



Temporal and spatial differences in deposition of organic matter and black carbon in Lake Michigan sediments over the period 1850–2010

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ABSTRACT

Inorganic carbon (IC), total organic carbon (OC), and black carbon (BC) were analyzed in eight sediment cores obtained from deep water (>30 m) sediments in the Chippewa and south Chippewa basins, as well as Green Bay in Lake Michigan. These cores were segmented at high resolution and radio-dated to reconstruct a detailed history of deposition to the lake both spatially and temporally since ca. 1850 CE. To help interpret the depositional record, cores were also characterized for stable isotopes (¹³C and ¹⁵N), as well as particle size distribution, density, organic matter (OM), and other parameters. Fine (silt and clay) sediment particles contained OM of primarily lacustrine algal biomass origin. Sedimentation fluxes showed large increases in OM and OC fluxes through much of the lake during the onset of industrialization and the period of rapid industrialization to onset of Great Lakes environmental legislation. In contrast, fluxes and loading of BC increased dramatically in the southern basin until the 1930's, then decreased substantially after the 1940's. This observation was due largely to results from site M009 nearest the steel mills and industrial zones of Chicago and northern Indiana. Together, whole lake loadings of OM and BC provide evidence that changing industrial activity and legislation intended to curb air pollution in the Great Lakes region have had a fairly rapid and dramatic impact. In contrast, legislation intended to decrease eutrophication through reductions in nutrient loading to the lake have not had a similar impact on sedimentation of OM in the lake.

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Introduction

Previous studies of sources and diagenesis of organic matter (OM) in Great Lakes sediment have shown that OM is a key paleo-environmental proxy for trophic state (Eadie et al., 1984; Meyers and Eadie, 1993; Meyers et al., 1980; Meyers and Ishiwatari, 1995; Meyers et al., 1984). OM in lacustrine sediments has two main sources: lacustrine primary production in the photic zone, where only a small fraction (<10%) is deposited in sediments (Dean and Gorham, 1998; Eadie et al., 1984;

Meyers and Eadie, 1993), and terrigenous sources that are transported directly to lakes via tributaries, runoff from land, or by atmospheric deposition (Meyers et al., 1984). Recent sedimentary records in the Laurentian Great Lakes show typical profiles of increasing OM over the past two centuries. The “cultural eutrophication” hypothesis argues that this trend is due to increasing loading of OM to sediments in quantities that exceed rates of early diagenesis. The increased OM load is a result of increased loading of anthropogenic nutrients which stimulates the concomitant increases of in-lake primary production (Meyers and Eadie, 1993; Meyers and Ishiwatari, 1993). This hypothesis is further supported by reports that most OM in lake sediments (~90%) results from in-lake (autochthonous) primary production, which is distinguishable from terrestrial OM derived from plants and atmospheric deposition-derived organic matter by analyses of patterns of stable isotopes (SIA) of carbon (C) and nitrogen (N) (Meyers and Ishiwatari, 1995) as well as C:N ratios. Differential transfer of ¹³C and ¹⁵N through trophic levels yield distinct ratios of isotopes of both C and N in lacustrine and terrestrial OM. The atomic C/N ratio has also been used to distinguish between autochthonous algal and terrestrial land-plant derived sedimentary OM (Meyers, 1994; Prah et al., 1980) because

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lacustrine algae are protein-rich and thus have low C/N ratios (≤ 10) compared with cellulosic OM that has larger C/N values (≥ 20) (Meyers, 1994, 2003).

Although there have been numerous studies of OM in the water column and sediments of Lake Michigan, important gaps in the data remain. To date, studies have usually consisted of only a few cores or sediment trap studies per lake (Eadie et al., 1984), which resulted in uncertainty when extrapolated to calculate whole-lake loadings. Furthermore, most studies have focused on OM (or perhaps OC), leaving out black C (BC) and inorganic C (IC) that comprise major components of sedimentary C (Lukasewycz and Burkhard, 2005). Finally, resolution of core segments might have been insufficient to accurately determine changes that might have occurred in deposition of C after major legislation first enacted in the 1960s–1970s that were aimed at reducing air and water pollution to the Great Lakes. These include primarily the 1972 Clean Water Act (PL 92–500 and major amendments in 1977 and 1987) and the 1963 Clean Air Act (PL 88–206 and various

amendments from 1965 to 1990), as well as more recent legislative action like the Great Lakes Legacy Act of 2002 (S. 2544).

To address some of these issues, a larger scale core-sampling program in Lake Michigan was conducted to estimate whole-lake loading over the period of cultural eutrophication. A secondary objective of this study was to determine whether observable decreases in loadings of OM and BC to Lake Michigan have occurred following enactment of legislation intended to reduce pollutant loading to the Great Lakes.

Materials and methods

Sampling and processing

Sampling was conducted to cover major depositional zones of Lake Michigan (Fig. 1). Land use surrounding the lake is diverse with sparsely populated forested regions in the north, and urbanized and industrial centers in the south that might influence deposition of BC, OC, and

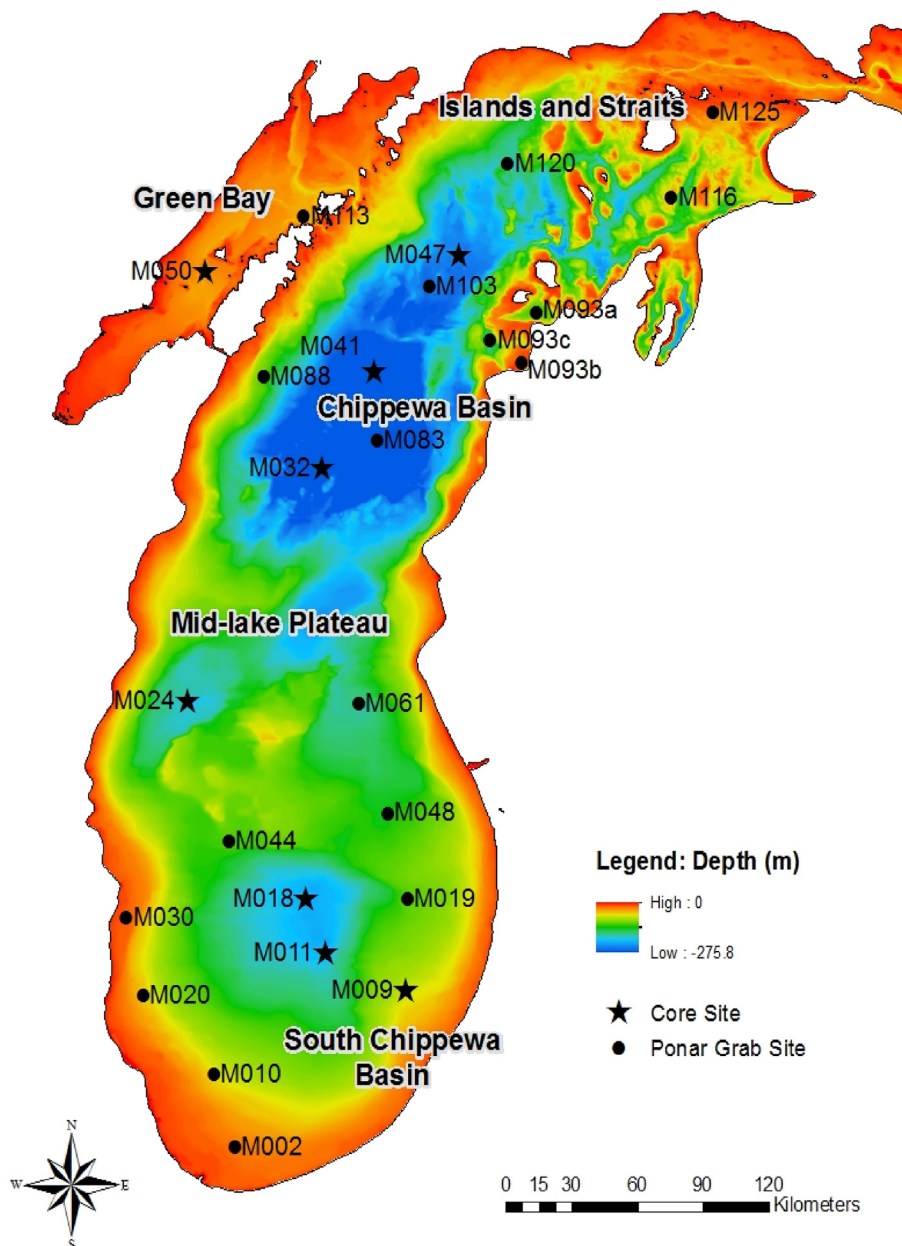


Fig. 1. Bathymetry map of Lake Michigan showing the five main regions. Coring sites are shown by stars and surface grab sample sites are shown by solid circles. Map created in ArcGIS using National Oceanic and Atmospheric Administration data.

OM. Green Bay is the largest bay in Lake Michigan, and is highly industrialized with the world's largest concentration of pulp and paper mills (Christensen and Chien, 1981). Its two major rivers provide >30% of Lake Michigan's tributary inflow (Christensen and Chien, 1981). Residence time of water within Lake Michigan is approximately 100 years (USEPA, 1995). Although Lake Michigan has been characterized as a large oligotrophic, freshwater lake (Dean and Gorham, 1998; Lehman, 1988), the southern basin of the lake has greater primary productivity than those typically found in oligotrophic lakes, which is most likely due to anthropogenic inputs of nutrients from the surrounding basin (Meyers and Eadie, 1993).

Sediments were collected from Lake Michigan in September 2010 and May 2011, onboard the US Environmental Protection Agency (USEPA) *R/V Lake Guardian* as part of the USEPA-funded Great Lakes Sediment Surveillance Program. Eight sampling sites were selected for coring (Fig. 1), based on likelihood of having a continuous record of deposition from analysis of data from previous sampling studies (Buckley et al., 2004; Li et al., 2006; Rockne et al., 2000). Sediment surface grab samples were also taken but are not discussed here. Core samples were obtained from a box corer (model BX-750, Ocean Instruments Inc., San Diego CA) or Ekman dredge (custom made in 1990) in the 2010 sampling campaign, or a four core multi-corer (model MC-400, Ocean Instruments, Inc., San Diego, CA) in the 2011 sampling. All coring devices used the same 10 cm × 60 cm polycarbonate core collection tubes (MC-400-4(P), Ocean Instruments Inc., San Diego, CA).

Sectioning of each core was performed immediately after retrieval in the general field laboratory of the *R/V Lake Guardian*. Cores were sectioned into 1-cm intervals from the surface to a depth of 10 cm, then in 2-cm increments for the remainder of the core. For most coring sites, 20 segments were obtained. Each core segment was homogenized in a clean Pyrex® container, and subsamples were stored in 50 mL plastic Falcon® tubes at 4 °C for subsequent analyses described below.

Characterization of sediments

Sediments were characterized for density, solids content, porosity, OM, IC, OC, and BC using *Standard Methods* (ASTM, 1998a, 1998b), and previously reported methods that were modified and validated for Lake Michigan sediment (Buckley et al., 2004; Li et al., 2006; Rockne et al., 2000). In brief, each sediment sample was split into three triplicate 3 mL sediment sub-samples from the homogenized sediment (Buckley et al., 2004). Each sample was weighed on a labeled tared aluminum tray, and then dried (105 °C, 48 h) to constant mass. Mass was determined ($\pm 10 \mu\text{g}$) on a calibrated analytical balance. Wet bulk density was determined from the wet mass and volume data. Samples were re-weighed after drying, and the dry sediment mass, moisture (%), and solids content (%) were determined.

