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An Ecological Network Analysis of nitrogen cycling in the Laurentian Great Lakes

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ABSTRACT

As water moves through the Laurentian Great Lakes system, it experiences a steep gradient in physical and chemical conditions between oligotrophic Lake Superior and eutrophic Lake Erie, likely affecting stocks and flows of nitrogen (N) across these lakes. We used published rates, supplemented by measurements conducted during a series of research cruises from 2010 to 2012, to construct three coupled 4-compartment N models for Lakes Superior, Huron, and Erie. Linear Inverse Modeling was used to identify plausible solutions to this model, and subsequent analysis focused on the most parsimonious model solution. For the most parsimonious model solution, we used Ecological Network Analysis (ENA) to analyze N flow and cycling in this steady-state model, and to examine the ultimate source of the N removed via denitrification within each lake. We also calculated denitrification efficiencies for each lake (the fraction of N removed through denitrification relative to all N exported) for 10,000 possible solutions to the underdetermined model. The average path length of N atoms in Lake Superior was 47.4, compared to 25.7 in Lake Huron and 15.2 in Lake Erie. Lake Superior's long (191 years) hydrologic residence time and relatively high N cycling rates allow for N atoms to have multiple opportunities to enter the sediment N pool and ultimately be removed through denitrification. Despite having a low areal denitrification rate, Lake Superior had a higher denitrification efficiency (86 ± 1%; mean ± 95% CI) compared to Lake Huron (64 ± 12%), and Lake Erie (48 ± 7%). This long residence time also makes Lake Superior highly sensitive to changes in loading rates and internal processes, probably contributing to the steady nitrate rise over the past century.

1. Introduction

The Laurentian Great Lakes are an ecologically- and economically-important resource, supporting tourism, fisheries, commercial shipping, recreation, and the provisioning of freshwater, which have been valued in the tens of billions of dollars (Krantzberg and de Boer, 2006). Excess nutrients are one important stressor that affects these lake ecosystems (Allan et al., 2012). Nutrient loading in the Great Lakes is the focus of numerous federal, state, and provincial regulations (Great Lakes Commission, 2012), and most attention has focused on phosphorus (P), which directly limits algal growth. As a non-limiting nutrient, nitrogen (N) has received less attention in the Great Lakes. However, N-levels are increasing in Lakes Superior, Huron, Michigan, and Ontario (Dove, 2009; EPA GLNPO; Sterner et al., 2007), and excess N contributes to downstream eutrophication (Howarth and Marino, 2006) and perhaps in Lake Erie as well (Rattan et al., 2012).

Nitrogen concentrations in lakes depend on input rates (e.g. runoff, deposition, fixation), removal rates (e.g. lake outflow, burial in sediments, and microbial removal via denitrification and anaerobic ammonium oxidation), and internal dynamics (e.g. uptake by phytoplankton, mineralization by heterotrophs). Nitrogen removal efficiencies in large lakes depend on lake trophic status; oligotrophic lakes are inefficient at removing N and are susceptible to increasing N concentrations resulting from decreased P loading (Finlay et al., 2013). As a result of these multiple controls, the concentration of various forms of N in the water column does not necessarily reflect the loading rates of those forms of N from tributaries and atmospheric deposition. For example, Lake Erie, which receives the highest levels of N loading among the Laurentian Great Lakes, has the lowest average spring nitrate (NO_3^-) + nitrite (NO_2^-) concentrations (<0.20 mg L^{-1}; EPA GLNPO). In contrast, Lake Superior, with the lowest N loading rates, has among the highest (~0.35 mg L^{-1}).

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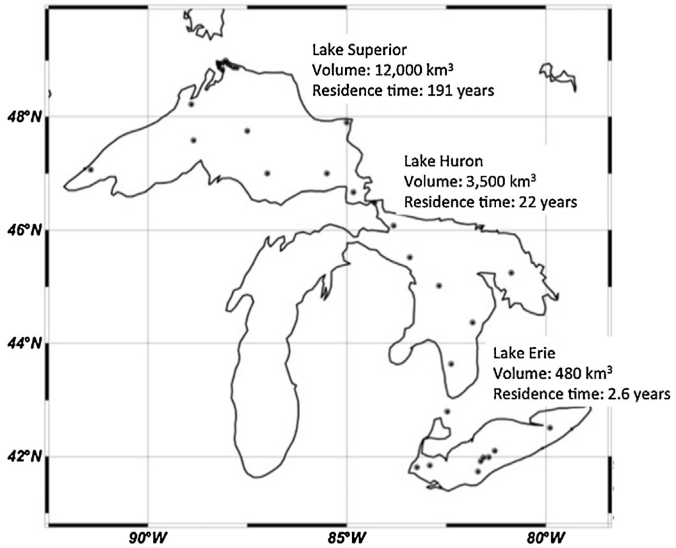

Fig. 1. Volumes and hydrologic residence times for Lakes Superior, Huron, and Erie. Circles depict locations of water column and sediment chemistry measurements during summer 2011.

