Effects of Hydrological Flow Regime on Sediment-water Interface and Water Column Nitrogen Dynamics in a Great Lakes Coastal Wetland (Old Woman Creek, Lake Erie)

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ABSTRACT. *Sediment-water interface nitrogen (N) transformations and water column ammonium cycling rates were measured along a stream to lake gradient at three sites within Old Woman Creek (OWC) and one near-shore Lake Erie site during two hydrological regimes: one with open flow to the lake after a rain event (July 2003), and another with a sand barrier blocking flow (July 2004). Net N_2 effluxes in OWC at all times and at the near-shore Lake Erie site in July 2003 suggest that sediments are a N sink via denitrification. Observed dissimilatory nitrate reduction to ammonium (DNRA) may counteract some of this N removal, particularly when the creek mouth is closed. Upstream, a closed creek mouth led to higher sediment oxygen demand, net N_2 flux, potential DNRA, and potential denitrification rates. The lake site exhibited lower rates of these processes with the creek mouth closed except denitrification potential, which was unchanged. Denitrification in OWC appeared to drive N limitation in the lower wetland when the sand barrier was blocking flow to the lake. Higher potential versus in situ denitrification estimates imply that water column NO_3^- limits and drives denitrification in OWC. Water column to sediment regeneration ratios suggest that sediment recycling may drive primary production in the OWC interior when the creek mouth is closed and new N inputs from runoff are absent, but more data are needed to confirm these apparent trends. Overall, hydrological regime in OWC appeared to have a greater impact on sediment N processes than on water column cycling.*

INDEX WORDS: *Old Woman Creek, Lake Erie, sediments, denitrification, DNRA, regeneration.*

INTRODUCTION

Coastal eutrophication has been implicated in several regional issues affecting human health and the environment, including harmful and nuisance algal blooms, altered food webs, and hypoxia (i.e., Vitousek *et al.* 1997, Nicholls *et al.* 2001, Beeton 2002, Rockwell *et al.* 2005). Coastal wetlands serve as 'metabolic gates' removing excess nutrients from

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runoff water (Wetzel 1992). Phosphorus (P) is considered the main nutrient limiting primary production in most freshwater systems (Schindler 1977). However, nitrogen (N) plays a significant role in driving productivity in all aquatic systems and has been reported as the limiting or co-limiting nutrient in some cases (i.e., Havens 1995). Consequently, identification and quantification of N sources, sinks, and links (An and Gardner 2002) is important to understand effects of anthropogenic eutrophication caused by increased nutrient inputs to aquatic systems.

Unlike P, N occurs in numerous organic and inorganic forms and oxidation states. Biological transformations at the sediment-water interface and in the water column affect N concentrations and distribution. For example, partitioning between two nitrate (NO_3^-) reduction pathways, denitrification and dissimilatory NO_3^- reduction to ammonium (DNRA), can have major feedback effects on system N conservation and availability (Brunet and Garcia-Gil 1996, An and Gardner 2002, Gardner *et al.* 2006). Denitrification, and other processes with N_2 as the end-product (i.e., Hulth *et al.* 2005), results in permanent N removal (a sink) from aquatic systems and may ameliorate eutrophication effects (Seitzinger 1988). N_2 must be fixed back into organic matter (a source) to become bioavailable to most organisms (Capone 2000). DNRA, in contrast, results in N conservation (a link) and converts N into a form (ammonium; NH_4^+) favored by most primary producers (Syrret 1981, Blomqvist *et al.* 1994, Vallino *et al.* 1996).

Old Woman Creek National Estuarine Research Reserve and State Nature Preserve (OWC) is located along the Ohio shoreline of Lake Erie (Fig. 1). OWC is a storm-driven, hypereutrophic coastal wetland with a diverse assemblage of aquatic biota (Klarer and Millie 1992, Lavrentyev *et al.* 2004). The watershed is 79 km^2 and drains primarily agricultural land (Klarer and Millie 1992). Tidal amplitude is insignificant, but wind-driven seiches can result in water level changes up to 0.7 m (http://nerrs.noaa.gov/OldWomanCreek/Tidal.html). A sand barrier created by Lake Erie wave action and along-shore currents blocks flow from OWC during low flow periods, particularly in summer (Tomaszek *et al.* 1997). Water depths are < 1 m in the lower estuary except at the mouth (near the highway bridge), which has depths up to 2 m. The upper estuary consists of a deep, narrow channel, and a railroad right-of-way divides the upper and lower estuary (Klarer and Millie 1992). Bottom
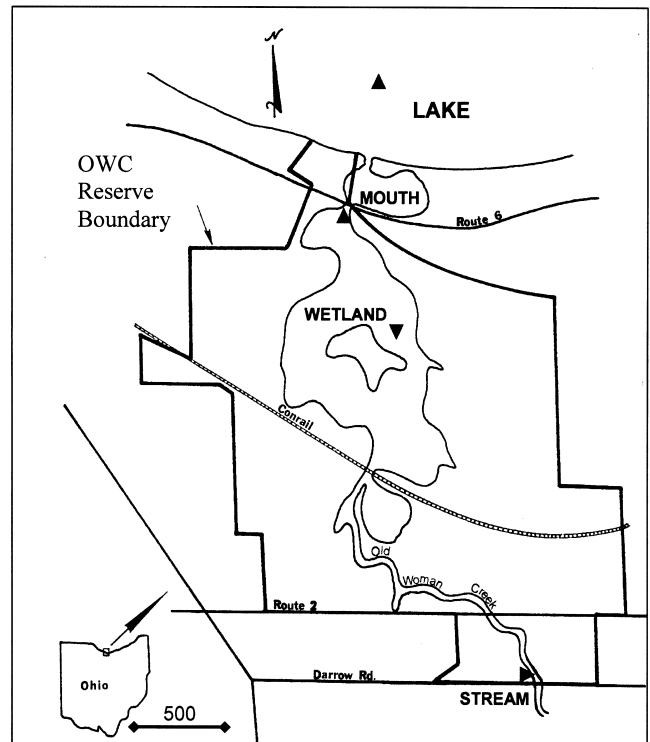
FIG. 1. Map showing location of sampling sites and position of Old Woman Creek relative to western Lake Erie (arrow on lower panel).

sediments often are resuspended by moderate wind events (Krieger 1984, cited by Klarer and Millie 1992).

