Nitrogen Removal and Greenhouse Gas Emissions from Constructed Wetlands Receiving Tile Drainage Water

Tyler A. Groh, Lowell E. Gentry, and Mark B. David*

Abstract

Loss of nitrate from agricultural lands to surface waters is an important issue, especially in areas that are extensively tile drained. To reduce these losses, a wide range of in-field and edge-of-field practices have been proposed, including constructed wetlands. We re-evaluated constructed wetlands established in 1994 that were previously studied for their effectiveness in removing nitrate from tile drainage water. Along with this re-evaluation, we measured the production and flux of greenhouse gases (GHGs) (CO₂, N₂O, and CH₄). The tile inlets and outlets of two wetlands were monitored for flow and N during the 2012 and 2013 water years. In addition, seepage rates of water and nitrate under the berm and through the riparian buffer strip were measured. Greenhouse gas emissions from the wetlands were measured using floating chambers (inundated fluxes) or static chambers (terrestrial fluxes). During this 2-yr study, the wetlands removed 56% of the total inlet nitrate load, likely through denitrification in the wetland. Some additional removal of nitrate occurred in seepage water by the riparian buffer strip along each berm (6.1% of the total inlet load, for a total nitrate removal of 62%). The dominant GHG emitted from the wetlands was CO₂, which represented 75 and 96% of the total GHG emissions during the two water years. The flux of N₂O contributed between 3.7 and 13% of the total cumulative GHG flux. Emissions of N₂O were 3.2 and 1.3% of the total nitrate removed from wetlands A and B, respectively. These wetlands continue to remove nitrate at rates similar to those measured after construction, with relatively little GHG gas loss.

Hypoxia in the benthic zone of the Gulf of Mexico occurs each summer and is driven by the decomposition of algae that grow to excess primarily from inputs of nitrate delivered via the Mississippi River (Rabalais et al., 1996; Mitsch et al., 2001; Turner et al., 2012). Much of the nitrate in the Mississippi River originates from the upper Midwest, where tile-drained corn and soybean fields are the dominant source (David et al., 2010). There is a wide range of in-field and edge-of-field methods that can be used in agricultural production systems to reduce these nitrate losses (USEPA, 2008). In-field methods include reducing fertilizer N rates, improving the synchrony of fertilizer application and crop uptake, using nitrification inhibitors, switching to slow release fertilizers, and using cover crops (USEPA, 2008). Edge-of-field N reduction methods provide farmers with an alternative way to reduce the amount of nitrate lost from their fields without having to change their farming practices and include drainage water management, saturated lateral buffers, woodchip bioreactors, and constructed wetlands (Woli et al., 2010; Chun et al., 2010; Robertson, 2010; Skaggs et al., 2012; Jaynes and Isenhart, 2014).

Constructed wetlands have been shown to be effective in removing nitrate from tile-drainage water (e.g., Kovacic et al., 2000; Crumpton et al., 2008). However, most studies have been conducted on wetlands in the first few years after construction, and their long-term effectiveness is poorly documented. Wetland nitrate removal processes include plant and periphyton uptake and microbial denitrification (Baker, 1998; Mitsch et al., 1999; Mitsch et al., 2000; Day et al., 2003; O’Geen et al., 2010). Previous research has shown that denitrification is the dominant nitrate removal mechanism for these wetlands (Xue et al., 1999; Kovacic et al., 2000; Larson et al., 2000; Hoagland et al., 2001). However, microbial denitrification may have a potential drawback: nitrous oxide (N₂O) emissions (Sylvia et al., 2005; Brady and Weil, 2008; Schlesinger and Bernhardt, 2013). Even though N₂O is often a small portion of the end product of denitrification, N₂O is a potent greenhouse gas (GHG) that is 310 times stronger than the warming potential of carbon dioxide (CO₂) (Xue et al., 1999; Sylvia et al., 2005; Solomon et al., 2007; Schlesinger and Bernhardt, 2013). Therefore, it is important...
to evaluate this potential environmental tradeoff between tile nitrate remediation and GHG emissions when considering the overall effectiveness of constructed wetlands receiving tile drainage water.

Other GHGs that are released by wetlands include CO$_2$ and methane (CH$_4$). Wetlands emit CO$_2$ via aerobic and anaerobic organic matter decomposition (Bernal and Mitsch, 2008; Brady and Weil, 2008). Wetlands have the tendency to build soil organic carbon during anaerobic periods, which could also be released as CO$_2$ during decomposition after wetland dry down (Mitsch and Gosselink, 2007). Methane production in wetlands generally follows the removal of nitrate from the water column because nitrate has been shown to have an inhibitory effect on methanogenesis (D’Angelo and Reddy, 1999; Stadmark and Bernhardt, 2013). Although the flux of CH$_4$ from wetlands is generally much less than CO$_2$, CH$_4$ is 21 times more potent as a GHG than CO$_2$ (Solomon et al., 2007).