Recent research has shed light on the importance of internal nutrient dynamics and denitrification in controlling N concentrations in the Great Lakes. In Lake Superior, the 5-fold rise in NO_3^- concentrations over the past century has been attributed to a combination of increased loading and altered internal dynamics (McDonald et al., 2010). Rates of internal cycling of N in Lake Superior are 50-fold greater than both external loading rates and the rate of long-term NO_3^- increase (Small et al., 2013a). Denitrification rates vary widely across the Great Lakes depending on sediment redox conditions; sediment in Lake Superior acts as a net source of NO_3^- to the water column, whereas Lake Erie sediment is a strong sink for water column NO_3^- (Small et al., 2013b). These results highlight the importance of understanding internal biogeochemical processing in conjunction with nutrient loading rates and physical properties of the lakes (e.g. residence time) to achieve a more complete picture of N dynamics in the Great Lakes.

Ecological Network Analysis (ENA) has been used to examine N cycling and its role in eutrophication in static biogeochemical models of several different coastal aquatic ecosystems (reviewed in Christian et al., 2011). For example, analyses of a model of N in the Neuse River Estuary have characterized the dominance of indirect effects due to cycling (Gattie et al., 2006) and described the role of sediment in alternately sequestering and releasing N (Whipple et al., 2014). ENA has been applied to a model of N cycling in the Cape Fear River estuary to estimate the coupling of nitrification and denitrification (Hines et al., 2012) and to compare analyses at different hierarchical levels (Hines and Borrett, 2014). Other studies have examined seasonal difference in N cycling indices in the Chesapeake Bay (Baird et al., 1995) and compared N cycling to cycling of carbon and phosphorus in the German Wadden Sea (Baird et al., 2008).

Here, we use published and unpublished data to produce three coupled four-compartment N models for Lakes Superior, Huron, and Erie. These lakes represent a range of environmental conditions, with notable differences in hydrologic residence times: 191 years in Lake Superior, 22 years in Lake Huron, and 2.6 years in Lake Erie (Fig. 1). Lake Superior is deep and perennially cold, with a small, mostly forested watershed with little agriculture or urbanization. Lake Erie is shallow and seasonally warm, with a relatively large watershed with extensive local influences of agriculture and urbanization. Lake Huron represents an intermediate level of N and P loading (Allan et al., 2012) and is mostly oligotrophic, with mesotrophic bays. We used Linear Inverse Modeling to construct plausible values, and to identify a parsimonious (best fit) solution, which was the focus of subsequent analysis. For this parsimonious model solution, we applied ENA tools (Fath and Patten, 1999) to follow the fate of N in this network, specifically with the aim of quantifying the ultimate sources of N removed through denitrification in each lake, and calculating denitrification efficiencies (the fraction of N removed from denitrification relative to total N export) for each lake.

2. Great Lakes nitrogen model

2.1. Model description

We constructed a simplified N budget for Lakes Superior, Huron, and Erie, representing three forms of bioavailable N in the water column (NO_3^-, NH_4^+, and organic N) and N in sediments. The organic N compartments include dissolved organic N, nonliving particulate N suspended in the water, and N in biotic compartments (e.g., phytoplankton and bacteria). The sediment N compartments included organic sedimentary N, as well as porewater dissolved N. Boundary flows include inputs of NO_3^-, NH_4^+, and organic N, and removal of N from the sediment compartment (via microbial denitrification or anaerobic ammonium oxidation). Downstream flows between lakes are represented for the three water column N compartments, including the outflow from Lake Erie (into Lake Ontario) as a boundary flow. Transformations represented in the model include nitrification, uptake of NO_3^- and NH_4^+ by phytoplankton, mineralization of organic N, and sedimentation. We did not consider N-fixation to be a significant contributor to the N-budgets of these lakes, as it has been shown to be barely detectable in Lakes Superior and Huron, and even in Western Lake Erie where moderately high N-fixation rates have been measured, this flux has been estimated to be only 2% of the N inputs entering the lake from Lake Huron (Mague and Burris, 1973). Likewise, we did not consider burial to be a permanent N-sink in this model. Although sedimentation rates are high in Lake Erie, net N efflux rates from sediment are also high (Small et al., 2013b). We discuss implications of this assumption in Section 4.

2.2. Parameterization

Storage values for each model compartment were assigned based on measurements from a series of research cruises from 2009 to 2012 on Lake Superior and Lake Erie, and a research cruise in 2011 that spanned Lakes Superior, Huron, and Erie. Measurements of water column and sediment N were thus conducted at multiple locations in each lake (Fig. 1). Sediment N values were based on N-content of sediment integrated over a depth of 10 cm from our surveys. From these measurements, mean concentrations (across depth and season) were used to estimate lake-wide values (Table 1).

Flow values were estimated using a Linear Inverse Modeling approach (Vézina and Platt, 1988), which can identify the range of plausible solutions given a set of constraints in the form of equalities and inequalities. Because ENA requires steady state conditions, this constraint was imposed on the model. Flows in the model were based on a combination of published values and estimates that we derived from published and unpublished values (Table 2). All flows are based on annual rates (i.e., the model is not seasonally explicit).

We calculated ranges for these flows by assigning a confidence interval to each based on our estimation of the combined effects of measurement error, and temporal and spatial variability on