Nitrogen Cycling and Fate in a Floodplain Backwater of the Upper Mississippi River

by William F. James

PURPOSE: Backwaters connected to large rivers efficiently retain nitrate and can play an important role in reducing downstream loading to coastal marine environments. However, biotic assimilation and transient storage can account for a significant portion of the nitrate uptake versus denitrification. The fate of this nitrogen (N) pool is largely unknown. Is assimilated nitrate stored temporarily and exported from the system later as another N species or is it eventually routed from recycling pathways to denitrification or burial? This information is critical for modeling and managing large river-floodplain systems. The objective of this research was to examine N fluxes and transformations in a backwater system of the Upper Mississippi River within the context of an N budget in order to provide more insight into the fate of nitrate.

BACKGROUND: High nitrate loading from agriculturally dominated large river systems has contributed substantially to impairment of sensitive coastal marine ecosystems (Vitousek et al. 1997; Rabalais 2002; Turner et al. 2006). For example, expansion of bottom water hypoxia in the northern Gulf of Mexico in recent decades has coincided with accelerated nitrate loading from the Mississippi River (Goolsby et al. 2001). In particular, Alexander et al. (2000) suggested that nitrogen (N) loads reaching the Mississippi River are transported to the Northern Gulf of Mexico with little uptake or transformation en route. Poor N processing efficiency is likely due to several factors. Headwater streams draining agricultural watersheds exhibit flashy hydrology during periods of high N runoff, resulting in very low contact time for uptake and transport of the majority of the load to larger river segments (Royer et al. 2004). N retention is lower in higher order river channels due to greater flow velocity, lower surface:volume ratio, and lack of suitable substrate for establishment of attached and sediment-dwelling biofilms. In addition, control structures that regulate pool elevation for navigation, agriculture, and flood control have reduced both geomorphic diversity and exchanges between large river segments and the adjoining floodplain (Sparks 1995), where N uptake and processing can be considerable (McClain et al. 2003; Richardson et al. 2004).

Floodplain features such as side channels, backwaters, and temporary ponds exhibit higher residence time in relation to large river channel segments, providing conditions for sediment accretion, submersed macrophyte growth, and greater contact time for N uptake. For instance, Tockner et al. (1999) reported high N uptake rates (estimated by mass balance input-output) for floodplain backwaters of the Danube River. Forshay and Stanley (2005) indicated that floodplain depressions of the Wisconsin River exhibited rapid N uptake rates during flood-pulse periods. Inundation of these features (representing 40,000 acres of the lower Wisconsin River) and N uptake was equivalent to 37 percent of the nitrate load transported by this river. James et al. (2008a) found that backwaters of the Upper Mississippi River (i.e., north of Cairo, Illinios) were

Report Documentation Page

Form Approved
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
SEP 2009		**00-00-2009 to 00-00-2009**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Nitrogen Cycling and Fate in a Floodplain Backwater of the Upper Mississippi River	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
U.S. Army Engineer Research and Development Center,Environmental Laboratory,3909 Halls Ferry Road,Vicksburg,MS,39180-6199	

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**15**	

very efficient (20-40 percent) at retaining N and could play a role in reducing N transport. Thus, evidence indicates that floodplain features provide an important ecological function in large river systems by retaining and processing N.

Less is known about the fate of nitrate that is retained in floodplain backwaters. However, this information is needed in order to better evaluate overall N processing efficiency. Dissimilatory reduction of nitrate to N_2 gas (denitrification) by bacterial communities under anoxic conditions represents a permanent N sink. However, nitrate can also be retained temporarily via biotic assimilation and conversion to particulate organic N, where it is transformed to ammonium via mineralization and can enter recycling pathways that include coupled nitrification-denitrification and biotic assimilation (as ammonium or nitrate) and transformation back to particulate organic N. James et al. (2008b) reported that only 27 percent of the summer nitrate retention could be accounted for by denitrification in a backwater lake of the Upper Mississippi River. In contrast, biotic assimilation and transformation represented the majority of the nitrate retained in the system, implying temporary storage and recycling to other forms. They observed net ammonium export from the system, which coincided with high concentrations of porewater sediment ammonium and high rates of ammonium release from sediments in excess of nitrification rates. Although net ammonium export was only equivalent to ~11 percent of the nitrate retention, these patterns suggested a linkage between biotic nitrate assimilation, organic N mineralization, and export as ammonium. If so, ammonium production and export rates should be factored into overall nitrate retention efficiency for backwater systems receiving high nitrate loads. The objectives of this research were to examine the role of organic N mineralization in sediments and ammonium fluxes to the water column in relation to an N budget that quantified N inflow-outflow, N sediment diffusive fluxes and nitrification-denitrification transformations in order to better understand the fate of nitrate in backwater systems of the Upper Mississippi River.