The objective of this project was to characterize N transformations at the sediment-water interface in Old Woman Creek and compare these results to water column N cycling rates. These data would be used to identify differences in sediment versus water column regeneration during different hydrological regimes (e.g., storm-driven flow versus no flow). It was hypothesized that sediment N regeneration (as the sum of dissolved inorganic N flux and denitrification) would be a more important driver of primary production during nutrient-depleted, "no flow" hydrology, and depth-normalized water column regeneration would increase in relative importance during nutrient-replete storm-driven flow.

METHODS

Field Sampling

Intact sediment cores and water were collected from four sites along a stream-to-lake gradient described previously (Lavrentyev *et al.* 2004). These

sites are referred to as stream, wetland, mouth, and lake (Fig. 1). Stream, wetland, and mouth collectively are referred to as "OWC sites" in some cases where exclusion of the Lake Erie site is informative. Stream and lake sometimes are referred to as "peripheral sites," and wetland and mouth sometimes are combined as "interior sites." Sampling occurred on 2 July 2003 a few days after a storm event, when the sand barrier was breached, allowing flow from the wetland to the lake. The second sampling event occurred on 10 July 2004 when the sand barrier had blocked flow for several weeks. Water samples for ambient nutrient (NH_4^+, NO_3^-, NO_2^-, and o-PO_4^{3-}) analyses were filtered on-site using a rinsed 0.2 μm syringe filter (Osmonics Cameo Nylon-66) and frozen for later analysis (see below). Other water quality data (temperature, pH, turbidity, and dissolved oxygen) were obtained from biweekly (April through October) monitoring results collected by OWC staff on 30 June 2003 and 6 July 2004 with a YSI Model 95 (temperature and dissolved oxygen), YSI Model 60 (pH), and Hach 2100 AN (turbidity). Water samples for NH_4^+ regeneration and potential uptake incubations were collected at each site in rinsed 1 L polyethylene bottles. Water for intact sediment core incubations was collected from each site in rinsed 20 L carboys. Intact sediment cores and overlying water were collected in duplicate at each site from small boats using a PVC handle and a one-way rubber valve (Gardner *et al*. 2006).

Sediment Core Incubations

Intact sediment cores (7.6 cm inner diameter, 15–20 cm length) and overlying water (~ 5 cm, 230 mL) were returned to the lab and fitted with a plunger with O-ring seal and Teflon flow tubes (Lavrentyev *et al*. 2000, An *et al*. 2001, McCarthy and Gardner 2003, Gardner *et al*. 2006). Cores were wrapped with aluminum foil to prevent light effects, submerged in a water bath to maintain temperature, and attached to a peristaltic pump (~1.2 mL min^{-1}) and aerated inflow reservoirs. Sampling began the next day after allowing the cores to reestablish "steady-state conditions" overnight. Inflow and outflow water samples were collected daily as described above for nutrient analyses in 14 mL snap-cap tubes (NO_3^-, NO_2^-, and o-PO_4^{3-}; Falcon) and 8 mL glass screw-cap vials (NH_4^+; Wheaton) to determine sediment-water interface nutrient fluxes. Inflow and outflow water samples for dissolved gas analysis (see below) were col-

lected daily in 15 mL ground-glass stoppered test tubes (Chemglass), preserved with 200 μL 50% $ZnCl_2$, and stored submerged in water (McCarthy *et al*. In Press). Outflow dissolved gas sample tubes were filled from the bottom to force a rising water column and allowed to overflow for at least 20 minutes prior to preservation, capping, and storage. These measures helped prevent atmospheric contamination during sample collection. Dissolved gas samples were analyzed within 1 week. After the first 2 days of incubation and sampling, the inflow reservoirs were enriched with 98+ atom % $^{15}NO_3^-$ (final concentration ~50 μM). Daily inflow and outflow sampling proceeded for another 2 days following isotope addition.

Water Column NH_4^+ Regeneration and Potential Uptake Incubations

Water column N cycling rates were determined in triplicate light and foil-wrapped, dark 70 mL clear polystyrene culture bottles (Corning) amended with 99 atom % $^{15}NH_4^+$. Final amendment concentrations, ambient concentrations, amendment percentage of ambient concentration, and incubation times are presented in Table 1. Biweekly monitoring data collected in preceding weeks by OWC staff were reviewed in an attempt to add a similar $^{15}NH_4^+$ concentration to estimated ambient NH_4^+ concentrations at each site (i.e., amendment percentage of ambient concentration ≅ 100). However, actual ambient concentrations differed from these estimates resulting in amendment percentages ranging from 47 to 409 (Table 1). These enrichment levels are well above the 10% threshold for "tracer" versus "saturating" additions (Paasche 1988). Tracer-level additions involve risk of complete substrate removal and under-estimation of uptake rates, but saturating additions may alter steady-state conditions (Glibert 1988, Paasche 1988). However, rates obtained using these techniques tend to converge in productive aquatic systems (Glibert *et al*. 1982). Ammonium uptake rates from saturating-level isotope additions in the present study were used to prevent complete substrate removal and are therefore qualified as "potential" rates.

