1997

Nitrate removal capacity of constructed wetlands

Richard Gregory Phipps
Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/rtd

Part of the Ecology and Evolutionary Biology Commons, Environmental Sciences Commons, and the Fresh Water Studies Commons

Recommended Citation

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6” x 9” black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor MI 48106-1346 USA
313/761-4700 800/521-0600
Nitrate removal capacity of constructed wetlands

by

Richard Gregory Phipps

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Water Resources

Major Professor: William G. Crumpton

Iowa State University

Ames, Iowa

1997
Graduate College
Iowa State University

This is to certify that the doctoral dissertation of

Richard Gregory Phipps

has met the thesis requirements of Iowa State University

Signature was redacted for privacy.

Major Professor

Signature was redacted for privacy.

For the Major Program

Signature was redacted for privacy.

For the Graduate College
<table>
<thead>
<tr>
<th>CHAPTER 1. GENERAL INTRODUCTION</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissertation Organization</td>
<td>4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER 2. FACTORS AFFECTING NITRATE LOSS IN CONSTRUCTED WETLANDS</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>5</td>
</tr>
<tr>
<td>Introduction</td>
<td>5</td>
</tr>
<tr>
<td>Methods</td>
<td>6</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>9</td>
</tr>
<tr>
<td>References</td>
<td>13</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER 3. THE EFFECTS OF HYDROLOGIC LOAD ON NITRATE LOSS IN CONSTRUCTED WETLANDS</th>
<th>23</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>23</td>
</tr>
<tr>
<td>Introduction</td>
<td>24</td>
</tr>
<tr>
<td>Methods</td>
<td>25</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>28</td>
</tr>
<tr>
<td>References</td>
<td>33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER 4. FATE OF NITROGEN LOADS IN EXPERIMENTAL WETLANDS</th>
<th>46</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>46</td>
</tr>
<tr>
<td>Introduction</td>
<td>47</td>
</tr>
<tr>
<td>Methods</td>
<td>48</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>51</td>
</tr>
<tr>
<td>Literature Cited</td>
<td>55</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER 5. GENERAL SUMMARY</th>
<th>62</th>
</tr>
</thead>
<tbody>
<tr>
<td>REFERENCES</td>
<td>63</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>67</td>
</tr>
</tbody>
</table>
CHAPTER 1. GENERAL INTRODUCTION

Agricultural applications of fertilizers and the subsequent contamination of surface and groundwaters has become a pressing environmental problem (Gianessi et al. 1986, Gray 1985, Keeney 1986). Nitrate is of concern because of its potential impacts on both public health and ecosystem function, and because of the widespread use of nitrogen in modern agriculture. Negative impacts associated with high nitrate loads include the health effects of high nitrate levels in drinking water, particularly for small children, and the eutrophication of downstream waters. Excess nitrate loads may stimulate algal blooms, which can reduce dissolved oxygen levels, reduce light penetration, and affect the taste of drinking water. The expense of building water purification facilities is often prohibitive.

The total amount of N applied in fertilizers far exceeds that of any other nutrient, and fertilizer application rates, particularly for corn in the Midwest, have grown from a negligible amount prior to World War II to 100 to 200 kg of N ha\(^{-1}\) yr\(^{-1}\) (David et al. 1997). Substantial amounts of the chemicals applied to farm fields are lost to surface and groundwaters in agricultural watersheds (Ommenik 1977, Keeney 1986). As much as 50% of the fertilizer nitrogen applied to cultivated crops may be lost in agricultural drainage water, primarily in the form of nitrate (Neely and Baker 1989). Streams draining agricultural watersheds are characterized by high nitrate loads, and considerably lower concentrations of organic nitrogen and ammonium. High nitrate loads result from the activities of nitrifying bacteria and subsequent leaching of nitrate. Ammonium cations readily bond to negatively charged clays and organic matter in soils. However, aerobic nitrifying bacteria transform considerable amounts of ammonium, converting it to the anion, nitrate. As surface water percolates through the soil profile, nitrate is readily leached to subsurface tile drains where nitrate-nitrogen concentrations frequently exceed 10 mg/l NO\(_3\)-N (Baker and Johnson 1981).

