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A reactive nitrogen budget for Lake Michigan

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ABSTRACT

The reactive (fixed) nitrogen (Nr) budget for Lake Michigan was estimated, making use of recent estimates of watershed and atmospheric nitrogen loads. Reactive N is considered to include nitrate, nitrite, ammonium, and organic N. The updated Nr load to Lake Michigan was approximately double the previous estimate from the Lake Michigan Mass Balance study for two reasons: 1) recent estimates of watershed loads were greater than previous estimates and 2) estimated atmospheric dry deposition and deposition of organic N were included in our budget. Atmospheric and watershed Nr loads were nearly equal. The estimated loss due to denitrification at the sediment surface was at least equal to, and possibly much greater than, the combined loss due to outflow and net sediment accumulation. Within the considerable uncertainty of the denitrification estimate, the budget was nearly balanced, which was consistent with the slow rate of accumulation of nitrate in Lake Michigan (~1%/yr). The updated loads were used to force the LM3-PP biogeochemical water quality model. Simulated water column concentrations of nitrate and organic nitrogen in the calibrated model were consistent with available observational data when denitrification was included at the sediment surface at a rate that is consistent with literature values. The model simulation confirmed that the estimated denitrification rate does not exceed the availability of settling organic N mass. Simulated increase (decrease) in nitrate concentration was sensitive to model parameters controlling supply of sediment organic N, highlighting the importance of internal processes, not only loads, in controlling accumulation of N.

Introduction

Reactive nitrogen (Nr) refers to forms of N that are readily available to support plant growth, primarily nitrate, nitrite, ammonium, and organic N, and excludes N_2. The availability of reactive N to ecosystems worldwide greatly increased over the 20th century through industrial production of N-rich fertilizers from atmospheric N_2, as well as through combustion of fossil fuels and biomass, which releases oxides of nitrogen (NO_X) to the atmosphere followed by deposition to terrestrial and aquatic ecosystems (Elser, 2011; Galloway et al., 2008). In the Laurentian Great Lakes, nitrate concentrations in Lake Superior increased fivefold between 1900 and 1980, while estimated Nr loads to Lake Michigan from its watershed increased threefold between 1900 and 2000 (Han and Allan, 2012).

Reactive nitrogen has received relatively little attention in the Laurentian Great Lakes because phosphorus (P) is considered to be the limiting nutrient for phytoplankton growth (Great Lakes Water Quality Board, 1978; Schelske, 1979; Schelske et al., 1974). However, Nr is also a required nutrient to support phytoplankton production, and individual taxa vary in their optimal N requirements for growth. Increased nitrate concentrations in oligotrophic lakes have been shown to alter phytoplankton community composition (Arnett et al., 2012), and to increase the severity of phosphorus limitation, not only for primary producers, but also for higher trophic levels (Elser et al., 2010). Any effects of altered N:P ratios in the Great Lakes that may have occurred were likely masked by concurrent ecosystem alteration due to increases in total nutrient loads and a series of invasive species introductions through the 20th century (e.g., Madenjian et al., 2002). Controversy continues regarding whether freshwater water quality management should focus entirely on P, or on N and P together; arguments for a dual control strategy include: 1) to reduce transport of N through drainage networks to aquatic ecosystems that may be N limited and 2) to avoid modification of algal community composition through altered N:P ratios (Lewis et al., 2011). Aside from eutrophication concerns, the seasonal drawdown of nitrate concentration can provide a time-integrated measure of primary production in lakes. Primary production and epilimnetic nitrate drawdown in Lake Michigan decreased in the early 2000s, coincident with the establishment of large populations of quagga mussels in Lake Michigan (Mida et al., 2010). In biogeochemical water quality models, accurate simulation of the concentrations of N species in the water column provides additional constraint on simulation of primary production. For these reasons, it is worthwhile to include N, and not to focus exclusively on P, in nutrient inventories and

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mass balance models that are used to diagnose ecosystem function and to inform management decisions.

In this paper, we develop a Nr budget for Lake Michigan, defining the system boundaries to include the water column and surface sediment. The cycling of reactive N in aquatic systems differs from that of P in two important ways: 1) exchange with the atmospheric reservoir of N_2 gas and 2) lack of adsorption to particles, which is important for P. Sources of Nr to water bodies include watershed runoff, atmospheric wet and dry deposition, and potential conversion of N_2 gas to ammonium by nitrogen-fixing organisms (N fixation). Losses of Nr from the system include outflow, burial to the deep sediment, and denitrification, a process through which heterotrophic organisms in an anoxic environment use nitrate as a terminal electron acceptor, reducing nitrate to N_2 gas through a series of intermediate steps.

Prior work devoted to quantifying components of the N budget of Lake Michigan has focused primarily on the watershed, with relatively little focus on in-lake processes. Watershed loads (Hall and Robertson, 1998) and atmospheric wet deposition of nitrate and total Kjeldahl N (Miller et al., 2000) were estimated from measurements for 1994–95 as part of the Lake Michigan Mass Balance (LMMB) study. More recently, nitrate was included in an update of nutrient loads to Lake Michigan for the period 1994–2008 (Dolan and Chapra, 2011, 2012). Robertson and Saad (2011) reported long-term annual mean Nr watershed load to Lake Michigan, using a SPARROW model to estimate contributions from unmonitored areas. Han et al. (2009) and Han and Allan (2012) developed Nr budgets on the watersheds of Lake Michigan, but did not develop a complete budget for Lake Michigan itself including loss processes.

The objective of this work is to estimate the values of the major components of the Nr budget for Lake Michigan (sources and sinks), and to test whether the net gain or loss associated with the estimated budget is consistent with the long-term trend in Lake Michigan water column nitrate concentration. This work is part of an effort to simulate the response of primary production in Lake Michigan to nutrient loading scenarios (Rowe et al., submitted for publication). Throughout this paper concentrations and masses of N species are given as mass of N, and nitrate concentrations are the sum of nitrite and nitrate. Loads are given in conventional units of metric tons (1000 kg) per year (MTA).