Initial samples were collected after spiking (filtered into 8-mL glass vials and frozen as above), and triplicate light and dark culture bottles were placed in a mesh bag and incubated in the creek for ~24 hours (Table 1), when final samples were collected. There has been considerable debate regarding merits and pitfalls of short- versus longer-term

TABLE 1.   Details of $^{15}NH_4^+$ amendments for water column NH_4^+ regeneration and potential uptake incubations. Ambient = initial NH_4^+ concentration (µM) from sampling sites. Amend = final $^{15}NH_4^+$ concentration (µM) in incubation bottles. %Amend = Amend/Ambient*100. Inc Time = total incubation time (h). N/A = not applicable.

Date	Station	Ambient	Amend	%Amend	Inc Time
2-Jul-03	Stream	5.3	16	301	24.9
	Wetland	25.2	16	63	24.7
	Mouth	34.3	16	47	24.5
	Lake	3.1	8	258	24.2
10-Jul-04	Stream	3.9	16	409	24.1
	Wetland	< 0.1	16	N/A	24.0
	Mouth	< 0.1	32	N/A	23.8
	Lake	< 0.1	4	N/A	23.6

incubations, but attempts to determine incubation length effects on NH_4^+ uptake and regeneration measurements have been inconclusive (Glibert 1988, Paasche 1988, Bode *et al.* 2002). In the present study, ~24 hour incubations were used to prevent incubation start/finish time effects by providing ambient day/night light availability. This approach may prevent over-estimation of rates from daylight-only incubations or under-estimation of rates from partial day/night or night-only incubations. Water column N cycling rates from July 2003 experiments were reported previously as associated with microbial food web patterns (Lavrentyev *et al.* 2004). In the present study, these data are combined with results from July 2004 and examined in the context of sediment-water interface N transformation rates and differing hydrological regimes.

Sample Analyses

All water samples were analyzed at the University of Texas Marine Science Institute (UTMSI). Filtered and frozen nutrient samples for NO_3^-, NO_2^-, and o-PO_4^{3-} were analyzed using a Lachat Quikchem 8000 flow injection analyzer. Atom % ^{15}N and total NH_4^+ concentration in samples from the sediment core and water column incubations were measured using high performance liquid chromatography (HPLC, Gardner *et al.* 1995a). Dissolved gases ($^{28}N_2$:Ar, O_2:Ar, $^{29}N_2$, and $^{30}N_2$) were measured using membrane inlet mass spectrometry (MIMS, Kana *et al.* 1994, Kana *et al.* 1998, An *et al.* 2001). The oxygen effect on N_2:Ar measurements associated with MIMS (Eyre *et al.* 2002, Kana and Weiss 2004) was evaluated on the instru-

ment at UTMSI using O_2 removal via Cu-reduction (Eyre *et al.* 2002), but this effect was not significant (McCarthy *et al.* In Press). No effort was made to distinguish between different N_2 production pathways, such as anammox (i.e., Dalsgaard *et al.* 2005) or oxygen-limited autotrophic nitrification-denitrification (OLAND, Kuai and Verstraete 1998). The terms "denitrification," "N_2 production," and "N removal" are intended to encompass all microbial processes with N_2 gas as the end-product.

Calculations and Statistical Analysis

Sediment-water interface N transformations and fluxes were determined by $(C_o - C_i) \times f / a$, where C_o is the outflow concentration in µM (µmol L^{-1}), C_i is the inflow concentration, f is the flow rate (0.072 L h^{-1}), and a is the sediment surface area (0.0045 m^2). Potential denitrification and N fixation (after $^{15}NO_3^-$ addition) calculations were based on the isotope pairing technique (Nielsen 1992) using $^{28, 29, 30}N_2$ measured using MIMS (An *et al.* 2001). Potential DNRA was determined as $^{15}NH_4^+$ production after $^{15}NO_3^-$ addition (An and Gardner 2002). Water column NH_4^+ regeneration and potential uptake were calculated using the Blackburn/Caperon isotope dilution technique (Blackburn 1979, Caperon *et al.* 1979). Water column NH_4^+ regeneration was depth-normalized for comparison with sediment-water interface recycling. Volumetric rates (µmol N L^{-1} h^{-1}) were converted to a depth-averaged areal rate (µmol N m^{-2} h^{-1}) by multiplying the volumetric rate by 1,000 (converting L^{-1} to m^{-3}) and water depth (converting m^{-3} to m^{-2}). Statistical differences between the two hydrological regimes

TABLE 2. *Water column characteristics along the stream-to-lake gradient at Old Woman Creek in July 2003 (Open = storm flow) and July 2004 (Closed = no flow). DO = dissolved oxygen. DIN = dissolved inorganic N = NH_4^+ + NO_3^- + NO_2^-. N/M = not measured.*

Parameter	Units	Stream Open	Closed	Wetland Open	Closed	Mouth Open	Closed	Lake Open	Closed
Temp	°C	20.4	22.5	22.9	22.8	23.4	22.6	20.2	22.9
pH		7.55	7.86	7.42	8.05	7.41	8.05	7.92	8.38
Turbidity	NTU	14.0	17.6	85.2	23.0	62.3	23.8	3.80	42.5
DO	mg L^{-1}	5.04	5.93	3.30	6.94	3.62	6.97	7.34	8.39
NH_4^+	μM	5.3	3.9	25.2	< 0.1	34.3	<0.1	3.1	< 0.1
NO_3^-	μM	74.5	47.2	18.5	2.7	9.8	2.7	54.1	33.3
NO_2^-	μM	0.50	< 0.03	1.03	< 0.03	1.62	< 0.03	0.32	0.27
o-PO_4^{3-}	μM	0.27	0.51	0.21	0.21	0.21	0.24	0.01	0.16
DIN:SRP		297	100	213	13	218	11	5750	210
NH_4^+:NO_x		0.07	0.08	1.30	N/A	3.00	N/A	0.06	N/A
chl *a*	μg L^{-1}	1.5	1.8	10.7	N/M	29.1	22.8	1.4	30.6

were determined using one-way analysis of variance (ANOVA; $p \leq 0.05$).

