ARTICLE IN PRESS

JGLR-00714; No. of pages: 12; 4C:

Journal of Great Lakes Research xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Journal of Great Lakes Research

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

Sediment nitrification and denitrification in a Lake Superior estuary

Brent J. Bellinger [a,*], Terri M. Jicha [a], LaRae P. Lehto [a], Lindsey R. Seifert-Monson [b,1], David W. Bolgrien [a], Matthew A. Starry [c,2], Theodore R. Angradi [a], Mark S. Pearson [a], Colleen Elonen [a], Brian H. Hill [a]

[a] U.S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Mid-Continent Ecology Division, 6201 Congdon Blvd., Duluth, MN 55804, USA
[b] Graduate Program in Integrative Biosciences, University of Minnesota, Duluth, MN 55812, USA
[c] SRA International, Inc., Duluth, MN 55804, USA

ARTICLE INFO

Article history:
Received 30 December 2013
Accepted 6 March 2014
Available online xxxx

Communicated by Joseph Makarewicz

Index words:
Laurentian Great Lakes
Denitrification
Nitrification
St. Louis River Estuary
Nitrous oxide

ABSTRACT

Inorganic nitrogen (N) transformations and removal in aquatic sediments are microbially mediated, and rates influence N-transport. In this study we related physicochemical properties of a large Great Lakes embayment, the St. Louis River Estuary (SLRE) of western Lake Superior, to sediment N-transformation rates. We tested for associations among rates and N-inputs, vegetation biomass, and temperature. We measured rates of nitrification (NIT), unamended base denitrification (DeNIT), and potential denitrification [denitrifying enzyme activity (DEA)] in 2011 and 2012 across spatial and depth zones. In vegetated habitats, NIT and DeNIT rates were highest in deep (ca. 2 m) water (249 and 2111 mg N m^{-2} d^{-1}, respectively) and in the upper and lower reaches of the SLRE (>126 and 274 mg N m^{-2} d^{-1}, respectively). Rates of DEA were similar among zones. In 2012, NIT, DeNIT, and DEA rates were highest in July, May, and June, respectively. System-wide, we observed highest NIT (223 and 287 mg N m^{-2} d^{-1}) and DeNIT (77 and 64 mg N m^{-2} d^{-1}) rates in the harbor and from deep water, respectively. Amendment with NO_3^- enhanced DeNIT rates more than carbon amendment; however, DeNIT and NIT rates were inversely related, suggesting the two processes are decoupled in sediments. Average proportion of N_2O released during DEA (23–54%) was greater than from DeNIT (0–41%). Nitrogen cycling rates were spatially and temporally variable, but we modeled how alterations to water depth and N-inputs may impact DeNIT rates. A large flood occurred in 2012 which temporarily altered water chemistry and sediment nitrogen cycling.

Introduction

Nitrogen (N) cycling, transport, and removal in aquatic systems occur in the water column and sediments via transformation of reduced and oxidized forms of N by plants into living biomass and through microbially mediated immobilization and mineralization (Reddy and DeLaune, 2008). Heterotrophic microbes degrade organic N-compounds into ammonia/ammonium (NH_3/NH_4^+), which can be oxidized by aerobic organisms by nitrification into nitrite and nitrate (NO_2^-/NO_3^-) or nitrous oxide (N_2O). Nitrate-N may be transported to downstream receiving waters, infiltrate groundwater, or released to the atmosphere as NOx, N_2O, and N_2 gas through reduction by facultative bacteria via denitrification.

Many aquatic systems receive anthropogenic N inputs in excess of removal rates (Howarth, 2008; Vitousek et al., 1997). Microbial denitrification (DeNIT), often coupled with nitrification (NIT), is an ecosystem service because it transforms and removes N, thereby reducing eutrophication, water treatment expenses, and potential health risks associated with elevated N-concentrations (Compton et al., 2011; Jordan et al., 2011; Russell and Greening, 2013). However, higher DeNIT rates increase N releases to the atmosphere influencing N-deposition, acid rain, stratospheric ozone depletion, or concentration of the potent greenhouse gas N_2O across an airshed (Compton et al., 2011; Smith, 1997; Vitousek et al., 1997).