As a nutrient loss reduction strategy, constructed wetlands need to be further evaluated for the potential environmental tradeoff between nitrate removal and GHG production (Thiere et al., 2011; Iowa Nutrient Reduction Strategy, 2013). Our objectives were (i) to determine nitrate removal for constructed wetlands receiving tile drainage after 18 yr of operation and (ii) to estimate GHG fluxes from terrestrial and inundated zones of the wetlands, focusing on N$_2$O emissions.

**Materials and Methods**

**Study Site**

Wetlands A and B are located in the Embarras River Watershed in east-central Illinois, 32 km south of Champaign, IL, and have been studied previously (Kovacic et al., 2000; Larson et al., 2000; Hoagland et al., 2001). They were constructed in 1994 on Colo series soil, a fine-silty, mixed, superactive, mesic Cumulic Endoaquoll in the floodplain of the Embarras River. Wetland A had swaths of soil excavated and removed, whereas the original soil profile (wetland B) remained undisturbed. The soil that was excavated from wetland A was used to build a berm around both wetlands A and B approximately 15.3 m from the Embarras River, which created a riparian buffer strip between the wetland and the river. The berms were compacted with a sheep’s foot roller to minimize water leakage/seepage; however, it was determined that substantial seepage occurred (Larson et al., 2000). Tile drainage areas for wetlands A and B were 15 and 5 ha, respectively, when constructed (Table 1). Before our study period, an additional 4 ha of drainage was added to the tile system of wetland B, for a total drainage area of 9 ha. These wetlands are typically inundated from late winter into early summer.

**Wetland Water Balance**

Precipitation data were obtained from a National Oceanic and Atmospheric Administration station at Philo, IL (~8 km northeast of the study site) (National Oceanic and Atmospheric Administration, 2014). Evapotranspiration data were from the Illinois State Water Survey station at Bondville, IL (Illinois State Water Survey, 2014). Each wetland inlet and outlet was equipped with v-notch weirs (Agri Drain structures), a pressure transducer, and a data logger to measure flow via the protocol from Chun and Cooke (2008). Flow data were collected every 30 min to determine daily average flow rates in and out of the wetlands. Wetland berms were overtopped by river flooding twice in 2013 when 119 mm of precipitation occurred during 16 to 19 April and again when 66 mm of precipitation occurred during 23 to 26 June. During flooding, outlet flow cannot be gaged, and we assume inlet flow equaled outlet flow. For wetland A, three transects of wells were installed (5.1-cm-diameter PVC) to determine seepage rates following Larson et al. (2000). Each transect had a well just inside the wetland along the berm (wetland wells), a well just outside of the wetland next to the berm (berm wells), and a well in the riparian area near the river (riparian wells). These wells were sampled beginning in March 2012. For wetland B, three wells were installed just inside of the wetland along the berm (berm wells), along with one riparian well. These wells were sampled beginning in January 2013. Well water depth was measured weekly using a water level meter (Solinst).

Seepage water volume exiting each wetland was determined by using the standard equation for water flow in a saturated soil (an abbreviated form of Darcy’s Law):

$$K \times A \times i$$

where $K$ is the apparent hydraulic conductivity, $A$ is the total effective seepage area, and $i$ is the hydraulic gradient (Larson et al., 2000). The apparent hydraulic conductivity was determined separately for wetlands A and B by analyzing periods of time with little to no precipitation, subtracting outlet from inlet flow adjusted for evapotranspiration for these time periods, and solving the equation given by adjusting the $K$ value until it equaled the amount of water missing. This is the same method used by Larson et al. (2000) in our previous work on these wetlands, which were included in the results of Kovacic et al. (2000). The hydraulic gradient for wetlands A and B was determined using the difference of water elevation between the wetlands and the Embarras River and dividing this difference by the average distance between the wetland berms and the river (i.e., 15.3 m). Continuous river water elevation was measured using an