RESULTS

Water Column Characteristics

Ambient physical and chemical conditions at the four sampling sites are presented in Table 2. Dissolved inorganic N (DIN) concentrations were higher in 2003 reflecting storm runoff into OWC. During no-flow sampling in 2004, DIN concentrations were low enough to cause DIN:o-PO_4^{3-} to be below the Redfield ratio (N:P = 16) at the wetland and mouth sites. High NO_3^- concentrations at stream and lake in both years led to DIN:o-PO_4^{3-} ≥

100. DIN was comprised almost entirely of NO_3^- at all times and sites except the OWC interior sites (wetland and mouth) during the open flow regime.

Sediment-water Interface Nutrient Fluxes

No significant differences in sediment-water interface nutrient fluxes (before isotope addition) were observed between the contrasting hydrological regimes. Fluxes were variable among duplicate cores and between sites (Table 3). The stream site was a minor o-PO_4^{3-} source in both years; more so during storm flow ($p < 0.05$) while other sites were a small o-PO_4^{3-} source during no flow. Only the lake site difference, however, was significant. Gen-

TABLE 3. *Sediment-water interface nutrient fluxes (in μmol N or P m^{-2} h^{-1}; before isotope addition) along the stream-to-lake gradient at Old Woman Creek in July 2003 (Open = storm flow) and July 2004 (Closed = no flow). SE = standard error (n = 4). Positive values indicate flux out of the sediment, and negative values represent flux from the water column into the sediment. Values with the same superscript are significantly different (ANOVA; $p \leq 0.05$).*

	Stream Open	Closed	Wetland Open	Closed	Mouth Open	Closed	Lake Open	Closed
o-PO_4^{3-}	6.48[a]	1.20[a]	−0.11	3.35	−3.57	4.05	−1.43[d]	0.40[d]
SE	1.79	0.48	1.41	1.11	0.96	4.93	0.63	0.14
NH_4^+	161[b]	267[b]	14[c]	151[c]	120	1310	32	−24
SE	22	16	43	20	35	839	41	6
NO_3^-	−147	−169	−28	2	−2	6	−80	8
SE	14	104	13	7	10	4	186	42
NO_2^-	5.11	−3.44	7.27	1.16	8.17	1.36	0.58	−1.61
SE	1.71	4.60	2.24	0.75	3.30	1.48	2.89	1.05

erally, OWC sediments (stream, wetland, and mouth) were an NH_4^+ source, particularly during no flow, although this trend was not significant at the mouth site. No appreciable NH_4^+ flux w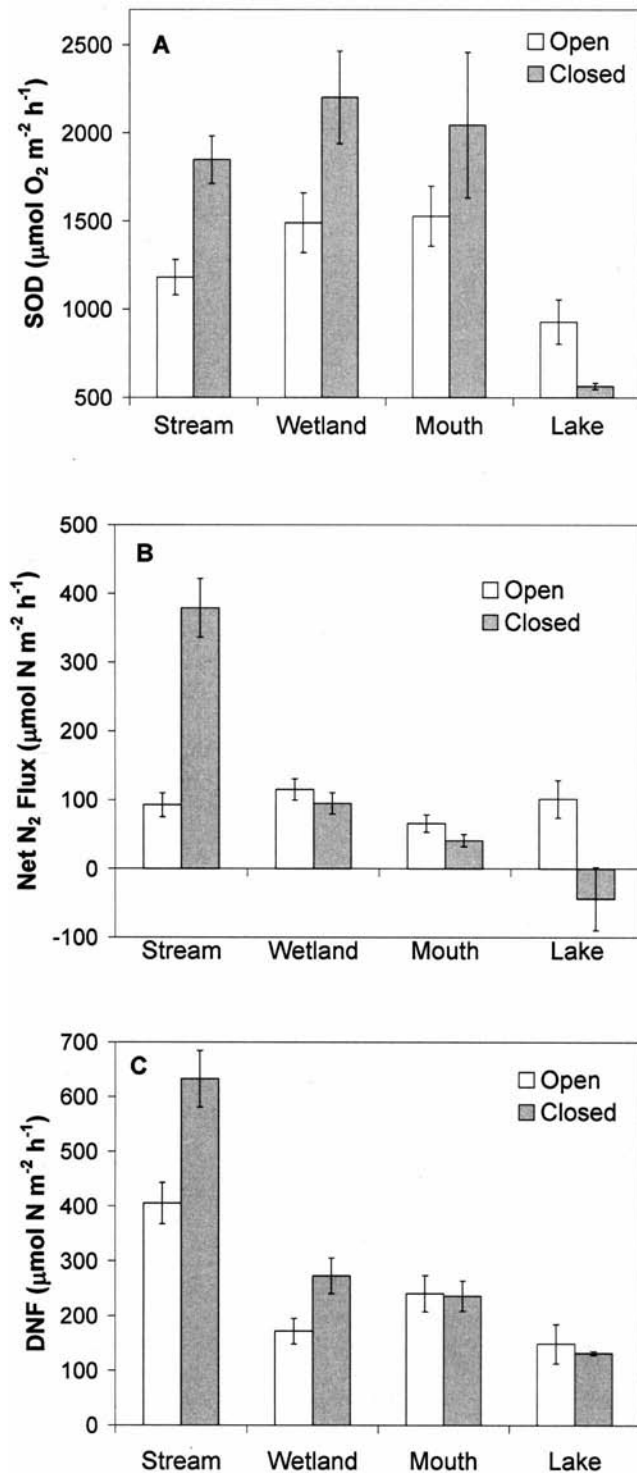as observed from near-shore Lake Erie sediments. The stream site was a NO_3^- sink in both years, and the wetland site was a NO_3^- sink during storm flow. All other NO_3^- fluxes were either very low (mouth site during no flow) or not different from zero due to high core variability. OWC sediments were a small, but significant, NO_2^- source during storm flow versus no flow.

