The carbon and nitrogen composition of suspended particulate matter in Lake Erie, selected tributaries, and its outflow

by

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Abstract

Since their introduction to Lake Erie, dreissenid mussels may have reengineered the cycling of nutrients in the lake so that the nearshore benthic community intercepts, retains, and recycles greater quantities of nutrients. This study traces particulate matter on a basin scale by characterizing the chemical composition (POC and PN concentrations, POC/PN mass ratios, $\delta^{13}C$ and $\delta^{15}N$) of suspended particulate matter in Lake Erie, three tributary inflows, and the lake outflow between May and October, 2002. The data are used to 1) determine the relative contributions of allochthonous and autochthonous sources to suspended particulate matter, 2) identify possible sources of suspended particulate matter, and 3) compare suspended particulate matter in the eastern basin of Lake Erie with that in the central and western basins. Mean POC concentrations range from 175 to 4494 µg/L and mean PN concentrations range from 33 to 812 µg/L in this system. Mean POC/PN mass ratios are similar across all sampling locations, ranging between 4.5 and 6.9, and indicate that suspended particulate matter at these sites is mainly derived from autochthonous sources, particularly plankton. The ranges of $\delta^{13}C$ (–34 to –22 ‰) and $\delta^{15}N$ (1 to 12 ‰) identify terrestrial plants and soil matter, aquatic macrophytes, phytoplankton, and sewage as possible sources of suspended particulate matter at all sites. Plankton is probably the dominant source of suspended particulate matter at each site, with smaller contributions from allochthonous and other autochthonous sources. Significant differences in the concentration and isotope data between inflow and lake or outflow sites indicate that tributary inflows may receive greater contributions from terrestrial plants and soils and aquatic macrophytes than the lake and outflow. $\delta^{15}N$ signatures also identify animal manure as a possible source of suspended particulate matter at the inflows. PN concentrations and $\delta^{15}N$ signatures suggest that the shallowest nearshore sites close to Peacock Point in the eastern basin receive PN from a source that is not present at the other eastern basin sites or at the sites in the central and western basins. This source may be related to dreissenid mussels at these nearshore sites recycling nitrogen back into the water column.

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I had no idea, at the beginning of this degree, that it was going to take me so long to work through it. I also didn't realize how much I was going to learn, both academically and personally, along the way. I would not have finished this thesis or have learned so much without the support of many people.

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Dedication

I dedicate this work to the memory of my friend Jane Almond.

Janer –

Thank you for many delightful shared moments and for contributing much to my non-academic learning during the course of this degree.

Love you,
B.

I wanted to know you
When we were both older
I thought there'd be more
Of those wonderful times

I could lie to myself
And say I like it
But I would love it
If you were here

- Sarah Harmer, *You Were Here*

Time goes by, the seasons change
And our lives go quickly by
The time we have is short to us
Yet we find it pays to try

And is it just imagination
Pictures in my mind
Just like waiting at some skybound station
For the train to bring us a peace we never find

- David Wiffen, *Skybound Station*

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Chapter 1: Introduction

1.1 Problem Statement

Increases in population, agricultural activity, and industrial development, coupled with the increasing use of detergents containing phosphate, resulted in a rapid decline in the water quality of Lake Erie after 1940 (Sly, 1976). These land-use and cultural changes led to the lake exhibiting highly eutrophic conditions in the 1970's (Sly, 1976). The eutrophication was largely attributed to high phosphorus loading, since phosphorus was most often the growth-limiting nutrient in the lake (Nicholls et al., 2001). In order to reduce the eutrophication of the lake, new methods were employed to remove phosphorus from wastewaters and legislation was passed to limit the phosphorus content of detergents (Nicholls et al., 2001). As a result, total phosphorus loading to the lake from point and non-point sources decreased by approximately 56 % between 1968 and 1982 (Fraser, 1987), the phosphorus concentrations in Lake Erie subsequently declined (Rosa, 1987), and lake water quality improved (Makarewicz and Bertram, 1991).

A non-native species of mussel, *Dreissena polymorpha* (commonly known as the zebra mussel), was found in the western basin of Lake Erie in 1988 (Leach, 1993). Within a few years of their arrival in the western basin, zebra mussels proliferated and spread to the central and eastern basins of Lake Erie (Mackie, 1991). A second dreissenid mussel, *D. bugensis* (quagga mussel), was also found in Lake Erie by 1989 (Mills et al., 1993) and *D. bugensis* is now the dominant species of mussel throughout most of the lake. Dreissenid mussels are filter feeders that remove suspended particles from the water column. Nutrients processed by dreissenids are used in mussel growth and reproduction, released to the water column in dissolved form, or deposited on the lake bottom in association with feces or pseudofeces (Arnott and Vanni, 1996). Concern has been raised regarding the effects of the invasive dreissenid mussels on native biota (Mackie, 1991; Griffiths, 1993), energy flow in the pelagic zone (Mackie, 1991; Hecky et al., 2004), and nutrient concentrations and distributions (Holland et al., 1995; Griffiths, 1993).

Previous research suggests that dreissenid mussels profoundly impact the nearshore environment of Lake Erie. Dreissenid mussels divert energy and nutrients from the water column to the benthos (Griffiths, 1993; Klerks et al., 1996), increasing the resources available to benthic organisms. The filtering action of the mussels enhances water clarity (Leach, 1993; Fahnenstiel et al., 1995; Holland, 1993; Howell et al., 1996), allowing light to penetrate to depths at which benthic algae, such as *Cladophora*, grow. Attaching themselves to the lake bottom, dreissenid mussels increase the roughness of the substrate, increasing the surface area available for the attachment of benthic algae and enhancing the retention of particulate matter in nearshore areas (Hecky et al., 2004).

Previous models of phosphorus in Lake Erie fail to explain the present conditions in the lake. Currently, the offshore environment of Lake Erie exhibits mesotrophic to oligotrophic conditions; however, there are signs of eutrophication, particularly abundant growth of the benthic filamentous alga *Cladophora*, in the nearshore environment (Hecky et al., 2004; Higgins et al., in press). Higher than normal particulate phosphorus concentrations have been reported at the lake outflow, but there is no evidence of increased phosphorus loading from external sources (Hecky et al., 2004).

Hecky et al. (2004) propose that dreissenid mussels have reengineered the cycling of nutrients in Lake Erie, which causes the nearshore benthic community to intercept, retain, and recycle greater quantities of nutrients. The nearshore shunt could also change the composition of particulate matter exported from the nearshore environment (Hecky et al., 2004). Figure 1.1 demonstrates this nearshore shunt hypothesis by illustrating the cycling of nutrients in Lake Erie before and after the introduction of dreissenid mussels to the lake. Prior to the dreissenid mussel invasion, the nearshore benthos only weakly retained nutrients and the nearshore water column was a net source of nutrients to the offshore environment (Hecky et al., 2004). Nutrients were mainly lost through sedimentation in the offshore water column to the offshore profundal region and nutrients discharged from the lake were derived from the offshore water column (Hecky et al., 2004). Since the dreissenid mussel colonization, nutrients supplied to the nearshore environment, from allochthonous sources and offshore areas, have been retained by the nearshore benthic community during the growing season of the mussels and benthic algae (Hecky et al., 2004). The offshore water column, therefore, has become a net source of nutrients to the nearshore environment. In the nearshore benthos, dreissenid mussel feeding activities package fine particulate matter and nutrients into larger, loosely-bound aggregates (feces and pseudofeces; Figure 1.2). These aggregates provide a source of nutrients following microbial degradation in the nearshore or they are available for resuspension, allowing transport to the offshore profundal zone or to the discharge under the influence of longshore currents (Hecky et al., 2004). The regeneration of nutrients through dreissenid mussel excretion or through microbial degradation of dreissenid feces and pseudofeces constitutes a new source of nutrients to sustain the early- and mid-summer growth of *Cladophora* (Hecky et al., 2004). *Cladophora* growth also results in larger particles being available for transport after the mid-summer die-off and during periods of higher turbulence and resuspension (Hecky et al., 2004). The net effect of the nearshore shunt is the production of larger particles from finer ones.

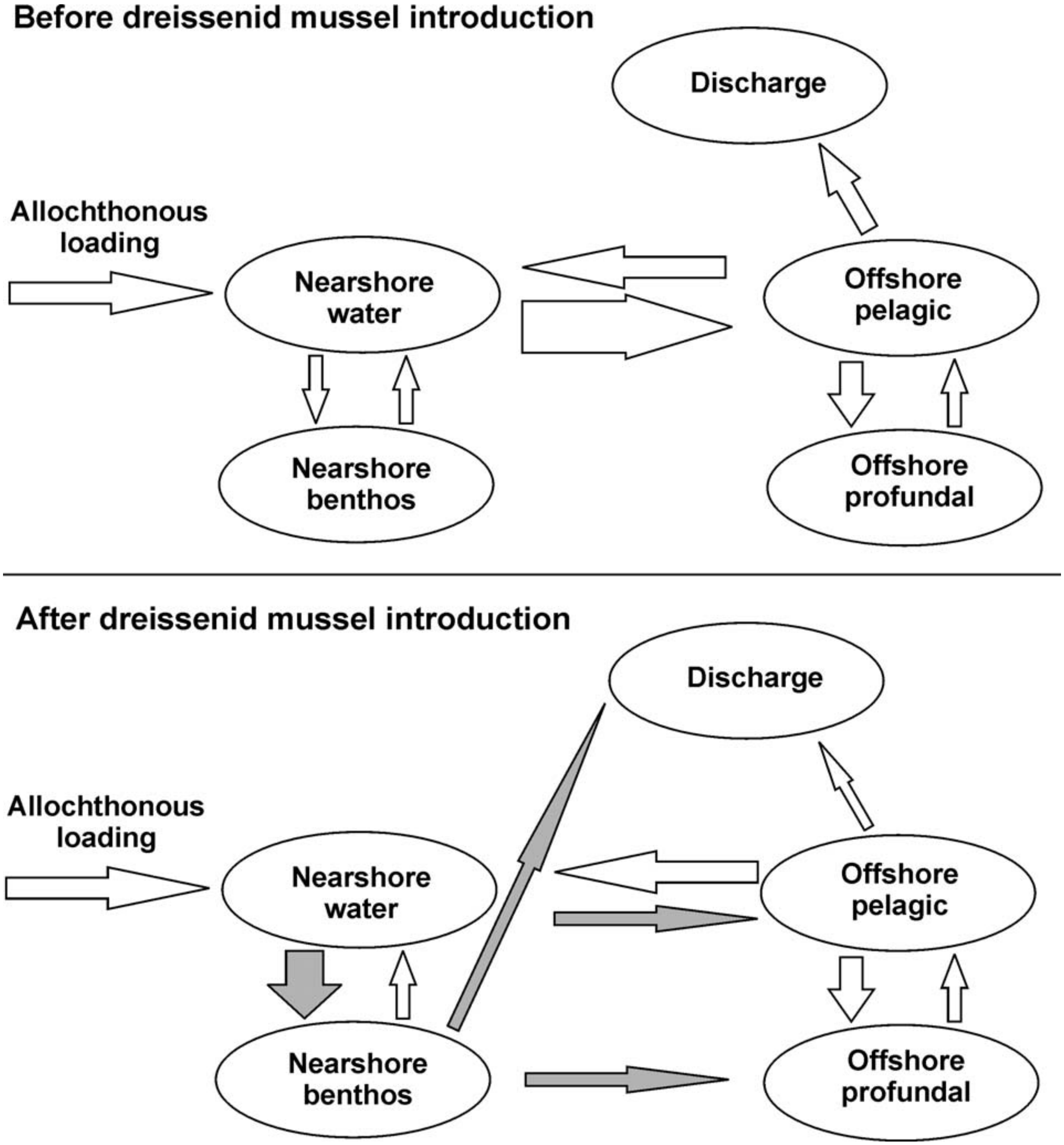


Figure 1.1: Diagram demonstrating the nearshore shunt hypothesis. The first panel shows conditions before dreissenid mussels were introduced into Lake Erie and the second panel shows conditions after their introduction. Ellipses represent the major compartments for nutrients and arrows show fluxes of nutrients into and out of the compartments. Arrow width indicates the relative magnitude of the flux. Shaded arrows highlight the fluxes that are most changed by the nearshore shunt. (Redrawn from Hecky et al., 2004.)

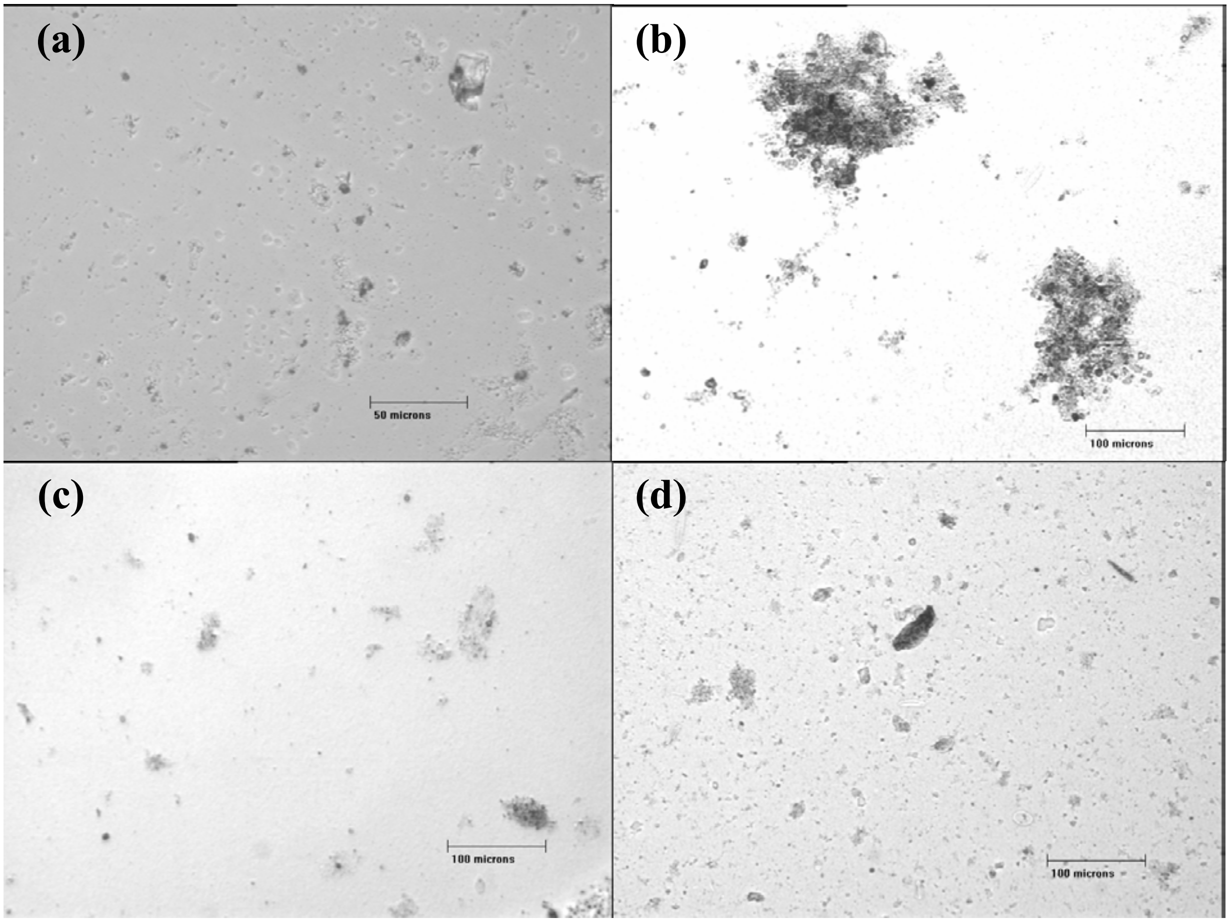


Figure 1.2: Photomicrographs of suspended particulate matter in July 2002 from (a) the Grand River, (b) the Lake Erie eastern basin nearshore above dreissenid mussel beds (5-m maximum depth), (c) the Lake Erie eastern basin offshore (62-m maximum depth), and (d) the Lake Erie outflow. The bar scale represents 50 microns in the Grand River image (a) and 100 microns in the other three images. Note the larger size and aggregated nature of particles present at the nearshore site compared with the other sites.

The present research contributes to the testing of the validity of the nearshore shunt hypothesis (Hecky et al., 2004) by using carbon and nitrogen as tracers on a basin scale to determine how particulate matter is cycled in Lake Erie. This is achieved by characterizing the absolute and relative concentrations and the isotopic composition of carbon and nitrogen associated with suspended particulate matter in the allochthonous loading (three tributary inflows), nearshore water, offshore pelagic, and discharge (lake outflow) compartments of the nearshore shunt model.

1.2 Particulate Organic Carbon and Particulate Nitrogen

For the purposes of this research, particulate organic carbon (POC) is the carbon associated with living and detrital organic material. Particulate nitrogen (PN) consists of both particulate organic nitrogen, which is the nitrogen associated with living and detrital organic material, and ammonium (a form of inorganic nitrogen) that adsorbs to particulate matter. Sources of POC and PN and processes involved in their cycling in a lake are shown in Figures 1.3 and 1.4, respectively. POC and PN in lakes can be derived from autochthonous (within-lake) organisms through processes such as photosynthesis or assimilation and degradation of aquatic organisms. POC and PN can also be derived from material transported to the lake from allochthonous (external) sources through processes including weathering and inflow from tributaries. The nearshore water column of Lake Erie receives POC and PN from a mixture of allochthonous sources, the nearshore benthos, and the offshore pelagic zone (Hecky et al., 2004). In contrast, the offshore water column of Lake Erie is not directly impacted by allochthonous sources, but can receive POC and PN through advection from the nearshore water column, from the offshore profundal zone during vertical mixing events, and primarily from autochthonous growth in the offshore (Hecky et al., 2004).

The ratio of carbon to nitrogen (C/N) has been widely used to distinguish between autochthonous and allochthonous origins of sedimentary organic matter in lakes (e.g. Meyers, 1994; Herczeg et al., 2001) and to infer the source of suspended particulate matter in freshwater environments (e.g. Meyers and Eadie, 1993; Kendall et al., 2001). This is possible because particulate matter derived from allochthonous sources tends to be more enriched in carbon relative to nitrogen than particulate matter derived from autochthonous aquatic sources due to the presence of cellulose in terrestrial vascular vegetation and its absence in algae (Meyers, 1994). For example, according to Wetzel (1983), organic matter resulting from the autochthonous source of decomposing plankton has a C/N ratio of approximately twelve, while allochthonous organic matter has a C/N ratio ranging from about forty-five to fifty. In a study of the Lake Geneva basin in Switzerland, Thomas et al. (1991) found that C/N ratios were useful in determining the origin of phosphorus and organic matter in lakes and lake systems. Kemp et al. (1977) showed that, in the Laurentian Great Lakes, C/N ratios are directly related to the provenance of sedimenting organic matter. The ratio of POC to PN is used in the present study to evaluate the relative contributions of allochthonous and autochthonous sources to suspended particulate matter in three tributary inflows, the outflow, and nearshore and offshore areas of Lake Erie. It is also used to identify possible origins of suspended particulate matter at these locations.

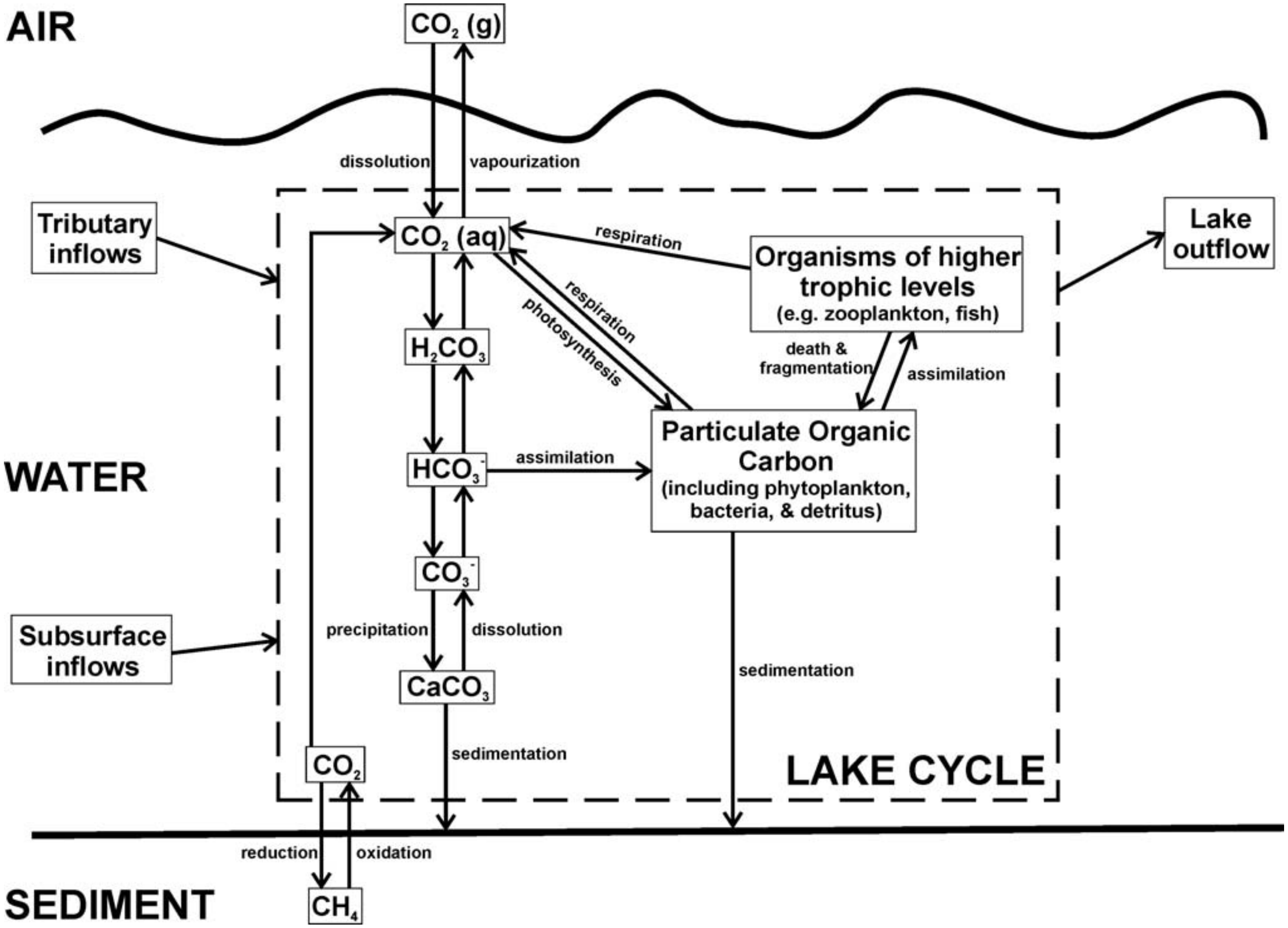


Figure 1.3: Diagram of the carbon cycle in a lake. The dashed line encloses the forms of carbon present and the processes occurring in the lake water column. The tributary inflows, subsurface inflows, and lake outflow compartments contain most or all forms of carbon found in the lake water column. (Drawn with reference to Kerr et al., 1972; Peterson and Fry, 1987; and Clark and Fritz, 1997.)

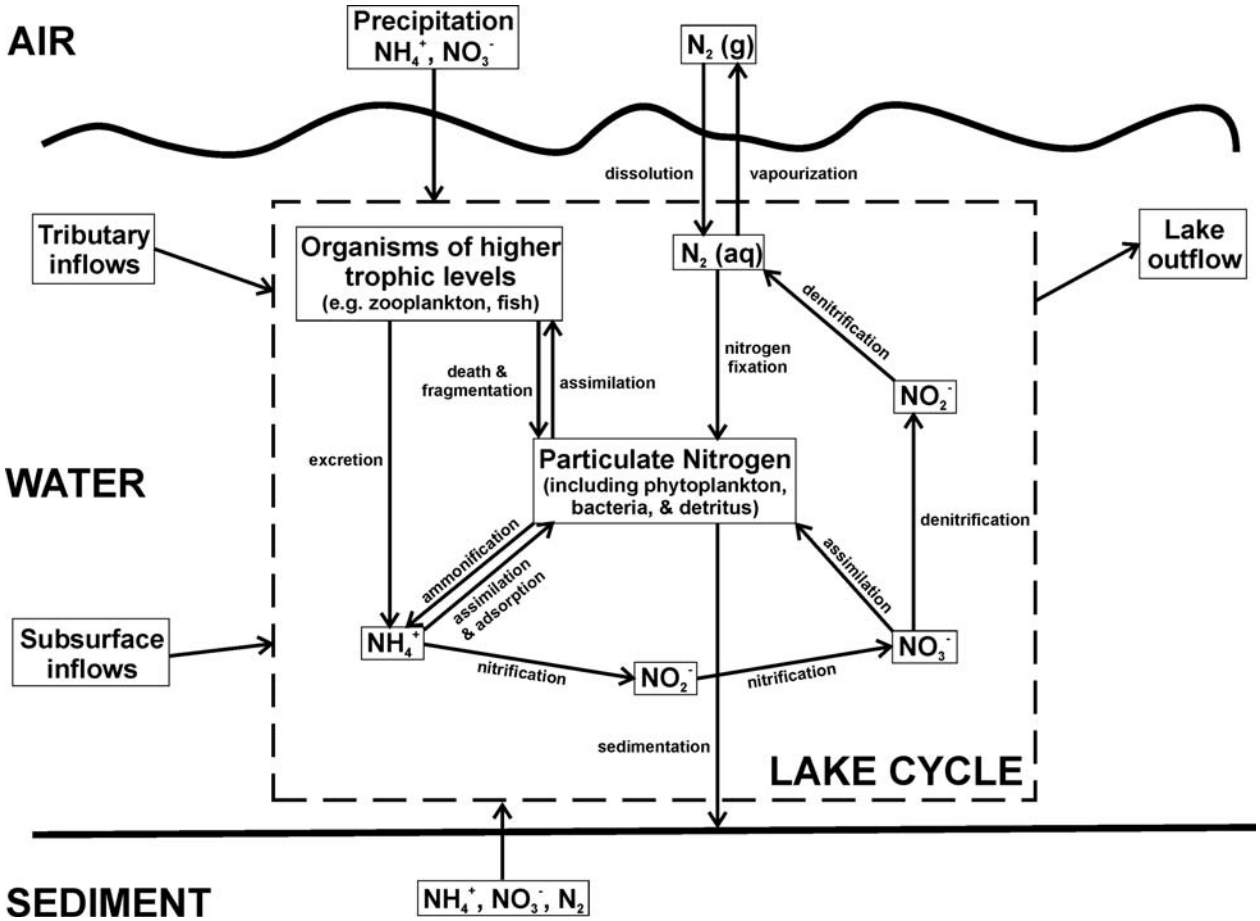


Figure 1.4: Diagram of the nitrogen cycle in a lake. The dashed line encloses the forms of nitrogen present and the processes occurring in the lake water column. The tributary inflows, subsurface inflows, and lake outflow compartments contain most or all forms of nitrogen found in the lake water column. (Drawn with reference to Keeney, 1973; Peterson and Fry, 1987; Newbold, 1992; Kendall, 1998.)

1.3 Carbon and Nitrogen Stable Isotopes

Isotopes are elements that have the same number of protons but a different number of neutrons in their nuclei (Hoefs, 1997). Stable isotopes do not spontaneously decay (Clark and Fritz, 1997). Carbon (C) and nitrogen (N) each have two stable isotopes:

^{12}C – 6 protons, 6 neutrons, 6 electrons ^{14}N – 7 protons, 7 neutrons, 7 electrons
^{13}C – 6 protons, 7 neutrons, 6 electrons ^{15}N – 7 protons, 8 neutrons, 7 electrons

The different number of neutrons among isotopes of the same element produces isotopes with different masses. The masses and relative abundances of carbon and nitrogen stable isotopes are shown in Table 1.1. The chemical behaviour of an element is determined by its electronic structure and, since isotopes of one element have the same number of electrons, they display similar chemical characteristics (Hoefs, 1997). The differing number of neutrons among isotopes of the same element results in isotopes with mass-dependent differences that affect vapour pressures, bond strengths, and reaction rates (Hoefs, 1997). Many reactions cause a change in the ratio of heavy to light isotopes between two substances or two phases of the same substance (Peterson and Fry, 1987). This is known as isotopic fractionation (Hoefs, 1997).

Table 1.1: Mass and average natural abundance of carbon and nitrogen stable isotopes. (Source: Ehleringer and Rundel, 1989; Holden, 2003)

Isotope	Mass (atomic mass units)	Average Natural Abundance (%)
^{12}C	12.000 000	98.89
^{13}C	13.003 355	1.11
^{14}N	14.003 074	99.63
^{15}N	15.000 108	0.37

Stable isotopes are measured as the ratio of the two most abundant isotopes for a given element, such as $^{13}C/^{12}C$ for carbon and $^{15}N/^{14}N$ for nitrogen (Clark and Fritz, 1997). The isotope abundances are reported relative to a standard value using the following equations for carbon and nitrogen, respectively:

$$\delta^{13}C = \frac{(^{13}C/^{12}C)_{\text{sample}} - (^{13}C/^{12}C)_{\text{standard}}}{(^{13}C/^{12}C)_{\text{standard}}} \times 1000\,‰ \qquad (1.1)$$

$$\delta^{15}N = \frac{(^{15}N/^{14}N)_{\text{sample}} - (^{15}N/^{14}N)_{\text{standard}}}{(^{15}N/^{14}N)_{\text{standard}}} \times 1000\,‰ \qquad (1.2)$$

Delta (δ) values indicate whether a sample is enriched or depleted in the heavier isotope relative to the standard (Fritz and Fontes, 1980). Positive values show that the sample is enriched in the heavier isotope relative to the standard, while negative values show depletion in the heavier isotope relative to the standard. Because isotopic fractionation does not cause large variations in isotopic concentration, δ values are multiplied by one thousand and expressed as per mil or parts per thousand (‰; Fritz and Fontes, 1980). The standard for carbon is Vienna PeeDee Belemnite (VPDB; $\delta^{13}C = 0$ ‰) and the standard for nitrogen is atmospheric nitrogen ($\delta^{15}N = 0$ ‰; Clark and Fritz, 1997).

Stable isotopes of carbon and nitrogen are useful in the study of hydrological, geological, and biological systems because these elements are naturally abundant and are involved in many biogeochemical processes (Clark and Fritz, 1997). Their use as tracers and to examine biogeochemical processes in these systems is also facilitated by the large relative mass difference between heavy and light isotopes of an element, which creates detectable changes in the partitioning of heavy and light isotopes (Clark and Fritz, 1997). In aquatic systems, stable isotopes of carbon and nitrogen fractionate in predictable ways as these nutrients cycle through biological processes affecting the production and degradation of particulate matter (Peterson and Fry, 1987). As a result, carbon and nitrogen stable isotopes are helpful in determining the source and fate, and processes influencing, particulate matter and associated nutrients in lakes (Peterson and Fry, 1987). It should be noted, however, that the use of stable isotopes as nutrient tracers is restricted to situations in which the source pool of a given nutrient is large relative to the demand for the nutrient. If most or all of the nutrient is removed from the source pool due to high demand, little or no fractionation will be evident (Kendall, 1998).

There are two principal effects that cause stable isotopes to fractionate: equilibrium effects and kinetic (non-equilibrium) effects. Equilibrium effects relate to temperature-dependent reactions. Heavier isotopes have greater bond strengths than lighter isotopes, requiring more energy to break bonds with other atoms (Clark and Fritz, 1997). Hence, the heavier isotopes generally partition into the relatively condensed phase (i.e. into the solid phase in mineral-solution reactions and into the aqueous phase in liquid-vapour reactions; Peterson and Fry, 1987). Fractionation tends to increase with decreasing temperature (Clark and Fritz, 1997).

Kinetic effects pertain to unidirectional, incomplete reactions in which mass differences in isotopes influence the rates of reactions (e.g. diffusion, biologically-mediated reactions; Hoefs, 1997). With respect to diffusion, molecules containing lighter isotopes generally diffuse more rapidly than those containing heavier isotopes (Hoefs, 1997). Biologically-mediated reactions preferentially incorporate lighter isotopes over heavier ones (Hoefs, 1997). For example, in photosynthesis, plants preferentially use ^{12}C over ^{13}C, resulting in the relative depletion of ^{13}C in organic matter compared to the carbon source (Hoefs, 1997). The magnitude of the kinetic effect in photosynthesis depends upon the carbon dioxide (CO_2) concentration and the type of metabolic process (i.e. Calvin, Hatch-Slack, Crassulacean Acid Metabolism; Hoefs, 1997).

The $\delta^{13}C$ signature of POC is governed by the $\delta^{13}C$ values of carbon sources to the POC pool and fractionation that occurs during processes of the lake carbon cycle (Figure 1.5). In photosynthesis, all plants preferentially assimilate lighter isotopes over heavier ones, producing plants with lower $\delta^{13}C$ values than their sources of carbon (Kendall et al., 2001). The carbon source for terrestrial plants is atmospheric CO_2 and these plants fall into two main categories, depending upon the photosynthetic pathway they use to convert inorganic carbon to organic carbon: C_3 plants, which follow the Calvin pathway, and C_4 plants, which follow the Hatch-Slack pathway (Kendall et al., 2001). About 90 % of all modern plants, including deciduous and coniferous trees, are C_3 plants (Hoefs, 1997). These plants use the ribulose biphosphate carboxylase oxygenase (RUBISCO) enzyme, which reacts with one molecule of CO_2 to produce three molecules of 3-phosphoglyceric acid (Hoefs, 1997). The C_4 group of plants includes, for example, corn and prairie grasses (Kendall et al., 2001). These plants use the phosphoenolpyruvate carboxylase (PEPC) enzyme, which initially assimilates CO_2 into four-carbon acids (Deines, 1980). C_3 plants fractionate more than C_4 plants do from their atmospheric carbon source, resulting in C_3 plants having lower $\delta^{13}C$ values than C_4 plants (Kendall et al., 2001). Some terrestrial plants use a Crassulacean Acid Metabolism (CAM) pathway for carbon fixation during photosynthesis. CO_2 fixation in these plants follows a diurnal cycle, using the Calvin pathway in light and the Hatch-Slack pathway in darkness (Osmond, 1975). The use of both the Calvin and Hatch-Slack pathways results in CAM plants having $\delta^{13}C$ values intermediate between C_3 and C_4 plants (Hoefs, 1997). The $\delta^{13}C$ of soil organic matter reflects the type of plant (i.e. C_3, C_4, CAM) growing on the soil (Kendall et al., 2001).

The source of carbon for aquatic plants is mainly dissolved inorganic carbon, which is derived from dissolved atmospheric CO_2, dissolution of carbonate rocks ($CaCO_3$), respiration of organisms, oxidation of methane, and water from surface and groundwater pathways (Kendall et al., 2001). Aquatic plants that use CO_2 as their carbon source have $\delta^{13}C$ values that overlap with the values for terrestrial plants (Krishnamurthy et al., 1986). The $\delta^{13}C$ values of aquatic plants can, however, be more variable than those of terrestrial plants due to boundary layer effects that are insignificant in air, but very significant in water and can result in less fractionation depending upon rates of photosynthesis (Osmond et al., 1981; Hecky and Hesslein, 1995). Aquatic plants using dissolved bicarbonate (HCO_3^-) tend to be more enriched in ^{13}C than those using CO_2 because the two-step reaction in which bicarbonate is formed ($CO_2(aq) + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$) enriches bicarbonate relative to CO_2

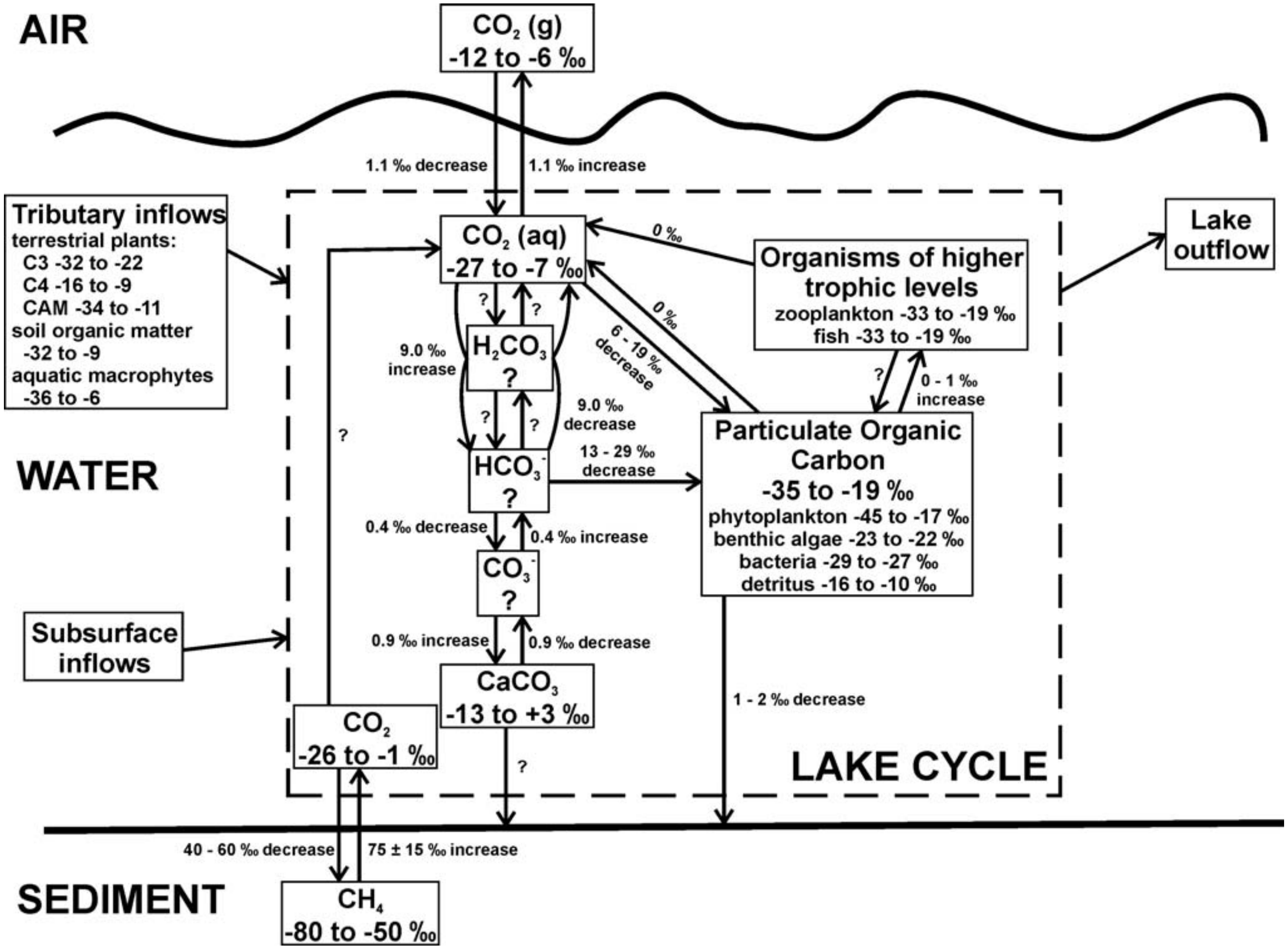


Figure 1.5: Diagram of the lake carbon cycle showing δ^{13}C values for the various forms of carbon and the change in δ^{13}C values associated with cycle processes. Fractionations for reactions occurring between CO_2(g) and $CaCO_3$ are for equilibrium conditions. (Drawn with reference to Deines, 1980; Osmond et al., 1981; Whiticar et al., 1986; Peterson and Fry, 1987; Fry and Sherr, 1989; Meyers and Eadie, 1993; Boschker et al., 1995; Hecky and Hesslein, 1995; Trumbore and Druffel, 1995; Clark and Fritz, 1997; Hoefs, 1997; Thorp et al., 1998; Embury, 2000; Grey et al., 2000; Kendall et al., 2001; Szabo, 2004).

