Tracing the Flow of Organic Matter from the Muskegon River Estuary System to Nearshore Lake Michigan: a Stable Isotope Analysis

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Abstract

The fate of inputs of organic matter from individual watersheds to the Great Lakes is poorly known. The goal of this study was to track the delivery of organic matter from the Muskegon River Estuary System (MRES) into nearshore Lake Michigan through a stable isotope analysis of water, sediment, and sources of primary production. The MRES is comprised of the lowest 90 km of the Muskegon River watershed from Croton Dam and includes Muskegon Lake, a drowned river mouth lake. Nutrients, total suspended material (TSM) and particular organic matter (POM) were measured from water samples collected monthly from May through October at five stations from Croton Dam to nearshore Lake Michigan, and carbon and nitrogen stable isotope signatures were analyzed. Sediments were collected at several sites in Muskegon Lake and nearshore Lake Michigan in May and September, and their grain size compositions and isotopic signatures were characterized. Values of TSM were significantly higher at the mouth of the Muskegon River (average 9.14 ± 1.67 mg/L) than in nearshore Lake Michigan (average 1.40 ± 0.17 mg/L), suggesting that much of the suspended material from Muskegon River was retained within Muskegon Lake. Isotopic signatures of POM collected in Muskegon Lake were depleted in $\delta^{13}C$ (-30.8‰) relative to the isotope signatures of POM from Lake Michigan (-26.2 ‰) or the mouth of the Muskegon River (-28.1 ‰), suggesting an additional source of depleted carbon was present in Muskegon Lake, likely biogenic methane. Sediments in Muskegon Lake were characterized by fine grains (< 63μm) with depleted $\delta^{13}C$ signatures (-28.9 ‰) compared to Lake Michigan sediments which were characterized by larger grains (>210 μm) with enriched $\delta^{13}C$ signatures (-24.1 ‰). Sediment $\delta^{15}N$ signatures increased on a strong east-to-west

gradient within Muskegon Lake itself, indicating significant microbial processing of nutrients occurring within the lake. Additionally, the west end of Muskegon Lake was characterized by sediment with higher levels of organic carbon and lower C/N ratios than measured either in Lake Michigan or Muskegon River, indicating an area of extensive aquatic production. The extent of nutrient uptake occurring in Muskegon Lake may have completely altered the chemical and isotopic characterization of organic matter flowing into the lake from Muskegon River. As such, there was no traceable impact of the carbon and nitrogen content of organic matter from Muskegon River to nearshore Lake Michigan.

Introduction

Organic matter (OM) is a mix of plant, animal, and microbial material in a dissolved or particulate state, and in various forms of decomposition, that serves as the base of food webs in aquatic ecosystems. OM in aquatic ecosystems can be derived from terrestrial (autochthonous) or aquatic (allocthonous) production. Tracing the delivery and fate of OM provides a critical means of understanding the linkage between terrestrial and aquatic systems. Since aquatic ecosystems are classified as "open" systems, they must have a continuous supply of new organic matter to satisfy the metabolic needs of that system (Wetzel 2001). As such, some scientists have argued that understanding and mapping the fate of organic matter in aquatic food webs is as critical as measuring biodiversity when evaluating the overall health of that system (Bunn et al. 1999). Many studies have examined the fate of riverine organic matter in estuaries and oceans (Eadie et al. 1984, Peterson and Howarth 1987, Canuel et al. 1995, Middleburg and Nieuwenhuize 1998, Alliot et al. 2003). However, virtually no studies have looked at the fate of riverine organic material from individual watersheds in the nearshore zone of the Laurentian Great Lakes.

Sources of organic matter can be differentiated using elemental and/or isotopic analyses, provided there has been little degradation of the source material (Middleburg and Nieuwenhuize 1998). Stable isotopes are increasingly being used to measure energy sources and transfers within aquatic food webs. This methodology measures natural ratios of heavy to light isotopes of a given element, expressed as δ values in units "per mil" or

‰. Increasing (enriched) δ values denote a greater presence of the heavier isotope. Multiple isotopes with different properties are often used to study energy sources and trophic levels of an ecosystem (Peterson and Fry 1987). Depending on the element, the isotope may change (fractionate) regularly with increasing trophic levels. Carbon isotopes are measured as the ratio of ^{13}C to ^{12}C, and have an average fractionation of 0 to 1‰ per trophic level (DeNiro and Epstein 1978). Given this small rate of fractionation, carbon is used as a means of tracing original energy sources in an ecosystem when there are at least two different sources of organic carbon with distinct isotopic signatures, such as terrestrial plants and phytoplankton (Peterson and Howarth 1987, Hamilton et al. 1992). In addition to tracing energy origins, carbon isotopes have also been successfully used to trace primary productivity and the effect of the phosphorus abatement program in the Great Lakes (Schelske and Hodell 1991, Hodell and Schelske 1998).

Nitrogen isotopes are measured as the ratio of ^{15}N to ^{14}N, and are assumed to fractionate regularly with increasing trophic position, with an average fractionation of 3.4‰ per trophic level (Minagawa and Wada 1984). However, this assumed fractionation can vary widely depending on nitrogen availability in food sources (Adams and Sterner 2000). Nitrogen isotopes are primarily used to assign trophic position to food web biota, although they are generally more difficult to interpret than carbon isotopes because the nitrogen cycle is more complicated than the carbon cycle (Bernasconi et al. 1997). Nitrogen isotopes are useful in identifying anthropogenic influences, which are typically enriched in ^{15}N (Cabana and Rasmussen 1996, Harvey and Kitchell 2000). In addition, previous research has shown that the process of denitrification results in nitrate that is

highly enriched in ^{15}N, and high levels of denitrification often occur in oxygen-depleted waters. This enriched ^{15}N gets incorporated into the food web, leading to higher $\delta^{15}N$ values for all food web components (Michener and Schell 1994). Increased $\delta^{15}N$ values in organic matter can reflect extensive degradation of the source material (Owens and Law 1989).

The Muskegon River is one of Lake Michigan's largest tributaries, and serves as a critical spawning and nursery area for many Great Lakes fishery species including walleye (*Sander vitreus*), Chinook salmon (*Oncorhynchus tshawytscha*), and steelhead (*Oncorhynchus mykiss*). This watershed also has recently been highlighted as an area where urban land usage is projected to significantly increase in the coming decades (Tang et al. 2005). The Muskegon River estuary system (MRES) includes the lower 90 km of the Muskegon River and the drowned river mouth, Muskegon Lake. The general purpose of this study was to trace the ecological "footprint" or signal of the MRES on nearshore Lake Michigan in an attempt to quantify contributions of riverine nutrients to nearshore Lake Michigan. The study sought to trace the delivery of nutrients (C, N, and P) from terrestrial/riverine habitats to nearshore Lake Michigan, and to use carbon and nitrogen stable isotopes as a means of characterizing MRES organic matter to determine the delivery and impact of this material on the coastal ecology of nearshore Lake Michigan. These objectives were designed to test two hypotheses. First, riverine inputs of nutrients and carbon to Lake Michigan had strong and measurable effects on the coastal ecology of nearshore Lake Michigan. Second, that carbon and nitrogen stable isotopes could be

successfully used to quantify these riverine nutrient contributions to nearshore Lake Michigan.

Methods

Site Description

The Muskegon River watershed (Figure 1) has the second largest catchment in Michigan with an area of ~5,900 km^2, and encompasses a 370 km-long river that terminates in Muskegon Lake. Mean annual discharge of the Muskegon River measured near the town of Newaygo is 55.8 cms, with average gradient of 0.49 m/km (O'Neal 1997). River habitat is varied, and warm, cool, and coldwater fish species are found throughout the mainstem of the Muskegon River (O'Neal 1997). The watershed predominately consists of forested (53.2%) and agricultural lands (23.0 %), with only a small percentage of urban land cover (4.2%). However, the Muskegon watershed is predicted to become significantly more urbanized, with the proportion of urbanized land potentially increasing to 11.5% by the year 2040 (Tang et al. 2005).

The study focused on the MRES. Riverine habitat in the upper portion of the study area (Croton Dam to Newaygo) is characterized by moderate-to-high water velocity, hard bottom substrates, and moderate river gradients (O'Neal 1997). This is one of the prime recreational fishing areas in Michigan, and supports the largest population of natural reproducing Chinook salmon in Michigan (Carl 1980). River habitats change dramatically downstream of Newaygo, with water velocity decreasing and bottom substrates becoming softer. The Muskegon River terminates in Muskegon Lake at one of the largest (40 km^2) wetlands in the Great Lakes region (O'Neal, 1997).

Muskegon Lake is a drowned river-mouth lake, with a mean depth of 7.1 meters, a maximum depth of 21 meters, and an estimated volume of 119 million m^3 given a low water datum mark of 173.35 m above sea level for Lake Michigan (Evans 1992). The mean hydraulic residence time in Muskegon Lake is 23 days (Carter 2002). Residence time can vary seasonally over a range of fourteen to seventy days, depending on discharge from Muskegon River (Brian Eadie, NOAA- Great Lakes Environmental Research Laboratory, personal communication). Muskegon Lake has been heavily impacted by industrial and human waste since settlement, prompting the Environmental Protection Agency to list it as an area of concern (AOC) in 1985 (US EPA 2007). Recently, water quality in Muskegon Lake has improved and the lake may be removed from the AOC listing within the next decade (Alexander 2005).

Lake Michigan is the third largest of the Laurentian Great Lakes, with a surface area of 57,800 km^2, a total volume of 4,920 km^3, and a hydraulic residence time of 62 years (Eadie 1997). The lake is divided into a northern and southern basin. Lake Michigan is oligotrophic, and productivity in the southern basin is higher than in the northern basin due to differences in geology and consequent nutrient supply from the respective drainage basins (Mackin et al. 1980, Meyers and Eadie 1993). Circulation in Lake Michigan is almost entirely wind-driven and consequently is extremely episodic (Kerfoot et al. 2004). Northerly winds in winter result in the formation of two counter-rotating gyres: a clockwise gyre in the northern portion of the lake, and a counter-clockwise gyre in the southern portion of the lake (Beletsky and Schwab 2001). Turbidity plumes have

been documented along the southern coast of the lake during high wind events in late winter and spring, re-suspending sediments for up to six weeks at a time (Schwab et al. 2000). Summer circulation patterns in Lake Michigan are also characterized by formation of a counter-clockwise gyre which can encompass the entire southern basin of the lake (Beletsky et al. 2006).

Sampling and Analysis

Measurements of average daily flow in Muskegon River were recorded by a USGS stream gage beneath Croton Dam. Whole water samples were collected for nutrient and particulate organic matter analysis monthly from March through October 2003 at five fixed stations (Figure 1). Two stations were located in the Muskegon River; at Pine Street boat launch near Croton Dam and in the North Channel at the Highway 120 Bridge (where the Muskegon River flows into Muskegon Lake). One station was located in Muskegon Lake, another in the shipping channel connecting Muskegon Lake to Lake Michigan, and the final sampling station was in the nearshore zone of Lake Michigan, 0.5 km directly west of the shipping channel. The Muskegon Lake, Lake Michigan, and North Channel stations were sampled using Niskin bottles to collect water samples from a depth of three meters. Samples were then transferred to acid-washed 4 L polyethylene bottles. At the Pine Street station (near Croton Dam), the sample was obtained by wading approximately 7 m into the river channel and collecting water directly in the polyethylene bottle. All samples were stored on ice until they could be processed within 24 hours of collection.

Water samples were processed by filtering whole water samples to prepare the following components for measurement: dissolved organic carbon (DOC), particulate organic matter (POM), total suspended material (TSM), total dissolved phosphorus (TDP), and nitrate (NO_3). Total phosphorous (TP) concentrations were obtained from un-filtered water samples. DOC samples were obtained by filtering 50 ml aliquots through pre-combusted 25 mm diameter Whatman GF/F filters and collecting the filtrate into Kimble amber glass vials (Fisher Scientific, Chicago, IL). The vials were then frozen and sent to G.G. Hatch Isotope Laboratories (Ottawa, Ontario, Canada) for analysis of DOC concentration (mg/L) and $\delta^{13}C$ signatures. POM samples were obtained by filtering 300 ml of whole water through pre-combusted 25 mm diameter Whatman GF/F filters (Fisher Scientific, Chicago, IL). POM filters were acidified with 2 N HCL and dried in an oven overnight at 60 ºC. The filters were then placed in Vycor tubes which had been pre-combusted at 900 ºC. Pre-combusted Cu powder and CuO wire were added to these tubes which were then evacuated and flame sealed. The samples were combusted at 650 ºC for 10 hours. Gases were purified by cryogenic vacuum distillation; H_2O was frozen into a dry-ice 2-propanol trap (~80 ºC), CO_2 was frozen into a sample tube and then immersed in liquid nitrogen and frozen into a sample bulb containing silica gel at liquid nitrogen temperature (approximately -195 °C). Stable isotopes of carbon and nitrogen were analyzed using a VG PRISM mass spectrometer. TSM samples were obtained by filtering 500-1000 ml of water (depending on turbidity of the sample) onto pre-weighed 47 mm diameter Whatman GF/F filters (Fisher Scientific, Chicago, IL). Filters were then stored frozen until they could be dried and weighed (0.1 mg) to determine TSM concentration (mg/L). TP samples were obtained by pouring 50 ml of whole water into acid-rinsed

Pyrex tubes and refrigerating the samples. TDP samples were collected by filtering a 20 ml aliquot of whole water through a 0.2 μm nylon syringe filter into an acid-rinsed Pyrex tube and refrigerating the sample. TP and TDP samples were digested in an autoclave after addition of potassium persulfate (5 % final concentration) and then measured for soluble phosphorus (Menzel and Corwin 1965). Nitrate concentrations (NO_3 +NO_2) were determined by the cadmium reduction method based on an azo dye reaction. Nutrient concentrations were measured using standard automatic colorimetric procedures on an Auto Analyzer II (Davis and Simmons 1979).

