Journal of Great Lakes Research 40 (2014) 192–201

Contents lists available at ScienceDirect

Journal of Great Lakes Research

journal homepage: www.elsevier.com/locate/jglr

A reactive nitrogen budget for Lake Michigan

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ARTICLE INFO

Article history:
Received 10 April 2013
Accepted 26 October 2013
Available online 19 December 2013

Communicated by: Carlo DeMarchi

Keywords:
Lake Michigan
Nutrient load
Nitrogen cycling
Nitrate
Mass-balance modeling
Denitrification

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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http://dx.doi.org/10.1016/j.jglr.2013.11.005

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 overlake 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}. Overlake 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