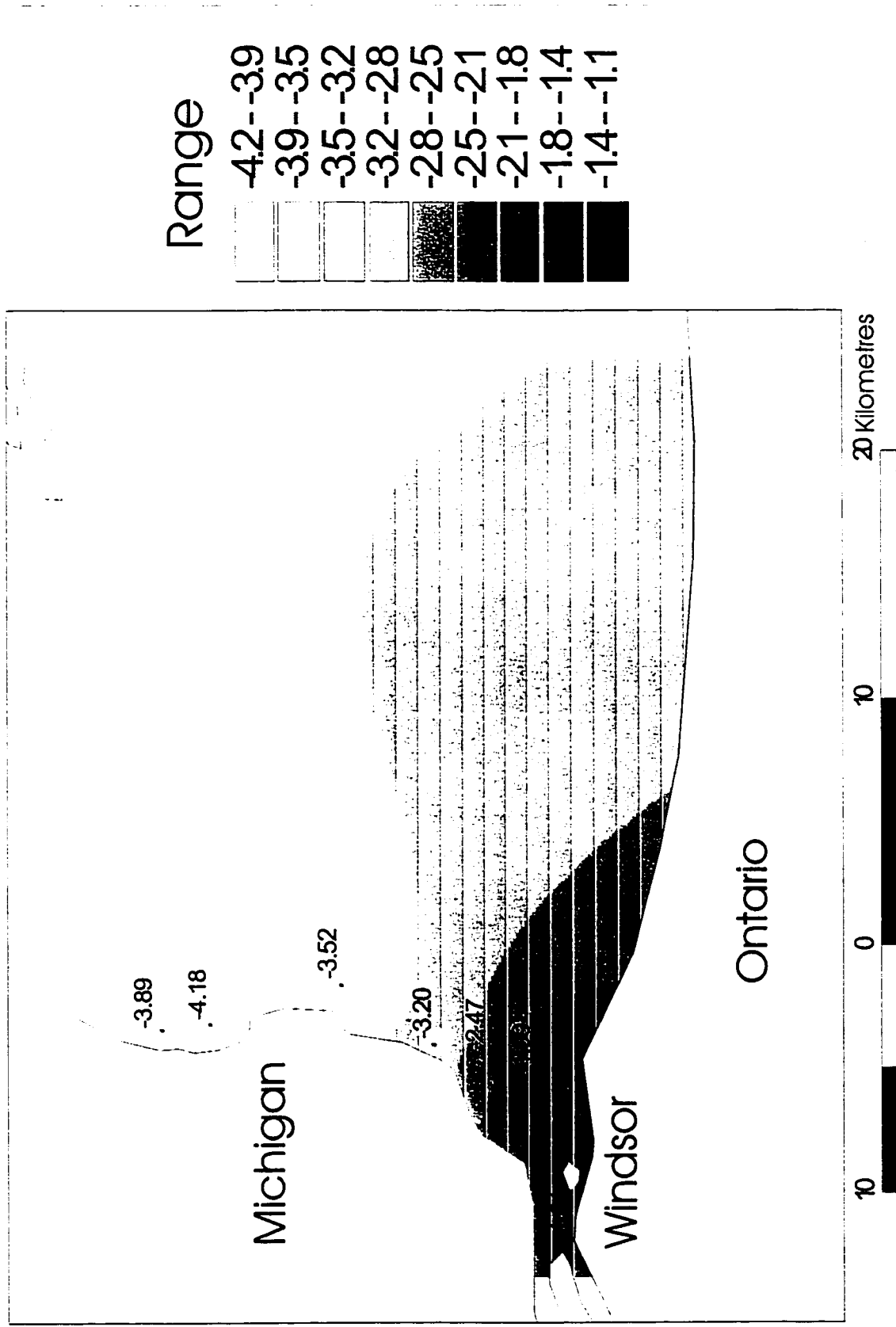
Figure 8.2: GIS Generated Map Showing the Distribution of $\delta^{13}C$ (‰VPDB) in Shells of *Dreissena polymorpha*.

the river head; the effect of producing the lighter $^{12}CO_2$ is more pronounced in the shallower coastal areas of western Lake St. Clair. Another reason may be the industrial discharges from the American side of the Detroit River head. Such industries might release carbon compounds that are enriched in their $\delta^{13}C$ composition, thus altering the carbon isotopic composition of the water and ultimately that of the shells.

8.4 Oxygen Isotopic Composition of *Dreissena polymorpha* Shells

In order to determine whether the *Dreissena polymorpha* shells were precipitated in isotopic equilibrium with the oxygen of the ambient water, the following equation, developed by Grossman and Ku (1986) was used:

$\delta^{18}O$ (a) - $\delta^{18}O$ (w)= 4.65 - 0.213 (T°C)

The t refers to the water temperature, while $\delta^{18}Oa$ and $\delta^{18}Ow$ refer to the isotopic composition of the aragonitic shell and water, respectively.

When an average $\delta^{18}O$ of -7.42 ± 0.19 ‰ (VSMOW) (n=13) for Lake St. Clair water is employed, the expected (equilibrium) $\delta^{18}O$ for the aragonitic shell will be -7.57 ‰. The actual average of -7.05 ± 0.69‰ (n=10) is slightly (0.5‰) enriched with respect to the equilibrium value. When other locations of the study area are taken separately, a similar scenario arises, where shells are only slightly enriched (0.5‰) with respect to the theoretical value which represents isotopic equilibrium with the ambient lake water. The only remarkable deviation from the equilibrium value is observed at the Detroit River head, where shells are enriched by 1.2‰.

One main factor that plays a role in the ^{18}O composition of lake water and consequently the aragonitic shells is temperature. The isotopic fractionation of oxygen is more dependent on temperature than that of carbon. This dependency translates into the higher temperature-dependent fractionation coefficient of 0.213 that is observed in the equilibrium fractionation equation developed by Grossman and Ku (1986).