In May and August of 2003, samples of dominant aquatic, emergent, and terrestrial plants from Muskegon River were collected to characterize sources of organic carbon inputs into Muskegon Lake and nearshore Lake Michigan. Samples were collected at every boat access point in the lower Muskegon River between Croton Dam and Muskegon Lake. When possible, three types of vegetation (terrestrial, aquatic, emergent) were collected at each location. Common plants collected included: *Salix nigra* (black willow), *Acer saccharum* (sugar maple), *Typha latifolia* (cattail), and *Elodea canadensis* (waterweed). All plants were stored in plastic bags on ice, transported to the lab, and rinsed with distilled deionized water. Plants were identified to the lowest possible taxonomic level and freeze dried. Dried samples were then ground with a mortar and pestle and weighed into aluminum boats for isotope analysis by species.

A ponar with a sampling area of 0.047 m^2 was used to sample sediments from five stations within Muskegon River and 25 stations along a transect in Muskegon Lake and

Lake Michigan in May 2003. In September 2003, 38 stations were sampled along a transect in Muskegon Lake and the nearshore zone of Lake Michigan with the same ponar. Ponar samples were carefully placed in a tub and emptied slowly to preserve the top layer of the sample. When possible, this top layer (encompassing several centimeters) was scraped from the ponar sample and placed in a plastic bag to isolate the most recently deposited materials. Samples were transported to the lab on ice where they were passed through a 500 μm screen to remove invertebrates and large debris. Samples were transferred into pre-weighed acetone rinsed containers and allowed to settle in a refrigerator for 24 hours, before the overlying water was siphoned off. Samples were then freeze-dried and sieved once again to isolate three size fractions: fine material (<63 μm), a mid-size fraction (63-210 μm), and a large size fraction (>210 μm). All visible particles of shells were removed and samples were ground into homogenized powder with a mortar and pestle and weighed. Carbonates were removed from sub-samples of approximately 0.2 g of sediment by adding several milliliters of 2 N HCL and mixing on a shaker table overnight. The sub-samples were then dried for 24 hours at 60ºC and ground once again with a mortar and pestle before analysis for organic carbon and nitrogen content (Carbo Erba elemental analyzer model 1110). Aliquots of acidified sediment were weighed into aluminum tins. Due to problems with lab processing, results from most of the May sediment samples collected from Lake Michigan and Muskegon Lake could not be used for this analysis.

Sediment contour plots were created using the natural neighbor gridding function of the Surfer 8 software for Windows (Golden Software Inc). This function enables the user to

generate a 3-dimensional continuous fit to irregularly spaced data. To create the fit, Surfer generates a grid of X (latitude), Y (longitude), and Z (data) values. Z values are interpolated or extrapolated for each grid node based on the existing data. The natural neighbor function uses a weighted average of the neighboring observations to generate the Z grid values, but does not extrapolate the Z values beyond the scope of the existing data.

Stable isotope analyses for carbon and nitrogen of plants and sediments were conducted by the Terrestrial Ecosystems Laboratory at the University of Michigan. Samples were converted to CO_2 or N_2 gas and analyzed for percentage of ^{15}N and ^{13}C atoms on a Delta Plus isotope ratio mass spectrometer with a Conflo II interface (Thermo Finnigan, San Jose, CA). The coefficient of variation for all replicate isotope samples was approximately 0.2 ‰ for $\delta^{13}C$ and 0.3 ‰ for $\delta^{15}N$. Stable isotope ratios were calculated using the following equation:

$$\delta X = \{(R_{sample} / R_{standard}) - 1\} \times 10^3$$

Where X is ^{13}C or ^{15}N, and R is the ratio of heavy to light isotope $^{13}C/^{12}C$ or $^{15}N/^{14}N$. The standard reference materials used to complete these calculations were PeeDee limestone for carbon, or atmospheric nitrogen gas for nitrogen (Peterson and Fry 1987).

All statistical analyses were run on SigmaStat Version 3.1. Differences in water chemistry concentrations (DOC, TSM, TP, TDP, POM, and NO_3) among sites and months were evaluated with two-way ANOVAs. Post-hoc pairwise comparisons of these two-way ANOVAs were made with Holm-Sidak tests. Differences among $\delta^{13}C$ and $\delta^{15}N$

signatures of sources of primary production in Muskegon River were analyzed with one-way ANOVA when the data were equally distributed, and a non-parametric Kruskal-Wallis ANOVA on ranks when the data were not normally distributed. Sediment samples were either analyzed with t-tests or Mann-Whitney tests on ranks to examine differences between transects from Muskegon Lake and Lake Michigan, depending on whether the equal variance assumption was met by the data. Results of statistical tests were considered significant at the $\alpha = 0.05$ level.

Results

Discharge of the Muskegon River at Croton Dam in 2003 was typical of river discharges during the 5-year period from 1999 to 2004. Discharge ranged from a low of 21.2 cms recorded on 11 September 2003 to a high of 115.2 cms on 5 November 2003, with a spring peak of 90.3 cms occurring on 21 April 2003 (Figure 2). Sediment values varied among sites (Two-way ANOVA: $F = 16.057$, $df = 4$, $p < 0.001$) but not among samples dates (Two-way ANOVA: $F = 0.810$, $df = 7$, $p = 0.586$) (Table 1 and Table 2). Average TSM at the North Channel site was much larger than that measured in Lake Michigan ($p < 0.001$), with concentrations at the North Channel ranging from 3 to 18 mg/L (Figure 3). A dramatic peak in TSM occurred in April at the North Channel when sampling corresponded with a spring flood event. TSM at other stations ranged between 1 and 5 mg/L.

Water chemistry values varied among sites and sample dates. Total phosphorus (TP) concentrations were significantly different among sites and months (Two-way ANOVA: Site $F = 11.177$, $df = 4$, $p < 0.001$; Month- $F = 3.493$, $df = 7$, $p = 0.008$) (Figure 4). TP was lower in Lake Michigan compared to other sites, and lower during April through August than in September and October. However, the highest TP concentration was measured at the North Channel site during a spring flood in April. Total dissolved phosphorus concentrations also varied significantly among months and sites. Lowest concentrations were found in Lake Michigan compared to other sites, and during April through July before increasing in late summer and fall (Two-way ANOVA; Site $F = 7.736$, $df = 4$, $p < 0.001$; Month- $F = 3.261$, $df = 7$, $p = 0.012$) (Figure 5).

Concentrations of dissolved organic carbon followed explicit temporal patterns, peaking at most sites in June or July and dramatically decreasing in late summer and fall (Figure 6). A two-way analysis of variance revealed that differences in DOC concentrations were statistically significant among sites and months (Two-way ANOVA Site: $F = 15.114$, $df = 4$, $p < 0.001$; Month- $F = 7.540$, $df = 7$, $p < 0.001$). In contrast, $\delta^{13}C$ isotopic signatures of DOC did not vary significantly among sites or months (Tables 1, 2) (Two-way ANOVA Site: $F = 2.521$, $df = 4$, $p = 0.063$; Month- $F = 1.511$, $df = 7$, $p < 0.204$).

Nitrate concentrations exhibited a general decline at all sampling stations throughout the sampling period (Figure 7). Though the nitrate data for the September sample date were lost, the general declining trend continued on through October. Differences in nitrate concentration were significant by site and month (Two-way ANOVA Site: $F = 5.745$, $df = 4$, $p = 0.002$; Month- $F = 27.676$, $df = 6$, $p < 0.001$). From March to June, nitrate concentrations were highest at North Channel and lowest in Lake Michigan. However, nitrate concentrations in Muskegon Lake and at Croton Dam fell below those measured in Lake Michigan beginning in July, and remained lower through the end of the sampling period.

Organic matter samples collected at the five water stations were characterized by clear site-specific patterns in the isotope data. A two-way ANOVA revealed no statistically significant pattern in monthly $\delta^{13}C$ signatures of POM ($F = 0.697$, $df = 7$, $p = 0.674$), but differences were statistically significant across sites (Two-way ANOVA; $F = 13.227$, $df = 4$, $p < 0.001$) (Figure 8). Multiple comparison tests between sites showed that $\delta^{13}C$

POM differences were significant between Muskegon Lake and Lake Michigan ($p < 0.001$), and between Muskegon Lake and North Channel and Croton Dam ($p = 0.003$), but not between Croton and North Channel ($p = 0.216$). $\delta^{15}N$ POM values varied significantly among months (Two-way ANOVA; $F = 4.744$, $df = 4$, $p = 0.001$) and sites (Two-way ANOVA: $F = 13.979$, $df = 4$, $p < 0.001$) (Figure 9). Multiple comparison tests revealed significant differences in the $\delta^{15}N$ of POM collected in March through July when compared to August ($p = 0.001$), September ($p < 0.001$) and October ($p < 0.001$). Site comparisons demonstrated a significant difference between $\delta^{15}N$ POM samples from Muskegon Lake and Lake Michigan ($p < 0.001$). However, differences in $\delta^{15}N$ of POM between Croton Dam and Muskegon Lake ($p = 0.078$) and Croton and North Channel ($p = 0.216$) were not significant. When $\delta^{13}C$ and $\delta^{15}N$ POM signatures were averaged by site for the entire sampling period, Lake Michigan POM was characterized by depleted $\delta^{15}N$ and enriched $\delta^{13}C$ relative to Muskegon Lake. POM $\delta^{13}C$ signatures for Muskegon River at Croton Dam and North Channel were intermediate between Muskegon Lake and Lake Michigan (Figure 10).

Isotope signatures of POM were compared with those of several different types of primary producers collected in the Muskegon River including aquatic plants, emergent vegetation, and terrestrial plants. Each plant type was characterized by a distinct isotopic signature within the Muskegon River (One-Way ANOVA: $\delta^{13}C$ $H = 25.791$, $df = 5$, $p < 0.001$; $\delta^{15}N$ $H = 35.294$, $df = 5$, $p < 0.001$). Generally, terrestrial plants were characterized by lower $\delta^{13}C$ and $\delta^{15}N$ signatures than aquatic vegetation, with POM having an intermediate value between the two types of vegetation. A single sample of

periphyton collected in the upper reaches of the lower Muskegon River had a high $\delta^{15}N$ and a low $\delta^{13}C$ signature (Table 3, Figure 11).

Surficial sediment samples from Muskegon River, Muskegon Lake, and Lake Michigan were analyzed to determine the fate of organic matter coming from Muskegon River. Size fractionation of surficial sediment samples showed that Muskegon Lake had a high proportion of fine (<63 μm) sediment, with most of the samples consisting of more than 60% fine grain (Figure 12). In contrast, surface sediments in nearshore Lake Michigan were primarily comprised of mid-size grains (63-210 μm), which were not prevalent in Muskegon Lake (Figure 13). Localized areas of coarse (>210 μm) sediment were present on shelf areas in both nearshore Lake Michigan and Muskegon Lake (Figure 14).

Stable isotope analysis of the fine-grain sediment revealed extensive differences in the isotopic carbon signature of surface sediments collected from Muskegon Lake and nearshore Lake Michigan. Fine sediment $\delta^{13}C$ signatures in Muskegon Lake were significantly lighter (-29 to -30‰) than those found in nearshore Lake Michigan (-23 to -26‰) (Mann-Whitney test on ranks, $T = 472.0$, $n = 16, 21$, $p < 0.001$) (Figure 15). Differences in $\delta^{15}N$ signatures between fine sediments from Muskegon Lake and Lake Michigan were not statistically significant ($p = 0.427$). However, sediment $\delta^{15}N$ values in fine sediments clearly increased along a gradient from east to west within Muskegon Lake (Figure 16). The eastern end of Muskegon Lake was characterized by significantly lighter $\delta^{15}N$ signatures (around 4‰) than the western end (maximum $\delta^{15}N$ values of 6‰),

reflecting the input of sediment from Muskegon River (t-test, $t = -6.586$, $df = 19$, $p < 0.001$).

Levels of organic carbon in surficial sediments (Figure 17) were significantly higher in Muskegon Lake compared to nearshore Lake Michigan stations (t-test, $t = -12.923$, $df = 34$, $p < 0.001$). C/N ratios of fine grained sediment in Lake Michigan were considerably lower than those measured in Muskegon Lake (Mann-Whitney test on ranks, $T = 159.00$, $n = 16, 20$, $p < 0.001$), although there were localized areas where low C/N ratios occurred in the surficial sediments of Muskegon Lake (Figure 18).

Discussion

The purpose of this study was to track the flow of nutrients and particulate organic matter (POM) from the Muskegon River Estuary System (MRES) into the nearshore zone of Lake Michigan. Peaks in TSM and TP concentrations at the mouth of the Muskegon River were associated with peaks in river discharge, but were not associated with corresponding peaks in either Muskegon Lake or Lake Michigan. Stable isotope ratios of POM samples collected from Muskegon River, Muskegon Lake, and Lake Michigan were all unique to these areas. POM collected at the mouth of the Muskegon River appeared to consist of a mixture of terrestrial and aquatic material, lacking in significant seasonal variation. In contrast, POM samples collected in Lake Michigan were defined by an enriched $\delta^{13}C$ signature relative to the MRES, which became more enriched in the summer during periods of high primary productivity. Muskegon Lake appears to be a sink for materials coming from Muskegon River, and as such, the POM isotope signature was highly depleted in $\delta^{13}C$ relative to either Muskegon River or Lake Michigan. This depleted POM $\delta^{13}C$ signature likely reflected the amount of nutrient processing occurring within the lake, and the resulting production of biogenic methane. No evidence of terrestrial organic matter was detected in nearshore Lake Michigan, indicating that organic matter originating from the MRES either doesn't reach nearshore Lake Michigan in significant quantities, or if it does, is quickly advected away.

