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)

Mark J. McCarthy¹*, Wayne S. Gardner¹, Peter J. Lavrentyev², Kenneth M. Moats², Frank J. Jochem³, and David M. Klarer⁴

¹The University of Texas at Austin
Marine Science Institute
750 Channel View Drive
Port Aransas, Texas 78373

²The University of Akron
Department of Biology
Akron, Ohio 44325

³Florida International University
Marine Biology Program
3000 NE 151 Street AC-1-379
North Miami, Florida 33181

⁴Old Woman Creek National Estuarine Research Reserve
2514 Cleveland Road
East Huron, Ohio 44839

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 N₂ 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 N₂ 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 NO₃⁻ 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
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 (Syrett 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 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 collected 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
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 instrument 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 $(C_o - C_i) x f / a$, 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 1. Details of $^{15}$NH$_4^+$ amendments for water column NH$_4^+$ regeneration and potential uptake incubations.

<table>
<thead>
<tr>
<th>Date</th>
<th>Station</th>
<th>Ambient</th>
<th>Amend</th>
<th>%Amend</th>
<th>Inc Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Jul-03</td>
<td>Stream</td>
<td>5.3</td>
<td>16</td>
<td>301</td>
<td>24.9</td>
</tr>
<tr>
<td></td>
<td>Wetland</td>
<td>25.2</td>
<td>16</td>
<td>63</td>
<td>24.7</td>
</tr>
<tr>
<td></td>
<td>Mouth</td>
<td>34.3</td>
<td>16</td>
<td>47</td>
<td>24.5</td>
</tr>
<tr>
<td></td>
<td>Lake</td>
<td>3.1</td>
<td>8</td>
<td>258</td>
<td>24.2</td>
</tr>
<tr>
<td>10-Jul-04</td>
<td>Stream</td>
<td>3.9</td>
<td>16</td>
<td>409</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td>Wetland</td>
<td>&lt; 0.1</td>
<td>16</td>
<td>N/A</td>
<td>24.0</td>
</tr>
<tr>
<td></td>
<td>Mouth</td>
<td>&lt; 0.1</td>
<td>32</td>
<td>N/A</td>
<td>23.8</td>
</tr>
<tr>
<td></td>
<td>Lake</td>
<td>&lt; 0.1</td>
<td>4</td>
<td>N/A</td>
<td>23.6</td>
</tr>
</tbody>
</table>
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$_4^{3-}\geq 100$. 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 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.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Stream Units</th>
<th>Open</th>
<th>Wetland Closed</th>
<th>Mouth Closed</th>
<th>Open</th>
<th>Lake Closed</th>
<th>Open</th>
<th>Closed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °C</td>
<td>20.4</td>
<td>22.5</td>
<td>22.9</td>
<td>22.8</td>
<td>23.4</td>
<td>22.6</td>
<td>20.2</td>
<td>22.9</td>
</tr>
<tr>
<td>pH</td>
<td>7.55</td>
<td>7.86</td>
<td>7.42</td>
<td>8.05</td>
<td>7.41</td>
<td>8.05</td>
<td>7.92</td>
<td>8.38</td>
</tr>
<tr>
<td>Turbidity NTU</td>
<td>14.0</td>
<td>17.6</td>
<td>85.2</td>
<td>23.0</td>
<td>62.3</td>
<td>23.8</td>
<td>3.80</td>
<td>42.5</td>
</tr>
<tr>
<td>DO mg L$^{-1}$</td>
<td>5.04</td>
<td>5.93</td>
<td>3.30</td>
<td>6.94</td>
<td>3.62</td>
<td>6.97</td>
<td>7.34</td>
<td>8.39</td>
</tr>
<tr>
<td>NH$_4^+$ µM</td>
<td>5.3</td>
<td>3.9</td>
<td>25.2</td>
<td>&lt; 0.1</td>
<td>34.3</td>
<td>&lt; 0.1</td>
<td>3.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>NO$_3^-$ µM</td>
<td>74.5</td>
<td>47.2</td>
<td>18.5</td>
<td>2.7</td>
<td>9.8</td>
<td>2.7</td>
<td>54.1</td>
<td>33.3</td>
</tr>
<tr>
<td>NO$_2^-$ µM</td>
<td>0.50</td>
<td>&lt; 0.03</td>
<td>1.03</td>
<td>&lt; 0.03</td>
<td>1.62</td>
<td>&lt; 0.03</td>
<td>0.32</td>
<td>0.27</td>
</tr>
<tr>
<td>o-PO$_4^{3-}$ µM</td>
<td>0.27</td>
<td>0.51</td>
<td>0.21</td>
<td>0.21</td>
<td>0.21</td>
<td>0.24</td>
<td>0.01</td>
<td>0.16</td>
</tr>
<tr>
<td>DIN:SRP</td>
<td>297</td>
<td>100</td>
<td>213</td>
<td>13</td>
<td>218</td>
<td>11</td>
<td>5750</td>
<td>210</td>
</tr>
<tr>
<td>NH$_4^+$:NO$_3^-$</td>
<td>0.07</td>
<td>0.08</td>
<td>1.30</td>
<td>N/M</td>
<td>3.00</td>
<td>N/A</td>
<td>0.06</td>
<td>N/A</td>
</tr>
<tr>
<td>chl $a$ µg L$^{-1}$</td>
<td>1.5</td>
<td>1.8</td>
<td>10.7</td>
<td>N/M</td>
<td>29.1</td>
<td>22.8</td>
<td>1.4</td>
<td>30.6</td>
</tr>
</tbody>
</table>