<table>
<thead>
<tr>
<th>Wetland</th>
<th>Surface area</th>
<th>Volume</th>
<th>Tile drainage area</th>
<th>Average depth</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ha</td>
<td>m$^2$</td>
<td>1995–1998</td>
<td>2012–2013</td>
</tr>
<tr>
<td>A</td>
<td>0.6</td>
<td>5400</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>B</td>
<td>0.3</td>
<td>1200</td>
<td>5</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 1. Dimensions for wetlands A and B based on water height at the bottom of the V-notched outlet weir along with drainage areas.
in-stream pressure transducer and data logger. Both wetlands’ water elevations were measured using the outlet pressure transducers during periods of outlet flow and by the wetland wells during periods of inundation without outlet flow. The water balance for each was determined as: \((\text{inlet} + \text{precipitation}) - (\text{outlet} + \text{seepage} + \text{evapotranspiration})\). A negative balance indicates unmeasured surface runoff; a positive balance indicates unmeasured water loss through the wetland emergency spillway during high-inlet flow events.

**Wetland and Well Water Sampling and Analyses**

An automatic water sampler (ISCO) was used to collect individual water samples at regular time intervals during tile flow events at each wetland inlet (as often as every 4 h, but typically once per day). During low flow periods, inlet grab samples were collected once per week. Grab samples were collected at the outlet structures during and after tile flow events until the wetland water level declined below the outlet v-notch weir. For wells in the riparian buffer strip, water was pumped out with a peristaltic pump (Solinst) and sampled at least 1 h later using a hand pump.

All water samples were transported to the laboratory, immediately filtered through a 0.45-µm filter, and separated into the appropriate aliquots. Wetland inlet and outlet water samples were measured for nitrate on a Dionex DX 120 Ion Chromatograph, and ammonium and total N were determined on a Quik Chem FIA+8000 Series Lachat following standard methods (APHA, 1998). Organic N was calculated by subtracting inorganic N from total N. Only nitrate was determined in well samples because we assumed this was the only mobile form of N in seepage water moving through the riparian zone.

**Wetland N Balance**

To determine wetland inlet and outlet nitrate, ammonium, and organic N loads, linear interpolation (SAS v. 9.2) was used to estimate the concentration values for each 30-min flow measurement recorded between water sampling times (SAS Institute, 2008). Total inlet and outlet N loads were determined by summing the loads of the three N species for each 30-min flow measurement (Zamyadi et al., 2007). Wetland seepage water N loads were determined by multiplying the average berm well nitrate concentration by the daily seepage rate from each wetland. The amount of nitrate removed by the riparian buffer was estimated by the difference in nitrate concentrations between berm wells and riparian wells (Larson et al., 2000). Early in 2012 (Jan.–Feb.), we did not have monitoring wells established in the riparian buffer strip of wetland A. There was one event that was important for the year that occurred in late January 2012, and this was a large percentage of the flow during this drought year. During that event the wetlands filled but had little outflow, and most water was lost through seepage. We calculated the seepage volume as above and assumed no nitrate removal. Given the cold winter temperatures and the lack of change in wetland nitrate concentrations between the inlet and outlet locations, we felt confident in estimating on the conservative side that nitrate was not removed in the buffer strip at this time. Monitoring wells were not installed in wetland B until 2013. Therefore, we estimated seepage in wetland B in 2012 by scaling the wetland B berm length by the wetland A berm length, the same approach used by Larson et al. (2000) for these two wetlands. We are assuming that seepage is a function of the length of the berm as a primary factor, and the water budget suggests we may have overestimated it by this method. However, this has little influence on the overall removal rate of nitrate that we calculated. Atmospheric N deposition estimates collected by the Illinois State Water Survey at Bondville, IL were used to complete the overall wetland N budget (NADP, 2014).

**Greenhouse Gas Sampling and Analyses**

Wetlands A and B were sampled for GHGs from 22 Mar. through 29 Oct. 2012 and from 3 Mar. through 20 Nov. 2013. The wetlands were sampled for terrestrial and inundated CO₂, CH₄, and N₂O fluxes via the GRACEnet protocol for chamber sampling (Blowes et al., 2003). Static PVC rings (20 cm diameter, 10 cm height inserted ~5 cm into the soil) were installed in transects perpendicular to the berm. Static rings that were not inundated were used to measure terrestrial GHG flux on a given date. When wetlands were dry, all static rings were sampled for terrestrial GHG flux. Wetland A had four transects of static rings in the 2012 and two transects in 2013. Wetland B had two transects of rings each year. There were five rings in each transect that were located approximately 1 m from the preceding one. The riparian buffer strip at wetland A also had two transects consisting of two rings each to determine the GHG flux. End caps made of PVC were outfitted with weather stripping, septa, and ventilation tubes and were made to fit on the PVC rings to complete the enclosed terrestrial chamber, which had overall head space volumes of 5 to 6 L (actual headspace was determined for each measurement on each ring). Vegetation, mostly reed canary grass (*Phalaris arundinacea* L.), was carefully removed, avoiding soil disturbance, from each terrestrial ring before sampling. Each ring was incubated for 30 min, and 15-mL samples were collected at 0, 10, 20, and 30 min with a syringe. The samples were placed into an evacuated 10-mL glass vial with a gray butyl septum. Soil temperature and moisture (gravimetric soil samples) were determined for each static ring during each sampling, with soil samples collected just outside each ring (within 50 cm of the ring).