TSM concentrations in nearshore Lake Michigan were consistently one tenth of those measured at the North Channel of the Muskegon River, indicating that either the vast majority of riverine material was either retained in Muskegon Lake or was advected out

of nearshore Lake Michigan. TSM concentrations at Croton Dam remained relatively constant, while TSM concentrations near the river mouth fluctuated in synchrony with peaks in river discharge, but these peaks were not evident in either Muskegon Lake or Lake Michigan. An examination of Muskegon River flow data measured between 1999 and 2004 indicates discharge during 2003 was typical until November when river flow dramatically increased after sampling had already ended. If sampling occurred in a year characterized by an atypical discharge pattern (either increased or decreased river discharge), there may have been corresponding changes in the amount of suspended material or total phosphorous measured at the mouth of the Muskegon River, but it is unlikely these changes would have been evident in Muskegon Lake or Lake Michigan. Although this study may have been compromised by the lack of replicate samples for water chemistry within a location and a month, trends were realistic and variances in water chemistry parameters averaged over the course of the study were low. Future sampling efforts should collect and analyze replicate water samples in order to ensure statistical power/significance.

One of the primary goals of this study was to demonstrate that stable isotopes could be effectively used to characterize organic matter originating from the MRES. Due to inherent difficulties with separating individual species of phytoplankton and characterizing their isotopic signatures, bulk measurements of POM are often used as a surrogate for phytoplankton in food web studies (Fry and Sherr 1984, del Giorgio and France 1996). This assumption may be problematic, particularly in riverine food webs where particulate matter can be a mixture of materials from autochthonous (i.e.

phytoplankton and periphyton) and allocthonous (i.e. decomposing tree leaves) sources. Indeed, isotopic analysis of several types of primary producers collected in lower Muskegon River demonstrated that POM collected at the mouth of the river had an isotopic signature intermediate to those of terrestrial and aquatic plants; indicating that terrestrial and aquatic plants were source materials for riverine POM. Unfortunately, one potential source of error in this study was low sample size of some types of riverine primary producers. For example, only one sample of stream periphyton was analyzed for the upper reaches of the lower Muskegon River, and no phytoplankton samples were collected and analyzed for isotopes. Regardless, it is clear both aquatic and terrestrial sources are contributing to the isotopic composition of Muskegon River organic matter. Further, this mixture of source materials may also explain the lack of seasonal variation in POM isotopic signatures at the river mouth. Future efforts should devote more attention to identifying the relative composition of primary producers in riverine bulk POM. For example, stream periphyton may contribute more significantly to the composition of POM near Croton Dam than in lower reaches of the river, as the reaches beneath the Dam are characterized by clear, fast-flowing water and a hard bottom.

In contrast to Muskegon River, POM from Lake Michigan was characterized by an enriched $\delta^{13}C$ signature that fluctuated seasonally, and a depleted $\delta^{15}N$ signature relative to the MRES. Over the entire sampling period, the average $\delta^{13}C$ ratio for Lake Michigan POM was -26.2‰, which was enriched compared to either Muskegon River (-28.1‰) or Muskegon Lake (-30.8‰). Previous isotopic studies of Great Lakes organic matter have demonstrated that algae and other primary producers preferentially use the lighter isotope

(^{12}C) during photosynthesis (Schelske and Hodell 1991). During periods of increased primary productivity, the ^{12}C in the dissolved inorganic carbon pool may be used up faster than it can be replaced, leaving only the ^{13}C to be used for photosynthesis (Schelske and Hodell 1991, Leggett et al. 1999). As a result, $\delta^{13}C$ signatures of phytoplankton become enriched during periods of high primary productivity; as seen in Lake Michigan POM samples collected for this study, which were enriched in $\delta^{13}C$ during spring and summer.

Interestingly, POM signatures measured at the Muskegon Lake station were unique, being depleted in $\delta^{13}C$ and enriched in $\delta^{15}N$ relative to either Muskegon River or Lake Michigan. TSM concentrations measured during this study indicated that large amounts of material coming from Muskegon River may be settling within Muskegon Lake. The fact that POM $\delta^{15}N$ was enriched in Muskegon Lake relative to Muskegon River may reflect the high amount of material being processed within the lake. In systems where high amounts of organic matter are present, microbial processing of this material can lead to a shortage of oxygen in sediments and overlying waters (Kiyashko et al. 2004). Low oxygen (hypoxic) waters are defined as having oxygen concentrations of less than 3 mg/L of dissolved oxygen (ESA, 2008). Dissolved oxygen concentrations as low as 2 mg/L were recorded in the bottom waters of Muskegon Lake during a monitoring period of 2002 thru 2007 (Bopiah Biddanda, Annis Water Resources Institute, personal communication). In the absence of sufficient oxygen, methanogenic bacteria process organic material, producing methane that is isotopically "light" (-60 to -80‰ $\delta^{13}C$) (Kiyashko et al. 2004). This $\delta^{13}C$ depleted methane is then oxidized to CO_2 in the water

column, and eventually makes its way into the food web via primary productivity (Wetzel 2001). Biogenic methane has been shown to be a critical source of carbon as well as a link between benthic and pelagic food webs in aquatic systems (Bastviken et al. 2003). Kiyahsko et al. (2004) reported depleted carbon isotope signatures in chironomids collected in Lake Biwa, Japan, where oxygen concentrations in the hypolimnion are ~3 mg/L during stratification. Through an analysis of the fatty acid compositions of the chironomids, these authors were able to determine that a large part of their diets consisted methanotrophic bacteria (Kiyashko et al. 2004). Future work should attempt to examine the extent of methane production in Muskegon Lake sediments and quantify the impact that this source of carbon has on food web.

While these data seemed to indicate the absence of MRES organic matter in Lake Michigan, another explanation for the lack of a watershed signal in nearshore Lake Michigan may be that materials originating in the Muskegon watershed are advected out of the nearshore zone of Lake Michigan into deeper water. Previous studies have demonstrated the delivery and use of land-derived organic materials in Lake Michigan. In a study of samples collected from a series of sediment traps deployed off the mouth of the Grand River in Lake Michigan, Meyers et al. (1984) used C/N ratios, lipids, and various other biomarkers to demonstrate the presence of a plume of materials of terrestrial origin off the mouth of the Grand River (Meyers et al. 1984). Using the same series of sediment traps, Eadie et al. (1984) demonstrated that surficial sediment organic carbon concentrations increased along with an increase in percentage of fine sediment with distance from shore (up to 35 km offshore), and proposed that terrestrial materials were

transported from near-bottom downslope to offshore. Meyers and Eadie (1993) found that organic matter $\delta^{13}C$ values increased at depth in sediment trap samples collected from a trap deployed at a depth of 145 meters. They theorized that lateral transport of organic matter from coastal regions with higher levels of productivity was the source of the enriched $\delta^{13}C$ (Meyers and Eadie 1993). Johengen et al. (2008) used field and laboratory experiments to demonstrate that seasonal inputs from the nearby St. Joseph River and episodic sediment resuspension events could enhance heterotrophic autotrophic production in nearshore Lake Michigan by 3-5 fold.

The delivery of terrestrial materials from watersheds into shallow, wide connecting basins may be characteristic of Muskegon Lake and other drowned river mouth tributaries feeding Lake Michigan, but is likely different in tributaries that feed directly into Lake Michigan or other Great Lakes basins. For example, the Grand River is characterized by a different geomorphology than the Muskegon River, and culminates in a river delta rather than a drowned river mouth lake. One might expect to find higher terrestrial signatures in Great Lakes areas such as Saginaw Bay, Green Bay or western Lake Erie where discharge from tributaries is high relative to the volume and depth of their receiving coastal waters. More intensive sampling around peak discharge events, that includes shorter sampling intervals and sampling at deeper depths in Lake Michigan may be needed to definitively answer whether materials from the MRES can be traced into Lake Michigan.

Whether or not OM from Muskegon River was transported into Lake Michigan, analysis of surficial sediment samples in Muskegon Lake indicated that Muskegon River materials undergo dramatic chemical alteration within Muskegon Lake. The $\delta^{13}C$ of surficial sediment in Muskegon Lake, like the particulate organic matter, was depleted relative to Lake Michigan, reflecting the influence of methane in this system. Analysis of the DOC, C/N ratios and $\delta^{15}N$ signatures in surficial sediments of Muskegon Lake supported conclusions reached by the $\delta^{13}C$ isotope results. The $\delta^{15}N$ signatures of surficial sediments increased on an east (near Muskegon River) to west (near Lake Michigan) gradient within Muskegon Lake, reflecting increasing amounts of microbial processing occurring within the sediments. The extent of microbial uptake of nutrients in Muskegon Lake was also confirmed by an analysis of organic carbon content and C/N ratios in surficial sediments. High levels of organic carbon in Muskegon Lake indicate the highly labile nature of the surficial sediments, as opposed to less labile material found in Lake Michigan sediments. In addition, higher C/N ratios of sediments in Muskegon Lake reflect the influence of terrestrial material being deposited from the watershed. At the west end of Muskegon Lake, there was one localized area of lower sediment C/N ratio, where coincidentally $\delta^{15}N$ signatures of sediments were highest, indicating an area of extensive aquatic biological production (Meyers and Ishiwatari 1993). C/N ratios in nearshore Lake Michigan were much lower, demonstrating the absence of terrestrial influence (Meyers and Ishiwatari 1993).

Stable isotope signatures of sediments estimated for shallow (< 2 m) stations may have been biased because these stations were not sampled at the margins of either Lake

Michigan or Muskegon Lake. Isotope data for the shallower margins of both lakes (Figures 12-18) were interpolated using the SURFER 8 contour plotting program, and may not represent actual values in these areas. Nonetheless, isotope values measured at nearby stations indicated that material coming from Muskegon River most likely underwent extensive chemical alteration in Muskegon Lake. More extensive sampling of the marginal areas of Muskegon Lake and Lake Michigan should be included in future studies to confirm these initial predictions.

Few studies have tried to track the flow of nutrients from individual watersheds and wetlands into the Great Lakes to determine the relevance and impact of these linkages. Brazner et al. (2001) attempted to demonstrate a significant linkage between a constricted coastal wetland and its corresponding offshore habitat in Lake Superior by tracking the fish-mediated transport of nutrients between the two habitats, but found that the flux of fish-mediated nutrients from the coastal wetland to Lake Superior was small relative to similar wetlands connected to the Atlantic coast. Several other studies have used stable isotope technology to study origins of Great Lakes organic matter. Most notably, Keough et al. (1996) demonstrated differences in stable isotope signatures of organic matter between nearshore and offshore food webs in Lake Superior, where the offshore food web was characterized by an enriched $\delta^{13}C$ of POM (-27 ‰) relative to the $\delta^{13}C$ of POM from the wetland (-31 ‰), even though primary producers in both food webs appeared to be phytoplankton. Though neither study found evidence of a significant transfer of materials between wetlands and the lake habitats to which they are connected, food web

linkages demonstrating fish usage of both wetland and offshore waters were identified using stable isotopes (Keough et al. 1996, Brazner et al. 2001).

Although stable isotope analysis has improved the ability to elucidate origins of Great Lakes organic matter, linkages between coastal wetlands and large lakes, and movements and fate of organic matter through these systems are still poorly understood (Keough et al. 1996, Brazner et al. 2001, Bouchard 2007). Great Lakes coastal wetlands can have multiple sources of energy (i.e. phytoplankton, periphyton, and terrestrial plants) depending on nutrient enrichment, hydrology, and wetland type (Kreiger 2003, Sierszen et al. 2004, Sierszen et al. 2006). Though coastal wetlands can serve as significant sources of organic carbon and other nutrients to nearshore lake zones, the actual transfer of material can be difficult to quantify, and can depend on a number of variables including the geomorphology, structure, size, and vegetation of a given wetland (Bouchard 2007).

The results of this study demonstrated that stable isotopes could be effectively used to characterize riverine organic matter as a mixture of aquatic and terrestrial source materials. However, the fate of organic matter produced in the MRES is unclear. The results of this study suggest that Muskegon River organic matter most likely settled and underwent extensive re-processing within Muskegon Lake, and thus was not traceable in Lake Michigan. Another explanation for the lack of a riverine signal in Lake Michigan may have been the lateral near-bottom downslope transport of materials that has been established through previous research on the Grand River. Regardless of the mechanism,

the lack of a traceable influence of Muskegon River organic matter on the nearshore zone of Lake Michigan was evident.

Though these results provided no evidence that terrestrial organic matter originating from the Muskegon River watershed influenced the coastal ecology of nearshore Lake Michigan, they do not preclude existence of watershed – Great Lakes connections. Even in areas such as Muskegon Lake, watershed interactions may occur primarily through biotic pathways rather than physical advection pathways. Many Great Lakes tributaries serve as spawning and nursery grounds for adfluvial fishes, which then migrate into nearshore waters to feed and grow. The influx of adult fishes from coastal waters to forage in Great Lakes tributaries, and the efflux of juvenile fishes such as suckers (Catostomidae), walleye and salmonids from watersheds to the Great Lakes are unknown for most systems but are likely substantial, and may have a more direct and concentrated impact on coastal ecosystems than transport of terrestrial POM.

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Tables

Table 1. Measured values for each water chemistry parameter sampled at five sites in the Muskegon River estuary and nearshore Lake Michigan, sampled monthly from March to October 2003. "NDC" designations indicate no data was collected.