(Krishnamurthy et al., 1986). The $\delta^{13}C$ signatures of aquatic animals are similar to or slightly enriched compared to their diets (Peterson and Fry, 1987).

Similar to carbon, the $\delta^{15}N$ signature of PN is controlled by the $\delta^{15}N$ values of nitrogen sources to the PN pool and fractionation that occurs in the lake nitrogen cycle (Figure 1.6). All plants preferentially assimilate the lighter nitrogen isotope in inorganic nitrogen compounds over the heavier one, producing terrestrial plants with lower $\delta^{15}N$ values than their sources of nitrogen (Kendall et al., 2001). The $\delta^{15}N$ of soil organic matter reflects that of the plants growing on the soil (Kendall et al., 2001).

The source of nitrogen for aquatic plants is mainly dissolved inorganic nitrogen in the form of ammonium (NH_4^+) and nitrate (NO_3^-; Talbot, 2001). Dissolved inorganic nitrogen is predominantly derived through the mineralization of organic matter (cellular-N → NH_4^+) and subsequent nitrification ($NH_4^+ \rightarrow NO_3^-$), but it also originates from agricultural fertilizer applications, livestock waste, and urban sewage (Kendall et al., 2001). With respect to nitrogen utilization, there are two major groups of primary producers: non-N-fixers that use the easily assimilated forms of nitrogen (NH_4^+, NO_3^-), and N-fixers that use dissolved atmospheric nitrogen (N_2(aq); Talbot, 2001). Most aquatic plants are non-N-fixers and the N-fixing group is largely composed of cyanobacteria (Talbot, 2001). N-fixers and non-N-fixers typically differ in their $\delta^{15}N$ values (Talbot, 2001). Little fractionation occurs, first, during the dissolution of atmospheric N_2 ($N_2(g) \rightarrow N_2(aq)$), and then, during nitrogen fixation ($N_2(aq)$ → cellular-N), producing N-fixers with $\delta^{15}N$ values close to that of atmospheric nitrogen (Talbot, 2001). By contrast, the assimilation of ammonium and nitrate by non-N-fixers can result in considerable isotopic fractionation (Talbot, 2001). The $\delta^{15}N$ value of aquatic plants is largely dependent upon three transformation processes affecting dissolved N_2 prior to fixation or ammonium and nitrate prior to assimilation: denitrification ($NO_3^- \rightarrow N_2(aq)$), ammonification (cellular-N → NH_4^+), and nitrification ($NH_4^+ \rightarrow NO_3^-$; Talbot, 2001).

The $\delta^{15}N$ signatures of aquatic animals are enriched compared to their diets (Peterson and Fry, 1987) due to catabolic pathways, which break down amino acids, that preferentially eliminate the lighter isotope (Létolle, 1980). For this reason, urinary nitrogen (NH_4^+) is depleted in ^{15}N (Peterson and Fry, 1987). The $\delta^{15}N$ signature of animal feces, however, is usually similar to that of the organism (Létolle, 1980).

Carbon and nitrogen stable isotopes have previously been used to determine the relative contributions of allochthonous and autochthonous sources of suspended particulate matter, and the sources of nutrients, in fluvial (Barth et al., 1998; Kendall et al., 2001) and lacustrine (Meyers and Eadie, 1993; Ostrom et al., 1998) environments. They have also been used to develop a better

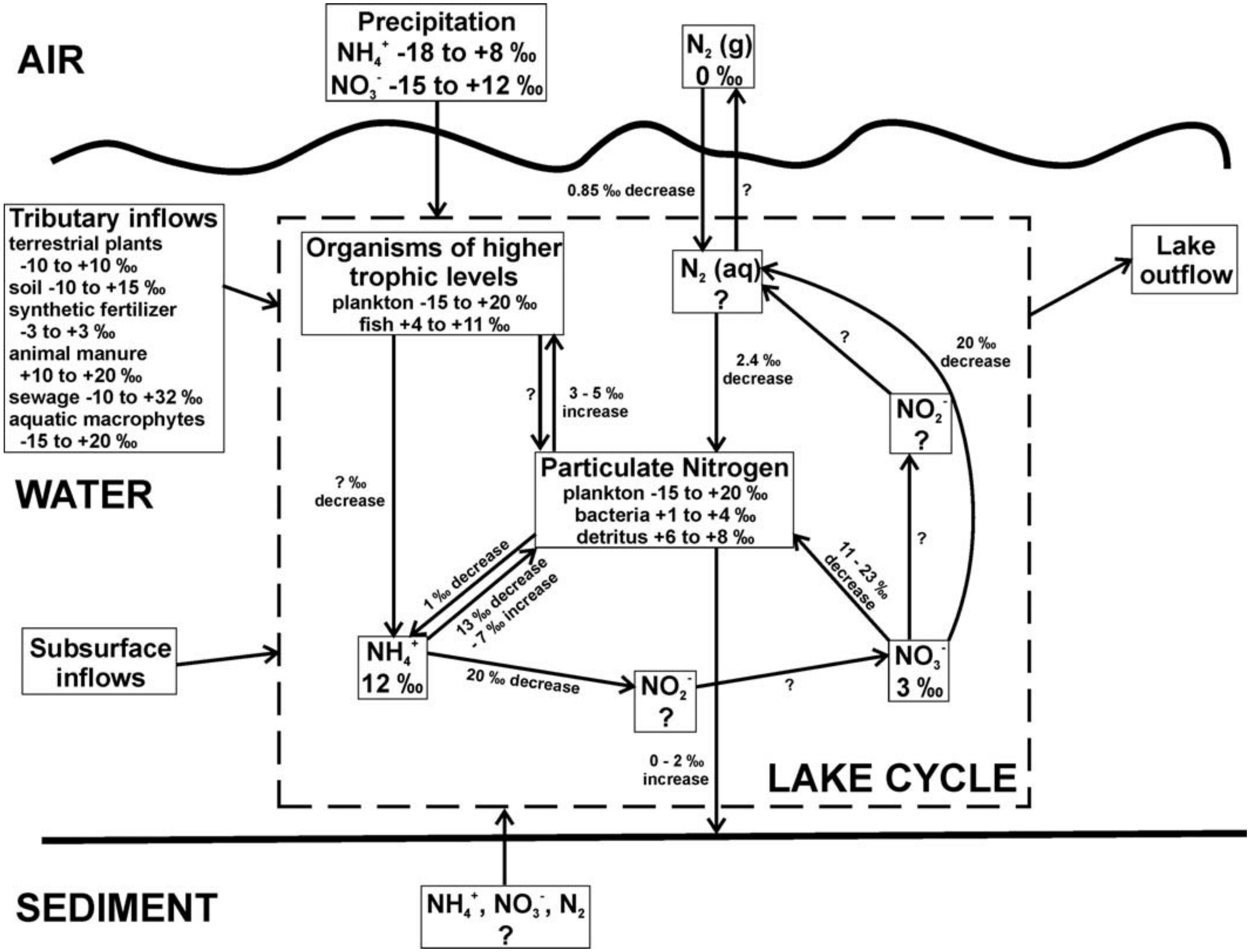


Figure 1.6: Diagram of the lake nitrogen cycle showing $\delta^{15}N$ values for the various forms of nitrogen and the change in $\delta^{15}N$ values associated with cycle processes. (Drawn with reference to Peterson and Fry, 1987; Hecky and Hesslein, 1995; Kendall, 1998; Ostrom et al., 1998; McCusker et al., 1999; Embury, 2000; Kendall et al., 2001; Talbot, 2001; Szabo, 2004.)

understanding of processes influencing suspended particulate matter in rivers (Kendall et al., 2001) and lakes (Hodell and Schelske, 1998; Leggett et al., 1999). In the present study, carbon and nitrogen stable isotopes are used to evaluate the relative contributions of allochthonous and autochthonous sources to suspended particulate matter in three tributary inflows, the outflow, and nearshore and offshore areas of Lake Erie. Furthermore, they are used to identify possible origins of suspended particulate matter at these locations.

1.4 Research Objectives

The objectives of this research are:

1. To characterize the chemical composition (POC and PN concentrations, POC/PN mass ratio, carbon and nitrogen stable isotopes) of suspended particulate matter in three tributary inflows, the outflow, and nearshore and offshore areas of the eastern basin of Lake Erie.

2. To determine the relative contributions of allochthonous and autochthonous sources to suspended particulate matter in three tributary inflows, the outflow, and nearshore and offshore areas of Lake Erie using the POC/PN mass ratio and carbon and nitrogen stable isotopes.

3. To identify possible sources of suspended particulate matter in three tributary inflows, the outflow, and nearshore and offshore areas of Lake Erie by comparing the POC/PN mass ratios and carbon and nitrogen stable isotopic signatures of suspended particulate matter at these sites to values from the literature for possible sources.

4. To determine how suspended particulate matter at the sampling locations in the eastern basin, which has high dreissenid mussel abundance, compares to that at sampling locations in the central and western basins.

To address the first and last objectives, the following null hypotheses (with numbers indicating the corresponding objectives) are tested using POC and PN concentration and carbon and nitrogen stable isotope data:

1. a) The chemical composition of suspended particulate matter entering Lake Erie through tributary inflows is not significantly different from that at nearshore sites in the eastern basin of the lake.

   b) The chemical composition of suspended particulate matter at eastern basin nearshore sites is not significantly different from that at eastern basin offshore sites.

   c) The chemical composition of suspended particulate matter at the lake outflow is not significantly different from that at eastern basin offshore sites.

4. The chemical composition of suspended particulate matter in the eastern basin of Lake Erie is not significantly different from that in the central and western basins.

1.5 Outline of Chapters

Chapter 2 contains a description of the study area. The experimental design, sampling locations, sampling and analytical methodology, supplementary data used in the research, and procedures for data analysis are also presented in this chapter.

In Chapter 3, the chemical composition of suspended particulate matter from the study sites is characterized using POC and PN concentrations and POC/PN mass ratios. The mass ratio data are also used to elucidate the relative contributions of allochthonous and autochthonous sources to suspended particulate matter, and to identify probable sources of this material, at these locations. Finally, the POC and PN concentrations and POC/PN mass ratios of suspended particulate matter in the eastern basin of Lake Erie are compared to those of suspended particulate matter in the central and western basins of the lake.

Carbon and nitrogen stable isotopes are used to characterize suspended particulate matter from the sampling locations in Chapter 4. The isotope data are also used to determine the relative contributions of allochthonous and autochthonous sources to suspended particulate matter, and to identify likely sources of this material, at these locations. Carbon and nitrogen stable isotopes of suspended particulate matter in the eastern basin of Lake Erie are then compared with those of suspended particulate matter in the central and western basins of the lake. Finally, the isotope data are synthesized with the POC and PN concentration and POC/PN mass ratio data from Chapter 3.

In Chapter 5, the main findings of the research are summarized and recommendations for future research are provided.

Chapter 2: Methodology

2.1 Experimental Design

The research is designed to evaluate the chemical composition of suspended particulate matter at a moderately large spatial scale in the eastern basin of Lake Erie, three tributary inflows, and the lake outflow, between May and October, 2002. The research compares sediment in fluvial and lacustrine environments to better understand particle composition and transport and their possible impact on nutrient dynamics in lakes. Several studies have evaluated chemical properties of particulate matter in tributaries to the Laurentian Great Lakes (e.g. Liaw and MacCrimmon, 1977; Mayer and Delos Reyes, 1996) and in Lake Erie (e.g. Mudroch, 1984; Williams et al., 1976). Little is known, however, about the chemical properties of particulate matter in both environments in relation to nutrient cycling. This research provides the first dataset combining the use of particulate organic carbon (POC) and particulate nitrogen (PN) concentrations, POC/PN mass ratios, and carbon and nitrogen stable isotopes to characterize suspended particulate matter in both fluvial and lacustrine environments of the Laurentian Great Lakes basin.

2.2 Lake Erie

Lake Erie is located in eastern North America and is bordered by Canada to the north and the United States of America (U.S.A.) to the south. It formed as a result of glacial activity about 12,600 years ago (Sly, 1976). The lake has a surface area of 25,300 km^2 and a volume of 470 km^3 (Sly, 1976). It is the southernmost and shallowest of the five Laurentian Great Lakes. Lake Erie receives the discharges from Lakes Superior, Michigan, and Huron through the Detroit River and drains into Lake Ontario through the Niagara River (Makarewicz and Bertram, 1991).

Lake Erie is divided into three basins (western, central, and eastern) that are separated by subaqueous moraines (Thomas et al., 1976). The western basin is the shallowest, with a maximum depth of eleven metres, while the central basin covers the largest surface area and has a maximum depth of twenty-five metres (Sly, 1976). The eastern basin is considerably deeper than the other two basins, with a maximum depth of sixty-four metres (Sly, 1976). The central and eastern basins thermally stratify each summer, while the western basin normally does not (Hartman, 1972).

Lake Erie has a catchment area of approximately 53,095 km^2 (Yaksich et al., 1985). Aside from the Detroit River, inflows from the Maumee River dominate the western basin, with smaller contributions from the Huron, Raisin, Portage, and Sandusky Rivers (Sly, 1976). The largest tributaries flowing into Lake Erie along the south shore of the central and eastern basins are the Cuyahoga River, the Grand River (Ohio), and Cattaraugus Creek (Sly, 1976). Along the north shore of the central and eastern basins, the Grand River (Ontario) is the only large tributary entering Lake Erie.

In the watershed surrounding Lake Erie, agricultural practice is intensive (Sly, 1976). Along the south shoreline, there are four large urban centres (Buffalo, Erie, Cleveland, and Toledo) with related industrial activity (Sly, 1976). By contrast, there are no large urban centres and less industrial activity along the north shoreline (Sly, 1976).

Lake Erie represents an important resource to the people living around the lake, as surrounding communities use the lake as a water source and for recreation. Lake Erie is also significant internationally, with respect to shipping and the lake's commercial fishery.

2.3 Sampling Locations

The locations of sampling sites in the eastern basin of Lake Erie, three tributary inflows, and the lake outflow are shown in Figure 2.1. The UTM coordinates of the sites and the maximum site depths (i.e. depth of the water column from the air-water interface to the sediment-water interface) are listed in Table 2.1. The Grand River, Sandusk Creek, and Nanticoke Creek were sampled as representative Canadian tributary inflows to the eastern basin. The Niagara River was sampled as the lake outflow at the Environment Canada site in Fort Erie. A series of six nearshore and five offshore sites, with maximum depths ranging between two and sixty-two metres, were sampled throughout the eastern basin. The twenty-metre contour line was used as the boundary between the nearshore and offshore areas as this is the approximate depth of the summer thermocline. Five of the eastern basin sites form a transect off Peacock Point, which is located between Sandusk and Nanticoke Creeks, along the north shore of the eastern basin. Three of the sites form a transect leading to the lake outflow. The remaining three eastern basin sites are located in the deepest area of the basin, near its boundary with the central basin. Samples were also collected from three sites in the central basin and two sites in the western basin to compare suspended particulate matter from those basins with that of the eastern basin (Figure 2.2, Table 2.1).

2.4 Sample Collection

Suspended particulate matter in the tributary inflows and the lake outflow was sampled bimonthly between May and October 2002 under baseflow conditions. The lake sites were sampled two to five times between June and October 2002. Table 2.2 provides greater detail concerning the depth, frequency, and timing of sample collection at each site. Wherever possible, samples were collected in triplicate, but the intended replicates are, in fact, almost entirely pseudo-replicates. The methodology

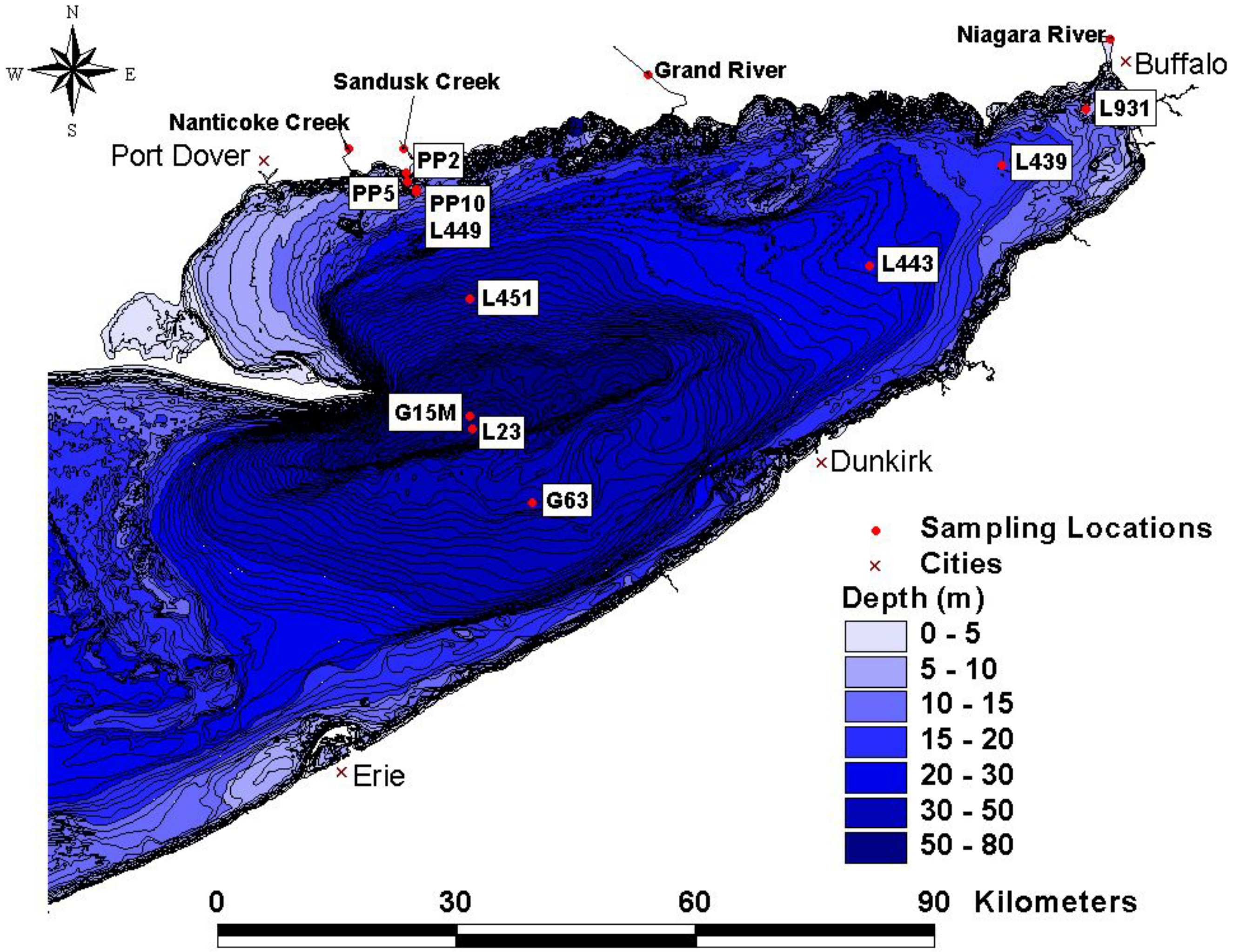


Figure 2.1: Bathymetric map of the eastern basin of Lake Erie with sampling locations indicated.

Table 2.1: Sampling location coordinates and maximum depth.

Site Grouping	Site	UTM Coordinates		Maximum Depth (m)
		Easting	Northing	
Tributary Inflows	Grand River	613520	4750500	N/A
	Sandusk Creek	582750	4741250	N/A
	Nanticoke Creek	575750	4741250	N/A
Lake Outflow	Outflow	671250	4755000	N/A
Eastern Basin Nearshore Peacock Point	PP2	583043	4738134	2
	PP5	583098	4737133	5
	PP10	584316	4736104	10
	L449	584290	4735728	11
Eastern Basin Nearshore Near Outflow	L931	668206	4746182	10
	L439	657649	4739080	19
Eastern Basin Offshore	L451	590966	4722329	41
	G15M	591044	4707742	62
	L23	591339	4706077	61
	G63	598805	4696909	44
	L443	641120	4726511	23
Central Basin Nearshore	GAsh	508617	4636575	5
Central Basin Offshore	G78M	479360	4662712	21
	G43	421343	4626888	20
Western Basin Nearshore	GSan	379055	4601386	11
	G91M	340906	4633824	8

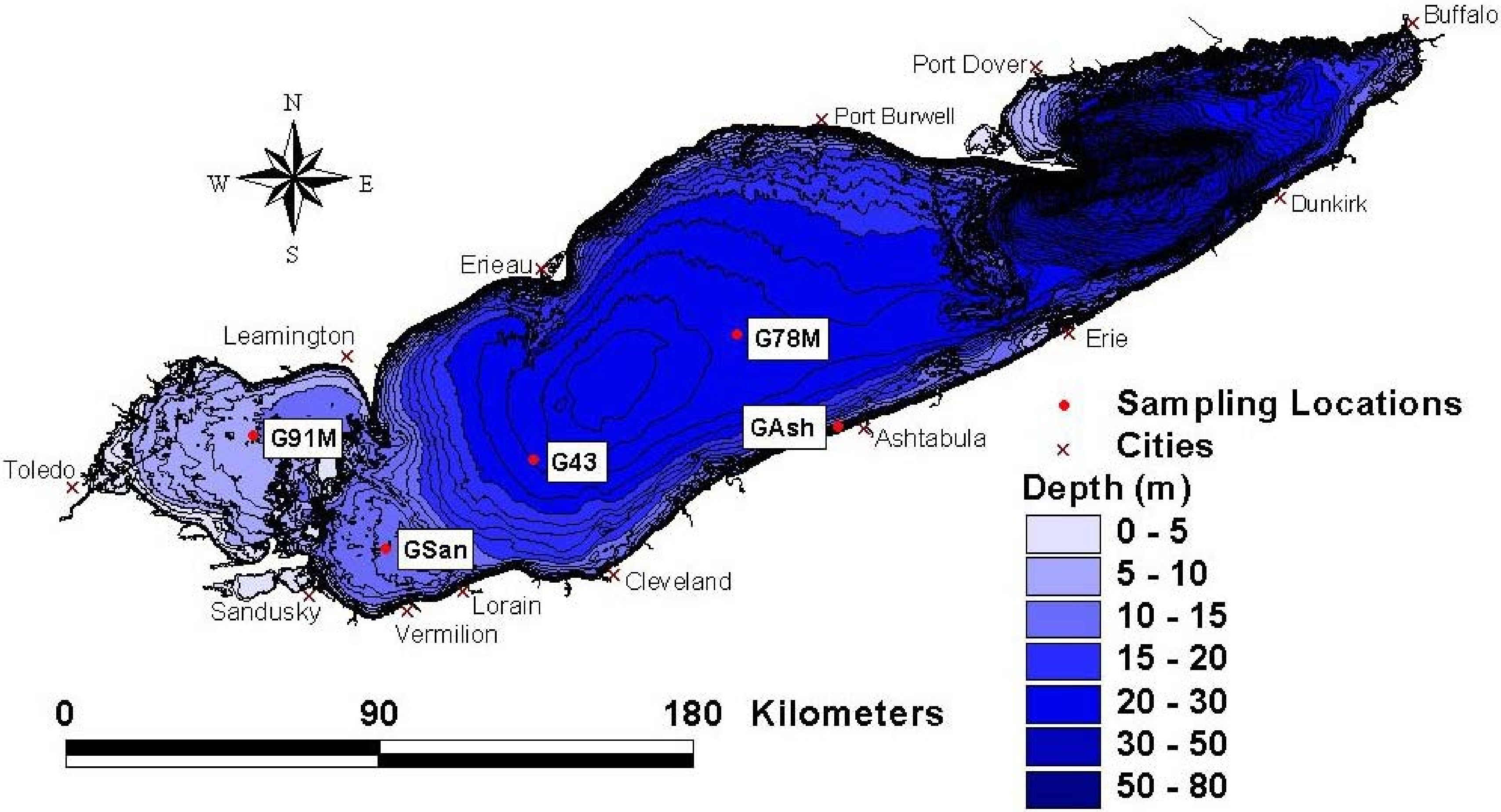


Figure 2.2: Bathymetric map of Lake Erie showing sites sampled in the central and western basins.

Table 2.2: Sampling depths, frequency, and duration for all sampling locations between May and October 2002.

Site Grouping	Site*	Depths Sampled (m)**	Sampling Frequency and Duration***					
			May	Jun	Jul	Aug	Sep	Oct
Tributary Inflows	Grand River	S	1	2	2	2	2	2
	Sandusk Creek	S	1	2	2	2	2	2
	Nanticoke Creek	S	1	2	2	2	2	2
Lake Outflow	Outflow	1.8	1	2	2	2	2	2
Eastern Basin Nearshore Peacock Point	PP2	0.5, 1			1	1		1
	PP5	2, 4			2			1
	PP10	4, 9			2			1
	L449	10		1	1		1	1
Eastern Basin Nearshore Near Outflow	L931	8			1		1	
	L439	17		1	1		1	1
Eastern Basin Offshore	L451	14, 24, 37		1	1		1	
	G15M	5-8.5, 59-60			1	1	1	
	L23	20, 40, 50, 60		1	1		1	1
	G63	5-10, 40-42			1	1	1	
	L443	15, 21		1	1		1	1
Central Basin Nearshore	GAsh	2.3-3			1	1	1	
Central Basin Offshore	G78M	5-10, 18-20			1	1	1	
	G43	7-10, 17-20			1	1	1	
Western Basin Nearshore	GSan	5.5-6			1	1	1	
	G91M	3.5-5			1	1	1	

* The L series of sites was sampled for stable isotopes, but not for POC and PN concentrations.
** S indicates that sediment was sampled from the water surface (at the air-water interface). The PP series of sites was sampled at two depths for POC and PN concentrations and at only the shallower depth for stable isotopes.
*** The number indicates the number of times that a given site was sampled during a particular month. The lake outflow was sampled in May for stable isotopes, but not for POC and PN concentrations.

for collecting suspended particulate matter varied across different groupings of sites and is described in Table 2.3.

While most of the particulate matter samples provide an instantaneous measure of chemical and physical parameters, at six sites in the eastern basin (the L series of sites), the suspended material was collected for carbon and nitrogen stable isotopes over a longer period of time (exposure time of 19 – 158 days) using sedimentation traps. In a review of the sedimentation trap technique, Bloesch and Burns (1980) argue that the exposure time of traps should be made as short as possible and should not exceed three weeks because particulate matter that sits in traps is subject to increased organic matter decomposition through bacterial mineralization. They also state that the results of analyses on organic matter collected using sedimentation traps are questionable if obtained from traps exposed for one month or longer. Carbon and nitrogen stable isotopic fractionations, however, are generally small during diagenetic processes acting on particulate organic matter (Boschker et al., 1995; Talbot, 2001). Consequently, within the context of this study, it may be reasonable to compare the carbon and nitrogen stable isotope signatures of material from samples collected using sedimentation traps with that from instantaneous samples.

Table 2.3: Methodology for collecting suspended particulate matter samples from various groupings of sites.

Site Grouping	Sampling Methodology
Tributary Inflows	- surface grab sample of water collected from bridges using bucket at centroid of flow, assuming uniform mixing
Lake Outflow	- water collected by pumping through permanent intake line from 1.8-m depth at centroid of flow, assuming uniform mixing
Eastern Basin	- at 3 sites (PP series), water collected from 2 depths using Van Dorn sampler - at 6 sites (L series), suspended solids collected using sedimentation traps deployed at various depths - at 2 sites (G series), water collected from 2 depths (epilimnion and hypolimnion) using Rosette sampler
Central and Western Basins	- water collected from 2 depths (epilimnion and hypolimnion) in stratified water columns and from 1 depth in mixed columns using Rosette sampler

2.5 Sample Preparation and Analysis

Suspended particulate matter was analyzed for POC and PN concentrations and for carbon and nitrogen stable isotopes. All replicates sampled were analyzed for POC and PN concentrations. The isotope laboratory was overwhelmed with samples and frequently experienced analyzer malfunction, causing lengthy delays in analysis. As a result, at least one set of isotope samples from each site was analyzed in triplicate, while the remaining samples were analyzed in duplicate. Table 2.4 outlines the sample preparation procedures for the analyses.

Particulate matter collected in sedimentation traps was initially stored in a refrigerator as a sediment-water mixture in 20-mL glass scintillation vials. In order to put this material on filters for the isotope analysis, the scintillation vial was agitated to create a homogeneous sample and a subsample (between 0.25 and 15 mL, depending upon the concentration of the sample) was extracted using a pipette. This subsample was resuspended in approximately 250 mL of deionized water, then filtered and stored according to the method described in Table 2.4.

In the present research, POC and PN are operationally defined as the carbon and nitrogen, respectively, retained on a GF/F filter (0.7-µm pore size) after acidification using 10 % hydrochloric acid (HCl). The POC and PN concentration analysis was performed in the Department of Biology at

Table 2.4: Sample preparation for the two analyses.

Analysis	Preparation
POC and PN Concentrations	1. Water sample filtered at 50-kPa pressure through pre-combusted (500°C for 4h) GF/F filter of 0.7-μm pore size until material visible on filter. 2. Filter stored in Petri dish in freezer. 3. Filter acidified to remove inorganic carbon in form of carbonate. Acidification performed on filter tower, using sufficient volume of 10% HCl solution to cover filter surface before filtering solution through. Similar volume of deionized water added, then filtered through. 4. Filter dried in open Petri dish in 50°C oven. 5. Filter stored in Petri dish in sealed plastic bag at room temperature. 6. Filter cut in half and packed into two nickel capsules using press. 7. Capsules stored in plastic tray in desiccator at room temperature until analysis.
Carbon and Nitrogen Stable Isotopes	1. Water sample filtered at 50-kPa pressure through pre-combusted (500°C for 6h) quartz fibre filter of 0.8-μm pore size until filter clogged. 2. Filter stored in Petri dish in freezer. 3. Filter acidified to remove inorganic carbon in form of carbonate. Acidification performed on filter tower, using sufficient volume of 10% HCl solution to cover filter surface before filtering solution through. Similar volume of deionized water added, then filtered through. 4. Filter dried in open Petri dish in 50°C oven. 5. Filter stored in Petri dish in sealed plastic bag at room temperature. 6. Depending upon amount of material on filter, quarter, half, or whole filter packed into tin capsule using press. 7. Capsule stored in plastic tray at room temperature until analysis.

the University of Waterloo, using a CHN/O/S Elemental Analyzer Model CE 440 with a PC Compatible/CE-490 Interface Unit, following the method described in Ehrhardt (1983). The carbon and nitrogen results are corrected to an acetanilide standard and for the instrument response to a blank filter (i.e. a pre-combusted filter without sample). The following equations were used to calculate the concentrations of POC and PN, respectively:

$$[\mathrm{POC}] = \frac{\dfrac{\mathrm{C_{read}} - \mathrm{C_{blank}}}{\mathrm{K_C}}}{\mathrm{V}} \times 1000\ \mathrm{mL/L} \qquad (2.1)$$

where [POC] = POC concentration (μg/L), C_{read} = instrument sample response for carbon (mV), C_{blank} = instrument blank response for carbon (mV), K_C = calibration factor for carbon (mV/μg), and V = sample volume (mL).

$$[\mathrm{PN}] = \frac{\dfrac{\mathrm{N_{read}} - \mathrm{N_{blank}}}{\mathrm{K_N}}}{\mathrm{V}} \times 1000\ \mathrm{mL/L} \qquad (2.2)$$

where [PN] = PN concentration (μg/L), N_{read} = instrument sample response for nitrogen (mV), N_{blank} = instrument blank response for nitrogen (mV), K_N = calibration factor for nitrogen (mV/μg), and V = sample volume (mL). The calibration factors are calculated using the equation:

$$K = \frac{RN - ZN - BN}{M \times N_a \times \frac{AW}{MW}} \tag{2.3}$$

where RN = average instrument response to standard (mV), ZN = instrument zero response (mV), BN = instrument blank response (mV), M = mass of standard material (μg), N_a = number of atoms of carbon or nitrogen in a molecule of standard material, AW = atomic weight of carbon (12.01) or nitrogen (14.01), and MW = molecular weight of standard material (135.2 for acetanilide). The analytical error range for both elements is ±0.3 %. The POC/PN mass ratio was calculated by dividing the POC concentration in μg/L by the PN concentration in μg/L.

The carbon and nitrogen stable isotope analysis was performed by the Environmental Isotope Laboratory at the University of Waterloo, using an Isochrom Continuous-flow Stable Isotope Mass Spectrometer (Micromass) coupled to a Carlo Erba Elemental Analyzer (CHNS-O EA 1108), according to the method outlined in Barrie and Lemley (1989). The carbon results are corrected to three standards: IAEA-CH6 (sugar), EIL-72 (cellulose), and EIL-32 (graphite). The nitrogen results are corrected to IAEA-N1 and IAEA-N2 (both ammonium sulphate). The normal error range for carbon is ±0.2 ‰ and for nitrogen is ±0.3 ‰.

2.6 Supplementary Data

It was not possible to obtain the absolute POC and PN concentration values for the samples collected using sedimentation traps from the L series of sites because the total sediment mass was not measured. The POC and PN concentration data for the L series of sites belong to, and are used with permission from, Stephanie Guildford (Department of Biology, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada). These data are derived from samples that were collected and processed similarly to the samples of the current study, except that water sampling was depth-integrated (rather than from a discrete depth) for some of the samples.

2.7 Data Analysis

Significant differences in the POC and PN concentrations and the carbon and nitrogen isotopic signatures between sites were determined through analysis of variance (ANOVA) tests. These tests were performed using the program SPSS, version 13.0.

Chapter 3: Particulate Organic Carbon and Particulate Nitrogen

Results of the particulate organic carbon (POC) and particulate nitrogen (PN) analyses on suspended matter samples from Lake Erie, three tributary inflows, and the lake outflow are presented and discussed in this chapter. The first section focuses on POC and PN concentration data and the second section explores POC/PN mass ratio data. Each section begins with a brief discussion of the descriptive statistics for each sampling location. In both sections, POC and PN data for the tributary inflows, lake outflow, and eastern basin of Lake Erie are compared, followed by a within-lake comparison of the eastern, central, and western basins of Lake Erie. The chapter ends with a section in which the important findings regarding the concentration and ratio data are synthesized and summarized.

3.1 POC and PN Concentrations

Mean, standard deviation, minimum, and maximum values of POC and PN concentrations for each sampling location are presented in Table 3.1. All concentration data are listed in Table A.1 of the Appendix.

All sites were sampled on at least three different dates, during at least two different months, between May and October 2002, and all sites show some temporal variability in POC and PN concentrations. Examination of the data, however, indicates that the mean POC and PN concentrations for individual sampling locations are not biased by using samples collected at different times in the calculation of the mean concentrations. The POC and PN concentrations at the three tributary inflows show similar temporal trends with a few exceptions (Figure 3.1). The ranges of POC and PN concentrations over time at the Grand River (e.g. POC: 1181 – 4285 µg/L) are lower than those at Sandusk (e.g. POC: 1773 – 9202 µg/L) and Nanticoke (e.g. POC: 1226 – 7268 µg/L) Creeks. Also, temporal trends in POC and PN concentrations are relatively delayed at Nanticoke Creek, (e.g. concentrations increase considerably in June 2002 at the Grand River and Sandusk Creek, but not until July 2002 at Nanticoke Creek). The lake outflow POC and PN concentrations have low-magnitude fluctuations, but relatively low variability over the season compared with the concentrations at the inflow sites (Figure 3.1). Within Lake Erie, sites consistently sampled on similar dates (those belonging to the same series of sites; i.e. PP, L, or G) show comparable temporal variation (Figures 3.2, 3.3). There is greater variation in temporal trends over depth at individual offshore sites, with the highest POC and PN concentrations occurring in the epilimnion, than across different sites. Therefore, only the POC and PN concentrations from the shallowest depth sampled at offshore sites were used to calculate the mean concentrations for those sites and in analysis of variance (ANOVA) tests.

Table 3.1: Mean, standard deviation (SD), minimum (Min), and maximum (Max) POC and PN concentration values for all sampling locations. The number of samples analyzed (n) is also indicated. The maximum site depths are given in brackets after the lake site names.

Site Grouping	Site	POC (µg/L)					PN (µg/L)				
		Mean	**SD**	**Min**	**Max**	**n**	**Mean**	**SD**	**Min**	**Max**	**n**
Inflows	Grand River	2672	1123	1181	4285	11	491	208	157	731	11
	Sandusk Creek	4494	2332	1773	9202	11	812	365	305	1448	11
	Nanticoke Creek	3211	2060	1226	7268	11	602	410	187	1408	11
Outflow	Outflow	175	32	135	237	10	33	7	24	49	10
Eastern Basin Nearshore Peacock Point	PP2 (2 m)	306	69	234	403	6	65	13	52	84	6
	PP5 (5 m)	318	80	232	436	6	71	20	52	103	6
	PP10 (10 m)	272	74	144	340	6	49	9	32	58	6
	L449* (11 m)	232	61	192	321	4	36	11	28	49	3
Eastern Basin Nearshore Near Outflow	L931 (10 m)	252	116	151	358	4	41	12	24	51	4
	L439 (19 m)	257	96	143	352	4	42	13	23	51	4
Eastern Basin Offshore	L451 (41 m)	304	119	198	451	4	49	21	28	75	4
	G15M (62 m)	228	69	151	281	3	39	11	28	49	3
	L23 (61 m)	319	115	186	476	5	51	18	32	78	5
	G63 (44 m)	250	46	197	277	3	43	8	33	48	3
	L443 (23 m)	280	67	189	332	4	45	14	30	63	4
Central Basin Nearshore	GAsh (5 m)	227	53	168	270	3	39	11	28	49	3
Central Basin Offshore	G78M (21 m)	277	67	202	333	3	49	15	32	59	3
	G43 (20 m)	346	84	250	406	3	63	14	49	76	3
Western Basin Nearshore	GSan (11 m)	395	179	196	543	3	79	41	36	117	3
	G91M (8 m)	618	102	545	734	3	123	24	97	145	3

* The sample for site L449 from 30/10/02 had an anomalously low PN concentration (8 µg/L) that was not used in the calculation of the mean PN concentration for this site.