Despite our best efforts, it is unlikely that these contamination problems can be solved by chemical management alone. The best solutions will involve a combination of on-field and off-field approaches. One of the most promising strategies for reducing nonpoint source contamination of surface and groundwaters is the use of constructed or restored wetlands specifically as sinks for ag-chemical contaminants (van der Valk and Jolly 1992).
Studies suggest that some wetlands are especially effective as sinks for nitrate loads from cultivated fields (Nixon and Lee 1986, Neely and Baker 1989). There is therefore considerable interest in the use of wetlands as sinks for nonpoint source nitrogen loads in these agricultural areas. If wetlands are to serve as long term sinks for nitrogen, differences in inputs and outputs must reflect net storage in the system through accumulation and burial in sediments, or net loss from the system through gaseous evolution of NH₃, N₂O, or N₂.

The sink capacity of wetlands for nitrogen may be affected by any number of factors. Aquatic plants (Reddy et al. 1989) and benthic invertebrates (Chatarpaul et al. 1980) may affect rates of microbial nitrogen transformations by altering fluxes of gases to and from anoxic sediments. Seasonal and even diurnal changes in factors such as temperature, nitrate concentration, and oxygen concentration can dramatically affect nitrogen transformations in sediments (Andersen et al. 1984, Christensen et al. 1989). The development of vegetation and litter may also reduce aeration of the water column and increase the area of anaerobic sites available for denitrification (Crumpton et al. in prep).

Nitrate sink capacity is due primarily to plant uptake, microbial assimilation, and denitrification. Most of the published papers dealing with wetlands and water quality note the probable importance of denitrification, with the resulting gaseous loss of N₂O and N₂. In fact, with rare exception, denitrification is cited as the primary reason wetlands may serve as nitrogen sinks (Nixon and Lee 1986, Bowden 1987, Seitzinger 1988, Neely and Baker 1989). In one study, approximately 20% of the nitrate load of ¹⁵N nitrate added to intact sediment microcosms was immobilized by emergent macrophytes and microbes, and 80% of ¹⁵N nitrate was unrecovered and presumed lost due to denitrification (Isenhart 1992, Isenhart and Crumpton in prep). However, there have been few actual measurements of denitrification in freshwater marshes (Nixon and Lee 1986, Bowden 1987, Seitzinger 1988, Neely and Baker 1989). As Neely and Baker (1989) note, denitrification is assumed to be an important process in many freshwater wetlands based largely on circumstantial evidence, first, that conditions in the wetlands are suitable for denitrification (anaerobic conditions and a large base of organic carbon) and second, that nitrate disappears rapidly from water overlying wetland sediment.
The Des Plaines Experimental Wetland Demonstration Project offered the opportunity to examine the capacity of flow through wetlands to remove nitrate nitrogen. These constructed wetlands were designed to receive regulated inflows pumped from the Des Plaines River. Three flow through wetlands were monitored for inflow and outflow of hydrologic loads and nitrogen. Seasonal mass balance and nitrate removal capacity were determined under different hydrologic loads during the 1991 and 1992 field seasons.

The 1990 and 1991 field work detailed here first considers the main factors that affect the sink capacity for nitrate including the availability of O₂, temperature, and nitrate concentration. These were thought to be the most significant variables affecting nitrate loss rates in the experimental wetlands. Loss rates measured in experimental microcosms were used to examine two potential models of nitrate flux in relation to nitrate concentration and temperature.

Areal loss rate coefficients (kₐ) (equation 2, ch. 3), determined from microcosms, represent the intrinsic loss rate capacity for a wetland. In 1991, the coefficient was referred to as the velocity of deposition. The velocity of deposition is analogous to the rate coefficient for a first order reaction in a continuously stirred tank reactor, and is a term commonly used in stream related literature. For work done in 1992, the coefficient is referred to as kₐ. These are the same terms.

Nitrate loss rate coefficients are important for the prediction of nitrate loss in response to varying nitrate concentrations and loading patterns. Increased nitrate loading to wetlands in agricultural watersheds might be expected to stimulate denitrification, but there are no reliable measurements of the effects of such loading or of the denitrification capacity of wetlands receiving agricultural loads (Nixon and Lee 1986, Bowden 1987, Seitzinger 1988, Neely and Baker 1989). Previous studies observed that prior exposure to nitrate produced a stimulatory effect in experimental wetland enclosures (Isenhart 1992, Moraghan 1993). Hydrologic and nitrogen loading rates may influence enzyme levels or populations of denitrifiers (Isenhart 1992). If so, the predictive power of the loss model would be reduced. The objective of the work in 1992 was to characterize nitrate loss coefficients over the field season in response to varying hydrologic and loading regimes.
Dissertation Organization

This dissertation consists of two papers written for journals and one written as a report to a funding agency.