Greenhouse gas fluxes were determined during periods of inundation using floating chambers. Our requirement for inundation was a water column depth of at least 10 cm. Floating chambers (headspace volume of 8 L) were made from plastic tubing and were outfitted with septa, a handle, and a piece of foam for buoyancy. These chambers were painted silver to reflect sunlight and minimize temperature increases within the chamber during sampling. Floating chambers were also incubated for 30 min, and 15-mL samples were collected at 0, 10, 20, and 30 min with a syringe and placed into an evacuated glass vial with a gray butyl septum. For each sampling location, three floating chambers were used to obtain an average flux of GHGs. When wetland areas were entirely inundated (i.e., during periods of outlet flow), only floating chambers were used to obtain GHG fluxes.

Overall, GHG measurements were made on 12 d in 2012 and on 24 d in the wetter year of 2013. Wetland A had inundated GHG measurements on 6 d in 2012 and on 19 d in 2013, whereas for wetland B the values were 0 d in 2012 (due to little tile flow and wetland water) and 16 d in 2013.
Gas samples were analyzed using a GC-2014 gas chromatograph with autosampler (Shimadzu) to determine $\text{N}_2\text{O}$ and $\text{CH}_4$ concentrations for terrestrial samples and $\text{CO}_2$, $\text{CH}_4$, and $\text{N}_2\text{O}$ for inundated samples. A LI-COR model LI-8100 was used to obtain a $\text{CO}_2$ flux from each terrestrial ring. Carbon dioxide was not measured in the floating chamber samples during the 2012 water year in wetland A due to technical problems with the gas chromatograph. Linear regression was used to determine the rate of gas emission during the 30-min incubation period from the concentration data, with individual values or fluxes discarded if there was a lack of linearity due to clear outliers (most $R^2$ values were >0.90 for large fluxes). Greenhouse gas concentrations were converted to a daily flux and scaled up from individual rings and floating chambers to the full area of the wetland by using the GPS location of each ring to estimate the portion of the wetland that was inundated. The average floating chamber flux for each gas measured was scaled up to the inundated area calculated, and the average terrestrial gas flux was used to scale up to the portion of the wetland that was not covered with water. Once mass per day was calculated for each portion of the wetland, the inundated and terrestrial masses were summed and divided by the area of the wetland to determine total daily flux. Linear interpolation was used to determine the values for daily fluxes between field measurements using SAS 9.2 (SAS Institute, 2008). The riparian buffer strip GHG fluxes were scaled up in a similar way from the transect measurements. All GHG fluxes were converted to $\text{CO}_2$–equivalent units ($\text{CO}_2$–e).

Results and Discussion

Wetland Water Balance

The study site received an estimated annual precipitation of 857 and 924 mm for the 2012 and 2013 water years, respectively. A severe drought occurred during the summer of the 2012 water year (June–July precipitation was 54 mm) after below-normal spring precipitation. This was followed by above-average precipitation in 2013 (603 mm, January–June). Tile flow (inlet) into wetlands A and B was 14,025 and 3400 m$^3$, respectively, in 2012 and 55,404 and 35,200 m$^3$, respectively, in 2013 (Table 2). In 2012, the largest inlet flow event of the year occurred in late January; however, there was no outlet flow for wetland B and only 11 m$^3$ of outlet flow for wetland A. With many large inlet flow events in 2013, outlet flow was substantial and accounted for 56% of the total inlet flow for wetland A and 37% of the inlet flow for wetland B. Wetland water that seeped through and under the berm and into the riparian buffer strip (seepage) accounted for 82 to 90% of the inlet volume in 2012 (Table 2). Total seepage was greater in 2013, accounting for 34 to 56% of the total inlet volumes for wetlands A and B, respectively. Our results show the importance of seepage, but this is a difficult value to accurately estimate and may have led to the water balances being different than zero. However, it was not possible to measure surface runoff and/or spillway losses after floods, and this may have led to some of the discrepancies.