STUDY SITE: Second Lake is a shallow backwater (surface area = 7.5 ha; mean depth = 0.4 m; maximum depth = 2.4 m) of the Finger Lakes complex located adjacent to the main channel in Navigation Pool 5 of the Upper Mississippi River (Figure 1). Construction of Lock and Dam 4 in the 1930's restricted hydraulic and constituent exchanges between the Finger Lakes and the Mississippi River until installation of gated culverts in 1994 to regulate flow into the backwater complex over a zero to ~ 2 m^3 s^{-1} range. The purpose of the culverts was to introduce low flows into the lake during winter periods to improve temperature and dissolved oxygen conditions for overwintering Centrarchid fish (Johnson et al. 1998). In 2006, the vertical slide gate controlling culvert (1.2 m dia) flows to Second Lake was adjusted to maintain flow at a constant 0.12 m^3 s^{-1}, resulting in a theoretical residence time of 3.3 days. External N loading to Second Lake is controlled by source water concentrations from the Mississippi River when culvert flow is held at a constant rate. Nitrogen species are dominated by nitrate (~ 2.0 mg l^{-1}; 70 percent of the total N). By comparison, ammonium loadings from the Mississippi River are low, with concentrations < 0.5 mg l^{-1}. Submersed macrophytes, dominated by *Ceratophyllum demersum*, *Lemna* sp., and *Potamogeton crispus* cover ~ 60 percent of the lake's surface area. The floating-leaved macrophyte *Nymphaea odorata* is located along the eastern and western shorelines of the lake. *C. demersum*, *Lemna*, and *N. odorata* senesce in late September through October while *P. crispus* dies back in June.
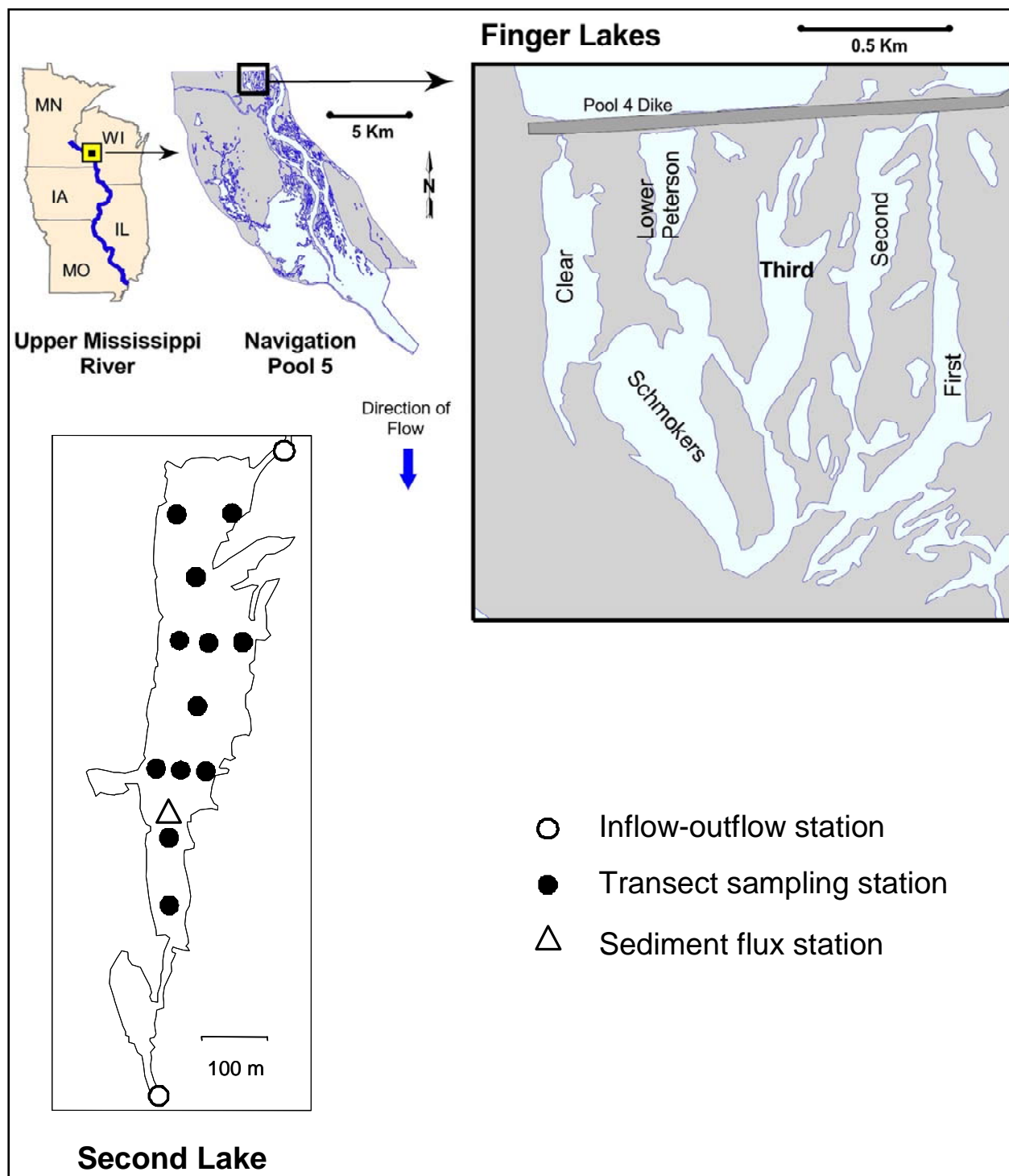
Figure 1. Location of the Finger Lakes backwater complex in Navigation Pool 5 of the Upper Mississippi River and sampling station locations in Second Lake.

METHODS: Culvert flow was measured continuously between May and October, 2006, using a combination electromagnetic velocity meter and pressure transducer (ISCO model 4150, Teledyne ISCO, Inc. Lincoln, Nebraska USA). Flow calibration was monitored weekly with a hand-held velocity meter (Flo-Mate model 2000; Marsh-McBirney Inc., Fredrick, Maryland USA). Discharge from the lake was not measured directly and assumed to equal inflow. Inflow-outflow chloride analyses indicated that dilution due to possible groundwater inputs did not occur.

Stations were established along the longitudinal and horizontal axis of the lake for sampling at biweekly intervals between May and October (Figure 1). Sampling was also conducted monthly in January through March, 2007. Poor ice conditions prevented access to the outflow of the lake in November and December, 2006. Water temperature, dissolved oxygen, pH, and conductivity were measured at 0.25-m depth intervals between the surface and 0.1 m above the sediment surface using a data sonde (Hydrolab Quanta monitoring system, Hach Co., Loveland, Colorado USA) that was calibrated against known standards and independently determined Winkler dissolved oxygen. Surface grab samples for total and total soluble N were predigested with potassium persulfate (American Public Health Association (APHA) 2005). Lake water was passed through a 0.45-µm syringe filter immediately after collection in the field prior to analysis of nitrate (as nitrate+nitrite-N) and ammonium. Colorimetric analyses of total and total soluble N, nitrate, and ammonium were performed on a Lachat QuikChem A/E using standard procedures (APHA 2005). Particulate organic N (PON) was equal to the difference between total N and total soluble N. Dissolved organic N (DON) was calculated as total soluble N minus the sum of nitrate and ammonium.

Constituent loading at the inflow and outflow was calculated as the product of concentration and flow. Net retention or export of loads was estimated as the difference between inflow and outflow loading. Gross retention or export was defined as the sum of inflow loading and internal sediment flux or transformation minus outflow loading. Percent efficiency was calculated as retention divided by input load and multiplied by 100.

Five replicate sediment cores were collected monthly at a station between June and September for examination of seasonal changes in exchangeable ammonium (Exch-N) concentration (Figure 1). The cores were sectioned at 2-cm intervals over the upper 10-cm layer and at 2.5- to 5.0-cm intervals over the lower 10 cm for analysis. Moisture content (percent) and density (g cm^{-3}) were determined gravimetrically by drying a known volume of sediment to a constant mass at 105 °C. Loss-on-ignition organic matter (percent) was estimated as the change in mass after combustion at 500 °C. Exch-N was extracted with 0.1 M NaCl (Bremner 1965) and analyzed using automated procedures (APHA 2005). Five additional replicate sediment cores were collected in July and sectioned as above for determination of total Kjeldahl N according to Plumb (1981). Sediment samples were digested with acidic red mercuric oxide and analyzed for N using automated colorimetric procedures.

Additional sediment cores were collected at the same station (Figure 1) in July to estimate nitrate and ammonium flux. The upper 10-cm sediment section was extruded intact into a 6.5-dia by 20-cm-long incubation sleeve. Water collected from the inflow and filtered through a glass fiber filter (2.0 µm nominal pore size; Gelman A/E) served as overlying water. Nitrate fluxes were estimated as a function of concentration (range = 0.5 to 4.0 mg l^{-1}) by adding KNO$_3$ to the overlying water. The oxidation-reduction environment of the overlying water was maintained by

gently purging either air (oxic) or nitrogen (anoxic) through an air stone positioned above the sediment surface. Water samples collected over a 3-day period were analyzed for nitrate and ammonium. Replacement water was preadjusted by purging with gas. Dissolved oxygen was measured periodically to ensure maintenance of anoxic conditions. Rates were calculated as the linear concentration change (corrected for dilution with replacement water) divided by time and core surface area. Since anoxia inhibited nitrification (aerobic conversion of ammonium to nitrate), differences between the oxic-anoxic ammonium flux were assumed to reflect rates of nitrification.