The first paper was published in the journal Ecological Engineering. Richard Phipps is the principal author and William G. Crumpton is the co-author. The paper describes the factors that affect nitrate loss in the Des Plaines wetlands. Microcosms are used to estimate loss rates under controlled laboratory conditions.

The second paper is written for submission to the journal Ecological Engineering. Richard Phipps is the main author and William G. Crumpton will be the co-author. This paper describes the effects of hydrologic loading on intrinsic loss rates (k_i) in these same wetlands.

The third paper was published as an Environmental Protection Agency Report with William G. Crumpton as principal investigator and with Richard Phipps as co-author. This paper contains experimental microcosm data and describes models of nitrate flux that are not seen in the first two papers. Richard Phipps was responsible for the microcosm loss rate measurements and W.G. Crumpton was responsible for the mathematical modeling.

A general summary follows the two papers; references cited in the General Introduction and General Summary are listed following the General Summary.
CHAPTER 2. FACTORS AFFECTING NITROGEN LOSS IN EXPERIMENTAL WETLANDS WITH DIFFERENT HYDROLOGIC LOADS

A paper accepted by the journal Ecological Engineering

Richard G. Phipps, William G. Crumpton

ABSTRACT

Constructed or restored wetlands have great potential for reducing nonpoint source contamination of surface and ground waters by agricultural chemical contaminants. The work reported here combines field and experimental studies of factors affecting nitrogen loss in the Des Plaines River Experimental Wetlands, Northeastern Illinois, USA. These wetlands receive approximately 5-36 cm/week of pumped river water with significant but seasonally variable loads of nitrate and organic nitrogen. On an annual basis, the wetlands removed 78-95% of the nitrate and 54-75% of the total nitrogen received. At the low hydrologic loading rate, organic nitrogen exports approximately equaled imports. However at the higher hydrologic loading rate, the wetlands exported 22-31% more organic nitrogen than received. Seasonal variation in nitrate and organic nitrogen loads had significant effects on the effectiveness of the wetlands as sinks for total nitrogen. The wetlands were nitrogen sinks during periods of high nitrate loading and nitrogen sources during periods of low nitrate loading. Experimental studies demonstrated the effects of nitrate concentration, temperature, and location on rates of nitrate loss. Results suggest that nitrate loading rates might influence not only nitrate loss rates but also loss rate coefficients.

INTRODUCTION

Studies suggest that wetlands may act as sinks for a variety of compounds (Howard-Williams, 1985; Nixon and Lee, 1986), and there is considerable interest in the use of wetlands as sinks for nonpoint nitrogen loads from rivers draining agricultural watersheds.
However, nitrogen transformations in wetlands involve complex spatial and temporal patterns, and wetlands differ greatly in their efficiency as nitrogen sinks, even when depth, area, and residence time are accounted for. If wetlands are to serve as sinks for nitrogen, differences in inputs and outputs must reflect net storage in the system through accumulation and burial in sediments, or net loss from the system through gaseous evolution of \( \text{NH}_3 \), \( \text{N}_2\text{O} \), or \( \text{N}_2 \). Wetlands are not equally effective at removing ammonium, nitrate, and organic nitrogen. In fact, with rare exception, denitrification of nitrate is cited as the primary reason wetlands may serve as nitrogen sinks (Neely and Baker, 1989).

Obviously the form and timing of nitrogen inputs can be expected to have considerable influence on the effectiveness of wetlands as sinks for nitrogen, and this may be especially important in the case of loads from rivers draining agricultural watersheds. Rivers draining agricultural watersheds may show dramatic seasonal patterns in organic and inorganic nitrogen loads, with nitrate concentrations typically highest during periods of high flow in the spring and late fall, and declining during periods of low flow (Christensen and Sorensen, 1988; W.G. Crumpton, unpublished data). Increased nitrate loading during periods of higher stream flow might be expected to stimulate denitrification, but there are no reliable measurements of the effects of such loading or of the denitrification capacity of wetlands receiving nonpoint source agricultural loads. The objectives of the work described here were to characterize nitrogen loads and exports to a series of constructed wetlands receiving controlled inputs of river water and to examine some of the factors affecting nitrogen loss in these wetlands.