8.5 Covariation of $\delta^{18}O$ and $\delta^{13}C$

A plot of $\delta^{13}C$ versus $\delta^{18}O$ of the *Dreissena polymorpha* shells (bulk analysis) is shown in Figure (8.3). It shows that there is a significant, positive linear relationship between $\delta^{18}O$ and $\delta^{13}C$ at the 0.05 level since the correlation coefficient, r (0.55), has a higher absolute value than the critical "r"(0.49). Correlation between $\delta^{18}O$ and $\delta^{13}C$ within individual shells (incremental analysis) was also strong. Factors inducing the covariation of the two isotopes are summarized in a paper by Talbot (1990).

The covariation between the two isotopes occurs as a result of the operation of factors that influence the two isotopes and their fractionation by about the same magnitude. Therefore factors such as temperature, and consequently evaporation, which exert an influence on one isotope and not the other will not result in isotope covariation. Higher temperatures result in increased evaporation, and since the lighter water molecules (H_2O^{16}) will preferentially evaporate as a result of their higher vapour pressure, the concentration of H_2O^{18} will increase, thus increasing the $\delta^{18}O$ value of the water. The oxygen isotopic composition of water will in turn affect the $\delta^{18}O$ value of the precipitated carbonates causing a shift towards more enriched values. However, most

studies show that carbon fractionation in biogenic aragonite exhibits only a slight temperature effect (Grossman and Ku 1986; Turner 1982). In fact Romanek et. al. (1992) concluded that the carbon fractionation is totally independent of temperature. Therefore, higher temperatures will increase $\delta^{18}O$ without significantly influencing the $\delta^{13}C$, and consequently covariation will not be observed.

Nonetheless, factors such as the residence time of water will influence both isotopes by about the same magnitude. Increased water residence time will allow for an increased CO_2 exchange with the atmospheric reservoir, thus causing the enrichment of both $\delta^{18}O$ and $\delta^{13}C$ (Talbot 1990). Other factors such as increased primary productivity and increased vegetation will also enrich both isotopes through the process of photosynthesis which preferentially consumes lighter CO_2 molecules.

Talbot (1990), however, makes a distinction between covariation in hydrologically open lakes and that in hydrologically closed lakes. He observed a stronger covariation in closed lakes (r>0.8) than in open lakes (r<0.7). Hydrologically open lakes do exhibit covariation but are also strongly influenced by the $\delta^{18}O$ composition of the inflowing water. Covariation of $\delta^{18}O$ and $\delta^{13}C$ in Lake St. Clair would be stronger if the lake were a closed one. However, Lake St. Clair has a short water residence time of 9.2 days and is influenced by the oxygen and carbon isotopic composition of inflowing water, especially the water of the St. Clair River.
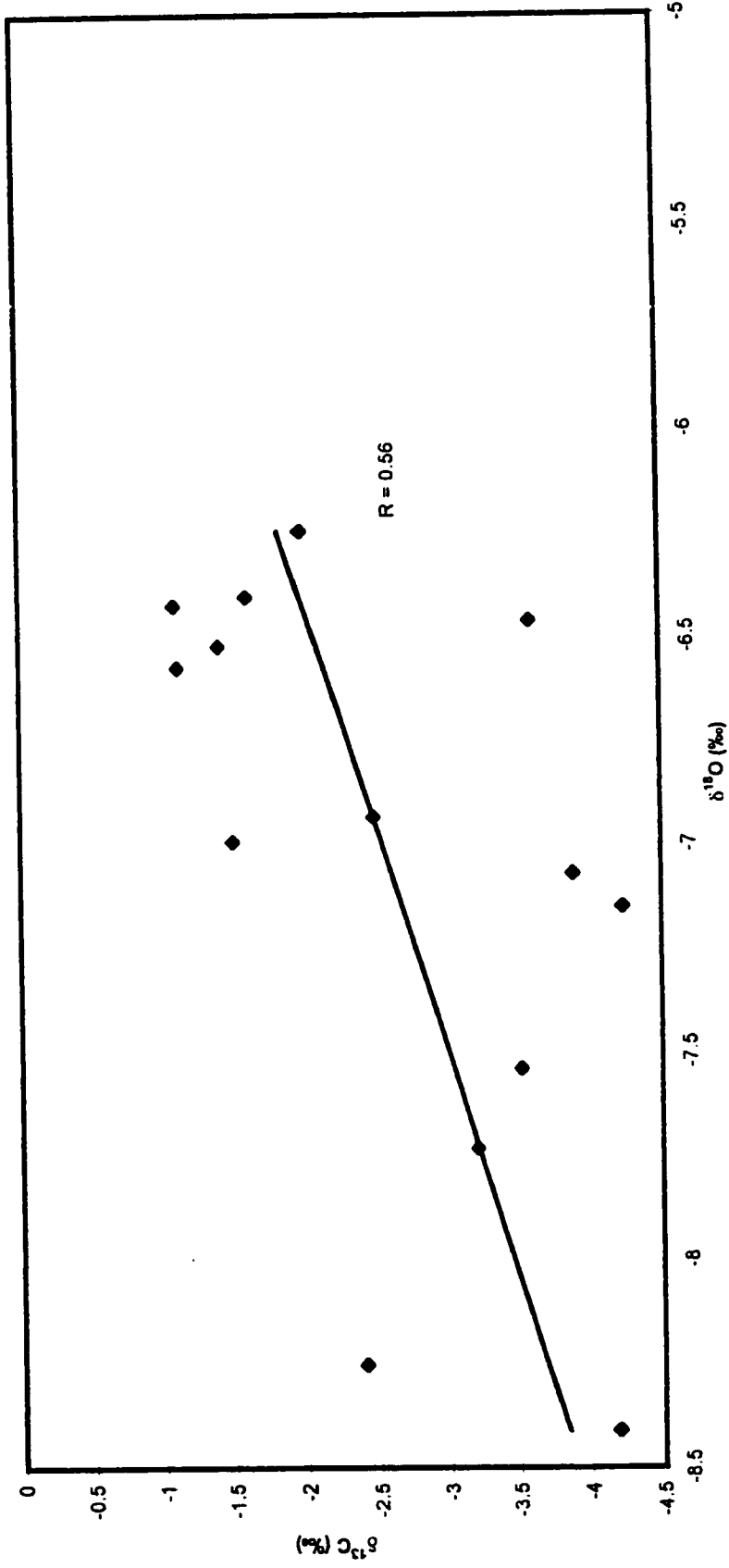
Figure 8.3: Scatter Plot of $\delta^{18}O$ (VPDB) and $\delta^{13}C$ (VPDB) in *Dreissena polymorpha* Shells