One dry sample was analyzed without further processing for Total Carbon (TC) and Nitrogen (TN). A second dried sample was analyzed for OC following complete removal of IC (described below), and a third sample was combusted (375 °C, 24 h) for determination of OM and BC. OM was operationally defined as the mass loss upon this low temperature combustion normalized to original dry mass by use of previously published methods (Rockne et al., 2002). The second and third samples were ground using a clean mortar and pestle for subsequent analysis of OC, IC, and BC.

A multistage acidification procedure was used to completely remove IC from samples prior to quantification of OC and BC (Lukasewycz and Burkhard, 2005). In a fume-hood, 50 μL of deionized water (DIW) was added to each dried sample in a 1.5 mL plastic microcentrifuge tube (Eppendorf N.A., Hauppauge, NY) to prevent violent bubbling during reaction of HCl with carbonate. A 10% HCl solution (1:1 dilution of 6 N HCl into DIW) was introduced in 50–100 μL aliquants up to the calculated target volume in excess after cessation of bubbling (8–10 μL HCl/mg dry sediment mass; e.g. 500 μL of HCl for 50 mg dry sediment). After decarbonation, each tube was closed tightly and vortexed for 2 min and then shaken for 24 h to ensure complete reaction. After 24 h, samples

were centrifuged again (5 min at 10,000 RPM at 20 °C) and the supernatant solution was removed by pipet. An additional 1 mL DIW was added to the sediment microcentrifuge tube, followed by vortexing for 2 min. Centrifugation, decanting of the supernatant, and DIW rinse was repeated at least three times until the sample had approximately neutral pH (tested with pH paper). After this, the sediment sample was placed in an oven at 40 °C for 48 h in preparation for analysis of OC or BC as described below (IC was thus equal to the difference between TC and OC). Complete removal of IC using this method was rigorously validated by looking for the presence of $\delta^{13}\text{C}$ values typical of IC or IC/OC mixtures (carbonates have little isotopic fractionation) in treated samples using isotope ratio mass spectrometry as described below (Bonina, 2016). This technique is sufficiently sensitive to see large discernable differences of $\delta^{13}\text{C}$ values in inadequately decarbonated sediments from the southern basin of Lake Michigan (Bonina, 2016).

Quantification of carbon, nitrogen and stable isotope ratios

Concentrations of C (TC, OC, and BC) and N were measured in triplicate by elemental analysis (EA). Ten to twenty mg of sample were placed in pre-tared tin combustion boats (CE Elantech Inc., Lakewood, NJ, USA), sealed and weighed. Elemental analysis was conducted using automated combustion/reduction (900 °C for C and N) followed by molecular sieve gas chromatography and thermal conductivity detection at 60 °C using a Carlo Erba Flash EA1112 (ThermoQuest/CE Elantech, Lakewood, NJ, USA) and quantified using 2,5-Bis-2(5-tert-butyl-benzoxalyl) thiophene standard.

Total concentrations of N ($\delta^{15}\text{N}_{\text{total}}$), and C ($\delta^{13}\text{C}_{\text{organic}}$ relative to PDB) were measured for all sites (except M050 because of lack of sufficient sample mass) by elemental analysis/isotope ratio mass spectrometry (EA/IRMS) using a Costech Analytical EA, ECS 4010 Elemental Combustion System with zero blank autosampler coupled to a ThermoFinnigan Delta Plus XL IRMS equipped with ConFlo III, Gas Bench II. C and N were quantified by comparison to acetanilide standard peak area using EAS Clarity ISODat 2.0 software. Caffeine (3,7 trimethylxanthine; 49.48 wt% C and 28.85 wt% N) was used as a secondary calibration standard to confirm results of the primary acetanilide standard. Authentic acetanilide and sediment sample replicates were run every ten samples to determine analytical accuracy and precision. Sediment samples with C or N outside the calibration curve were re-analyzed with a lower mass sample.

Grain size analysis

Sediment samples for particle size distribution measurement were pre-treated to remove OM agglomeration by addition of H_2O_2 (10%) to the wet sediment until absence of reaction as shown by bubble cessation. Samples were then suspended and homogenized in a 1 L beaker of DIW until the refractive index reading was stable prior to analysis using a Malvern laser diffraction particle velocimeter (Malvern Instruments, Worcestershire, UK).

Dating of sediment cores

Profiles of rates of accumulation of masses of sediments (i.e., sedimentation rates) and calendar dates were determined from measurements of ^{210}Pb , ^{226}Ra , and ^{137}Cs by gamma ray spectroscopy using instrumentation and previously described methods (Corcoran, 2013; Smalley, 2013; Corcoran et al., 2018). Sediment focusing factors (FF) were determined from cumulative activities of ^{210}Pb and ^{137}Cs in each core compared with their integrated atmospheric depositional fluxes (Eadie et al., 2008). A FF value <1 indicates sediment loss, and a FF value >1 implies sediment gain, by horizontal sediment transport processes (Eadie et al., 2008).

Depositional fluxes and loadings

Fluxes and loadings were calculated from concentrations and profiles of radionuclide activities. Net depositional flux was calculated by

dividing the product of the concentration and the sedimentation rate by the FF. Whole lake loading (in metric tons per year, t/yr) was calculated using the surface integration of the flux over the whole lake using the Inverse Distance Weighting (IDW) method for multivariate interpolation. Whole-lake loadings and fluxes were determined as a function of time and plotted and mapped using the ArcMap component of the software geographic information system (ArcGIS, v.10.3, ESRI, Redlands, CA, USA).

Results and discussion

Geochemical characterization of Lake Michigan sediments

Sampling sites were divided into four geographically distinct groups: northern Chippewa basin sites M047, M041, and M032, mid-lake plateau site M024, Green Bay site M050, and southern Chippewa basin sites M018, M011, and M009 (Fig. 1). The relatively small “islands and straits” region at the northern end of Lake Michigan is relatively shallow, contains many rocky reefs, and lacks soft sediment depositional basins. Because of these characteristics, cores were collected primarily from the four other regions.

Mixing of sediments within the water column occurs at some locations (sites M011, M024, M047, M050) as a result of physical lake processes that result in large-scale re-suspension and horizontal transport of sediments from depositional areas and temporary repositories on the lake margins (Corcoran, 2013). Post-depositional processes that might affect sediment layers include annual lake turnover (destratification), storm events, and upwelling (Bell and Eadie, 1983; Eadie et al., 2008; Eadie et al., 1990; Plattner et al., 2006). However, on

a net deposition basis as recorded in the sedimentary cores, differences between and among sites were observed.

Loading of TC is less in the open lake than in Green Bay (M050), and an enrichment of TC and IC relative to OC has occurred at M050 during the last four decades (Fig. 2a–d). Although sedimentation rates vary among sampling sites, ranging from 0.065 g/cm²/yr at M009 to 0.018 g/cm²/yr at M018 (Electronic Supplementary Material (ESM) Table S1), similar temporal trends in concentrations were evident at some sites (Fig. 2a–d). There was a pronounced increase in concentrations of TC observed from north to south (Fig. 2a–c), with greatest concentrations in the southern Chippewa basin. TC ranged from 4%–5% at most sites, with sites M050 and M009 being notably enriched in TC at depth in the core (Fig. 2a). In general, there was a pronounced increase in concentrations of TC in more recently deposited sediments, increasing from approximately 5% near the bottom to 9% in top layers of site M050. Although M009 had greater concentrations of TC in deeper core segments, concentrations did not increase towards the top of the core as they did in M050. Most of the other sites had concentrations of TC in the range of 4–5% (Fig. 2a). Similarly for OM and OC, concentrations were similar at most locations (1–3% for OC and 4–8% for OM), with greater concentrations of OC and OM in sediments from M050 (6–8% OC and 10–15% OM, respectively).

In the southern Chippewa basin, sites M018, M009, and M011 might be influenced by their proximity to areas with more urbanization and intensive agricultural land use, although differences between site M009 and sites M011 and M018 are evident (Fig. 2a–c). All have greater concentrations of TC, OC, and OM during the period 1850–1930. However, M009 had a shallow gradient with depth, while a decline in OC concentration occurs at approximately mid-core at sites M011 and

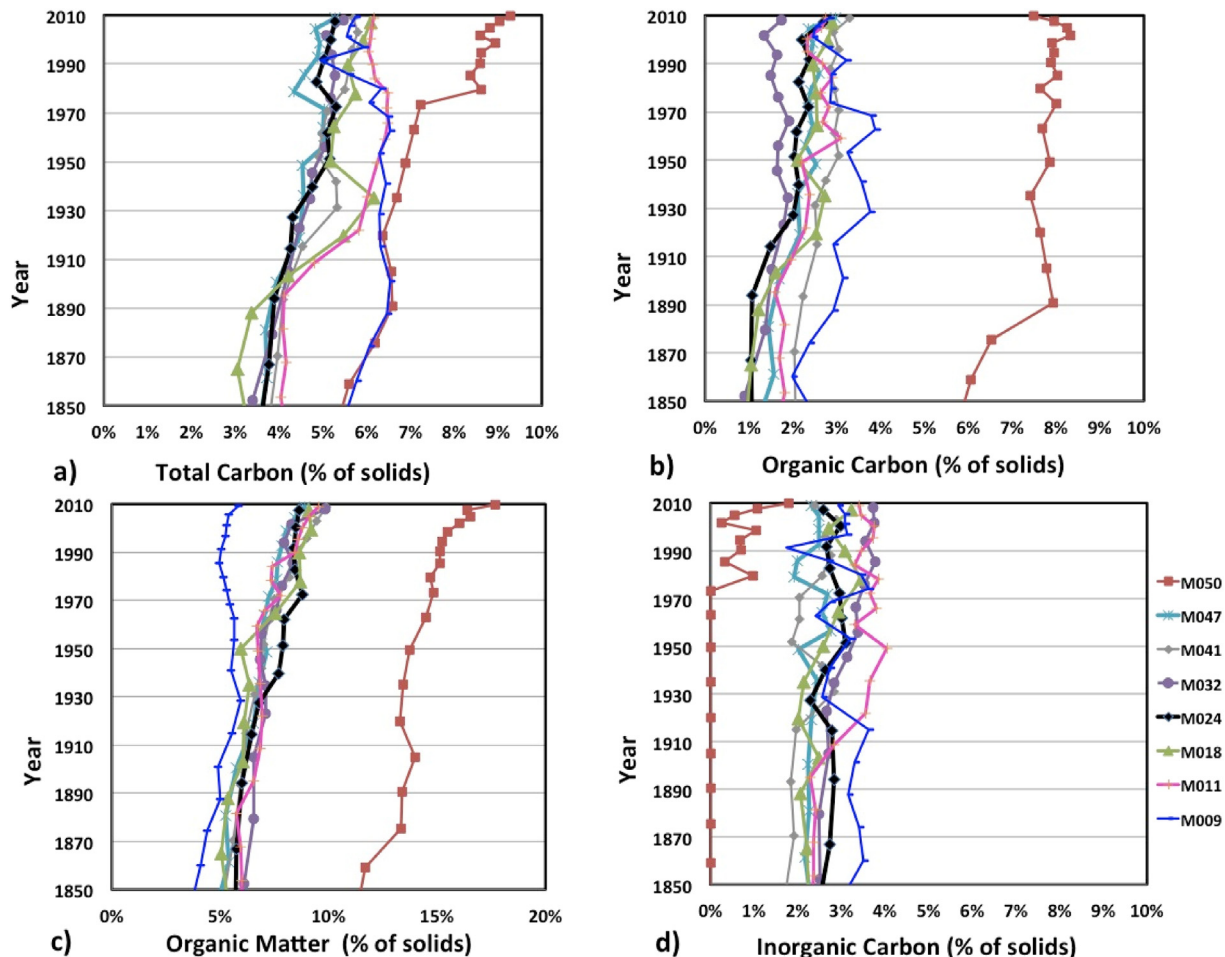


Fig. 2. Concentrations of a) total carbon (TC), b) organic carbon (OC), c) organic matter (OM), and d) inorganic carbon (IC) versus sedimentation year in Lake Michigan coring sites.