Methods

Site description

Lake Michigan is an oligotrophic lake with a surface area of 57,800 km^2, a watershed area of 118,000 km^2, a volume of 4947 km^3, a maximum depth of 281 m, and a hydraulic residence time of 99 years (Chapra et al., 2009; Coordinating Committee on Great Lakes Basic Hydraulic and Hydrologic Data, 1977). The annual mean over-lake precipitation for Lake Michigan is 804 mm, which exceeds the annual mean runoff from the watershed of 622 mm over the lake surface (data source: www.glerl.noaa.gov/data/arc/hydro/mnth-hydro.html, accessed 1-19-2011), highlighting the importance of direct interaction with the atmosphere for this system. The primary outflow occurs by two-way exchange with Lake Huron through the Straits of Mackinac, with a minor outflow through the Chicago diversion (Fig. 1). Land cover in the Lake Michigan basin was 46% agricultural, 36% forest, 11% wetland, and 4% urban for the 1970s through 1980s (Han and Allan, 2012). The three tributaries delivering the greatest proportion of the watershed nitrate load (35,000 MTA, 1994–2008 mean) to Lake Michigan were the agriculturally-dominated watersheds of the Grand River (26%), St. Joseph River (23%), and the Fox River (7%), while point sources discharging directly to the lake contributed 9% of the watershed nitrate load (data from, Dolan and Chapra, 2011). Robertson and Saad (2011) estimated that the proportion of the watershed Nr load to Lake Michigan from each land use type was 29% atmospheric deposition to the watershed, 22% point sources, 18% farm fertilizers, 18% manure, and 13% additional agricultural sources.

Atmospheric dry deposition of Nr from the CMAQ model

An atmospheric deposition data product for Nr from the Community Multiscale Air Quality (CMAQ) model was provided by USEPA Atmospheric Modeling and Analysis Division (Appel et al., 2011; Dennis et al., 2010). Monthly values of four variables were provided for the period 2002 to 2006 on a 12-km grid: dry deposition of oxidized N (DDOXN), dry deposition of reduced N (DDREDN), wet deposition of oxidized N (WDOXN), and wet deposition of reduced N (WDREDN).

The CMAQ output was for a deposition-only treatment of ammonia exchange with the surface. A bidirectional treatment of ammonia exchange, and contribution of lightning to NO_X were planned in future versions of CMAQ. CMAQ N deposition included both gaseous and particulate species, and differing deposition velocity models for land and water. CMAQ deposition to Lake Michigan was taken from cells having land cover type of >90% water to ensure that the values applied to Lake Michigan were representative of deposition to water, not to land. Oxidized N dry deposition consisted of total-nitrate (TNO_3 = nitric acid + coarse and fine particulate nitrate) plus deposition of NO_X ($NO_X = NO + NO_2$) and other oxides of N. Reduced N dry and wet deposition was comprised of ammonia gas and particulate ammonium.

NADP atmospheric nitrogen wet deposition

Data were downloaded from the National Atmospheric Deposition Program-National Trends Network (http://nadp.sws.uiuc.edu/, accessed 4-27-2011) for all stations in the states bordering Lake Michigan (Michigan, Wisconsin, Indiana, and Illinois) for 1994–2008. NADP reports monthly values of precipitation-volume-weighted mean nitrate and ammonium (based on weekly measurements), as well as monthly total precipitation depth measured at each site. NADP concentration and precipitation depth were converted to kg N ha^{-1} mo^{-1}. Over-lake wet deposition was estimated using Thiessen polygon interpolation using the stations that met the NADP data quality parameters for each month.

Watershed reactive nitrogen load

Dolan and Chapra (2011) produced estimates of annual watershed nitrate loads to Lake Michigan for the period 1994–2008. Loads were estimated based on water quality data from the US Geological Survey and the USEPA STORET database. Point source data were obtained from the USEPA PCS and ICIS databases. Loads for unmonitored tributaries were estimated using a Unit Area Load (UAL) method. The methods used have been documented elsewhere (Dolan and Chapra, 2012; Dolan and McGunagle, 2005; Dolan et al., 1981).

Robertson and Saad (2011) reported an estimate of 70,000 MTA for the long-term annual average watershed Nr load to Lake Michigan. Their estimate was described as representing a long-term mean because their method normalized out the hydrologic contribution to interannual variation in the load, and used explanatory land use variables representative of a base year of 2002. Use of their estimate as a representative mean over the period 1994–2008 assumes that N-related land use variables did not change significantly over that time period, which is consistent with Han and Allan (2012) who found that N imports to the Lake Michigan watershed changed little from 1980 to 2002. To minimize bias in their estimate, Robertson and Saad (2011) used observations of Nr concentration and discharge for all monitored tributaries in addition to observed direct-to-lake point sources, and only used their SPARROW model to estimate the contribution of unmonitored areas. In this way, their estimate makes use of all available observations, while representing the total (monitored and unmonitored) watershed load delivered to Lake Michigan. Han and

Fig. 1. Map of Lake Michigan and its watershed. Tributaries included in the nutrient loads of Dolan and Chapra (2011) are indicated with triangles. Tributaries are named along with the Straits of Mackinac and Chicago diversion. The USEPA GLNPO monitoring stations are indicated with circles, and NDBC buoy with a cross. The boundaries of our reactive N budget include the water column and surface sediment, and exclude the watershed.

Allan (2012) estimated a watershed Nr load to Lake Michigan of ~59,000 MTA (their Fig. 6, 1993 to 2002 mean) using a regression model for major tributaries; their estimate may be affected by model bias, and does not include contributions from unmonitored areas and direct-to-lake point sources. Han and Allan (2012) focused on trends over time, rather than on a total accounting of the watershed load delivered to Lake Michigan.

Lake Michigan Mass Balance (LMMB) study atmospheric and watershed loads

Atmospheric wet deposition (Miller et al., 2000) and watershed loads (Hall and Robertson, 1998) of nitrate and total Kjeldahl N ($TKN = NH_3 + NH_4^+ +$ organic N) were estimated as part of the 1994–1995 Lake Michigan Mass Balance study. These data were obtained from the USEPA internal databases that were used to generate input files for the LM3-Eutro model (Rossmann, 2006).

Lake Michigan water column concentration measurements

During LMMB, nitrate and TKN were measured in the Lake Michigan water column at nearshore (<40-m depth) and offshore stations during most months of the year for 1994 and 1995. For the period 1996–2008, nitrate concentrations were obtained from the USEPA GLNPO spring and summer surveys (data source: www.epa.gov/greatlakes/monitoring/data_proj/glenda, accessed 11-1-2012) at 11 offshore stations (Fig. 1). Ammonium and TKN were not included in the GLNPO monitoring program.