8.6 Isotopic Analysis of *Dreissena polymorpha* Growth Rings

Most studies that dealt with stable isotope analysis of molluscs focused on whole shell isotopic compositions, until more recent studies (Abell and Williams 1989; Al-Aasm et al. 1998; Dettman and Lohmann 1993) revealed some large variations in the isotopic composition of carbon within single mollusc shells over several years of growth. The results of sequential growth ring analysis of *Driessena polymorpha* shells in this study also showed annual variations in the isotopic composition of carbon and oxygen. The growth rings closest to the umbo in shells 5 (Mitchell's Bay), 8 (Grosse Point), and 13 (St. Clair Shores) exhibit depleted $\delta^{13}C$ and $\delta^{18}O$ values. These growth rings are definitely not in isotopic equilibrium with the ambient water. The repetitive nature of this early depletion in $\delta^{13}C$ and $\delta^{18}O$, and the fact that it is independent of the year in which growth started implies that it is not caused by ambient environmental factors.

One hypothesis that could account for this disequilibrium is that not only DIC but also metabolically light carbon is incorporated into the bivalve's shell. In a 1974 study by Fritz and Poplawski which included seven lakes in southern Ontario, it was found that the mollusk shells are in isotopic equilibrium with the lake DIC. However, other studies determined that 35 to 85% of the shell's ^{13}C was metabolic (Tanaka et al. 1986). Additional research showed that the isotopic composition of carbon in the shell is controlled by the rate of the metabolic activity of the mantle (Killingley and Berger 1979; Klein et al. 1996). The depleted $\delta^{13}C$ and $\delta^{18}O$ values during the first year of growth could be reflecting a period of high metabolic activity during which metabolically light

CO_2 is being actively supplied by the mantle and readily incorporated into the shell. A recent study by Schwarcz et al. (1998) investigated stable carbon isotope variations in the annual layers of aragonitic otoliths of the Atlantic cod (Gadus morhua). Results of the study indicated a depletion in the $\delta^{13}C$ of the first few layers of the otoliths, afterwhich the $\delta^{13}C$ continuously rises until the age of approximately six years. This trend of increasing $\delta^{13}C$ with age was attributed to a combination of a decrease in the amount of metabolic oxidized carbon in the fishes' blood as they mature and a shift in their dietary habits directed towards foods from higher trophic levels with higher $\delta^{13}C$.

Another possible cause for the observed depletion during the first year could be kinetic fractionation. Erez (1977, 1978) found that the $\delta^{13}C$ and the $\delta^{18}O$ of the carbonate shell decrease with increasing calcification rate in *Montipora verrucosa*. Planktonic foraminifera were also found to undergo quick initial shell nucleation, during which the test is depleted in ^{18}O and ^{13}C, that is later followed by slower thickening of the test (Al-Aasm and Bornhold 1986). Many other benthic organisms, including the deep-sea corals Bathypsammia (Emiliani et al. 1978) and Nautilus (Landman et al. 1983) exhibit strong kinetic isotopic disequilibria during early (rapid) growth. Such kinetic isotopic disequilibria, as defined by McConnaughey (1988), always involve the simultaneous depletion of ^{18}O and ^{13}C during early growth.

After the first year of growth, the zebra mussel growth rings still displayed some variation in the $\delta^{13}C$ and $\delta^{18}O$ signatures, but the values observed in the subsequent growth rings are never as low as the value of the first growth ring. All the shells in Lake St. Clair that were sampled for individual growth rings exhibited this phenomenon.

This finding was reconfirmed when a comparison between large and small *Dreissena polymorpha* shells was made. The terms juvenile and adult are avoided since the organism is said to enter the adult stage as soon as it settles after the completion of the planktonic stage. The small shells, which consisted of three growth rings, were depleted in ^{18}O and ^{13}C with respect to the larger shells, which consisted of seven growth rings (Table 7.3). The difference is due to the altered uptake of metabolic CO_2 throughout the life cycle of the zebra mussel. The depleted $\delta^{18}O$ and $\delta^{13}C$ values of the first growth ring carry more weight in determining the bulk $\delta^{18}O$ and $\delta^{13}C$ values of the small shells than in the larger shells since, in the former case, the first growth ring constitutes a higher percentage of the shell volume. Other studies by Berger et al. (1978) and Khan and Williams (1981) also showed that $\delta^{13}C$ in planktonic foraminifera decreases with decreasing size.

The ontogenetic method of sampling was also applied to a shell from the mouth of the Detroit River. The isotopic variation in this shell, however, does not conform to the pattern observed in the shells from Lake St.Clair. It was observed that the first growth ring of shell 17 (Fig 7.11) is not depleted in ^{13}C with respect to the subsequent growth rings This observation does not imply that the *Dreissena polymorpha* samples from the mouth of the Detroit River differ metabolically from those in Lake St. Clair. It is probably a reflection of the differing environmental conditions of the two areas. One significant difference that has to be taken into account is that isotopic analysis of bulk shells and DIC in water samples from the mouth of the Detroit River area showed a clear enrichment in ^{13}C relative to other locations of the study area. In this case, this ^{13}C enriched DIC could have accounted for a large percentage of the carbon used in the

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formation of the organism's shell during the first and later years of growth. The presence of the ^{13}C enriched DIC, which was utilized in the formation of the shell, masked the presence of metabolic carbon that is usually extensively used in the calcification process during the first year of growth.