M018. The IC data also show a pronounced difference between the southern and northern Chippewa basins (Fig. 2d). IC concentrations were largely between 2 and 4% by mass, but usually larger in southern basin sites M009 and M011. In addition, IC represents a substantial fraction of the TC, frequently ~50% by mass (with the exception of M050).

Most sediments at all sites were classified as silt (2–63 μm) that constituted 50–60% of the sediment (Fig. 3). Clay-sized particles also constituted a large percentage of the sediment, between 25 and 50% by mass. Only site M050 (in Green bay) had a sand-sized particle fraction exceeding a few percent. Together, these data show that nearly all sediment is fine-grained in Lake Michigan (even at near shore sites M050 and M009). These particle sizes are consistent with an open water deposition process, where coarser terrigenous material is deposited near shore, leaving only finer-sized particles at the deeper-water sites sampled for this study. Within cores, the sediment followed a general trend of increasing bulk density and solids content with depth (data not shown), which was indicative of compaction of the sediment with increasing overburden.

Stable isotope analysis

Analyses of stable isotopes can provide information on fixation of C in OM, based on differential transport of stable isotopes across membranes and through differential affinity for light and heavy isotopes by metabolic enzymes. Results of the SIA in nearly all Lake Michigan sediments are consistent with in-lake algal production as the dominant source of OM to the sediment (Fig. 4a). All sediments had $\delta^{13}\text{C}$ values of -25 to -27% within the range of lacustrine algae, and C/N ratios clustered near the Redfield ratio of algae (Meyers, 1994).

N isotopes are also fractionated during biological uptake and metabolism (and through trophic transfer), and thus a more detailed resolution of these data can be obtained by comparing $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values (Fig. 4b). Lesser $\delta^{15}\text{N}$ values, ranging from 3 to 6‰ at some locations suggests that sediment OM might originate from a mixture of lacustrine algae and terrestrial plants (Fig. 4b).

Spatial trends in SIA indicate that sites M009, M041, and M047 have more terrigenous OM compared to sites M011, M018, M024, and M032, which have an almost exclusively lacustrine algal OM source. Interestingly, the SIA data suggest a slight change in OM from primarily autochthonous (lacustrine) sources in the past, to increasing allochthonous (terrestrial) sources from outside the Lake in more recently deposited sediments. It is not immediately clear what accounts for these observations. Reasons include a change in OM source, differential degradation of post-depositional sediment OM in situ, or a combination of the two processes. Results of sediment trap studies suggest that in Lake Michigan, labile algal-OM can be preferentially degraded (Eadie et al.,

1984), possibly affecting the isotope ratio in the deposited sediments (Meyers and Lallier-Vergès, 1999). Continued preferential degradation of algal-derived OM in situ would result in increases of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values, while the C/N ratio would decrease. Conversely, preferential degradation of C3 OM in situ would be expected to have the opposite effect of decreasing $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values, with concomitant increasing C/N ratios. Neither is entirely consistent with findings of this study, suggesting that changes in OM source to the lake (e.g. increasing terrigenous OM) has likely occurred in recent times.

Analysis of depositional trends

The proportion of the sediment OC pool that is potentially biodegradable can be estimated by comparing OC loading to sediment surface area relative to the “monolayer equivalent” (MLE). The MLE represents the equivalent surface area (SA) coverage of one molecule thickness of adsorbed OC, an amount that is typically observed in continental shelf sediments and other oligotrophic depositional environments. In this study, OC coverage was many times greater than the MLE of $\sim 1 \text{ mg/m}^2$ (Fig. 5). The OC/SA ratios clustered from 1 to 10 mg/m^2 for all depositional sites, and were much greater (as much as 50 mg/m^2) at site M050 in Green bay (Fig. 5).

Comparisons of concentrations of OC and OM within each core confirmed that across the lake there has been an increase in OM in sediment in recent decades (particularly in Green Bay) compared with OM and OC levels in deeper sediment, when presumably lake nutrient input was less. This interpretation is consistent with comparisons of loading of OC to that of OM or loading of OC to TN (Fig. 6a–b, respectively). Sites having greater C surface coverage (e.g., M050) have a correspondingly larger ratio of OC:OM approaching 1:2; similar to what would be expected in new OM (Fig. 6a). However, site M009 has less OM than M050 and a large OC/TN ratio of 20:1. This suggests that site M009 has sources of C that are relatively poor in N and likely resistant to biodegradation. Conversely, most other sites have OC:OM ratios between 1:2 and 1:5 with decreasing OC relative to TN in sediment (Fig. 6b), which is consistent with a lacustrine algal OM source.

Comparison with sediment trap data

Results of sediment trap studies indicate that continuous oxidative alteration and degradation of re-suspended sediment OM was considerable ($\sim 80 \text{ g OC/m}^2/\text{yr}$ at 100 m depth in the southern basin); approximately ten times the annual OC flux at the lake bottom layer (Eadie et al., 1984; Meyers and Eadie, 1993; Meyers et al., 1984). Net masses of C buried in sediment are related to net primary production (NPP),

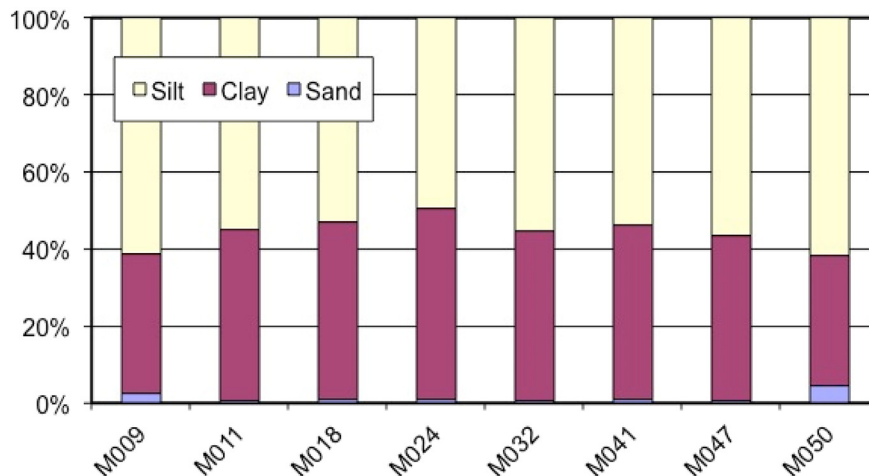


Fig. 3. Whole-core average particle size fraction of clay (<2 μm), silt (2–63 μm), and sand (>63 μm) in sediments from all coring sites in Lake Michigan.

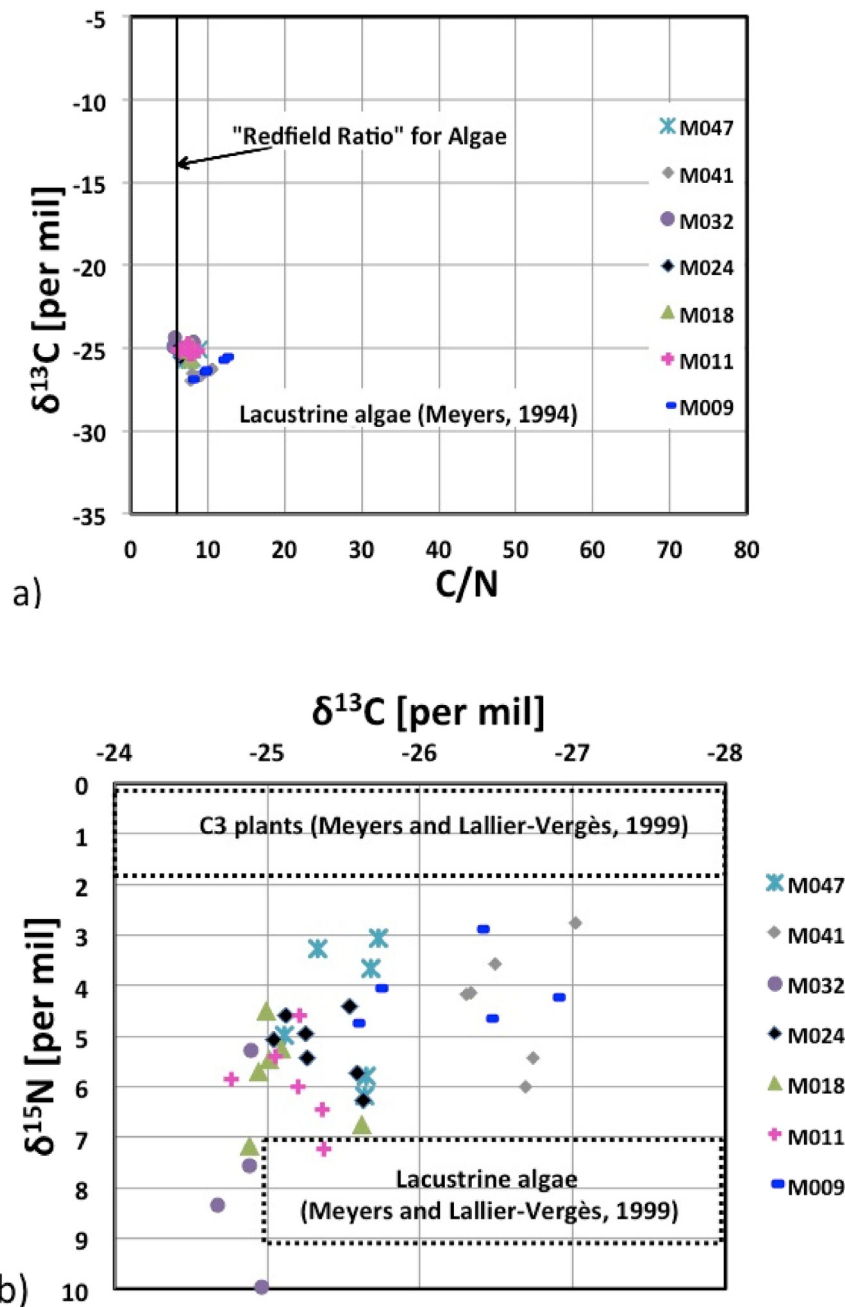


Fig. 4. Comparison of a) $\delta^{13}\text{C}$ to C/N molar ratio, and b) $\delta^{15}\text{N}$ to $\delta^{13}\text{C}$ in Lake Michigan sediment samples. Also shown are the molar C/N "Redfield ratio" for algae, and the range of reported $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values for lacustrine algae and terrestrial C3 plants for comparison.

which was $\sim 8 \text{ g C}_{\text{org}}/\text{m}^2/\text{yr}$ (Eadie et al., 1984) and thus only a small percentage of NPP was ultimately buried in the sediment as OM.