Atmospheric reactive nitrogen load estimate

Atmospheric deposition consists of dry and wet deposition. Here, wet deposition refers to particulate and dissolved constituents associated with precipitation, while dry deposition refers to gaseous and particulate deposition not associated with precipitation. Atmospheric deposition of Nr includes nitrate, ammonium, and organic N. The CMAQ model estimates both dry and wet deposition of primarily nitrate and ammonium, but does not include organic N. NADP reports measured wet deposition of nitrate and ammonium, but does not include dry deposition or organic N. LMMB reported measured wet deposition of nitrate and TKN, which includes organic N, but only for 1994–95.

To estimate total atmospheric N deposition to Lake Michigan for 1994–2008, we elected to use NADP for wet deposition because it is more directly based on measurements than CMAQ. NADP provided monthly wet nitrate and ammonium loads for 1994–2008. For dry deposition we elected to use CMAQ because it is necessary to use a model to estimate dry deposition to water bodies. The CASTNET network does report N dry deposition; however, deposition is estimated from measured atmospheric concentrations using a deposition velocity model for plant canopies and land surfaces with parameters specific to land cover at each CASTNET station (Schwede et al., 2011); therefore, the CASTNET data product is not directly applicable to water bodies. Deposition velocities of particles and gases to land surfaces differ significantly from neighboring water bodies because of differences in aerodynamic roughness, atmospheric stability, and chemical speciation at the surface (e.g., Zhang et al., 2002).

It was necessary to add an estimated contribution of organic N to both dry and wet deposition, based on literature values. A review by Cornell et al. (2003) reported dissolved organic N in precipitation of 38 +/− 19% (mean, s.d.) of Nr for North America, from measurements in 51 locations. An estimate of organic N wet deposition to Lake Michigan can be obtained by subtracting NADP ammonium deposition from LMMB TKN deposition, which gives 20 and 24% of Nr as organic N for 1994 and 1995, respectively, which is at the low end of the range reported by Cornell et al. We elected to use the mean value reported by Cornell et al. because it was based on a relatively large data set. A quantity of organic N was added to the N load, equal to 61% of the nitrate + ammonium wet load, to produce 38% of Nr as organic N.

To estimate dry deposition, CMAQ modeled dry deposition to Lake Michigan was averaged over the five available years of CMAQ model output. As mentioned previously, a significant portion of N in wet deposition is organic N. Since the origin of organic N in wet deposition is from organic particles and gases in the atmosphere, one may suspect that organic N is also a significant portion of dry deposition, even though we are not aware of any data to quantify the dry deposition of organic N. For lack of a better estimate, we made the same assumption for dry deposition of organic N as for wet deposition of organic N, and added a quantity to the CMAQ dry deposition so that dry deposition of organic N was 38% of the total Nr dry deposition.

Sediment burial rate for organic nitrogen

The annual lakewide loss of organic N by burial was estimated by obtaining a sediment net accumulation rate (cm/year) on a 5-km grid, then multiplying by the organic N concentration of Lake Michigan sediment. Robbins et al. (1999) reported the values of several variables measured from box core samples at 55 locations in the depositional and transitional regions of Lake Michigan during LMMB, including net accumulation rate of sediment solids, sediment solid concentration (dry mass per bulk volume), and thickness of the surface sediment mixed layer from radioisotope measurements. Several nutrient species, including organic N, were measured in Lake Michigan sediment and reported as fraction of sediment dry mass (mg/g) at 130 locations as part of the LMMB study (Johengen, 1996) (data source: www.epa.gov/greatlakes/monitoring/data_proj/glenda, accessed 11-1-2012). Sediment radioisotope data from Robbins et al. (1999) were used to calculate burial velocity (Zhang et al., 2008), which was interpolated to the 5-km grid, and set to zero outside the depositional areas identified by Cahill (1981). Sediment mass fraction organic N was multiplied by bulk density at each sample location (Eadie and Lozano, 1999; Robbins et al., 1999) to obtain concentration, which was interpolated to the 5-km grid. Sediment organic N measurements were from surface sediment: 0 to 1.5-cm depth for box cores or from Ponar samples.

Outflow estimate

Loss of N by outflow was estimated by multiplying the concentration in the water column by net flow rate at the outlets of Lake Michigan at the Straits of Mackinac and the Chicago diversion. Net outflow rates were estimated as 40.47 and 2.98 km^3/yr at Mackinac and Chicago, respectively for 1996–2005 (Chapra et al., 2009). Concentration of nitrogen species in the water column was estimated as the median of LMMB study measurements from 1994 to 1995 for the spring isothermal period (water temperature <4 °C) when the water column is expected to be vertically well mixed.

LM3-PP model

LM3-PP is a revised version of the LM3-Eutro model. The LM3-Eutro model is a high-resolution, mechanistic, numerical water quality model of Lake Michigan (Melendez et al., 2009; Pauer et al., 2008, 2011; Rossmann, 2006). LM3-Eutro and LM3-PP share a common model grid and set of state variables. Both models include 17 state variables: two phytoplankton classes, diatom and non-diatom phytoplankton, zooplankton, labile and refractory N, P, and C detritus particles; dissolved organic N, P, and C; phosphate, ammonium, nitrate + nitrite; and dissolved and particulate silica. Hydrodynamic transport in the model is driven by output from the Princeton Ocean Model for 1994–95 (Schwab and Beletsky, 1998). The 1994–95 hydrodynamics are assumed to be representative (Rossmann, 2006), and are repeated for simulation of subsequent years. The model grid has 5-km horizontal resolution and 19 sigma layers. The model time step is ~1.3 h. Estimated daily watershed loads are input at 38 tributary locations. Spatially-varying atmospheric loads are applied at a monthly temporal resolution.

In comparison to LM3-Eutro, LM3-PP included updated nutrient loads and updated biogeochemical process parameterizations to better simulate primary production (PP) of newly-fixed organic carbon in addition to chlorophyll and nutrient concentrations. In addition, LM3-PP included a sediment biogeochemical submodel that simulated settling, resuspension, and mineralization of organic matter as well as diffusive exchange of dissolved nutrients. Resuspension was driven by benthic shear stress. The resuspension rate constant was calibrated to result in sediment organic N concentrations that were comparable to measured values (Rowe et al., submitted for publication). Denitrification was estimated in LM3-PP using an assumption based on the sediment core studies by Gardner et al. (1987); it was assumed that 95% of N mineralized in the sediment was transformed to N_2 gas (a loss from the model). By applying the assumption in this way, the actual denitrification loss in LM3-PP was limited by the availability of settling organic N. Specifically, denitrification was limited by the rate of mineralization of organic N in the sediment: the product of sediment organic N concentration and a rate constant. Sediment organic N concentration, in turn, depended on the balance between settling, resuspension, burial, and mineralization rates. Development, calibration, and skill assessment of LM3-PP were described in detail in a separate manuscript (Rowe et al., submitted for publication).