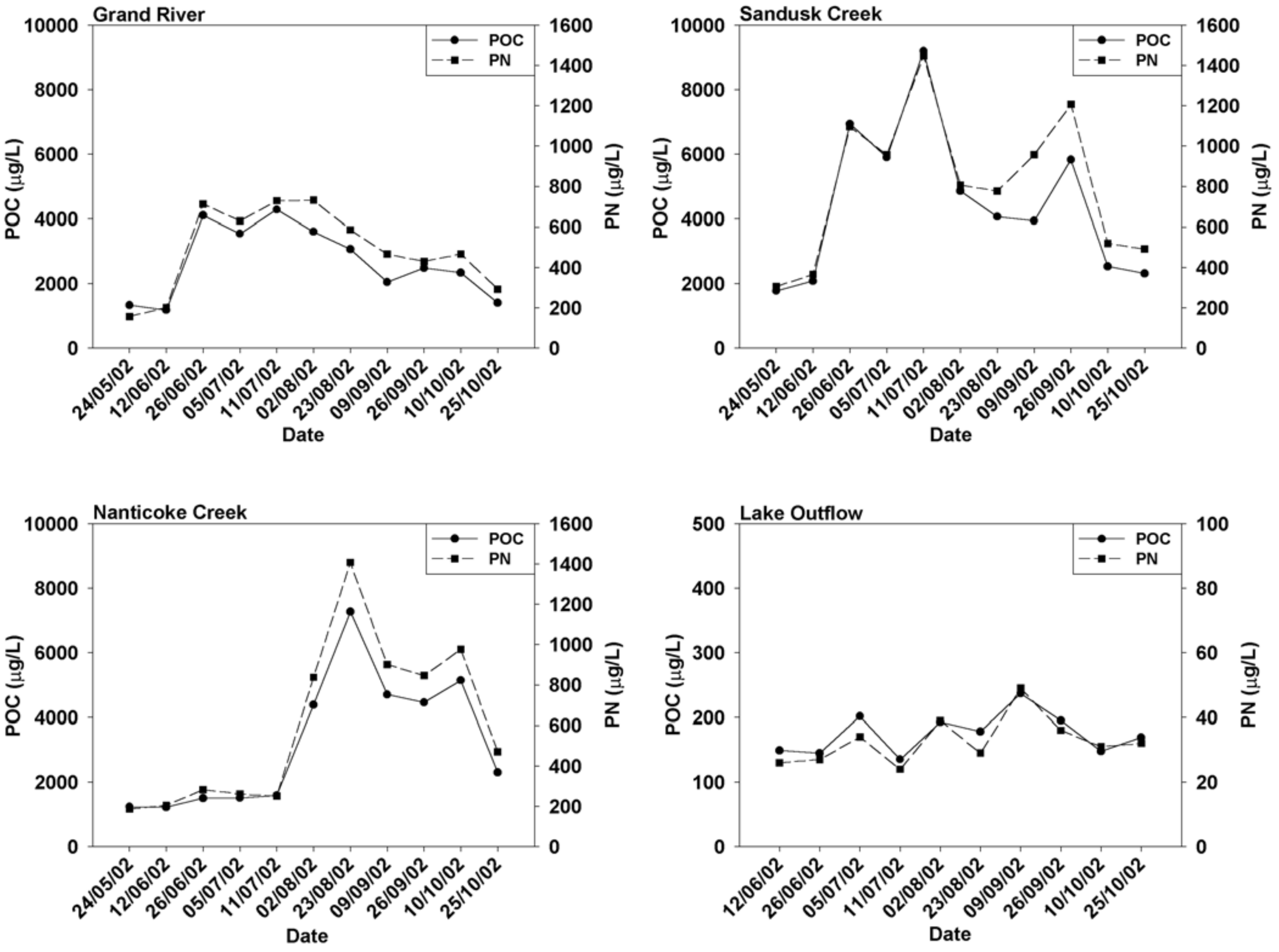


Figure 3.1: Temporal variation in POC and PN concentrations for the three tributary inflows and the lake outflow. Note the change in scales for the lake outflow graph.

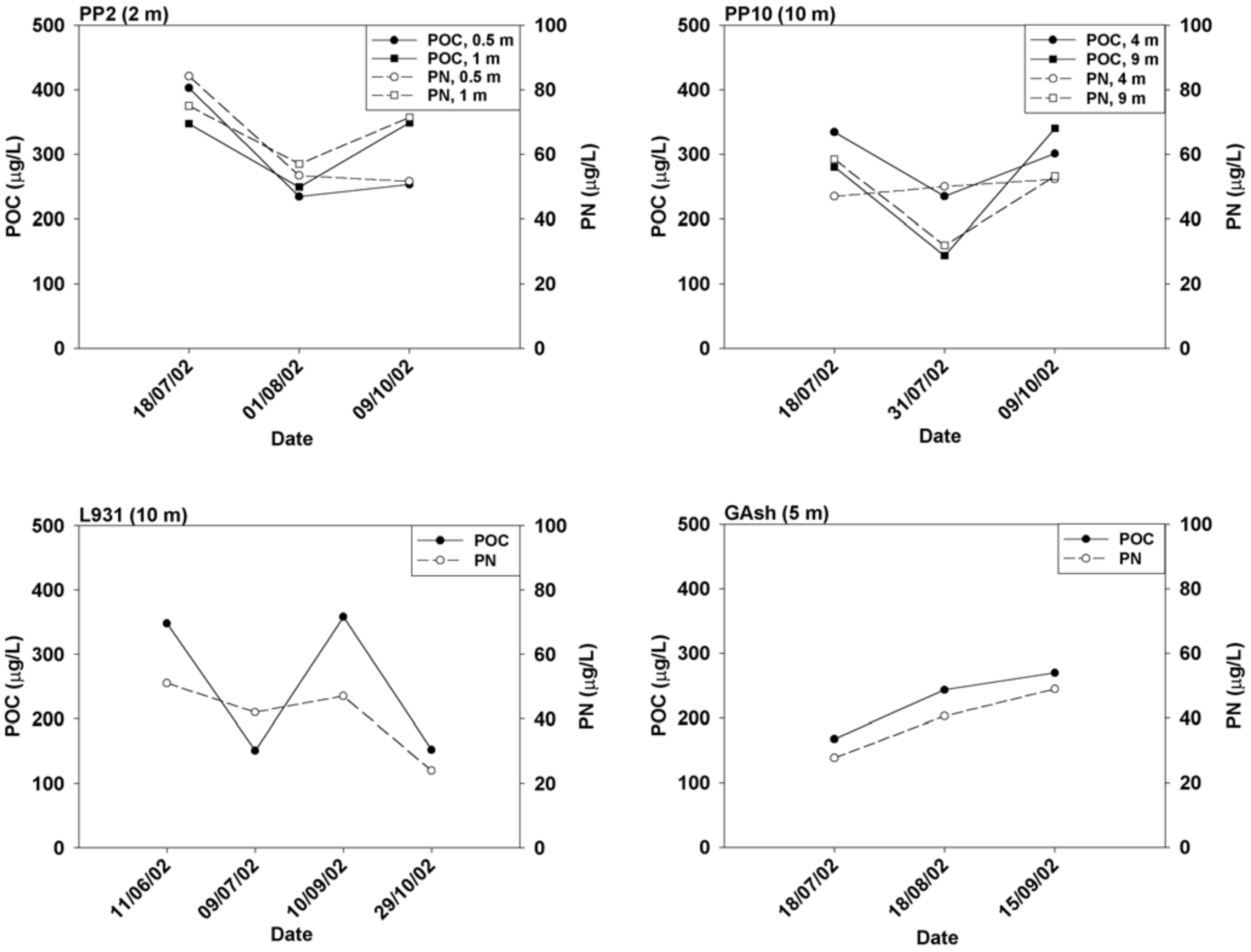


Figure 3.2: Temporal variation in POC and PN concentrations for four nearshore sites in Lake Erie. The maximum site depths are given after the site names.

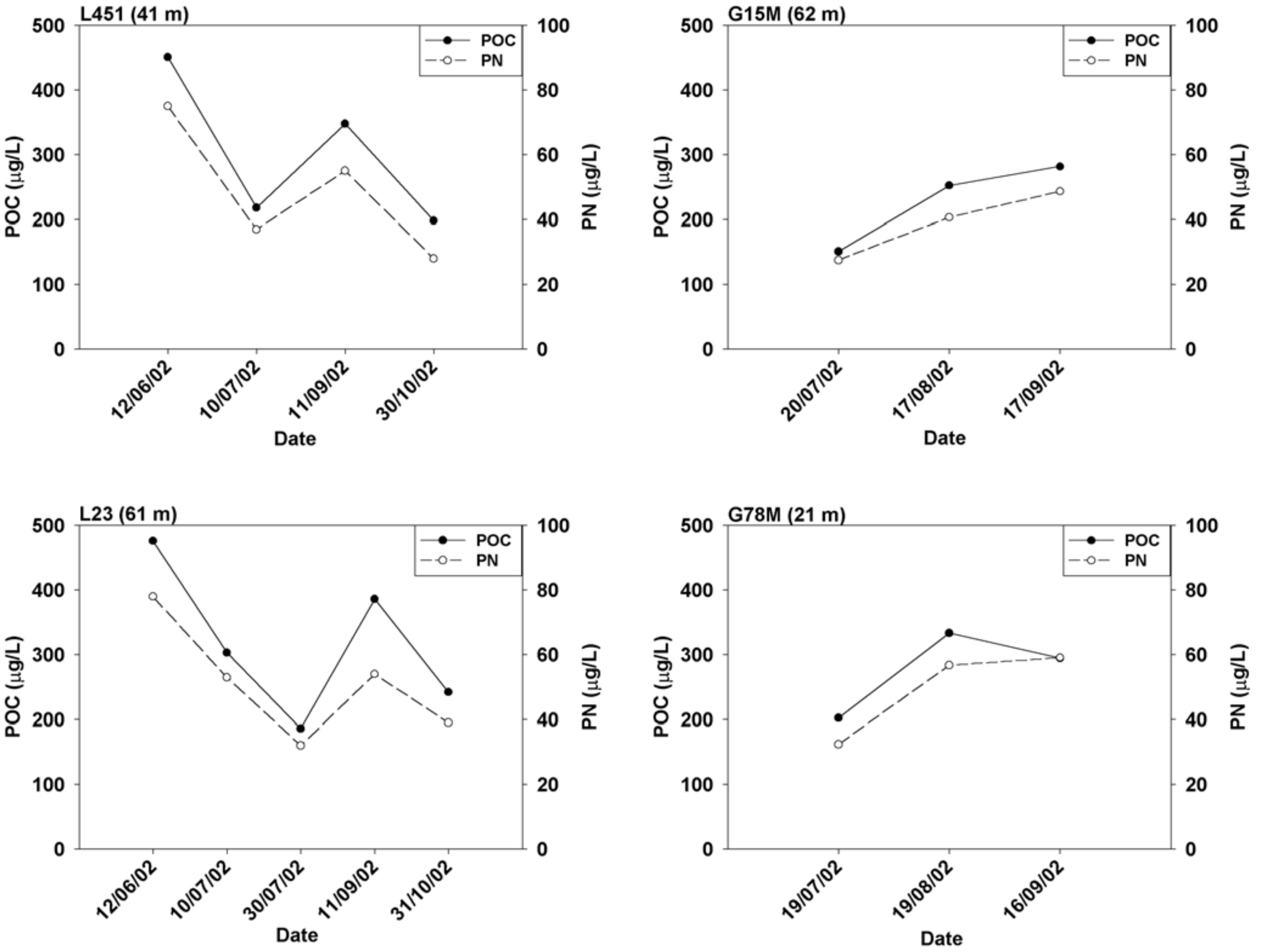


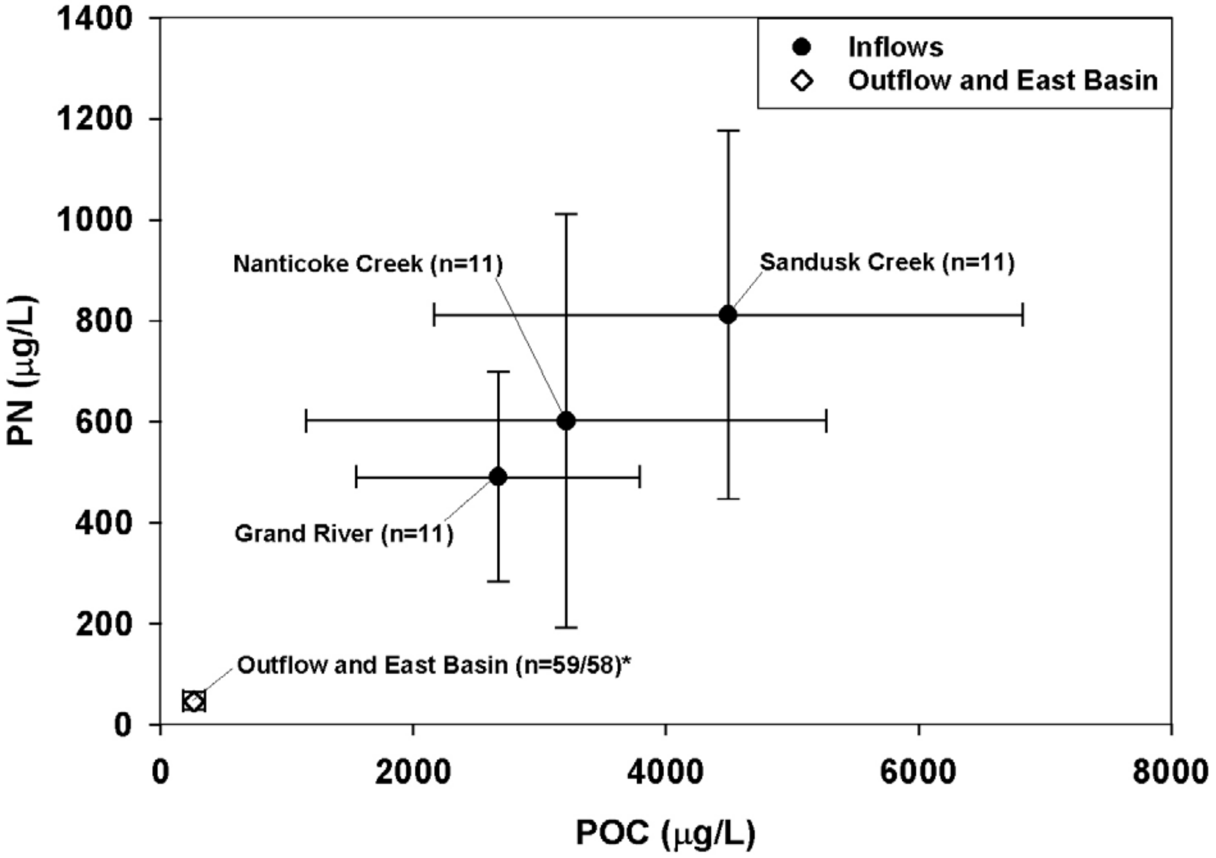
Figure 3.3: Temporal variation in POC and PN concentrations for four offshore sites in Lake Erie. The maximum site depths are given after the site names.

An anomalous PN concentration (8 μg/L) was measured for site L449 on 30/10/02 and is 4.5 times lower than the mean of the other observations at that site (36 μg/L). The anomalous value is considered an outlier and was not included in the calculation of the mean PN concentration for site L449 or in statistical tests.

3.1.1 Tributary Inflows, Lake Outflow, and Eastern Basin of Lake Erie

The POC and PN concentrations of the tributary inflows are approximately thirteen times higher than those of the lake outflow and all eastern basin sites (Figure 3.4) and these differences are statistically significant (ANOVA, $F_{POC} = 10.41$, $F_{PN} = 10.91$, $\alpha = 0.05$; Tables 3.2, 3.3). Although the lake outflow sampling location is located in the Niagara River, the POC and PN concentrations at this site show more similarity to the lake concentrations than to the concentrations found at the tributary inflows in this study. The similarity in POC and PN concentrations at the outflow and lake sampling locations may be due to similarities in the sources of particulate matter at these sites. Particulate matter in the tributary inflows is largely derived from a mixture of agricultural, municipal, and industrial sources. Barth et al. (1998) determined that POC in the main channel of the St. Lawrence River is largely derived from Great Lakes *in situ* photosynthetic production. Therefore, particulate matter in the eastern basin and lake outflow of the present study may partly result from *in situ* photosynthetic production in Lake Erie.

Several researchers have evaluated POC concentrations in rivers and lakes (e.g. Meybeck, 1982; Hessen et al., 2003), but fewer studies have reported POC concentrations for suspended particulate matter of rivers and lakes in the Laurentian Great Lakes basin. It is apparent from previously published data for the Laurentian Great Lakes basin that rivers typically have higher POC concentrations than lakes (Table 3.4). The mean POC concentration of the Grand River (Liaw and MacCrimmon, 1977) is approximately two to eighteen times higher than the mean POC concentrations of the Great Lakes (Table 3.4). The middle of this range is comparable to the difference in mean POC concentrations observed between tributary inflows and the eastern basin of Lake Erie in 2002. The mean POC concentration of the Nith River (Stone and Droppo, 1994) is up to six times higher than the mean POC concentrations for the Great Lakes (Table 3.4), with the exception of the eutrophic Inner Saginaw Bay, Lake Huron (Johengen et al., 1995), which has a higher mean POC concentration than the Nith River. The difference in mean POC concentrations between the Nith River (Stone and Droppo, 1994) and the Great Lakes (Table 3.4) is not as marked as the 13-fold difference between the tributary inflows and Lake Erie in the present study. This may relate to differences in the type of soil in the watersheds surrounding these rivers. According to Droppo and Stone (1994), both sandy loam and



* n=59 for POC and n=58 for PN

Figure 3.4: Mean POC and PN concentrations for three tributary inflows and for the lake outflow and eastern basin sites. Error bars indicate standard deviation.

Table 3.2: Results of a univariate ANOVA comparing the mean POC concentrations of different sites using all sampling locations ($F = 10.41$, $\alpha = 0.05$). The symbol ✱ indicates that there is a significant difference in the concentration between sites.

Site	GR	SC	NC	Out	PP2	PP5	PP10	L449	L931	L439	L451	G15M	L23	G63	L443	GAsh	G78M	G43	GSan	G91M
GR		✱		✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱
SC	✱		✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱
NC		✱		✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱
Out	✱	✱	✱																	
PP2	✱	✱	✱																	
PP5	✱	✱	✱																	
PP10	✱	✱	✱																	
L449	✱	✱	✱																	
L931	✱	✱	✱																	
L439	✱	✱	✱																	
L451	✱	✱	✱																	
G15M	✱	✱	✱																	
L23	✱	✱	✱																	
G63	✱	✱	✱																	
L443	✱	✱	✱																	
GAsh	✱	✱	✱																	
G78M	✱	✱	✱																	
G43	✱	✱	✱																	
GSan	✱	✱	✱																	
G91M	✱	✱	✱																	

Table 3.3: Results of a univariate ANOVA comparing the mean PN concentrations of different sites using all sampling locations (F = 10.91, α = 0.05). The symbol ❋ indicates that there is a significant difference in the concentration between sites.

Site	GR	SC	NC	Out	PP2	PP5	PP10	L449	L931	L439	L451	G15M	L23	G63	L443	GAsh	G78M	G43	GSan	G91M
GR		❋		❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋
SC	❋		❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋
NC		❋		❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋
Out	❋	❋	❋																	
PP2	❋	❋	❋																	
PP5	❋	❋	❋																	
PP10	❋	❋	❋																	
L449	❋	❋	❋																	
L931	❋	❋	❋																	
L439	❋	❋	❋																	
L451	❋	❋	❋																	
G15M	❋	❋	❋																	
L23	❋	❋	❋																	
G63	❋	❋	❋																	
L443	❋	❋	❋																	
GAsh	❋	❋	❋																	
G78M	❋	❋	❋																	
G43	❋	❋	❋																	
GSan	❋	❋	❋																	
G91M	❋	❋	❋																	

Table 3.4: POC concentration data from previously published research for rivers and lakes in the Laurentian Great Lakes basin. Mean, standard deviation (SD), minimum (Min), and maximum (Max) values are provided, as well as the number of samples used in calculating these values.

System	Reference	Location	Date	POC (µg/L)					Notes
				Mean	SD	Min	Max	n	
River	Liaw and MacCrimmon, 1977	Grand River, Ontario	May – November 1970 & 1971	2280	—	970	3320	—	—
	Stone and Droppo, 1994	Nith River, Ontario	July 1993	783	48	728	834	5	- calculated from values at 5 points over cross-section
Lake	Bloesch, 1982	Eastern Basin, Lake Erie (1 nearshore, 2 offshore sites)	June – October 1978	500	200	200	1000	34	- calculated from sample values depicted in graph
	Charlton and Rao, 1983	Eastern Basin, Lake Erie (5 offshore sites)	May – September 1979	260	80	210	320	2	- calculated from time-weighted averages for epilimnion and hypolimnion
		Central Basin, Lake Erie (10 offshore sites)	May – September 1979	360	10	350	360	2	
	Johengen et al., 1994	Lake Ontario (1 offshore site)	Summer 1981 – 1992	429	108	310	630	12	- calculated from summer means
	Johengen et al., 1995	Inner Saginaw Bay, Lake Huron (18 sites)	April – October 1991 – 1993	1335	163	1220	1450	3	- calculated from annual means
		Outer Saginaw Bay, Lake Huron (8 sites)	April – October 1991 – 1993	440	71	390	490	3	
	Halfon, 1984	Lake Superior (15 nearshore, 12 offshore sites)	May – October 1973	130	30	91	157	5	- calculated from monthly means
	Hecky et al., 1993	Lake Superior	ice-free season 1990	193	—	—	—	6	—

clay soils are present in the Nith River watershed, while the Sandusk and Nanticoke Creek watersheds are dominated by clay soils and the Grand River watershed in the area of sampling is dominated by clay soils, with sandy soils further upstream (Presant and Acton, 1984). The sandy soils in the Nith River watershed could lead to lower POC concentrations in this river relative to the tributary inflows of the current research.

Very few researchers have published PN concentration data for suspended matter in the Great Lakes (e.g. Bloesch et al., 1982; Hecky et al., 1993). No previously published PN concentrations were found in the literature for rivers of the Laurentian Great Lakes basin. The data are therefore insufficient to determine whether or not, similar to POC, PN concentrations are routinely much higher in rivers than lakes of the Laurentian Great Lakes basin.

For both POC and PN, the order of the inflows from lowest to highest concentration is: Grand River < Nanticoke Creek < Sandusk Creek. Also in terms of both POC and PN concentrations, the Grand River and Nanticoke Creek do not differ significantly from one another, but both are significantly lower than Sandusk Creek (ANOVA, $F_{POC} = 10.41$, $F_{PN} = 10.91$, $\alpha = 0.05$; Tables 3.2, 3.3).

The POC concentration data for the tributary inflows in this study are compared with data reported previously for Lake Erie tributaries in Table 3.5. The mean POC concentration for the Grand River in the early 1970's (Liaw and MacCrimmon, 1977) is lower than, but comparable to, that in 2002. The lower mean concentration in the 1970's could, at least in part, be related to the type of filters used in the collection of particulate matter for POC analysis. Liaw and MacCrimmon (1977) used Gelman Type A glass fibre filters, which have a larger pore size than the GF/F glass fibre filters used in the present study. With their lower porosity, GF/F filters collect smaller particles that pass through Type A filters. GF/F filters thus result in higher POC concentrations for a water sample than Type A filters, when all other parameters are held constant. Liaw and MacCrimmon (1977) also used a different analytical technique (quantitative dichromate oxidation) than the current study to determine POC concentrations; however, it is not known how this difference in technique could influence the comparability of the mean concentrations from the two studies. The mean POC concentration for the Grand River, Sandusk Creek, and Nanticoke Creek in July 2002 is 5.5 times higher than that for the Nith River, a tributary of the Grand River, in July 1993 (Stone and Droppo, 1994). In general, the POC concentrations measured for three tributary inflows in 2002 are greater than those previously measured for the Grand (Liaw and MacCrimmon, 1977) and Nith (Stone and Droppo, 1994) Rivers. Nevertheless, the POC concentrations of the Grand River in the early 1970's (Liaw and MacCrimmon, 1977) are more comparable to those of the tributary inflows in 2002 than the concentrations of the Nith River in 1993. This probably relates to the fact that the Nith River was sampled in its headwaters (M.

Table 3.5: POC concentration data for Great Lakes tributary inflows and outflows from this and other studies. Mean, standard deviation (SD), minimum (Min), and maximum (Max) values are provided, as well as the number of samples used in calculating these values. Thicker lines are inserted between rows to group together the values being compared.

System	**Reference**	**Location**	**Date**	**POC (µg/L)**				
				Mean	**SD**	**Min**	**Max**	**n**
Tributary Inflows	Upsdell, 2005	Grand River	May – October 2002	2672	1123	1181	4285	11
	Liaw and MacCrimmon, 1977	Grand River	May – November 1970 & 1971	2280	—	970	3320	—
	Upsdell, 2005	Grand River, Sandusk Creek, Nanticoke Creek	July 2002	4339	2909	1509	9202	6
	Stone and Droppo, 1994*	Nith River, Ontario	July 1993	783	48	728	834	5
Lake Outflow	Upsdell, 2005	Lake Erie outflow	11 July 2002	135	—	—	—	1
	Barth et al., 1998	St. Lawrence River (Lake Ontario outflow)	14 July 1994	102	—	—	—	1
	Upsdell, 2005	Lake Erie outflow	10 October 2002	148	—	—	—	1
			25 October 2002	169	—	—	—	1
	Barth et al., 1998	St. Lawrence River (Lake Ontario outflow)	17 October 1995	76	—	—	—	1

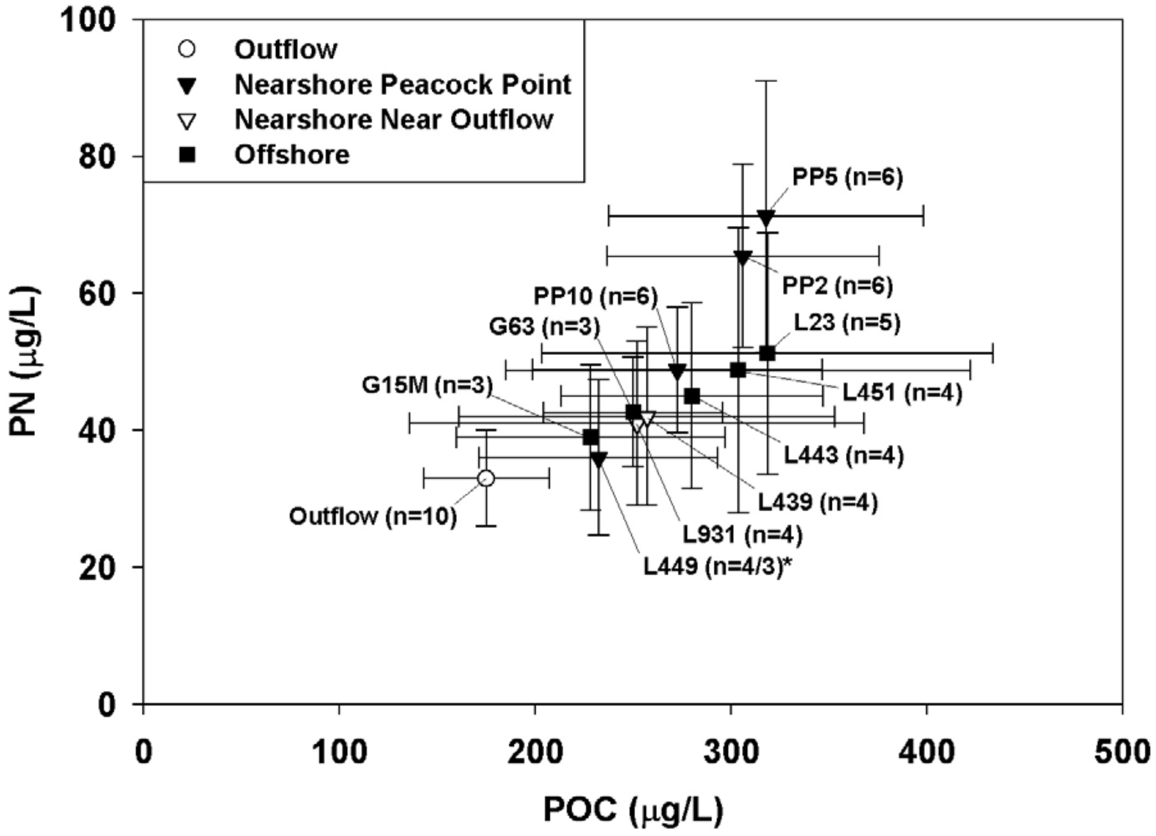
* The values presented here are calculated from the concentrations at five points over a cross-section of the river.

Stone, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, N2L 3G1, Canada, personal communication) while the tributary inflows of the present research were sampled close to their mouths. According to Vannote et al. (1980), particulate matter collected from river headwaters differs in size and chemical composition from that collected from the river mouth. No previously published data were found for PN concentrations of Great Lakes tributary inflows.

Table 3.5 also shows a comparison of POC concentrations at the Lake Erie outflow from this study with those reported previously for the St. Lawrence River, the outflow of Lake Ontario. The POC concentrations for the Lake Erie and Lake Ontario outflows are more similar than those for tributary inflows, but the Lake Erie outflow data from 2002 (135 – 169 µg/L) are still higher than those for the Lake Ontario outflow in 1994 and 1995 (76 – 102 µg/L; Barth et al., 1998). Barth et al. (1998) collected particulate matter for POC analysis from the Lake Ontario outflow using GF/C glass fibre filters, which have a larger pore size than the GF/F filters used in the current study. As a result, the higher POC concentrations of the Lake Erie outflow, compared with the Lake Ontario outflow, may be partly due to the difference in pore size of the filters used for the two sites. No previously published data were found for PN concentrations of Great Lakes outflows.

Figure 3.5 depicts the POC and PN concentrations of the lake outflow and eastern basin sites with the inflow sites removed. Among the eastern basin nearshore sites (maximum depth < 20 m), the two shallowest Peacock Point sites (PP2, PP5) have the highest mean POC and PN concentrations, while the two deeper Peacock Point sites (PP10, L449) and the two sites close to the lake outflow (L931, L439) have lower mean concentrations. Due to the tributary inflows having much higher POC and PN concentrations than the lake and outflow sites, a second test of ANOVA, using only lake and outflow sites, was performed to determine whether significant differences in the concentrations occur among the lake and outflow sites (Tables 3.6, 3.7). There are no significant differences in the POC concentrations among the eastern basin nearshore sites (ANOVA, $F = 4.89$, $\alpha = 0.05$). With respect to PN concentrations, however, sites PP2 and PP5 are both significantly higher than sites L449, L931, and L439 (ANOVA, $F = 7.04$, $\alpha = 0.05$). The PN concentration at site PP5 is also significantly higher than that at site PP10 (ANOVA, $F = 7.04$, $\alpha = 0.05$).

Regarding the eastern basin offshore sites (maximum depth ≥ 20 m), sites L451 and L23 have the highest mean POC and PN concentrations, while site G15M has the lowest (Figure 3.5). Sites G15M and L23 are the deepest sites sampled in the eastern basin and yet these deep sites, of similar maximum depth, respectively exhibit the lowest and highest mean POC and PN concentrations observed at the eastern basin offshore sites. There are no significant differences among the offshore sites in terms of either POC or PN concentrations (ANOVA, $F_{POC} = 4.89$, $F_{PN} = 7.04$, $\alpha = 0.05$).



* n=4 for POC and n=3 for PN

Figure 3.5: Mean POC and PN concentrations for the lake outflow and all sites in the eastern basin. Error bars indicate standard deviation.

Table 3.6: Results of a univariate ANOVA comparing the mean POC concentrations of different sites using only the outflow and lake sampling locations (F = 4.89, α = 0.05). The symbol ❋ indicates that there is a significant difference in the concentration between sites.

Site	Out	PP2	PP5	PP10	L449	L931	L439	L451	G15M	L23	G63	L443	GAsh	G78M	G43	GSan	G91M
Out		❋	❋	❋				❋		❋		❋			❋	❋	❋
PP2	❋																❋
PP5	❋																❋
PP10	❋															❋	❋
L449																❋	❋
L931																❋	❋
L439																❋	❋
L451	❋																❋
G15M																❋	❋
L23	❋																❋
G63																❋	❋
L443	❋																❋
GAsh																❋	❋
G78M																	❋
G43	❋																❋
GSan	❋			❋	❋	❋	❋		❋		❋		❋				❋
G91M	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	

Table 3.7: Results of a univariate ANOVA comparing the mean PN concentrations of different sites using only the outflow and lake sampling locations (F = 7.04, α = 0.05). The symbol ✱ indicates that there is a significant difference in the concentration between sites.

Site	Out	PP2	PP5	PP10	L449	L931	L439	L451	G15M	L23	G63	L443	GAsh	G78M	G43	GSan	G91M
Out		✱	✱							✱					✱	✱	✱
PP2	✱				✱	✱	✱		✱		✱		✱				✱
PP5	✱			✱	✱	✱	✱	✱	✱	✱	✱	✱	✱				✱
PP10			✱													✱	✱
L449		✱	✱												✱	✱	✱
L931		✱	✱													✱	✱
L439		✱	✱													✱	✱
L451			✱													✱	✱
G15M		✱	✱													✱	✱
L23	✱		✱													✱	✱
G63		✱	✱													✱	✱
L443			✱													✱	✱
GAsh		✱	✱													✱	✱
G78M																✱	✱
G43	✱				✱												✱
GSan	✱			✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱			✱
G91M	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	✱	

Bloesch (1982) measured POC concentrations at sites in Lake Erie with maximum depths similar to those of sites in the current research (Table 3.8). At sites of comparable depths, the mean POC concentrations reported by Bloesch (1982) in 1978 range from 1.5 to 2.6 times greater than those determined for similar timeframes in 2002. The mean POC concentration quantified by Charlton and Rao (1983) for five offshore sites in the eastern basin of Lake Erie in 1979 is 1.1 times greater than that for the five offshore sites studied in 2002 (Table 3.8). The POC concentration reported by Charlton and Rao (1983) is thus more comparable than the 1978 values of Bloesch (1982) to the mean concentrations determined in 2002. Both Bloesch (1982) and Charlton and Rao (1983) collected particulate matter for POC analysis on GF/C filters. Since their POC concentrations are higher than those determined in 2002 using GF/F filters, the difference is not caused by filter type and suggests that the concentrations were, in fact, lower in the eastern basin in 2002 than in the late 1970's. This could partly reflect the decreased total phosphorus concentrations of Lake Erie over time (Makarewicz and Bertram, 1991), resulting from reduced phosphorus loadings to the lake since the Great Lakes Water Quality Agreement was signed in 1972 (Dolan, 1993).

Bloesch (1982) also measured PN concentrations at Lake Erie sites with maximum depths similar to those in the present study (Table 3.9). At sites of comparable depths, the mean PN concentrations determined by Bloesch (1982) in 1978 range from 4.5 to 8.9 times greater than those determined for similar timeframes in 2002. This difference is larger than that observed for mean POC concentrations. Means of the PN concentrations quantified by Lean et al. (1983) in 1979 for an eastern basin site are approximately 1.5 times greater than the mean PN concentrations in 2002 at sites of similar maximum depth (Table 3.9). Hence, the Lean et al. (1983) mean PN concentrations are more similar than those of Bloesch (1982) to the mean PN concentrations determined in 2002, but are still higher than the 2002 mean concentrations. Both Bloesch (1982) and Lean et al. (1983) collected particulate matter for PN analysis on GF/C filters. Because their PN concentrations are higher than those determined in 2002 using GF/F filters, the higher concentrations are not caused by the type of filters used and must indicate that, similar to POC, the PN concentrations were actually lower in the eastern basin in 2002 than in the late 1970's.

The mean POC and PN concentrations for nearshore and offshore sites in the eastern basin are compared in Figure 3.5. The nearshore and offshore sites have similar ranges of POC concentrations and there are no significant differences in concentrations between nearshore and offshore sites (ANOVA, $F = 4.89$, $\alpha = 0.05$; Table 3.6). Except for the shallowest nearshore sites (PP2, PP5), the nearshore and offshore sites also have similar ranges of PN concentrations. Site PP2 has significantly higher PN concentrations than two offshore sites (G15M, G63), while site PP5 has significantly higher

Table 3.8: POC concentration data for the eastern basin of Lake Erie from this and other studies. Mean, standard deviation (SD), minimum (Min), and maximum (Max) values are provided, as well as the number of samples used in calculating these values. Thicker lines are inserted between rows to group together the values being compared.

Depth Range	Reference	Maximum Depth	Location	Date	POC (µg/L)				
					Mean	**SD**	**Min**	**Max**	**n**
9 – 11 m	Upsdell, 2005	10 m	Peacock Point (PP10)	July & October 2002	272	74	144	340	6
	Bloesch, 1982*	9 m	Port Dover	July & October 1978	400	100	400	600	4
	Upsdell, 2005	11 m	Peacock Point (L449)	June – October 2002	232	61	192	321	4
		10 m	near outflow (L931)	June – October 2002	252	116	151	358	4
	Bloesch, 1982*	9 m	Port Dover	June – October 1978	600	200	400	900	8
19 – 25 m	Upsdell, 2005	19 m	near outflow (L439)	June – October 2002	257	96	143	352	4
		23 m	near outflow (L443)	June – October 2002	280	67	189	332	4
	Bloesch, 1982*	25 m	Port Dover	June – October 1978	500	200	300	1000	8
40 – 44 m	Upsdell, 2005**	41 m	Peacock Point (L451)	June – October 2002	216	123	92	451	8
	Bloesch, 1982*	40 m	Port Dover	June – October 1978	400	100	200	500	9
	Upsdell, 2005**	44 m	near central basin (G63)	July – September 2002	158	105	58	277	6
	Bloesch, 1982*	40 m	Port Dover	July – September 1978	400	100	300	600	10
Offshore	Upsdell, 2005	≥ 20 m	5 sites	June – September 2002	282	89	151	476	19
	Charlton and Rao, 1983***	≥ 20 m	5 sites	May – September 1979	320	—	—	—	1

* The values presented here are approximate because they are calculated from sample values depicted in a graph.

** The values were adjusted to include POC concentrations at sampling depths similar to those used in Bloesch (1982) rather than only the shallowest sampling depth.

*** The value presented here is the time-weighted average for the epilimnion.

Table 3.9: PN concentration data for the eastern basin of Lake Erie from this and other studies. Mean, standard deviation (SD), minimum (Min), and maximum (Max) values are provided, as well as the number of samples used in calculating these values. Thicker lines are inserted between rows to group together the values being compared.

Depth Range	Reference	Maximum Depth	Location	Date	PN (µg/L)				
					Mean	SD	Min	Max	n
9 – 11 m	Upsdell, 2005	10 m	Peacock Point (PP10)	July & October 2002	49	9	32	58	6
	Bloesch, 1982*	9 m	Port Dover	July & October 1978	220	40	170	280	5
	Upsdell, 2005	11 m	Peacock Point (L449)	June – September 2002	36	11	28	49	3
	Bloesch, 1982*	9 m	Port Dover	June – September 1978	240	30	190	280	7
	Upsdell, 2005	10 m	near outflow (L931)	June – October 2002	41	12	24	51	4
	Bloesch, 1982*	9 m	Port Dover	June – October 1978	230	40	170	280	9
19 – 25 m	Upsdell, 2005	19 m	near outflow (L439)	June – October 2002	42	13	23	51	4
		23 m	near outflow (L443)	June – October 2002	45	14	30	63	4
	Bloesch, 1982*	25 m	Port Dover	June – October 1978	220	40	180	280	8
40 – 44 m	Upsdell, 2005**	41 m	Peacock Point (L451)	June – October 2002	33	22	14	75	8
	Bloesch, 1982*	40 m	Port Dover	June – October 1978	230	40	180	290	9
	Upsdell, 2005**	44 m	near central basin (G63)	July – September 2002	27	18	11	48	6
	Bloesch, 1982*	40 m	Port Dover	July – September 1978	240	40	200	300	11
61 – 62 m	Upsdell, 2005	62 m	near central basin (G15M)	July – September 2002	39	11	28	49	3
	Lean et al., 1983*	61 m	near central basin (L23)	July – September 1979	60	20	50	90	4
	Upsdell, 2005	61 m	near central basin (L23)	June – October 2002	51	18	32	78	5
	Lean et al., 1983*	61 m	near central basin (L23)	June – October 1979	75	35	45	140	6

* The values presented here are approximate because they are calculated from sample values depicted in a graph.

** The values were adjusted to include POC concentrations at sampling depths similar to those used in Bloesch (1982) rather than only the shallowest sampling depth.

PN concentrations than all five offshore sites (ANOVA, F = 7.04, α = 0.05, Table 3.7). The PN concentrations at the four other nearshore sites do not differ significantly from those at the five offshore sites (ANOVA, F = 7.04, α = 0.05). In general, there is no consistent trend between POC or PN concentration and the maximum site depth. Only one study has previously evaluated differences in POC and PN concentrations in nearshore versus offshore sites of a Laurentian Great Lake. Bloesch (1982) studied a transect of nearshore-to-offshore sites, with maximum depths ranging from nine to forty metres, in the eastern basin of Lake Erie between June and October 1978. The 1978 data are generally higher than the 2002 data reported in the present study. Unlike the 2002 data, the 1978 POC concentrations decreased from nearshore to offshore (Bloesch, 1982). Similar to the 2002 data, however, the 1978 PN concentrations did not show a consistent trend with depth (Bloesch, 1982).