Sediment Oxygen Demand and Net N_2 Flux

Sediment oxygen demand in OWC sediments (before isotope addition) was higher during no flow conditions (Fig. 2A, $p = 0.01$). However, including data from the Lake Erie site, which was higher during storm flow, eliminates the statistical significance. No significant difference was observed in net N_2 flux among sites for the two hydrological regimes ($p = 0.80$). Considered separately, the stream site had almost four times higher net N_2 flux during no flow versus storm flow, while the lake site had positive net N_2 flux during storm flow and no apparent flux during no flow (Fig. 2B).

Potential Denitrification, N Fixation, and DNRA

Potential denitrification (after $^{15}NO_3^-$ addition) was higher during no flow at stream and wetland, but no difference was observed at mouth or lake (Fig. 2C). Ratios of potential denitrification fueled by ^{15}N versus ^{14}N (Fig. 3A) show that, in most cases, added $^{15}NO_3^-$ was a more important substrate than ambient $^{14}NO_3^-$, with the lake site as a notable exception. Despite observing negative net N_2 flux before isotope addition in one lake core during no flow conditions, calculations failed to identify any potential N fixation at any site in either year. No potential DNRA was observed at the near-shore Lake Erie site, but positive DNRA was observed at OWC sites (Fig. 3B). A large spike in

FIG. 2. *Sediment-water interface process rates in Old Woman Creek and near-shore Lake Erie sediments in July 2003 (Open = storm flow) and July 2004 (Closed = no flow). A. Sediment oxygen demand (SOD; in μmol O_2 m^{-2} h^{-1}; before isotope addition). Means for the two hydrological regimes are significantly different (ANOVA; p = 0.01) if the Lake Erie site is excluded. B. Net N_2 flux (in μmol N m^{-2} h^{-1}; before isotope addition). C. Potential denitrification (in μmol N m^{-2} h^{-1}; after $^{15}NO_3^-$ addition).*

potential DNRA was observed at mouth during no flow conditions, but duplicate core variability was high. Overall, there were no statistical differences between the two flow regimes for either potential denitrification or DNRA, even after excluding the lake site.
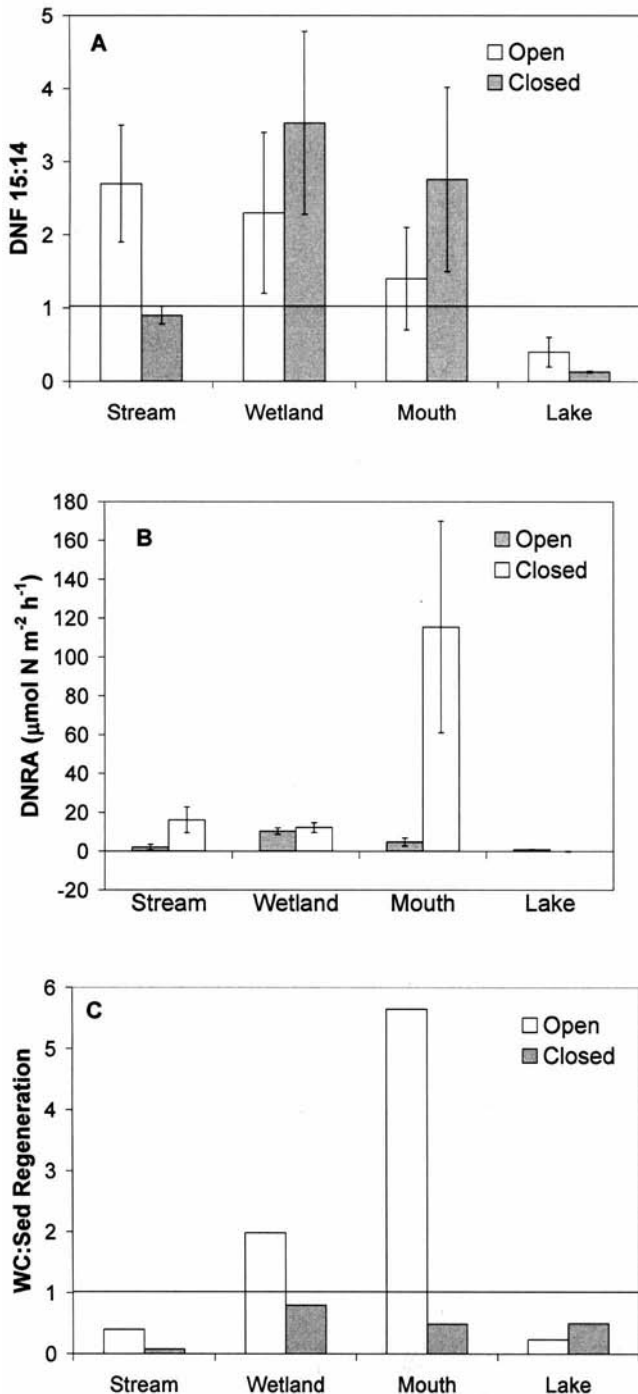
Water Column NH_4^+ Regeneration and Potential Uptake

Hereafter, NH_4^+ regeneration and potential uptake will be referred to as "regeneration" and "uptake." No significant differences were observed in light or dark water column N cycling rates between the two hydrological regimes for the system as a whole. However, light uptake was higher than dark uptake when there was no flow and the near-shore Lake Erie site was excluded. Also, consideration of sites individually (Table 4) or grouped as "interior" (wetland and mouth) and "peripheral" (stream and lake) resulted in some differences. All water column N cycling rates were significantly higher at the OWC interior sites than peripheral sites. Light uptake was higher than dark uptake in all cases except the lake site during storm flow, and light uptake was higher than light regeneration in all cases except the lake site during no flow. Depth-averaged water column NH_4^+ regeneration was lower than areal sediment regeneration at all sites during no flow (WC:Sed < 1, Fig. 3C) but two to nearly six times higher than sediment regeneration at interior sites during storm flow.