For input into the LM3-PP model, organic N was evenly divided between the dissolved organic and refractory organic model state variables based on references cited by Berman and Bronk (2003), indicating that between 20 and 75% of the DON in atmospheric deposition at continental sites in North America is bioavailable in short term assays. The 1994–2008 mean Nr watershed load was set to 70,000 MTA (Robertson and Saad, 2011). To estimate a time-varying Nr load for input into the model, a ratio of Nr to nitrate of 70,000/38,000 = 1.8 was calculated where 38,000 was the 1994–2008 mean Dolan and Chapra lakewide annual nitrate load. Nr was estimated from daily nitrate by multiplying by the Nr/nitrate ratio of 1.8; this method ensured that the long-term mean Nr watershed load was fixed to the Robertson and Saad (2011) value. The Dolan and Chapra annual nitrate loads were disaggregated to daily loads by multiplying the daily fraction of annual discharge from USGS gages at each tributary (http://waterdata.usgs.gov/nwis/rt, accessed 3-31-2011). Speciation to LM3-PP state variables was estimated first by using the Dolan and Chapra nitrate load, then partitioning the remaining portion of Nr among organic N and ammonium according to tributary-specific ratios derived from LMMB measurements.

Results and discussion

Historical water column nitrate concentrations

The spring isothermal period (vertically-mixed water column) nitrate concentration in Lake Michigan increased at a rate of 1%/year (Fig. 2) over the period 1983–2008 (slope = 0.003 mg/L/yr, $p < 0.001$). Ammonium and TKN were measured in 1994–95 during LMMB, but only nitrate was measured as part of the USEPA long term monitoring program. The LMMB data indicate that nitrate accounts for 67% of Nr in the water column. If we assume that the trend in nitrate represents the trend in Nr, then we expect the N budget to nearly balance in order to result in water column N concentrations that vary little over a period of 25 years.

Atmospheric load estimate

The spatial distribution of atmospheric Nr deposition to Lake Michigan is shown in Fig. 3. There is a north–south gradient apparent

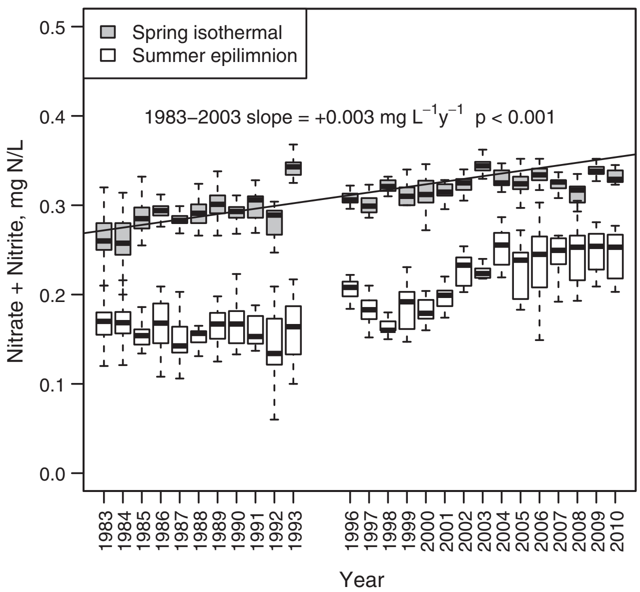

Fig. 2. Nitrate concentration measured by the USEPA GLNPO monitoring program at offshore stations in Lake Michigan during the spring isothermal period (all sample depths) and summer stratified period (sample depth <11 m). Results of linear regression on the spring data are shown. Boxplots indicate the median and interquartile range with whiskers to furthest data point within 1.5 times interquartile range. Outliers were not plotted, but all data were used in the linear regression.

in wet and dry deposition of both ammonium and nitrate. In the case of wet deposition, a north–south gradient in annual mean precipitation is partly responsible, although the difference in precipitation depth between northern and southern Lake Michigan is <20% (Daly et al., 2008), while the gradient in atmospheric N deposition is >20% (Fig. 3). The annual precipitation depth on the east side of Lake Michigan is ~10% greater than on the west side (Daly et al., 2008); a slight east–west gradient is visible in Fig. 3 for wet deposition of nitrate, but not for ammonium. North–south gradients in emissions of NO_X (Hudman, 2007) and ammonia (Goebes et al., 2003) to the atmosphere also contribute to the gradient in deposition. The short atmospheric lifetime of ammonia results in a spatial pattern of dry deposition simulated by CMAQ that is closely associated with source regions of ammonia from fertilizer applications in intensive agriculture regions located to the southwest of Lake Michigan in Illinois and Indiana and near the south end of Green Bay in Wisconsin (Goebes et al., 2003). An interesting nearshore–offshore gradient in dry deposition of oxidized N is predicted by CMAQ, and may result from greater wind speed offshore or by gradients in lake surface temperature and their effects on atmospheric stability and deposition velocity.

The seasonal distribution of atmospheric Nr deposition is shown in Fig. 4. Ammonia emissions from fertilizer applications peak in April–June with a lesser peak in fall (Goebes et al., 2003). Peaks of NH_3 deposition in spring and fall are apparent in Fig. 4, but the seasonal distribution is further complicated by seasonal variation in atmospheric stability and precipitation. Precipitation is least in Jan., Feb., and March (data source: www.glerl.noaa.gov/data/arc/hydro, accessed 1-19-2011), which is consistent with lower wet deposition during those months. Dry deposition of nitrate from CMAQ is consistent with the monthly distribution of atmospheric stability, as quantified by the bulk Richardson number calculated from air–water temperature difference and wind speed from the National Data Buoy Center southern Lake Michigan buoy (Rowe, unpublished data).