By assuming that the sites in studies were sufficiently near to each other and largely representative of the area, and that net C burial as recorded in the sediment is similar to what had occurred then (i.e. there has not been substantial degradation of OC in situ during the past 20–30 years), comparisons can be made between results of sediment trap studies conducted in the 1980's and 1990's, and the current study. Taking two sites, one in the north and one in south of the lake, that correspond closely to those studied in a previous study (Meyers and Eadie, 1993) and the present study, changes over this period were calculated. In the southern basin, the historical limit of net flux of OC in the upper layer was estimated to be $22.6 \text{ g}/\text{m}^2/\text{yr}$ (Meyers and Eadie, 1993) and $3.75 \text{ g}/\text{m}^2/\text{yr}$ in the present study. In the northern basin, net fluxes of OC during earlier and current studies were 9.9 and $3.5 \text{ g}/\text{m}^2/\text{yr}$,

respectively. These results suggested that there was continuous degradation in the hypolimnion, thus making it difficult to estimate net sedimentation flux of OC in the southern basin from the available data because the rate of resuspension of sediments obfuscates hypolimnetic processes. In contrast, in the northern basin there was less resuspension. If it is assumed that a similar 67% hypolimnetic oxidation of OC occurred (comparing $24 \text{ g C}_{\text{org}}/\text{m}^2/\text{yr}$ to $8 \text{ g C}_{\text{org}}/\text{m}^2/\text{yr}$) as in Eadie et al. (1984), a NPP of $7 \text{ g}/\text{m}^2/\text{yr}$ was estimated for the southern basin and $3.3 \text{ g}/\text{m}^2/\text{yr}$ in the northern basin.

Comparison of the OC $\delta^{13}\text{C}$ values from sediment trap results and this study at similar locations of the South Chippewa and Chippewa basins of Lake Michigan (Table 1) exhibits a pattern of isotopic changes consistent with a decrease in OM lost during sinking through the water column. The initial $\delta^{13}\text{C}$ values were -26 to -27‰ , which are similar to those determined in this study, but decreased to -29‰ in

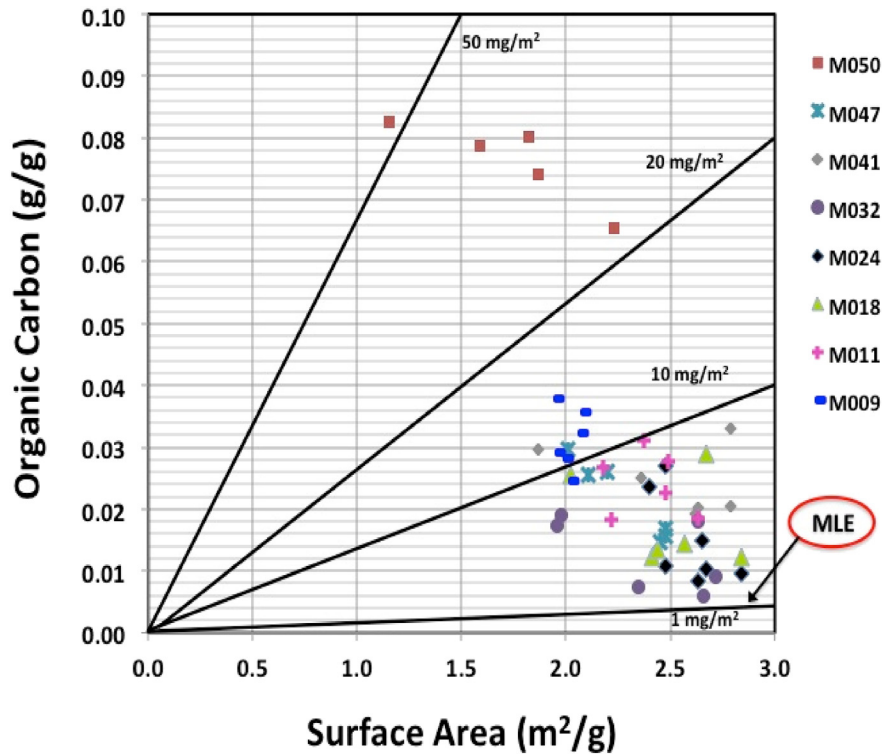


Fig. 5. Loading of OC as a function of sediment particle surface area in Lake Michigan sediments. Shown also are relative coverage ratios and the carbon mono-layer equivalent (MLE) of approximately 1 mg C/m^2 for comparison.

the upper water column where losses of OC were greater. This is to be expected in the photic zone, where primary productivity is greatest. These results of OM isotopic composition are consistent with observed changes in biomarker compositions that reveal selective losses of algal components in the epilimnion water column (Meyers and Eadie, 1993). Isotopic variations similarly reflect progressive diagenetic reduction of algal OM and survival of the most resistant OM fractions. There was no substantial diagenetic change in $\delta^{13}\text{C}$ values with depth in sediment cores where the hypolimnion OM is not as dominated by algal-derived OM (Rea et al., 1980).

Depositional fluxes

Depositional fluxes (in $\text{mg/cm}^2/\text{yr}$) were calculated for all measured parameters for each site by combining concentration data and radionuclide data plotted against the sediment deposition year to test the hypothesis that enrichment of OM and OC has occurred in more recently deposited sediments. The flux of OM doubled from $0.5\text{--}1 \text{ mg/cm}^2/\text{yr}$ for most cores, $1\text{--}1.5 \text{ mg/cm}^2/\text{yr}$ at M009, and $1\text{--}2 \text{ mg/cm}^2/\text{yr}$ at M050 (Fig. S.1). OC, IC, and TN fluxes had a largely similar relationship (Fig. 7a–c), with OC fluxes ranging from $0.4\text{--}0.5 \text{ mg/cm}^2/\text{yr}$ at most sites, IC fluxes from $0.3\text{--}0.5 \text{ mg/cm}^2/\text{yr}$, and TN fluxes $\sim 0.05 \text{ mg/cm}^2/\text{yr}$ at most locations. Fluxes of OC and TN at sites M009 and M050 were typically much greater than those at other locations. The OC flux and radionuclide data at site M050 both indicated that a change in deposition rate had occurred around 1980. A possible factor might be that in 1977, the US Army Corps of Engineers built an artificial island in the Fox River to receive sediment dredged from the river and other locations, and resultant changes in river flow and sedimentation likely occurred.

Among analytes, fluxes of BC exhibited some of the largest differences among cores (Fig. 7d). Fluxes of BC for most sites were $0.01\text{--}0.05 \text{ mg/cm}^2/\text{yr}$, whereas fluxes of BC at site M009 were typically $0.5 \text{ mg/cm}^2/\text{yr}$ and peaked at $\sim 1.5 \text{ mg/cm}^2/\text{yr}$ in the 1940s (Fig. 7d). Fluxes of BC at M009 were comparable to fluxes of OC at other sites, which demonstrated the major effects of industrial activity in the

southern basin of the lake. This time frame in the sediment deposition record corresponds to the period of intense steel production during the build-up and maximum industrialization associated with WW II.

Whole lake loading

Whole lake loading (t/yr) of OM, OC, IC, BC, and TN to the sediment was calculated by using surface integration of the flux over the whole lake, by use of the Inverse Distance Weighting (IDW) model and then plotting against deposition year (Fig. 8a–d). The increase of total loading for OM (Fig. 8a) in more recent sediments is quite evident, increasing from $\sim 400,000 \text{ t/yr}$ ($=400 \times 10^6 \text{ kg/yr}$) up to $500,000\text{--}600,000 \text{ t/yr}$ ($=500\text{--}600 \times 10^6 \text{ kg/yr}$) in the 1970s, where loading leveled off until another recent increase in OM load in 2010. A similar trend of total OC loading ranged from $150,000 \text{ t OM/yr}$ ($=150 \times 10^6 \text{ kg/yr}$) in 1850 to $250,000 \text{ t OM/yr}$ ($=250 \times 10^6 \text{ kg/yr}$) in 1930, followed by a plateau that lasted for several decades, until increasing again to $>300,000 \text{ t OM/yr}$ ($=300 \times 10^6 \text{ kg/yr}$) in 2010 (Fig. 8b). The recent increase in both OM and OC load to the lake in the most recent sediments requires further analysis, but is clearly due to an increased OM and OC concentration in the top-most layer of sediment. There are three possible explanations for this abrupt increase: mussel invasion, labile OM deposition, or a combination of the two. First, the increase may result from the impact of *Dreissena* spp. invasions that have occurred over the past two decades. Although sestonic phytoplankton has decreased markedly over this time (Mida et al., 2010; Pilcher et al., 2017), algal biomass may become incorporated more rapidly in the sediment through filter feeding by mussels. A second possibility is that increased OM in the surface layer results from recently deposited labile OM that is still undergoing early diagenetic alteration. This OM is clearly present as a coating at the sediment-water interface upon core retrieval. If this newly deposited OM is in the process of being biodegraded, we can estimate the abrupt “increase” in whole lake loading as representing the amount of labile OM that is degraded during net burial. Over an approximate timeframe of 10 years, this represents $\sim 5000 \text{ t OM/yr}$ ($=5$

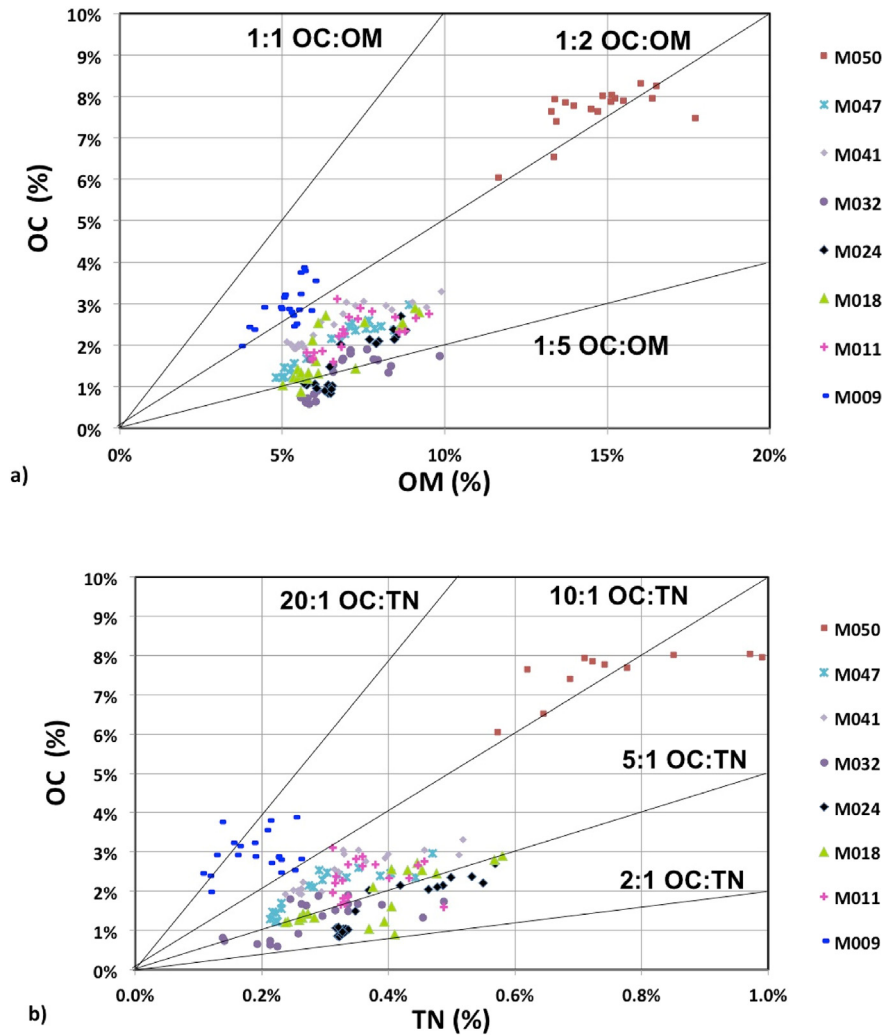


Fig. 6. Comparison of a) organic carbon (OC) to organic matter (OM) ratio, and b) OC to total nitrogen (TN) ratio in Lake Michigan sediments.