		TSM	δ^{13}C POM	δ^{15}N POM	DOC	δ^{13}C DOC	TP	TDP	NO3
Sampling Date	Location	(mg/L)	(‰)	(‰)	ppm	(‰)	(µg/L)	(µg/L)	(mg/L)
3/27/2003	Croton	3.38	-27.2	2.63	3.98	-26.49	19.3	11.6	0.79
	North Channel	9.65	-27.3	4.45	4.20	-27.13	29.5	14.8	0.88
	Muskegon Lake	2.94	-29.9	3.42	3.03	-29.74	26.3	9.7	0.78
	Muskegon Channel	2.02	ndc	ndc	2.96	-30.47	21.7	6.2	0.72
	Lake Michigan	1.21	-27.0	2.51	1.88	-33.41	5.8	2.0	0.38
4/21/2003	Croton	2.91	-29.6	5.12	3.02	-30.54	20.3	4.6	0.74
	North Channel	18.45	-28.4	5.81	3.83	-25.87	48.0	10.7	0.67
	Muskegon Lake	2.13	-29.1	6.04	3.03	-30.04	18.3	4.8	0.74
	Muskegon Channel	1.68	-30.1	5.87	3.94	-26.35	16.8	4.8	0.74
	Lake Michigan	1.71	-28.2	4.23	1.90	-28.91	7.0	6.4	0.48
5/19/2003	Croton	1.51	-28.1	4.49	4.97	-27.30	14.0	5.3	0.55
	North Channel	7.32	-28.6	4.84	5.55	-28.19	24.8	7.6	0.62
	Muskegon Lake	2.41	-34.0	6.59	5.85	-25.92	23.0	6.5	0.48
	Muskegon Channel	2.01	-27.4	6.05	4.95	-27.42	19.6	7.6	0.50
	Lake Michigan	1.51	-25.6	4.31	2.15	-28.85	8.3	2.0	0.42
6/11/2003	Croton	1.37	-27.4	ndc	6.04	-26.06	11.1	6.1	0.53
	North Channel	7.77	-28.4	4.52	5.54	-26.64	21.8	7.3	0.64
	Muskegon Lake	2.23	-31.6	5.03	5.18	-25.41	19.8	6.8	0.43
	Muskegon Channel	2.11	-30.8	5.75	4.28	-30.56	20.4	6.0	0.43
	Lake Michigan	2.37	-27.5	4.08	2.61	-33.32	10.9	3.1	0.37
7/7/2003	Croton	1.36	-29.9	5.68	6.77	-27.40	7.5	8.4	0.30
	North Channel	13.12	-27.6	4.85	3.24	-30.30	16.0	10.4	0.42
	Muskegon Lake	2.54	-30.8	5.50	4.95	-25.52	14.1	7.2	0.23
	Muskegon Channel	2.56	-29.9	5.17	5.97	-24.37	10.0	5.8	0.23
	Lake Michigan	0.94	-25.2	ndc	2.45	-37.25	2.6	2.1	0.30
8/26/2003	Croton	1.12	-28.9	5.49	3.82	-30.76	19.9	14.5	0.21
	North Channel	6.10	-27.8	4.82	3.60	-30.8	23.6	9.7	0.40
	Muskegon Lake	4.62	-29.4	8.11	3.87	-30.76	36.0	6.0	0.10
	Muskegon Channel	2.33	-27.7	6.32	3.24	-29.80	23.2	8.5	0.13
	Lake Michigan	0.85	-24.1	3.61	1.52	-31.50	4.9	2.0	0.26
9/11/2003	Croton	1.75	-29.7	7.23	3.37	-31.22	42.9	23.3	ndc
	North Channel	3.17	-28.8	4.92	3.33	-31.26	24.4	8.7	ndc
	Muskegon Lake	3.12	-30.5	7.24	3.10	-29.06	28.5	7.3	ndc
	Muskegon Channel	4.20	-30.8	7.70	2.18	-28.64	29.6	6.4	ndc
	Lake Michigan	1.29	-25.8	3.86	1.43	-28.36	9.4	2.7	ndc
10/11/2003	Croton	0.79	-28.6	6.68	2.70	-31.41	30.3	26.3	0.20
	North Channel	7.51	-27.9	4.94	3.48	-32.02	32.2	15.9	0.30
	Muskegon Lake	2.61	-31.5	8.54	4.09	-30.71	29.7	11.0	0.18
	Muskegon Channel	1.36	-29.0	ndc	3.08	-31.52	28.0	18.1	0.16
	Lake Michigan	1.29	-26.2	3.22	1.58	-31.88	10.5	3.2	0.23

Table 2. Average values (± 1 standard error) of water chemistry variables at five stations in the Muskegon River estuary and nearshore Lake Michigan, sampled monthly from March to October 2003.

	Croton	North Channel	Muskegon Lake	Muskegon Outflow	Lake Michigan
TSM (mg/L)	1.77 ± 0.32	9.14 ± 1.67	2.83 ± 0.28	2.28 ± 0.30	1.40 ± 0.17
δ13C POM	-28.62 ± 0.40	-28.10 ± 0.19	-30.85 ± 0.55	-29.79 ± 0.62	-26.20 ± 0.47
δ15N POM	6.27 ± 0.44	4.89 ± 0.15	6.31 ± 0.60	6.08 ± 0.43	3.41 ± 0.35
DOC (mg/L)	4.33 ± 0.52	4.10 ± 0.33	4.14 ± 0.38	3.83 ± 0.43	0.43 ± 0.15
δ13C DOC	-28.90 ± 0.81	-29.03 ± 0.83	-28.40 ± 0.84	-28.64 ± 0.86	-31.69 ± 1.06
TP (μg/L)	21.23 ± 4.02	27.54 ± 3.39	24.46 ± 2.50	21.16 ± 2.19	7.43 ± 1.02
TDP (μg/L)	12.78 ± 2.94	10.64 ± 1.12	7.41 ± 0.71	7.93 ± 1.51	2.94 ± 0.53
NO3 (mg/L)	0.47 ± 0.09	0.56 ± 0.08	0.42 ± 0.10	0.42 ± 0.10	0.35 ± 0.03

Table 3. Sample sizes (n), means (+ 1 standard error), and ranges of carbon and nitrogen stable isotopes values of plants (sorted by type) collected throughout the Muskegon River from March thru October 2003.

		$\delta^{13}C$ (‰)			$\delta^{15}N$ (‰)		
Plant Type	**n**	**Mean**	**Std Error**	**Range**	**Mean**	**Std Error**	**Range**
Terrestrial Plant	20	-29.0	0.3	-31.2 to -25.9	1.5	0.6	-3.8 to 9.9
Emergent (Wetland)	11	-28.4	0.4	-30.5 to -26.5	6.7	0.8	1.0 to 10.4
Aquatic Macrophyte	10	-25.1	0.7	-27.6 to -22.4	8.4	0.5	5.2 to 10.0
Periphyton	1	-30.9			8.6		
Particulate Organic Matter	17	-28.3	0.2	-29.9 to-26.8	5.0	0.3	2.6 to 6.7

Figures

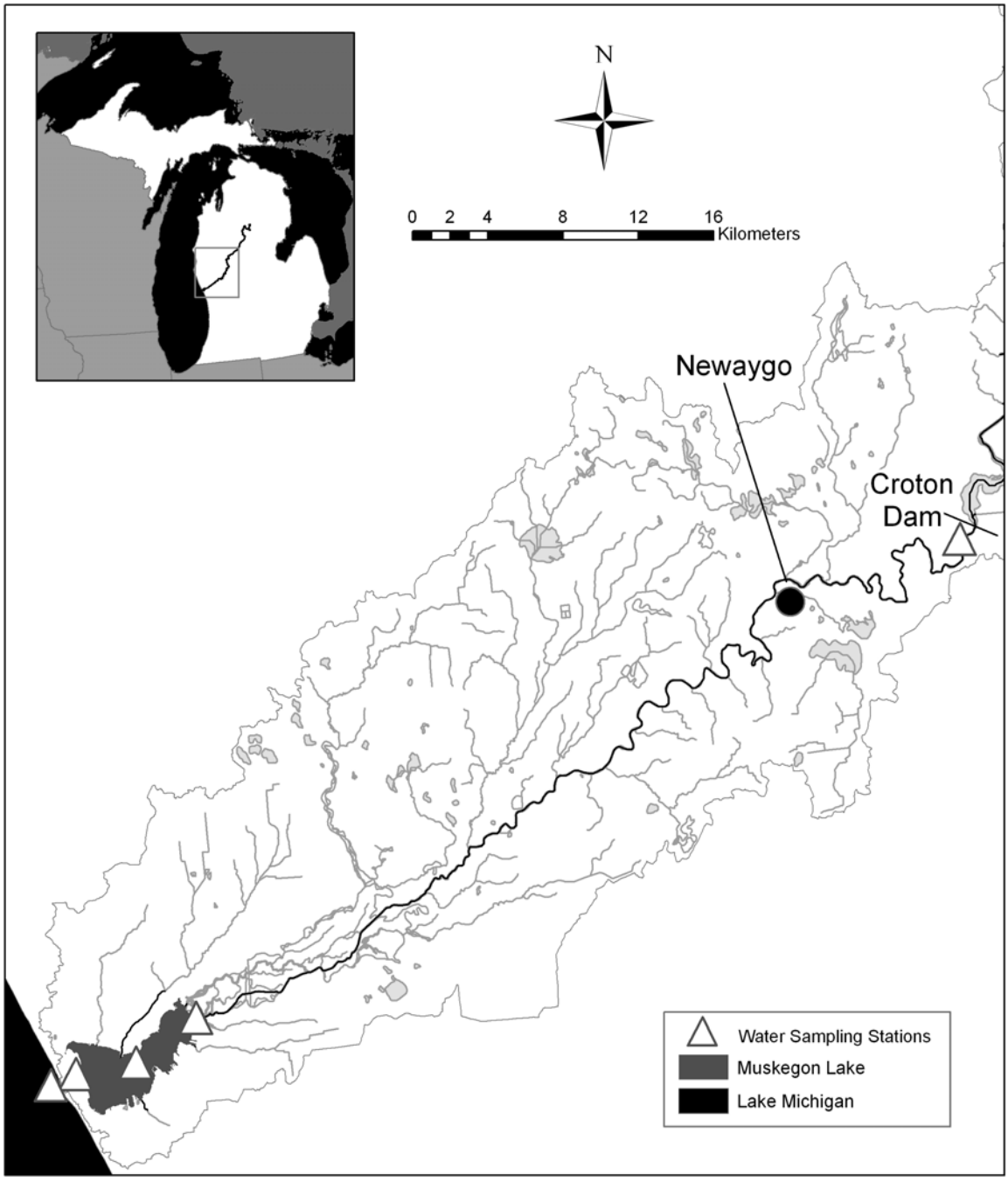

Figure 1. A map of the Muskegon River watershed, western lower peninsular Michigan, U.S.A. Water sampling stations are noted with open circles.

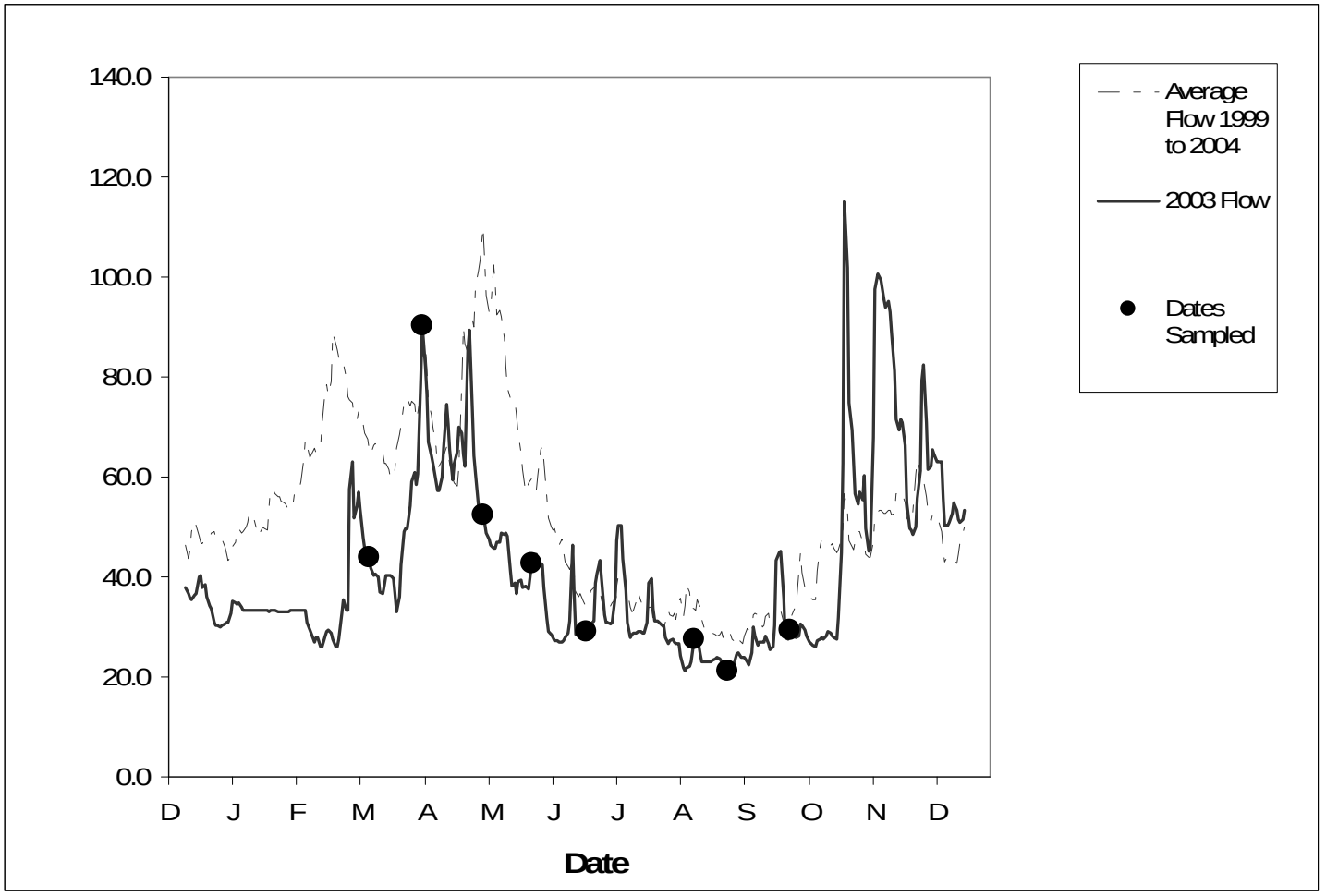

Figure 2. Average daily discharge (cms, Y-Axis) for the Muskegon River beneath Croton Dam as measured by a USGS stream gage, 2003. The solid line represents average daily flows measured in 2003, with the dots representing sampling dates for water chemistry. The dashed line represents average daily flows (cms) averaged over a period of five years from 1999 through 2004.