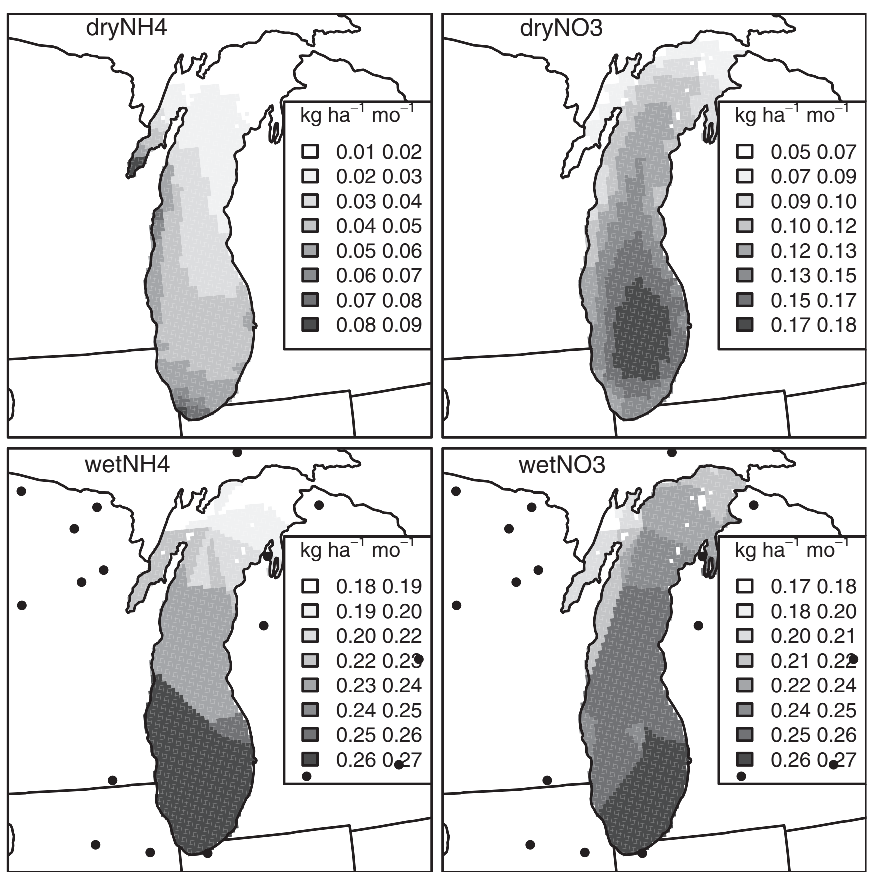

Fig. 3. Spatial distribution of atmospheric dry deposition of reduced nitrogen (dryNH4) and oxidized nitrogen (dryNO3) to Lake Michigan simulated by the CMAQ model (2002–2006 mean). Atmospheric wet deposition of ammonium (wetNH4) and nitrate + nitrite (wetNO3) interpolated over Lake Michigan from surrounding stations of the NADP network (black circles), averaged over 1994–2008.

Watershed reactive nitrogen load estimate

Watershed nitrate and total Nr load estimates are compared in Fig. 5. The recent estimates of 38,000 MTA nitrate (1994–2008 mean) by Dolan and Chapra and of 70,000 MTA Nr by Robertson and Saad (2011) were greater than the LMMB 1994–95 mean load estimates by 41 and 28%, respectively. The Dolan and Chapra nitrate loads show considerable year-to-year variation (26% relative standard deviation), but no significant temporal trend is present over the 15-year period ($R^2 = 0.06$, $p = 0.38$). The LMMB Nr loads for 1994 and 1995 are less than the Robertson and Saad (2011) long-term mean Nr load, which is consistent with expectations given that LMMB nitrate loads for 1994 and 1995 were below the long-term mean nitrate load (Fig. 5), providing evidence that 1994–95 were below average years for Nr watershed load.

Sediment burial of organic nitrogen

The spatial distribution of organic N net sediment accumulation is shown in Fig. 6. Net sediment accumulation is confined to deep, depositional basins. The net sediment accumulation rate of organic N was estimated as 36,870 MTA.

Outflow estimate

The median water column concentrations for the spring isothermal period of LMMB (1994–95) were 0.15 mg/L TKN (unfiltered water), 0.30 mg/L nitrate + nitrite, and 0.02 mg/L ammonium (included in TKN); thus 67% of Nr in the spring water column is nitrate, 29% is organic N, and 4% is ammonium (Table 1). The outflow loss of Nr from Lake Michigan was estimated as 19,553 MTA.

Nitrogen fixation

Some taxa of cyanobacteria and bacteria are capable of fixing atmospheric N_2 to ammonium. However, N fixation is expected to be negligible in lakes when the water column N:P concentration mass ratio is >30 (Patoine et al., 2006; Schlesinger, 1997). There is a high energy cost to N fixation, so N fixation is not competitive when ammonium or nitrate is

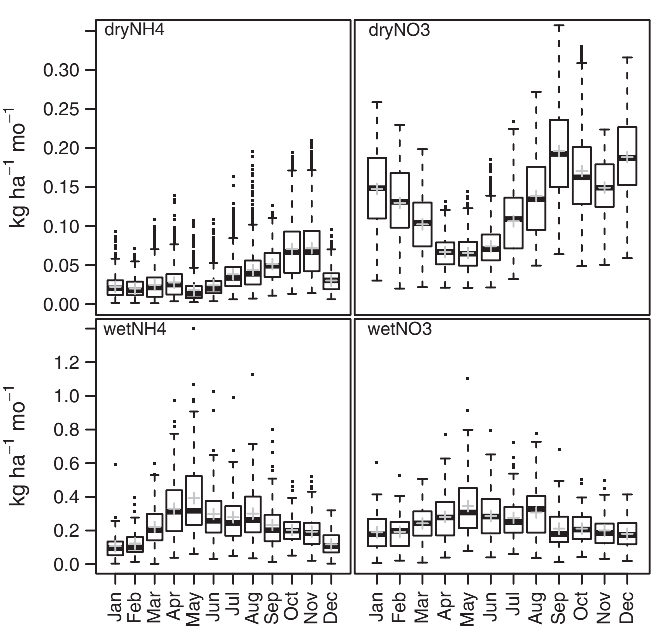

Fig. 4. Seasonal distribution of atmospheric deposition of nitrogen species to Lake Michigan for 2002 to 2006 (data from Fig. 3). Boxplots are defined in Fig. 2, with mean indicated by plus symbol.