The mean POC and PN concentrations at the lake outflow are lower than those at the eastern basin sites (Figure 3.5). In terms of both POC and PN concentrations, the lake outflow is significantly lower than the two shallowest nearshore sites at Peacock Point (PP2, PP5) and offshore site L23 (ANOVA, $F_{POC} = 4.89$, $F_{PN} = 7.04$, α = 0.05; Tables 3.6, 3.7). The POC concentrations at the lake outflow are also significantly lower than those at nearshore site PP10 and at two other offshore sites (L451, L443; ANOVA, F = 4.89, α = 0.05). Generally, the POC and PN concentrations at the lake outflow are more similar to the concentrations at deeper nearshore and some offshore sites rather than at shallower nearshore sites, such as those near Peacock Point.

Within the eastern basin, nearshore sites generally have greater PN concentrations relative to POC concentrations than offshore sites (Figure 3.6). Regression analysis shows that the relationship between POC and PN is best described for nearshore sites by the quadratic equation

$$y = 94.569 - 0.742x + 0.002x^2 \tag{3.1}$$

and for offshore sites by the linear equation

$$y = 10.581 + 0.126x \tag{3.2}$$

where y = PN concentration (μg/L) and x = POC concentration (μg/L) in both equations. In the nearshore, deeper sites (up to 20 m) are less enriched than shallower ones at Peacock Point in PN relative to POC. The offshore sites, by contrast, show a more consistent relationship between POC and PN. Based upon this relationship, the eastern basin sites can be divided into three groups. The shallowest nearshore sites (2-5 m maximum depth), which are most enriched in PN relative to POC, form the first group. The second group consists of the deeper nearshore sites (10-19 m maximum depth), which are moderately enriched in PN relative to POC. The offshore sites (23-62 m maximum depth), least enriched in PN relative to POC, make up the third group. The POC and PN concentration data for Lake Erie that were published by Bloesch (1982) show a different trend: while the mean POC

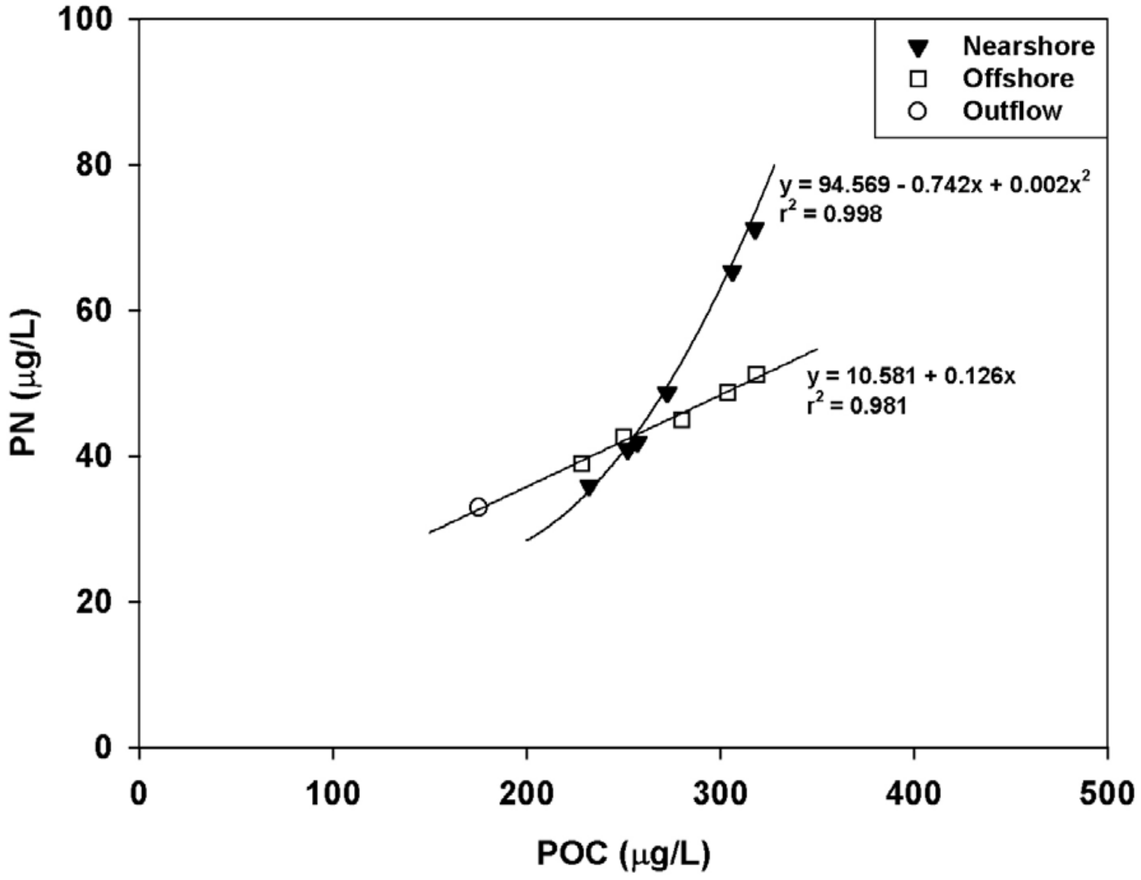


Figure 3.6: Mean POC and PN concentrations for the lake outflow and all sites in the eastern basin, with regression lines for the nearshore and offshore groupings of sites added to the graph. The corresponding regression equation and r^2-value are shown next to each line.

concentration decreased from nearshore to offshore, the mean PN concentration remained relatively constant across the sites. This resulted in offshore sites having greater PN concentrations relative to POC than nearshore sites in 1978 (Bloesch, 1982). As will be shown later in this chapter, Bloesch (1982) reports unusually low POC/PN mass ratios when compared with ratios for Lake Erie and other temperate lakes in the existing literature, rendering Bloesch's (1982) values somewhat suspect.

The identification of three groups of sites, based upon POC and PN concentrations and the relationship between the two parameters, may reflect the origin and processing of particulate matter found at the different sites. The shallowest nearshore sites at Peacock Point may have a greater proportion of allochthonous particulate matter, originating from nearby tributary inflows such as Nanticoke Creek, than the other sites. By contrast, autochthonous particulate matter may dominate at the offshore sites. The influences of allochthonous material, which passed through the shallower nearshore, and autochthonous material, which formed in the offshore, may overlap at the deeper nearshore sites. Although the tributary inflows are more enriched in PN relative to POC than the offshore sites, they are still not as enriched as the shallowest nearshore sites. This suggests that there may be an additional source of PN at the shallowest nearshore sites that is not present at the inflows or at deeper sites in the lake. Dreissenid mussels were present at sites PP2 and PP5 at the time of sampling. They may recycle PN back into the water column by excreting ammonium (Arnott and Vanni, 1996), which strongly adsorbs to particulate matter (Wetzel, 1983) or can be taken up by benthic algae and nearshore phytoplankton. This enhanced availability of nitrogen through regeneration by dreissenids may account for the higher PN concentrations relative to POC concentrations at the shallowest sites.

With regard to the processing of particulate matter, material that has travelled from allochthonous sources, through the nearshore, to the offshore may have undergone more degradation processes within the lake than the material delivered directly to the nearshore sites. Since nitrogen-rich proteins and lipids are labile and decompose relatively rapidly compared with other components of living particulate organic matter (Talbot, 2001), there would be less PN relative to POC in the offshore allochthonous material than in the nearshore allochthonous material.

The lake outflow shows a relationship between POC and PN that is similar to that observed at the offshore sites (Figure 3.6). Therefore, particulate matter at the lake outflow is likely to be composed of autochthonous materials derived from the offshore environment rather than allochthonous materials from the nearshore.

3.1.2 Eastern, Central, and Western Basins of Lake Erie

Mean POC and PN concentrations for nearshore and offshore sites in the central and western basins of Lake Erie are shown in Figure 3.7. In the central basin, the shallowest and nearshore site has lower mean POC and PN concentrations than the offshore sites, but differences among the central basin site concentrations are not statistically significant (ANOVA, $F_{POC} = 4.89$, $F_{PN} = 7.04$, $\alpha = 0.05$; Tables 3.6, 3.7). This trend is opposite from that found among eastern basin sites of comparable maximum depths. Only nearshore sites were sampled in the western basin, with deeper site GSan having significantly lower concentrations than shallower site G91M (ANOVA, $F_{POC} = 4.89$, $F_{PN} = 7.04$, $\alpha = 0.05$).

In Figure 3.7, the mean POC and PN concentrations of sampling locations in the central basin are also compared to those of sampling locations in the eastern basin. The mean POC and PN concentrations at central basin nearshore site GAsh fall at the lower end of the data ranges for eastern basin nearshore and offshore sites. While POC concentrations at site GAsh do not differ significantly from any sites in the eastern basin, the PN concentrations are significantly lower than two nearshore eastern basin sites (PP2, PP5; ANOVA, $F_{POC} = 4.89$, $F_{PN} = 7.04$, $\alpha = 0.05$). This difference is interesting because, with respect to maximum site depth, these two sites are the most comparable of all the eastern basin sites to site GAsh. Each of these three sites has a rocky substrate. Dreissenid mussels were present at sites PP2 and PP5 at the time of sampling, but not at site GAsh. Therefore, a possible source of higher PN concentrations at sites PP2 and PP5, relative to site GAsh, is recycling and increased availability of dissolved ammonium from dreissenids. The mean POC and PN concentrations at central basin offshore site G78M are not significantly different from those at eastern basin sites (ANOVA, $F = 4.89$, $\alpha = 0.05$). While the mean POC concentrations at central basin offshore site G43 are not significantly different from those at all eastern basin sites, the PN concentrations at this site are significantly greater than those at eastern basin nearshore site L449 (ANOVA, $F = 7.04$, $\alpha = 0.05$).

The central basin POC and PN concentration data in this study are compared with previously published values for the central basin in Table 3.10. The mean POC concentration reported by Charlton and Rao (1983) using GF/C filters for ten central basin offshore sites in 1979 is greater than that determined for two central basin offshore sites in this study using GF/F filters. The difference in mean POC concentrations between these sampling years is likely underestimated because of the use of different filters, but it may also be influenced by inconsistencies in the spatial and temporal coverage of the sampling in the two studies. Charlton and Rao (1983) found that mean POC concentrations in the central basin offshore were greater than those in the eastern basin offshore. In 2002, one of the central basin offshore sites (G43) has a greater mean POC concentration than the eastern basin offshore

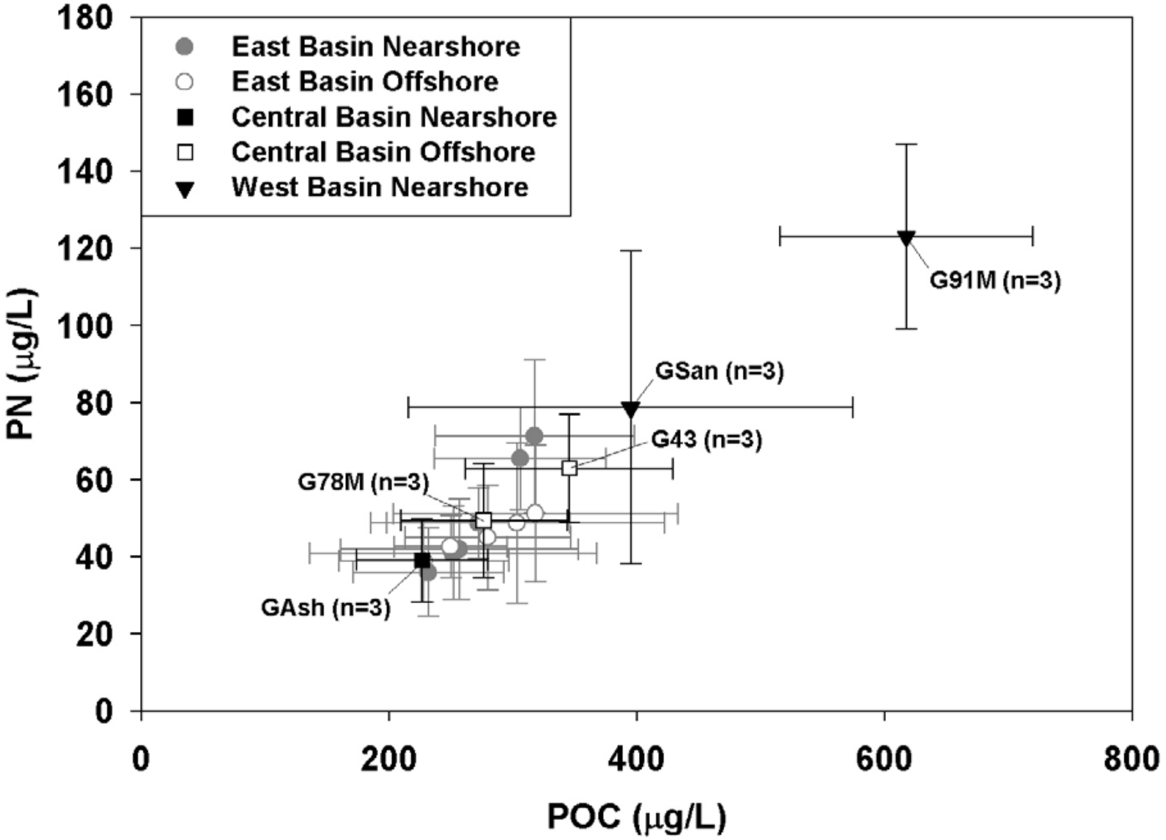


Figure 3.7: Mean POC and PN concentrations for nearshore and offshore sites in the eastern, central, and western basins. Error bars indicate standard deviation.

Table 3.10: POC and PN concentration data for the central basin of Lake Erie from this and other studies. Mean, standard deviation (SD), minimum (Min), and maximum (Max) values are provided, as well as the number of samples used in calculating these values.

Parameter	Reference	Maximum Depth	Location	Date	POC or PN (µg/L)				
					Mean	SD	Min	Max	n
POC	Upsdell, 2005	≥ 20 m	2 sites	July – September 2002	311	78	202	406	6
	Charlton and Rao, 1983*	≥ 20 m	10 sites	May – September 1979	360	—	—	—	1
PN	Upsdell, 2005	≥ 20 m	near west basin (G43)	July – September 2002	63	14	49	76	3
	Lean et al., 1983**	—	near west basin (G43)	July – September 1979	60	10	50	80	4

* The value presented here is the time-weighted average for the epilimnion.

** The values presented here are approximate because they are calculated from sample values depicted in a graph.

sites; however, the other site (G78M) has a mean POC concentration that is greater than only two of the five eastern basin offshore sites. The mean PN concentration determined by Lean et al. (1983) for one sampling location in the central basin in 1979 is similar to that for the same site in 2002. Since Lean et al. (1983) used GF/C filters to collect particulate matter, their mean PN concentration may actually be greater than that from 2002.

Figure 3.7 shows how mean POC and PN concentrations of sampling locations in the western basin compare with those of sampling locations in the eastern basin. The POC concentrations at western basin nearshore site GSan are most similar to those at the two shallowest nearshore sites in the eastern basin (PP2, PP5) and are significantly greater than those at the remaining nearshore sites and two offshore sites (G15M, G63) in the eastern basin (ANOVA, $F = 4.89$, $\alpha = 0.05$). The PN concentrations at GSan are not significantly different from those at sites PP2 and PP5, but they are significantly greater than those at all of the other sites in the eastern basin (ANOVA, $F = 7.04$, $\alpha = 0.05$). The POC and PN concentrations at western basin site G91M are remarkable in that they are significantly greater than those at all other sites in the lake (ANOVA, $F_{POC} = 4.89$, $F_{PN} = 7.04$, $\alpha = 0.05$), although they are still much lower than the concentrations at the tributary inflows. The elevated concentrations at this site may be caused by resuspension of deposited materials in the western basin due to its shallow depth (Lick et al., 1994). Alternatively, higher summer algal productivity in the western basin compared with the central and eastern basins (personal observation; Charlton et al., 1999) may maintain these high concentrations of POC and PN. No comparable POC or PN concentration values for the western basin were found in previously published work.

3.2 POC/PN Mass Ratios

Mean, standard deviation, minimum, and maximum values of POC/PN mass ratios for each sampling location are presented in Table 3.11. All ratio data are provided in Table A.1 of the Appendix.

All sites show some temporal variability in POC/PN mass ratios; however, examination of the data indicates that the mean POC/PN mass ratios for individual sampling locations are not biased by using samples collected at different times in the calculation of the mean ratios. The Grand River has the largest range of POC/PN mass ratios (4.39 – 8.48) of all the sampling locations (Figure 3.8). The mass ratios at the other tributary inflows and at the lake outflow range between 4.0 and 7.0 (Figure 3.8). In the Lake Erie nearshore (Figure 3.9), all but site L931 have POC/PN mass ratios that range between 4.0 and 7.5. Site L931 has a larger range of ratios (3.6 – 7.6) than all of the other lake sampling locations. The POC/PN mass ratios in the Lake Erie offshore (Figure 3.10) have a smaller range (5.0 –

Table 3.11: Mean, standard deviation (SD), minimum (Min), and maximum (Max) POC/PN mass ratios for all sampling locations. The number of samples analyzed (n) is also indicated. The maximum site depths are given in brackets after the lake site names.

Site Grouping	**Site**	**POC/PN (mass ratio)**				
		Mean	**SD**	**Min**	**Max**	**n**
Inflows	Grand River	5.61	1.07	4.39	8.48	11
	Sandusk Creek	5.47	0.76	4.11	6.35	11
	Nanticoke Creek	5.55	0.55	4.89	6.64	11
Outflow	Outflow	5.4	0.5	4.7	6.2	10
Eastern Basin Nearshore Peacock Point	PP2 (2 m)	4.7	0.2	4.4	4.9	6
	PP5 (5 m)	4.5	0.5	4.1	5.3	6
	PP10 (10 m)	5.5	1.1	4.5	7.1	6
	L449* (11 m)	6.9	0.3	6.6	7.2	3
Eastern Basin Nearshore Near Outflow	L931 (10 m)	6.1	1.7	3.6	7.6	4
	L439 (19 m)	6.2	1.0	4.8	6.9	4
Eastern Basin Offshore	L451 (41 m)	6.3	0.5	5.9	7.1	4
	G15M (62 m)	5.8	0.4	5.5	6.2	3
	L23 (61 m)	6.2	0.6	5.7	7.1	5
	G63 (44 m)	5.9	0.1	5.7	6.0	3
	L443 (23 m)	6.3	1.0	5.2	7.5	4
Central Basin Nearshore	GAsh (5 m)	5.9	0.3	5.5	6.0	3
Central Basin Offshore	G78M (21 m)	5.7	0.6	5.0	6.3	3
	G43 (20 m)	5.5	0.4	5.2	6.0	3
Western Basin Nearshore	GSan (11 m)	5.1	0.4	4.6	5.4	3
	G91M (8 m)	5.1	0.6	4.5	5.6	3

* The anomalous ratio for site L449 from 30/10/02 (POC/PN = 20) was not used in the calculation of the mean ratio for this site.

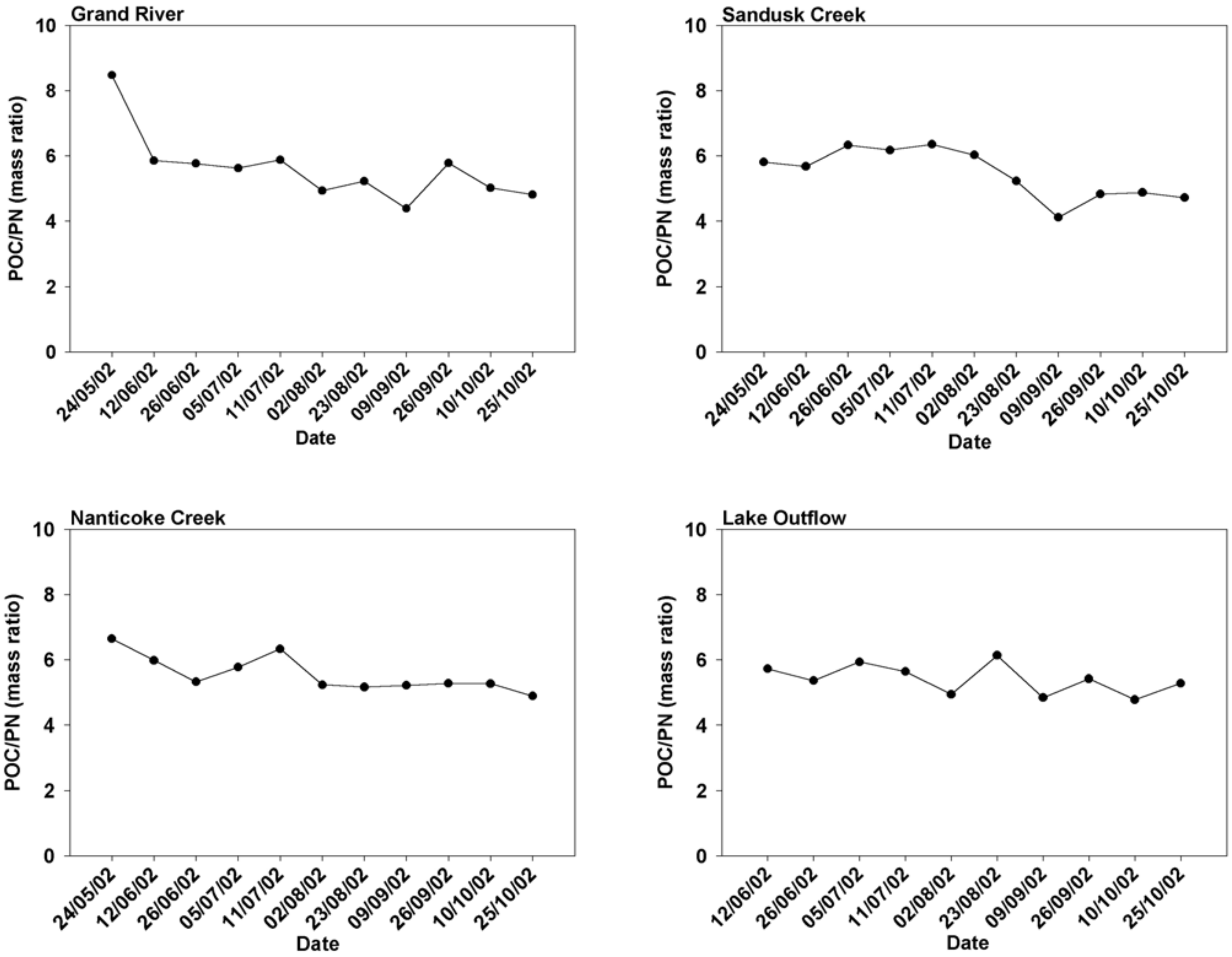


Figure 3.8: Temporal variation in POC/PN mass ratios for the three tributary inflows and the lake outflow.

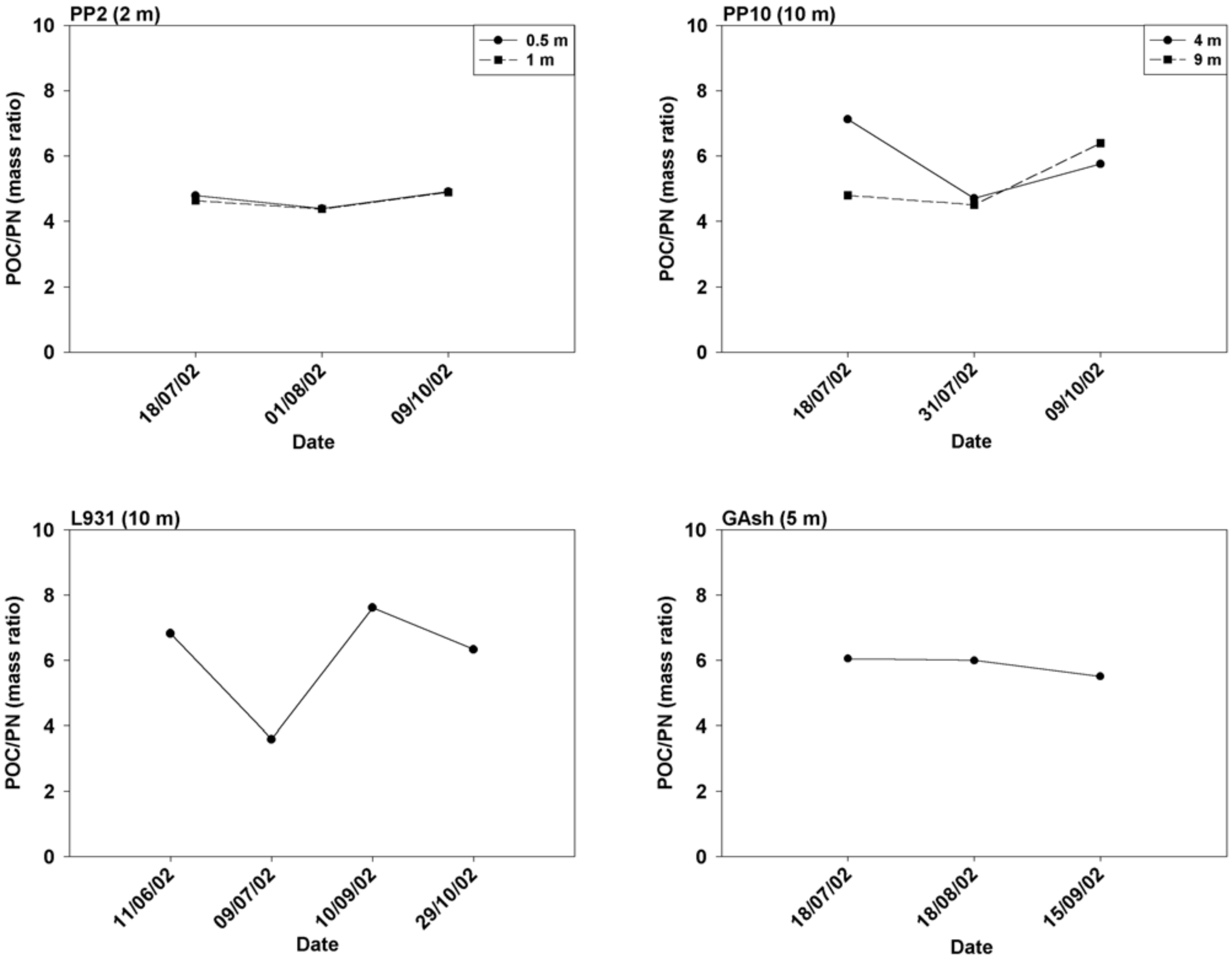


Figure 3.9: Temporal variation in POC/PN mass ratios for four nearshore sites in Lake Erie. The maximum site depths are given after the site names.

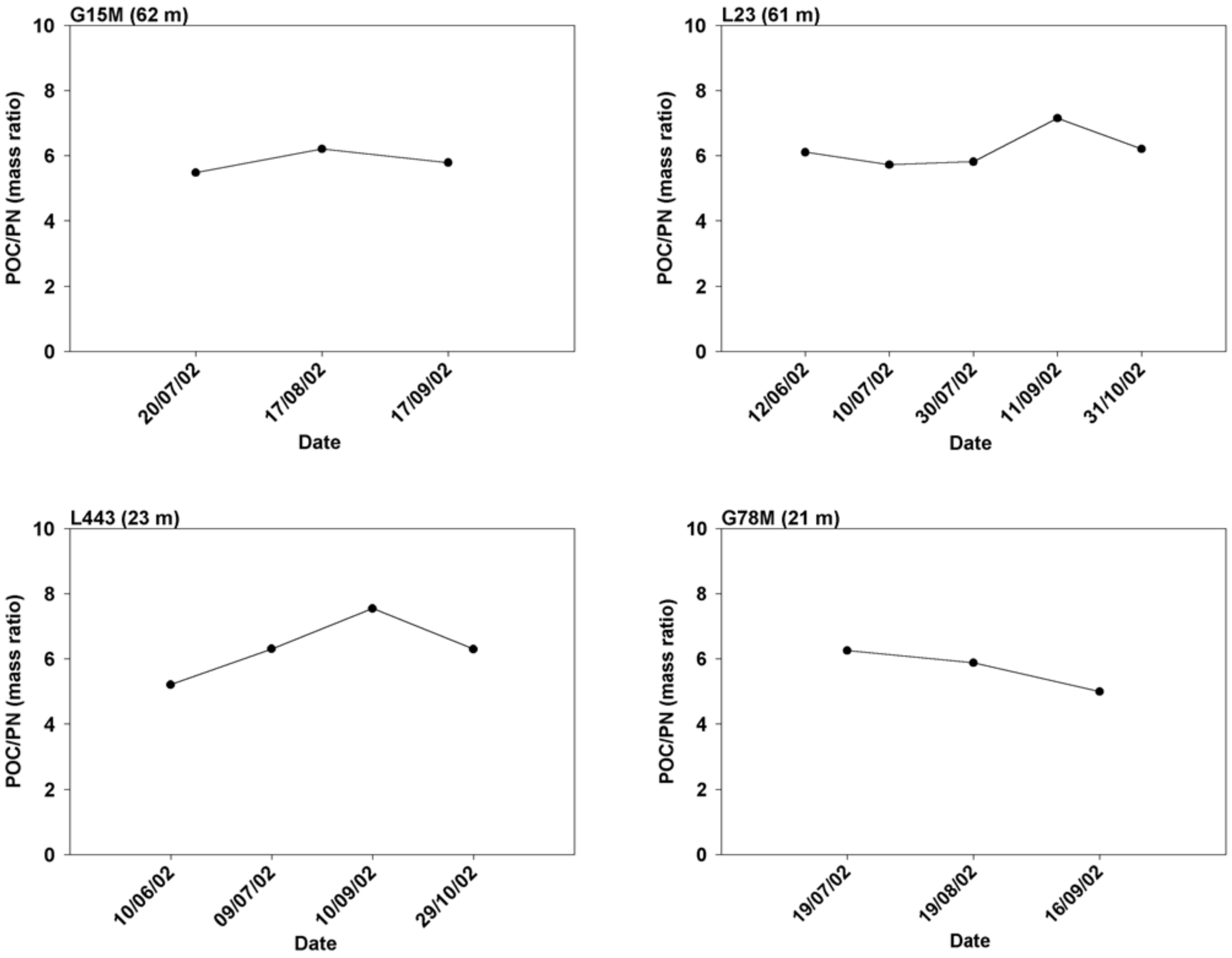


Figure 3.10: Temporal variation in POC/PN mass ratios for four offshore sites in Lake Erie. The maximum site depths are given after the site names.

7.5) than the rivers and the lake nearshore. Therefore, at most, the POC/PN mass ratios at a particular site vary temporally over a value of approximately four.

The anomalous PN concentration value from site L449 on 30/10/02 resulted in a POC/PN mass ratio of twenty for that site and date. This ratio is anomalous compared to the mean ratio of approximately seven for the other samples at that site. The anomalous ratio is considered an outlier and was not included in the calculation of the mean POC/PN mass ratio for site L449.

3.2.1 Tributary Inflows, Lake Outflow, and Eastern Basin of Lake Erie

The three tributary inflows have similar mean POC/PN mass ratios, ranging from 5.47 at Sandusk Creek to 5.61 at the Grand River (Figure 3.11). Unlike POC and PN concentrations, the lake outflow mean POC/PN mass ratio (5.4) is similar to those at the tributary inflows. Hence, although the mean POC and PN concentrations are approximately nineteen times greater at the three tributary inflows than at the outflow, the relative proportions of POC and PN are similar at these four sites.

The range of mean POC/PN mass ratios for the tributary inflows is smaller than, and is at approximately the centre of, the range of mean POC/PN mass ratios for all of the eastern basin sites (4.5 – 6.9; Figure 3.11). The two shallowest nearshore Peacock Point sites (PP2, PP5) have lower mean POC/PN mass ratios than the tributary inflows, while nearshore Peacock Point site PP10 has a mean ratio that is similar to those at the inflows. The deepest nearshore Peacock Point site (L449), nearshore sites close to the lake outflow, and offshore sites all have higher mean POC/PN mass ratios than the tributary inflows.

Numerous researchers have evaluated carbon/nitrogen (C/N) ratios in rivers (e.g. Meybeck, 1982), but no previously published POC/PN mass ratios were found in the literature for suspended particulate matter in tributaries of the Great Lakes. Many researchers have also evaluated C/N ratios in lakes (e.g. Hecky et al., 1993), but few studies have reported POC/PN mass ratios for suspended particulate matter in the Laurentian Great Lakes. This discussion of POC/PN mass ratios for Lake Erie and three of its tributary inflows therefore draws on previously published data for other lakes and rivers in areas with temperate climates in addition to data for the Laurentian Great Lakes. Similar to the current research, the range of previously published mean POC/PN mass ratios for temperate rivers (6.79 – 11.2) is within the range of previously published mean ratios for temperate lakes (2 – 11.4; Table 3.12). Unlike the Lake Erie tributary inflows, however, the mean POC/PN mass ratios for temperate rivers are at the higher end, rather than the centre, of the range of mean ratios for temperate lakes.

The POC/PN mass ratio data for the tributary inflows in this study are compared with data reported previously for temperate rivers in Table 3.13. The mean ratio for three relatively pristine

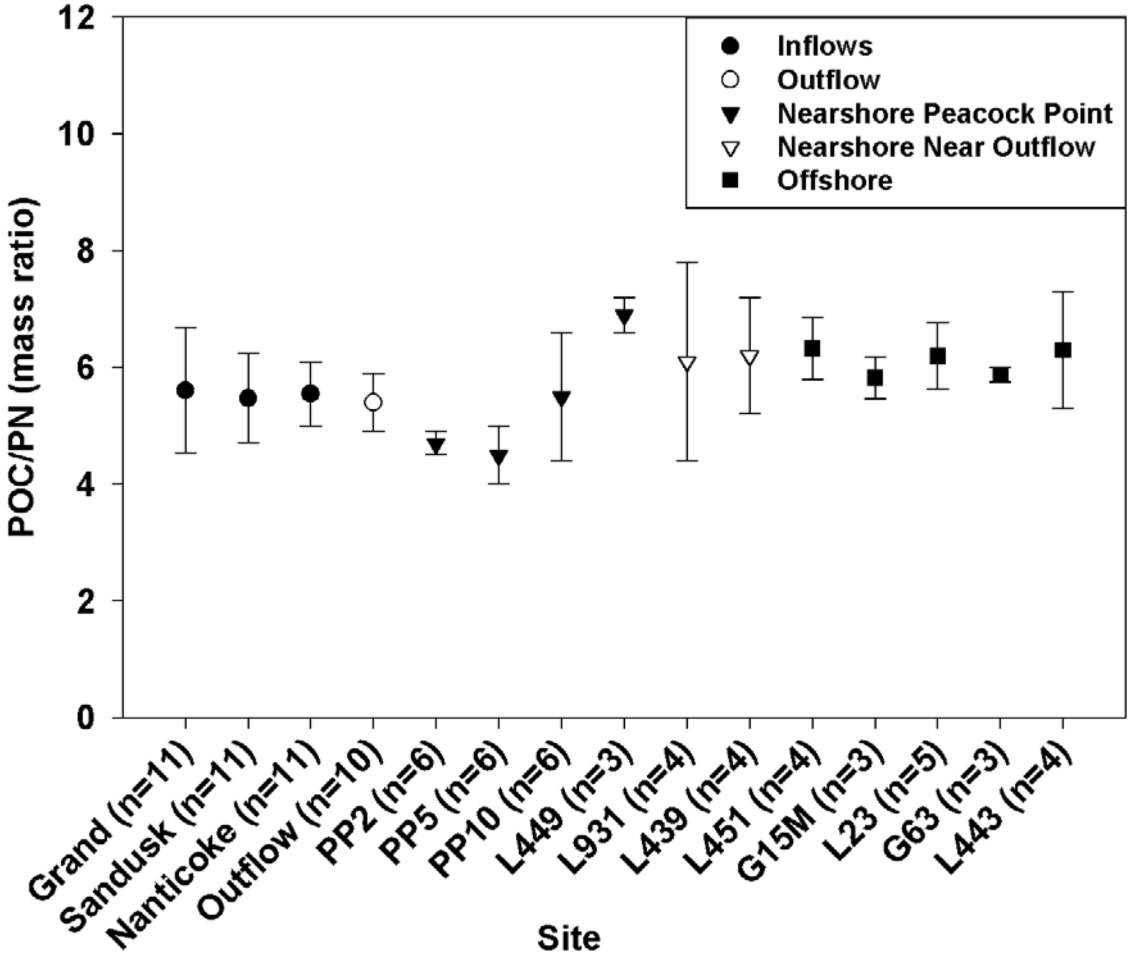


Figure 3.11: Mean POC/PN mass ratios for three tributary inflows, the lake outflow, and nearshore and offshore sites in the eastern basin. Error bars indicate standard deviation.

Table 3.12: POC/PN mass ratio data from previously published research for temperate rivers and lakes. Mean, standard deviation (SD), minimum (Min), and maximum (Max) values are provided, as well as the number of samples used in calculating these values.

System	Reference	Location	Date	POC/PN (mass ratio)					Notes
				Mean	SD	Min	Max	n	
River	Hecky et al., 1993	3 ELA* streams, Ontario	1987 – 1989	11.2	0.7	10.5	12.2	5	- calculated from median values
	Rostad et al., 1997	Mississippi River (9 sites) and 4 tributaries (1 site each), U.S.A.	July or August 1991	6.9	0.7	6.0	8.8	13	—
	Lartiges et al., 2001	Rhine River, France	May – July 1996 & 1997	6.79	2.15	2.63	8.18	6	—
Lake	Bloesch, 1982	Eastern Basin, Lake Erie (1 nearshore, 2 offshore sites)	June – October 1978	2	1	1	4	34	- calculated from sample values depicted in graph
	Lean et al., 1983	Eastern Basin, Lake Erie (1 offshore site)	May – October 1979	6.7	1.0	5.0	8.0	7	- calculated from sample values depicted in graph
		Central Basin, Lake Erie (1 offshore site)	May – October 1979	6.5	0.5	6.0	7.0	7	
	Burns and Ross, 1972	Central Basin, Lake Erie (25 sites)	July – August 1970	6.56	0.74	5.36	7.54	6	- for epilimnion
	Halfon, 1984	Lake Superior (15 nearshore, 12 offshore sites)	May – October 1973	7.14	0.80	6.21	8.29	5	- calculated from monthly means
	Hecky et al., 1993	Lake Superior	ice-free season 1990	9.7	—	—	—	6	- seasonal mean
		Lake Nipigon, Ontario		8.6	—	—	—	6	
		12 ELA* lakes, Ontario		11.4	2.1	7.1	15.3	13	- calculated from seasonal means
		6 NOLSS** lakes, Ontario		9.9	0.7	8.9	11.0	6	
	Hessen et al., 2003	109 temperate lakes, southeastern Norway	May – August 1991 & 1992	8.07	—	—	—	1	- calculated from seasonal mean POC and PN concentrations for all 109 lakes

* ELA = Experimental Lakes Area

** NOLSS = Northwestern Ontario Lake Size Series

Table 3.13: POC/PN mass ratio data for the three tributary inflows from this study compared with data for temperate rivers from other studies. Mean, standard deviation (SD), minimum (Min), and maximum (Max) values are provided, as well as the number of samples used in calculating these values. Thicker lines are inserted between rows to group together the values being compared.