Physicochemical factors, such as dissolved oxygen and organic carbon (DOC), NO_3^- concentration, and temperature that control microbial N-cycling rates vary in aquatic systems with vegetation, depth, season, and sediment characteristics (Piña-Ochoa and Álvarez-Cobelas, 2006; Rysgaard et al., 1995; Seitzinger, 1988). The physicochemical characteristics of an aquatic ecosystem affect its inherent capacity to mitigate excess nutrients through mineralization and removal (Jørgensen and Sørensen, 1985).

Ecosystem physicochemical characteristics are not static over interannual time scales. Urbanization and intensification of agriculture and, to a lesser extent ecosystem restoration, are altering watershed characteristics throughout the Great Lakes basin (Great Lakes Commission, 2013; Larson et al., 2013). Climate change may lead to warmer temperatures

---

[*] Corresponding author. Tel.: +1 218 529 5247.
E-mail address: bellinger.brent@epa.gov (B.J. Bellinger).
[1] Current address: Sappi Fine Paper, 20 North 22nd St., Cloquet, MN 55720, USA.
[2] Current address: Superior Water, Light and Power Company, 2915 Hill Ave., Superior, WI 54880, USA.

http://dx.doi.org/10.1016/j.jglr.2014.03.012
0380-1330/Published by Elsevier B.V. on behalf of International Association for Great Lakes Research.

Please cite this article as: Bellinger, B.J., et al., Sediment nitrification and denitrification in a Lake Superior estuary, J Great Lakes Res (2014), http://dx.doi.org/10.1016/j.jglr.2014.03.012

and altered water depths in the Great Lakes which could increase DeNIT and NIT rates due to increased nutrient concentrations and biological activity, longer ice-free periods, and altered oxic regimes (Hall and Stuntz, 2007).

Nutrient management in the Great Lakes, especially in coastal and estuary ecosystems, requires an understanding of the drivers of sediment N-cycling rates in order to implement adaptive management plans that enhance ecosystem services (Seitzinger et al., 2006). Few studies have quantified N-mineralization and N-removal rates, or the associated environmental conditions in coastal Great Lakes systems (Knuth and Kelly, 2011; Sierszen et al., 2012). In this study, we measured N-transformation rates and estimated N$_2$O production from DeNIT in sediments of the St. Louis River Estuary (SLRE). We summarized rates across the estuary by zones and months in relation to site physicochemical attributes, and we determined if NO$_3^-$ and C availability were limiting N-processing rates. We hypothesized that NIT, ambient DeNIT, and potential DeNIT rates would be positively related to temperature, vegetation biomass, water depth, and inputs of NO$_3^-$-rich Lake Superior water. We also expected rates to be higher in the lower reaches of the SLRE receiving anthropogenic N-loadings from the twin ports of Duluth, MN, and Superior, WI.

Materials and methods

Study area

The SLRE is a drowned river-mouth estuary at the western end of Lake Superior, bordering the cities of Duluth, MN, and Superior, WI, USA (Fig. 1). The St. Louis River is the largest U.S. tributary to Lake Superior (watershed area >10,000 km^2, mean annual discharge about 70 m^3 s^{-1}; Fig. 1). River and lake waters mix in the lower SLRE. The SLRE extends 37 river km from Fond du Lac dam to its outlet to Lake Superior at the Superior Entry. The main tributaries are the St. Louis (>90% of flow), Red, Pokegama, and Nemadji Rivers. The lower reach (0–13 river km), which includes the twin ports of Duluth and Superior, an international seaport, has been extensively modified by bank stabilization, dredging, wetland fill, and shoreline development. The SLRE is mostly shallow (~56% <2 m) but shipping channels (depth >6 m) are maintained in the harbor up to about river km 20. The upper river 20 km is bordered by forest and wetland with scattered residential development (SLRCAC, 2002). Concentrations entering the SLRE for nitrite/nitrate (<150 μg NO$_x^-$-N/L) are low, and total phosphorus (TP; ~20 μg P/L) and total nitrogen (TN; 500–>1000 μg N/L) are high relative to Lake Superior (~400 μg NO$_3^-$-N/L, <5 μg TP/L, and ~600 μg TN/L) (Guildford and Hecky, 2000; Sterner, 2011). Watershed-derived and estuarine ammonium/ammonia-N (NH$_4$-N) concentrations may vary from <30–170 μg NH$_4$-N/L (this study) but are always higher than in Lake Superior (<15 μg NH$_4$-N/L) (Small et al., 2013).