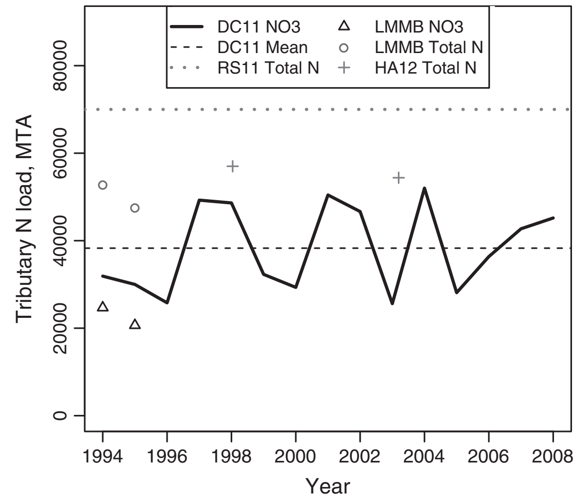

Fig. 5. Tributary loads of nitrate + nitrite and total reactive nitrogen to Lake Michigan from four sources: DC11, Dolan and Chapra (2011); RS11, Robertson and Saad (2011); LMMB, Lake Michigan Mass Balance study (Rossmann, 2006); and HA12, Han and Allan (2012).

available. The mass ratio of nitrate to dissolved P in Lake Michigan is >30, and has increased since the 1990s to be >100 (Fig. 7), so N fixation is not expected to be significant. Even so, there is some evidence for N fixation in Lake Michigan. MacGregor et al. (2001) reported molecular biology and isotope ratio evidence that N fixation may occur in the cyanobacterial community of the metalimnion in Lake Michigan, but did not estimate a rate. Insufficient information exists to estimate a contribution of N fixation to the N budget of Lake Michigan; however the possibility cannot be excluded that N fixation may occur under certain conditions.

Denitrification estimate from sediment core incubation measurements

Denitrification has been observed in nearly all river, lake, and coastal marine ecosystems that have been studied (Seitzinger, 1988). Lake Michigan is oligotrophic, resulting in low community oxygen demand, and has dissolved oxygen concentrations in the water column that remain near equilibrium with the atmosphere even in the hypolimnion (data source: www.epa.gov/greatlakes/monitoring/data_proj/glenda, accessed 11-1-2012). Hypoxia does occur on a limited spatial and

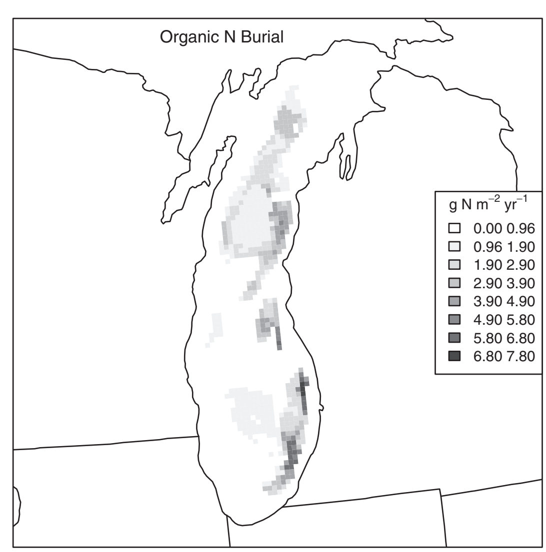

Fig. 6. Net accumulation rate of sediment organic nitrogen in Lake Michigan, estimated from interpolated sediment organic N concentration and sediment net accumulation rate.

Table 1
Median water column concentration (mg/L) and inventory (1000s of metric tons) of nitrogen species from Lake Michigan Mass Balance study measurements for the isothermal periods (T < 4 °C) of 1994–95 (n = 300). Organic N was estimated as unfiltered TKN concentration minus ammonium concentrations.
Organic N in surficial sediment (1 cm) is included in the inventory.

	Concentration	Inventory
Nitrate + nitrite	0.30	1484
Organic N	0.13	643
Ammonium	0.02	99
Sediment organic N	–	178

temporal extent in Green Bay, which is not explicitly accounted for in our whole-lake, annual mean budget analysis. Hypoxia in the water column is not required for denitrification to occur; coupled nitrification–denitrification is effective at the sediment–water interface where diagenesis of organic matter in the subsurface sediment provides ammonium, which is nitrified at the oxic sediment surface, then promptly denitrified by bacteria occupying nearby anoxic microenvironments. In the studies of rivers and lakes reviewed by Seitzinger (1988), N_2 gas accounted for 76–100% of the sediment–water N flux. Gardner et al. (1987) measured denitrification rates in Lake Michigan sediment cores in the range 15–50 μmol N m^{-2} h^{-1} (Fig. 8), which is within the range of values reported for lakes across a range of trophic states (Piña-Ochoa and Álvarez-Cobelas, 2006). Gardner et al. (1987) found that N_2 gas accounted for 93–98% of the sediment–water flux of inorganic N, which is consistent with the review by Seitzinger (1988).

We used the fluxes reported by Gardner et al. (1987) to estimate the lakewide loss of Nr to denitrification. The spatial distribution of denitrification in Lake Michigan is unknown. We assume that denitrification occurs mainly in sediments that are richer in organic matter, and so apply the denitrification rate only to the depositional and transitional areas of Cahill (1981), which are 32 and 21% of the total lake area, respectively. This assumption results in a lakewide denitrification estimate of 55,858–186,194 MTA, using the low and high rates of Gardner et al. (1987), respectively. The actual long-term average rate of denitrification must be limited by the rate at which settling organic N is supplied to the sediment. To obtain an estimate of denitrification that is subject to this constraint, we applied the LM3-PP model.

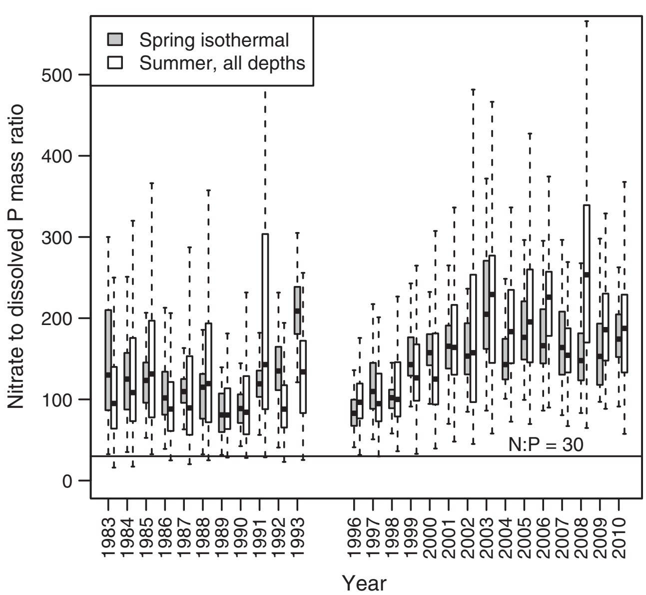

Fig. 7. The mass ratio of nitrate + nitrite to dissolved phosphorus in the Lake Michigan water column from US EPA GLNPO monitoring measurements at offshore stations for spring and summer surveys. All sample depths included. A line indicates N:P ratio of 30, above which N fixation is not expected to occur (see text). Boxplots are defined in Fig. 2.