Reference	**Location**	**Date**	**POC/PN (mass ratio)**				
			Mean	**SD**	**Min**	**Max**	**n**
Upsdell, 2005	Grand River, Sandusk Creek, Nanticoke Creek	May – October 2002	5.54	0.80	4.11	8.48	33
Hecky et al., 1993*	3 ELA** streams, Ontario	1987 – 1989	11.2	0.7	10.5	12.2	5
Upsdell, 2005	Grand River, Sandusk Creek, Nanticoke Creek	July & August 2002	5.66	0.50	4.93	6.35	12
Rostad et al., 1997	Mississippi River (9 sites) and 4 tributaries (1 site each), U.S.A.	July or August 1991	6.9	0.7	6.0	8.8	13
Upsdell, 2005	Grand River, Sandusk Creek, Nanticoke Creek	May – July 2002	6.13	0.73	5.32	8.48	15
Lartiges et al., 2001	Rhine River, France	May – July 1996 & 1997	6.79	2.15	2.63	8.18	6

* The values presented here were calculated from median values.

** ELA = Experimental Lakes Area

rivers in the Experimental Lakes Area (ELA) of northwestern Ontario (Hecky et al., 1993) is about twice that for the three Lake Erie tributary inflows, which are impacted by agricultural land uses (Ontario Ministry of Agriculture and Food, 1983a, 1983b). The lower ratio for the Lake Erie tributaries could reflect higher inputs of nitrogen from fertilizers applied to cropland and from manure in areas grazed by cattle. The mean ratios for the Mississippi River and its tributaries (Rostad et al., 1997) and for the Rhine River (Lartiges et al., 2001) are each greater than, but comparable to, those of the three Lake Erie tributary inflows for corresponding time periods. Both Rostad et al. (1997) and Lartiges et al. (2001) used a continuous-flow centrifuge to collect particulate matter for POC and PN analysis rather than collecting the material on a filter as in the present study. The POC/PN mass ratios of Rostad et al. (1997) and Lartiges et al. (2001) could, in part, be higher than those of this study because centrifugation would collect smaller particles that pass through filters. Rostad et al. (1997) found that POC/PN mass ratios for riverine particulate matter were in the same range as those for algae, fungi, soil biomass, and microbial cells. They concluded that the primary source of particulate matter in the Mississippi River and its tributaries is aquatic microorganisms rather than allochthonous particulate inputs. The low POC/PN mass ratios in the three Lake Erie tributary inflows of the present study may similarly indicate that a large proportion of the particulate matter in these tributaries is derived from autochthonous, rather than allochthonous, particulate sources. Allochthonous sources of particulate matter to rivers include terrestrial plants and soils. Thorp et al. (1998) found that particulate carbon/particulate nitrogen (PC/PN) mass ratios for terrestrial plants in the Ohio River watershed, U.S.A., range from 17.06 to 51.84. Herczeg et al. (2001) determined that terrestrial soil matter collected adjacent to Lake Alexandrina and the River Murray in South Australia has PC/PN mass ratios ranging from 21 to 44. The ratios for these allochthonous sources are at least three times higher than the seasonal mean POC/PN mass ratio for particulate matter in three Lake Erie tributary inflows. This suggests that other sources, with lower POC/PN ratios, must contribute significantly to the pool of suspended particulate matter in the tributaries.

Among the eastern basin nearshore sites, mean POC/PN mass ratios follow a trend opposite to that for mean POC and PN concentrations. The two shallowest Peacock Point sites (PP2, PP5) have the lowest mean POC/PN mass ratios, while the deepest Peacock Point site (L449) has the highest mean ratio (Figure 3.11). Peacock Point site PP10 and the two sites close to the lake outflow have intermediate mean ratios. Thus, POC and PN concentrations do not increase proportionately at the nearshore sites. Instead, PN concentrations increase at a faster rate than POC concentrations, as maximum site depth decreases in the nearshore environment. As was previously discussed in relation to Figure 3.6, recycling of dissolved ammonium by dreissenid mussels may increase the PN concentration and lower the POC/PN mass ratio at sites PP2 and PP5.

The eastern basin offshore sites show much less variability in terms of mean POC/PN mass ratios than the nearshore sites (Figure 3.11). All of the offshore sites have mean ratios of approximately six, which is similar to the mean ratios at nearshore sites close to the lake outflow.

Bloesch (1982) calculated POC/PN mass ratios for Lake Erie sites with maximum depths similar to those in the present study (Table 3.14). At sites of comparable depths, the mean ratios determined in 2002 average about three times greater than those determined by Bloesch (1982) for similar timeframes in 1978. The mean POC/PN mass ratios reported by Lean et al. (1983) for an eastern basin site in 1979 are greater than, but comparable to, the mean ratios at sites of similar maximum depth in 2002 (Table 3.14). Unlike the current study, Lean et al. (1983) did not acidify particulate matter samples used in the determination of POC and PN concentrations in order to remove inorganic carbon in the form of carbonate. This inclusion of carbonate minerals could result in the POC/PN mass ratios of Lean et al. (1983) being somewhat higher than the ratios for 2002. Unlike Lean et al. (1983) and the present study, Bloesch (1982) used sedimentation traps to collect particulate matter; however, this difference in methodology likely would not account for Bloesch's (1982) ratios from 1978 being so much lower than those determined by Lean et al. (1983) for 1979 and in the present research for 2002. In fact, no POC/PN mass ratios for other temperate lakes in the literature (Table 3.12) were as low as those for Bloesch (1982). The ratios of Bloesch (1982) seem to be extreme outliers from data reported for temperate lakes, including the data of the current study. In a broader comparison with temperate lakes (Table 3.15), the eastern basin of Lake Erie has lower POC/PN mass ratios than Lake Superior (Halfon, 1984; Hecky et al., 1993), other temperate lakes in northwestern Ontario (Hecky et al., 1993), and 109 temperate lakes in southeastern Norway (Hessen et al., 2003).

It is generally accepted that the carbon/nitrogen (C/N) molar ratio of marine phytoplankton is approximately 6.6 (Redfield, 1958) and this is known as the Redfield ratio. C/N ratios of freshwater phytoplankton, however, are more variable than marine phytoplankton due to variations in the availability of nitrogen and phosphorus for phytoplankton growth (Hecky et al., 1993). According to Kendall et al. (2001), freshwater particulate matter samples dominated by plankton have C/N molar ratios of less than eight, which corresponds to a C/N mass ratio of less than 7. The POC/PN mass ratios in the eastern basin of Lake Erie, ranging from 3.6 to 7.6, are more similar to the C/N mass ratio for freshwater plankton (< 7) than to the range of PC/PN mass ratios for benthic algae (8.19 – 10.11; Thorp et al., 1998), aquatic macrophytes (10.59 – 12.23; Thorp et al., 1998), terrestrial plants (17.06 – 51.84; Thorp et al., 1998), and terrestrial soil matter (21 – 44; Herczeg et al., 2001). Thus, the particulate

Table 3.14: POC/PN mass ratio data for the eastern basin of Lake Erie from this and other studies. Mean, standard deviation (SD), minimum (Min), and maximum (Max) values are provided, as well as the number of samples used in calculating these values. Thicker lines are inserted between rows to group together the values being compared.

Depth Range	Reference	Maximum Depth	Location	Date	POC/PN (mass ratio)				
					Mean	SD	Min	Max	n
9 – 11 m	Upsdell, 2005	10 m	Peacock Point (PP10)	July & October 2002	5.5	1.1	4.5	7.1	6
	Bloesch, 1982*	9 m	Port Dover	July & October 1978	2	0	2	3	4
	Upsdell, 2005	11 m	Peacock Point (L449)	June – September 2002	6.9	0.3	6.6	7.2	3
	Bloesch, 1982*	9 m	Port Dover	June – September 1978	2	1	2	3	6
	Upsdell, 2005	10 m	near outflow (L931)	June – October 2002	6.1	1.7	3.6	7.6	4
	Bloesch, 1982*	9 m	Port Dover	June – October 1978	2	1	2	3	8
19 – 25 m	Upsdell, 2005	19 m	near outflow (L439)	June – October 2002	6.2	1.0	4.8	6.9	4
		23 m	near outflow (L443)	June – October 2002	6.3	1.0	5.2	7.5	4
	Bloesch, 1982*	25 m	Port Dover	June – October 1978	2	1	1	4	8
40 – 44 m	Upsdell, 2005**	41 m	Peacock Point (L451)	June – October 2002	6.8	1.1	5.9	9.3	8
	Bloesch, 1982*	40 m	Port Dover	June – October 1978	2	1	1	2	9
	Upsdell, 2005**	44 m	near central basin (G63)	July – September 2002	5.7	0.3	5.2	6.0	6
	Bloesch, 1982*	40 m	Port Dover	July – September 1978	2	0	1	3	10
61 – 62 m	Upsdell, 2005	62 m	near central basin (G15M)	July – September 2002	5.8	0.4	5.5	6.2	3
	Lean et al., 1983*	61 m	near central basin (L23)	July – September 1979	6.3	1.0	5.0	7.5	4
	Upsdell, 2005	61 m	near central basin (L23)	June – October 2002	6.2	0.6	5.7	7.1	5
	Lean et al., 1983*	61 m	near central basin (L23)	June – October 1979	6.6	1.1	5.0	8.0	6

* The values presented here are approximate because they are calculated from sample values depicted in a graph.

** The values were adjusted to include POC/PN mass ratios at sampling depths similar to those used in Bloesch (1982) rather than only the shallowest sampling depth.

Table 3.15: POC/PN mass ratio data for the eastern basin of Lake Erie from this study and for other temperate lakes from other studies. Mean, standard deviation (SD), minimum (Min), and maximum (Max) values are provided, as well as the number of samples used in calculating these values. Thicker lines are inserted between rows to group together the values being compared.

Reference	**Location**	**Date**	**POC/PN (mass ratio)**					**Notes**
			Mean	**SD**	**Min**	**Max**	**n**	
Upsdell, 2005	Eastern Basin, Lake Erie (6 nearshore, 5 offshore sites)	June – October 2002	5.7	1.0	3.6	7.6	48	—
Halfon, 1984	Lake Superior (15 nearshore, 12 offshore sites)	June – October 1973	7.28	0.85	6.21	8.29	4	- calculated from monthly means
Hecky et al., 1993	Lake Superior	ice-free season 1990	9.7	—	—	—	6	- seasonal mean
	Lake Nipigon, Ontario		8.6	—	—	—	6	
	12 ELA* lakes, Ontario		11.4	2.1	7.1	15.3	13	- calculated from seasonal means
	6 NOLSS** lakes, Ontario		9.9	0.7	8.9	11.0	6	
Upsdell, 2005	Eastern Basin, Lake Erie (6 nearshore, 5 offshore sites)	June – August 2002	5.4	1.0	3.6	7.1	29	—
Hessen et al., 2003	109 temperate lakes, southeastern Norway	May – August 1991 & 1992	8.07	—	—	—	1	- calculated from seasonal mean POC and PN concentrations for all 109 lakes

* ELA = Experimental Lakes Area

** NOLSS = Northwestern Ontario Lake Size Series matter in the eastern basin of Lake Erie is likely derived primarily from plankton rather than other aquatic plants and allochthonous sources.

3.2.2 Eastern, Central, and Western Basins of Lake Erie

Mean POC/PN mass ratios for sampling locations in the central basin are compared with those for sampling locations in the eastern basin in Figure 3.12. In the central basin, the mean ratios are higher in the nearshore than in the offshore, ranging from 5.5 to 5.9. The mean POC/PN mass ratio for the central basin nearshore site is at the centre of the range of ratios for eastern basin nearshore sites and is higher than the ratios at sites of similar maximum depth in the eastern basin (PP2, PP5). As was previously discussed in the section regarding POC and PN concentrations, the difference in ratios between site GAsh and sites PP2 and PP5 suggests that there is a source of PN, such as recycling of dissolved ammonium by dreissenid mussels, at sites PP2 and PP5 that is not present at site GAsh. The mean ratios at the central basin offshore sites are slightly lower than those at the eastern basin offshore sites. The central basin POC/PN mass ratio data in this study are compared with previously published values for the central basin in Table 3.16. Burns and Ross (1972) and Lean et al. (1983) both found mean POC/PN mass ratios for the central basin that are higher than, but comparable to, those of the present study. Neither Burns and Ross (1972) nor Lean et al. (1983) acidified their particulate matter samples to remove carbonate, which could partly account for their ratios being higher than the current research. Both studies used coarser filters than the current research, which may also affect the POC/PN mass ratios in some unknown manner.

Figure 3.12 also shows how mean POC/PN mass ratios of sampling locations in the western basin compare with those of sampling locations in the eastern basin. The two western basin nearshore sites have low mean ratios of 5.1, which are most similar to those at nearshore sites PP2 and PP5 in the eastern basin. Despite the higher POC and PN concentrations at western basin site G91M compared with the other sites in Lake Erie, the POC/PN mass ratios at this site are similar to the other lake sites. Therefore, POC and PN are present in similar proportions at site G91M as at the other sites. No POC/PN mass ratios for the western basin were found in previously published work.

Similar to the eastern basin, the range of POC/PN mass ratios for the central and western basins (4.5 – 6.3) is more similar to values for freshwater plankton than to those for benthic algae, aquatic macrophytes, terrestrial plants, and terrestrial soil matter. Hence, the particulate matter in the central and western basins of Lake Erie is also likely derived to a greater extent from plankton than from other aquatic plants and allochthonous sources.

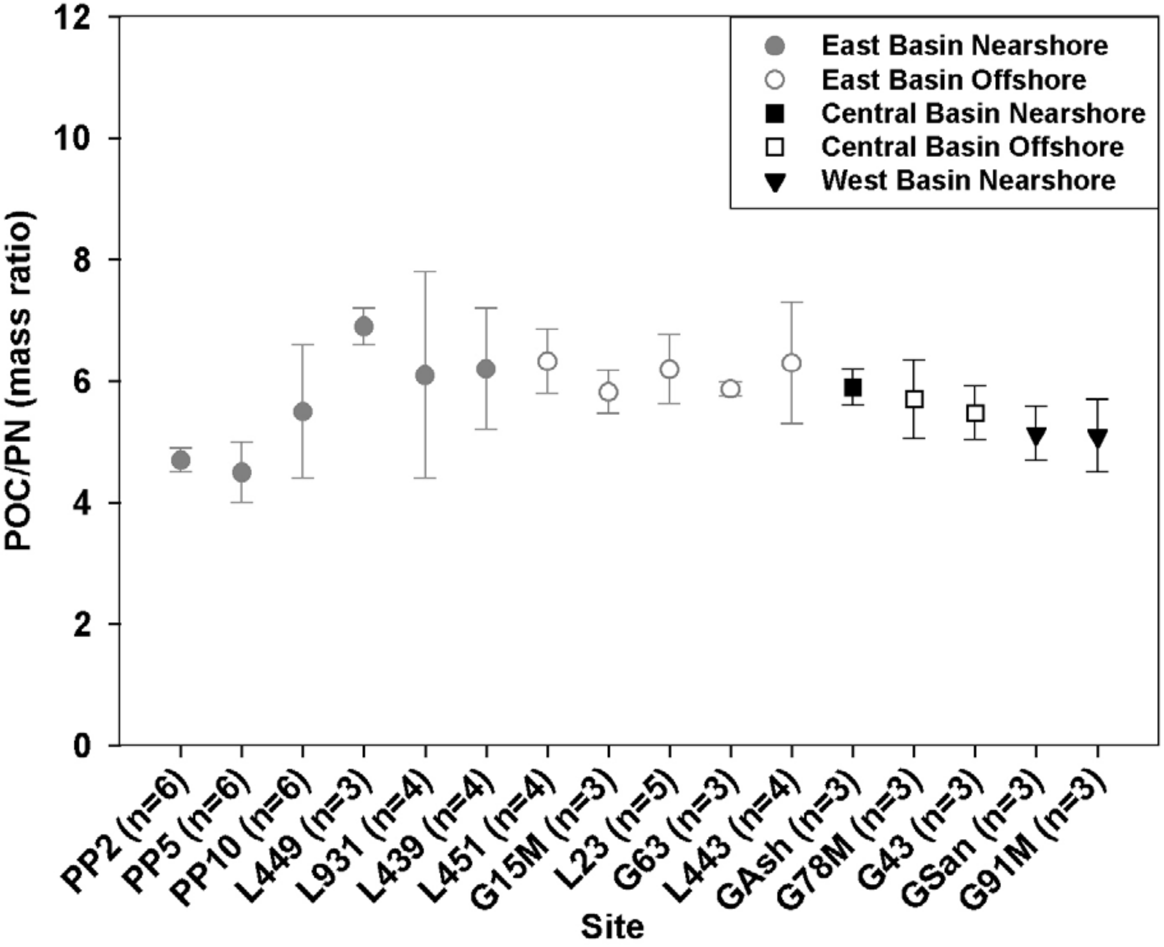


Figure 3.12: Mean POC/PN mass ratios for nearshore and offshore sites in the eastern, central, and western basins. Error bars indicate standard deviation.

Table 3.16: POC/PN mass ratio data for the central basin of Lake Erie from this and other studies. Mean, standard deviation (SD), minimum (Min), and maximum (Max) values are provided, as well as the number of samples used in calculating these values. Thicker lines are inserted between rows to group together the values being compared.

Reference	Maximum Depth	Location	Date	POC/PN (mass ratio)				
				Mean	SD	Min	Max	n
Upsdell, 2005	≥ 20 m	2 sites	July – August 2002	5.8	0.5	5.2	6.3	4
Burns and Ross, 1972*	—	25 sites	July – August 1970	6.56	0.74	5.36	7.54	6
Upsdell, 2005	≥ 20 m	near west basin (G43)	July – September 2002	5.5	0.4	5.2	6.0	3
Lean et al., 1983**	—	near west basin (G43)	July – September 1979	6.5	0.6	6.0	7.0	4

* The values presented here are for the epilimnion.

** The values presented here are approximate because they are calculated from sample values depicted in a graph.

3.3 Synthesis and Summary

3.3.1 Tributary Inflows, Lake Outflow, and Eastern Basin of Lake Erie

POC and PN concentrations and POC/PN mass ratios determined in the present study are summarized in the context of nutrient compartments involved in the nearshore shunt concept in Figure 3.13. The mean POC and PN concentrations at the tributary inflows are significantly higher (by approximately thirteen times) than those in the eastern basin of Lake Erie and the lake outflow, which may reflect differences in the sources of particulate matter between these two groupings of sites. Within the grouping of eastern basin and outflow sites, the outflow has significantly lower POC and PN concentrations than some nearshore and offshore sites in the eastern basin. The mean POC/PN mass ratios, however, are similar among the tributary inflows, eastern basin, and lake outflow. The range of POC/PN mass ratios for all sampling locations are generally comparable to those for freshwater plankton, including bacteria, and less than those for benthic algae, aquatic macrophytes, terrestrial plants, and terrestrial soil matter. The mean POC/PN mass ratios at the Lake Erie tributary inflows are lower than those at more pristine tributaries in northwestern Ontario, suggesting that the Lake Erie inflows are largely influenced by autochthonous materials, while the more pristine tributaries are more affected by allochthonous plant and soil materials. Particulate matter at the Lake Erie tributary inflows is likely derived from a mixture of autochthonous materials and somewhat enriched in PN due to fertilizer applied to cropland and manure from grazing cattle. The eastern basin and lake outflow particulate matter is probably dominated by autochthonous sources, including *in situ* photosynthetic production.

In the eastern basin of Lake Erie, POC and PN concentrations for 2002 are lower than those previously reported for the late 1970's, probably as a result of reduced phosphorus loadings that decreased total phosphorus concentrations in the lake. Also in the eastern basin, the POC concentrations are not significantly different across sites, while the PN concentrations are significantly greater at the two shallowest sampling locations, PP2 and PP5, than at some or all, respectively, of the other sites. As a result, the mean POC/PN mass ratios are lower at sites PP2 and PP5 than at the other eastern basin sites. The greater PN concentrations relative to POC concentrations at sites PP2 and PP5 than at the other sites suggests that there is a source of PN at the shallowest sites that is not present at other sites. The additional source of PN at sites PP2 and PP5 could be recycling of dissolved ammonium back into the water column by dreissenid mussels and subsequent uptake into particulate matter.

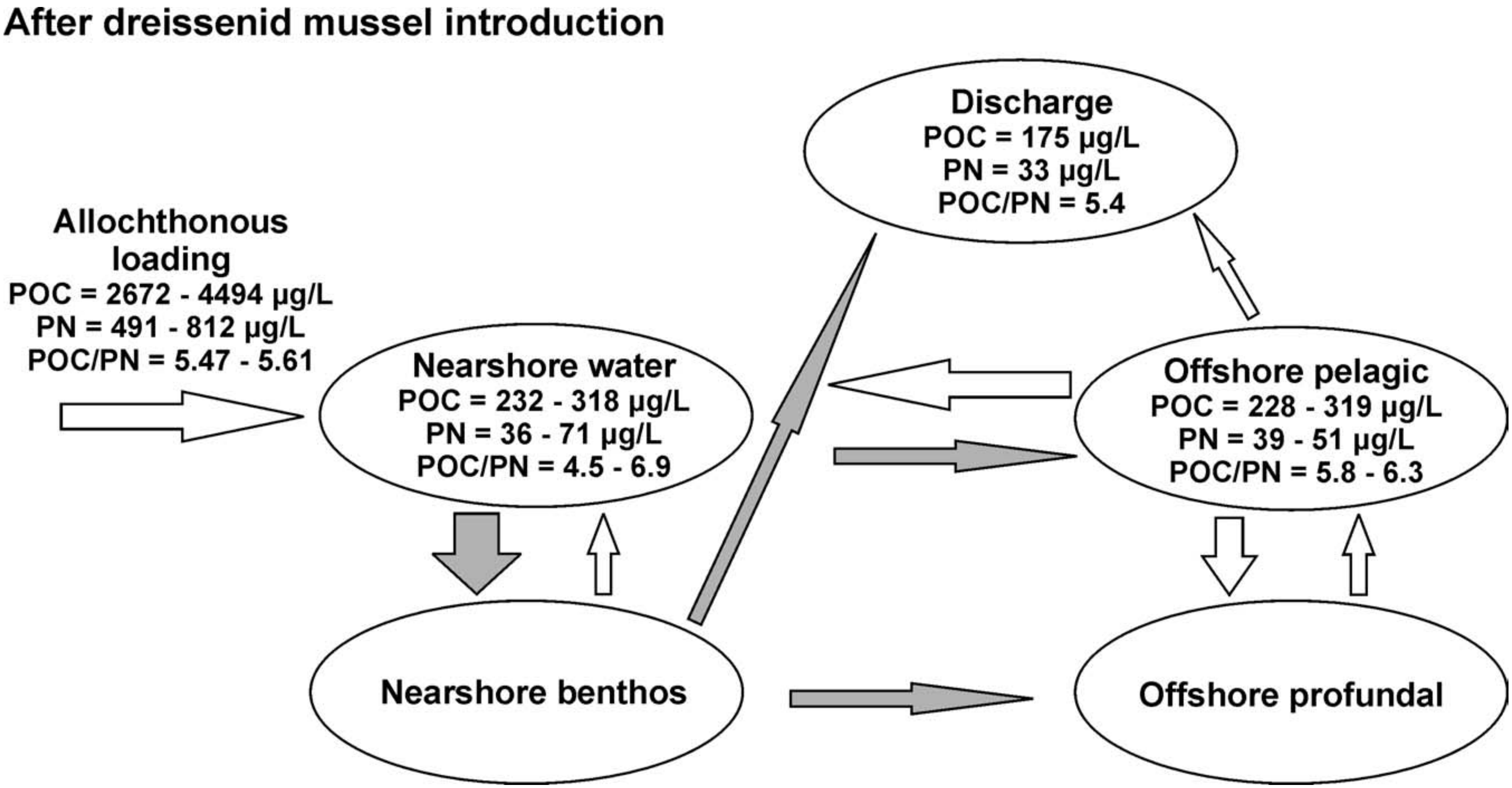


Figure 3.13: Diagram showing the nearshore shunt concept with mean values (or ranges of mean values in the cases of multiple sites per compartment) of POC and PN concentrations and POC/PN mass ratios determined in the present study for four of the six nutrient compartments. The nearshore water and offshore pelagic compartments contain data for sites in the eastern basin of Lake Erie.

3.3.2 Eastern, Central, and Western Basins of Lake Erie

Similar to the eastern basin, there is evidence that central basin POC and PN concentrations from 2002 are lower than those reported for the late 1970's. Sampling locations in the eastern and central basins do not differ significantly in terms of POC concentrations, but there are some significant differences in PN concentrations between eastern and central basin sites. Both POC and PN concentrations show significant differences between eastern and western basin sites. In fact, the POC and PN concentrations are significantly higher at western basin site G91M than at all of the other sites in Lake Erie. This is likely related to the resuspension of deposited materials and high summer algal productivity in the shallow western basin.

As in the eastern basin, the POC/PN mass ratios in the central and western basins are low and on the order of those for freshwater plankton, including bacteria. Therefore, particulate matter in the central and western basins is also probably derived primarily from autochthonous sources. In general, there is little evidence, based on either gradients in POC and PN concentrations or on the ratio of these two elements, of terrestrial plant debris and soils making a significant direct contribution to the particulate matter in Lake Erie.

Chapter 4: Carbon and Nitrogen Stable Isotopes

Carbon and nitrogen stable isotope data ($\delta^{13}C$ and $\delta^{15}N$) for samples of suspended matter collected from Lake Erie, three tributary inflows, and the lake outflow are presented and discussed in this chapter. The chapter begins with a brief discussion of the descriptive statistics for each sampling location. The isotope data are compared for the tributary inflows, lake outflow, and eastern basin of Lake Erie. Then, further within-lake comparisons of the eastern, central, and western basins of Lake Erie are made with respect to $\delta^{13}C$ and $\delta^{15}N$. The chapter concludes with a summary of the important findings from the isotope data, followed by a synthesis of the isotope data with the POC and PN concentration and POC/PN mass ratio data.

4.1 Carbon and Nitrogen Stable Isotopes

The $\delta^{13}C$ and $\delta^{15}N$ data for each sampling location are summarized in Table 4.1 and all isotope data are listed in Table A.2 of the Appendix. The data show some temporal variability in $\delta^{13}C$ and $\delta^{15}N$, but this variability is within the range of previously published $\delta^{13}C$ and $\delta^{15}N$ values for possible sources of particulate matter in freshwater systems (Tables 4.2, 4.3). For example, $\delta^{13}C$ values for the lake sites range from –26.84 to –20.51 (Table 4.1) and values in this range reflect signatures of terrestrial C_3 and CAM plants, soil organic matter, aquatic macrophytes, phytoplankton, and sewage particulate organic matter (Table 4.2). The $\delta^{15}N$ values for the lake sites range from 1.62 to 8.76 (Table 4.1) and values in this range have been reported for terrestrial plants, soil, synthetic fertilizer, sewage, aquatic macrophytes, plankton, and bacteria (Table 4.3). The mean $\delta^{13}C$ and $\delta^{15}N$ values are not skewed by single high or low values.

The $\delta^{13}C$ and $\delta^{15}N$ signatures of particulate matter from tributary inflows change over time due to shifts in the relative contributions of different carbon and nitrogen sources (Barth et al., 1998), such as terrestrial plant debris and soil, animal and human waste, and algal production. Temporal trends in $\delta^{13}C$ and $\delta^{15}N$ differ among the three inflows (Figure 4.1). At the Grand River, $\delta^{13}C$ increases as $\delta^{15}N$ decreases over the study period. By contrast, $\delta^{13}C$ and $\delta^{15}N$ vary similarly over time at Sandusk Creek and in an unrelated manner over time at Nanticoke Creek. $\delta^{13}C$ and $\delta^{15}N$ values at the lake outflow do not exhibit similar temporal trends to the values at any of the tributary inflows and the outflow $\delta^{13}C$ and $\delta^{15}N$ signatures are less variable than the inflow signatures (Figure 4.1).

Within Lake Erie, the $\delta^{13}C$ and $\delta^{15}N$ signatures of particulate matter change over time due mainly to the availability of different forms of carbon and nitrogen used in primary production and to degradation processes (Hodell and Schelske, 1998; McCusker et al., 1999). Signatures of $\delta^{13}C$ and $\delta^{15}N$ are variable over depth at individual sites in the lake, so only data for the shallowest depth sampled at

Table 4.1: Mean, standard deviation (SD), minimum (Min), and maximum (Max) δ^{13}C and δ^{15}N values for all sampling locations. The number of samples analyzed (n) is also indicated. The maximum site depths are given in brackets after the lake site names.

Site Grouping	Site	δ^{13}C (‰)					δ^{15}N (‰)				
		Mean	SD	Min	Max	n	Mean	SD	Min	Max	n
Inflows	Grand River	-30.79	0.90	-31.88	-29.48	11	9.85	1.31	8.30	12.05	11
	Sandusk Creek	-30.05	2.02	-32.19	-25.52	11	7.87	1.74	4.84	9.83	11
	Nanticoke Creek	-30.22	2.07	-33.31	-27.45	11	10.10	1.43	6.37	11.67	11
Outflow	Outflow	-23.29	0.92	-25.15	-22.16	11	5.88	0.99	4.27	7.94	11
Eastern Basin Nearshore Peacock Point	PP2 (2 m)	-24.25	0.97	-25.07	-23.18	3	7.65	0.21	7.51	7.89	3
	PP5 (5 m)	-24.73	1.15	-26.05	-24.04	3	7.84	0.57	7.31	8.44	3
	PP10 (10 m)	-24.94	1.29	-25.91	-23.48	3	8.14	0.59	7.58	8.76	3
	L449* (11 m)	-23.78	0.81	-24.45	-22.66	4	5.02	2.33	1.62	6.71	4
Eastern Basin Nearshore Near Outflow	L931* (10 m)	-24.74	0.32	-24.97	-24.51	2	3.76	2.09	2.28	5.23	2
	L439* (19 m)	-25.65	0.44	-26.30	-25.32	4	3.51	0.82	2.63	4.59	4
Eastern Basin Offshore	L451* (41 m)	-24.82	0.81	-25.74	-24.18	3	5.76	2.41	3.06	7.72	3
	G15M (62 m)	-25.57	0.72	-26.31	-24.86	3	5.48	1.10	4.38	6.58	3
	L23* (61 m)	-25.69	0.69	-26.56	-24.94	4	6.82	1.88	4.13	8.16	4
	G63 (44 m)	-24.77	1.21	-25.94	-23.54	3	5.42	0.74	4.79	6.24	3
	L443* (23 m)	-25.48	0.68	-26.25	-24.60	4	5.15	1.68	2.68	6.28	4
Central Basin Nearshore	GAsh (5 m)	-24.16	3.28	-26.84	-20.51	3	5.98	0.75	5.11	6.46	3
Central Basin Offshore	G78M (21 m)	-25.21	1.47	-26.24	-23.52	3	5.26	0.34	4.90	6.58	3
	G43 (20 m)	-25.54	0.76	-26.40	-24.97	3	6.26	1.41	5.29	7.87	3
Western Basin Nearshore	GSan (11 m)	-24.54	0.84	-25.29	-23.63	3	6.43	0.23	6.24	6.69	3
	G91M (8 m)	-23.42	1.28	-24.68	-22.13	3	5.29	1.13	4.62	6.60	3

* Particulate organic matter was sampled using a sedimentation trap.

Table 4.2: Ranges of previously published δ^{13}C values for various sources of particulate matter to rivers and lakes.

Source		δ^{13}C Range (‰)	Reference	Notes
Terrestrial Plants	C_3	-32 to -22	Kendall et al., 2001	- compiled from various sources - typical average value = -27 ‰
	C_4	-16 to -9	Kendall et al., 2001	- compiled from various sources - typical average value = -13 ‰
	CAM	-34 to -11	Deines, 1980	- compiled from various sources
Soil Organic Matter		-32 to -9	Kendall et al., 2001	- based upon typical ranges for C_3 and C_4 plants, since δ^{13}C of soil organic matter reflects δ^{13}C of plants growing on soil
Aquatic Macrophytes		-36 to -6	Deines, 1980	- compiled from various sources
Phytoplankton		-36 to -16	LaZerte, 1983; Grey et al., 2000	- for Lake Memphremagog, Québec, and 16 lakes in United Kingdom
Bacteria		-29 to -27	Embury, 2000	- for water column of Lake 164, Experimental Lakes Area in northern Ontario
Sewage Particulate Organic Matter		-29 to -21	Maksymowska et al., 2000	- compiled from various sources

Table 4.3: Ranges of previously published δ^{15}N values for various sources of particulate matter to rivers and lakes.

Source	δ^{15}N Range (‰)	Reference	Notes
Terrestrial Plants	-10 to +10	Kendall et al., 2001	—
Soil	-10 to +15	Kendall, 1998	—
Synthetic Fertilizer	-3 to +3	Kendall, 1998	—
Animal Manure	+10 to +20	Kendall et al., 2001	- compiled from various sources
Sewage	-10 to +32	Kendall, 1998	- compiled from various sources
Aquatic Macrophytes	-10 to +11	Talbot, 2001; Thorp et al., 1998	- partly, for the Ohio River
Phytoplankton	0 to +11	Cloern et al., 2002	- for freshwater areas of San Francisco Bay estuarine system
Bacteria	+1 to +4	Embury, 2000	- for water column of Lake 164, Experimental Lakes area in northern Ontario

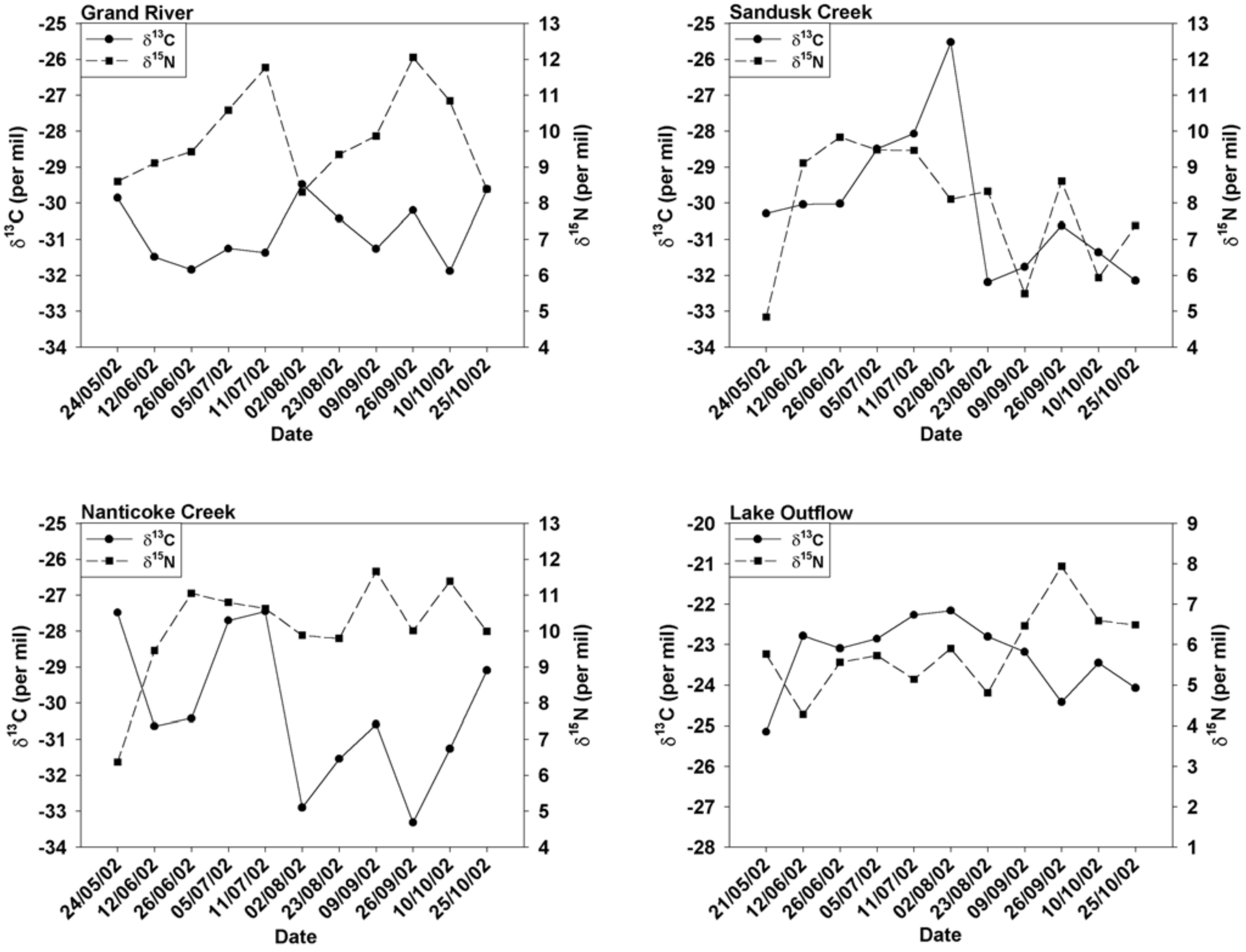


Figure 4.1: Temporal variation in $\delta^{13}C$ and $\delta^{15}N$ for the three tributary inflows and the lake outflow. Note the change in scales for the lake outflow graph.

each lake site were used in the calculation of the site mean $\delta^{13}C$ and $\delta^{15}N$. $\delta^{13}C$ and $\delta^{15}N$ values of the Lake Erie sites consistently sampled on similar dates (those belonging to the same series of sites; i.e. PP, L, or G) do not always vary in a similar manner over time like the POC and PN concentration data for these sites do (Figures 4.2, 4.3). Similar to the lake outflow, the $\delta^{13}C$ and $\delta^{15}N$ signatures at the lake sites are less variable than the inflow signatures.

4.1.1 Tributary Inflows, Lake Outflow, and Eastern Basin of Lake Erie

The mean $\delta^{13}C$ values for the three tributary inflows range between –31 and –30 ‰, while those for the eastern basin range between –26 and –23 ‰ and the lake outflow mean value is approximately –23 ‰ (Figure 4.4). The inflows have significantly lower $\delta^{13}C$ signatures than the eastern basin and outflow (ANOVA, $F = 20.15$, $\alpha = 0.05$; Table 4.4), which suggests that the sources of, or processes influencing, particulate matter at the inflow sites differ from those at the eastern basin and outflow sites.

The mean $\delta^{15}N$ values for the three tributary inflows range between 7 and 11 ‰, while those for the eastern basin range between 3 and 9 ‰ and the lake outflow mean value is approximately 6 ‰ (Figure 4.4). The mean $\delta^{15}N$ value for Nanticoke Creek is significantly higher than those at all eastern basin sites and the lake outflow, while the mean $\delta^{15}N$ value for the Grand River is significantly higher than those at all but one site (PP10) in the eastern basin and than that at the lake outflow (ANOVA, $F = 10.03$, $\alpha = 0.05$; Table 4.5). The mean $\delta^{15}N$ value for Sandusk Creek is significantly greater than those at most eastern basin sites and the lake outflow; however, it is not significantly different from those at three nearshore Peacock Point sites (PP2, PP5, PP10) and one offshore site (L23; ANOVA, $F = 10.03$, $\alpha = 0.05$). Hence, the $\delta^{15}N$ signatures of the tributary inflows are not as distinct from those of the eastern basin and lake outflow as the $\delta^{13}C$ signatures are. This suggests that, in addition to differences in the sources of particulate matter between the inflows and the eastern basin sites, there may also be differences in the sources, or in the relative proportions of the sources, of particulate matter among the inflow and eastern basin groupings of sites. Since the $\delta^{13}C$ signatures of the tributary inflows and the eastern basin sites point toward these two groups of sites having different sources of particulate matter and the $\delta^{15}N$ signatures are very heterogeneous among the eastern basin sites (Table 4.5), the variation in $\delta^{15}N$ is strongly influenced by within-lake processes.