As previously mentioned, there still is some variation in the isotopic signatures of both oxygen and carbon after the first year of growth. This variation is due to a combination of changes in the $\delta^{13}C_{DIC}$, $\delta^{18}O$ of the lake water, and the metabolic activity of the organism. Higher resolution sampling can even reveal more seasonal isotopic variations. This can be accomplished by multiple sampling of the same growth ring, moving away from the umbo. Such a method of sampling will give the isotopic composition values of carbon and oxygen for different seasons of the year. Since metabolic activity is at its lowest during late fall, the percent of metabolically derived carbon that is incorporated into the shell is close to zero. Therefore the $\delta^{13}C$ of the shells during this period is, to a large degree, a true reflection of the $\delta^{13}C$ of the DIC of lake water, and a useful tool for paleoenvironmental studies.

The approach of incremental sampling undertaken in this study proved to be important and essential for the proper understanding of variables that control the isotopic composition of a shell. The method allows for a direct observation of variations in the shell isotopic composition that occur during the development of the organism. In this case, it was concluded that after the first year of growth, intrinsic factors within the organism play a much smaller role in determining the shell's isotopic composition, and extrinsic environmental factors seem to become the primary ingredient governing the shell's isotopic composition.

8.7 Heavy Metals, Major and Minor Elements in Water and Shells

Previous literature is full of studies dealing with heavy metal bioaccumulation in the soft tissue of mussels (e.g. Busch 1991; De Kock 1986). However, studies involving the use of carbonate shells for monitoring heavy metal pollution are scarce compared to those involving the use of soft body tissues (Imlay 1982). Bourgoin (1989) suggested that shell analysis offers numerous advantages over soft body analysis because : (1) shells are easier to collect, clean, and preserve, (2) shell analysis techniques are easier to standardize, and finally (3) shell metal concentrations usually have smaller variance, thus yielding more significant statistical inferences.

8.7.1 Iron

Iron is incorporated into the aragonitic lattice in its reduced state (Tucker et al. 1990). Its average concentration in water (dissolved and particle-adsorbed species) within the study area was 244 ± 116 ppb, compared to an average shell concentration of 149 ± 102 ppm. Therefore, the resulting [Fe shell]/[Fe water] ratio is 611 (Table 8.1). The ratio of an element's concentration in the shell with respect to its concentration in the water is referred to as the accumulation factor. The significantly higher shell concentration is indicative of the occurrence of heavy metal accumulation, whereby iron from the water accumulates to high concentrations in the shell. Results showed that *Dreissena polymorpha* shells from Lake St. Clair exhibited a mean iron concentration of $(162 \pm 107$ ppm, n=11) and shells from the Detroit River mouth displayed and average of $(139 \pm 96$ ppm, n=3). A t-test was performed and indicated that there was no statistical difference between the two means $(p < 0.05)$. It was expected that shells from the Detroit River mouth would show higher concentrations of iron, knowing that steel plants

are found extensively along the American shore of the Detroit River. However, results suggest that heavy metal contamination levels in Lake St. Clair are comparable to those at the Detroit River mouth, probably due to the fact that the lake receives a high level of industrial discharges, mainly from the Chemical Valley in Sarnia, via the St. Clair River. The highest iron concentration in the shell was observed in shell 5 at Mitchell's Bay (392 ppm), which coincided with one of the highest iron concentration in the water. The elevated iron concentrations in Mitchell's Bay could be associated with the high level of organic material therein. Treated sewage water that is high in Fe content could be introduced by the rivers that flow into Mitchell's Bay. The concentration of iron in the study area was higher than that in Lake Erie. The latter concentration was determined by Nriagu et al. (1996) to be in the range 120-5048 ng/L. However, the samples in this study were not filtered and therefore the higher values probably reflect the combined adsorbed and dissolved ion concentrations of iron. The pollution factor (PF) for iron within the study area, which compares the highest concentration value to the lowest value displayed by the mussels within the study area, was calculated to be 10 (Table 8.1). The PF value is an indication of the extent of contamination in a water body; higher values indicate higher levels of pollution (Mersch et al. 1992)

The following equation, developed by McIntire (1963) and later modified by Kinsman (1969), was used to determine the distribution coefficient of iron, D, which controls the incorporation of trace elements into a carbonate lattice:

$$(^{m}Me/ ^{m}Ca)s = D (^{m}Me/ ^{m}Ca)w$$

where m stands for the molar concentration, Me signifies the trace element, and "s" and "w" indicate the solid phase and water, respectively. The distribution coefficient of iron

was determined to be 0.06 (Table 8.1). The average iron and calcium concentrations in both the shells and the water were used in the equation. The above equation is used based on the assumption that the system being examined is at equilibrium, a condition which is understood to exist whenever the amount of the solid phase is much smaller than the volume of the water, since the concentration of the element in the water doesn't noticeably change as it would if the volume of water was small (Veizer 1983). A "D" value of less than one implies that the solid phase contains a lower iron concentration, relative to Ca, than the water from which it precipitated.

Table 8.1: List of the accumulation factors, pollution factors, and the distribution coefficients of elements analyzed by ICP-OES.

Element Analyzed	Accumulation Factor	Polution Factor	Distribution Coefficient
Fe	611	10	0.06
Zn	130	10	0.04
Mn	2,300	5	0.20
Ca	11,500	–	–
Mg	9	–	–

8.7.2 Zinc

The average concentration of zinc in water within the study area was 70 ± 52 ppb (n=18), while the average shell concentration was 9 + 8 ppm (n=15). This yields a [Zn shell]/[Zn water] ratio of 130, which is also indicative of the high accumulation of zinc in the shell. A t-test indicated that there is no significant difference between the mean Zn concentration in shells taken from Lake St. Clair and that in shells taken from the mouth

of the Detroit River, again showing that Lake St. Clair contamination levels are comparable to those of the Detroit River mouth. Lake St. Clair is highly influenced by the industrial activities of the Ontario Chemical Valley, which regularly discharges industrial waste that is enriched in heavy metals. Nriagu et al. (1996) determined the average concentration of zinc in the Great Lakes to be 87-277 ng/L, which is much lower than the concentration determined in this study. The difference in concentrations is probably due to the fact that the samples in this study were not filtered. The pollution factor (PF) for Zn within the study area was also 10, however the anomalously high value at site 6 (382 ppm) was not considered in the calculation. The distribution coefficient was determined to have a low value of 0.04. Such values can be useful in estimating the concentrations of trace metals in the water during shell formation, assuming all the other variables in the equation are known, especially knowing that metal concentrations in freshwater systems may fluctuate, and a concentration that is determined during the time of sampling may not be reflecting the metal's actual concentration during the time the shell was formed. Therefore more laboratory and in situ studies can be beneficial in determining accurate values for distribution coefficients.