During the past two decades, there has been no change to the watershed (i.e., field tile drainage system) for wetland A; therefore, we can make a direct comparison with past research results. Water inputs and outputs for wetland A in 2013 were similar to those reported by Kovacic et al. (2000) during the 1995 through 1997 water years, especially 1997, when the inlet, outlet, and seepage volumes were 54,300, 27,700, and 23,600 m$^3$, respectively. The similar values for inputs and outputs as well as the overall water balances suggest that the hydrology of wetland A has not changed since the time of construction. More importantly, roots from trees along the berm or animal burrows have not led to an increase in seepage losses through time.

Wetland N Removal

Tile N loads into the wetlands were much greater in 2013 compared with 2012 and followed a similar pattern as inlet water volumes, indicating that flow was a more important factor than nitrate concentration in determining tile N load (Table 3). Total N loads ranged from 52 kg for wetland B in 2012 during the dry year to 642 kg for wetland A in the wet year. Nitrate accounted for more than 96% of the inlet N load but was 89% of the total outlet N load, suggesting some organic N production within the wetland during inundation. Subtracting outlet and seepage exports from inlet loads allows for the determination of the total amount of N removed and percent removal from each wetland. Percent removal of total N was >50% for both wetlands in both years. However, due to the low hydraulic loading in 2012, wetlands A and B removed a combined total of only 118 kg N ha$^{-1}$ in 2012, compared with 639 kg N ha$^{-1}$ in 2013. Overall, wetland A and B nitrate removal was 56% of the inlet load for the study period.

Wetland seepage under the berm connects the wetland with the riparian buffer, increasing the potential for nitrate removal by the entire wetland/riparian buffer complex (Kovacic et al., 2000; Larson et al., 2000). As water moved under the berm it passed through a 15.3-m strip of riparian soils along the river that had both herbaceous and woody vegetation. This flow path would allow for plant uptake of nitrate and for further denitrification.

### Table 2. Water budget for wetlands A and B for the 2012 and 2013 water years.

<table>
<thead>
<tr>
<th></th>
<th>Inlet Precipitation</th>
<th>Outlet</th>
<th>Seepage</th>
<th>ET†</th>
<th>Balance‡</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m$^3$</td>
<td>m$^3$</td>
<td>m$^3$</td>
<td>m$^3$</td>
<td>m$^3$</td>
</tr>
<tr>
<td>Wetland A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2012</td>
<td>14,025</td>
<td>1,999</td>
<td>11</td>
<td>13,087</td>
<td>3,126</td>
</tr>
<tr>
<td>2013</td>
<td>55,404</td>
<td>3,696</td>
<td>33,108</td>
<td>20,118</td>
<td>2,601</td>
</tr>
<tr>
<td>Wetland B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2012</td>
<td>3,400</td>
<td>954</td>
<td>0</td>
<td>3,926</td>
<td>1,394</td>
</tr>
<tr>
<td>2013</td>
<td>35,200</td>
<td>2,032</td>
<td>13,892</td>
<td>20,658</td>
<td>1,558</td>
</tr>
</tbody>
</table>

† Evapotranspiration.
‡ Negative balances come from surface runoff entering the wetlands that was not quantified in the water budget. Positive balances indicate a portion of the inlet flow exited through the wetland’s emergency spillway.
Table 3. Annual nitrate and total N budgets for wetlands A and B in 2012 and 2013. Total N includes nitrate, ammonium, and organic N in tile inlets and in outlet flow, as well as wet and dry atmospheric deposition added to the inlet load.

<table>
<thead>
<tr>
<th></th>
<th>Inlet load</th>
<th>Outlet export</th>
<th>Seepage export through berm†</th>
<th>Removal by wetland</th>
<th>Removal rate per ha of wetland‡</th>
<th>Inlet + deposition load</th>
<th>Outlet export</th>
<th>Seepage export through berm</th>
<th>Removal by wetland</th>
<th>Removal rate per ha of wetland</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wetland A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2012</td>
<td>147</td>
<td>0.1</td>
<td>56 (51)</td>
<td>91</td>
<td>152 (62)</td>
<td>0.1</td>
<td>56</td>
<td>96</td>
<td>160 (63)</td>
<td></td>
</tr>
<tr>
<td>2013</td>
<td>619</td>
<td>246</td>
<td>38 (15)</td>
<td>335</td>
<td>558 (54)</td>
<td>642</td>
<td>278</td>
<td>38</td>
<td>326</td>
<td>543 (51)</td>
</tr>
<tr>
<td>Wetland B</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2012</td>
<td>50</td>
<td>0</td>
<td>23 (20)</td>
<td>27</td>
<td>90 (54)</td>
<td>52</td>
<td>0</td>
<td>23</td>
<td>29</td>
<td>97 (56)</td>
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<tr>
<td>2013</td>
<td>544</td>
<td>114</td>
<td>126 (65)</td>
<td>304</td>
<td>555</td>
<td>127</td>
<td>38</td>
<td>126</td>
<td>302</td>
<td>1007 (54)</td>
</tr>
</tbody>
</table>

† Values in parentheses indicate percent removal.
‡ Values in parentheses indicate percent removal.