Researchers have characterized suspended particulate matter using carbon stable isotopes in the ocean (Ostrom et al., 1997), estuaries (Cloern et al., 2002), lakes (Grey et al., 2000), and rivers (Onstad et al., 2000). Few studies, however, report $\delta^{13}C$ signatures for suspended particulate matter of lakes in areas with temperate climates, including the Laurentian Great Lakes. No previously published $\delta^{13}C$ values were found for rivers flowing into the Laurentian Great Lakes, but some data are available for

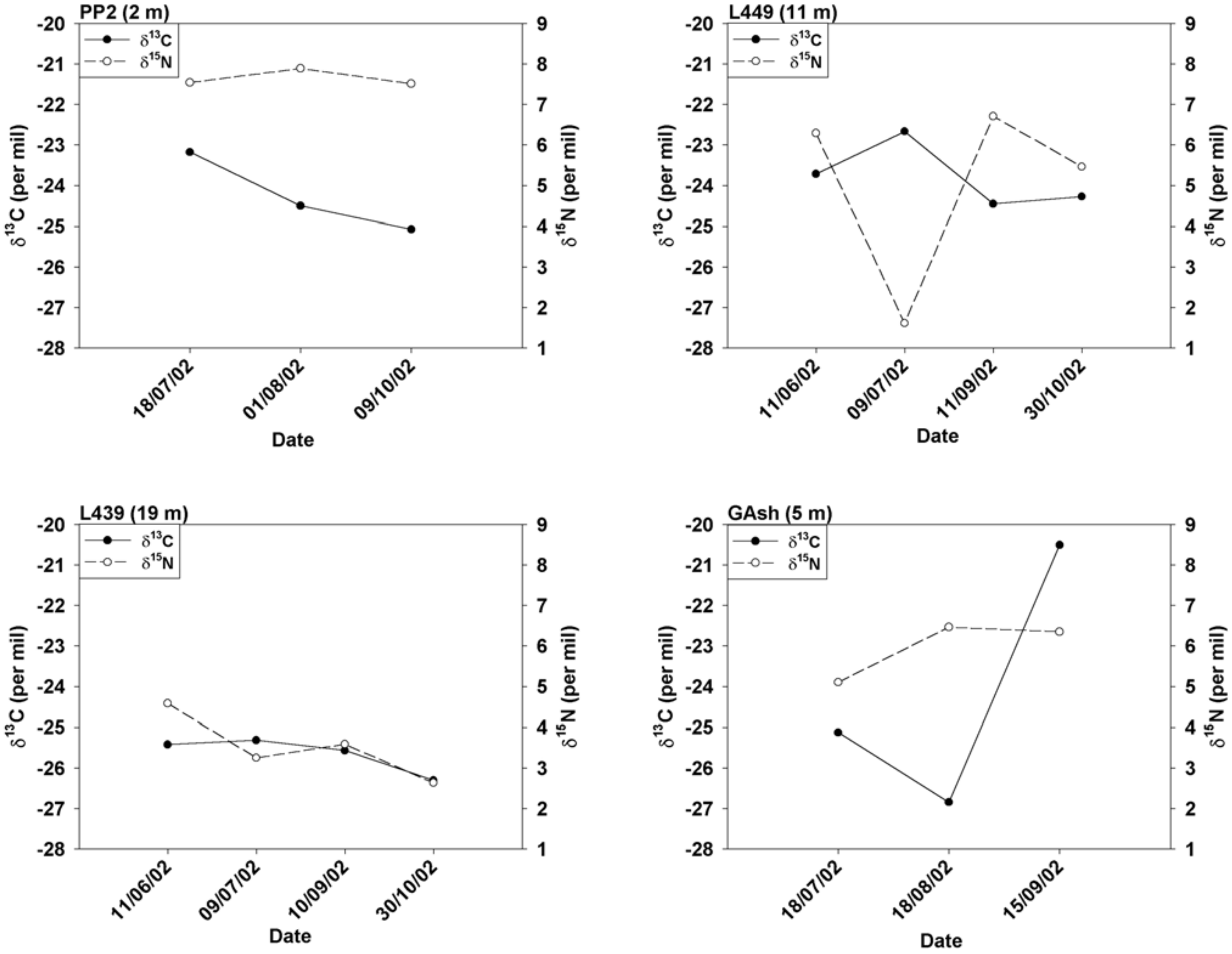


Figure 4.2: Temporal variation in $\delta^{13}C$ and $\delta^{15}N$ for four nearshore sites in Lake Erie. The maximum site depths are given after the site names.

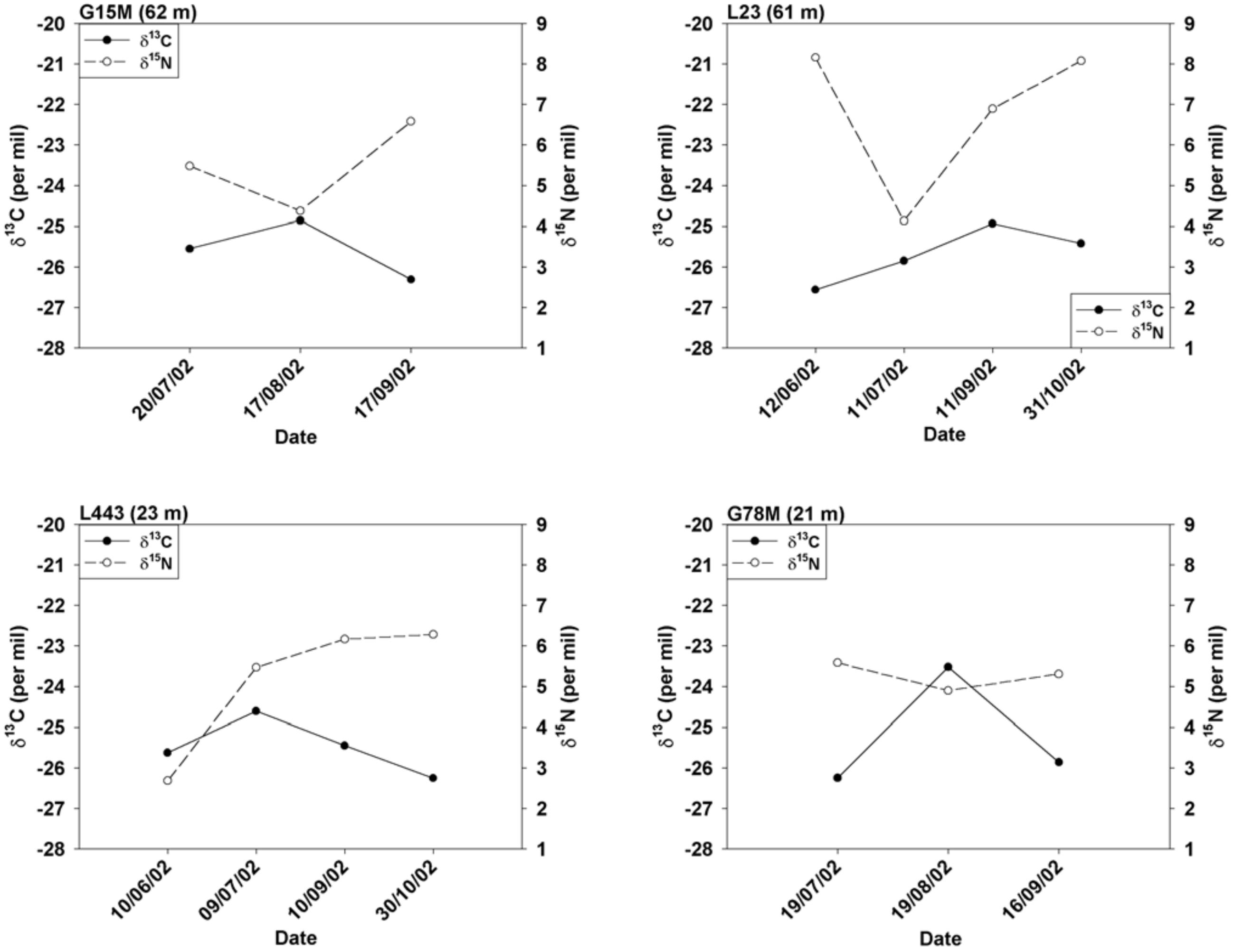


Figure 4.3: Temporal variation in $\delta^{13}C$ and $\delta^{15}N$ for four offshore sites in Lake Erie. The maximum site depths are given after the site names.

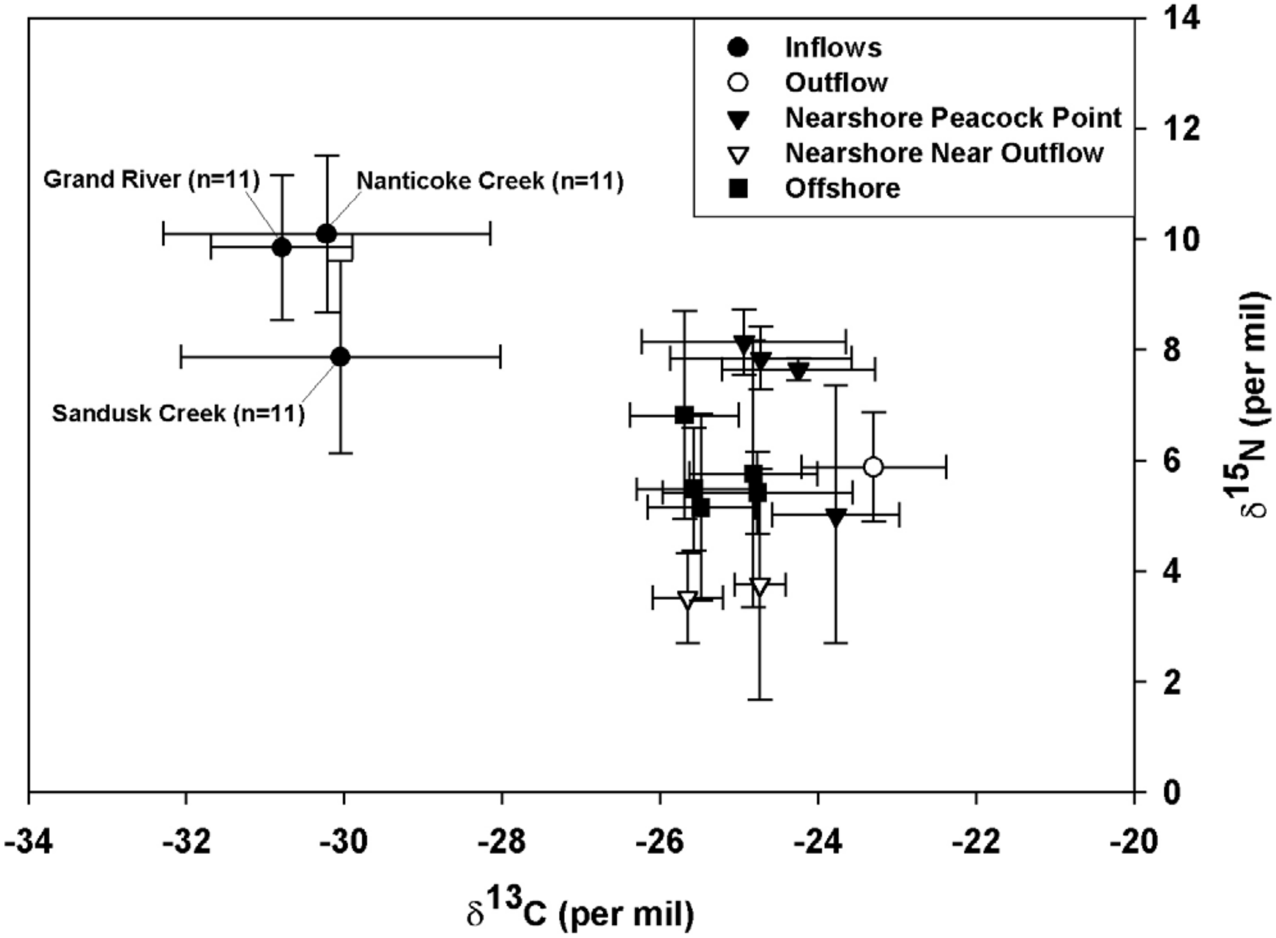


Figure 4.4: Mean δ^{13}C and δ^{15}N for three tributary inflows, the lake outflow, and all sites in the eastern basin. Error bars indicate standard deviation.

Table 4.4: Results of a univariate ANOVA comparing the mean $\delta^{13}C$ values of different sites ($F = 20.15$, $\alpha = 0.05$). The symbol ❋ indicates that there is a significant difference in the $\delta^{13}C$ between sites.

Site	GR	SC	NC	Out	PP2	PP5	PP10	L449	L931	L439	L451	G15M	L23	G63	L443	GAsh	G78M	G43	GSan	G91M
GR				❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋
SC				❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋
NC				❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋
Out	❋	❋	❋							❋		❋	❋		❋		❋	❋		
PP2	❋	❋	❋																	
PP5	❋	❋	❋																	
PP10	❋	❋	❋																	
L449	❋	❋	❋																	
L931	❋	❋	❋																	
L439	❋	❋	❋	❋																❋
L451	❋	❋	❋																	
G15M	❋	❋	❋	❋																
L23	❋	❋	❋	❋																❋
G63	❋	❋	❋																	
L443	❋	❋	❋	❋																
GAsh	❋	❋	❋																	
G78M	❋	❋	❋	❋																
G43	❋	❋	❋	❋																
GSan	❋	❋	❋																	
G91M	❋	❋	❋							❋			❋							

Table 4.5: Results of a univariate ANOVA comparing the mean $\delta^{15}N$ values of different sites ($F = 10.03$, $\alpha = 0.05$). The symbol ❋ indicates that there is a significant difference in the $\delta^{15}N$ between sites.

Site	GR	SC	NC	Out	PP2	PP5	PP10	L449	L931	L439	L451	G15M	L23	G63	L443	GAsh	G78M	G43	GSan	G91M
GR		❋		❋	❋	❋		❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋
SC	❋		❋	❋				❋	❋	❋	❋	❋		❋	❋	❋	❋			❋
NC		❋		❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋	❋
Out	❋	❋	❋			❋	❋		❋	❋										
PP2	❋		❋					❋	❋	❋					❋		❋			❋
PP5	❋		❋	❋				❋	❋	❋		❋		❋	❋		❋			❋
PP10			❋	❋				❋	❋	❋	❋	❋		❋	❋		❋			❋
L449	❋	❋	❋		❋	❋	❋													
L931	❋	❋	❋	❋	❋	❋	❋						❋						❋	
L439	❋	❋	❋	❋	❋	❋	❋				❋		❋			❋		❋	❋	
L451	❋	❋	❋				❋			❋										
G15M	❋	❋	❋			❋	❋													
L23	❋		❋						❋	❋										
G63	❋	❋	❋			❋	❋													
L443	❋	❋	❋		❋	❋	❋													
GAsh	❋	❋	❋							❋										
G78M	❋	❋	❋		❋	❋	❋													
G43	❋		❋							❋										
GSan	❋		❋						❋	❋										
G91M	❋	❋	❋		❋	❋	❋													

temperate rivers. While the tributary inflows of the present study have lower δ^{13}C signatures than the eastern basin of Lake Erie, temperate rivers in general have mean δ^{13}C signatures that fall within the range of those for temperate lakes (Table 4.6).

Relative to carbon stable isotopes, fewer researchers have characterized suspended particulate matter using nitrogen stable isotopes. δ^{15}N has been used in varied environments, including the ocean (Ostrom et al., 1997), estuaries (Cloern et al., 2002), lakes (Hodell and Schelske, 1998), and rivers (Kendall et al., 2001). Nevertheless, few studies report the δ^{15}N composition of suspended particulate matter in the Laurentian Great Lakes. While no previously published δ^{15}N values were found for rivers flowing into the Laurentian Great Lakes, some data are available for other temperate rivers. In the present study, the range of mean δ^{15}N signatures for tributary inflows and the eastern basin of Lake Erie partially overlap, with the range for the inflows extending above that of the eastern basin and the range for the eastern basin extending below that of the inflows (Figure 4.4). δ^{15}N data for temperate rivers and lakes, however, are similar in the two environments (Table 4.7).

There are no significant differences in δ^{13}C among the tributary inflows (ANOVA, $F = 20.15$, $\alpha = 0.05$; Table 4.4) and the order from lowest to highest is: Grand River < Nanticoke Creek < Sandusk Creek. The δ^{13}C values for the three inflows range from about –34 to –25 ‰ and this range corresponds to the range of values previously published for terrestrial C_3 and CAM plants, soil organic matter, aquatic macrophytes, phytoplankton, bacteria, and sewage particulate organic matter (Table 4.2). It does not correspond to the range of values reported for terrestrial C_4 plants (Table 4.2).

While the δ^{15}N signatures of the Grand River and Nanticoke Creek do not differ significantly from one another, both are significantly higher than that of Sandusk Creek (ANOVA, $F = 10.03$, $\alpha = 0.05$; Table 4.5). The order of the tributary inflows from lowest to highest δ^{15}N signature is: Sandusk Creek < Grand River < Nanticoke Creek. The δ^{15}N values for the three inflows range from approximately four to twelve per mil, which corresponds to the range of values previously reported for terrestrial plants, soil, animal manure, sewage, aquatic macrophytes, phytoplankton, and bacteria, but not to the range of values reported for synthetic fertilizer (Table 4.3).

Since no previously published δ^{13}C data are available for rivers flowing into Lake Erie or into the other Laurentian Great Lakes, the δ^{13}C data for the tributary inflows in the present study are compared with data previously published for other temperate rivers (Table 4.8). Kendall et al. (2001) measured δ^{13}C in suspended particulate matter of five temperate river systems in the U.S.A. The mean δ^{13}C values for those five systems range between two and five per mil greater than the mean δ^{13}C value for the three tributary inflows in the current study. The differences in δ^{13}C may be partially related to the timing of sampling, as Kendall et al. (2001) sampled particulate matter throughout the year, while

Table 4.6: $\delta^{13}C$ data from previously published research for temperate rivers and lakes. Mean, standard deviation (SD), minimum (Min), and maximum (Max) values are provided, as well as the number of samples used in calculating these values.

System	Reference	Location	Date	$\delta^{13}C$ (‰)				
				Mean	SD	Min	Max	n
River	Kendall et al., 2001	Missouri River (5 sites) and 2 tributaries (1 site each), U.S.A.	October 1996 – September 1997	-26.2	3.1	-32.1	-22.6	7
		Ohio River (3 sites) and 2 tributaries (1 site each), U.S.A.		-27.4	0.9	-28.6	-26.3	5
		Mississippi River (3 sites)		-25.5	0.9	-26.4	-24.6	3
		Colorado River (1 site) and 2 tributaries (1 site each), U.S.A.		-25.8	1.1	-26.6	-24.5	3
		Columbia River (4 sites) and 2 tributaries (1 site each), U.S.A.		-28.0	0.4	-28.6	-27.7	6
	Martinotti et al., 1997	Po River (2 sites), Italy	September 1995	-26.3	0.2	-26.4	-26.1	2
	Maksymowska et al., 2000*	Vistula River, Poland	May – October 1996	-28.5	1.0	-29.5	-27.0	5
Lake	Hodell and Schelske, 1998*	Eastern Basin, Lake Ontario (1 offshore site)	May – October 1993 – 1995	-26.0	1.4	-28.9	-23.4	30
	Leggett et al., 1999	Lake Ontario (2 offshore sites)	May – June 1995	-28.9	0.7	-29.4	-27.8	5
	Meyers and Eadie, 1993**	Lake Michigan (2 offshore sites)	June – November 1980	-27.6	0.9	-29.2	-26.2	10
	McCusker et al., 1999*	Grand Traverse Bay, Lake Michigan (2 offshore sites)	May – September 1997	-27.2	1.8	-30.0	-25.0	13
	Ostrom et al., 1998*	Lake Superior (3 offshore sites)	June 1994	-27.3	0.5	-27.7	-26.7	3
	Grey et al., 2000	13 lakes, United Kingdom	May – July 1998	-25.6	3.5	-30.8	-21.1	13
		11 lakes, United Kingdom	May – October 1998	-23.6	4.1	-35.0	-19.5	22

* The values presented here are approximate because they are calculated from sample values depicted in a graph.

** The values presented here are calculated from sample values for material collected over 142 days using 5 sediment traps, deployed at different depths, for each site.

Table 4.7: $\delta^{15}N$ data from previously published research for temperate rivers and lakes. Mean, standard deviation (SD), minimum (Min), and maximum (Max) values are provided, as well as the number of samples used in calculating these values.

System	Reference	Location	Date	$\delta^{15}N$ (‰)				
				Mean	SD	Min	Max	n
River	Kendall et al., 2001	Missouri River (5 sites) and 2 tributaries (1 site each), U.S.A.	October 1996 – September 1997	4.0	2.7	-0.8	7.5	7
		Ohio River (3 sites) and 2 tributaries (1 site each), U.S.A.		5.3	1.2	4.0	6.7	5
		Mississippi River (3 sites)		7.7	1.5	6.7	9.4	3
		Colorado River (1 site) and 2 tributaries (1 site each), U.S.A.		5.0	0.6	4.3	5.5	3
		Columbia River (4 sites) and 2 tributaries (1 site each), U.S.A.		2.0	1.9	-1.0	3.8	6
	Martinotti et al., 1997	Po River (2 sites), Italy	September 1995	6.3	1.0	5.6	7.0	2
	Maksymowska et al., 2000*	Vistula River, Poland	May – October 1996	4.7	2.6	2.5	9.0	5
Lake	Hodell and Schelske, 1998*	Eastern Basin, Lake Ontario (1 offshore site)	May – October 1993 – 1995	7.6	1.7	4.7	10.8	30
	Leggett et al., 1999	Lake Ontario (2 offshore sites)	May – June 1995	4.4	1.7	2.5	7.2	5
	Meyers and Eadie, 1993**	Lake Michigan (2 offshore sites)	June – November 1980	3.9	0.8	3.3	5.2	5
	McCusker et al., 1999*	Grand Traverse Bay, Lake Michigan (2 offshore sites)	May – September 1997	5.1	2.2	3.0	11.5	13
	Ostrom et al., 1998*	Lake Superior (2 offshore sites)	June 1994	1.7	2.1	0.2	3.2	2

* The values presented here are approximate because they are calculated from sample values depicted in a graph.

** The values presented here are calculated from sample values for material collected over 142 days using 5 sediment traps, deployed at different depths, for each site.

Table 4.8: δ^{13}C data for the three tributary inflows and lake outflow from this study compared with data for temperate rivers from other studies. Mean, standard deviation (SD), minimum (Min), and maximum (Max) values are provided, as well as the number of samples used in calculating these values. Thicker lines are inserted between rows to group together the values being compared.

System	Reference	Location	Date	δ^{13}C (‰)				
				Mean	**SD**	**Min**	**Max**	**n**
Tributary Inflows	Upsdell, 2005	Grand River, Sandusk Creek, Nanticoke Creek	May – October 2002	-30.35	1.72	-33.31	-25.52	33
	Kendall et al., 2001	Missouri River (5 sites) and 2 tributaries (1 site each), U.S.A.	October 1996 – September 1997	-26.2	3.1	-32.1	-22.6	7
		Ohio River (3 sites) and 2 tributaries (1 site each), U.S.A.		-27.4	0.9	-28.6	-26.3	5
		Mississippi River (3 sites)		-25.5	0.9	-26.4	-24.6	3
		Colorado River (1 site) and 2 tributaries (1 site each), U.S.A.		-25.8	1.1	-26.6	-24.5	3
		Columbia River (4 sites) and 2 tributaries (1 site each), U.S.A.		-28.0	0.4	-28.6	-27.7	6
	Upsdell, 2005	Grand River, Sandusk Creek, Nanticoke Creek	September 2002	-31.29	1.14	-33.31	-30.20	6
	Martinotti et al., 1997	Po River (2 sites), Italy	September 1995	-26.3	0.2	-26.4	-26.1	2
	Upsdell, 2005	Grand River, Sandusk Creek, Nanticoke Creek	May – October 2002	-30.35	1.72	-33.31	-25.52	33
	Maksymowska et al., 2000*	Vistula River, Poland	May – October 1996	-28.5	1.0	-29.5	-27.0	5
Lake Outflow	Upsdell, 2005	Lake Erie outflow	21 May 2002	-25.15	—	—	—	1
	Barth et al., 1998	St. Lawrence River (Lake Ontario outflow)	29 May 1995	-30.0	—	—	—	1
	Upsdell, 2005	Lake Erie outflow	11 July 2002	-22.27	—	—	—	1
	Barth et al., 1998	St. Lawrence River (Lake Ontario outflow)	14 July 1994	-27.4	—	—	—	1
	Upsdell, 2005	Lake Erie outflow	10 October 2002	-23.45	—	—	—	1
			25 October 2002	-24.07	—	—	—	1
	Barth et al., 1998	St. Lawrence River (Lake Ontario outflow)	17 October 1995	-28.5	—	—	—	1

* The values presented here are approximate because they are calculated from sample values depicted in a graph.

particulate matter at the three Lake Erie tributaries were sampled between May and October. Kendall et al. (2001) state that many of their sampling locations show a decrease in $\delta^{13}C$ signatures between early spring and late fall, so it is possible that the period during which the Lake Erie inflows were sampled corresponds to the half of the year when particulate matter tends to be depleted in ^{13}C relative to the other half of the year. Other factors that could account for Kendall et al. (2001) having higher mean $\delta^{13}C$ values than the present research include the locations of sampling along the rivers (headwaters versus river mouths), variations in the amount of precipitation and runoff in the catchment areas, and differences in watershed land use. Similar to the rivers discussed in Kendall et al., (2001), the Po River in Italy (Martinotti et al., 1997) has a mean $\delta^{13}C$ value that is five per mil greater, and the Vistula River in Poland (Maksymowska et al., 2000) has a mean $\delta^{13}C$ value that is approximately two per mil greater, than that for the three tributary inflows of the current research. These differences could be influenced by variations in the type and pore size of the filters used to collect particulate matter and in acidification methodology. Particulate matter was collected from the Po (Martinotti et al., 1997) and Vistula (Maksymowska et al., 2000) Rivers using GF/F glass fibre filters of 0.7-µm pore size; whereas, particulate matter was collected from the Lake Erie inflows using QM/A quartz fibre filters of 0.8-µm pore size. Maksymowska et al. (2000) acidified the filters by fuming them with 6 N HCl, while the filters of the present study were acidified by filtering 10 % HCl through them. It is more likely, however, that differences in the $\delta^{13}C$ signatures between the tributary inflows of the current research and the Po and Vistula Rivers are related to differences in the characteristics of the rivers and their catchment areas. For example, the Po River passes through heavily industrialized areas of Italy (Martinotti et al., 1997), while the tributary inflows of the present study are surrounded by predominantly agricultural areas. Nevertheless, the data generally indicate that the three Lake Erie tributary inflows are less enriched in ^{13}C than other temperate rivers.

The Lake Erie outflow $\delta^{13}C$ signatures from this study are compared with previously reported data for the St. Lawrence River, which is the Lake Ontario outflow, in Table 4.8. The Lake Erie outflow has mean $\delta^{13}C$ values that are consistently about four to five per mil greater than those for the Lake Ontario outflow (Barth et al., 1998). The dissimilarity in the $\delta^{13}C$ signatures of the two outflows may be partly related to the type and pore size of the filters used to collect particulate matter. While the present study used QM/A quartz fibre filters of 0.8-µm pore size, Barth et al. (1998) used GF/C glass fibre filters of 1.2-µm pore size to collect particulate matter. It is not known, however, how differences in filter type and pore size influence the $\delta^{13}C$ signatures of particulate matter. The difference in $\delta^{13}C$ signatures between the two outflows may also reflect variability in the within-lake processes between Lakes Erie and Ontario.

No previously published $\delta^{15}N$ data were found for rivers flowing into Lake Erie or into the other Laurentian Great Lakes. The $\delta^{15}N$ data for tributary inflows in the present study are compared with data reported previously for temperate rivers (Table 4.9). The five river systems in the U.S.A. studied by Kendall et al. (2001) have mean $\delta^{15}N$ values that are one to eight per mil lower than the mean value for the three Lake Erie inflows. The differences in $\delta^{15}N$ could be partly related to variation in the sampling periods of the two studies. Kendall et al. (2001) note that there was an increase in $\delta^{15}N$ values at many of their sites during the growing season. $\delta^{15}N$ signatures at Lake Erie tributary inflows may be similarly inflated during the growing season. If the three inflows of the current research had been sampled throughout the year, as per Kendall et al. (2001), $\delta^{15}N$ during the November-to-April period may have reduced the mean $\delta^{15}N$. Variations in the locations of sampling along the rivers, the amount of precipitation and runoff in the catchment areas, and watershed land use could also lead Kendall et al. (2001) to have lower mean $\delta^{15}N$ values than the current research. The Po (Martinotti et al., 1997) and Vistula (Maksymowska et al., 2000) Rivers have mean $\delta^{15}N$ signatures that are approximately three and five per mil lower, respectively, than the mean signature for the three Lake Erie inflows. Similar to $\delta^{13}C$, these differences could be influenced by several factors. These include variations in the type and pore size of the filters used to collect particulate matter, acidification methodology, land use in the river watersheds, and the sources and cycling of nutrients in these systems. Generally, the data indicate that the three Lake Erie tributary inflows are more enriched in ^{15}N than other temperate rivers. No previously published $\delta^{15}N$ data are available for lake outflows.

Figure 4.5 depicts the $\delta^{13}C$ and $\delta^{15}N$ isotopic signatures of the eastern basin and outflow sites with the tributary inflow data removed. Among the eastern basin nearshore sites, the mean $\delta^{13}C$ signatures range between –25.65 (L439) and –23.78 ‰ (L449) and there are no significant differences between the sites in terms of $\delta^{13}C$ (ANOVA, $F = 20.15$, $\alpha = 0.05$; Table 4.4). The mean $\delta^{15}N$ signatures for eastern basin nearshore sites range from between three and four per mil at sites close to the lake outflow to approximately eight per mil at the three shallowest sites at Peacock Point (PP2, PP5, PP10). The deepest nearshore Peacock Point site has a mean $\delta^{15}N$ signature of approximately five per mil, lower than those for the other Peacock Point sites. The $\delta^{15}N$ values at nearshore Peacock Point sites PP2, PP5, and PP10 are significantly greater than those at nearshore Peacock Point site L449 and those at nearshore sites close to the lake outflow (ANOVA, $F = 10.03$, $\alpha = 0.05$; Table 4.5). Variation in $\delta^{15}N$ of particulate matter among nearshore sites may be related to the forms of nitrogen used in primary production, the frequency with which nitrogen cycles through the food web, and the amount of ammonium adsorbed to particulate matter. Primary producers assimilating ammonium will be more enriched in ^{15}N than those assimilating nitrate (McCusker et al., 1999). The sequential processes of

Table 4.9: $\delta^{15}N$ data for the three tributary inflows from this study compared with data for temperate rivers from other studies. Mean, standard deviation (SD), minimum (Min), and maximum (Max) values are provided, as well as the number of samples used in calculating these values. Thicker lines are inserted between rows to group together the values being compared.

Reference	**Location**	**Date**	**$\delta^{15}N$ (‰)**				
			Mean	**SD**	**Min**	**Max**	**n**
Upsdell, 2005	Grand River, Sandusk Creek, Nanticoke Creek	May – October 2002	9.27	1.77	4.84	12.05	33
Kendall et al., 2001	Missouri River (5 sites) and 2 tributaries (1 site each), U.S.A.	October 1996 – September 1997	4.0	2.7	-0.8	7.5	7
	Ohio River (3 sites) and 2 tributaries (1 site each), U.S.A.		5.3	1.2	4.0	6.7	5
	Mississippi River (3 sites)		7.7	1.5	6.7	9.4	3
	Colorado River (1 site) and 2 tributaries (1 site each), U.S.A.		5.0	0.6	4.3	5.5	3
	Columbia River (4 sites) and 2 tributaries (1 site each), U.S.A.		2.0	1.9	-1.0	3.8	6
Maksymowska et al., 2000*	Vistula River, Poland	May – October 1996	4.7	2.6	2.5	9.0	5
Upsdell, 2005	Grand River, Sandusk Creek, Nanticoke Creek	September 2002	9.62	2.38	5.49	12.05	6
Martinotti et al., 1997	Po River (2 sites), Italy	September 1995	6.3	1.0	5.6	7.0	2

* The values presented here are approximate because they are calculated from sample values depicted in a graph.

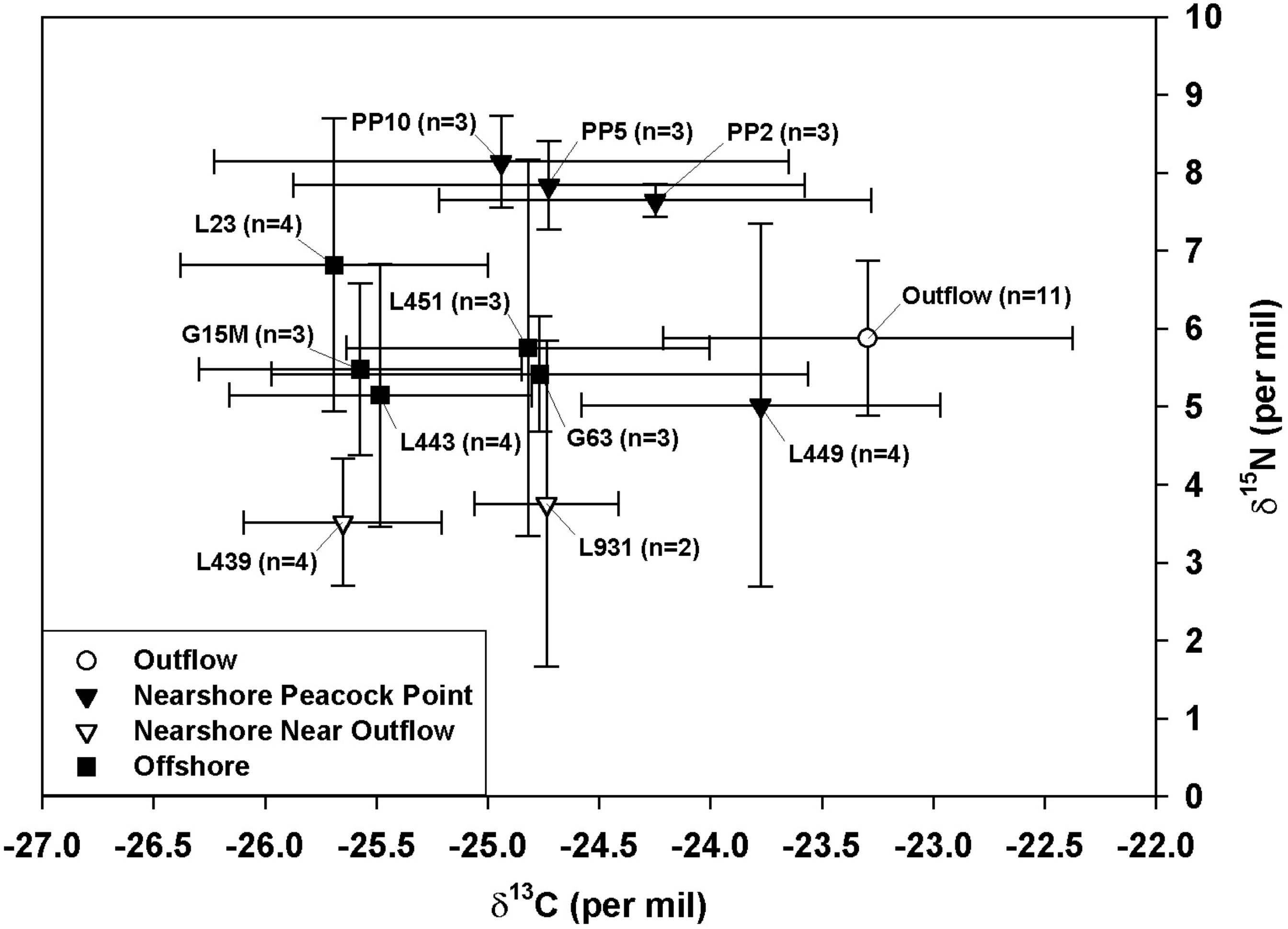


Figure 4.5: Mean $\delta^{13}C$ and $\delta^{15}N$ for the lake outflow and all sites in the eastern basin. Error bars indicate standard deviation.

plant assimilation, animal assimilation, and eventual ammonification or excretion result in a net decrease in δ^{15}N, rendering recycled pools of ammonium and nitrate depleted in ^{15}N relative to the original pools (Figure 1.6). Ammonium adsorbed to particulate matter is more enriched in ^{15}N than assimilated ammonium (Figure 1.6). The high δ^{15}N values at sites PP2, PP5, and PP10, relative to the other nearshore sites, may suggest that there is an additional source of nitrogen at these sites that is not present at the other nearshore sites. This source may be related to recycling of nitrogen back into the water column by dreissenid mussels that are present at sites PP2, PP5, and PP10. The mussels excrete ammonium (Arnott and Vanni, 1996), which is ^{15}N-enriched compared to nitrate (McCusker et al., 1999), that becomes a part of the particulate matter pool when it is used in primary production and when it adsorbs to particulate matter (Wetzel, 1983). Animal feces usually have δ^{15}N signatures similar to that of the organism (Létolle, 1980), enriched three to five per mil compared to the organism's diet (Peterson and Fry, 1987). Therefore, dreissenid mussel feces, which can be resuspended into the water column by wave action and regenerated as relatively ^{15}N-enriched ammonium or nitrate, could also increase the δ^{15}N signatures of particulate matter at sites PP2, PP5, and PP10. Additionally, the isotope data indicate that particulate matter at sites PP2, PP5, and PP10 might be a mixture of particulate matter from tributary inputs and dreissenid mussel biodeposits (Figure 4.6). The δ^{13}C values for particulate matter at these sites (–25 to –24 ‰) are about halfway between the δ^{13}C values for particulate matter at the three tributary inflows (–31 to –30 ‰) and the value for biodeposits of mussels (–19.19 ‰; Szabo, 2004) from the three Peacock Point sites. The δ^{15}N signatures for particulate matter at the three Peacock Point sites (7.5 to 8.5 ‰) are about halfway between the δ^{15}N signatures for particulate matter at the Grand River and Nanticoke Creek (9.5 to 10.5 ‰) and the signature for the mussel biodeposits (6.47 ‰; Szabo, 2004), and are similar to the signature for Sandusk Creek (7.87 ‰).

Regarding eastern basin offshore sites, the mean δ^{13}C signatures range between –25.69 (L23) and –24.77 ‰ (G63), while the mean δ^{15}N signatures range from 5.15 (L443) to 6.82 ‰ (L23;). There are no significant differences among the offshore sites in terms of either δ^{13}C or δ^{15}N signatures (ANOVA, $F_{\delta^{13}C} = 20.15$, $F_{\delta^{15}N} = 10.03$, $\alpha = 0.05$).