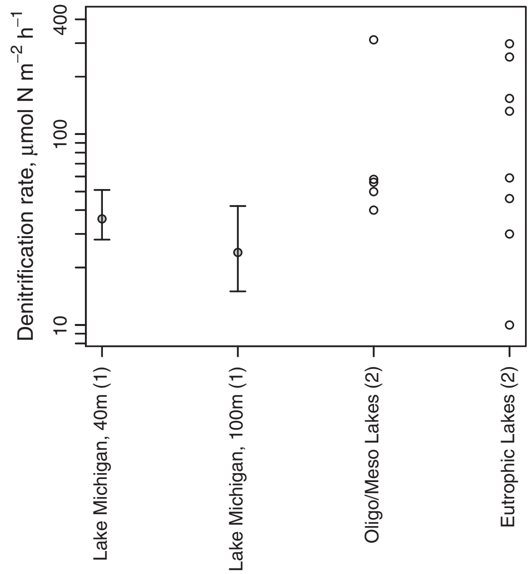

Fig. 8. Denitrification rates (molar) measured in Lake Michigan and in other lakes at the sediment surface: 1) Gardner et al. (1987) and 2) Piña-Ochoa and Álvarez-Cobelas (2006). Error bars indicate the mean and range of measured values.

Components of the reactive N budget for Lake Michigan

The Nr load to Lake Michigan is nearly equally divided between watershed and atmospheric loads (Fig. 9). Among the loss processes, denitrification is almost certainly greater than burial and outflow although the lakewide denitrification rate cannot be quantified with certainty given the few measurements available. Han and Allan (2012) reported estimates of atmospheric deposition of Nr to Lake Michigan, and also found that atmospheric deposition was nearly equal to the tributary load, although their estimate of ~50,000 MTA (their Fig. 6) was less than our estimate of 71,000 MTA (1994–2008 mean). Han and Allan (2012) focused on the N budget of the watershed, and did not report in detail their methods for estimating direct-to-lake N deposition; therefore it is not clear whether they considered the differing deposition velocity for dry deposition between land (plant canopies) and water, and whether they included a contribution of organic N.

Even though our estimate of the Nr load is twice the value estimated in the LMMB, the N budget can balance within the range of denitrification rate estimates (Fig. 9). We estimated the average annual Nr watershed plus atmospheric load to be 141,356 MTA, compared to a value of 69,663 that was derived from the LMMB study (Rossmann, 2006). There are several contributions to the greater load estimate in the present

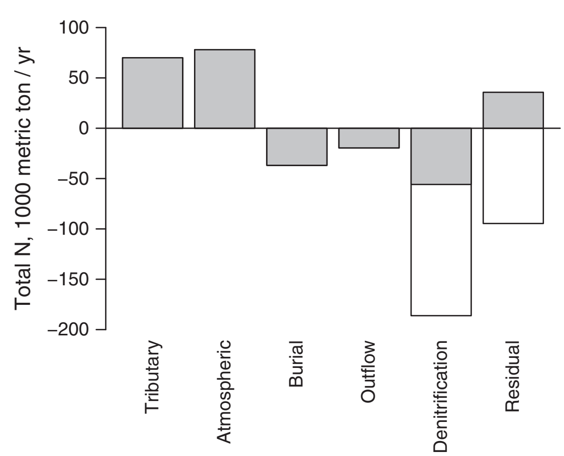

Fig. 9. Components of the nitrogen budget of Lake Michigan. Open and filled bars represent the high and low estimates of the denitrification rate.

study: 1) watershed nitrate and Nr loads were higher in recent studies, compared to the LMMB (Fig. 5); 2) the LMMB loads used an estimate of atmospheric wet deposition of nitrate and TKN based on Miller et al. (2000), but did not attempt to estimate the contribution of dry deposition; and 3) atmospheric dry deposition of organic N was not included in the LMMB loads although our estimate was only speculative.

Lakewide inventory and residence time for reactive N

The lakewide inventory of N was estimated using a lake volume of 4947 km^3 (Chapra et al., 2009) and the concentrations shown in Table 1. In addition, the inventory of organic N in the surface 1 cm of sediment was estimated using the interpolated values of sediment organic N concentration. Nitrate and organic N in the water column make up the majority of the N inventory (Table 1). If it is assumed that the slow rate of change in the nitrate concentration (1%/yr, Fig. 2) is representative of the Nr inventory, then an imbalance in the budget of only 24,000 MTA is required to produce the observed rate of change. This imbalance is a small fraction of the estimated denitrification rate, or of the loading rate, which highlights the importance of internal processes in addition to loads in determining water column N concentrations. In their N budget for Lake Superior, McDonald et al. (2010) similarly concluded that internal process rates may be as influential as loads to the N budget although they did not attempt to estimate the denitrification rate directly. The residence time of Nr in Lake Michigan water and surface sediment (inventory/total loss rate) is 10 to 20 years for the high and low denitrification rate estimates, respectively. The residence time indicates that Nr inventory in Lake Michigan may change on a decadal time scale, which is much shorter than the hydraulic residence time of ~100 years.