Table 1
OC sedimentation rates and sediment geochemical characteristics obtained from water column sediment traps reported in Meyers and Eadie (1993) compared to values obtained from dated sediment cores from the present study.

| Site location/depth | TOC (%) | Atomic C/N | $\delta^{13}\text{C}$ (‰) | $\delta^{15}\text{N}$ (‰) | TOC flux (g/m ² /yr) | Sampling/depositional date (Year) |
|---|---------|------------|---------------------------|---------------------------|---------------------------------|-----------------------------------|
| Sedimentation rate based on sediment traps (Meyers and Eadie, 1993) | | | | | | |
| Meyers and Eadie site 4 (South Chippewa Basin) | | | | | | |
| 15 m | 16.0 | 19.8 | -27.7 | 5.2 | 23.4 | 1980 |
| 35 m | 14.2 | 22.5 | -28.8 | ND | 25.6 | 1980 |
| 80 m | 6.4 | 8.7 | -26.8 | 3.6 | 22.6 | 1980 |
| 120 m | 4.8 | 10.7 | -26.2 | 4.3 | 33.9 | 1980 |
| 140 m | 8.8 | 21.2 | -26.6 | ND | 120 | 1980 |
| Meyers and Eadie site 11 (Chippewa Basin) | | | | | | |
| 11 m | 38.1 | 13.1 | -29.2 | ND | 9.9 | 1980 |
| 31 m | 45.8 | 20.9 | -28.1 | ND | 43.4 | 1980 |
| 91 m | 10.9 | 16.5 | -27.5 | ND | 16.4 | 1980 |
| 146 m | 4.8 | 8.1 | -27.4 | 3.3 | 9.9 | 1980 |
| 166 m | 5.7 | 13.3 | -27.8 | 3.3 | 24.1 | 1980 |
| Net sedimentation rate based on dated coring (present study) | | | | | | |
| This study site M011 (South Chippewa Basin) | | | | | | |
| M011-01 | 2.76 | 6.05 | -25.4 | 7.2 | 3.75 | 2009 |
| M011-05 | 2.68 | 7.08 | -25.4 | 6.5 | 3.64 | 1990 |
| M011-07 | 2.63 | 7.33 | -25.3 | 6.3 | 3.57 | 1978 |
| This study site M047 (Chippewa Basin) | | | | | | |
| M047-01 | 2.97 | 6.31 | -25.6 | 6.2 | 3.50 | 2009 |
| M047-05 | 2.60 | 7.38 | -25.5 | 5.8 | 3.07 | 1986 |
| M047-07 | 2.36 | 7.05 | -25.4 | 5.5 | 2.78 | 1972 |

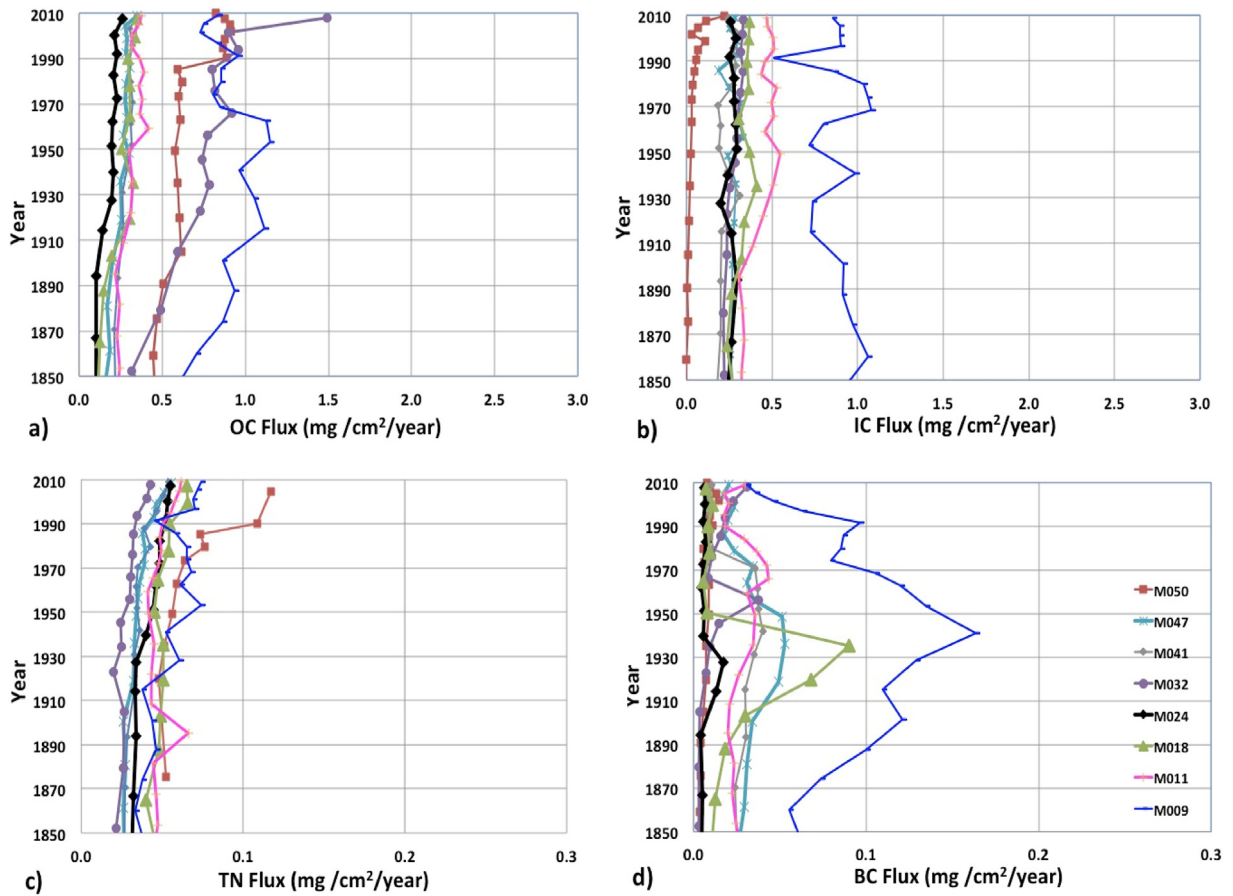


Fig. 7. Flux of a) organic carbon (OC), b) inorganic carbon (IC), c) total nitrogen (TN), and d) black carbon (BC) as a function of sediment deposition year for each core site in Lake Michigan.

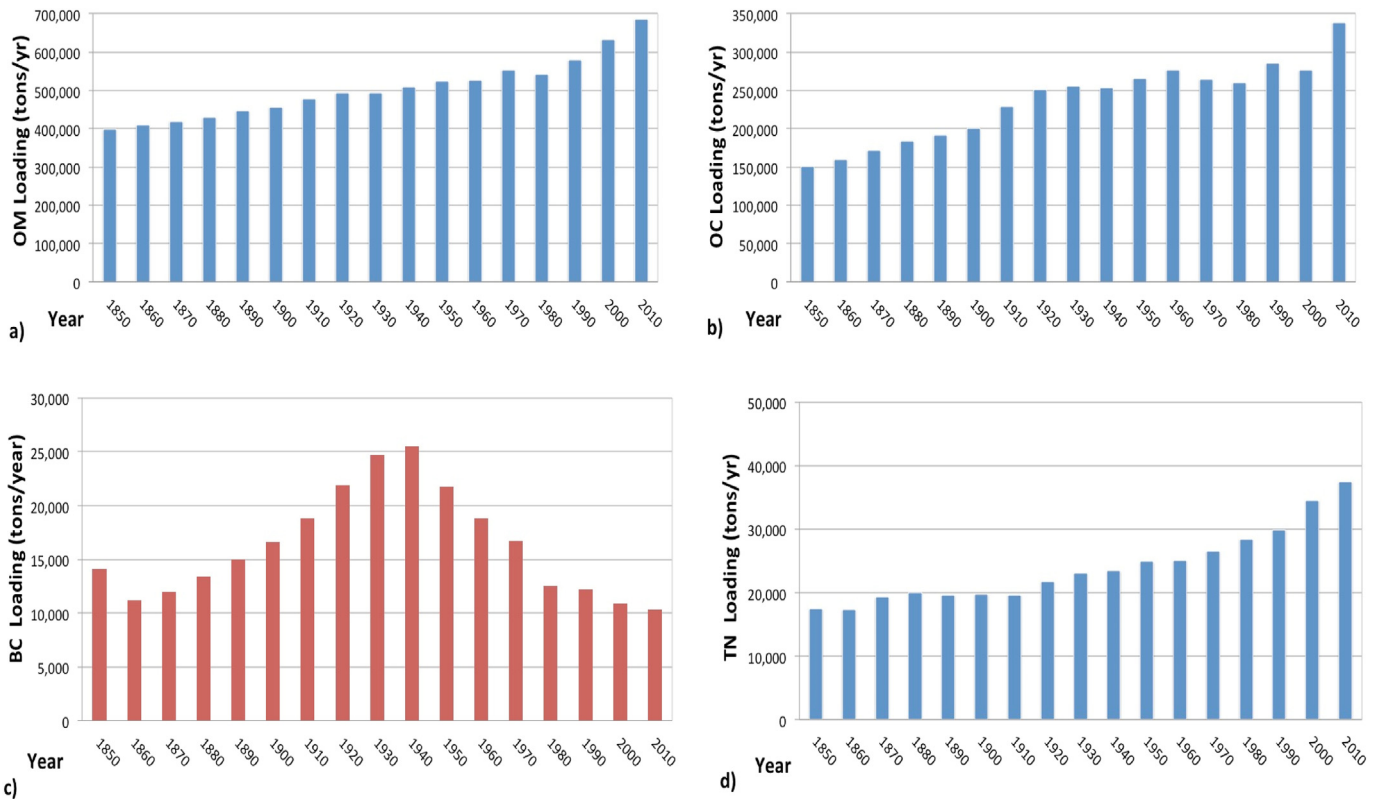


Fig. 8. Annual net loading (t/yr) of a) organic matter (OM), b) organic carbon (OC), c) black carbon (BC), and d) total nitrogen (TN) to Lake Michigan over decadal periods from 1850 to 2010.

$\times 10^6$ kg OM/yr). The third possibility is that both processes (mussel invasion and labile OM deposition) may account for the resulting high OM found in surficial sediments of Lake Michigan.

Among analytes, whole lake BC loading (Fig. 8c) followed an approximately symmetric peak, showing an increase from 10,000 t BC/yr ($= 100 \times 10^6$ kg/yr) during the early industrial revolution in the mid 1800's to the 1940's, and then followed by a decrease from 1950 to present. Greatest loading of BC was in the 1930's and 1940's, likely as a result of wartime, fuel driven production, manufacturing, and shipping. Lesser loading of BC might be related to decreasing production and the onset of improved pollution prevention following federal Clean Air Act legislation starting in the 1960's. Also likely affecting loading of BC is the change in electricity generation during the period covered in this study. Early in the industrialization period coal was the predominant source of electricity generation. More recently, electricity generation shifted to oil and gas, both of which release much less BC through more complete combustion compared to coal (Hosseini, 2016).

Unlike the large increase and subsequent decrease in loading of BC, TN loading has increased steadily with time starting from the 1850's and almost doubling by 2010 (Fig. 8d). This is similar to the trend in OM loading over this time period (Fig. 8a), suggesting a similar sedimentation process. In contrast to the case with all other analytes, whole lake loading of IC was largely unchanged throughout Lake Michigan during the entire period from 1850 to 2010 (data not shown), with annual loading of $194,000 \pm 8500$ t/yr ($= 19 \times 10^6$ kg/yr) (mean \pm 95% CI).