The δ^{13}C signatures of particulate matter at sampling locations in the eastern basin range between –27 and –22 ‰, which corresponds to the range of signatures reported by other researchers for terrestrial C_3 and CAM plants, soil organic matter, aquatic macrophytes, phytoplankton, bacteria, and sewage particulate organic matter, but not to the range for terrestrial C_4 plants (Table 4.2). The δ^{15}N signatures of particulate matter at the eastern basin sites range between one and nine per mil. This range corresponds to the range of signatures previously reported for terrestrial plants, soil, synthetic

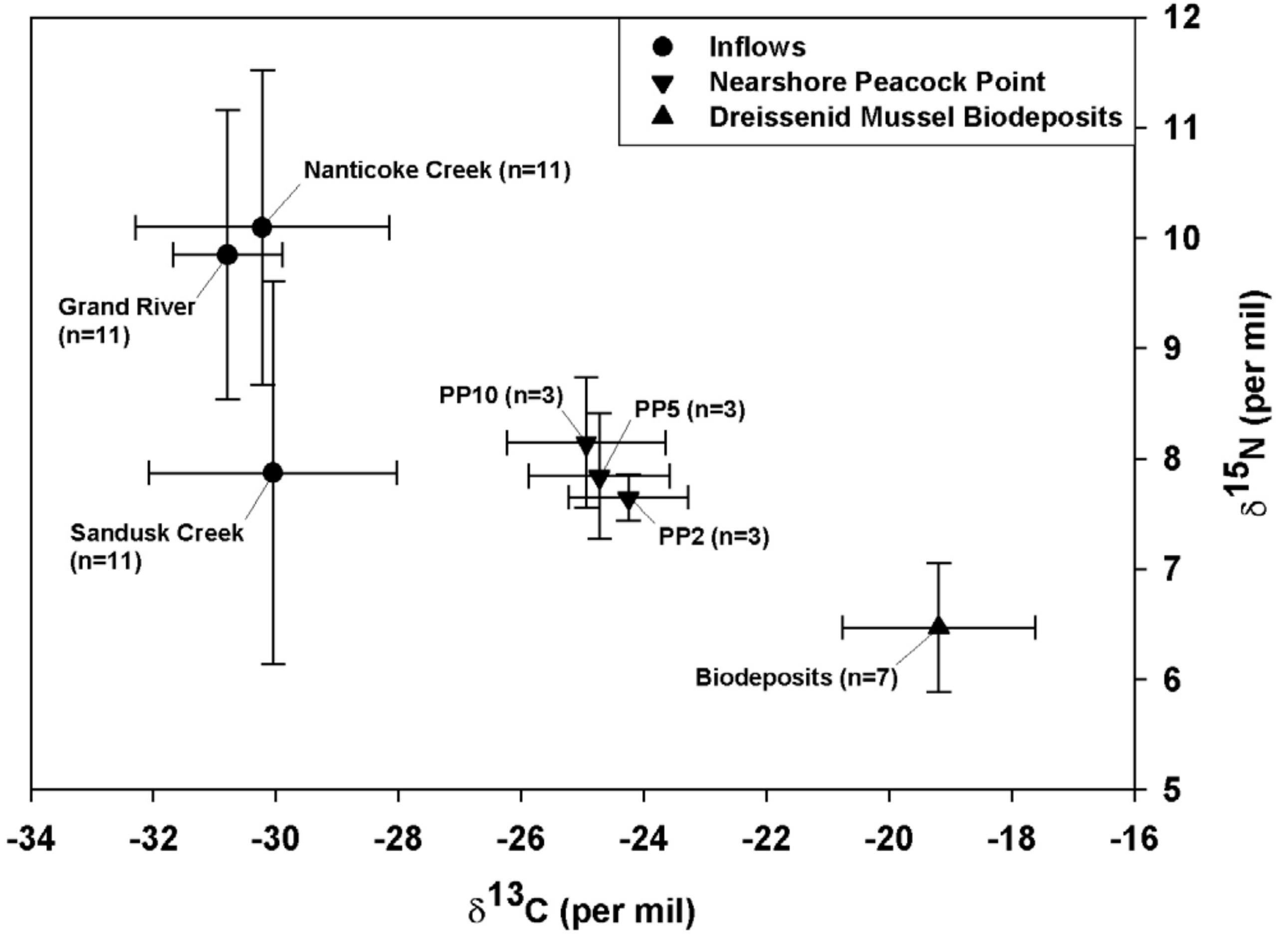


Figure 4.6: Mean δ^{13}C and δ^{15}N for particulate matter from three tributary inflows and the three shallowest nearshore sites at Peacock Point and for dreissenid mussel biodeposits from mussels collected at the nearshore sites. (Biodeposit data from Szabo, 2004.)

fertilizer, sewage, aquatic macrophytes, phytoplankton, and bacteria, but not to the range for animal manure (Table 4.3).

There are no previously published $\delta^{13}C$ and $\delta^{15}N$ data for suspended particulate matter in Lake Erie, but Schelske and Hodell (1995) determined $\delta^{13}C$ signatures for sediment cores from Lake Erie. In Table 4.10, the $\delta^{13}C$ value reported by Schelske and Hodell (1995) for surficial bottom sediment from one core is compared with the $\delta^{13}C$ composition of suspended particulate matter from the present study for the two eastern basin sites closest to the core site. The suspended particulate matter, from all of the depths sampled at sites G15M and L23 in 2002, is slightly enriched in ^{13}C, by no more than 1.1 ‰, than the surficial bottom sediment collected by Schelske and Hodell (1995) in 1987. A core collected by Schelske and Hodell (1995) in 1993 from another Lake Erie site showed sharply increasing $\delta^{13}C$ values from 1990 onwards, coincident with the introduction of dreissenid mussels to the lake. Thus, in terms of $\delta^{13}C$, Lake Erie surficial bottom sediment in 2002 could be less similar than the surficial bottom sediment of 1987 to suspended sediment in 2002.

Table 4.10: $\delta^{13}C$ data for the eastern basin of Lake Erie from this study and from Schelske and Hodell (1995).

Reference	**Location**	**Maximum Depth**	**Date**	**Sampling Depth**	**$\delta^{13}C$ (‰)**
Upsdell, 2005	near central basin (G15M)	62 m	20 July 2002	5 m	-25.55
				60 m	-25.76
	near central basin (L23)	61 m	12 June 2002	20 m	-26.56
				40 m	-26.03
				50 m	-26.02
				60 m	-26.21
Schelske and Hodell, 1995*	near central basin	65 m	29 May 1987	surficial bottom sediment	-26.65

* The value presented here is approximate because it is estimated from a sample value depicted in a graph.

Since no previously published $\delta^{13}C$ values were found for suspended particulate matter in Lake Erie, the $\delta^{13}C$ values of the current research are compared to those for suspended particulate matter of other temperate lakes (Table 4.11). With a few exceptions, the mean $\delta^{13}C$ signatures for the eastern basin of Lake Erie are within two per mil of those for other temperate lakes (Hodell and Schelske, 1998; Ostrom et al., 1998; McCusker et al., 1999; Grey et al., 2000). Particulate matter collected from three Lake Erie offshore sites in June 2002 is approximately 3.4 ‰ more enriched in ^{13}C than particulate matter collected from two Lake Ontario offshore sites in June 1995 (Leggett et al., 1999). This discrepancy in $\delta^{13}C$ values, however, could be related to differences in sample collection

Table 4.11: $\delta^{13}C$ data for the eastern basin of Lake Erie from this study and for other temperate lakes from other studies. Mean, standard deviation (SD), minimum (Min), and maximum (Max) values are provided, as well as the number of samples used in calculating these values. Thicker lines are inserted between rows to group together the values being compared.

Reference	**Location**	**Date**	**$\delta^{13}C$ (‰)**				
			Mean	**SD**	**Min**	**Max**	**n**
Upsdell, 2005*	Eastern Basin, Lake Erie (1 offshore site – L23)	June – October 2002	-25.75	0.51	-26.31	-25.21	4
Hodell and Schelske, 1998**	Eastern Basin, Lake Ontario (1 offshore site)	June – October 1993 – 1995	-25.7	1.4	-28.9	-23.4	24
Upsdell, 2005	Eastern Basin, Lake Erie (3 offshore sites)	June 2002	-25.46	1.20	-26.56	-24.18	3
Leggett et al., 1999	Lake Ontario (2 offshore sites)	June 1995	-28.9	0.9	-29.4	-27.8	3
Ostrom et al., 1998**	Lake Superior (3 offshore sites)	June 1994	-27.3	0.5	-27.7	-26.7	3
Upsdell, 2005	Eastern Basin, Lake Erie (5 offshore sites)	June – October 2002	-25.30	0.81	-26.56	-23.54	17
Meyers and Eadie, 1993***	Lake Michigan (2 offshore sites)	June – November 1980	-28.5	1.1	-29.2	-27.7	2
Upsdell, 2005	Eastern Basin, Lake Erie (5 offshore sites)	June – September 2002	-25.23	0.83	-26.56	-23.54	15
McCusker et al., 1999**	Grand Traverse Bay, Lake Michigan (2 offshore sites)	June – September 1997	-26.7	1.4	-28.5	-25.0	11
Upsdell, 2005	Eastern Basin, Lake Erie (6 nearshore, 5 offshore sites)	June – July 2002	-24.7	1.1	-26.6	-22.7	16
Grey et al., 2000	7 mesotrophic lakes, United Kingdom	May – July 1998	-26.4	2.3	-29.7	-24.0	7
Upsdell, 2005	Eastern Basin, Lake Erie (6 nearshore, 5 offshore sites)	September – October 2002	-25.4	0.7	-26.3	-24.3	15
Grey et al., 2000	1 mesotrophic lake, United Kingdom	September – October 1998	-24.4	—	—	—	1

* The values were adjusted to include $\delta^{13}C$ signatures at sampling depths similar to those used in Hodell and Schelske (1998) rather than only the shallowest sampling depth.

** The values presented here are approximate because they are calculated from sample values depicted in a graph.

*** The values presented here are calculated from sample values for material collected over 142 days using a sediment trap at each site.

methodology. Leggett et al. (1999) collected particulate matter using a centrifuge and determined $\delta^{13}C$ on particles in the 0.45- to 44-μm size range, while particulate matter for the present study was collected by sedimentation traps and subsequent filtration, and represents particles in the > 0.8-μm size range. The mean $\delta^{13}C$ value for five offshore sites in Lake Erie in 2002 is 3.2 ‰ greater than that for two offshore sites in Lake Michigan in 1980 (Meyers and Eadie, 1993). This discrepancy in $\delta^{13}C$ values could also be related to differences in sample collection methodology. Meyers and Eadie (1993) collected particulate matter using sedimentation traps without subsequently filtering the material; therefore, their samples could have included particles of a smaller size range than the current research.

The $\delta^{15}N$ data can also be compared to data for other temperate lakes (Table 4.12) since no previously published $\delta^{15}N$ values were found for Lake Erie. The mean $\delta^{15}N$ signatures for the eastern basin of Lake Erie are within two per mil of the mean signatures from three of the five studies of temperate lakes listed in Table 4.12 (Hodell and Schelske, 1998; Meyers and Eadie, 1993; McCusker et al., 1999). By contrast, particulate matter collected from three Lake Erie offshore sites in June 2002 is approximately 2.4 ‰ more enriched in ^{15}N than particulate matter collected from two Lake Ontario offshore sites in June 1995 (Leggett et al., 1999) and about 4 ‰ more enriched in ^{15}N than particulate matter collected from two Lake Superior offshore sites in June 1994 (Ostrom et al., 1998). Similar to $\delta^{13}C$, the discrepancy in $\delta^{15}N$ values between the current study and that of Leggett et al. (1999) could be related to differences in sample collection methodology. The difference in $\delta^{15}N$ signatures between the present research and that of Ostrom et al. (1998) could be related to the different trophic states of the two lakes. Lake Erie is presently considered to be mesotrophic, while Ostrom et al. (1998) indicate that Lake Superior is ultra-oligotrophic. It is not known how lake trophic state relates to $\delta^{15}N$, but in their study of twenty-four lakes in the United Kingdom, Grey et al. (2000) found that particulate organic matter in oligotrophic lakes was generally more enriched in ^{13}C than particulate organic matter in mesotrophic lakes. Other factors that could account for Lakes Erie and Superior differing in terms of $\delta^{15}N$ include the watershed substrate (soil versus rock, soil type), land use, and population density, which all influence the nature of sediment material in, and nutrient inputs to, lakes.

The mean $\delta^{13}C$ and $\delta^{15}N$ signatures for nearshore and offshore sites in the eastern basin are compared in Figure 4.5. Most of the nearshore sites have mean $\delta^{13}C$ values that are in the same range as the offshore sites. While nearshore sites PP2 and L449 have higher mean $\delta^{13}C$ values than the other eastern basin sites, there are no significant differences in $\delta^{13}C$ signatures between nearshore and offshore sites (ANOVA, $F = 20.15$, $\alpha = 0.05$). In terms of $\delta^{15}N$, the nearshore sites have a greater range of mean values than the offshore sites, with the offshore range lying at approximately the centre of the overall nearshore range. The three shallowest nearshore Peacock Point sites (PP2, PP5, PP10) have

Table 4.12: $\delta^{15}N$ data for the eastern basin of Lake Erie from this study and for other temperate lakes from other studies. Mean, standard deviation (SD), minimum (Min), and maximum (Max) values are provided, as well as the number of samples used in calculating these values. Thicker lines are inserted between rows to group together the values being compared.

Reference	Location	Date	$\delta^{15}N$ (‰)				
			Mean	**SD**	**Min**	**Max**	**n**
Upsdell, 2005*	Eastern Basin, Lake Erie (1 offshore site – L23)	June – October 2002	5.70	1.82	4.17	7.89	4
Hodell and Schelske, 1998**	Eastern Basin, Lake Ontario (1 offshore site)	June – October 1993 – 1995	7.3	1.8	4.7	10.8	23
Upsdell, 2005	Eastern Basin, Lake Erie (3 offshore sites)	June 2002	5.77	2.81	2.68	8.16	3
Leggett et al., 1999	Lake Ontario (2 offshore sites)	June 1995	3.4	0.8	2.5	4.0	3
Ostrom et al., 1998**	Lake Superior (2 offshore sites)	June 1994	1.7	2.1	0.2	3.2	2
Upsdell, 2005	Eastern Basin, Lake Erie (5 offshore sites)	June – October 2002	5.75	1.60	2.68	8.16	17
Meyers and Eadie, 1993***	Lake Michigan (1 offshore site)	June – November 1980	5.2	—	—	—	1
Upsdell, 2005	Eastern Basin, Lake Erie (5 offshore sites)	June – September 2002	5.56	1.57	2.68	8.16	15
McCusker et al., 1999**	Grand Traverse Bay, Lake Michigan (2 offshore sites)	June – September 1997	5.1	2.3	3.0	11.5	11

* The values were adjusted to include $\delta^{15}N$ signatures at sampling depths similar to those used in Hodell and Schelske (1998) rather than only the shallowest sampling depth.

** The values presented here are approximate because they are calculated from sample values depicted in a graph.

*** The value presented here represents material collected over 142 days using a sediment trap at the site.

higher mean δ^{15}N values than the offshore sites, while the nearshore sites close to the lake outflow have lower mean δ^{15}N values than the offshore sites. The deepest nearshore Peacock Point site (L449) has a mean δ^{15}N signature that is similar to that at offshore site L443. All but one of the nearshore sites (L449) have significantly different δ^{15}N signatures than at least one offshore site (ANOVA, F = 10.03, $\alpha = 0.05$). Nearshore site PP2 has significantly higher δ^{15}N values than offshore site L443, while nearshore site PP5 has significantly higher values than three offshore sites (G15M, G63, L443), and nearshore site PP10 has significantly higher values than four offshore sites (L451, G15M, G63, L443; ANOVA, F = 10.03, $\alpha = 0.05$). The data suggest that the additional source of nitrogen to the PN pool at sites PP2, PP5, and PP10 is probably not present at the offshore sites. For nearshore sites close to the lake outflow, site L931 has significantly lower δ^{15}N signatures than offshore site L23, and site L439 has significantly lower signatures than offshore sites L451 and L23 (ANOVA, F = 10.03, $\alpha = 0.05$). It is not known why the nearshore sites close to the outflow are generally depleted in ^{15}N compared with the other eastern basin sites. No previously published research has compared carbon and nitrogen stable isotope signatures between nearshore and offshore sites.

The mean δ^{13}C signature of –23.29 ‰ at the lake outflow is greater than those at the eastern basin sites, which range from –25.69 to –23.78 ‰ (Figure 4.5). The lake outflow has significantly greater δ^{13}C values than nearshore site L439 and three offshore sites (G15M, L23, L443; ANOVA, F = 20.15, $\alpha = 0.05$). Particulate matter at the lake outflow has δ^{13}C values that range from –26 to –22 ‰. This range fits within the ranges of values previously published for terrestrial C_3 and CAM plants, soil organic matter, aquatic macrophytes, phytoplankton, and sewage particulate organic matter, but not within the ranges for terrestrial C_4 plants and bacteria (Table 4.2).

In terms of δ^{15}N, the lake outflow has a mean value of 5.88 ‰ that is similar to those at eastern basin offshore sites and nearshore site L449. The outflow has significantly lower δ^{15}N signatures than nearshore Peacock Point sites PP5 and PP10 and significantly greater values than the two nearshore sites in the vicinity of the outflow (ANOVA, F = 10.03, $\alpha = 0.05$). The mean δ^{15}N value at the lake outflow (5.88 ‰) is approximately halfway between the values for the three shallowest nearshore sites at Peacock Point (7.5 to 8.5 ‰) and the values for the nearshore sites close to the outflow (3.5 to 4.0 ‰; Figure 4.5). The data suggest that particulate nitrogen at the lake outflow may be derived from material at the offshore sites rather than material at the majority of nearshore sites or it may represent a mixture of material from the nearshore sites at Peacock Point and the nearshore sites close to the outflow. Outflow particulate matter has δ^{15}N values in the range of four to eight per mil, corresponding to the ranges of values previously reported for terrestrial plants, soil, sewage, aquatic macrophytes, phytoplankton, and bacteria, but not to the ranges for synthetic fertilizer and animal manure (Table 4.3).

4.1.2 Eastern, Central, and Western Basins of Lake Erie

Mean $\delta^{13}C$ and $\delta^{15}N$ signatures for nearshore and offshore sites in the central and western basins of Lake Erie are shown in Figure 4.7. In the central basin, the nearshore site has a higher mean $\delta^{13}C$ value than the offshore sites, but differences in $\delta^{13}C$ among the central basin sites are not statistically significant (ANOVA, $F = 20.15$, $\alpha = 0.05$; Table 4.4). All three central basin sites have mean $\delta^{15}N$ values that range between 5.0 and 6.5 ‰ and there are no significant differences in $\delta^{15}N$ among these sites (ANOVA, $F = 10.03$, $\alpha = 0.05$, Table 4.5). The two nearshore sites in the western basin have mean $\delta^{13}C$ signatures that range between –25 and –23 ‰ and mean $\delta^{15}N$ signatures that range between five and seven per mil. There are no significant differences in $\delta^{13}C$ or $\delta^{15}N$ among the western basin sites (ANOVA, $F_{\delta^{13}C} = 20.15$, $F_{\delta^{15}N} = 10.03$, $\alpha = 0.05$). Particulate matter at sites in the central and western basins has $\delta^{13}C$ signatures that range between –26 and –23 ‰, which fits within the ranges of signatures previously published for terrestrial C_3 and CAM plants, soil organic matter, aquatic macrophytes, phytoplankton, and sewage particulate organic matter, but not within the ranges for terrestrial C_4 plants and bacteria (Table 4.2). $\delta^{15}N$ signatures for particulate matter at central and western basin sites range from five to seven per mil, within the previously reported ranges for terrestrial plants, soil, sewage, aquatic macrophytes, and phytoplankton, but not within those for synthetic fertilizer, animal manure, or bacteria (Table 4.3). No previously published $\delta^{13}C$ or $\delta^{15}N$ data for the central or western basin of Lake Erie were found for comparison with the data from this research.

In Figure 4.7, the mean $\delta^{13}C$ and $\delta^{15}N$ signatures of sampling locations in the central basin are also compared to those of sampling locations in the eastern basin. The mean $\delta^{13}C$ value for the central basin nearshore site is higher than those for the eastern basin offshore sites and within the range of mean values for eastern basin nearshore sites. The two central basin offshore sites have mean $\delta^{13}C$ values that are within the range of mean values for eastern basin offshore sites and at the lower end of the range of mean values for eastern basin nearshore sites. There are no significant differences in $\delta^{13}C$ signatures between the central and eastern basin sites (ANOVA, $F = 20.15$, $\alpha = 0.05$). Regarding $\delta^{15}N$, the central basin nearshore site has a mean value that is approximately in the middle of the range of mean values for eastern basin nearshore and offshore sites. The two central basin offshore sites have mean $\delta^{15}N$ values that are within the range of mean values for both eastern basin nearshore and offshore sites. $\delta^{15}N$ signatures at nearshore site GAsh and offshore site G43 in the central basin are significantly greater than those at eastern basin nearshore site L439 (ANOVA, $F = 10.03$, $\alpha = 0.05$). Conversely, central basin offshore site G78M has $\delta^{15}N$ signatures that are significantly lower than those at three eastern basin nearshore sites (PP2, PP5, PP10; ANOVA, $F = 10.03$, $\alpha = 0.05$).

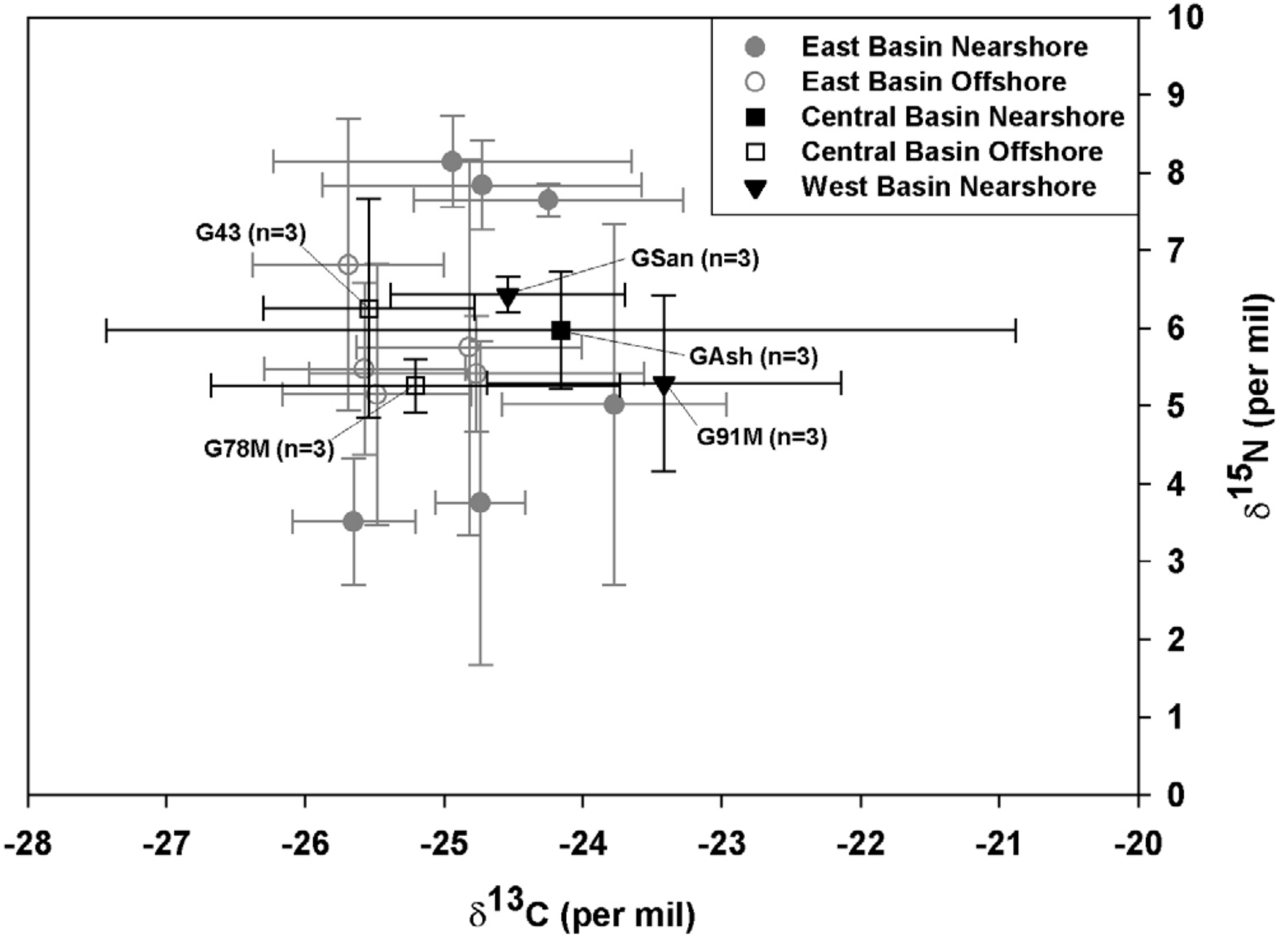


Figure 4.7: Mean δ^{13}C and δ^{15}N for nearshore and offshore sites in the eastern, central, and western basins. Error bars indicate standard deviation.

Figure 4.7 shows how mean $\delta^{13}C$ and $\delta^{15}N$ signatures of sampling locations in the western basin compare with those of sampling locations in the eastern basin. The mean $\delta^{13}C$ value for western basin nearshore site GSan is within the range of mean values for eastern basin nearshore sites and greater than the mean values for eastern basin offshore sites. Particulate matter at western basin nearshore site G91M is, on average, more enriched in ^{13}C than particulate matter at all of the eastern basin sites. While $\delta^{13}C$ values for site GSan do not differ significantly from those of any eastern basin sites, $\delta^{13}C$ values for G91M are significantly greater than those of eastern basin nearshore site L439 and eastern basin offshore site L23 (ANOVA, $F = 20.15$, $\alpha = 0.05$). The mean $\delta^{15}N$ signatures at the two western basin nearshore sites are within the range of mean values for both eastern basin nearshore and offshore sites. $\delta^{15}N$ values at western basin nearshore site GSan are significantly greater than those at eastern basin nearshore sites in the vicinity of the lake outflow (L931, L439; ANOVA, $F = 10.03$, $\alpha = 0.05$). By contrast, western basin nearshore site G91M has $\delta^{15}N$ values that are significantly lower than those at three eastern basin nearshore sites at Peacock Point (PP2, PP5, PP10; ANOVA, $F = 10.03$, $\alpha = 0.05$). The source of nitrogen that increases $\delta^{15}N$ values at sites PP2, PP5, and PP10 is therefore not likely a dominant source of nitrogen at site G91M in the western basin.

4.2 Summary and Synthesis

4.2.1 Tributary Inflows, Lake Outflow, and Eastern Basin of Lake Erie

Carbon and nitrogen stable isotope signatures determined in the present research are summarized in the context of nutrient compartments involved in the nearshore shunt concept in Figure 4.8. Since particulate matter from the tributary inflows has significantly lower $\delta^{13}C$ values than particulate matter from the eastern basin of Lake Erie and the lake outflow, the sources of, or processes influencing, particulate matter at the inflow sites probably differ from those at the eastern basin and outflow sites. While there are significant differences in the nitrogen signatures, $\delta^{15}N$ values of particulate matter are less distinct, relative to $\delta^{13}C$, between the tributary inflows and the eastern basin and lake outflow. Hence, there are also probably differences in the sources, or in the relative proportions of the sources, of particulate matter among the inflow and eastern basin groupings of sites. Given that $\delta^{13}C$ signatures indicate that the tributary inflows and the eastern basin likely have different sources of particulate matter and given that $\delta^{15}N$ signatures are very heterogeneous among eastern basin sites, the variations in $\delta^{15}N$ in the eastern basin must be strongly influenced by within-lake processes.

Suspended particulate matter collected from the eastern basin of Lake Erie in 2002 is slightly enriched in ^{13}C, by a maximum of 1.1 ‰, compared to bottom sediment collected from the eastern basin in 1987. Among the eastern basin sites, there are no significant differences in $\delta^{13}C$. There are,

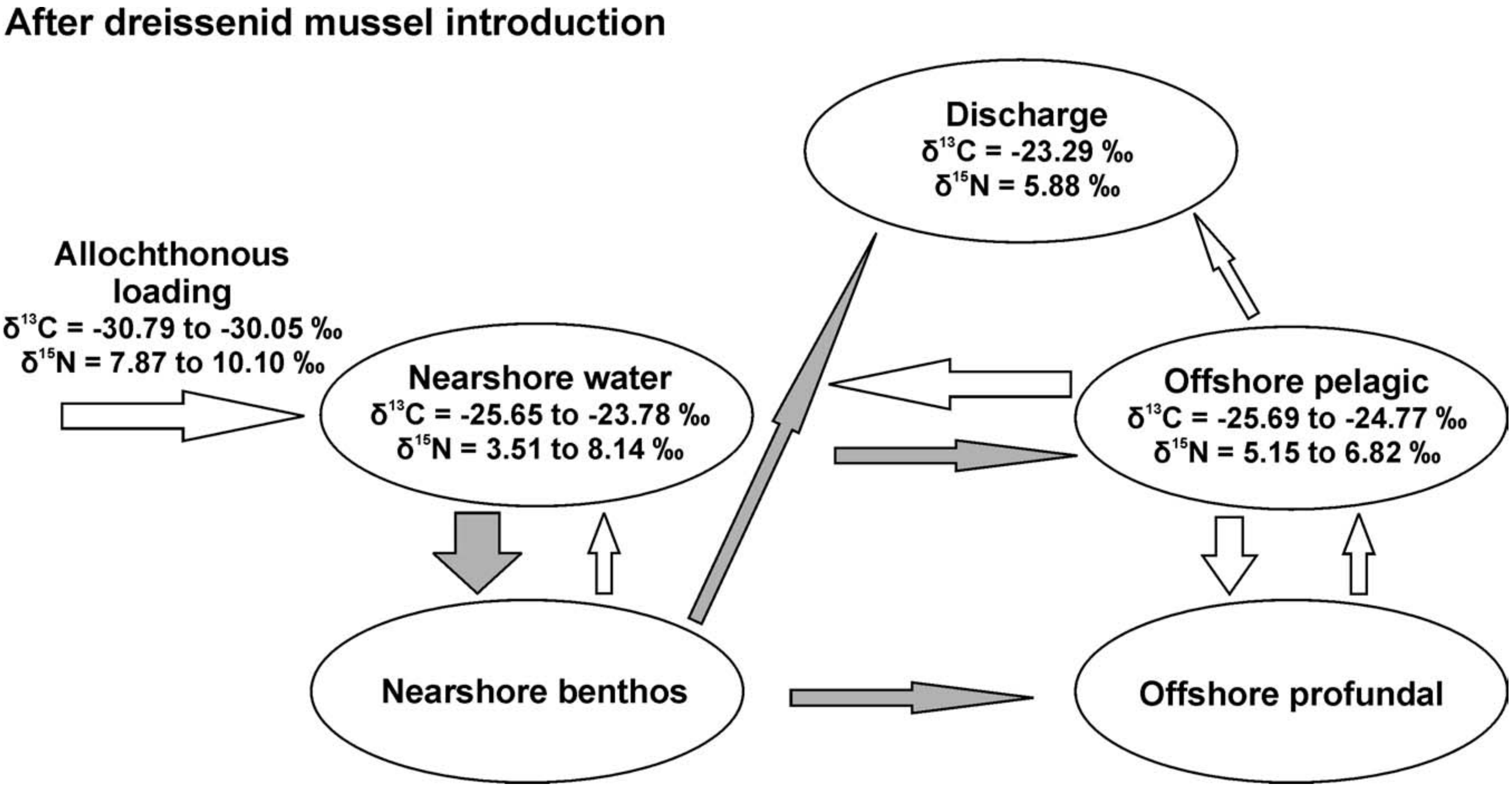


Figure 4.8: Diagram showing the nearshore shunt concept with mean values (or ranges of mean values in the cases of multiple sites per compartment) of δ^{13}C and δ^{15}N determined in the present study for four of the six nutrient compartments. The nearshore water and offshore pelagic compartments contain data for sites in the eastern basin of Lake Erie.

however, some significant differences in $\delta^{15}N$ between nearshore and offshore sites and among nearshore sites. $\delta^{15}N$ values of particulate matter at the three shallowest nearshore sites close to Peacock Point (PP2, PP5, PP10) are significantly higher than those of particulate matter at the other nearshore sites and at some of the offshore sites. Recycling of nitrogen back into the water column by dreissenid mussels may enrich particulate matter in ^{15}N at sites PP2, PP5, and PP10 and may be a source of nitrogen at these sites that is not present at the other sites in the eastern basin. Particulate matter at these three sites near Peacock Point could also be derived from a mixture of particulate matter from tributary inputs and dreissenid mussel biodeposits. Nearshore sites close to the lake outflow are depleted in ^{15}N compared with the other eastern basin sites, but the reason for this is not known.

The lake outflow differs significantly in terms of $\delta^{13}C$ from some of the eastern basin offshore sites. It does not differ significantly with respect to $\delta^{15}N$ from the eastern basin offshore sites, so PN at the outflow may be derived from material in offshore areas of the eastern basin. PN at the outflow may also be a mixture of material derived from nearshore sites at Peacock Point (enriched in ^{15}N compared to the outflow) and nearshore sites close to the outflow (depleted in ^{15}N compared to the outflow).

$\delta^{13}C$ signatures indicate that terrestrial C_4 plants are not a major source of POC to the tributary inflows, eastern basin of Lake Erie, or lake outflow. Based on the $\delta^{13}C$ data, bacteria do not comprise a dominant proportion of POC at the outflow, but bacteria could be more relevant as a POC source than the data suggest because the $\delta^{13}C$ data for bacteria are limited.

$\delta^{15}N$ signatures show that synthetic fertilizer is not a major source of PN at the tributary inflows or the lake outflow. While animal manure probably contributes to the PN at the tributary inflows, it is not a primary source of PN in the eastern basin of Lake Erie or at the lake outflow.

$\delta^{13}C$ signatures and POC/PN mass ratios for the tributary inflows, eastern basin, and lake outflow are compared in Figure 4.9. $\delta^{13}C$ of particulate matter is clearly distinct between the tributary inflows and the eastern basin and outflow. This difference is not apparent in the POC/PN mass ratios. Figure 4.10 shows a comparison of $\delta^{15}N$ signatures and POC/PN mass ratios for the inflows, eastern basin, and lake outflow. There is much variation in $\delta^{15}N$ (mean values range over about six per mil) over a small range of POC/PN mass ratios (mean values range over approximately three). Hence, the $\delta^{15}N$ data provide information that is not as clear in the mass ratio data.

POC/PN mass ratios are similar across the inflow, eastern basin, and outflow sites and indicate that particulate matter at these sites is probably derived from mainly autochthonous sources, particularly plankton. $\delta^{13}C$ and $\delta^{15}N$ signatures show that possible sources of particulate matter at the inflow, eastern basin, and outflow sites include terrestrial plants and soil matter, aquatic macrophytes,

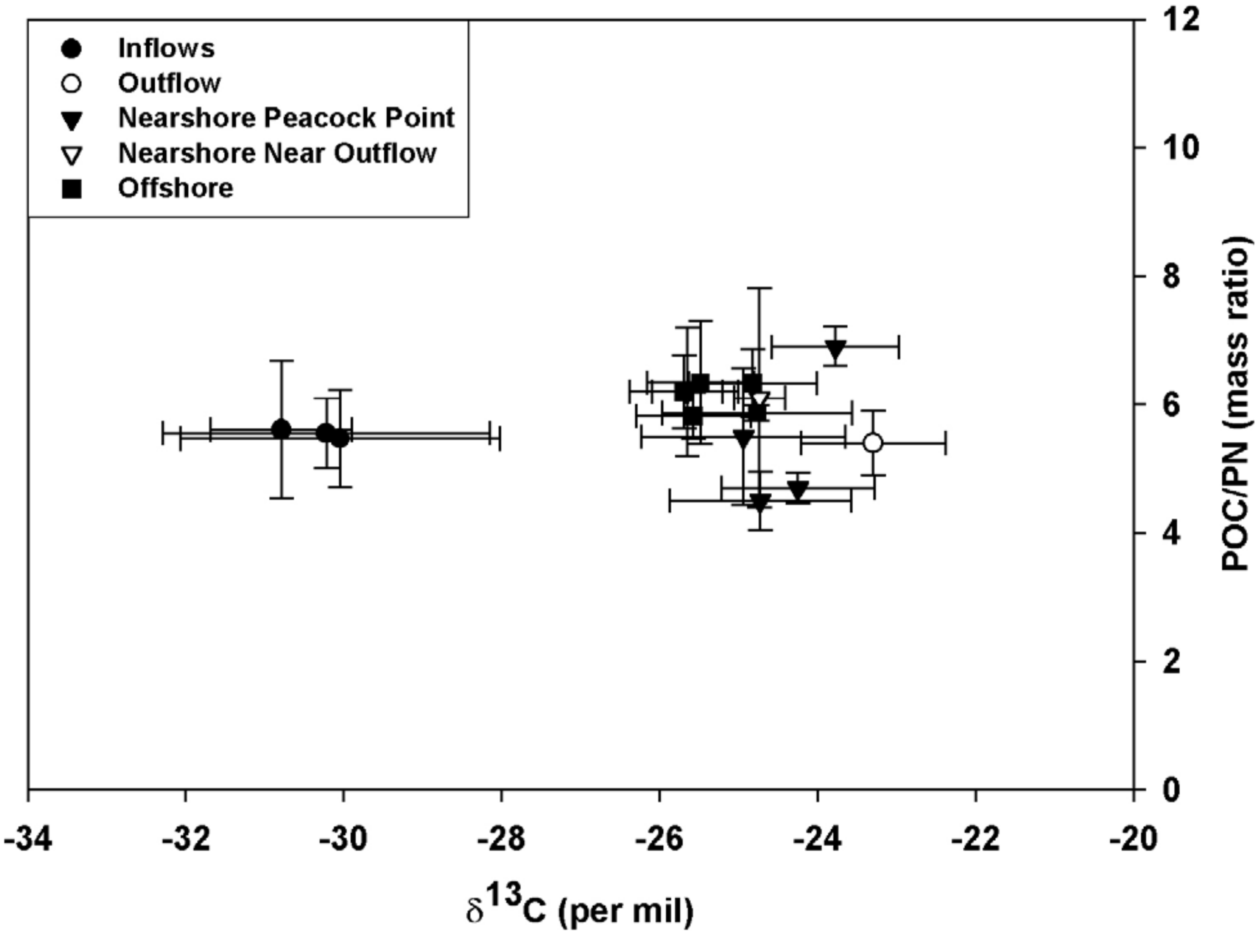


Figure 4.9: Mean δ^{13}C and POC/PN mass ratios for three tributary inflows, the lake outflow, and all sites in the eastern basin. Error bars indicate standard deviation.

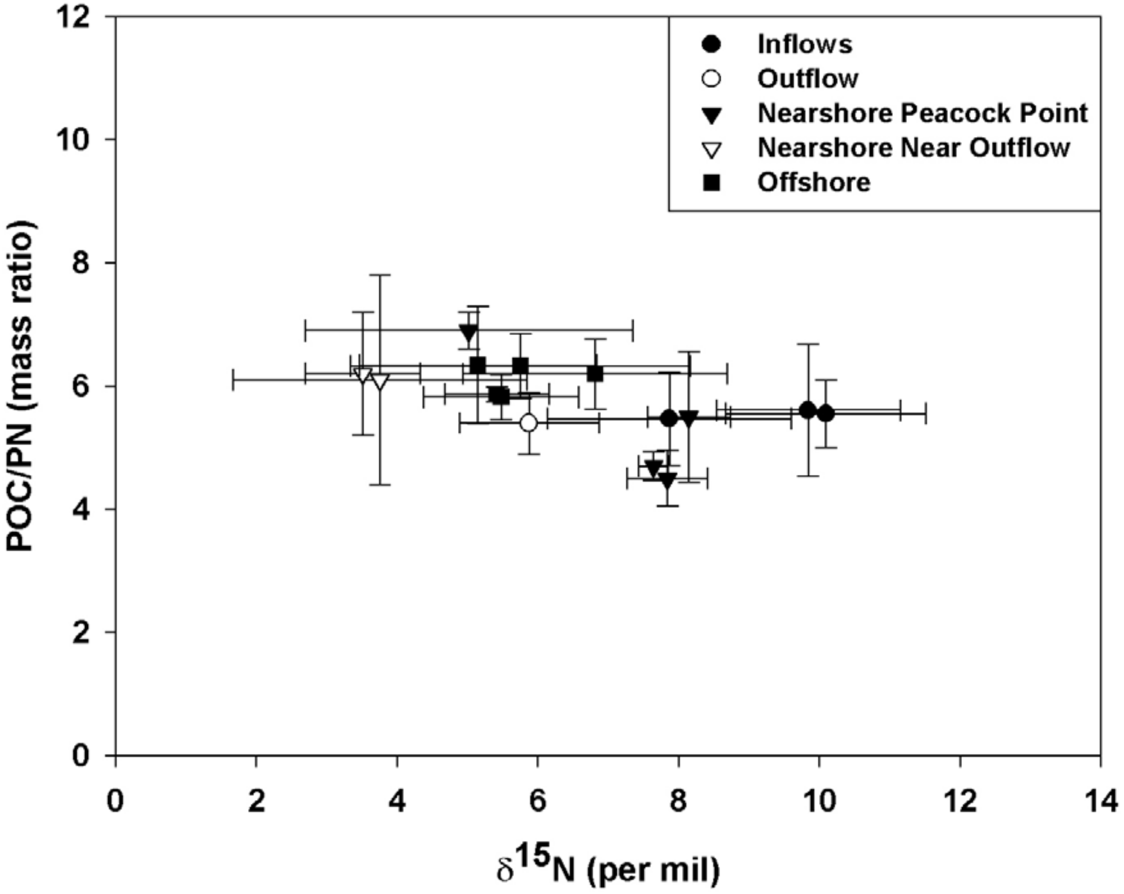


Figure 4.10: Mean δ^{15}N and POC/PN mass ratios for three tributary inflows, the lake outflow, and all sites in the eastern basin. Error bars indicate standard deviation.

phytoplankton, and sewage. Since the POC/PN mass ratios point towards plankton, it is probably the primary source of particulate matter at all of the sampling locations.