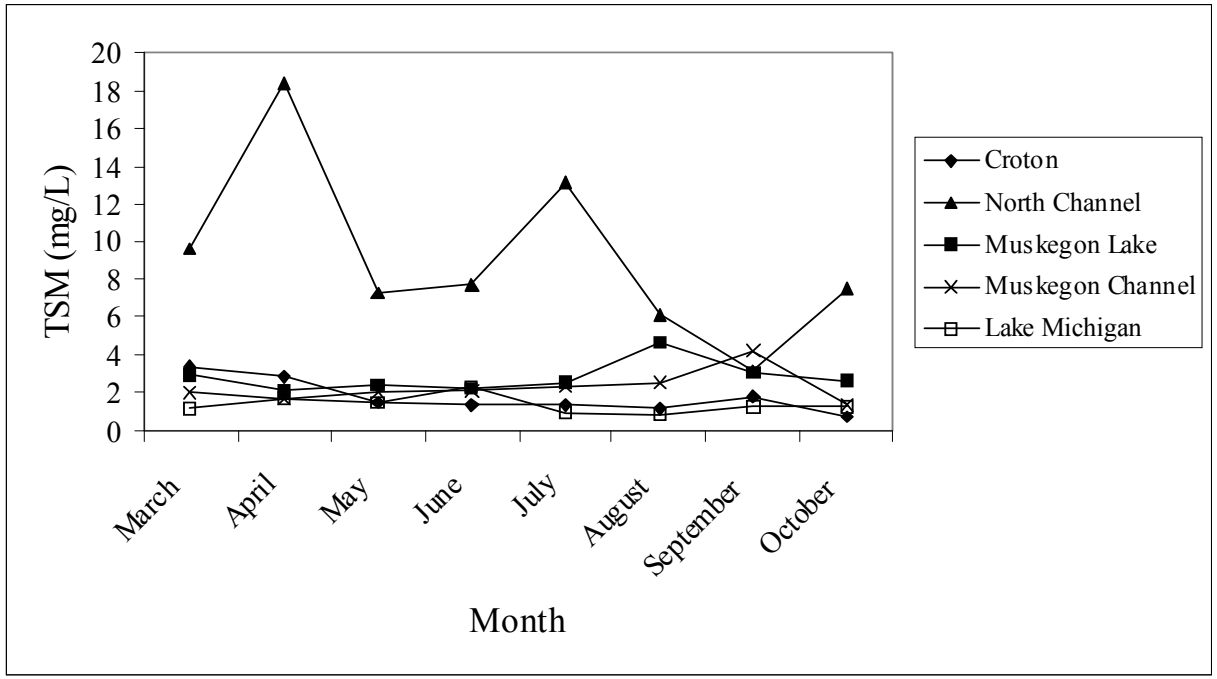

Figure 3. Total suspended material (TSM) concentrations (mg/L) at five sites in the Muskegon watershed and nearshore Lake Michigan, March to October, 2003. A two-way ANOVA using site and month comparisons revealed significant differences among sites ($p < 0.001$), but not among months ($p = 0.586$). A Holm-Sidak multiple comparison test revealed that the TSM concentrations measured at North Channel were significantly higher than at any of the other sites. Statistical significance is shown by the following pattern, where underlining indicates a lack of significant difference; NC ML MC CD LM. 'NC' stands for North Channel, 'ML' is Muskegon Lake, 'MC' is Muskegon Channel, 'CD' is Croton Dam, and 'LM' is Lake Michigan.

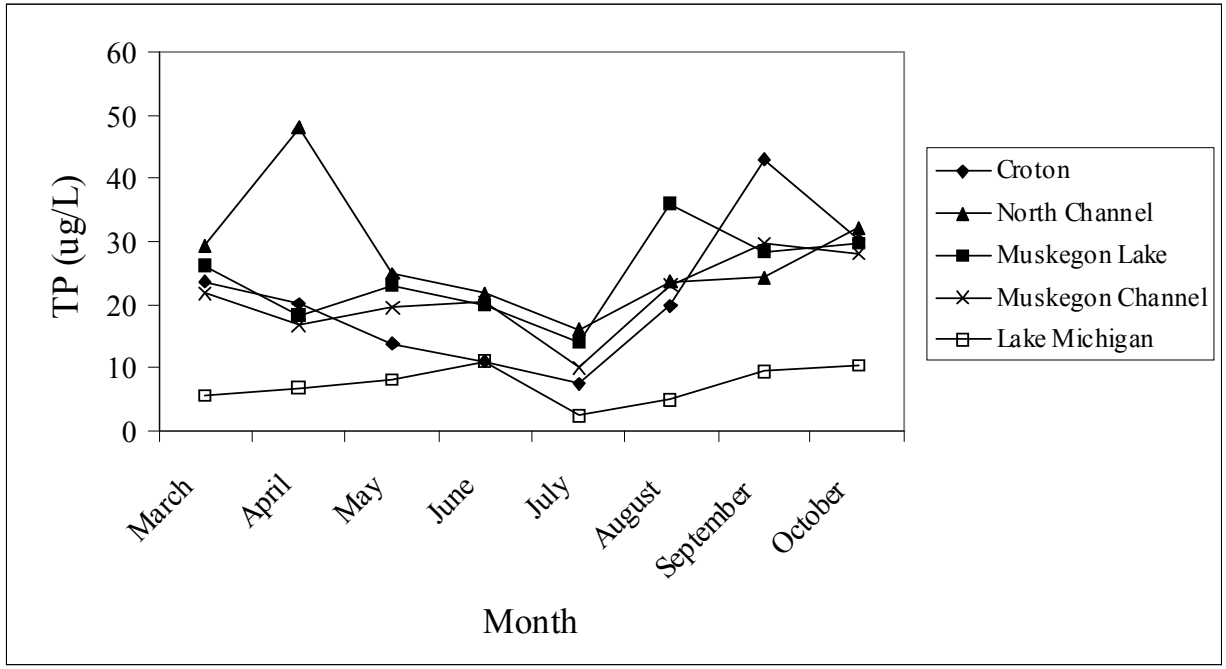

Figure 4. Total phosphorus (TP) concentrations (µg/L) at five sites in the Muskegon watershed and nearshore Lake Michigan, March-October, 2003. A two way ANOVA using site and month comparisons revealed significant differences among sites ($p < 0.001$) and months ($p = 0.008$). Holm-Sidak multiple comparison tests were conducted on the data aggregated by site and month. The tests showed that TP concentrations measured at Lake Michigan were significantly lower than those measured at any other site. TP concentrations in September and October were similar significantly higher than in any other month. Statistical significance patterns are as follows, where underlining indicates a lack of significant difference: for site NC ML CD MC LM; and for month Sep Oct Apr Mar May Jun Jul.

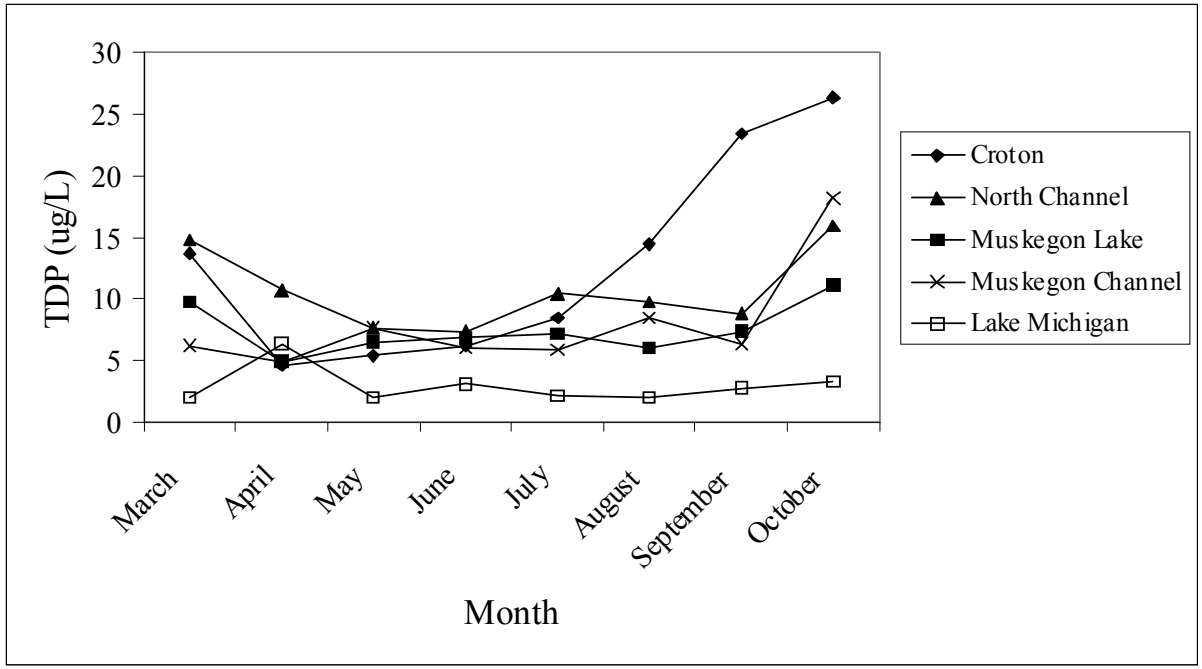

Figure 5. Total dissolved phosphorus (TDP, µg/L) concentrations measured at five sites in the Muskegon watershed and nearshore Lake Michigan, March-October, 2003. A two way ANOVA using site and month comparisons revealed significant differences among sites ($p < 0.001$) and months ($p = 0.012$). Holm-Sidak multiple comparison tests were conducted on the data aggregated by site and month. The tests showed that TDP concentrations measured at Croton Dam and North Channel were statistically similar, and were significantly higher than at other stations. Statistical significance patterns are as follows, where underlining indicates a lack of significant difference: for site CD NC MC ML LM; and for month
Oct Sep Mar Aug Jul Apr Jun May

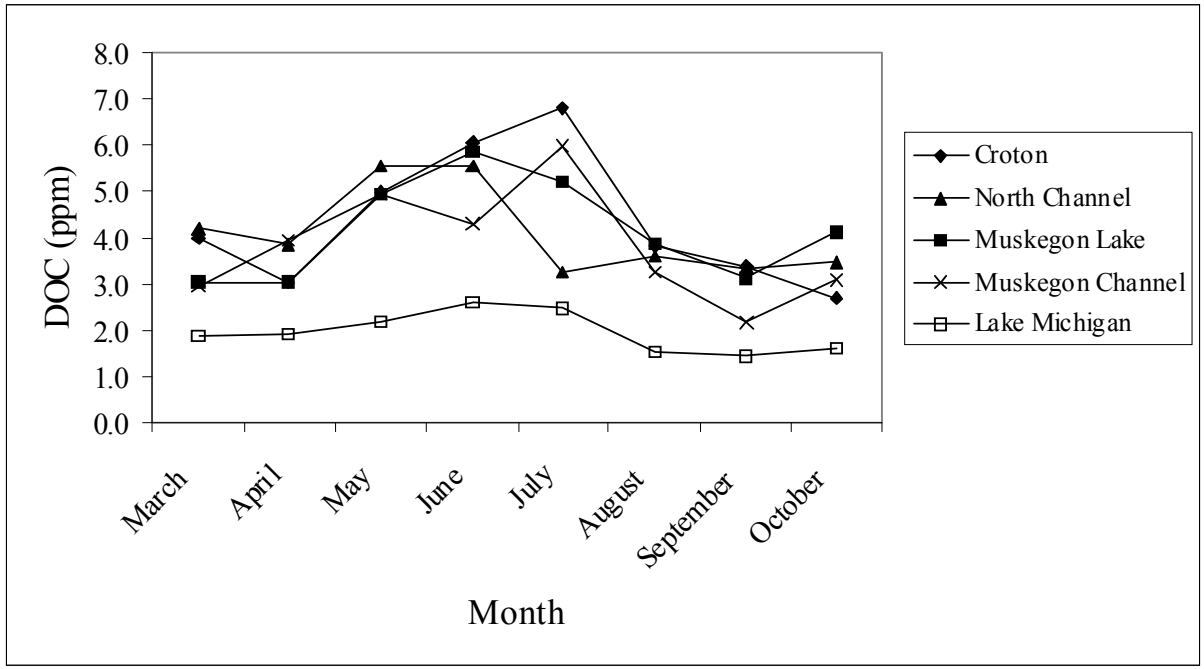

Figure 6. Dissolved organic carbon (DOC) concentrations (ppm) at five sites in the Muskegon watershed and nearshore Lake Michigan, March-October, 2003. A two way ANOVA using site and month comparisons revealed significant differences among sites ($p < 0.001$) and months ($p < 0.001$). Holm-Sidak multiple comparison tests were conducted on the data aggregated by site and month. The tests showed that Lake Michigan was characterized by significantly lower DOC concentrations than at any other station, and that DOC concentrations were significantly higher in the summer months. Statistical significance patterns are as follows, where underlining indicates a lack of significant difference: for site CD ML NC MC LM; and for month: Jun Jul May Aug Mar Apr Oct Sept.