DISCUSSION

Water Chemistry and Nutrient Limitation

In most cases, water chemistry (Table 2) supported the general observation that P limits primary production (i.e., DIN: o-PO_4^{3-} > 16) in temperate freshwater systems (Schindler 1977). Despite ele-

FIG. 3. *A. Ratio of denitrification fueled by added $^{15}NO_3^-$ (measured as $^{29\&30}N_2$) to denitrification of the ambient $^{14}NO_3^-$ pool, including originating from nitrification, in Old Woman Creek and near-shore Lake Erie sediments in July 2003 (Open = storm flow) and July 2004 (Closed = no flow). A value above 1 indicates a higher importance for overlying water NO_3^-, and a value below 1 indicates a higher reliance on denitrification coupled to nitrification. B. Potential dissimilatory NO_3^- reduction to NH_4^+ (DNRA; measured as $^{15}NH_4^+$ production; in µmol N m^{-2} h^{-1}; after $^{15}NO_3^-$ addition). C. Ratio of depth-averaged water column (WC) to sediment (Sed) regeneration (sum of DIN flux and denitrification). A value above 1 indicates a higher importance for water column regeneration as a driver of primary production.*

TABLE 4.   Water column NH_4^+ regeneration and potential uptake (in µmol N L^{-1} h^{-1}) along the stream-to-lake gradient at Old Woman Creek in July 2003 (Open = storm flow) and July 2004 (Closed = no flow). SE = standard error (n = 3). Values with the same superscript are significantly different (ANOVA; p ≤ 0.05).

	Stream Open	Closed	Wetland Open	Closed	Mouth Open	Closed	Lake Open	Closed
Reg (L)	0.075[l]	0.091[n]	0.381[b,p]	0.570[b,r]	0.548[t]	0.381[v]	0.048[g,w]	0.116[g]
SE	0.037	0.023	0.036	0.007	0.115	0.025	0.004	0.005
Reg (D)	0.044	0.106	0.415	0.432	0.497[e]	0.373[e]	0.084[h]	0.113[h]
SE	0.082	0.011	0.072	0.023	0.071	0.032	0.006	0.002
Uptake (L)	0.151[a,k,l]	0.531[a,m,n]	0.683[c,o,p]	1.247[c,q,r]	1.820[f,s,t]	1.089[f,u,v]	0.068[i,w]	0.120[i,x]
SE	0.031	0.009	0.049	0.014	0.131	0.049	0.002	0.007
Uptake (D)	0.061[k]	0.183[m]	0.195[d,o]	0.482[d,q]	0.251[s]	0.244[u]	0.068[j]	0.041[j,x]
SE	0.096	0.007	0.090	0.030	0.073	0.004	0.007	0.005

mental ratios mostly suggesting P limitation, observed total nutrient concentrations were high and may argue against nutrient limitation in OWC, as suggested by Heath (1992). However, when the sand barrier was blocking flow from OWC to Lake Erie, results suggested that the OWC interior (wetland and mouth) may become N limited (or co-limited). DIN:o-PO_4^{3-} at these sites were below the Redfield ratio at 13.1 and 11.4, respectively, during no flow. DIN:o-PO_4^{3-} may not be the best proxy for nutrient limitation (Dodds 2003), but total N and P data were not available for this study.

DIN was comprised almost entirely of less-favored NO_3^- (Syrret 1981, Table 2), despite higher sediment NH_4^+ efflux (includes DNRA, Table 3). Predominance of NO_3^- also was observed in July 1994 in the OWC interior (NO_3^- > 300 µM, NH_4^+ ≅ 0.5 µM, Tomaszek *et al.* 1997). Most algae prefer NH_4^+ to NO_3^- for growth (Dugdale and Goering 1967), and without new N inputs from runoff, it follows that NH_4^+ would be depleted before NO_3^-. Diatoms, which are superior competitors for NO_3^- (Syrret 1981), historically have dominated the phytoplankton community in OWC (Klarer and Millie 1992). However, the phytoplankton assemblage during storm flow was comprised mostly of cryptophytes, euglenophytes, and chlorophytes (Lavrentyev *et al.* 2004), which presumably prefer NH_4^+. Macrophytes also are abundant in the OWC interior (Klarer and Millie 1992, Francko and Whyte 1999), and these plants probably were a large factor in observed NH_4^+ depletion as well. Despite the presence of DIN as NO_3^-, primary pro-

ducers may need to compete for scarce, but more suitable, NH_4^+, especially during no flow, and may effectively be N limited regardless of elemental ratios.

Denitrification and Apparent N Limitation

Since N fixation was not quantified by calculations, it is reasonable to assume that net N_2 flux before isotope addition represents an estimate of in situ denitrification. Excluding the lake site (net N_2 flux not different from zero), these estimates ranged from 41 to 380 µmol N m^{-2} h^{-1} during no flow conditions (Fig. 2B). Net N_2 flux was not higher at OWC interior sites during no flow conditions, but nearly four times higher N removal at the stream site (Figs. 2C) may contribute to apparent N limitation at these sites. Unless atmospheric N_2 is fixed back to organic matter, denitrification results in permanent removal from the system and can drive systems toward N limitation (Seitzinger 1988) in the absence of new inputs, such as during no flow in OWC. Results from Taihu Lake (China, McCarthy *et al.* In press) and a constructed wetland in Texas (Dr. Thad Scott, Baylor University, unpublished data) showed a similar pattern of denitrification upstream perhaps driving downstream N deficiency.