RESULTS:

Nitrogen Loading and Water Column Patterns: Total N inflow loading was dominated by nitrate throughout the summer (64.5 percent $\pm$ 3.9 S.E.; Figure 2). Inflow nitrate was greatest (> 2 mg l^{-1}) during May-June in conjunction with spring runoff from the Upper Mississippi River watershed and accounted for 82.6 percent ($\pm$ 4.3 S.E.) of the total N load. Concentrations declined to < 1 mg l^{-1} during the drier period of August-October. Net nitrate retention occurred throughout the summer, representing ~55 percent of the inflow load (Figure 2; Table 1). Ammonium inflow concentrations and loading were negligible by comparison (Figure 2). However, ammonium outflow loading exceeded inflow loading throughout the summer, resulting in net export from the system (Figure 2; Table 1). PON and DON represented < 30 percent of the total N inflow load (Table 1). Forty percent of the summer PON inflow load was retained in the system while DON was exported in excess of DON inflow load (Table 1). PON inflow concentrations were greatest in late June through July, exceeding PON outflow concentration by a factor of 3 to 4 (Figure 2). As a result, net retention of PON was greatest during that period (Figure 2). DON concentrations in the inflow and outflow exhibited a peak in May followed by a decline to relatively constant concentrations in July through October (Figure 2). Although net DON export occurred throughout the summer, it was greatest in May and July (Figure 2). Annual inflow-outflow loading exhibited similar patterns of net retention or export (Table 1).

Longitudinal declines in nitrate concentration in Second Lake were regulated by inflow concentration at the culvert and uptake during transport to the outflow (Figure 3a). Concentration gradients were greatest in May-July in conjunction with high inflow nitrate and lower during the late summer period. Ammonium increased from near zero at the inflow to a mid-lake peak between 200 and 600 m downstream of the culvert. Concentrations near the outflow declined from mid-lake peaks in May, June, and September. With the exception of Station 5 (Figure 1; 575 m downstream of the culvert), located near the deepest point in the lake (i.e., ~2.4 m deep; ~1 percent of the surface area), near-bottom dissolved oxygen concentrations were greater than 1 mg l^{-1} throughout the summer. Bottom water anoxia (dissolved oxygen < 1 mg l^{-1}) was observed at Station 5 in July and August.

Sediment Nitrogen Characteristics and Fluxes: Mean sediment constituent concentrations in July were relatively uniform within the upper 20-cm sediment layer (Table 2). Moisture content was greater than 80 percent, while sediment density was low, indicating a fine-grained particle size distribution. Organic matter content was moderate at ~ 15 percent. Total Kjeldahl N was high relative to ranges and means reported in Barko and Smart (1986) for a variety of lake and reservoir sediments in North America (range = 0.3 to 24.1 mg g^{-1}; mean = 7.8 mg g^{-1}). Exch-N averaged ~0.09 mg g^{-1} and represented less than 1 percent of the total Kjeldahl N.
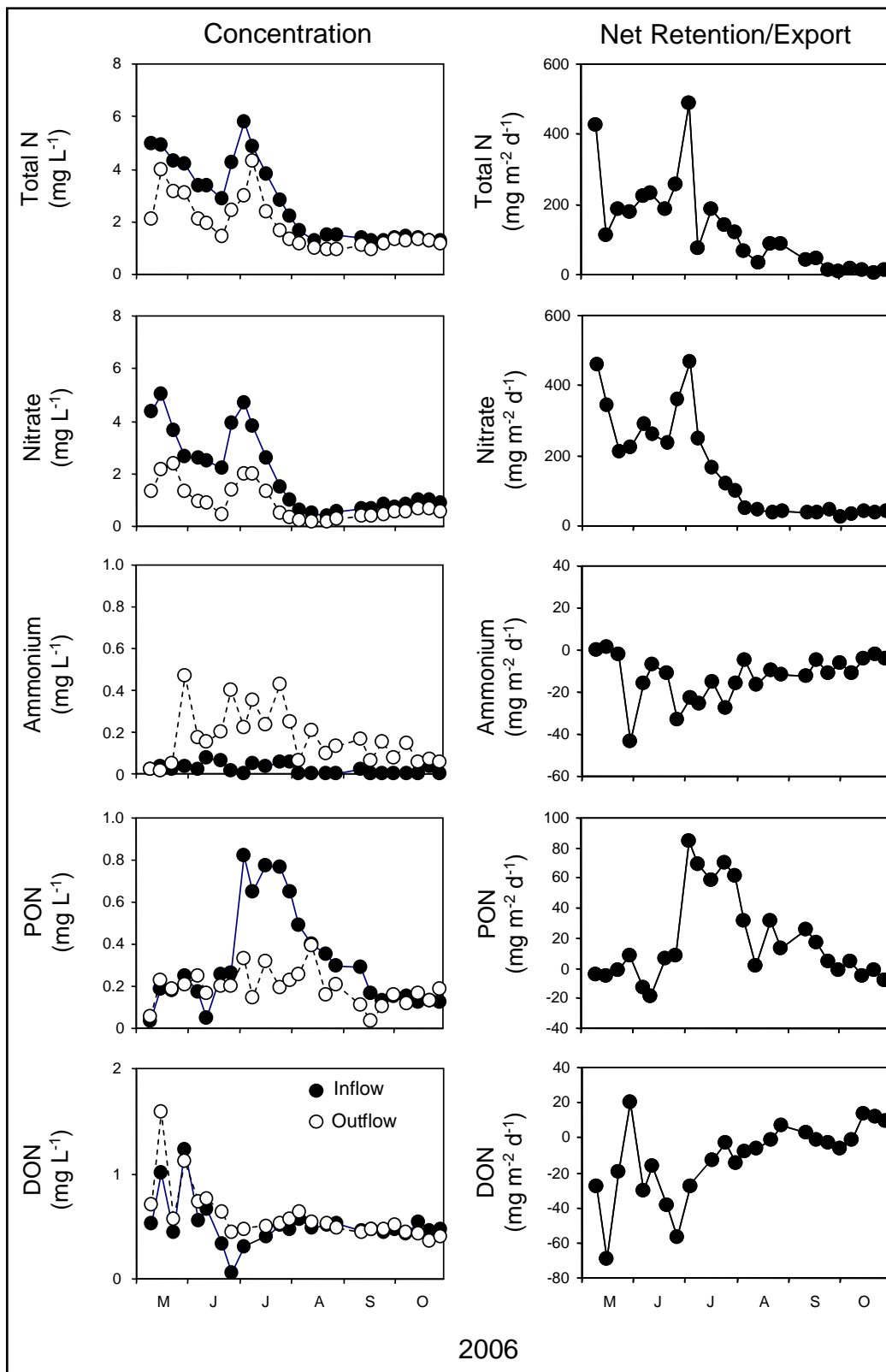
Figure 2. Seasonal variations in concentration and net retention or export loading for total nitrogen (N), particulate organic N (PON), nitrate, ammonium, and dissolved organic N (DON).