8.7.3 Manganese

Manganese displayed the highest tendency among the heavy metals to accumulate in the shell, with an [Mn shell]/[Mn water] ratio of 2300. The average water and shell concentrations were 6 ± 2 ppb (n=18) and 14 ± 7 ppm (n=15), respectively. Older literature presents many cases where mussels displayed an accumulation of manganese in their shells (Williams and Powell 1974). Manganese displayed an average concentration of 16 ± 6 ppm (n=11) in shells from Lake St. Clair and 10 ± 5 ppm (n=3) in shells from

the Detroit river mouth, with no statistical difference between the two means. Nriagu et al. (1996) determined the concentration of Mn in Lake Ontario within the range 8-449 ng/L. Again, the higher values obtained in this study can be attributed to the fact that the water samples were not filtered. The pollution factor (PF) within the study area was the lowest for manganese, with a value of 5, indicating it has the lowest contamination level amongst the three studied heavy metals within the study area. In this case the, distribution coefficient that controls the incorporation of manganese into the aragonitic shell was the highest, having a value of 0.20. The published value for the distribution coefficient of Mn in aragonite from marine environments (0.86) is still within the same order of magnitude of the value determined in this study (Brand and Veizer 1983).

A GIS generated map displaying the distribution of Mn in *Dreissena polymorpha* shell samples from the western shore of Lake St. Clair is shown in Figure (8.4). The map shows a higher concentration of manganese at the Detroit River head than along the western shore. This might be indicative of a higher level of industrial waste discharge at the Detroit River head from industrial plants along the American shore.

8.7.4 Calcium and Magnesium

While, in terms of abundance, calcium is considered as a major element, magnesium is only a minor element. The shell/water ratios for Ca and Mg were 11,500 and 9, respectively (Table 8.1). Magnesium, therefore, displays the lowest accumulation amongst all the elements analyzed. Previous literature cites examples of mollusc discrimination against Mg, which might be the reason behind its observed low level of accumulation in the shell (Veizer 1983). In the scope of this discussion, the two

Concentration Range

	4.1 - 6.0
	6.0 - 7.9
	7.9 - 9.8
	9.8 - 11.7
	11.7 - 13.6
	13.6 - 15.5
	15.5 - 17.4
	17.4 - 19.3
	19.3 - 21.2

Michigan

Ontario

Windsor

10   0   10   20 Kilometres
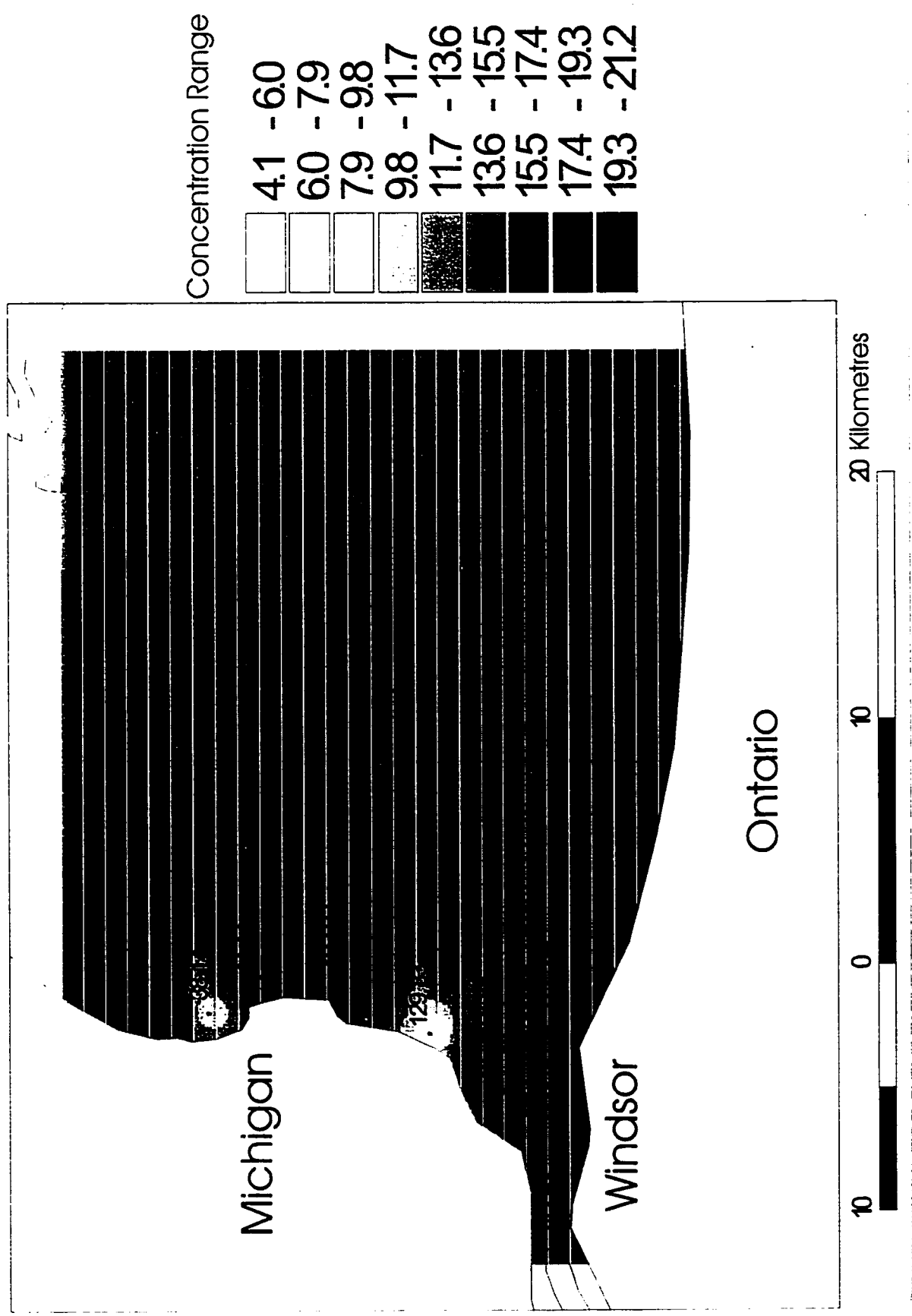
Figure 8.4: GIS Generated Map Showing the Distribution of Mn (ppm) in Shells of *Dreissena polymorpha*.