Temporal variability in flux data suggests three distinct periods of loading of OM and BC occurred during the period 1850–2010: Period I from ca. 1850 until 1910 (ESM Figs. S2 and S5), Period II from ca. 1920–1970, which corresponds to the period of rapid industrialization to the start of Great Lakes legislation intended to decrease pollutant loading to the lakes (ESM Figs. S3 and S6), and Period III from 1980 onward corresponding to the post-legislation period (ESM Figs. S4 and S7). Fluxes of OM during Period I were typically 1 mg/cm²/yr in the south and ~ 0.5 mg/cm²/yr at other sites, while BC fluxes were typically < 0.04 mg/cm²/yr except for the more south-eastern portion of the southern Chippewa basin. Fluxes of both OM and BC were greater in the northern basin during Period II, typically in the 0.5 – 1 mg/cm²/yr for OM and 0.04 – 0.07 mg/cm²/yr for BC. Finally, fluxes of OM during Period III were similar in the south basin, but somewhat lower in the middle part of the northern basin. In great contrast, lake-wide fluxes of BC decreased substantially in Period III. For all three periods, site M009 in the south basin typically had the greatest fluxes of OM and BC, while M050 in Green Bay exhibited the greatest fluxes of OM. Whole-lake loading at open-lake and the remaining north basin sites was uniformly lesser than those at other sites.

Conclusions

Lake Michigan sediments have C/N ratios that are greater than or equal to lacustrine algae, and lower than those found in terrestrial plants. Further, $\delta^{13}\text{C}$ of Lake Michigan sediment is similar to both lacustrine algae and C3 land plants. Sediment OM/OC ratios of 2.1 ± 2.4 and OC/N ratios 6.4 ± 1.6 are consistent with the algal Redfield ratio for OM. Together, these findings suggest that algae are the dominant source of OM to Lake Michigan sediments, while possible terrigenous sources are important in the southern Chippewa basin site M009 and in the northern Chippewa basin site M041. Fluxes of BC were unusual in that the loading looks like a shallow bell curve, peaking during the WW II war effort in the 1940's. In contrast to the case with OM, OC, and BC, IC sedimentation has been relatively constant in Lake Michigan since at least the 1850's. This indicates that IC deposition is unaffected by changes in industrial, urban, or agricultural practices in the watershed that have occurred in the last 150 years or longer.

Overall, whole lake loading followed a trend of increasing loading of OM and BC in Period I, followed by a more rapid increase during Period

II. Interestingly, there is no convincing evidence that legislation intended to curb waterborne eutrophication had a strong impact on decreasing OM loading in the sediment record of the current study. Thus, we can conclude that reductions in nutrient loading were not sufficient to decrease OM loading during the ~ 40 years since legislation. In marked contrast, whole lake loading of BC decreased dramatically following WW II. In the latest core segments, BC loading is at or near where it was prior to any urbanization of the Great Lakes region. Within the context of legislation, it would appear that air pollution reduction strategies have been particularly successful for BC. The reason for the disparity between OM and BC loading might result from the fact that the residence time of BC in the water column is quite low, and thus reductions in emissions result in rapid decreases of BC in the water column. In contrast, reductions in nutrient loads to the lake would not result in immediate decreases in OM loading because the residence time of the lake is on the order of 100 years, and thus we would expect a substantial delay until reductions in whole-lake loading of OM can occur.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jglr.2018.03.001>.

References

- ASTM, 1998a. American Society for Testing and Materials. Standard Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock. ASTM D2216-92, Philadelphia, PA.
- ASTM, 1998b. American Society for Testing and Materials. Standard Test Method for Specific Gravity of Soils. ASTM D854-92, Philadelphia, PA.
- Bell, G.L., Eadie, B.J., 1983. Variations in the distribution of suspended particles during an upwelling event in Lake Michigan in 1980. *J. Great Lakes Res.* 9 (4), 559–567.
- Bonina, S.M.C., 2016. Carbon Loading to Lake Michigan Sediments. (PhD Thesis). University of Illinois at Chicago.
- Buckley, D.R., Rockne, K.J., Li, A., Mills, W.J., 2004. Soot deposition in the Great Lakes: implications for semi-volatile hydrophobic organic pollutant deposition. *Environ. Sci. Technol.* 38 (6), 1732–1739.
- Christensen, E.R., Chien, N.-K., 1981. Fluxes of arsenic, lead, zinc, and cadmium to Green Bay and Lake Michigan sediments. *Environ. Sci. Technol.* 15 (5), 553–558.
- Corcoran, M.B., 2013. Variations in Sedimentation Rate and Sediment Focusing in Lake Michigan Using Radionuclide Profiles. (Master of Science Thesis). University of Illinois at Chicago.
- Corcoran, M.B., Sturchio, N.C., Sherif, M., Smalley, C., Poghossyan, A., Li, A., Rockne, K.J., Giesy, J.P., 2018. New Survey of Great Lakes Sediment Chronologies from Radionuclide Profiles (This issue).
- Dean, W.E., Gorham, E., 1998. Magnitude and significance of carbon burial in lakes, reservoirs, and peatlands. *Geology* 26 (6), 535–538.
- Eadie, B.J., Chambers, R.L., Gardner, W.S., Bell, G.L., 1984. Sediment trap studies in Lake Michigan: resuspension and chemical fluxes in the southern basin. *J. Great Lakes Res.* 10 (3), 307–321.
- Eadie, B.J., Vanderploeg, H.A., Robbins, J.A., Bell, G.L., 1990. Significance of sediment resuspension and particle settling. *Large Lakes*. Springer, pp. 196–209.
- Eadie, B.J., Robbins, J.A., Klump, J.V., Schwab, D.J., Edgington, D.N., 2008. Winter-spring storms and their influence on sediment resuspension, transport, and accumulation patterns in southern Lake Michigan. *Oceanography* 21 (4), 118–135.

- Hosseini, S., 2016. Implications of Carbon Deposition on the Fate of Semi-Volatile Organic Pollutants in the Great Lakes. (PhD Thesis). University of Illinois at Chicago.
- Lehman, J.T., 1988. Algal Biomass Unaltered by Food-web Changes in Lake Michigan.
- Li, A., Rockne, K.J., Sturchio, N.C., Mills, W.J., Song, W., Ford, J.C., Buckley, D.R., 2006. Chronology of PBDE air deposition in the great lakes from sedimentary. (Retrieved from). Great Lake Atmospheric Deposition Program. USEPA Region V.
- Lukasewycz, M.T., Burkhard, L.P., 2005. Complete elimination of carbonates: a critical step in the accurate measurement of organic and black carbon in sediments. *Environ. Toxicol. Chem.* 24 (9), 2218–2221.
- Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chem. Geol.* 114 (3), 289–302.
- Meyers, P.A., 2003. Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. *Org. Geochem.* 34 (2), 261–289.
- Meyers, P.A., Eadie, B.J., 1993. Sources, degradation and recycling of organic matter associated with sinking particles in Lake Michigan. *Org. Geochem.* 20 (1), 47–56.
- Meyers, P.A., Ishiwatari, R., 1993. Lacustrine organic geochemistry—an overview of indicators of organic matter sources and diagenesis in lake sediments. *Org. Geochem.* 20 (7), 867–900.
- Meyers, P.A., Ishiwatari, R., 1995. Organic matter accumulation records in lake sediments. *Physics and Chemistry of Lakes*. Springer, pp. 279–328.
- Meyers, P.A., Lallier-Vergès, E., 1999. Lacustrine sedimentary organic matter records of Late Quaternary paleoclimates. *J. Paleolimnol.* 21 (3), 345–372.
- Meyers, P.A., Edwards, S.J., Eadie, B., 1980. Fatty acid and hydrocarbon content of settling sediments in Lake Michigan. *J. Great Lakes Res.* 6 (4), 331–337.
- Meyers, P.A., Leenheer, M.J., Eaoie, B.J., Maule, S.J., 1984. Organic geochemistry of suspended and settling particulate matter in Lake Michigan. *Geochim. Cosmochim. Acta* 48 (3), 443–452.
- Mida, J.L., Scavia, D., Fahnenstiel, G.L., Pothoven, S.A., Vanderploeg, H.A., Dolan, D.M., 2010. Long-term and recent changes in southern Lake Michigan water quality with implications for present trophic status. *J. Great Lakes Res.* 36, 42–49.
- Pilcher, D.J., McKinley, G.A., Kralj, J., Bootsma, H.A., Reavie, E.D., 2017. Modeled sensitivity of Lake Michigan productivity and zooplankton to changing nutrient concentrations and quagga mussels. *J. Geophys. Res. Biogeosci.* 122, 2017–2032.
- Plattner, S., Mason, D.M., Leshkevich, G.A., Schwab, D.J., Rutherford, E.S., 2006. Classifying and forecasting coastal upwellings in Lake Michigan using satellite derived temperature images and buoy data. *J. Great Lakes Res.* 32 (1), 63–76.
- Prahl, F.G., Bennett, J.T., Carpenter, R., 1980. The early diagenesis of aliphatic hydrocarbons and organic matter in sedimentary particulates from Dabob Bay, Washington. *Geochim. Cosmochim. Acta* 44 (12), 1967–1976.
- Rea, D.K., Bourbonniere, R.A., Meyers, P.A., 1980. Southern Lake Michigan sediments: changes in accumulation rate, mineralogy, and organic content. *J. Great Lakes Res.* 6 (4), 321–330.
- Rockne, K.J., Taghon, G.L., Kosson, D.S., 2000. Pore structure of soot deposits from several combustion sources. *Chemosphere* 41 (8), 1125–1135.
- Rockne, K.J., Shor, L.M., Young, L., Taghon, G.L., Kosson, D.S., 2002. Distributed sequestration and release of PAHs in weathered sediment: the role of sediment structure and organic carbon properties. *Environ. Sci. Technol.* 36 (12), 2636–2644.
- Smalley, C.C., 2013. Radioisotope Geochronology of Lake Superior Sediments. (Master of Science Thesis). University of Illinois at Chicago.
- USEPA, 1995. The great lakes. An Environmental Atlas and Resource Book, 3th ed. National Service Center for Environmental Publications (NSCEP).