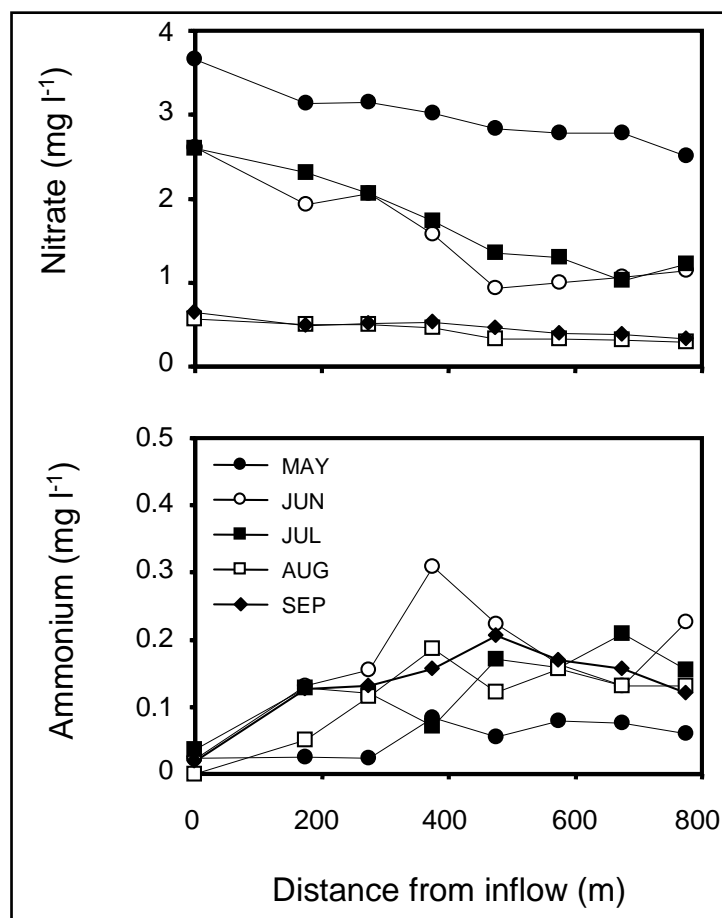|				
Table 1. Summer and annual inflow and outflow loading, net retention (positive rate) or export (negative rate), and efficiency for total nitrogen (N), particulate organic N (PON), dissolved organic nitrogen (DON), nitrate, and ammonium.				
N Species	**Inflow (mg m^{-2} d^{-1})**	**Outflow (mg m^{-2} d^{-1})**	**Net Retention/Export (mg m^{-2} d^{-1})**	**Efficiency (%)**
May – October				
Total N	396	268	128	32
PON	45	27	18	40
DON	72	92	-20	-128
Nitrate	285	127	158	55
Ammonium	2	15	-13	-750
Annual				
Total N	364	267	97	27
PON	31	18	13	42
DON	63	72	-9	-114
Nitrate	267	154	113	42
Ammonium	5	14	-9	-280

Figure 3.   Longitudinal variations in nitrate and ammonium concentrations.

Table 2. Variations in means (n = 5) and standard errors (SE) for sediment moisture content, density, organic matter content, total Kjeldahl nitrogen (N), and exchangeable N (Exch-N) as a function of sediment depth.

Depth (cm)	Moisture Content (%)		Density (g cm^{-3})		Organic Matter (%)		Total Kjeldahl N (mg g^{-1})		Exch-N (mg g^{-1})	
	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
2	88.4	0.5	1.074	0.003	15.3	0.4	9.10	0.25	0.049	0.012
4	87.2	0.4	1.082	0.006	14.9	0.3	9.31	0.33	0.066	0.006
6	86.5	0.3	1.078	0.012	14.4	0.2	9.39	0.33	0.073	0.010
8	86.7	0.1	1.078	0.013	14.9	0.2	9.12	0.38	0.102	0.017
10	86.5	0.4	1.082	0.008	14.8	0.2	9.23	0.24	0.115	0.019
12.5	85.1	0.7	1.089	0.006	14.9	0.1	9.15	0.42	0.110	0.021
15	83.5	0.7	1.078	0.005	15.2	0.3	9.05	0.07	0.088	0.011
20	81.8	0.4	1.101	0.005	15.6	0.4	8.78	0.26	0.078	0.010

Nitrate influx from overlying water to the sediment in laboratory incubation systems varied logarithmically as a function of nitrate concentration in the overlying water column (Figure 4). Lower nitrate influx under oxic conditions was probably related to a longer diffusional gradient through the oxic microzone and additional nitrate input via bacterial nitrification. In contrast, anoxic conditions inhibited bacterial nitrification and coupled nitrification-denitrification. Thus, nitrate influx under anoxic conditions approximated denitrification of external inputs. Under an assumption that nitrate influx occurred primarily under oxic conditions in Second Lake, the mean inflow nitrate concentration of 1.866 mg l^{-1} ($\pm$ 0.398 SE; n = 14) translated into a summer nitrate influx of 81.6 mg m^{-2} d^{-1}, based on regression relationships developed between laboratory-derived nitrate influx under oxic conditions and the overlying water concentration (Figure 4).
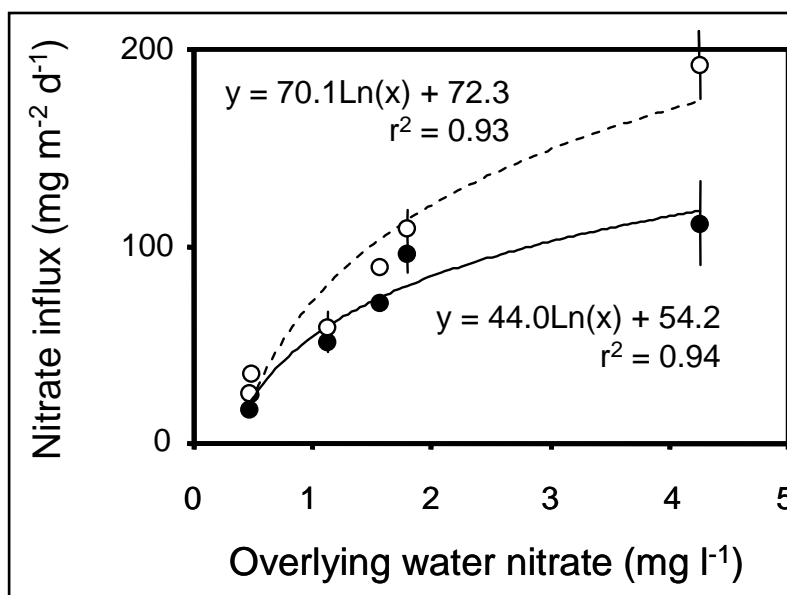

Figure 4. Variations in mean (n = 5) nitrate influx to sediment under oxic (solid dot) and anoxic (circle) for different initial nitrate concentrations in the overlying water. Vertical lines represent ± 1 standard error.