elements are best described as a ratio of Mg/Ca. It would be expected that the ratio of Mg/Ca in water is higher than that in the aragonitic shell of *Dreissena polymorpha*. As expected, the Mg/Ca ratio in the water, with an average of 0.28, was around a thousand fold higher than in the shell, the latter having an average of 0.00022. Moreover, the Mg/Ca ratios in the shell and in the water were uniform and statistically not different throughout all the locations within the study area.

8.8 Large versus Small Shells of *Dreissena polymorpha*

It was previously mentioned that smaller *Dreissena polymorpha* shells were depleted in ^{18}O and ^{13}C with respect to larger shells taken from the same locations (Table 7.3). Additionally, metal analysis revealed that smaller shells had noticeably lower concentrations of iron, manganese, and zinc (Fig.7.15). The shells were collected from northern Lake St. Clair, the head, and the mouth of the Detroit River.

At first glance, these observations might seem to constitute an interesting correlation between metal content and the carbon and oxygen isotopic composition of the shells, implying that larger shells are more enriched in both their metal content and their isotopic composition relative to the smaller and younger shells. However, although the isotopic depletion observed in smaller shells can be attributed to the extensive incorporation of metabolic carbon in the first year of growth, the lower metal concentrations of the smaller shells require a different explanation.

Detailed examination of growth rings within single shells revealed that the first growth ring, which represents the first year of growth, displayed higher concentrations of iron, than the other growth rings (Fig. 7.6, 7.8, 7.10). Consequently, depletion of iron in the smaller shells with respect to larger shells cannot be accounted for by a lower incorporation of iron in the early years of the organism's life. After the first two growth rings, iron concentrations decreased in the third and fourth ring, and then increased in subsequent rings. Zinc and manganese behaved differently in each of the individual shells analyzed. For example, the extensive cyclical variation of zinc that is observed in shell 5 is not found in the other shells.

Variation of metal concentrations within the growth rings of a shell seems to reflect changes in the metal concentration of the ambient water, metal concentrations of the sediment, water temperature and other factors that depend on the ambient environment of the zebra mussel and its position in the mussel colony. Growth rate and other intrinsic factors within the organism have been previously shown to have minimal effects on shell metal content (Forstner and Wittmann 1983).

If the intrinsic processes occurring within the organism played an important role in determining the metal content of the shell, one would expect to see a correlation between metal concentrations of the shell and those of the soft body; the latter has repeatedly been shown to be affected by such internal processes (Bryan 1973). Nevertheless, there has been little or no evidence of such a correlation. Van Der Velde et al. (1992) found no correlation between the concentrations of Cd, Zn, and Cu in the soft body and the shell of *Dreissena polymorpha*. Previous studies present many cases where

an increase in the metal concentration of the shell was accompanied by a decrease in the metal concentration of the soft body of the mussel (Romeril 1971).

The enrichment of Fe in the central (umbonal) part of the shell is similar to results from Schettler and Pcarcc (1996). Previous experiments conducted by katticairn and Salih (1992) indicated that bivalves react to stress caused by high levels of pollution or a reduction in oxygen levels by closing their shell valves and switching to anaerobic metabolism, thereby avoiding severe, short-term pollution events, especially during their first year of growth when they are least tolerant to environmental stresses. Shcettler and Pcarcc (1996) utilized this documented bivalve's reaction to stress to explain the metal enrichment of Cu, Zn, and Pb in the umbonal area of *Dreissena polymorpha* shells. They indicated that as the mussels are undertaking anaerobic metabolism, the acidic products of anaerobic glycolysis can be neutralized by partial dissolution of the carbonate shell. Once the mussels return to aerobic respiration, carbonate deposition is continued. This cycle of dissolution and deposition may be repeated many times as a reaction to environmental pollution, thus concentrating heavy metals to a certain part of the shell (the umbo in this case). However, the process of partial shell dissolution and acid neutralization has not been observed to operate in *Dreissena polymorpha* yet. It has been observed in the mussel *Mytilus mercenaria*, occurring mainly within the palial line (Crenshaw 1980).

Although each analyzed pair of small and large shells was collected from the same sampling site, the observed difference in heavy metal concentration between the two sizes can still be accounted for by variations in environmental conditions. The larger shells may have witnessed higher levels of pollution during the first three to four years of

growth, a period during which the smaller shells still did not exist. Following the first four years of the organism's life, heavy metal pollution levels might have decreased in sites 3, 7, and 15; this depletion in heavy metal concentrations would have been reflected in the smaller shells, resulting in the observed heavy metal enrichment in the larger shells in comparison to the smaller shells (bulk analysis).

Being the efficient filter-feeders they are, zebra mussels preferentially consume particles in the range of 15 to 40 μm (Winkel and Davids 1982). Depending on the speciation of the metals bound to food particles or dissolved in the water, some forms are bioavailable to the organism and are therefore retained. Generally, the dissolved species of the heavy metal have a higher bioavailability than the forms that are particle bound (Busch et al. 1992). Nonbioavailable species are not incorporated into the organism's tissues. A study by Fisher et al. (1996) came to the conclusion that metals obtained from food sources are mostly associated with the soft body of the mussel, whereas dissolved metals are primarily associated with the shell.