Particulate matter at the tributary inflows has POC and PN concentrations and $\delta^{13}C$ signatures that are distinct from those of particulate matter in the eastern basin and at the lake outflow. This is likely due to terrestrial-derived material forming a greater proportion of the particulate matter at the inflows than at the other sites. In particular, $\delta^{15}N$ signatures identify animal manure as a possible source of PN at the inflows, but not in the eastern basin or at the outflow. Terrestrial plant and soil material and aquatic macrophytes may also contribute more substantially to the inflow particulate matter than to the eastern basin and outflow particulate matter.

In the eastern basin, particulate matter at the shallower nearshore sites close to Peacock Point has significantly higher PN concentrations and lower POC/PN mass ratios, and is enriched in ^{15}N, relative to other sites in the basin. This is evidence of an additional source of PN at the nearshore Peacock Point sites that is not present at the other sampling locations. Dreissenid mussels at the Peacock Point sites may contribute the additional source of PN by recycling nitrogen back into the water column.

4.2.2 Eastern, Central, and Western Basins of Lake Erie

Sampling locations in the eastern and central basins do not differ significantly in terms of $\delta^{13}C$, but there are some significant differences in $\delta^{15}N$ between eastern and central basin sites. Both $\delta^{13}C$ and $\delta^{15}N$ signatures show significant differences between eastern and western basin sites. $\delta^{15}N$ values at western basin nearshore site G91M are significantly different from those at eastern basin nearshore sites PP2 and PP5. Therefore, the higher PN concentrations relative to POC concentrations at site G91M are probably not due to the same source as that which causes higher PN relative to POC concentrations at sites PP2 and PP5.

POC/PN mass ratios indicate that particulate matter in the central and western basins is probably mainly derived from autochthonous sources, particularly plankton. Possible sources of particulate matter in these basins based upon the isotope data include terrestrial plants and soil matter, aquatic macrophytes, phytoplankton, and sewage. Combining the source information provided by the ratio and isotope data, plankton is likely the dominant source of particulate matter in the central and western basins of Lake Erie.

Chapter 5: Conclusion

The conclusions of this study are presented in this chapter. They are followed by a brief discussion of the relevance of this research to the broader concept of the nearshore shunt hypothesis. The chapter concludes with some recommendations for future research.

5.1 Conclusions

In this study, the absolute and relative concentrations and the isotopic composition of carbon and nitrogen are used to characterize the chemical composition of suspended particulate matter in three tributary inflows, nearshore and offshore sites in Lake Erie, and the lake outflow. Carbon and nitrogen are also used as tracers, on a basin scale, to determine the probable sources of particulate matter at the sampling locations and how particulate matter is cycled in Lake Erie. This is the first larger-scale study to determine POC and PN concentrations, POC/PN mass ratio, $\delta^{13}C$, and $\delta^{15}N$ simultaneously in fluvial and lacustrine environments of the Laurentian Great Lakes basin. The conclusions of this research are provided below in association with the relevant objectives and null hypotheses.

Objective 1: To characterize the chemical composition (POC and PN concentrations, POC/PN mass ratio, carbon and nitrogen stable isotopes) of suspended particulate matter in three tributary inflows, the outflow, and nearshore and offshore areas of the eastern basin of Lake Erie.

Hypothesis 1. a) The chemical composition of suspended particulate matter entering Lake Erie through tributary inflows is not significantly different from that at nearshore sites in the eastern basin of the lake.

With respect to the POC and PN concentrations of suspended particulate matter, the three tributary inflows are significantly higher than nearshore sites in the eastern basin. $\delta^{13}C$ signatures of suspended particulate matter in the tributary inflows are significantly lower than those of suspended particulate matter at eastern basin nearshore sites. $\delta^{15}N$ signatures of suspended particulate matter from the inflows are significantly higher than those of suspended particulate matter from some (Grand River, Sandusk Creek) or all (Nanticoke Creek) of the nearshore sites in the eastern basin. Distinct isotopic signatures between the inflows and nearshore areas of the eastern basin indicate that, while nearshore sites may receive inputs from tributary inflows, they are also influenced by other sources of particulate matter or by processes that affect the composition of particulate matter.

Hypothesis 1. b) The chemical composition of suspended particulate matter at eastern basin nearshore sites is not significantly different from that at eastern basin offshore sites.

In the eastern basin, POC concentrations and $\delta^{13}C$ signatures of suspended particulate matter at nearshore sites are not significantly different from POC concentrations and $\delta^{13}C$ signatures, respectively, of suspended particulate matter at offshore sites. PN concentrations of suspended particulate matter at two nearshore sites (PP2, PP5) are significantly higher than those of suspended particulate matter at some (PP2) or all (PP5) offshore sites. δ^{15}N signatures of suspended particulate matter at three nearshore sites (PP2, PP5, PP10) are significantly higher than those of suspended particulate matter at some offshore sites, while δ^{15}N signatures of suspended particulate matter at two nearshore sites (L931, L439) are significantly lower than those of suspended particulate matter at some offshore sites. The PN concentration and δ^{15}N data suggest that the shallowest nearshore sites close to Peacock Point receive PN from a source that is not present at the offshore sites in the eastern basin.

Hypothesis 1. c) The chemical composition of suspended particulate matter at the lake outflow is not significantly different from that at eastern basin offshore sites.

Suspended particulate matter at the lake outflow is significantly lower in terms of POC and PN concentrations than that at some offshore sites in the eastern basin. δ^{13}C signatures of suspended particulate matter at the lake outflow are significantly higher than those of suspended particulate matter at some eastern basin offshore sites. δ^{15}N signatures of suspended particulate matter at the outflow do not differ significantly from those of suspended particulate matter at eastern basin offshore sites. δ^{13}C signatures indicate that the suspended particulate matter at the lake outflow is probably not derived from offshore sites in the eastern basin, but δ^{15}N signatures support the possibility of the outflow and offshore sites having similar sources of PN.

Objective 2: To determine the relative contributions of allochthonous and autochthonous sources to suspended particulate matter in three tributary inflows, the outflow, and nearshore and offshore areas of Lake Erie using the POC/PN mass ratio and carbon and nitrogen stable isotopes.

While δ^{13}C and δ^{15}N signatures show that both allochthonous and autochthonous sources may contribute to suspended particulate matter at all sampling locations, POC/PN mass ratios indicate a dominance of autochthonous contributions to suspended particulate matter at all sites.

Objective 3: To identify possible sources of suspended particulate matter in three tributary inflows, the outflow, and nearshore and offshore areas of Lake Erie by comparing the POC/PN mass ratios and carbon and nitrogen stable isotopic signatures of suspended particulate matter at these sites to values from the literature for possible sources.

POC/PN mass ratios point towards plankton as the main source of suspended particulate matter at all sampling locations. Based upon δ^{13}C and δ^{15}N signatures, likely sources of particulate matter at all sites include terrestrial plants and soil matter, aquatic macrophytes, phytoplankton, and sewage. Therefore, plankton is probably the primary source of particulate matter at each site, with smaller contributions possible from other sources. Terrestrial plants and soils and aquatic macrophytes may contribute more significantly to the particulate matter at the tributary inflows than to the particulate matter in the eastern basin and at the lake outflow. Animal manure is also a possible source of PN at the inflow sites. In the eastern basin, dreissenid mussels may contribute an additional source of PN to the suspended matter at the shallower nearshore sites close to Peacock Point by recycling nitrogen back into the water column.

Objective 4: To determine how the suspended particulate matter at the sampling locations in the eastern basin, which has high dreissenid mussel abundance, compares to that at sampling locations in the central and western basins.

Hypothesis 4. The chemical composition of suspended particulate matter in the eastern basin of Lake Erie is not significantly different from that in the central and western basins.

With respect to the POC concentrations and $\delta^{13}C$ signatures of suspended particulate matter, eastern basin sites do not differ significantly from central basin sites. Regarding the PN concentrations and $\delta^{15}N$ signatures of suspended particulate matter, however, some eastern basin sites differ significantly from at least one central basin site. Central basin sites show no evidence of an additional source of PN like that found at eastern basin nearshore sites colonized by dreissenid mussels.

POC and PN concentrations of suspended particulate matter at all eastern basin sites are significantly lower than those of suspended particulate matter at at least one of the two western basin sites. Suspended particulate matter at two eastern basin sites (L439, L23) has significantly lower $\delta^{13}C$ signatures than suspended particulate matter at one western basin site (G91M). $\delta^{15}N$ signatures of suspended particulate matter at some eastern basin sites differ significantly from those of suspended particulate matter at a western basin site. $\delta^{15}N$ signatures indicate that high PN concentrations relative to POC concentrations at western basin site G91M are probably not due to the same source of nitrogen (i.e. dreissenid mussels) that likely causes this trend at eastern basin sites near Peacock Point.

5.2 Relevance to Nearshore Shunt Hypothesis

This research contributes to the testing of the hypothesis, proposed by Hecky et al. (2004), that dreissenid mussels have reengineered the cycling of nutrients in Lake Erie, causing the nearshore benthic community to intercept, retain, and recycle greater quantities of nutrients. The carbon and nitrogen composition has been characterized for particulate matter in four of the six compartments of the nearshore shunt concept (Figures 3.13, 4.8). The data indicate that contributions from catchment sources to nutrients retained by the nearshore shunt are minor compared to contributions from phytoplankton. The data also suggest that dreissenid mussels may be recycling nitrogen back into the water column. Therefore, the mussels may, indeed, have reengineered the cycling of nitrogen in Lake Erie.

5.3 Recommendations for Future Research

Much further work is required in order to test the validity of the nearshore shunt hypothesis. Some suggestions for future research that stem from the current study are:

1. To obtain a more comprehensive picture of nutrient cycling in the whole system, determine the chemical composition of material in the nearshore benthos and offshore profundal compartments of the nearshore shunt model and compare this to the chemical composition of material in the four compartments examined in the present study.

2. To determine whether or not the benthic community is intercepting and retaining nutrients, compare the chemical composition of material from the nearshore water and nearshore benthos compartments of the nearshore shunt model.

3. To determine whether or not the material from the nearshore benthos is being transported directly to the discharge by long-shore currents, compare the chemical composition of material from the nearshore benthos and discharge compartments of the nearshore shunt model.

4. To obtain a better understanding of the contributions of various sources of particulate matter, determine the POC/PN mass ratios and carbon and nitrogen isotopic signatures of possible sources of suspended particulate matter that are specific to this system.

5. In the present study, tributary inflows were sampled under baseflow conditions only. Since suspended solid and associated nutrient concentrations in tributaries can vary over orders of magnitude due to changes in flow (Droppo and Jaskot, 1995), determining the chemical composition of suspended particulate matter under stormflow conditions may help in understanding the sources and cycling of nutrients in Lake Erie.

Two other datasets were compiled as part of this study, but have not yet been analyzed. One contains concentrations of total particulate phosphorus, non-apatite inorganic phosphorus, organic phosphorus, and apatite phosphorus. The other contains data with respect to particle size distribution and particle morphology. Analysis of the phosphorus dataset may provide information concerning the sources and cycling of phosphorus in Lake Erie. The particle size and morphology dataset may be helpful in determining whether or not dreissenid mussels package the material they process into larger aggregates. It may also be useful in understanding the cycling and fate of material previously processed by the mussels.

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Appendix

Table A. 1: Mean, standard deviation (SD), minimum (Min), and maximum (Max) POC and PN values for all of the depths and dates sampled at each site. The number of replicates analyzed (n) and POC/PN values are also indicated.

Site	Depth (m)	Date	POC (µg/L)					PN (µg/L)					POC/PN
			Mean	SD	Min	Max	n	Mean	SD	Min	Max	n	
Grand River	N/A	24/05/02	1328	698	789	2117	3	157	35	120	190	3	8.46
		12/06/02	1181	93	1076	1254	3	202	26	175	227	3	5.86
		26/06/02	4110	270	3928	4421	3	713	55	656	765	3	5.76
		05/07/02	3543	174	3353	3695	3	630	29	598	653	3	5.63
		11/07/02	4285	129	4144	4398	3	729	13	716	742	3	5.88
		02/08/02	3604	96	3518	3708	3	731	20	708	744	3	4.93
		23/08/02	3062	93	2958	3139	3	586	23	568	612	3	5.23
		09/09/02	2046	17	2027	2060	3	466	22	449	490	3	4.39
		26/09/02	2482	88	2395	2572	3	429	82	335	482	3	5.78
		10/10/02	2340	208	2113	2522	3	467	47	413	500	3	5.01
		25/10/02	1408	88	1321	1497	3	292	26	266	317	3	4.82
Sandusk Creek	N/A	24/05/02	1773	156	1615	1927	3	305	44	260	348	3	5.81
		12/06/02	2080	48	2041	2133	3	366	11	357	379	3	5.68
		26/06/02	6938	246	6676	7163	3	1096	66	1030	1162	3	6.33
		05/07/02	5905	248	5640	6131	3	956	41	909	985	3	6.18
		11/07/02	9202	528	8639	9687	3	1448	74	1365	1506	3	6.35
		02/08/02	4859	374	4612	5289	3	807	48	769	861	3	6.02
		23/08/02	4064	152	3892	4180	3	777	32	742	804	3	5.23
		09/09/02	3935	1108	2662	4681	3	957	257	661	1106	3	4.11
		26/09/02	5827	841	5218	6787	3	1207	179	1071	1410	3	4.83
		10/10/02	2528	404	2256	2992	3	519	61	464	585	3	4.87
		25/10/02	2316	13	2301	2328	3	491	7	484	498	3	4.72
Nanticoke Creek	N/A	24/05/02	1241	130	1121	1378	3	187	18	166	200	3	6.64
		12/06/02	1226	206	1006	1415	3	205	43	163	249	3	5.98
		26/06/02	1501	25	1486	1530	3	282	11	274	289	2	5.32
		05/07/02	1509	357	1102	1773	3	261	71	180	311	3	5.77
		11/07/02	1589	11	1577	1598	3	251	6	246	257	3	6.33
		02/08/02	4384	86	4300	4472	3	838	61	799	908	3	5.23

Site	Depth (m)	Date	POC (µg/L)					PN (µg/L)					POC/PN
			Mean	SD	Min	Max	n	Mean	SD	Min	Max	n	
Nanticoke Creek, continued	N/A	23/08/02	7268	649	6848	8016	3	1408	127	1324	1554	3	5.16
		09/09/02	4699	104	4579	4764	3	901	34	863	926	3	5.21
		26/09/02	4461	859	3559	5271	3	846	149	688	984	3	5.27
		10/10/02	5144	615	4488	5707	3	976	78	912	1063	3	5.27
		25/10/02	2301	130	2163	2420	3	471	15	454	483	3	4.89
Lake Outflow	N/A	12/06/02	149	15	137	166	3	26	6	23	33	3	5.6
		26/06/02	145	7	138	151	3	27	4	24	32	3	5.4
		05/07/02	202	31	172	234	3	34	5	28	37	3	5.9
		11/07/02	135	6	132	142	3	24	2	22	25	3	5.6
		02/08/02	193	5	187	197	3	39	2	37	42	3	4.9
		23/08/02	178	25	150	199	3	29	3	26	31	3	6.2
		09/09/02	237	10	226	245	3	49	1	48	51	3	4.8
		26/09/02	195	18	184	216	3	36	2	35	38	3	5.4
		10/10/02	148	5	145	153	3	31	1	31	32	3	4.7
		25/10/02	169	11	161	182	3	32	1	31	33	3	5.3
PP2	0.5	18/07/02	403	51	346	441	3	84	2	83	86	3	4.8
		01/08/02	234	7	228	242	3	53	3	52	57	3	4.4
		09/10/02	253	11	247	265	3	52	7	47	60	3	4.9
	1	18/07/02	347	48	293	377	3	75	11	63	83	3	4.6
		01/08/02	249	14	235	263	3	57	1	55	58	3	4.4
		09/10/02	349	18	335	369	3	71	13	62	87	3	4.9
PP5	2	18/07/02	436	6	430	440	3	103	1	102	104	3	4.2
		31/07/02	232	7	224	236	3	52	5	48	57	3	4.4
		09/10/02	250	5	246	255	3	53	6	49	60	3	4.8
	4	18/07/02	348	32	311	370	3	86	10	75	92	3	4.1
		31/07/02	268	13	255	282	3	64	7	58	72	3	4.2
		09/10/02	373	9	365	382	3	71	1	70	71	3	5.3
PP10	4	18/07/02	334	30	310	369	3	47	23	21	60	3	7.1
		31/07/02	235	2	232	237	3	50	3	47	53	3	4.7
		09/10/02	301	71	249	382	3	52	16	42	71	3	5.8

Site	Depth (m)	Date	POC (µg/L)					PN (µg/L)					POC/PN
			Mean	SD	Min	Max	n	Mean	SD	Min	Max	n	
PP10, continued	9	18/07/02	280	29	248	305	3	58	3	57	62	3	4.8
		31/07/02	144	10	134	154	3	32	4	28	36	3	4.5
		09/10/02	340	111	247	463	3	53	8	47	62	3	6.4
L449	10	12/06/02	321				1	49				1	6.6
	12	10/07/02	192				1	28				1	6.9
	13	11/09/02	222				1	31				1	7.2
	0-11	30/10/02	194				1	8				1	20
L931	0-9	11/06/02	348				1	51				1	6.8
	0-8	09/07/02	151				1	42				1	3.6
	0-7	10/09/02	358				1	47				1	7.6
	0-7	29/10/02	152				1	24				1	6.3
L439	0-14	11/06/02	352				1	51				1	6.9
	18	09/07/02	215				1	45				1	4.8
	17	10/09/02	318				1	47				1	6.8
	0-16	29/10/02	143				1	23				1	6.2
L451	11	12/06/02	451				1	75				1	6.0
	14	10/07/02	218				1	37				1	5.9
	10	30/10/02	198				1	28				1	7.1
	30	12/06/02	198				1	36				1	5.5
	22	10/07/02	230				1	42				1	5.5
	27	11/09/02	138				1	24				1	5.8
	25	30/10/02	212				1	31				1	6.8
	39	12/06/02	123				1	20				1	6.2
	39	10/07/02	148				1	16				1	9.3
	38	11/09/02	92				1	14				1	6.6
	38	30/10/02	151				1	21				1	7.2
G15M	5	20/07/02	151	60	81	186	3	28	11	15	35	3	5.5
	8	17/08/02	252	8	245	262	3	41	1	39	42	3	6.2
	8.5	17/09/02	281	11	271	293	3	49	5	45	54	3	5.8
	60	20/07/02	61	42	35	109	3	11	7	6	19	3	5.5

Site	**Depth (m)**	**Date**	**POC (µg/L)**					**PN (µg/L)**					**POC/PN**
			Mean	**SD**	**Min**	**Max**	**n**	**Mean**	**SD**	**Min**	**Max**	**n**	
G15M, continued	60	17/08/02	57	7	50	65	3	12	2	10	13	3	4.9
	59	17/09/02	63	8	55	72	3	16	2	13	18	3	4.0
L23	15	12/06/02	476				1	78				1	6.1
	16	10/07/02	303				1	53				1	5.7
	19	30/07/02	186				1	32				1	5.8
	20	11/09/02	386				1	54				1	7.1
	20	31/10/02	242				1	39				1	6.2
	40	12/06/02	472				1	78				1	6.1
	35	10/07/02	136				1	22				1	6.2
	37	30/07/02	126				1	18				1	7.0
	35	11/09/02	138				1	19				1	7.3
	40	31/10/02	171				1	29				1	5.9
	52	10/07/02	117				1	12				1	9.8
	48	30/07/02	197				1	35				1	5.6
	48	11/09/02	89				1	12				1	7.4
	50	31/10/02	101				1	16				1	6.3
	60	12/06/02	107				1	19				1	5.6
	60	10/07/02	107				1	13				1	8.2
	60	30/07/02	111				1	20				1	5.6
	59	11/09/02	83				1	10				1	8.3
	59	31/10/02	114				1	16				1	7.1
G63	5	20/07/02	197	6	191	204	3	33	0	33	34	3	5.9
	10	17/08/02	275	5	273	281	3	46	1	45	47	3	6.0
	10	17/09/02	277	9	267	284	3	48	4	44	52	3	5.7
	40	20/07/02	58	35	36	98	3	11	5	7	17	3	5.5
	42	17/08/02	77	14	68	93	3	15	2	13	17	3	5.2
	40	17/09/02	64	17	44	74	3	11	3	8	13	3	5.8
L443	20	10/06/02	328				1	63				1	5.2
	20	09/07/02	271				1	43				1	6.3
	18	10/09/02	332				1	44				1	7.5

Site	Depth (m)	Date	POC (µg/L)					PN (µg/L)					POC/PN
			Mean	SD	Min	Max	n	Mean	SD	Min	Max	n	
L443, continued	0-20	29/10/02	189				1	30				1	6.3
GAsh	3	18/07/02	168	2	166	170	3	28	1	26	28	3	6.0
	2.5	18/08/02	243	5	238	248	3	41	1	40	41	3	6.0
	2.3	15/09/02	270	19	247	284	3	49	2	47	51	3	5.5
G78M	5	19/07/02	202	5	197	207	3	32	1	32	33	3	6.3
	7	19/08/02	333	15	319	349	3	57	2	55	58	3	5.9
	10	16/09/02	295	13	280	306	3	59	3	57	62	3	5.0
	20	19/07/02	197	17	184	216	3	38	4	35	42	3	5.2
	20	19/08/02	258	12	246	270	3	49	3	47	52	3	5.3
	18	16/09/02	292	4	287	294	3	60	1	58	61	3	4.9
G43	7	17/07/02	250	25	234	278	3	49	7	44	57	3	5.2
	10	20/08/02	382	14	366	390	3	64	2	61	66	3	6.0
	10	14/09/02	406	18	392	427	3	76	4	74	81	3	5.3
	17	17/07/02	296	127	219	443	3	40	1	39	42	3	7.3
	20	20/08/02	297	11	291	310	3	53	2	52	55	3	5.6
GSan	6	21/07/02	196	91	91	259	3	36	18	16	49	3	5.4
	6	21/08/02	447	26	418	469	3	82	3	79	85	3	5.4
	5.5	18/09/02	543	8	537	548	2	117	1	116	118	3	4.6
G91M	5	21/07/02	545	15	534	555	2	97	4	94	100	2	5.6
	4	21/08/02	734	22	716	758	3	145	4	140	149	3	5.1
	3.5	18/09/02	574	26	552	603	3	127	5	124	133	3	4.5

Table A. 2: Mean, standard deviation (SD), minimum (Min), and maximum (Max) δ^{13}C and δ^{15}N values for all of the depths and dates sampled at each site. The number of replicates analyzed (n) is also indicated.

Site	Depth (m)	Date	δ^{13}C (‰)					δ^{15}N (‰)				
			Mean	SD	Min	Max	n	Mean	SD	Min	Max	n
Grand River	N/A	24/05/02	-29.85	0.22	-30.11	-29.71	3	8.60	0.17	8.41	8.71	3
		12/06/02	-31.49	0.50	-32.06	-31.12	3	9.11	0.12	9.00	9.23	3
		26/06/02	-31.84	0.04	-31.89	-31.81	3	9.43	0.22	9.20	9.63	3
		05/07/02	-31.26	0.18	-31.46	-31.15	3	10.59	0.42	10.21	11.04	3
		11/07/02	-31.37	0.14	-31.47	-31.27	2	11.77	0.05	11.74	11.80	2
		02/08/02	-29.48	0.01	-29.49	-29.47	2	8.30	0.1	8.23	8.37	2
		23/08/02	-30.43	0.39	-30.70	-30.15	2	9.35	0.08	9.30	9.41	2
		09/09/02	-31.26	0.02	-31.28	-31.25	2	9.87	0.78	9.31	10.42	2
		26/09/02	-30.20	0.16	-30.31	-30.09	2	12.05	0.72	11.54	12.56	2
		10/10/02	-31.88	0.13	-31.97	-31.79	2	10.84	0.06	10.80	10.89	2
		25/10/02	-29.61	0.37	-29.88	-29.35	2	8.38	0.6	7.96	8.81	2
Sandusk Creek	N/A	24/05/02	-30.29	0.15	-30.44	-30.14	3	4.84	0.09	4.79	4.94	3
		12/06/02	-30.04	0.09	-30.13	-29.96	3	9.11	0.04	9.07	9.14	3
		26/06/02	-30.02	0.06	-30.08	-29.96	3	9.83	0.06	9.77	9.87	3
		05/07/02	-28.49	0.30	-28.84	-28.29	3	9.48	0.11	9.36	9.58	3
		11/07/02	-28.07	0.08	-28.13	-28.01	2	9.46	0.06	9.42	9.51	2
		02/08/02	-25.52	0.22	-25.67	-25.37	2	8.10	0.01	8.09	8.11	2
		23/08/02	-32.19	0.25	-32.37	-32.01	2	8.33	0.08	8.28	8.38	2
		09/09/02	-31.76	0.25	-31.94	-31.59	2	5.49	4.82	2.08	8.89	2
		26/09/02	-30.62	0.28	-30.82	-30.42	2	8.61	0.11	8.53	8.69	2
		10/10/02	-31.36	0.25	-31.54	-31.19	2	5.93	1.66	4.76	7.11	2
		25/10/02	-32.15	0.97	-32.83	-31.46	2	7.38	0.31	7.16	7.60	2
Nanticoke Creek	N/A	24/05/02	-27.48	0.15	-27.60	-27.31	3	6.37	0.15	6.24	6.53	3
		12/06/02	-30.64	0.22	-30.88	-30.46	3	9.46	0.10	9.35	9.54	3
		26/06/02	-30.43	0.08	-30.48	-30.34	3	11.05	0.13	10.97	11.20	3
		05/07/02	-27.70	0.80	-28.45	-26.85	3	10.80	0.58	10.23	11.38	3
		11/07/02	-27.45	0.16	-27.57	-27.34	2	10.62	0.05	10.59	10.66	2
		02/08/02	-32.90	0.28	-33.10	-32.70	2	9.88	0.22	9.73	10.04	2

Site	**Depth (m)**	**Date**	**δ^{13}C (‰)**					**δ^{15}N (‰)**				
			Mean	**SD**	**Min**	**Max**	**n**	**Mean**	**SD**	**Min**	**Max**	**n**
Nanticoke Creek, continued	N/A	23/08/02	-31.54	0.24	-31.71	-31.37	2	9.79	0.04	9.76	9.82	2
		09/09/02	-30.59	0.09	-30.65	-30.52	2	11.67	0.93	11.00	12.33	2
		26/09/02	-33.31	0.18	-33.44	-33.19	2	10.01	0.12	9.93	10.10	2
		10/10/02	-31.27	0.08	-31.33	-31.21	2	11.39	1.25	10.51	12.28	2
		25/10/02	-29.09	0.22	-29.24	-28.94	2	9.99	0.08	9.93	10.05	2
Lake Outflow	N/A	21/05/02	-25.15	0.15	-25.31	-25.02	3	5.76	0.22	5.53	5.96	3
		12/06/02	-22.79	0.17	-22.97	-22.65	3	4.27	0.15	4.10	4.36	3
		26/06/02	-23.09	0.20	-23.27	-22.87	3	5.56	0.26	5.33	5.84	3
		05/07/02	-22.86	0.06	-22.90	-22.79	3	5.73	0.19	5.58	5.95	3
		11/07/02	-22.27	0.11	-22.34	-22.19	2	5.14	0.04	5.11	5.17	2
		02/08/02	-22.16	0.42	-22.46	-21.86	2	5.90	0.17	5.78	6.02	2
		23/08/02	-22.81	0.03	-22.83	-22.79	2	4.81	1.39	3.82	5.79	2
		09/09/02	-23.18	0.11	-23.25	-23.10	2	6.46	0.63	6.02	6.91	2
		26/09/02	-24.43	0.01	-24.43	-24.42	2	7.94	0.76	7.40	8.47	2
		10/10/02	-23.45	0.43	-23.76	-23.15	2	6.59	0.63	6.14	7.04	2
		25/10/02	-24.07	0.19	-24.21	-23.94	2	6.49	0.29	6.28	6.70	2
PP2	0.5	18/07/02	-23.18	0.07	-23.25	-23.13	3	7.54	0.10	7.43	7.64	3
		01/08/02	-24.50	0.19	-24.68	-24.30	3	7.89	0.12	7.77	8.02	3
		09/10/02	-25.07	0.07	-25.15	-25.02	3	7.51	0.08	7.47	7.60	3
PP5	2	18/07/02	-24.09	0.43	-24.46	-23.62	3	7.31	0.36	6.90	7.58	3
		31/07/02	-24.04	0.14	-24.13	-23.87	3	7.78	0.24	7.50	7.92	3
		09/10/02	-26.05	0.25	-26.34	-25.87	3	8.44	0.32	8.12	8.76	3
PP10	4	18/07/02	-23.48	0.40	-23.94	0.40	3	8.10	0.21	7.95	8.34	3
		31/07/02	-25.91	0.23	-26.17	0.23	3	7.58	0.20	7.39	7.78	3
		09/10/02	-25.43	0.08	-25.51	0.08	3	8.76	0.19	8.62	8.97	3
L449	10	11/06/02	-23.71	0.41	-24.00	-23.43	2	6.29	0.53	5.91	6.67	2
		09/07/02	-22.66	0.02	-22.68	-22.65	2	1.62	0.21	1.47	1.76	2
		11/09/02	-24.45	0.04	-24.48	-24.42	2	6.71	1.22	5.85	7.57	2
		30/10/02	-24.27	0.05	-24.31	-24.21	3	5.46	0.84	4.81	6.41	3
L931	8	09/07/02	-24.97	0.14	-25.06	-24.87	2	2.28	0.16	2.17	2.40	2

Site	Depth (m)	Date	$\delta^{13}C$ (‰)					$\delta^{15}N$ (‰)				
			Mean	**SD**	**Min**	**Max**	**n**	**Mean**	**SD**	**Min**	**Max**	**n**
L931, continued	8	10/09/02	-24.51	0.01	-24.51	-24.50	2	5.23	0.56	4.84	5.63	2
L439	17	11/06/02	-25.42	0.06	-25.46	-25.38	2	4.59	0.15	4.48	4.70	2
		09/07/02	-25.32	0.30	-25.53	-25.10	2	3.25	1.06	2.51	4.00	2
		10/09/02	-25.57	0.24	-25.74	-25.39	2	3.59	0.51	3.22	3.95	2
		30/10/02	-26.30	0.13	-26.42	-26.16	3	2.63	0.66	1.87	3.06	3
L451	14	12/06/02	-24.18	0.86	-24.79	-23.57	2	6.48				1
		10/07/02	-24.54				1	3.06				1
		11/09/02	-25.74	0.06	-25.78	-25.69	2	7.72	0.24	7.55	7.90	2
	24	12/06/02	-24.81	0.04	-24.84	-24.78	2					
		10/07/02	-25.06	0.08	-25.11	-25.00	2	4.61	0.05	4.58	4.65	2
		11/09/02	-25.73	0.14	-25.83	-25.63	2	7.45	1.28	6.54	8.35	2
	37	12/06/02	-25.10	0.81	-25.68	-24.53	2	6.06	0.45	5.74	6.38	2
		10/07/02	-25.07	0.06	-25.11	-25.03	2	3.26	0.08	3.21	3.32	2
		11/09/02	-25.59	0.07	-25.64	-25.54	2	8.78	0.13	8.68	8.87	2
G15M	5	20/07/02	-25.55	0.05	-25.61	-25.50	3	5.48	0.17	0.17	5.67	3
	8	17/08/02	-24.86	0.21	-25.01	-24.71	2	4.38	0.12	4.29	4.46	2
	8.5	17/09/02	-26.31	0.10	-26.38	-26.24	2	6.58	0.21	6.43	6.73	2
	60	20/07/02	-25.76	0.18	-25.95	-25.59	3	7.26	0.61	0.61	7.94	3
	60	17/08/02	-25.24	0.19	-25.38	-25.10	2	8.94	0.30	8.73	9.15	2
	59	17/09/02	-26.55	0.23	-26.72	-26.39	2	9.97	0.15	9.87	10.08	2
L23	20	12/06/02	-26.56	1.88	-27.89	-25.23	2	8.16	0.26	7.97	8.35	2
		11/07/02	-25.85	0.02	-25.86	-25.84	2	4.13	0.06	4.09	4.18	2
		11/09/02	-24.94	0.15	-25.04	-24.83	2	6.89	0.03	6.87	6.91	2
		31/10/02	-25.42	0.36	-25.79	-25.06	3	8.08	0.49	7.60	8.57	3
	40	12/06/02	-26.03	0.05	-26.07	-26.00	2	7.89	0.34	7.64	8.13	2
		11/07/02	-25.21	0.28	-25.41	-25.02	2	4.23	0.33	3.99	4.46	2
		11/09/02	-25.45	0.12	-25.53	-25.36	2	6.50	0.24	6.33	6.67	2
		31/10/02	-26.31	0.22	-26.55	-26.13	3	4.17	3.51	0.12	6.37	3
	50	12/06/02	-26.02	0.03	-26.04	-26.00	2	4.52	0.35	4.27	4.76	2
		11/07/02	-24.91	0.18	-25.03	-24.78	2	3.06	0.21	2.91	3.21	2

Site	Depth (m)	Date	δ^{13}C (‰)					δ^{15}N (‰)				
			Mean	**SD**	**Min**	**Max**	**n**	**Mean**	**SD**	**Min**	**Max**	**n**
L23, continued	50	11/09/02	-25.71	0.08	-25.77	-25.66	2	4.40	0.41	4.11	4.69	2
		31/10/02	-26.40	0.15	-26.54	-26.24	3	7.12	0.95	6.05	7.84	3
	60	12/06/02	-26.21	0.18	-26.33	-26.08	2	4.49	0.38	4.22	4.77	2
		11/07/02	-25.31	0.04	-25.34	-25.28	2	4.21	0.86	3.60	4.81	2
		11/09/02	-25.91	0.03	-25.93	-25.89	2	4.50	0.29	4.29	4.70	2
		31/10/02	-26.26	0.14	-26.36	-26.10	3	9.59	0.85	8.65	10.30	3
G63	5	20/07/02	-24.82	0.29	-25.11	-24.54	3	4.79	0.18	0.18	5.00	3
	10	17/08/02	-23.54	0.53	-23.91	-23.16	2	5.23	0.52	4.86	5.59	2
	10	17/09/02	-25.94	0.07	-25.99	-25.90	2	6.24	0.21	6.08	6.39	2
	40	20/07/02	-26.53	0.11	-26.65	-26.45	3	5.40	0.19	0.19	5.57	3
	42	17/08/02	-23.81	0.35	-24.06	-23.56	2	8.62	0.18	8.50	8.75	2
	40	17/09/02	-26.08	0.19	-26.21	-25.95	2	9.03	0.57	8.62	9.44	2
L443	15	10/06/02	-25.62	0.08	-25.68	-25.57	2	2.68	0.32	2.46	2.91	2
		09/07/02	-24.60	0.10	-24.67	-24.54	2	5.46	0.74	4.94	5.99	2
		10/09/02	-25.45	0.19	-25.59	-25.32	2	6.17	0.23	6.00	6.33	2
		30/10/02	-26.25	0.02	-26.27	-26.23	3	6.28	2.38	3.97	8.72	3
	21	10/06/02	-25.47	0.08	-25.53	-25.42	2	4.19	0.56	3.79	4.59	2
		09/07/02	-24.86	0.02	-24.88	-24.85	2	3.21	0.04	3.18	3.24	2
		10/09/02	-25.56	0.04	-25.59	-25.53	2	6.72	0.66	6.25	7.18	2
		30/10/02	-26.08	0.25	-26.27	-25.80	3	4.28	0.26	4.03	4.55	3
GAsh	3	18/07/02	-25.13	0.02	-25.15	-25.10	3	5.11	0.62	0.62	5.71	3
	2.5	18/08/02	-26.84	0.18	-26.97	-26.71	2	6.46	0.16	6.35	6.58	2
	2.3	15/09/02	-20.51	0.02	-20.52	-20.49	2	6.35	0.25	6.18	6.53	2
G78M	5	19/07/02	-26.24	0.08	-26.33	-26.19	3	5.58	0.56	0.56	5.97	3
	7	19/08/02	-23.52	0.15	-23.63	-23.41	2	4.90	0.24	4.73	5.07	2
	10	16/09/02	-25.86	0.06	-25.90	-25.81	2	5.31	0.21	5.16	5.46	2
	20	19/07/02	-25.53	0.08	-25.59	-25.44	3	6.89	0.15	0.15	7.06	3
	20	19/08/02	-24.26	0.58	-24.67	-23.85	2	5.08	0.59	4.66	5.50	2
	18	16/09/02	-25.38	0.03	-25.40	-25.36	2	5.48	0.34	5.24	5.73	2
G43	7	17/07/02	-26.40	0.10	-26.51	-26.33	3	5.61	0.74	0.74	6.15	3

Site	**Depth (m)**	**Date**	**δ^{13}C (‰)**					**δ^{15}N (‰)**				
			Mean	**SD**	**Min**	**Max**	**n**	**Mean**	**SD**	**Min**	**Max**	**n**
G43, continued	10	20/08/02	-24.97	0.01	-24.98	-24.97	2	5.29	0.12	5.21	5.37	2
	10	14/09/02	-25.25	0.13	-25.35	-25.16	2	7.87	0.14	7.77	7.97	2
	17	17/07/02	-25.58	0.31	-25.93	-25.37	3	4.50	0.25	0.25	4.66	3
	20	20/08/02	-25.38	0.14	-25.48	-25.28	2	7.00	0.00	7.00	7.00	2
GSan	6	21/07/02	-24.70	0.09	-24.79	-24.61	3	6.24	0.61	0.61	6.80	3
	6	21/08/02	-25.29	0.40	-25.58	-25.01	2	6.37	0.18	6.25	6.50	2
	5.5	18/09/02	-23.63	0.03	-23.65	-23.61	2	6.69	0.08	6.63	6.74	2
G91M	5	21/07/02	-22.13	0.19	-22.33	-21.94	3	6.60	0.31	0.31	6.96	3
	4	21/08/02	-23.44	0.01	-23.44	-23.43	2	4.62	0.06	4.58	4.67	2
	3.5	18/09/02	-24.68	0.08	-24.74	-24.63	2	4.66	0.26	4.48	4.85	2