Sources of NO_3^- for Denitrification

Potential denitrification rates (after $^{15}NO_3^-$ addition) during no flow at OWC sites ranged from 240 to 630 µmol N m^{-2} h^{-1}, and rates at stream and wetland were significantly higher compared to storm

flow conditions (Fig. 3C). Nitrification and denitrification often proceed at rates far below their potential but may accelerate under appropriate conditions (Bowden 1987). Higher potential versus *in situ* denitrification estimates in OWC (e.g., $^{15}NO_3^-$ addition stimulated N_2 production) suggest that nitrification does not provide as much NO_3^- as the ambient denitrifying population can process. The ratio of potential denitrification at OWC sites from added $^{15}NO_3^-$ (as $^{29\ or\ 30}N_2$) versus the ambient $^{14}NO_3^-$ pool (as $^{28}N_2$, Fig. 3A), including NO_3^- originating from nitrification, further suggests that overlying water is the primary NO_3^- source driving denitrification (i.e., 15:14 > 1). Ambient water column NO_3^- concentrations during no flow were lower than during storm flow, but NO_3^- still was present in the water column (range 2.7–47 µM, Table 2).

Comparison with Previously Reported Denitrification Rates in OWC

The rates reported above are much lower than dark incubation rates estimated in July 1994 (no flow) using an in vitro N_2 flux technique (~730 µmol N m^{-2} h^{-1}) and an *in situ* benthic chamber (~1,000 µmol N m^{-2} h^{-1}, Tomaszek *et al.* 1997). The temperature of the incubations in July 1994 was 28°C versus 20.2–23.4°C in the present study, and denitrification rates in OWC increased by four times over a temperature range of 13–27°C (Tomaszek *et al.* 1997). This factor seems a likely caveat to comparison between rates from the present and referenced studies.

Perhaps the most noteworthy methodological difference between N removal results from the present study and those referenced is the use of a continuous-flow incubation system versus static systems, respectively. The continuous-flow system was designed to maintain oxic overlying water in the intact sediment cores during the 5 day incubation, and water flowing out of the intact core chambers remained oxic throughout the incubation. Minimal change in O_2 penetration depth over 5 days was observed in the incubation system versus large changes in O_2 penetration depth in a static incubation lasting just 6 hours (Bernot *et al.* 2003). The shallow, wind-mixed water column in OWC rarely becomes hypoxic (Heath 1992). Thus, higher denitrification rates (as in Tomaszek *et al.* 1997) might be expected if lower O_2 concentration, and perhaps sulfate reduction (Joye and Hollibaugh 1995, Brunet and Garcia-Gil 1996), inhibits nitrification and/or shortens the diffusive distance for overlying

water NO_3^- in static incubations. However, the dark static chambers used in July 1994 remained aerobic after 3 days (294 µM initial to 200 µM final) despite SOD's ranging from 2,100 to 3,000 µmol O_2 m^{-2} h^{-1} (Tomaszek *et al.* 1997). This result implies O_2 contamination either in the incubation chambers or samples between collection and analysis, since a tight system with these SOD's should go anoxic quickly without new O_2 added (as in continuous flow chambers). Measured SOD's at OWC sites in the present study (~1,200 to 2,200 µmol O_2 m^{-2} h^{-1}; Fig. 2A) were similar to the lower end of rates reported in Tomaszek *et al.* (1997).

Water Column NH_4^+ Regeneration and Uptake

Light NH_4^+ regeneration and uptake rates in OWC (lake site excluded) were similar to rates, determined by comparable methods, from subtropical, eutrophic Taihu Lake (China, McCarthy *et al.* In Press) and south Texas coastal estuaries (McCarthy *et al.* unpublished data), lower than rates from tropical, eutrophic Lake Maracaibo (Gardner *et al.* 1998), and higher than rates from Lake Erie (this study and McCarthy *et al.* unpublished data), Lake Michigan (Gardner *et al.* 2004), Saginaw Bay (Lake Huron, Gardner *et al.* 1995b), Florida Bay (Gardner *et al.* unpublished data), and the Mississippi River plume (Gulf of Mexico, Gardner *et al.* 1997).

Considering the effects of hydrological regime, light uptake was higher during storm flow conditions at the mouth site (Table 4), which was unexpected considering the absence of water column NH_4^+ during no flow and high NH_4^+ concentration during storm flow (Table 2). In the absence of NH_4^+, phytoplankton might be expected to respond more vigorously to added NH_4^+ than when NH_4^+ is available. This expectation was met at the wetland and lake sites, which also had no measurable water column NH_4^+ during no flow (Table 2).

System residence times are lower, and turbidity and turbulence are higher, in OWC during storm flow (Klarer and Millie 1989, 1994). With the exception of the mouth site, higher uptake rates during no flow may reflect a more favorable light climate under static conditions within OWC, particularly at the narrow stream site, and much longer system residence times. During storm flow, short system residence times and a poor light climate due to resuspended sediments may give primary producers less opportunity to use nutrients discharged into OWC by runoff. In contrast, long residence times during no flow lead to near-complete removal

of available NH_4^+ via phytoplankton/plant and bacterial (i.e., nitrification) uptake. System flushing and dilution of phytoplankton biomass (Klarer and Millie 1994) also may cause lower NH_4^+ cycling rates during storm flow.