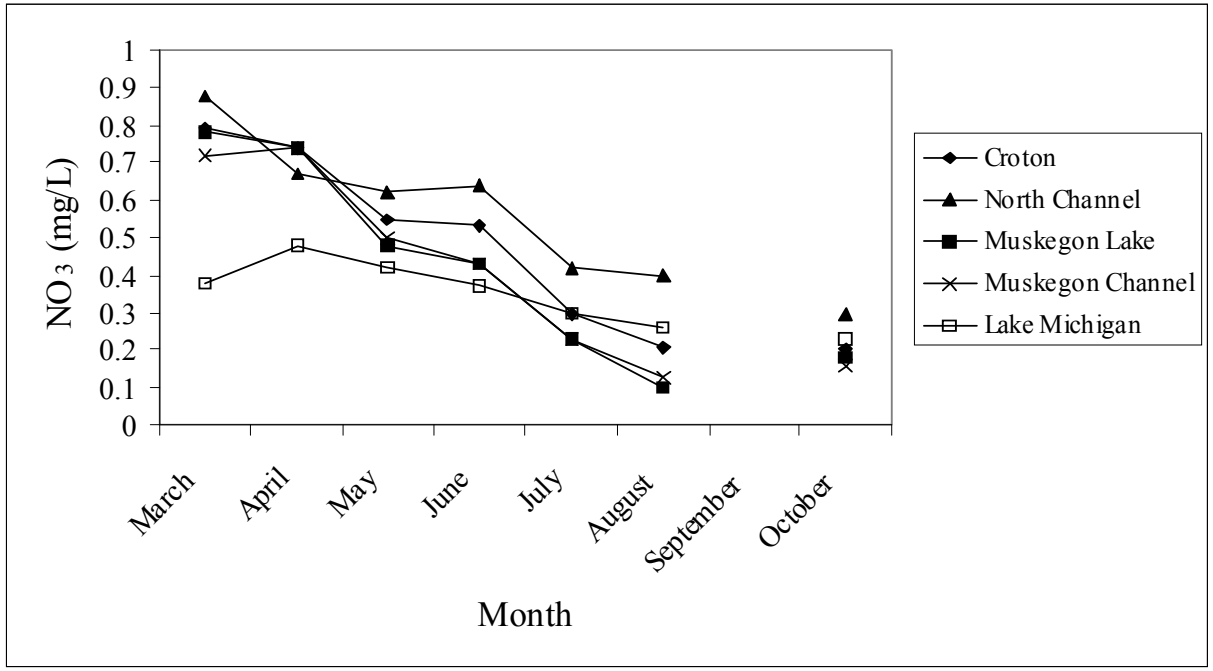

Figure 7. Nitrate (NO_3) concentrations (mg/L) at five sites in the Muskegon watershed and nearshore Lake Michigan, March-October 2003. Data from September were lost. A two way ANOVA using site and month comparisons revealed significant differences among sites ($p = 0.002$) and months ($p < 0.001$). Holm-Sidak multiple comparison tests were conducted on the data aggregated by site and month. The tests showed that NO_3 concentrations were significantly higher at the North Channel than at either the Muskegon Lake or Lake Michigan stations. In addition, NO_3 values in March and April were statistically similar, and higher than in May and June, or July through October. Statistical significance patterns are as follows, where underlining indicates a lack of significant difference: for site NC CD ML MC LM; and for month Mar Apr May Jun Jul Aug Oct.

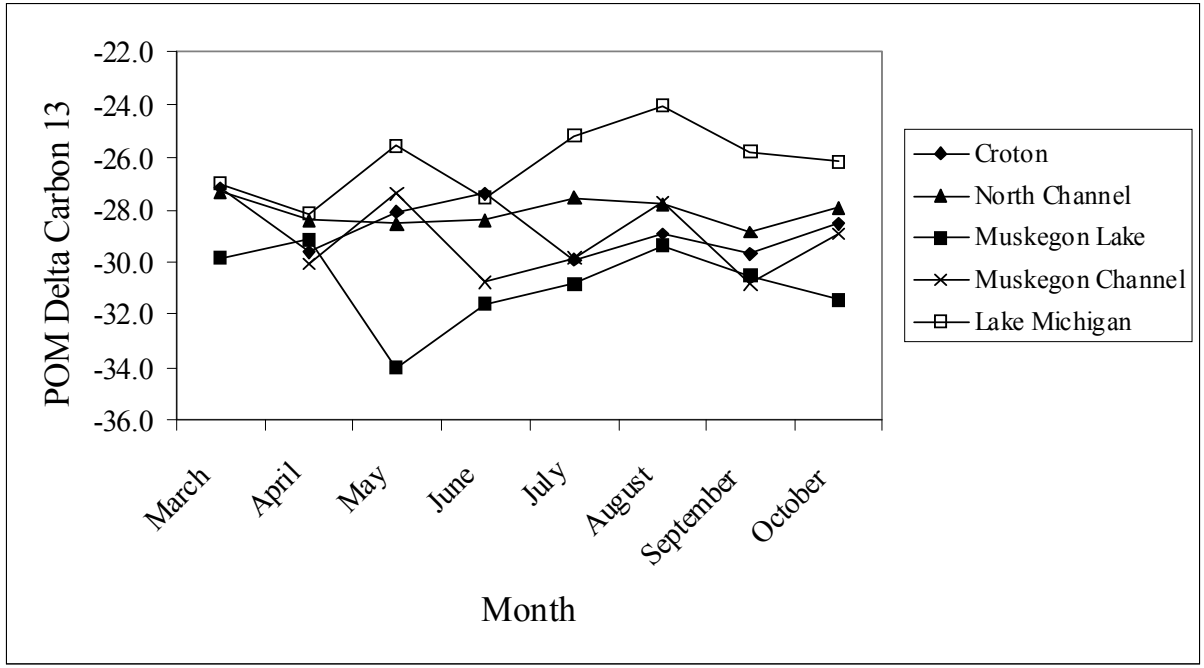

Figure 8. $\delta^{13}C$ values for particulate organic matter samples (POM) collected at five sites in the Muskegon watershed and nearshore Lake Michigan, March-October, 2003. A two way ANOVA using site and month comparisons revealed significant differences among sites ($p < 0.001$) but not among months ($p = 0.674$). Holm-Sidak multiple comparison tests were conducted on the data aggregated by site, and showed that Lake Michigan had a significantly enriched $\delta^{13}C$ signature compared to the other stations, and that the $\delta^{13}C$ signatures at both Muskegon Lake and Muskegon Channel were statistically similar. Statistical significance patterns are as follows, where underlining indicates a lack of significant difference: for sites LM NC CD MC ML.

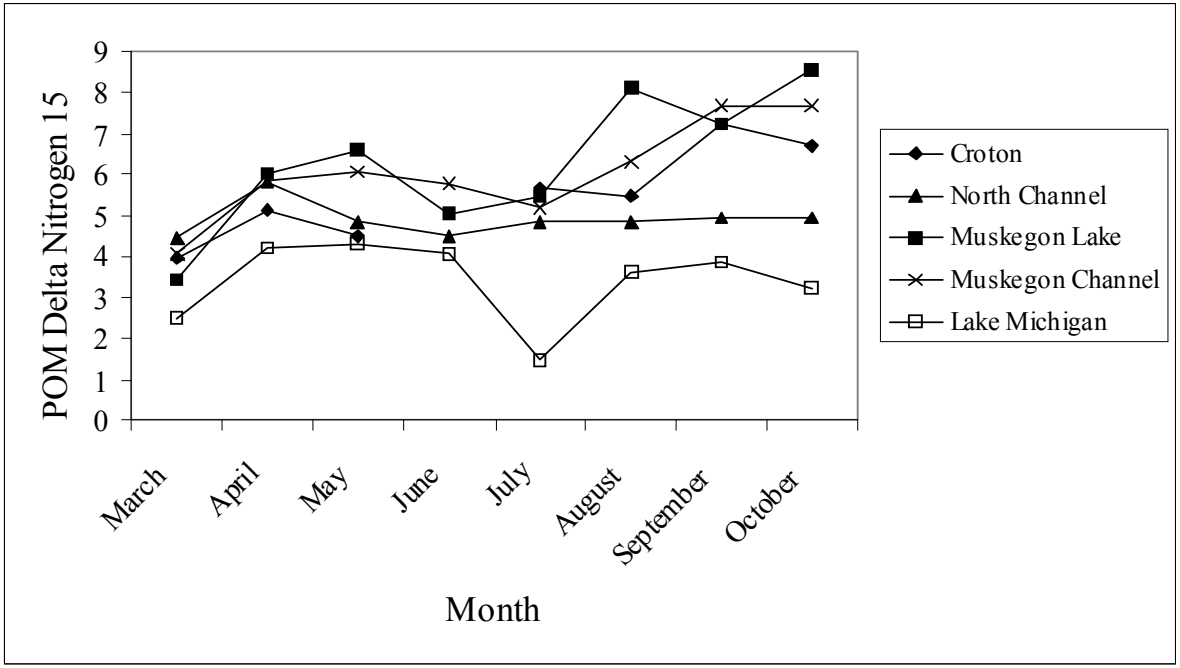

Figure 9. $\delta^{15}N$ values for particulate organic matter samples (POM) collected at five sites in the Muskegon watershed and nearshore Lake Michigan, March-October, 2003. A two way ANOVA using site and month comparisons revealed significant differences among sites ($p < 0.001$) and months ($p < 0.001$). Holm-Sidak multiple comparison tests were conducted on the data aggregated by site and by month. These tests showed that $\delta^{15}N$ at the Lake Michigan site was significantly lower than at other stations, and that Muskegon Lake and Muskegon Channel were characterized by similar $\delta^{15}N$ values. In addition, aggregate $\delta^{15}N$ values were significantly higher in October, September and August. Statistical significance patterns are as follows, where underlining indicates a lack of significant difference: for site ML MC CD NC LM; and for month Oct Sep Aug Apr May Jun Jul Mar.

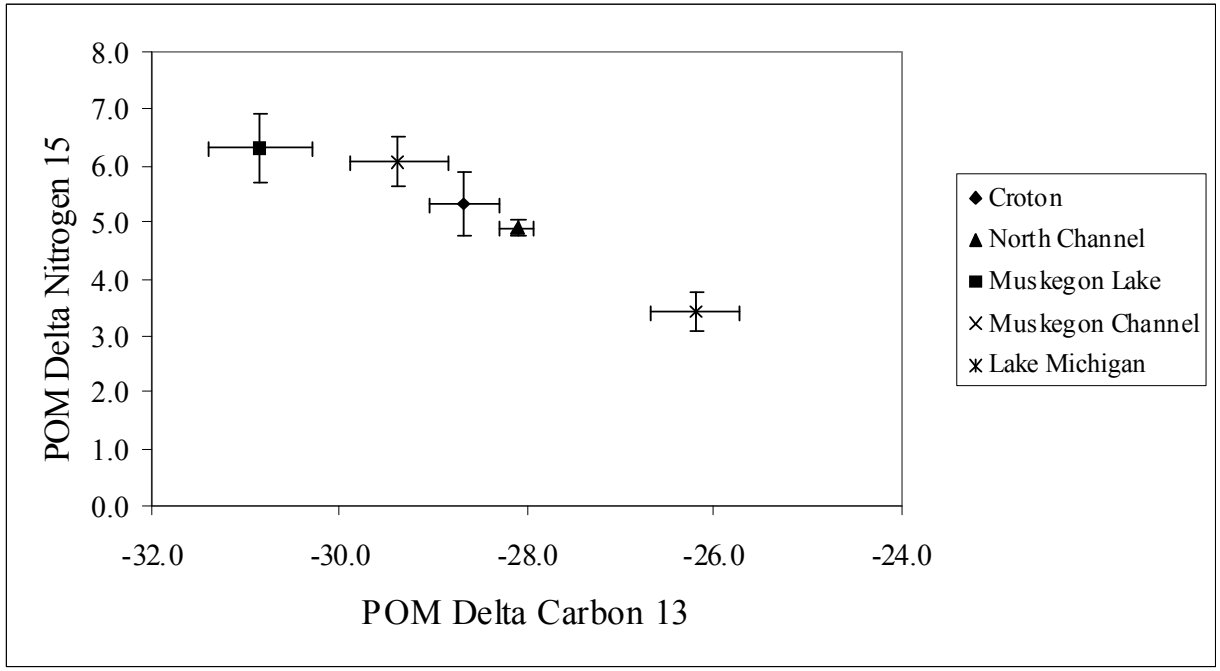

Figure 10. Average $\delta^{13}C$ and $\delta^{15}N$ isotopic signatures of POM collected at five sites in the Muskegon watershed and nearshore Lake Michigan, March-October, 2003. Error bars represent one standard error. A one-way ANOVA indicated differences in $\delta^{13}C$ signatures among sites were significant ($p < 0.001$). Multiple comparisons conducted with a Tukey test procedure demonstrated the following pattern of statistical significance (underlining indicates non-significance) LM ML NC CD ML. The $\delta^{15}N$ values were analyzed using a non-parametric Kruskal-Wallis test on ranks, and differences among sites were significant ($p < 0.001$). A Dunn's method multiple comparison test resulted in the following significance pattern: MC ML CD NC LM.