Ammonium efflux from sediment was 56.2 mg m^{-2} d^{-1} (± 1.8 SE; n = 8) under anoxic conditions and 27.1 mg m^{-2} d^{-1} (± 3.2 SE; n = 8) under oxic conditions. Efflux did not vary as a function of nitrate concentration in the overlying water column. Since anoxia inhibited nitrification, the difference between the two rates approximated nitrification. The summer nitrification rate estimate was 29.1 mg m^{-2} d^{-1}. A denitrification rate was estimated as the sum of nitrate influx under oxic conditions and the nitrification rate, assuming that the entire nitrate pool produced via nitrification diffused into the anoxic sediment and was transformed into N$_2$ via denitrification (i.e., coupled nitrification-denitrification). The denitrification rate was 110.7 mg m^{-2} d^{-1}.

Exch-N exhibited a concentration peak in June and declining values between July and September within the upper 2-cm sediment layer (Figure 5a). Below 2 cm, concentrations were low and relatively uniform with depth in June, increased steadily between July and August, and declined in September. Thus, rates of change in Exch-N were negative for the upper 2-cm layer and positive for deeper layers over the June-September period (Figure 5b). Concentrations integrated over the upper 20-cm sediment layer followed a similar trend of increasing mass over the summer period, resulting in a net Exch-N accumulation rate of 7.4 mg m^{-2} d^{-1} between June and September (Figure 6). By comparison, the nitrification and oxic ammonium effluxes were nearly four times greater.
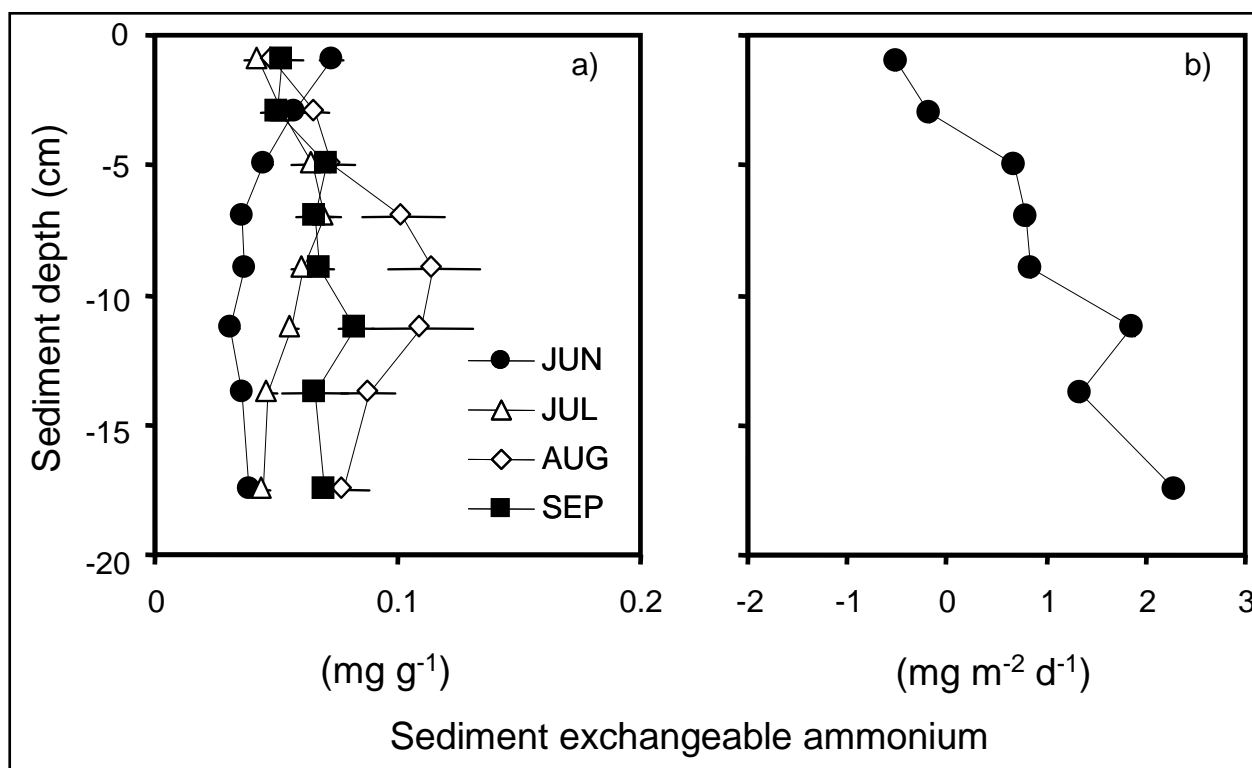

Figure 5.   Seasonal and vertical variations in mean (n = 5) sediment exchangeable ammonium concentration (a) and net rates of concentration change between June and September 2006. Horizontal lines represent ± 1 standard error.
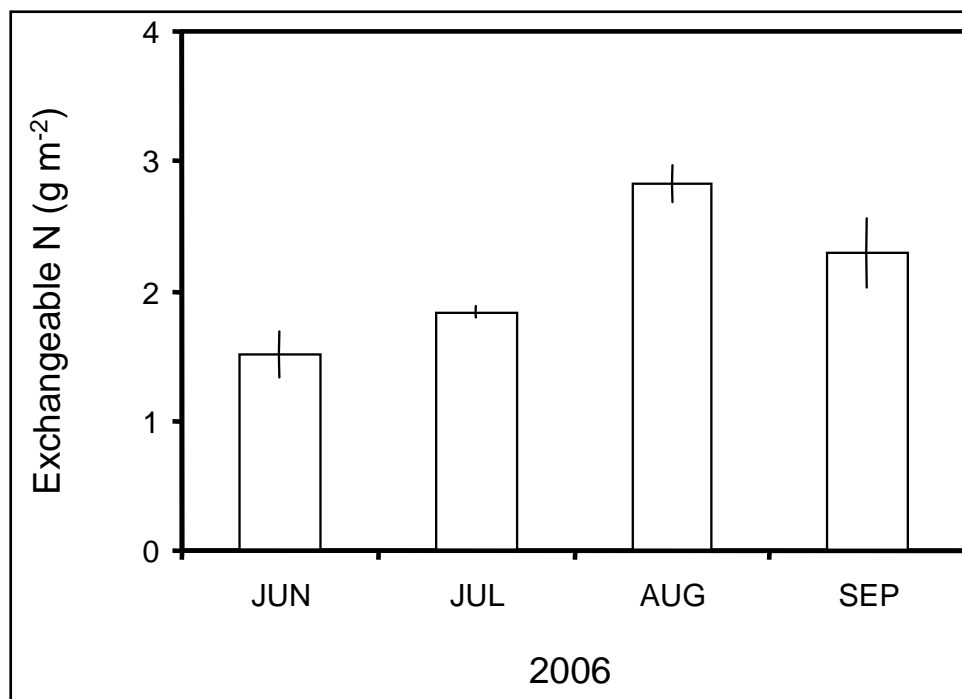
Figure 6.   Seasonal variations in mean (n = 5) sediment exchangeable
ammonium concentrations integrated over the upper 20-cm sediment
layer. Vertical lines represent ± 1 standard error.