Electronic Supplementary Material

Temporal and spatial differences in deposition of organic matter and black carbon
in Lake Michigan sediments over the period 1850-2010

Table S1

and

Figures S1-S7

Table S1. Sedimentation rates and ^{210}Pb focusing factors determined from cores obtained of Lake Michigan sediments. Data from Corcoran (2013) and Corcoran et al. (this issue).

| Site ID | Location in Lake | Water Depth | Sedimentation Rate | Focus Factor ^{210}Pb |
|----------------|----------------------------------|--------------------|---------------------------|--|
| | | (m) | (g/cm ² /yr) | |
| M009 | South Chippewa Basin, near shore | 62 | 0.065 | 2.20 |
| M011 | South Chippewa Basin | 164 | 0.041 | 2.99 |
| M018 | South Chippewa Basin | 165 | 0.018 | 1.52 |
| M024 | Mid-Lake Plateau | 150 | 0.019 | 1.98 |
| M032 | Chippewa Basin | 257 | 0.018 | 2.09 |
| M041 | Chippewa Basin | 272 | 0.022 | 2.11 |
| M047 | North End, Chippewa Basin | 200 | 0.031 | 2.64 |
| M050 | Green Bay | 33 | 0.020-0.043 | 2.85 |

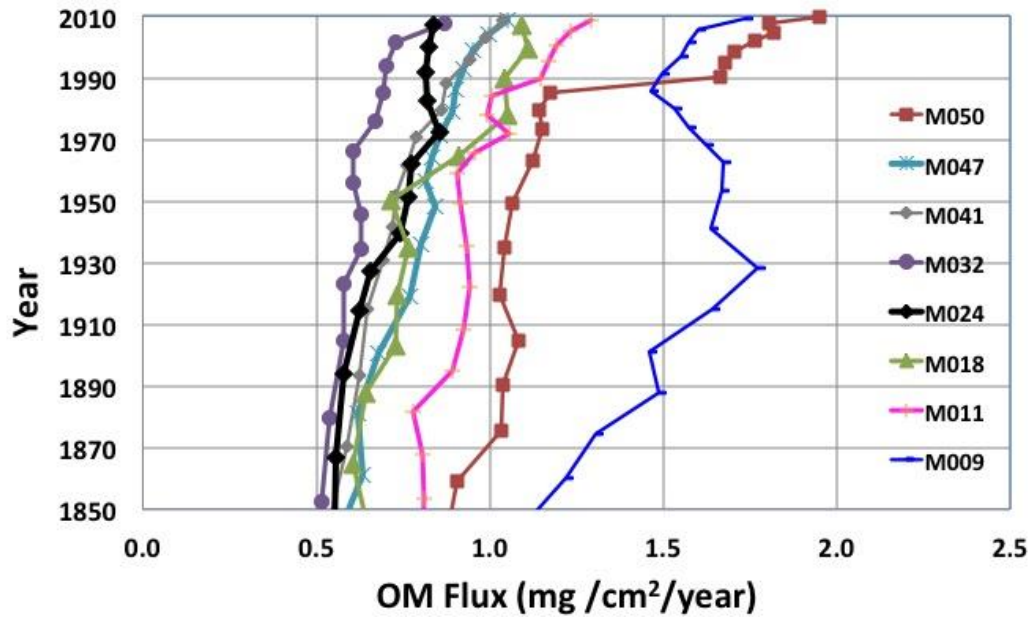


Figure S1. Flux of Organic Matter (OM) as function of sediment deposition year for each core site in Lake Michigan.

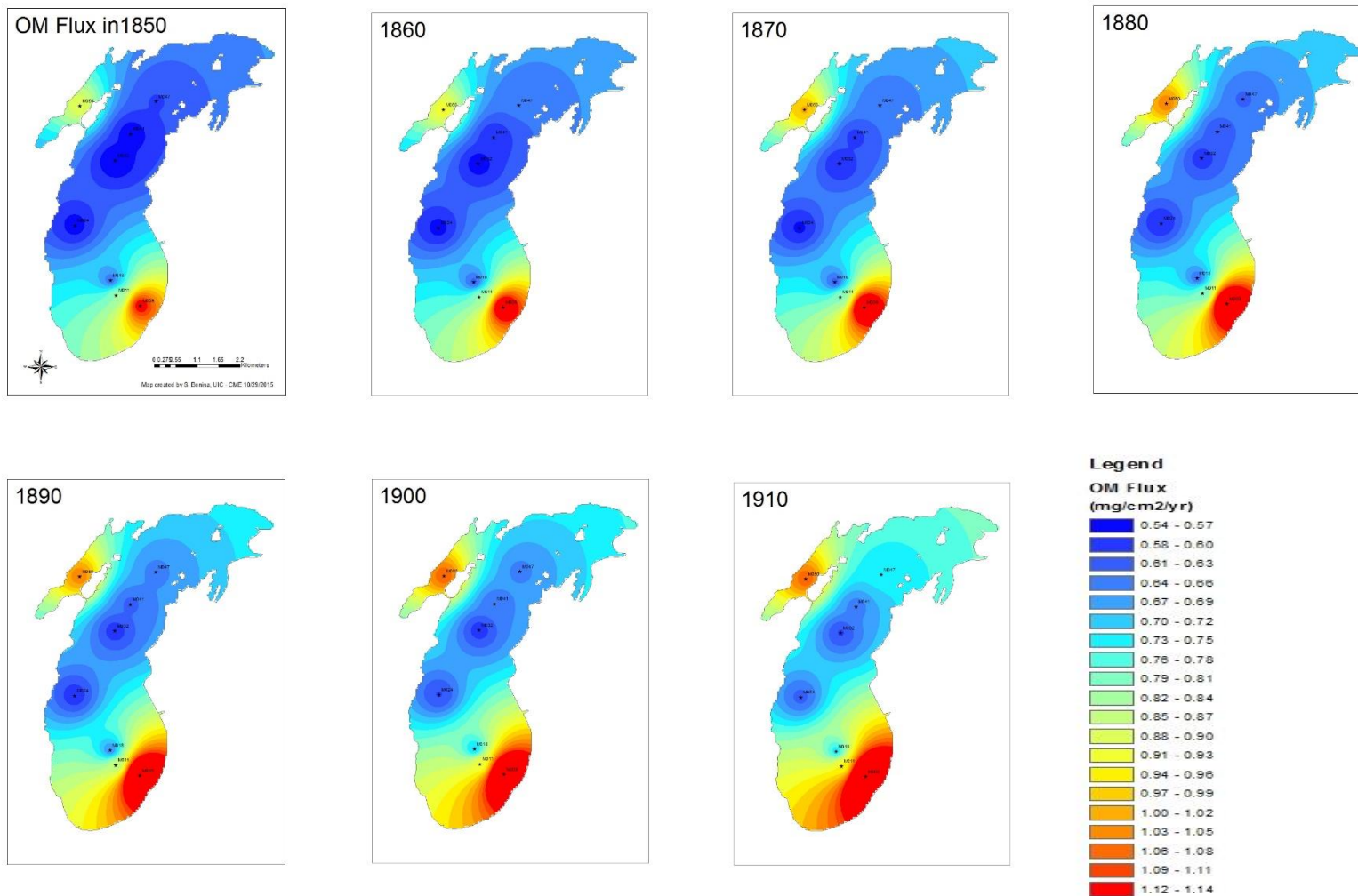


Figure S2. Net annual fluxes (by decade) of Organic Matter (OM) to Lake Michigan sediment for Period I from 1850 to 1910 during the period prior to rapid industrialization.

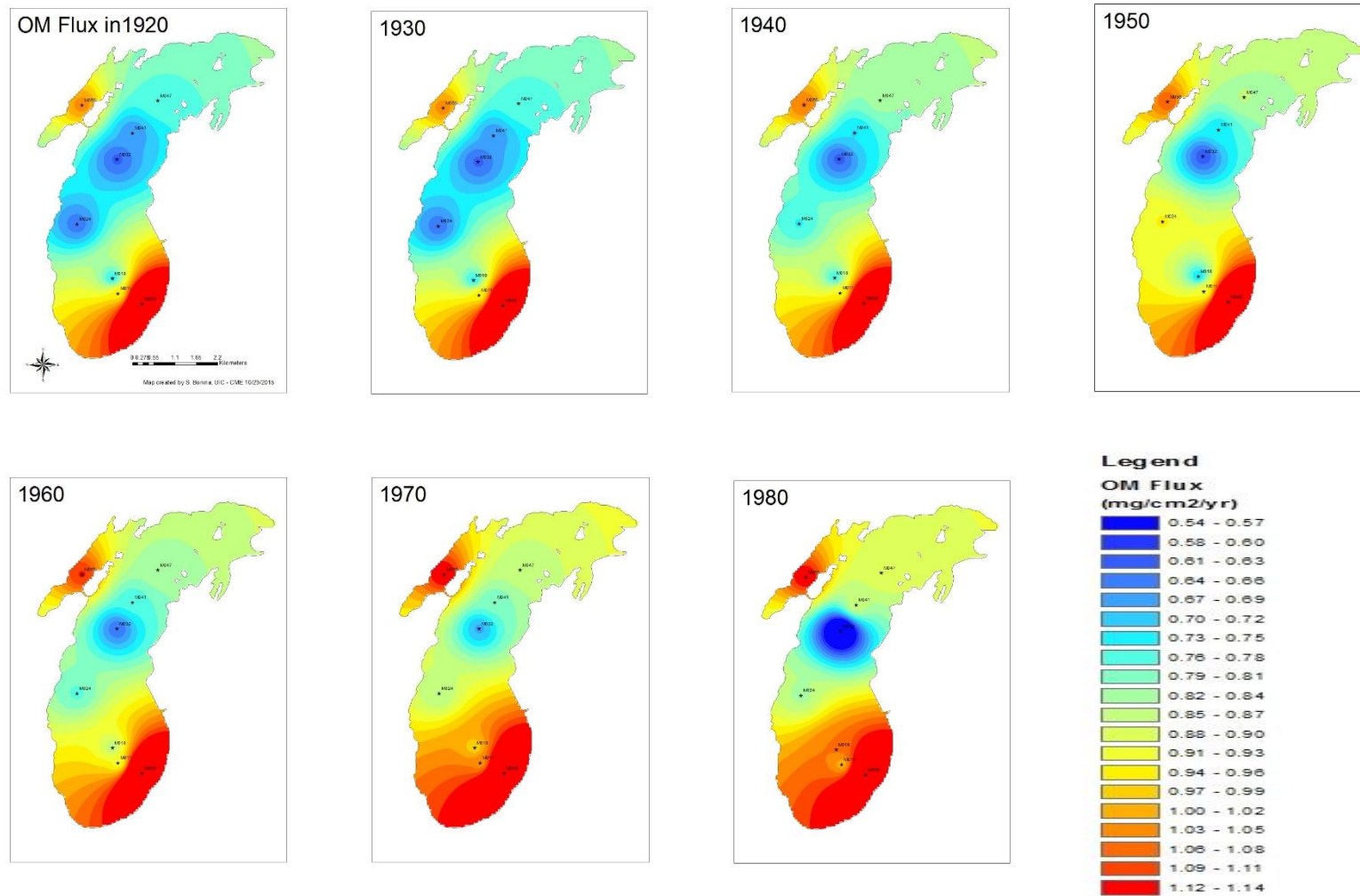


Figure S3. Net annual flux (by decade) of Organic Matter (OM) to Lake Michigan sediment for Period II from 1920 to 1980 during the time of rapid industrialization up to enactment of Great Lakes legislation.

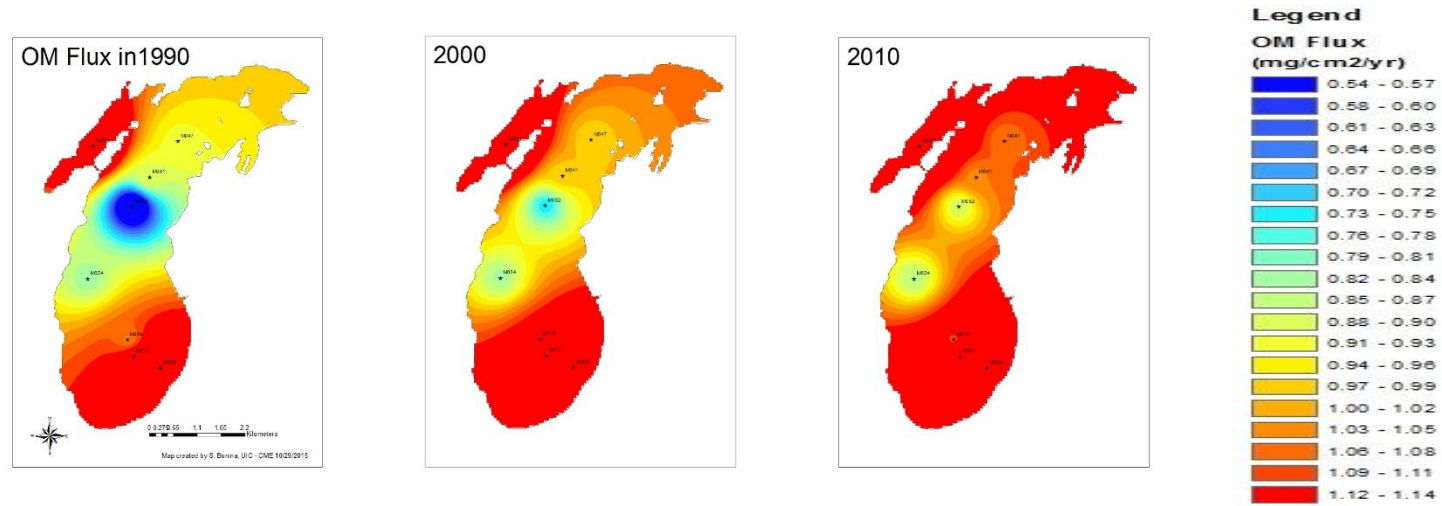


Figure S4. Net annual flux (by decade) of Organic Matter (OM) to Lake Michigan sediment for Period III from 1990 to 2010 during the post-Great Lakes legislation period.