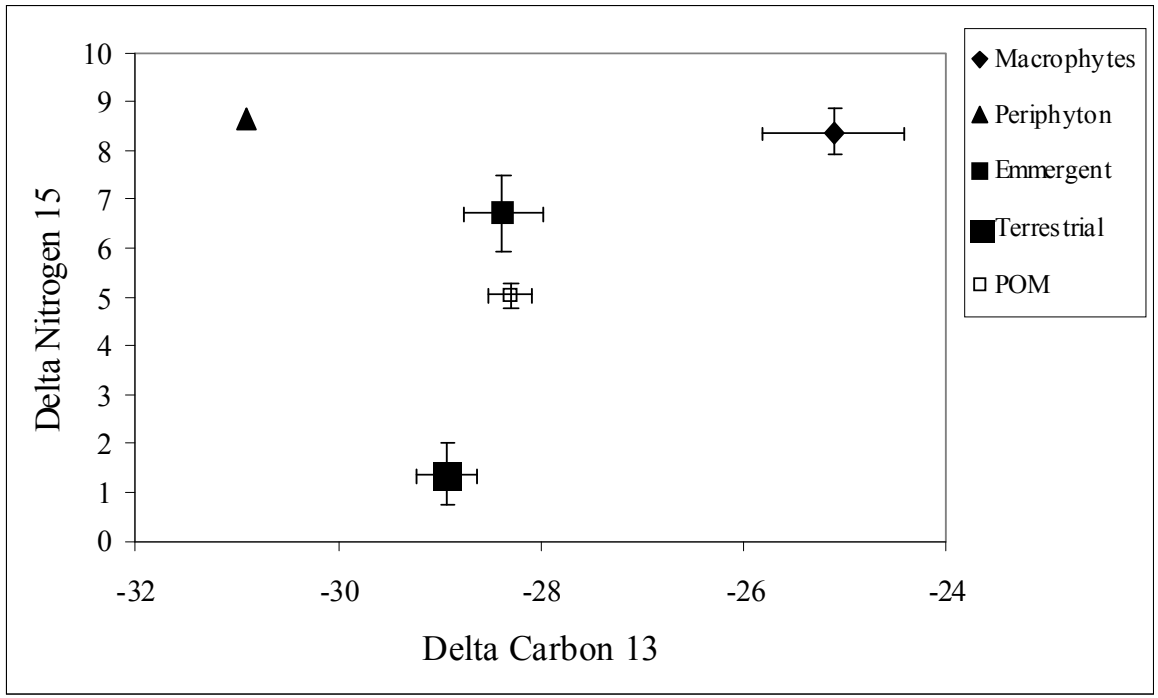

Figure 11. Average isotopic signatures of primary producers collected from Muskegon River, March-October, 2003. Error bars represent one standard error. A one-way ANOVA test indicated that differences among sites were significant in both $\delta^{13}C$ ($p < 0.001$) and $\delta^{15}N$ ($p < 0.001$) values.

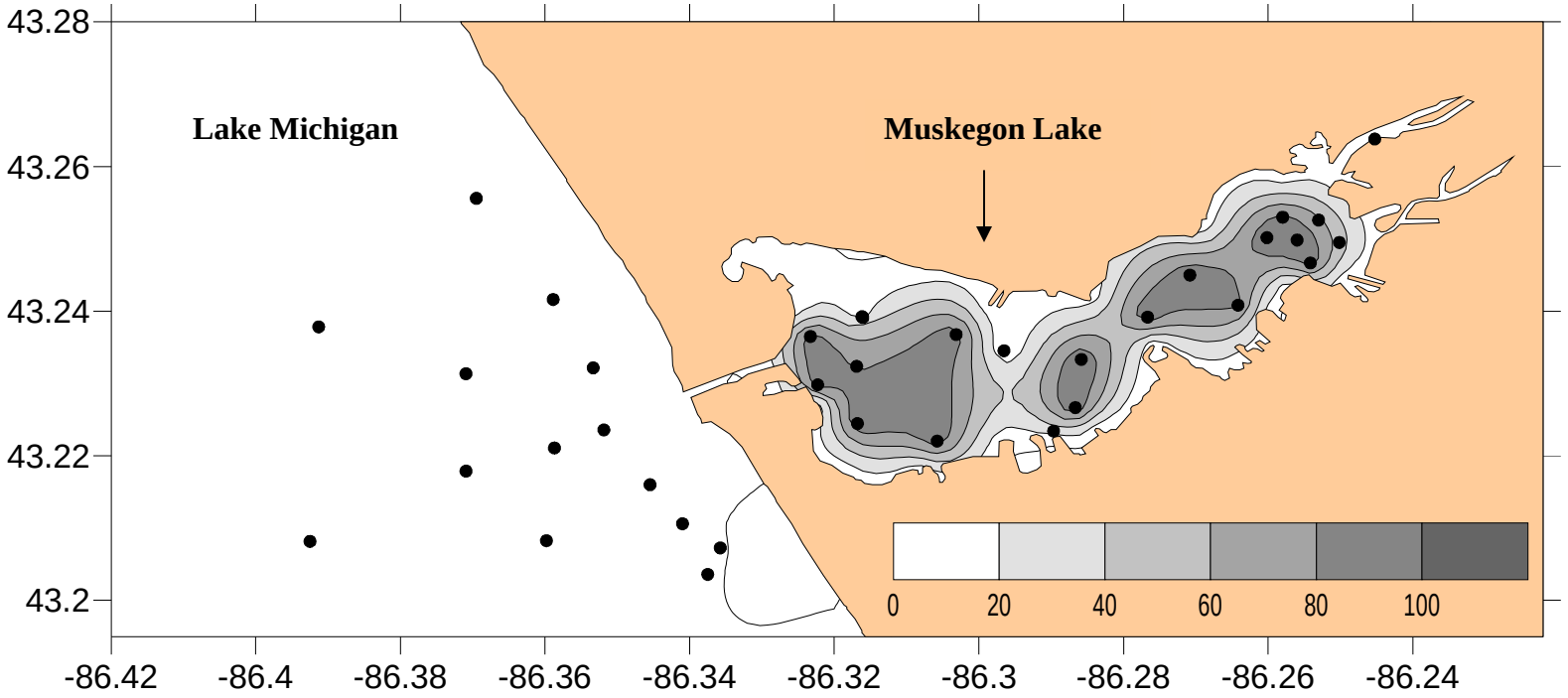

Figure 12. Contour plot showing percentage of fine-grained sediment (<63µm) throughout Muskegon Lake and nearshore Lake Michigan. Samples were collected in September, 2003. X and Y axes represent longitude and latitude coordinates, respectively.

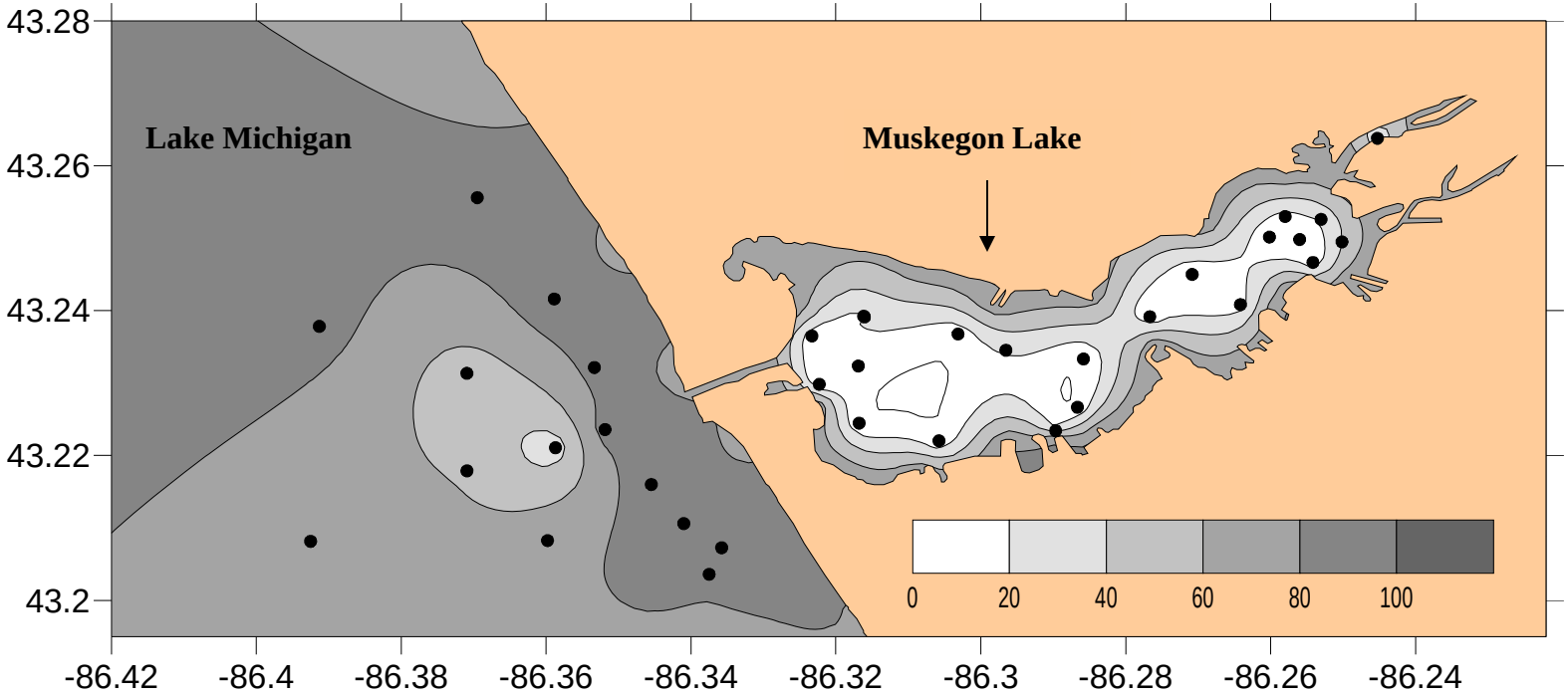

Figure 13. Contour plot showing the percentage of mid-grained sediment (63-210 µm) throughout Muskegon Lake and nearshore Lake Michigan. Samples were collected in September, 2003. X and Y axes represent longitude and latitude coordinates, respectively.

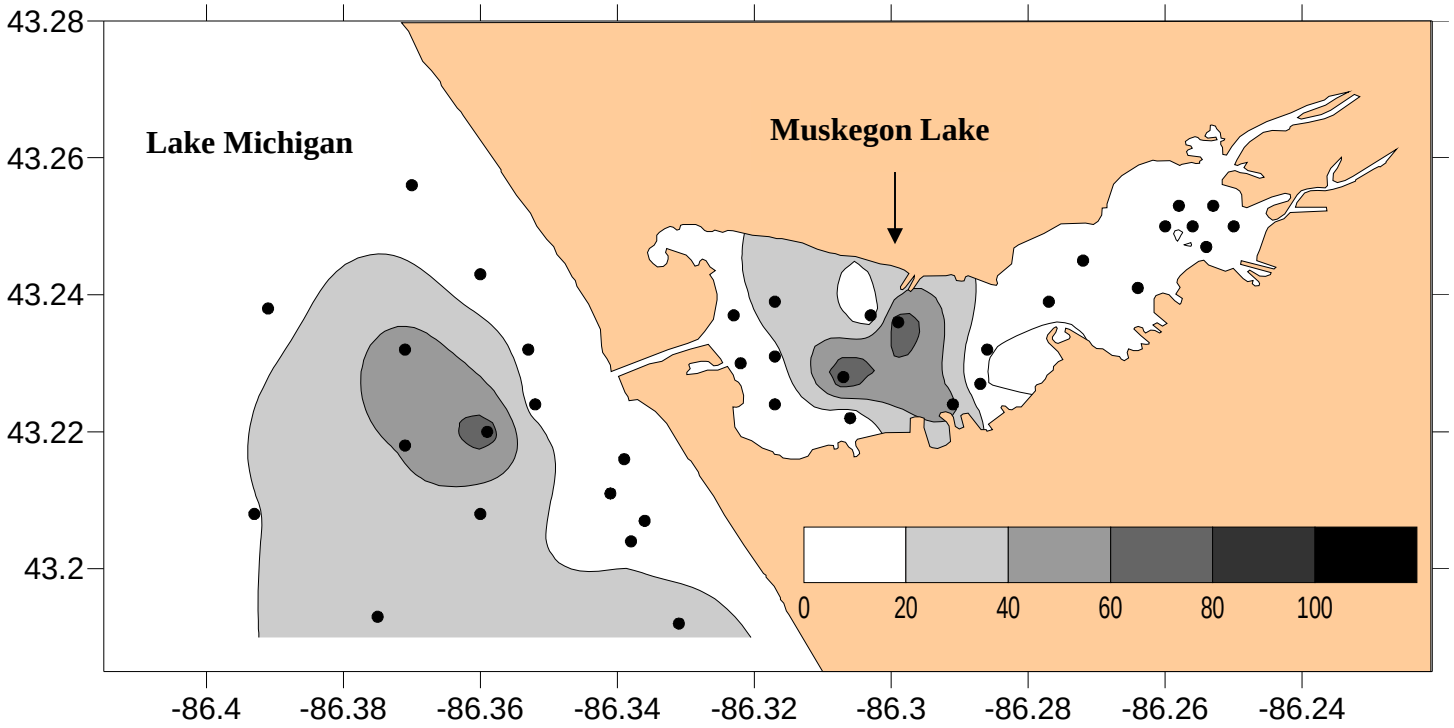

Figure 14. Contour plot showing the distribution of coarse sediment (>210 µm) throughout Muskegon Lake and nearshore Lake Michigan. Samples were collected in September, 2003. X and Y axes represent longitude and latitude coordinates, respectively.