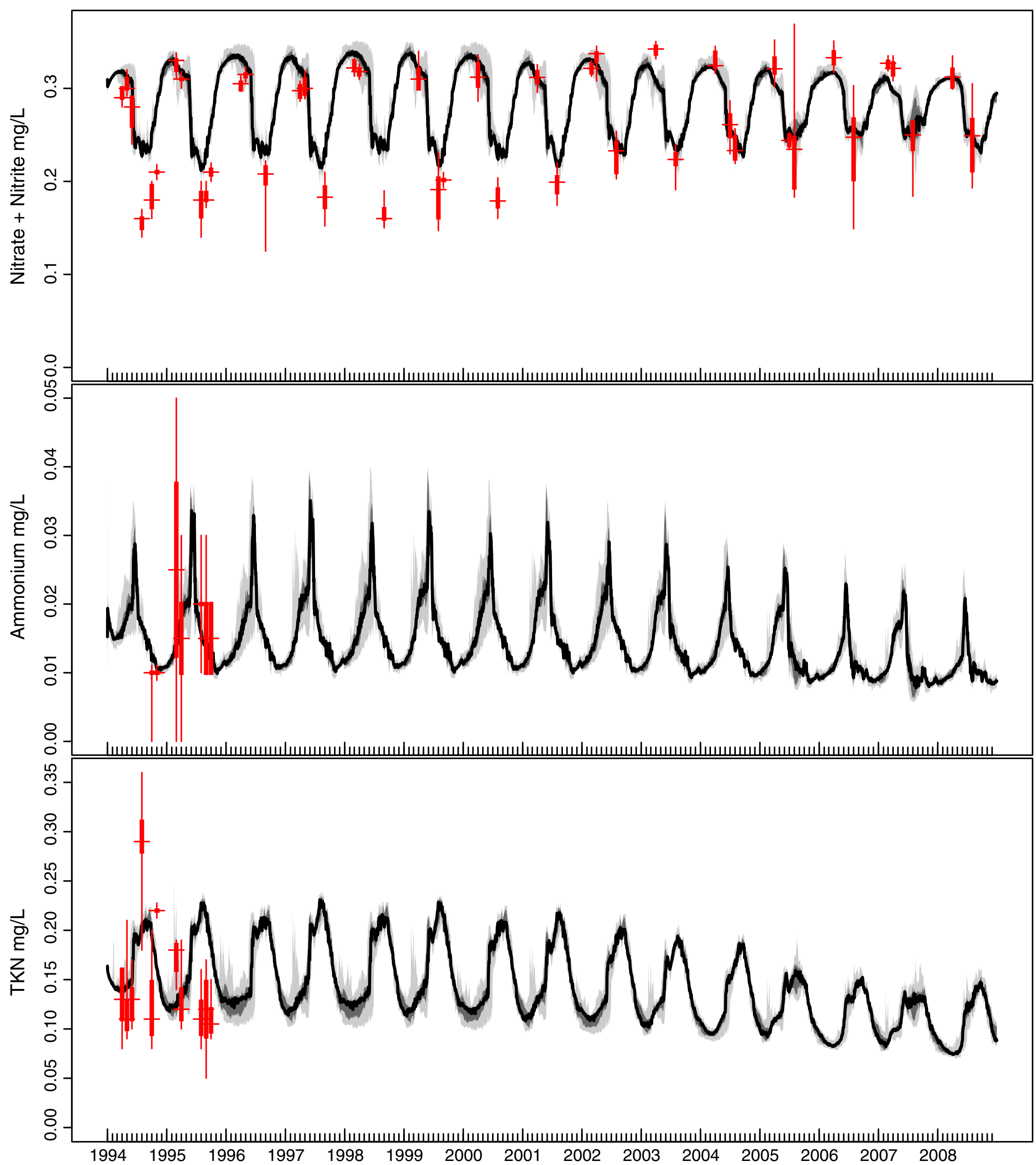

Fig. 10. Comparison of LM3-PP model output to observations at the 11 USEPA GLNPO offshore monitoring stations. Observed and simulated concentration data for nitrogen species are from the surface to 10-m sample depth. The black line, dark shading, and light shading represent the median, interquartile, and minimum–maximum simulated values of all stations. The crosses, wide, and narrow vertical bars represent the median, interquartile range, and minimum–maximum observed values.

Simulating the reactive nitrogen budget with the LM3-PP model

The mass balance framework and phytoplankton growth model within LM3-PP can assess whether the supply of organic N to the sediment is sufficient to sustain the estimated denitrification rate. The simulated settling flux of organic N was verified to be within the range of values measured in sediment trap experiments during LMMB (Rowe et al., submitted for publication). Simulated nitrate concentration in the calibrated model was comparable to observations in the water column for the 1994–2008 period. There was little long-term trend in simulated and observed nitrate concentration (Fig. 10), which was a result of a nearly-balanced N budget. The observed and simulated seasonal drawdown of nitrate in the epilimnion was reduced after ~2004 (Fig. 10), which has been attributed to the reduction of the spring diatom bloom by invasive, filter-feeding quagga mussels (Mida et al., 2010). Quagga mussel filter feeding impacts were included in the model simulation. The average annual simulated denitrification loss was 99,000 MTA, which is within the range that was estimated based on the denitrification rates measured by Gardner et al. (1987). This result indicates that the supply of organic N to the sediment can be sufficient to sustain the denitrification rates estimated based on the measurements of Gardner et al.

General discussion

The large influence of denitrification on the N budget highlights the importance of internal processes (not only external loads) in determining the accumulation of N in Lake Michigan and similar aquatic systems. The simulated rate of denitrification in the LM3-PP model was sensitive to minor adjustments in parameters that influenced the accumulation of sediment organic N. For example, minor adjustments to parameters specifying the fractions of phytoplankton that are converted to labile particles, refractory particles, or dissolved state variables upon mortality resulted in increasing or decreasing trends in nitrate over the 15-year simulation. This behavior is consistent with the budget analysis summarized in Fig. 9, indicating that the budget residual may be positive or negative within the range of estimated denitrification rates.

The rate of increase in nitrate concentration appears to have slowed in the period 2004–2010 (Fig. 2), which is coincident with other changes observed after large populations of quagga mussels became established in Lake Michigan (Mida et al., 2010). The rapid expansion of the quagga mussel population in Lake Michigan over the period 2000–2010 has changed the benthic landscape (Nalepa et al., 2010), and resulted in reduced phytoplankton biomass in the water column (Fahnenstiel et al., 2010). By transferring increasing amounts of organic N from the water column to the sediment in the form of feces and pseudofeces, it is reasonable to hypothesize that quagga mussels may act to increase the rate of denitrification in Lake Michigan and to alter the trend of gradually increasing nitrate concentration. By a similar mechanism, restoration of oyster beds has been suggested as a means to reverse eutrophication in Chesapeake Bay through enhanced denitrification (Cerco and Noel, 2007). Additional years of observations will be required to determine if the trend in nitrate accumulation has indeed been altered in Lake Michigan.

Acknowledgments

We wish to posthumously recognize our co-author, Dr. David M. Dolan, for his contributions to this publication and to nutrient loading studies in the Laurentian Great Lakes. His efforts on the mathematical and statistical treatment of Great Lakes phosphorus loads are widely recognized, as he was the established international expert on the topic. Less known are his recent contributions to our knowledge of nitrogen loading, 1994–2008, which is pursuant to this publication. His research has left an indelible imprint on Great Lakes ecosystem management and will influence its direction for years to come. We wish to thank Robin Dennis and Ellen Cooter, USEPA, for CMAQ N deposition data. The information in this document has been funded wholly by the U.S. Environmental Protection Agency. It has been subjected to review by the National Health and Environmental Effects Research Laboratory and approved for publication. Approval does not signify that the contents reflect the views of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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