A sediment net PON mineralization rate to ammonium of 63.6 mg m^{-2} d^{-1} was estimated over the upper 20-cm sediment layer as the sum of the Exch-N accumulation rate, nitrification rate, and oxic ammonium efflux (i.e., 7.4 + 29.1 + 27.1 mg m^{-2} d^{-1}). This rate may have been underestimated because root uptake by macrophytes was not factored into the estimate. However, a large portion of the macrophyte-epiphyton community in Second Lake has rudimentary root structures (i.e., *Lemna* and *C. demersum*; Rogers et al. 2000; James unpubl.[1]) and probably sequestered N primarily from the water column rather than sediment. Since sediments were anoxic below the 2-cm depth, it was assumed that the Exch-N accumulation rate within these strata reflected PON mineralization under anoxic conditions (1.3 mg m^{-2} d^{-1}). Thus, most of the PON mineralization occurred within the upper 2-cm sediment layer (54.0 mg m^{-2} d^{-1}) and either diffused into the water column as ammonium or was converted to nitrate by nitrifying bacteria.

Summer Budgetary Analysis: Inflow loading was the dominant source of nitrate to the system versus nitrification (Table 3). Gross nitrate retention represented ~60 percent of the nitrate inputs to the system. Denitrification accounted for 59 percent of the gross nitrate retention and was a permanent sink for nitrate. Thus, unmeasured assimilation by biotic components (i.e., macrophytes, epiphyton, phytoplankton) and transformation to PON represented 41 percent of the gross nitrate retention.

---

[1] Unpublished macrophyte abundance data. 2006. William F. James, Research Aquatic Biologist, U.S. Army Engineer Research and Development Center, Eau Galle Aquatic Ecology Laboratory, Spring Valley, WI.

Table 3. Summer nitrate, ammonium, and particulate organic nitrogen budget (PON) for Second Lake.									
Fluxes	**Nitrate**			**Ammonium**			**PON**		
	Source	mg m^{-2} d^{-1}	% input	Source	mg m^{-2} d^{-1}	% input	Source	mg m^{-2} d^{-1}	% input
Input	Inflow	285		Inflow	2		Inflow	45	
	Sediment nitrification	29		Sediment PON mineralization	64		Biotic assimilation to PON	91	
Transformation	Sediment denitrification	111	35	Sediment nitrification	29	44	Sediment PON mineralization	64	47
	Biotic assimilation to PON	76	24	Biotic assimilation to PON	15	23			
Storage or burial				Sediment Exch N accumulation	7	11	PON deposition	45	33
Output	Outflow	127	40	Outflow	15	23	Outflow	27	20
Gross retention[a]		187	60		51	77		109	80

PON mineralization overwhelmingly dominated ammonium inputs to Second Lake. Forty-four percent of the mineralized sediment PON was nitrified while the remainder either accumulated in the sediment as Exch-N or diffused into the water column. Gross ammonium retention accounted for 77 percent of the ammonium input. Biotic assimilation of ammonium to PON accounted for 29 percent, while transformation to nitrate via nitrification accounted for 57 percent of the gross ammonium retention. Accumulation of Exch-N in anoxic sediment represented 14 percent of the gross ammonium retention. Net export (i.e., inflow minus outflow) of ammonium from the lake occurred as an apparent result of PON mineralization, efflux into the water column in excess of nitrification, and advective transport to the outflow in excess of biotic uptake (Table 1).

DON flux and transformation information was incomplete for Second Lake and was not included in the budgetary analysis. PON inputs were dominated by biotic assimilation of nitrate and ammonium (i.e., 67 percent of the PON input; Table 3). Most of the biotic assimilation was accounted for by nitrate that originated from external loading to the lake (84 percent). Ammonium sources for biotic assimilation were probably linked to diffusive efflux from sediment since ammonium culvert loading was minor. Gross PON retention represented 80 percent of the input, suggesting that most of the PON contribution remained within the system during the summer period. For budgetary purposes, biotic assimilation and PON mineralization were assumed to be relatively constant annually and a PON deposition or storage rate was calculated as the difference between gross PON retention and mineralization (Table 3). PON mineralization and deposition represented 59 and 41 percent of the gross PON retention rate, respectively.

DISCUSSION: Although summer net nitrate retention efficiency was high in Second Lake, denitrification accounted for only ~60 percent of the uptake, suggesting that a large percentage of the load was assimilated by biotic components, representing transient storage. While denitrification was a permanent sink for nitrate, assimilated nitrate was subject to transformation, burial, and export from the system as PON or a dissolved N form. It was likely that submersed aquatic macrophytes (*C. demersum* and *Lemna*) and associated epiphyton accounted for most of the

biotic assimilation in Second Lake, suggesting temporary storage as macrophyte biomass over the growing season. Fragmented macrophyte PON could have been exported during senescence in September-October; however, PON did not increase in the outflow over summer concentrations and net PON retention occurred during the autumn period. Monthly monitoring in January through March 2007 indicated PON retention during winter months, suggesting overall annual net PON retention rather than export as fragmented macrophyte PON.

The PON mineralization rate of 64 mg m^{-2} d^{-1} fell within ranges reported by others (Kadlec and Knight 1996; Reddy and DeLaune 2008). Assuming minimal mineralization in the winter, an annual rate for Second Lake of 11.8 g m^{-2} y^{-1} would fall within the upper range reported for north-temperate wetlands (Kadlec and Knight 1996). The PON mineralization rate was lower by ~ 40 percent than the gross PON retention rate. This pattern could have been attributed to at least two factors. First, much of the nitrate assimilated over the growing season was not immediately available for mineralization. Instead, it was tied up as living submersed macrophyte biomass (versus detritus) that did not die back until autumn. Under these circumstances, PON sources for mineralization may be largely derived from submersed macrophyte biomass that was produced during the previous growing season, deposited to the sediment, and stored over the winter. Second, with the exception of a thin oxic microzone, anoxic conditions probably existed throughout most of the vertical sediment column in Second Lake, limiting rates of PON mineralization to anaerobic metabolism. Gross PON retention in excess of net mineralization would eventually become buried under this scenario.

Nitrification represented a minor source of nitrate to the system because inputs were dominated by external loading. High nitrate concentrations in the overlying water column implied that nitrate produced by nitrifiers most likely diffused downward into anoxic sediment, becoming denitrified, rather than diffusing out of the sediment. Under these conditions, coupled nitrification-denitrification would approximate the nitrification rate for Second Lake. This scenario contrasted with systems receiving lower external nitrate loads, where nitrification can represent much greater source to denitrifiers and may exceed coupled nitrification-denitrification, resulting in net nitrate diffusion into the overlying water column (Jensen et al. 1994; Risgaard-Petersen 2003).