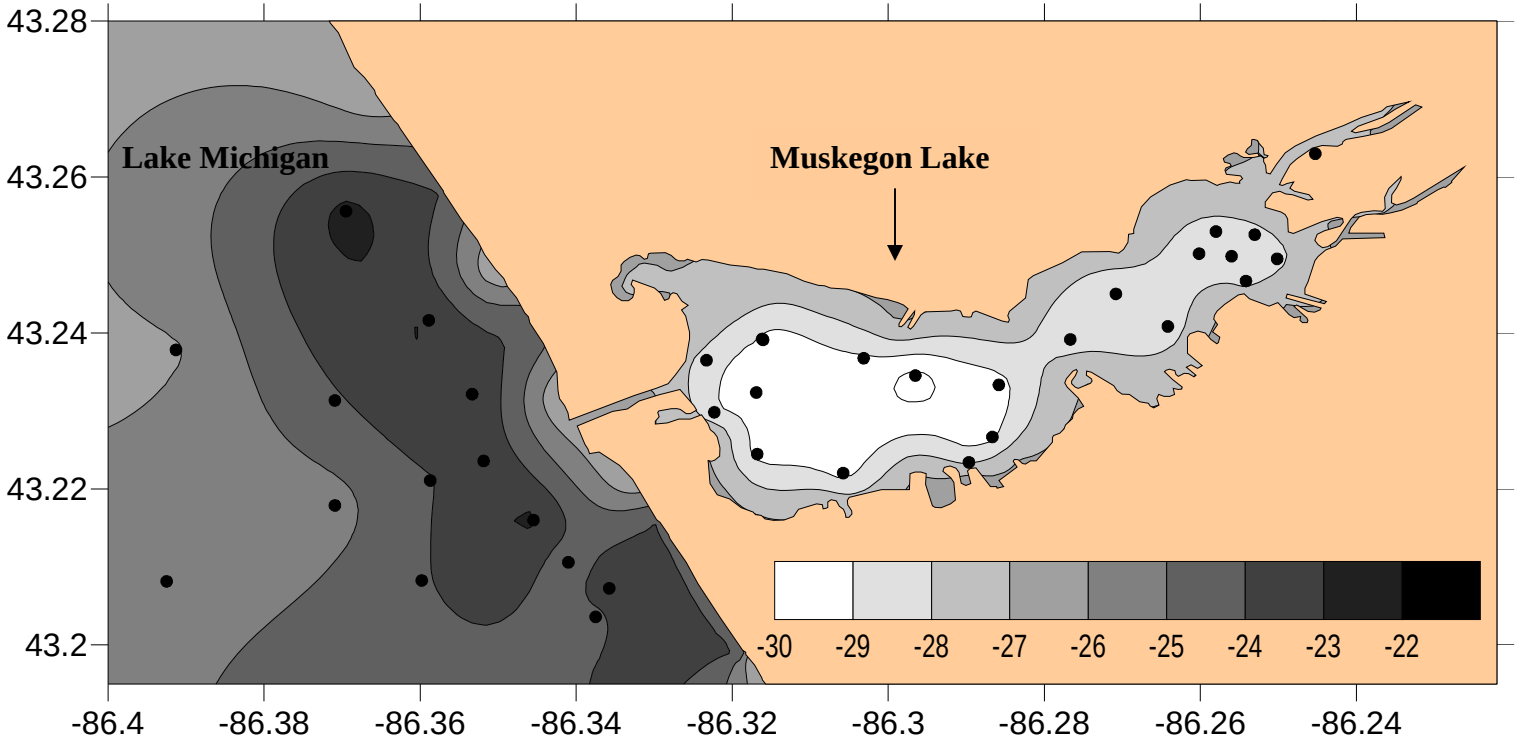

Figure 15. Contour plot showing the $\delta^{13}C$ values of fine-grained (<63 µm) surface sediments from Muskegon Lake and nearshore Lake Michigan. Samples were collected in September, 2003. X and Y axes represent longitude and latitude coordinates, respectively.

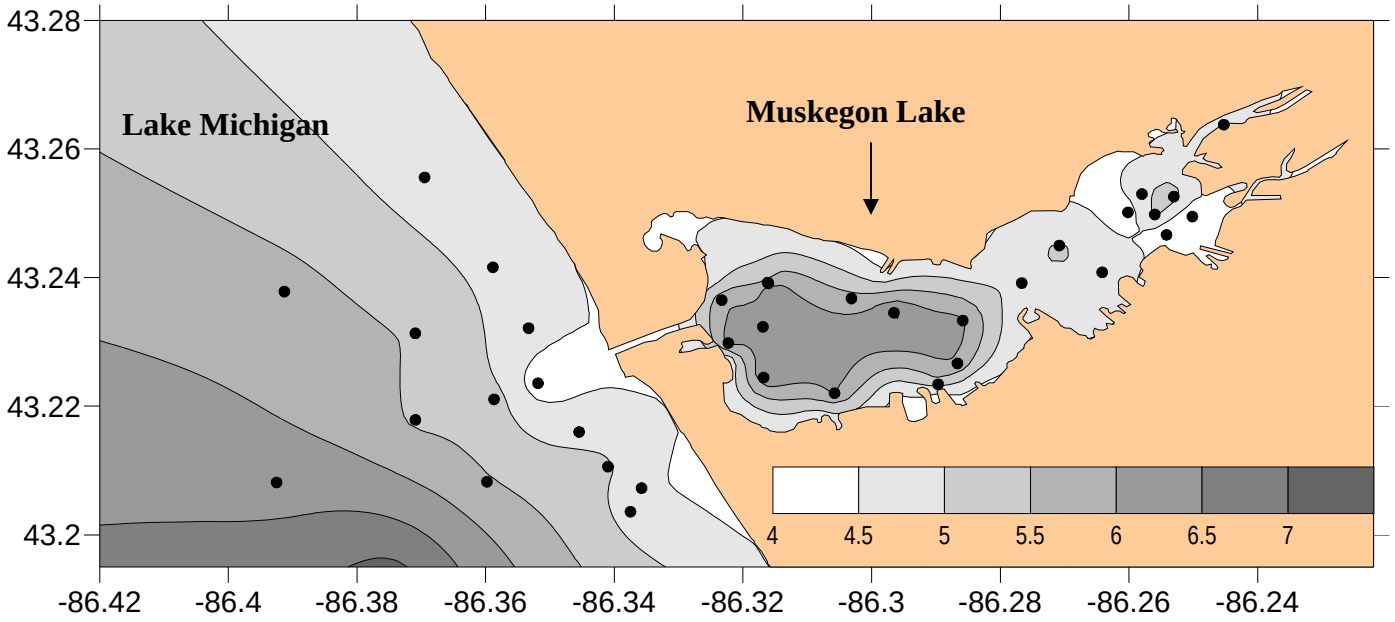

Figure 16. Contour plot showing δ^{15}N values of fine–grained (<63 µm) surface sediments in Muskegon Lake and nearshore Lake Michigan. Samples were collected in September, 2003. X and Y axes represent longitude and latitude coordinates, respectively.

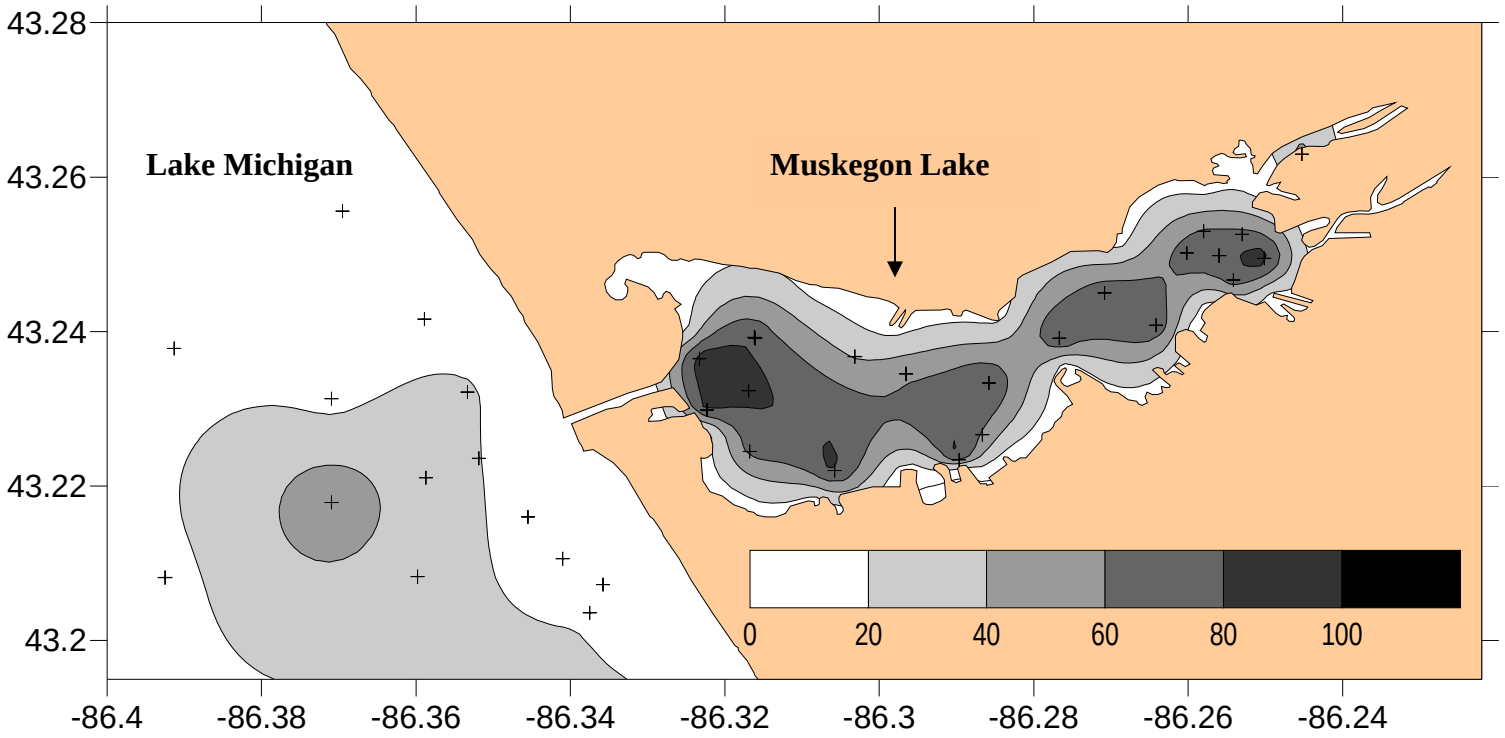

Figure 17. Levels of organic carbon (mg C/g) measured in fine-grained surface sediments collected in Muskegon Lake and nearshore Lake Michigan, September 2003. X and Y axes represent longitude and latitude coordinates, respectively.

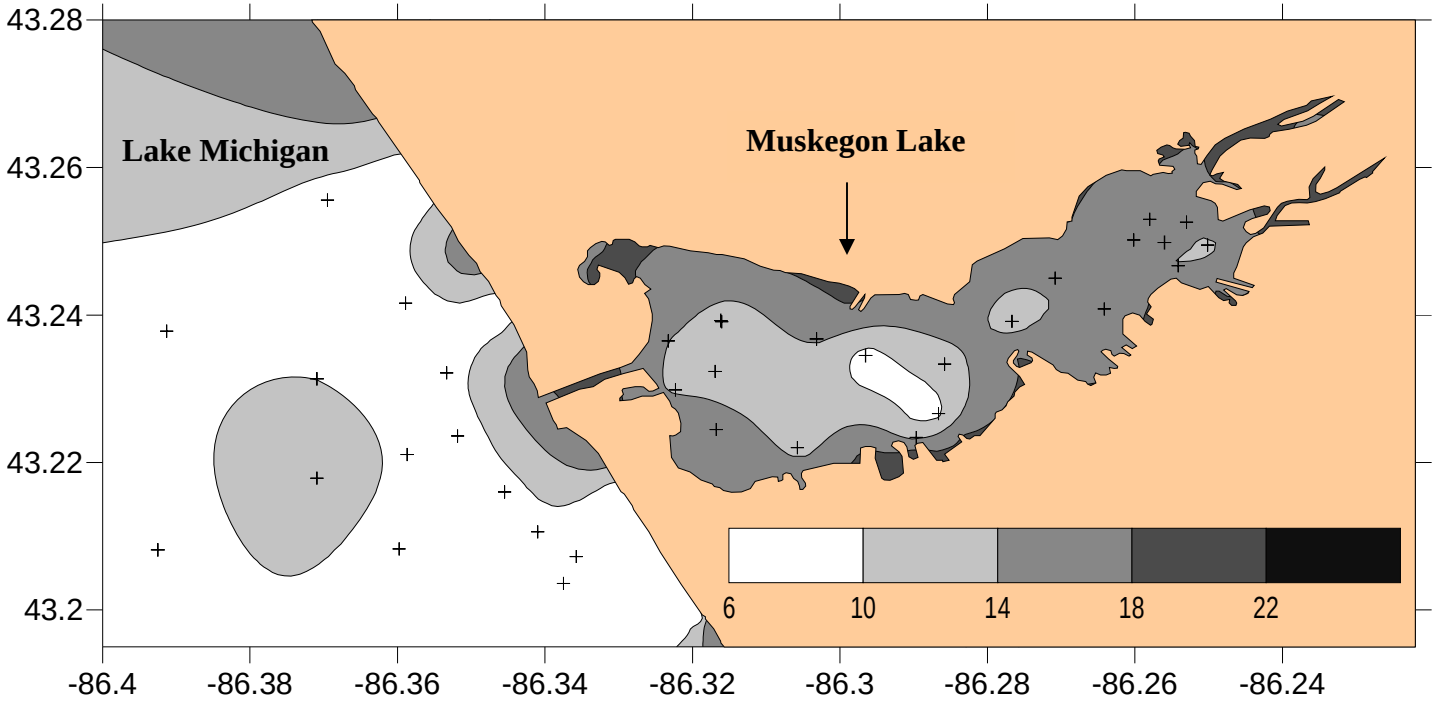

Figure 18. Carbon to nitrogen (C/N) ratios measured in surficial sediments in Muskegon Lake and nearshore Lake Michigan, September 2003. X and Y axes represent longitude and latitude coordinates, respectively.