A drawback to bottle incubations for measuring nutrient cycling rates is isolation from physical and atmospheric factors (i.e., Schindler 1977). However, whole-system measurements often are not practical, particularly for stable isotope techniques. It seems intuitive that bottle incubations during no flow represent *in situ* conditions better than those during storm flow. The enclosure of turbulent and turbid water may have allowed more efficient use of available nutrients, perhaps leading to over-estimation of uptake rates. Settling of suspended solids after enclosure also may have provided a more suitable light environment, again leading to over-estimation of uptake rates. Assuming that such bottle effects are larger for storm flow incubations, it follows that differences between hydrological regimes (i.e., higher rates during no flow than storm flow) are conservative except at the mouth site (higher rates during storm flow).

Water Column Versus Sediment Regeneration

We hypothesized that water column regeneration would increase in importance during storm flow, while sediment regeneration would drive primary production during no flow due to water column nutrient depletion. Depth-averaged water column NH_4^+ regeneration rates were lower than sediment regeneration rates (WC:Sed < 1 in Fig. 3C) in all cases except at the wetland and mouth sites during storm flow. These observations support our hypothesis in the OWC interior but not at peripheral sites, which are more physically dynamic. Dark incubations during storm flow demonstrated that bacteria contribute to water column NH_4^+ regeneration within the creek proper when N is abundant (Lavrentyev *et al.* 2004). Significant sediment DIN efflux was not observed at the lake site in either year or the wetland site during storm flow (Table 3). In these cases, water column regeneration was the only internal N source available for primary producers. Although denitrification is a regeneration process, resulting N_2 is not immediately available to most primary producers. If denitrification is excluded, water column regeneration also exceeded sediment DIN efflux at the stream site during storm flow and at the wetland site during no flow.

Potential DNRA was observed at all OWC sites, but only the mouth site during no flow exhibited any significant contribution from DNRA relative to denitrification (DNF:DNRA = 2; all others > 17; data not shown). DNRA usually is associated with sulfidic marine sediments (Brunet and Garcia-Gil 1996) but also can account for 30% of NO_3^- reduction in some lake sediments (Tiedje 1988). DNRA contributed significant but generally small amounts of sediment NH_4^+ efflux in Taihu Lake (McCarthy *et al.* In Press) and a Texas wetland (Dr. Thad Scott, Baylor University, unpublished data).

Since sediment NH_4^+ efflux (includes DNRA) comprised the largest proportion of total sediment regeneration readily available for primary producers (i.e., excluding denitrification), it is useful to compare depth-averaged water column NH_4^+ regeneration to sediment NH_4^+ efflux (WC:sNH_4^+). No significant NH_4^+ flux in either direction during storm flow and NH_4^+ influx during no flow make this comparison impossible at the lake site. However, some interesting observations emerge within OWC. At the stream site, WC:sNH_4^+ was 0.28 and 0.20 during storm and no flow, respectively. Water column NH_4^+ regeneration was not significantly different at this site during the two hydrological regimes (Table 4), but sediment NH_4^+ efflux was higher during no flow (Table 3), which explains the decrease in WC:sNH_4^+. At the wetland site during storm flow, sediment NH_4^+ efflux was not different from zero (Table 3), and water column regeneration was high. Water column NH_4^+ regeneration increased and still exceeded sediment NH_4^+ efflux during no flow (WC:sNH_4^+ = 2.3), although the sediment component increased in importance. The wetland site has many rooted macrophytes, which may provide refuge for water column grazers (i.e., regenerators, Klarer and Millie 1994) and absorb NH_4^+ mineralized in the sediments through their roots (i.e., Brix *et al.* 2002), thus increasing the water column component while decreasing the sediment component, respectively.

The mouth site provided the best fit for our hypothesis regarding water column versus sediment regeneration during storm and no flow. Water column regeneration far exceeded sediment NH_4^+ efflux during storm flow (WC:sNH_4^+ = 9.1), but the opposite was observed during no flow (WC:sNH_4^+ = 0.6). Neither the water column (Table 4) nor sediment (Table 3) component changed significantly from storm to no flow, but lower water column regeneration and, especially, increased sediment regeneration perhaps were masked by high replicate variability. This site is too deep for rooted macro-

phytes (~2 m) and furthest from inflows via the stream, so organic matter moving downstream may accumulate here when flow to Lake Erie is blocked. Ultimately, sediment NH_4^+ efflux in OWC, particularly at the stream and mouth sites, may have a more important role in driving primary production than water column regeneration during no flow conditions.

o-PO$_4^{3-}$ Flux and Hydrological Regime

During storm flow conditions, sediments at the stream site were a five-fold higher o-PO$_4^{3-}$ source than during no flow conditions (Table 3). This observation may reflect sediment P release driven by physical resuspension in the narrow stream channel. In contrast, no significant differences in sediment P flux were observed between storm and no flow conditions in the broader OWC interior (wetland and mouth). Higher water column total P concentrations were observed in mesocosms deployed in OWC with benthivorous fish driving sediment resuspension (Havens 1991). However, higher sediment P release at the stream site during storm flow in the present study did not lead to higher o-PO$_4^{3-}$ concentration at the site or downstream (Table 2). The opposite trend was observed at the near-shore Lake Erie site, which was an o-PO$_4^{3-}$ sink during storm flow and a small source during no flow. At this site, observed sediment P release did coincide with higher water column o-PO$_4^{3-}$ concentration.

CONCLUSIONS

Ambient nutrient ratios indicated that sites in the broad OWC interior may become N limited when flow from OWC to Lake Erie is blocked by a sand barrier. This observation may be due in part to increased denitrification and N uptake by plants and phytoplankton, particularly at upstream sites. Results from this study suggest an important role for internal nutrient recycling in OWC, particularly during no flow conditions. Further, the magnitude and relative importance of sediment-generated internal nutrients increased during no flow hydrology. This observation was particularly the case for NH_4^+, which was released from OWC sediments via mineralization and, to a lesser extent, DNRA.

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