Efflux from sediments largely accounted for net ammonium export from Second Lake during the summer. Rates measured here were similar to those reported by James et al. (2008b) for a neighboring backwater lake (16.9 and 55.4 mg m^{-2} d^{-1} under oxic and anoxic conditions, respectively) and within ranges reported for systems receiving agricultural inputs (2.1 to > 36.3 mg m^{-2} d^{-1}; Reddy et al. 2001; Malecki et al. 2004). It was unusual that net ammonium efflux occurred under oxygenated conditions in excess of nitrification (Rysgaard et al. 1994; Risgaard-Petersen 2003). In contrast, others have observed decreases in ammonium concentration in laboratory sediment systems under oxic conditions due to nitrification (Malecki et al. 2004). Patterns for Second Lake suggested that nitrifying bacterial communities were probably saturated with respect to ammonium fluxes into the aerobic microzone via PON mineralization and ammonium diffusion from anaerobic sediment, resulting in net efflux to the overlying water.

Net ammonium and DON export from the system implied that a portion of the retained nitrate was actually discharged from the system after biotic assimilation and transformation. This was a

reasonable hypothesis given that nitrate dominated biotically available inorganic N sources to the system. Thus, gross nitrate retention efficiency would be overestimated due to transformation and export as ammonium or DON. Combined ammonium and DON export was small relative to the summer gross nitrate retention rate (i.e., ~ 15 percent). Assuming that exported ammonium and DON were derived entirely from assimilated nitrate, the corrected gross retention rate and retention efficiency were less than original estimates (Table 3) at 153 mg m^{-2} d^{-1} and 49 percent, respectively. Nevertheless, corrected values indicated that backwater retention efficiency was high and comparable to wetlands and other floodplain systems (Tockner et al. 1999; Mitsch et al. 2001; Friedrich et al. 2003; Forshay and Stanley 2005). Overall, the fate of nitrate in Second Lake during the summer period was primarily conversion to N$_2$ via denitrification (Figure 7). For biotically assimilated nitrate, deposition as PON (primarily as senescent macrophyte biomass in the autumn) accounted for 24 percent while transformation and export as ammonium or DON represented 17 percent.
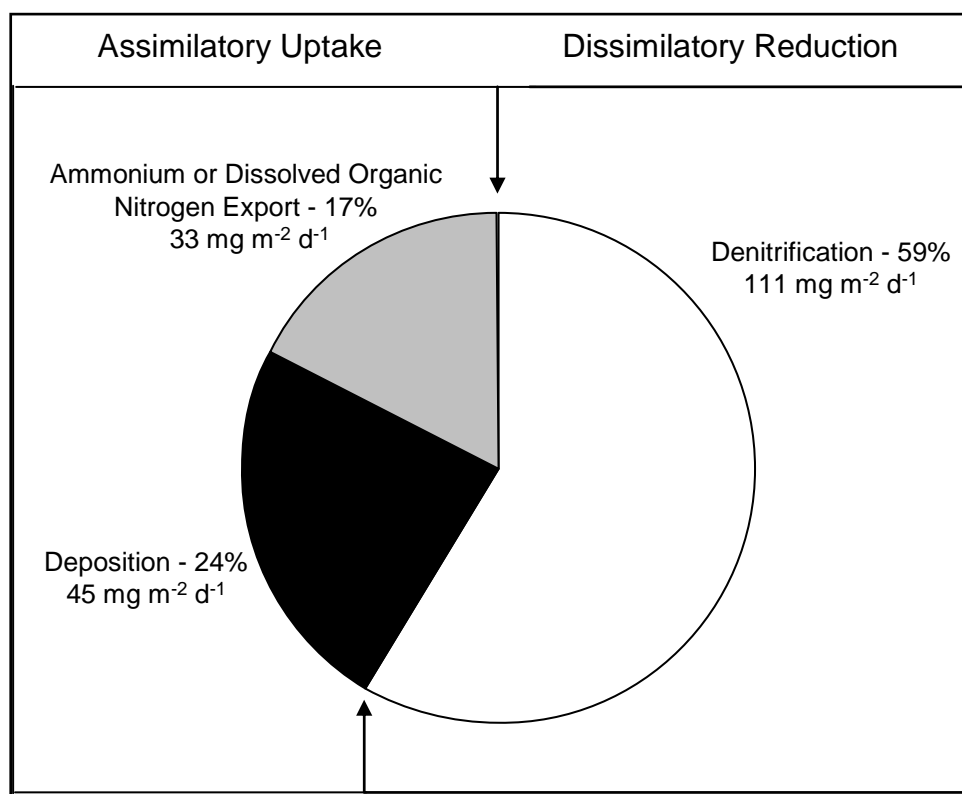

Figure 7.   Fate of summer nitrate in Second Lake.

Others have found that biotic assimilation represented a significant portion of the nitrate uptake in various aquatic systems (Webster et al. 2003; Mulholland et al. 2004; Arango et al. 2008). However, little is known about the fate of assimilated nitrate. A scenario where assimilated nitrate is ultimately transported downstream as a different form (i.e., nutrient spiraling) rather than permanently retained would imply that backwaters are not as effective in reducing nitrate loading to sensitive coastal ecosystems as once thought. Although assimilated N was subject to recycling pathways, the N budget for Second Lake suggested that more that half (57 percent) stayed within the system while 43 percent was exported. These results indicated that floodplain backwaters are efficient sinks for nitrate rather than transient storage areas.

ADDITIONAL INFORMATION: This technical note was prepared by William F. James, Research Aquatic Biologist, Eau Galle Aquatic Ecology Laboratory, Environmental Laboratory, U.S. Army Engineer Research and Development Center. The study was conducted as an activity of the Nutrient Algorithms work unit of the System-Wide Water Resources Program (SWWRP). For information on SWWRP, please consult *https://swwrp.swwrp.army.mil/* or contact the Program Manager, Dr. Steven L. Ashby at *Steven.L.Ashby@usace.army.mil*. This technical note should be cited as follows:

> James, W. F. 2009. *Nitrogen cycling and fate in a floodplain backwater of the Upper Mississippi River.* SWWRP Technical Notes Collection. ERDC TN-SWWRP-09-8, Vicksburg, MS: U.S. Army Engineer Research and Development Center. *https://swwrp.usace.army.mil/*

REFERENCES

Alexander, R. B., R. A. Smith, and G. E. Schwarz. 2000. Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. *Nature* 403: 758-761.

American Public Health Association (APHA). 2005. *Standard methods for the examination of water and wastewater.* 21th ed., Washington, DC.

Arango, C. P., J. L. Tank, L. T. Johnson, and S. K. Hamilton. 2008. Assimilatory uptake rather than nitrification and denitrification determined nitrogen removal patterns in streams of varying land use. *Limnology and Oceanography* 53: 2558-2572.