Wetland B had a larger seepage N load and a greater N removal rate than wetland A during 2013, although it had a shorter berm and lower effective seepage area. This likely occurred due to the greater inlet nitrate concentrations entering into wetland B compared with wetland A (15.5 and 11.2 mg nitrate-N L$^{-1}$, respectively, for 2013) as well as flow events that kept wetland B full much of the spring (maximizing seepage). We estimated that the riparian buffers removed between 3.4 to 11.2% of the inlet nitrate load in the two wetlands in 2012 and 2013 and increased the overall removal percentage of the inlet load to 62%. This is shown in Table 3 by the difference in seepage export through the berm minus the amount that reached the river, which is the amount removed by the buffer strip. The percentage removal is that value divided by the inlet load of nitrate. More wells and nitrate measurements in the riparian zone would have improved these estimates but likely would not change the overall conclusion of the role of seepage losses in terms of nitrate removal for the overall wetland/riparian buffer complex.

Overall, the wetlands continued to remove nitrate at the same capacity as when they were created. Nitrate removal as a function of hydraulic loading was similar to that measured by Kovacic et al. (2000) and Larson et al. (2000) in the 4 yr after construction of the wetlands (Fig. 1). A strong linear relationship ($r^2 = 0.82$) was observed between hydraulic loading and the mass of nitrate removed. The hydraulic loading in 2012 was less than we had seen previously between 1994 and 1998, whereas the hydraulic loading in 2013 was larger than in our previous work. However, even with this increase in the range of hydraulic loading rates measured, all mass removal rates of nitrate fell on the same trend line.

Wetland and Riparian Buffer Greenhouse Gas Fluxes

The majority of the total cumulative GHG fluxes for wetlands A and B in both study years came from the terrestrial portions of the wetlands (Fig. 2). The largest terrestrial CH$_4$ and N$_2$O fluxes occurred during the final dry-down (last time areas of the wetlands were inundated) of the wetlands (Fig. 3). During this time, the soils were still saturated and were thought to be anaerobic. In addition, once the water receded, the soil was exposed to a greater amount of solar radiation, thus warming the soil. These greater soil temperatures likely increased microbial activity, increasing the amount of CH$_4$ and N$_2$O emitted. There is evidence that soil temperatures of <15°C can severely limit the rate of denitrification (Stanford et al., 1975).

The inundated fluxes for each GHG measured accounted for only a small portion of the total cumulative flux. The largest combined GHG inundated flux, which accounted for 14% of the total year flux, occurred in wetland A in 2013 (Table 4). Assuming that the 2013 water year was a more typical water year than 2012, wetland A had a greater inundated flux of CH$_4$ (1050 kg CO$_2$-e ha$^{-1}$ yr$^{-1}$) than N$_2$O (930 kg CO$_2$-e ha$^{-1}$ yr$^{-1}$). Conversely, wetland B had a greater inundated N$_2$O flux (802 kg CO$_2$-e ha$^{-1}$ yr$^{-1}$) than inundated CH$_4$ flux (273 kg CO$_2$-e ha$^{-1}$ yr$^{-1}$). This may have been due to the nitrate concentration in the wetlands. Wetland B was smaller, with a larger inlet nitrate flow-weighted mean in 2013 (15.5 mg nitrate-N L$^{-1}$), thus providing ample nitrate to the denitrifying communities. Wetland A was larger, with a smaller inlet nitrate flow-weighted mean (11.2 mg nitrate-N L$^{-1}$), thus giving the denitrifiers more opportunity to remove all or most of the nitrate in the water. This was especially true for the inundated area sampled near wetland A’s outlet, where nitrate concentrations were typically much less. For example, during flow events in May and June 2013, concentrations were decreased by about 50% halfway along the flow path of the wetland and were at 0 mg nitrate-N L$^{-1}$ in the outlet flow. When nitrate in the water column was completely depleted before the water exited the wetland, the anaerobic microbes would have had to move to another terminal electron
acceptor. Eventually, the wetlands became reduced enough so that CH$_4$-producing microbes took over. These microbes can reduce CO$_2$ and other carbonaceous material to CH$_4$. This shift from inundated N$_2$O to CH$_4$ production was further confirmed by the relationship between inundated N$_2$O and CH$_4$ fluxes and nitrate concentration. The inundated CH$_4$ flux was negatively related to the nitrate concentration in the wetland water ($n = 97; r = -0.50; p < 0.0001$), whereas the N$_2$O flux was positively related to the nitrate concentration ($n = 97; r = 0.42; p < 0.0001$). This was probably because methanogens cannot survive in conditions that provide more energetically favorable electron acceptors. Both relationships were relatively weak, but high CH$_4$ fluxes were only measured when nitrate concentrations were near zero. This supports the observation that nitrate inhibits CH$_4$ production that has been found by a similar study (Stadmark and Leonardson, 2005).