Biogenic carbonates, as other natural, non-biogenic carbonates, incorporate metal ions into their lattice by ways of substitution for calcium ions, occupation of free lattice positions, and adsorption to satisfy surface charges (McIntire 1963; Zemann 1969). The kinetics of incorporation depend on many environmental factors, such as the pH of the surrounding environment and the temperature of the ambient water which can speed up and increase metal incorporation during warmer years, thus producing the annual variation observed in the growth rings of the zebra mussel. As stated earlier, annual changes in the metal concentration of the ambient water also take part in producing the observed annual variations in the metal concentrations of growth rings. It is also

important to point out that changes in the water concentration of one metal can affect the incorporation of other metals into the shell. Romeril (1971) observed that the zinc concentrations in mussel shells increased with the addition of iron and cobalt to the water. Other studies show that the uptake of Cd by the mussel is inhibited by the presence of Zn or Cu (Hemelraad et al. 1987)

8.9 Relationship between Element Concentrations in the Shell and the Water

To determine the relationship between metal concentration in the shell and that in the water, the metal concentrations in the shell were plotted against the metal concentrations in the water. Correlation coefficients, which are listed in Table 8.2, were determined for each plot. There was no significant correlation between the water and the mussel samples. This lack of correlation was also observed by Mersch et al. (1992), who found a poor correlation between *Dreissena polymorpha* samples and the water of the Mosel River, with respect to Cd, Cr, and Zn. Therefore, the sessile mussel samples must be considered more reliable in reflecting metal pollution levels in the study area than single water samples. The water samples do not always reflect the mean contamination level of a site.

There were, however, significant correlations between element concentrations in the water (Table 8.2). Iron concentrations were significantly correlated with those of Mn, Ca, and Mg, Mn correlated significantly with Zn, Ca, and Mg, and calcium concentration was strongly correlated with that of magnesium. The correlation

Table 8.2:   List of correlation coefficients (r) between the analyzed elements. "S" stands for shell and "W" stands for water. Absolute values that are higher than 0.48 (critical r) are significant at the 5% level.

Element	Fe (S)	Mn (S)	Zn (S)	Ca (S)	Mg (S)	Fe (W)	Mn (W)	Zn (W)	Ca (W)	Mg (W)
Fe (S)	1.00	0.31	-0.20	-0.14	-0.35	0.08	0.40	-0.15	0.38	0.31
Mn(S)		1.00	-0.38	-0.42	0.19	-0.59	-0.52	-0.37	-0.49	-0.42
Zn (S)			1.00	0.36	0.09	0.12	0.08	-0.30	0.61	0.57
Ca (S)				1.00	0.21	0.41	0.36	-0.12	0.45	0.52
Mg(S)					1.00	-0.08	-0.33	-0.27	-0.24	-0.09
Fe (W)						1.00	0.80	0.45	0.57	0.64
Mn(W)							1.00	0.52	0.60	0.66
Zn (W)								1.00	-0.09	-0.07
Ca (W)									1.00	0.94
Mg(W)										1.00

observed between heavy metal concentrations in the water is probably suggesting their common origin from industrial discharges that find their way into the study area. The correlation between Fe and Mn could also be explained by their connected geochemical cycles, whereby manganese acts as a scavenger and adsorbs iron.

8.10 Relationship between Metal Concentrations and the Isotopic Composition of the Shells

Bulk shell analysis yielded no correlation between the isotopic composition of the shell ($\delta^{18}O$ and $\delta^{13}C$) and the concentration of the three heavy metals (Fe, Mn, and Zn) in the shell, as shown in Table 8.3. Correlation between stable isotopes and heavy metals was also weak within individual shells (incremental analysis). Factors affecting both the isotopic composition and the heavy metal content, such as temperature, can in some instances be responsible for their covariation, as shown in a study by Al-Aasm et al. (1998). In the latter study, periods of stable isotope enrichment correlated with higher heavy metal concentrations; such periods probably corresponded with relatively higher temperatures during which metal ions were easier to incorporate into the aragonitic shell.

Table 8.3 : Correlation coefficients between heavy metal concentrations and $\delta^{18}O$ and $\delta^{13}C$ values in Dreissena polymorpha shells.

Element	$\delta^{13}C$	$\delta^{18}O$
Fe	0.004	0.41
Mn	0.26	0.43
Zn	-0.43	-0.01

The lack of correlation between the stable isotopes and the heavy metals can be in part due to the different factors governing their distribution during the first year of the organism's life. Growth rate seems to be a factor that greatly affects the isotopic composition of the shell during the first year. The higher growth rate during the first year is probably responsible for the occurrence of kinetic fractionation that favors the incorporation of lighter CO_2 into the shell, thus depleting the $\delta^{18}O$ and the $\delta^{13}C$ values. Another factor that depletes the $\delta^{13}C$ and $\delta^{18}O$ during the first year is the incorporation of metabolically derived carbon into the shell. The two aforementioned factors, however, did not affect the metal concentration of the shell. Metal concentrations in the shell were instead primarily affected by the ambient environmental conditions, including temperature, pH, and the metal content of the surrounding water.

After the first year of the mussel's life, the isotopic composition of the shell becomes affected by a combination of environmental and metabolic factors, although metabolic factors become less important at this stage because metabolism and the growth rate have slowed down. It is important to consider the fact that there are many environmental factors that can affect either the metal content or the isotopic composition of the shell, but not both. Examples of such factors are nearby photosynthetic activities that could enrich $\delta^{13}C_{DIC}$ and $\delta^{18}O$ of the water without influencing the metal concentrations, and high metal concentrations in the water column that could increase the metal content of the shells without affecting the shell's isotopic composition.

CHAPTER 9

CONCLUSIONS

1. Isotopic analysis of bulk *Dreissena polymorpha* shells indicated that they are deposited close to isotopic equilibrium with the ambient water. The mean $\delta^{18}O$ value in Lake St. Clair was -7.05 ± 0.69‰ (n=10) VPDB, and the mean $\delta^{13}C$ value was -2.98 ± 1.11‰ (n= 10) VPDB, the latter being depleted by 0.7‰ with respect to the equilibrium value. This slight depletion could be due to the incorporation of metabolically derived carbon. Being close to equilibrium, the isotopic composition of the shell reflects changes in the environmental conditions occurring within the surrounding area of the zebra mussel.