METHODS

Site Description

Research was conducted at the Des Plaines River Wetlands Demonstration Project near Wadsworth, Illinois, USA. Upstream of the site, the Des Plaines River drains approximately 520 km\(^2\) of mainly agricultural land (80%) in southeastern Wisconsin and northeastern Illinois. Wetland construction and restoration at the site began in 1986 and the four experimental wetlands (EW3, EW4, EW5, and EW6) used in the research described
below were completed in October, 1988. These wetlands range between approximately 1.9 hectares (EW5) and 3.4 hectares (EW6) in area. Wetlands EW3 and EW4 are 2.4 hectares. Average depths are 61 cm for EW3, 72 cm for EW4, 69 cm for EW5, and 56 cm for EW6. Detailed descriptions of the site and the experimental wetlands, including detailed hydrology, can be found in Hey et al. (1994a). A pump station installed on the Des Plaines river is used to deliver controlled amounts of river water to each of the wetlands, and wetland water levels and discharge are controlled by a weir at the outlet of each wetland. During the current study, the wetlands were assigned to one of two hydrologic loading rates which were held constant for the duration of the study. From April through November, 1991, two high flow wetlands (EW3 and EW5) received approximately 36 cm of river water per week while two low flow wetlands (EW4 and EW6) received approximately 5 cm of river water per week (Hey et al., 1994a). These loading rates resulted in average detention times of approximately 12 days for the high flow wetlands and approximately 95 days for the low flow wetlands. Because of excessive loss to ground water, EW6 seldom had outflows and was dropped from the experimental design for the purposes of the analyses described below.

Field Studies

Replicate 60 mL samples were collected at weekly intervals from the Des Plaines River, from wetland inlets, and from wetland outlets, and acidified to pH<2 using H₂SO₄. Samples were assayed for a range of constituents including nitrate, ammonium, organic nitrogen, and total nitrogen (Hey et al., 1994b). Ammonium was determined using the indophenol method (Scheiner, 1976). Nitrate, organic nitrogen and total nitrogen were determined using second derivative spectroscopy (Crumpton et al., 1992). The weekly inlet and outlet monitoring data were used to assess the forms of nitrogen loaded to the experimental wetlands and the loss of different forms of nitrogen. River stage was measured each week and flows calculated from a stage-discharge formula for the site (Hey et al., 1994a).
Experimental microcosms were used to examine the effects of temperature, nitrate concentration, and sampling location on nitrate flux. The microcosms used in this study were developed in our laboratory for measurements of benthic microbial processes, and consist of 5 cm diameter, polycarbonate cores enclosing intact sediment and overlying water. The microcosms are designed for both sampling and incubation, so it is possible to measure processes in intact sediment-water systems with minimal disturbance.

Between June and August, a series of experiments were conducted to examine the effects of temperature, nitrate concentration, and location on nitrate loss. Cores were collected from open water or lightly vegetated areas in EW3, EW4, and EW5 and used in a series of three-way ANOVAs (2 X 2 X 2 designs for concentration, temperature, and location). In EW3, cores were taken both from the upper reach, 15-40 meters from the inlet, and from the lower reach, 15-80 meters from the outlet. In EW4 and EW5, cores were taken from middle reaches. To obtain cores, polycarbonate cylinders (5.1 cm ID, 30.5 cm long) were pushed into the sediment to depths of at least 7 cm and their tops sealed using rubber stoppers. The cores with intact sediment were then pulled up and their lower ends stoppered. Cores were placed in coolers as soon as they were collected and transferred to water baths immediately upon return to the laboratory. EW4 outlet water, which was always low in NO$_3^-$, was added to the baths until the tops of the cores were overlain by approximately 2 cm of water. Two circulating, thermostated water baths maintained constant water temperature of approximately 20 or 30°C, depending on the experimental treatment. Water overlying each core was bubbled with air to allow thorough mixing and the baths drained to 3-4 cm below the cylinder tops. Overlying water within the cores was adjusted to approximately 6 cm above the sediment water interface. Cores were spiked with NaNO$_3$ to provide initial concentrations of approximately 3 or 6 mg NO$_3^-$-N/L, depending on the experimental treatment. Cores were sampled, incubated in the dark for a 6 hour period, and sampled again. Initial and final samples were preserved with HCl and analyzed for nitrate nitrogen using second derivative ultraviolet spectroscopy (Crumpton et al., 1992). Nitrate flux rates were calculated based on changes in concentration during incubation and scaled to an areal basis.
Sediment organic content was determined for the upper 2 cm in sediment cores collected from each of the sampling sites as described above. Two cm of surface sediment was extruded from the cylinder, collected, and wet sediment volume and weight were recorded. Sediment was then dried at 70°C for 48-72 hours and weighed. Dried sediment was mixed, ground, and subsamples were weighed before and after combustion in a muffle furnace at 550°C for 60 minutes, or until there was no further weight loss. Percentage weight loss on ignition was calculated as a measure of organic content.