Experimental design and site selection

We used different survey designs in 2011 and 2012. Both designs were based on area-weighted probability sampling methods, similar to those developed for EPA's Environmental Monitoring and Assessment Program (EMAP) (Crane et al., 2005; Stevens and Olsen, 2003, 2004). Sampling sites were assigned to spatial zones: “harbor” (river km 0–13), “bay” (river km 13–24), or “river” (river km 24–35) (Fig. 1). Sites were also grouped by depth zones (“shallow,” <1 m; “intermediate,” 1–2 m; and “deep,” >2 m). In 2011 (“vegetated-habitat survey”), the sample frame consisted of areas of emergent and submergent vegetation in the SLRE as determined from field observation (J. Lindgren, MN Department of Natural Resources, pers. comm.) and delineated in available state and national wetland inventories (U.S. Fish and Wildlife Service; www.fws.gov/wetlands/) in ARCGIS (ESRI Co., v. 9.3, Redlands, CA, USA). Inclusion of emergent vegetation beds in the sample frame was contingent on surface water connectivity and exchange with the SLRE. Based on

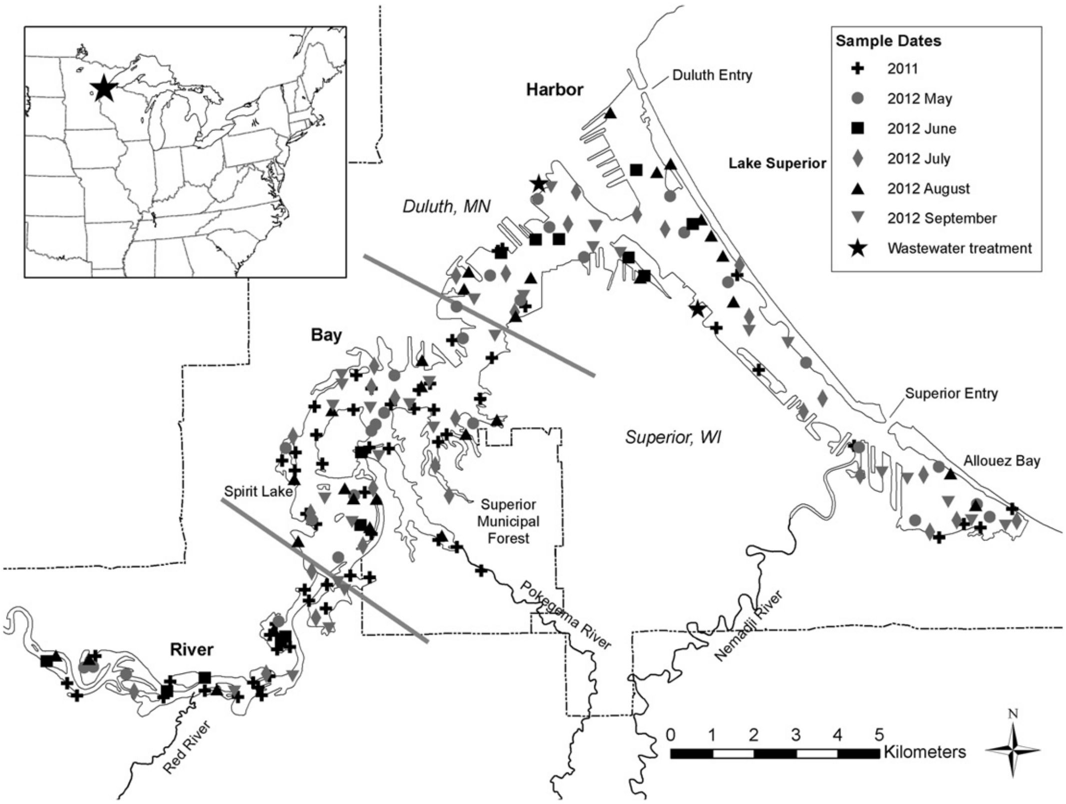

Fig. 1. Map of sampling locations in the St. Louis River Estuary in 2011 and 2012. Water treatment plants are the Western Lake Superior Sanitary District and Superior Municipal Water Treatment Plant.

Please cite this article as: Bellinger, B.J., et al., Sediment nitrification and denitrification in a Lake Superior estuary, J Great Lakes Res (2014), http://dx.doi.org/10.1016/j.jglr.2014.03.012