### 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; \( p \leq 0.05 \)).

<table>
<thead>
<tr>
<th></th>
<th>Stream Open</th>
<th>Closed</th>
<th>Wetland Open</th>
<th>Closed</th>
<th>Mouth Open</th>
<th>Closed</th>
<th>Lake Open</th>
<th>Closed</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-PO$_4^{3-}$</td>
<td>6.48$^a$</td>
<td>1.20$^a$</td>
<td>-0.11</td>
<td>3.35</td>
<td>-3.57</td>
<td>4.05</td>
<td>-1.43$^d$</td>
<td>0.40$^d$</td>
</tr>
<tr>
<td>SE</td>
<td>1.79</td>
<td>0.48</td>
<td>1.41</td>
<td>1.11</td>
<td>0.96</td>
<td>4.93</td>
<td>0.63</td>
<td>0.14</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>161$^b$</td>
<td>267$^b$</td>
<td>14$^c$</td>
<td>151$^c$</td>
<td>120</td>
<td>1310</td>
<td>32</td>
<td>-24</td>
</tr>
<tr>
<td>SE</td>
<td>22</td>
<td>16</td>
<td>43</td>
<td>20</td>
<td>35</td>
<td>839</td>
<td>41</td>
<td>6</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>-147</td>
<td>-169</td>
<td>-28</td>
<td>2</td>
<td>-2</td>
<td>6</td>
<td>-80</td>
<td>8</td>
</tr>
<tr>
<td>SE</td>
<td>14</td>
<td>104</td>
<td>13</td>
<td>7</td>
<td>10</td>
<td>4</td>
<td>186</td>
<td>42</td>
</tr>
<tr>
<td>NO$_2^-$</td>
<td>5.11</td>
<td>-3.44</td>
<td>7.27</td>
<td>1.16</td>
<td>8.17</td>
<td>1.36</td>
<td>0.58</td>
<td>-1.61</td>
</tr>
<tr>
<td>SE</td>
<td>1.71</td>
<td>4.60</td>
<td>2.24</td>
<td>0.75</td>
<td>3.30</td>
<td>1.48</td>
<td>2.89</td>
<td>1.05</td>
</tr>
</tbody>
</table>
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 was 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-
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 noflow. 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$_3^-$ (Syrett 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$_3^-$ (Syrett 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 producers 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

**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; $p \leq 0.05$).

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