RESULTS AND DISCUSSION

Field Studies

Ammonium concentrations were consistently low at all sites throughout the study, rarely exceeding 0.05 mg/L. Nitrate and organic nitrogen were clearly the dominant forms of nitrogen loaded to the wetlands. However, the relative contribution of nitrate and organic nitrogen to the total nitrogen load entering the wetlands varied seasonally due to changes in nitrate and organic nitrogen concentrations in the river. Nitrate concentrations in the river were highest during periods of high stream flow early and late in the season and declined to near detection limits during periods of low stream flow in the summer and early fall (Figure 1). This pattern is very common in systems like the Des Plaines River which receive significant nonpoint source agricultural inputs. During periods of low flow, instream processes can remove significant amounts of nitrate nitrogen from agricultural streams (Hill, 1983, Isenhart and Crumpton, 1989, Bachmann et al., 1990). Instream loss rates of nitrate nitrogen reported for agricultural streams generally range between about 0.1 and 1 g NO₃-N / m² / day (Hill, 1983).

The seasonal variation in nitrate and organic nitrogen concentrations in river water entering the wetlands had a significant effect on the quality of water exiting the wetlands. Nitrate concentrations in water exiting the wetlands were consistently reduced relative to inlet concentrations (Figure 2). However, concentrations of organic nitrogen were frequently higher in water exiting the wetlands than in water entering the wetlands (Figure 3). As a result, during periods of high nitrate load, when nitrate comprised most of the total nitrogen
load, the wetlands were effective sinks for total nitrogen (Figure 4). In contrast, during periods of low nitrate loading in the summer, when organic nitrogen comprised most of the total nitrogen load, the wetlands were frequently sources for total nitrogen.

On an annual basis, all of the wetlands were sinks for nitrate, with high flow wetlands removing 78-84% of the nitrate received and the low flow wetland removing 95% of the nitrate received (Table 1). For EW4, organic nitrogen exports approximately equaled imports, with the wetland removing 8% of the organic nitrogen received. The higher organic nitrogen concentrations in EW4 outlet water relative to inlet water apparently reflect the concentrating effect of net evaporative losses, which accounted for 13% of the water budget for this wetland (Hey et al., 1994a). Net evaporative loss accounted for only 2-3% of the water budget for the high flow wetlands (Hey et al., 1994a). The high flow wetlands not only exported higher concentrations of organic nitrogen than received, but were net sources for organic nitrogen on an annual basis, exporting 22-31% more mass of organic nitrogen than received (Table 1). The fact that all three wetlands were net sinks for total nitrogen on an annual basis (Table 1) can be attributed to the high nitrate loads and losses early and late in the year (Figure 2). Clearly the effectiveness of the wetlands as nitrogen sinks is closely related to nitrate loading rate.