A concern with installing constructed wetlands to remove nitrate from tile lines is the release of N$_2$O during denitrification. Of the total nitrate removed by the wetlands, 3.2 and 1.3% was released as N$_2$O in 2012 and 2013, respectively. Most of the N$_2$O loss was from the terrestrial portions of the wetlands, which were much larger during the drought year of 2012. Little N$_2$O was emitted from inundated areas, suggesting strongly anaerobic conditions where only N$_2$ gas is released, similar to what was measured previously in these wetlands (Xue et al., 1999). As wetland water recedes and soil is exposed, terrestrial portions of the wetland appear to be the source of the N$_2$O production.

Wetland A for both water years and wetland B for the 2013 water year had roughly the same total cumulative GHG flux values (Table 4). Wetland B had a lower cumulative flux in 2012. Wetland A had cuts excavated into its bottom when it was constructed to form the berms, whereas the bottom of wetland B was undisturbed. Being lower in the landscape, cuts in wetland A usually had greater moisture content, providing greater potential for GHG fluxes in 2012. Dry soils, like those in wetland B, would have less microbial activity, and therefore less GHG flux, than moist soil conditions.

Similar to the wetlands’ cumulative GHG flux, the riparian buffer strip along wetland A had a cumulative GHG flux that consisted mostly of CO$_2$, with little N$_2$O or CH$_4$ produced (Fig. 4). The majority of the soil profile in the buffer strip for wetland A was saturated for most of the year due to the hydraulic head between wetland A and the Embarras River. Therefore, any nitrate denitrified was likely converted to N$_2$. 

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**Fig. 2.** Cumulative fluxes of CO$_2$, CH$_4$, and N$_2$O for wetlands A and B separating the terrestrial source of each gas from the total cumulative flux. The orange lines outline the final dry down of each wetland for both water years. The first orange line in each water year represents the last day of outlet flow, and the second orange line represents when the wetlands are completely dry.
Greenhouse gas emissions are driven by microbial processes; therefore, temperature is an important controlling variable. For the wetlands’ CH₄ and N₂O fluxes, surface water and soil temperature were important in inundated and terrestrial fluxes, respectively (Fig. 5 and 6). Inundated CH₄ and N₂O fluxes had a threshold at 18°C, similar to the 15°C value described by Stadmark and Leonardson (2005) for CH₄. Any flux that occurred in water temperature below 18°C was limited when compared with fluxes that were emitted in water above 18°C. This same trend was observed for terrestrial CH₄ and N₂O fluxes. However, the temperature threshold for terrestrial fluxes was centered around 15°C. Carbon dioxide did not seem to have the same threshold characteristics, similar to what Stadmark and Leonardson (2005) observed. As summarized by O’Geen et al. (2010), the optimum temperature range for denitrification is 20 to 25°C, with the rate decreasing below 15°C due to reduced diffusion rates and microbial activity. Sirivedhin and Gray (2006) measured a >100 times increase in denitrification rates as temperature increased from 4 to 25°C. For wetlands in east-central Illinois, where there is often winter tile flow, denitrification rates are low, with corresponding poor efficiency in nitrate removal during these flow periods.