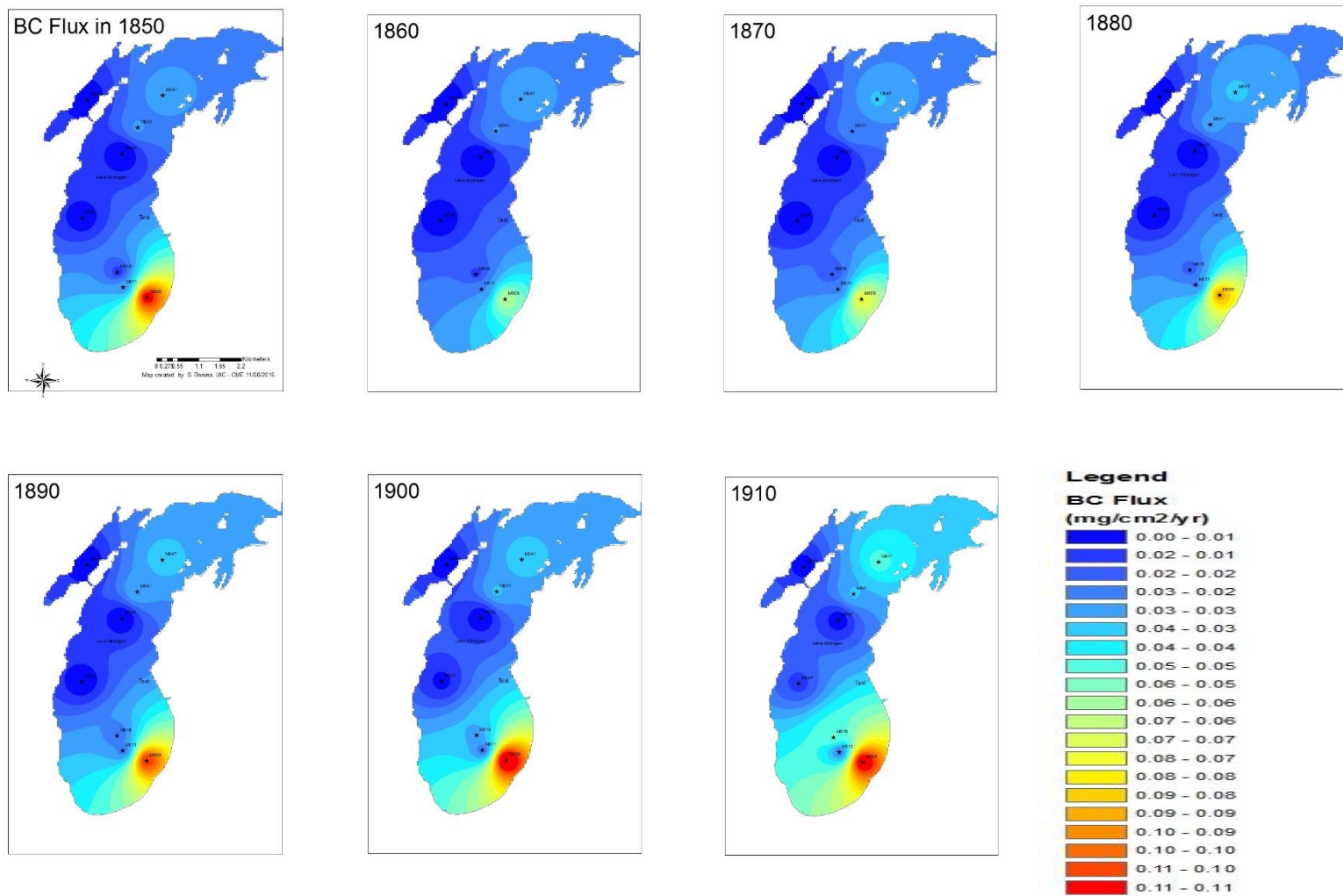


Figure S5. Net annual fluxes (by decade) of Black Carbon (BC) to Lake Michigan sediment for Period I from 1850 to 1910 during the period prior to rapid industrialization.

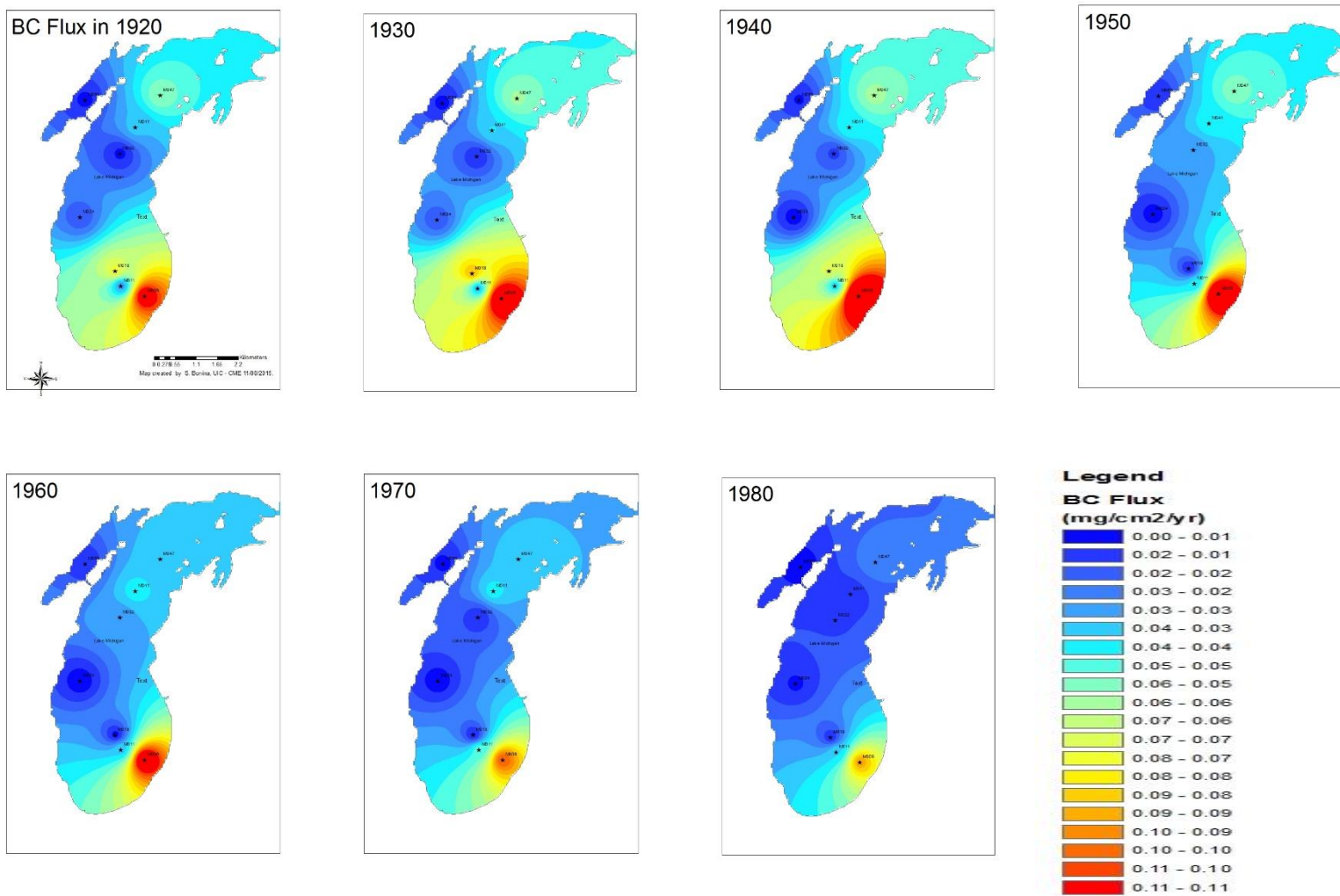


Figure S6. Net annual flux (by decade) of Black Carbon (BC) to Lake Michigan sediment for Period II from 1920 to 1980 during the time of rapid industrialization up to enactment of Great Lakes legislation.

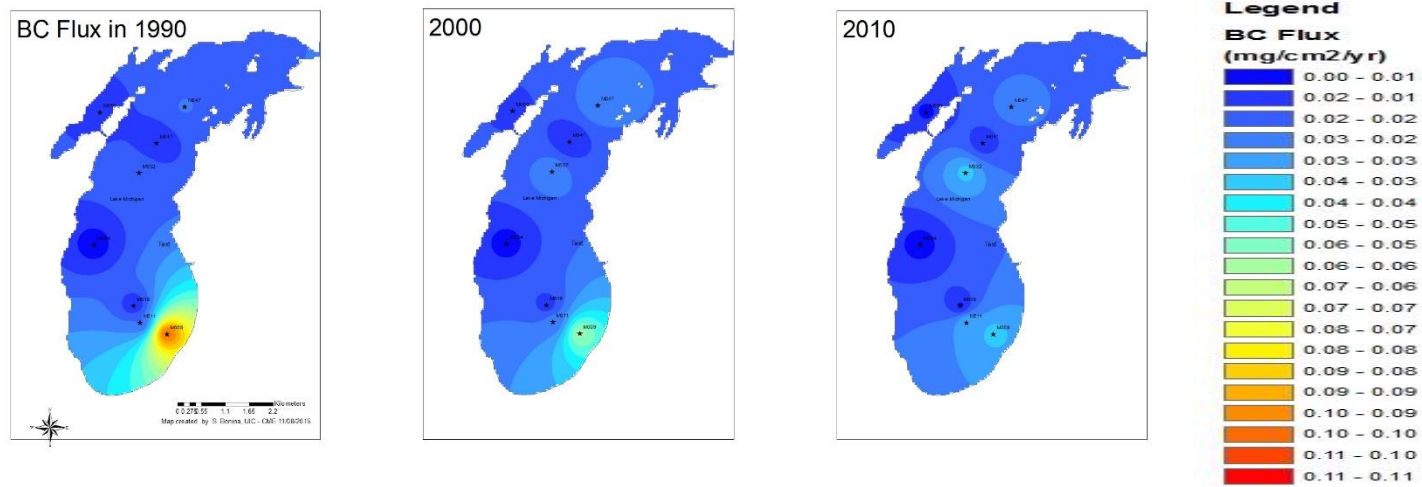


Figure S7. Net annual flux (by decade) of Black Carbon (BC) to Lake Michigan sediment for Period III from 1990 to 2010 during the post-Great Lakes legislation period.