Barko, J. W., and R. M. Smart. 1986. Sediment-related mechanisms of growth limitation in submersed macrophytes. *Ecology* 67**:** 1328-1340.

Bremner, J. M. 1965. Inorganic forms of nitrogen. In *Methods of soil analysis, Part 2: Chemical and microbiological properties*, ed. C. A. Black, 1179-1237. Madison, WI: Am. Soc. Agron.

Forshay, K. J., and E. H. Stanley. 2005. Rapid nitrate loss and denitrification in a temperate river floodplain. *Biogeochemistry* 75: 43-64.

Friedrich, J., C. Dinkel, E. Grieder, S. Rada, D. Secrieru, S. Steingruber, and B. Wehrli. 2003. Nutrient uptake and benthic regeneration in Danube delta lakes. *Biogeochemistry* 64: 373-398.

Goolsby, D. A., W. A. Battaglin, B. T. Aulenbach, and R. P. Hooper. 2001. Nitrogen input to the Gulf of Mexico. *Journal of Environmental Quality* 30: 329-336.

James, W. F., W. B. Richardson, and D. M. Soballe. 2008a. Effects of residence time on summer nitrate uptake in Mississippi River flow-regulated backwaters. *River Research and Applications* 24: 1206-1217.

James, W. F., W. B. Richardson, and D. M. Soballe. 2008b. Contribution of sediment fluxes and transformations to the summer nitrogen budget of an Upper Mississippi River backwater system. *Hydrobiologia* 598: 95-107.

Jensen, K., N. P. Sloth, N. Risgaard-Petersen, S. Rysgaard, and N. P. Revsbech. 1994. Estimation of nitrification and denitrification from microprofiles of oxygen and nitrate in model sediment systems. *Applied and Environmental Microbiology* 60: 2094-2100.

Johnson, B. L., B. C. Knights, J. W. Barko, R. F. Gaugush, D. M. Soballe, and W. F. James. 1998. Estimating flow rates to optimize winter habitat for Centrarchid fish in Mississippi River (USA) backwaters. *Regulated Rivers: Research and Management* 14:499-510.

Kadlec, R. H., and R. L. Knight. 1996. *Treatment wetlands.* CRC Press LLC. Lewis Publishers.

Malecki, L. M., J. R. White, and K. R. Reddy. 2004. Nitrogen and phosphorus flux rates from sediment in the Lower St. Johns River estuary. *Journal of Environmental Quality* 33: 1545-1555.

McClain, M. E., E. W. Boyer, C. L. Dent, S. E. Gergel, N. B. Grimm, P. M. Groffman, S. C. Hart, J. W. Harvey, C. A. Johnston, E. Mayorga, W. H. McDowell, and G. Pinay. 2003. Biogeochemical hot spots and hot moments at interface of terrestrial and aquatic ecosystems. *Ecosystems* 6:301-312.

Mitsch, W. J., J. W. Day, J. W. Gilliam, P. M. Groffman, D. L. Dey, G. W. Randall, and N. Wang. 2001. Reducing nitrogen loading to the Gulf of Mexico from the Mississippi River basin: Strategies to counter a persistent ecological problem. *Bioscience* 51**:** 373-388.

Mulholland, P. J., H. M. Valett, J. R. Webster, S. A. Thomas, L. W. Cooper, S. K. Hamilton, and B. J. Peterson. 2004. Stream denitrification and total nitrate uptake rates measured using a field ^{15}N tracer addition approach. *Limnology and Oceanography* 49: 809-820.

Plumb, R. H. 1981. *Procedures for handling and chemical analysis of sediment and water samples.* Technical Report EPA/CE-81-1. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.

Rabalais, N. N. 2002. Nitrogen in aquatic ecosystems. *Ambio* 31: 102-112.

Reddy, K. R., and R. D. DeLaune. 2008. *Biogeochemistry of wetlands: Science and applications*. Boca Raton, FL: CRC Press, Taylor & Francis Group.

Reddy, K. R., M. M. Fisher, H. Pant, P. Inglett, and J. R. White. 2001. Nutrient exchange between sediment and overlying water column. In *Indian River lagoon hydrodynamics and water quality model: Nutrient storage and transformations in sediments*. St. Johns River Water Management District, Gainsville, FL: 4-1 to 4-52.

Richardson, W. B., E. A. Strauss, L. A. Bartsch, E. M. Monroe, J. C. Cavenaugh, L. Vingum, and D. M. Soballe. 2004. Denitrification in the Upper Mississippi River: Rates, controls, and contribution to nitrate flux. *Canadian Journal of Fisheries and Aquatic Sciences* 61**:** 1102-1112.

Risgaard-Petersen, L. 2003. Coupled nitrification-denitrification in autotrophic and heterotrophic estuarine sediments: On the influence of benthic algae. *Limnology and Oceanography* 48: 93-105.

Rogers, S. J., J. S. Sauer, and S. E. Weick. 2000. Responses of aquatic vegetation to hydrologic modification in the Finger Lakes system. In *Evaluation of hydrologic modification for habitat improvement: The Finger Lakes habitat rehabilitation and enhancement project biological response study.* St. Paul, MN: U.S. Army Corps of Engineers.

Royer, T. V., J. L. Tank, and M. B. David. 2004. Transport and fate of nitrate in headwater agricultural streams in Illinois. *Journal of Environmental Quality* 33: 1296-1304.

Rysgaard, S., N. Risgaard-Petersen, N. P. Sloth, K. Jensen, and L. P. Nielsen. 1994. Oxygen regulation of nitrification and denitrification in sediments. *Limnology and Oceanography* 39: 1643-1652.

Sparks, R. E. 1995. Need for ecosystem management of large rivers and their floodplains. *BioScience* 45**:**168-182.

Tockner, K., D. Pennetzdorfer, N. Reiner, F. Schiemer, and J. V. Ward. 1999. Hydrological connectivity and the exchange of organic matter and nutrients in a dynamic river-floodplain system (Danube, Austria). *Freshwater Biology* 41: 521-535.

Turner, R. E., N. N. Rabalais, and D. Justic. 2006. Predicting summer hypoxia in the northern Gulf of Mexico: Riverine N, P, and Si loading. *Marine Pollution Bulletin* 52: 139-148.

Vitousek, P. M., J. D. Aber, R. W. Howarth, G. E. Likens, P. A. Matson, D. W. Schindler, W. H. Schlesinger, and D. G. Tilman. 1997. Human alteration of the global nitrogen cycle: Sources and consequences. *Ecological Applications* 7:737-750.

Webster, J. R., P. J. Mulholland, J. L. Tank, H. M. Valett, W. K. Dodds, B. J. Peterson, W. B. Bowden, C. N. Dahm, S. Findlay, S. V. Gregory, N. B. Grimm, S. K. Hamilton, S. L. Johnson, E. Marti, W. H. McDowell, J. L. Meyer, D. D. Morrall, S. A. Thomas, and W. M. Wollheim. 2003. Factors affecting ammonium uptake in streams – an inter-biome perspective. *Freshwater Biology* 48: 1329-1352.