Similar to the temperature threshold, the wetland terrestrial CH₄ and N₂O fluxes had a soil moisture threshold at ~25% (Fig. 7). Terrestrial CH₄ and N₂O fluxes remained at a baseline level until soil moisture was at 25% or greater. Also, similar to the temperature threshold, CO₂ did not respond to this soil moisture threshold.
Greenhouse Gas Flux Comparisons with Other Studies

It is important to know how these GHG fluxes compare with other studies and other environmental conditions. This proved difficult because many studies do not report GHG fluxes on an annual basis. Smith et al. (2013) looked at cumulative N₂O fluxes from corn, Miscanthus x giganteus, switchgrass (Panicum virgatum L.), and mixed prairie. The cumulative flux from these systems had ranges of 1656 to 3751, 292 to 682, 390 to 689, and 195 to 341 kg CO₂-e ha⁻¹ yr⁻¹, respectively. Corn plots had the largest N₂O fluxes; however, this was the only treatment that received the application of N fertilizer. Regardless, the range of corn N₂O fluxes was comparable to the range of N₂O fluxes found in this study (992–5270 kg CO₂-e ha⁻¹ yr⁻¹). This comparison with Smith et al. (2013) suggests that, on a per-hectare basis, our constructed wetlands had relatively large N₂O fluxes that were comparable to fertilized corn. However, the wetland areas were quite small, and the amount of nitrate denitrified was large. If the flux is divided by the drainage areas, the fluxes become much less than those from fertilized corn and suggest that these N₂O losses are not large compared with corn production and are not an environmental concern.

Altor and Mitsch (2006) measured CH₄ fluxes from two constructed wetlands in Ohio under flashy hydrology with dry periods during the water year. The permanently inundated portions of the wetlands in Altor and Mitsch, (2006) had a cumulative flux of 11,760 kg CO₂-e ha⁻¹ yr⁻¹, whereas the terrestrial portions exposed during dry periods had a cumulative flux of 3528 kg CO₂-e ha⁻¹ yr⁻¹. The CH₄ flux from the permanently inundated portions were well above the maximum CH₄ flux measured in this study (4746 kg CO₂-e ha⁻¹ yr⁻¹), which came from wetland A during 2013. However, the large CH₄ fluxes from Altor and Mitsch (2006) were from permanently flooded portions of their wetlands during much of the year. They could control the flow of water and kept portions of their wetlands inundated, whereas we had precipitation-driven tile flow as our control on inundation. Therefore, the length and duration of our inundation periods were small in comparison to Altor and Mitsch (2006). Taken together, the Altor and Mitsch (2006) results and our own suggest that the major controlling factor on CH₄ production is the amount of time the wetland is inundated. However, if the inundation period were reduced, nitrate removal would likely decrease as well, which is why the wetlands were created.

Thiere et al. (2011) examined the estimated nitrate retention and CH₄ emissions from wetland creation across a watershed in southern Sweden. They used intensive data from a few wetlands as well as a wetland survey to examine the two processes. Their conclusion was that the wetlands did remove nitrate with a relatively low CH₄ emission but that many factors explained the differences between wetlands (e.g., temperature, aquatic plant cover, and wetland age). Thiere et al. (2011) concluded from this
work that large-scale wetland creation would make an important reduction in N fluxes with little environmental risk. Our results fit well with Thiere et al. (2011), given the magnitude of our GHG emissions compared with the large nitrate removal rates we measured.

Conclusions

The wetlands studied here had nitrate removal rates of between 90 and 1013 kg N ha\(^{-1}\) yr\(^{-1}\) and between 54 and 62% N removal of the tile loads. Overall, the wetlands seemed to have the same nitrate removal potential as when they were created, with hydraulic loading the primary regulating factor. The majority of the GHG flux came from the terrestrial portions of the wetland, not the flooded areas. This was especially true during the final dry down periods of wetlands A and B in both sampling years. Nitrous oxide emissions were 3.2 and 1.3% of the overall nitrate removal in 2012 and 2013, respectively. When comparing the GHG fluxes from this study with other studies, the N\(_2\)O fluxes from these wetlands were comparable to those from a fertilized corn field on a per-hectare basis. However, given the small size of the wetlands compared with their drainage areas, the added GHG emissions were small when considering the overall production system and the amounts of nitrate removed.

Acknowledgments

We thank the farm cooperator who made this study possible, Morgan Davis and Tito Lavaire for field assistance, and Corey Mitchell for laboratory analysis and data summaries. This work was partially funded by the USDA National Institute of Food and Agriculture under agreements no. 2011-039568-31127 and 2011-51130-31120. Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the authors and do not necessarily reflect the view of the USDA.

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Fig. 6. Terrestrial CO\(_2\) (top), CH\(_4\) (middle), and N\(_2\)O (bottom) fluxes plotted with soil temperature for wetlands A and B in 2012 and 2013.

Fig. 7. Terrestrial CO\(_2\) (top), CH\(_4\) (middle), and N\(_2\)O (bottom) fluxes plotted with percent soil moisture for wetlands A and B in 2012 and 2013.


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