2. *Dreissena polymorpha* shells at the Detroit River mouth exhibited the most enriched $\delta^{13}C$ values. Water samples from this area also displayed the highest $\delta^{13}C_{DIC}$. One of the possible causes for the observed isotopic enrichment is the discharge of chemicals that are enriched in $\delta^{13}C$ from the heavily industrialized Detroit River shores.

3. The $\delta^{18}O$ composition of Lake St. Clair water and consequently *Dreissena polymorpha* shells was relatively uniform. This could be due to the relatively uniform depth within the lake, which minimizes temperature differences that could otherwise produce oxygen isotope fractionation.

4. The heavy metals tended to strongly accumulate in the shells of the zebra mussels. Accumulation factors were 611, 130, and 2300 for Fe, Zn, and Mn, respectively. There was no statistical difference between the mean concentration of each of the

heavy metals in shells taken from Lake St. Clair and those taken from the Detroit River mouth. This implies that the heavy metal contamination level in Lake St. Clair is comparable to that at the Detroit River mouth. The lake regularly receives industrial discharges from the Ontario Chemical Valley, via the St. Clair River.

5. The incremental analysis of the shells revealed annual variations in the heavy metal concentrations and the carbon and oxygen isotopic composition. While heavy metal concentrations in *Dreissena polymorpha* shells seemed to be primarily affected by environmental factors, the isotopic composition was affected by a combination of environmental factors and intrinsic factors, such as growth rate and the incorporation of metabolically derived carbon. The latter factors were especially significant during the first year of growth, causing an appreciable depletion in the $\delta^{13}C$ and the $\delta^{18}O$ values.

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APPENDIX 1

Results of $\delta^{18}O$ and $\delta^{13}C$ for whole shell (bulk) samples of *Dreissena polymorpha*.

Site Number	$\delta^{18}O$ (VSMOW) ‰	$\delta^{18}O$ (VPDB) ‰	$\delta^{13}C$ (VPDB) ‰	Shell Length (mm)
1	24.31	-6.40	-1.61	19.50
1s	22.09	-8.55	-1.83	10.25
3	24.47	-6.24	-1.99	20.00
3s	21.85	-8.79	-2.23	9.75
5-A	23.87	-6.83	-3.77	19.25
5-B	24.65	-6.08	-3.43	19.00
6	23.54	-7.15	-4.23	22.00
7	24.14	-6.57	-1.11	19.75
7s	21.91	-8.73	-1.60	11.75
8	23.77	-6.93	-2.47	18.75
9	22.94	-7.73	-3.20	22.00
10	23.14	-7.54	-3.52	22.75
12	22.24	-8.41	-4.18	22.50
13	23.62	-7.07	-3.89	18.00
14	22.41	-8.25	-2.39	19.00
16	23.70	-6.99	-1.50	18.75
16s	23.76	-6.94	-1.26	8.25
17-A	24.32	-6.39	-1.10	21.25
17-B	24.27	-6.44	-1.07	22.00
18-A	24.30	-6.42	-1.13	20.50
18-B	24.10	-6.62	-1.68	19.00

Results of $\delta^{18}O$ and $\delta^{13}C$ for the Sequential Sampling Procedure of
Dreissena polymorpha **Growth Rings (commencing with GR1, closest to umbo, and moving outwards).**

Shell Site Number	Growth Ring Number	$\delta^{18}O(VPDB)$ ‰	$\delta^{13}C(VPDB)$ ‰
5 (Mitchell's Bay)	GR1	-10.08	-5.74
	GR2	-7.74	-4.42
	GR3	-6.97	-3.43
	GR4	-6.57	-3.21
	GR5	-6.68	-4.46
	GR6	-6.43	-4.68
	GR7	-7.88	-3.98
8 (Grosse Point)	GR1	-21.82	-10.39
	GR2	-6.97	-2.65
	GR3	-6.73	-2.73
	GR4	-8.26	-3.67
	GR5	-7.85	-3.72
13 (St. Clair Shores)	GR1	-18.49	-9.22
	GR2	-10.70	-3.02
	GR3	-8.29	-2.17
	GR4	-11.11	-3.74
	GR5	-9.15	-2.48
	GR6	-8.34	-2.45
17 (Mouth of Detroit River)	GR1	-7.01	-1.32
	GR2	-7.38	-1.21
	GR3	-4.98	-0.15
	GR4	-10.81	-3.14
	GR5	-6.75	-1.50
	GR6	-6.98	-1.90

APPENDIX 3

Results of $\delta^{18}O$ and $\delta^{13}C_{DIC}$ for Water Samples

SAMPLE SITES	$\delta^{18}O$ (VSMOW)	$\delta^{13}C$ (VPDB)
1	-7.44	-3.71
2	-7.44	-4.33
3	-7.49	-2.32
4	-7.41	-2.17
5	-7.56	-9.74
6	-7.62	-5.12
7	-7.36	-2.90
8	-7.27	-4.46
9	-7.26	-3.76
10-A	-7.44	-2.75
10-B	-7.46	N/A
11	-8.01	-2.77
12	-7.41	-2.85
13	-7.38	-2.63
14	-7.33	-3.68
15	-7.32	-1.86
16	-6.94	-1.39
17	-7.12	N/A
18	-7.19	-1.85

APPENDIX 4

Heavy metal concentrations in water (ppb) and *Dreissena polymorpha* shells (ppm)

Location	Fe (shell)	Fe (water)	Mn (shell)	Mn (water)	Zn (shell)	Zn (water)
1	143	220	21	5	13	47
2	N/A	157	N/A	4	N/A	95
3	120	161	20	4	5	65
4	N/A	106	N/A	4	N/A	78
5	393	438	9	9	12	77
6	75	309	4	7	383	22
7	174	110	22	3	35	21
8	274	204	21	8	6	92
9	130	165	8	5	7	24
10	265	160	19	7	8	60
11	90	204	19	6	7	62
12	38	152	10	5	3	51
13	78	171	19	5	N/A	32
14	48	221	5	7	7	202
15	N/A	181	N/A	6	N/A	144
16	76	495	8	9	7	181
17	91	449	7	8	6	72
18	249	206	16	8	4	52

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