Microcosm Studies

The field data demonstrate the considerable capacity of the wetlands as nitrate sinks but provide little insight regarding factors affecting rates of nitrate loss. The experimental microcosm studies were designed to examine the effects of nitrate concentration, temperature, and location on nitrate loss rates in the experimental wetlands. These were thought to be among the most significant variables affecting nitrate loss in the experimental wetlands. Previous studies have demonstrated that temperature and nitrate concentrations can significantly affect nitrate loss rates in a range of aquatic systems, although most of the published literature deals with rivers, lakes, and estuaries (Andersen, 1977; van Kessel, 1977; Nedwell, 1982; Seitzinger, 1988; Cerco, 1989). The results of these experiments are summarized in Table 2. The effect of nitrate concentration was highly significant (p<0.001)
in all experiments, but the effect of temperature was significant in only three out of six experiments. These results are consistent with previous studies which generally report significant effects of nitrate concentration on nitrate loss rate in a variety of aquatic systems, but less frequently report an effect of temperature (Andersen, 1977; Knowles, 1982; Cerco, 1989).

Location was considered a potentially important variable for the current study because the experimental wetlands differ in hydrologic and nitrate loading rate as well as in sediment characteristics. EW3 and EW5 receive approximately seven times more water and nitrate load than EW4 (Table 3). In addition, the wetlands differ considerably in the organic content of their bottom sediment, ranging from 8.8% in EW4 to 28.1% in EW3 (Table 3). Previous studies have demonstrated the importance of organic matter availability for denitrification (Knowles, 1982) and it was expected that differences in percent sediment organic matter between locations would cause a significant location effect in most experiments. However, the effect of location was significant in only two out of the six experiments, and the effect was not related to percent organic matter in the sediment (Table 3). The effect of location was not significant when comparing cores from the high flow wetlands despite a three fold difference in percent sediment organic matter among the sites. The effect of location was significant only when comparing cores from high flow and low flow wetlands, with cores from the high flow wetlands having consistently higher rates of nitrate loss than cores from the low flow wetland (Table 3).

Further analysis shows that cores from the high flow wetlands had not only higher nitrate loss rates but also higher rate coefficients for nitrate loss. This is illustrated by comparing the velocity of deposition for cores from high flow and low flow wetlands. The velocity of deposition for each core was calculated based on the formula

\[ v_g = \frac{F}{C} \]

where \( v_g \) = the velocity of deposition in m/day, \( F \) = the loss rate of nitrate in g N m\(^{-2}\) day\(^{-1}\), and \( C \) = the concentration of nitrate in g N m\(^{-3}\).

Although expressing the nitrate removal capacity in meters per day, \( v_g \) is analogous to the rate coefficient for a first order reaction in a continuously stirred tank reactor. As was
the case for nitrate loss rate, velocity of deposition was unrelated to percent sediment organic matter but does seem related to loading rate (Table 4). Cores from the high flow wetlands had consistently higher vgs than cores from the low flow wetland, suggesting that higher loading rates might have increased nitrate removal capacity in the high flow wetlands. This interpretation is consistent with recent studies suggesting that nitrate loads to wetlands might significantly stimulate the activities and/or population densities of denitrifying bacteria (Isenhart, 1992; Moraghan, 1992). Moraghan (1992) found that prior addition of antecedent KNO$_3$ to natural wetlands with controlled inflows and outflows increased apparent denitrification (as unaccounted for K$^{15}$NO$_3$) from 56 to 83%. Moraghan suggested that addition of nitrate might have stimulated synthesis of dissimilatory nitrate reductase or inhibited competitive reactions, in either case resulting in increased denitrification. Isenhart (1992) drew similar conclusions from an observed increase in the nitrate assimilative capacity of experimental wetland mesocosms following dosage with NaNO$_3$. Isenhart (1992) observed a four fold increase in the velocity of deposition of nitrate within a few days following the addition of approximately 10 mg NO$_3$-N/L and suggested that nitrate addition stimulated the activities and/or population densities of denitrifying bacteria. Isenhart (1992) also suggested that the nitrate removal capacity of wetlands might be enhanced by sustained nitrate loads, a suggestion consistent with our results for the Des Plaines River Experimental Wetlands.

Although intriguing, the general significance of nitrate loading effects is still unclear, and in the case of the Des Plaines River Wetlands, factors other than nitrate loading might be involved. The high flow and low flow wetlands differ also in hydrologic loading rate, dissolved organic carbon loading rate, and nutrient loading rate, any of which might affect nitrate assimilative capacity. Clearly further research into controls over nitrate assimilative capacity in these wetlands is needed. In particular, the effect of hydrologic and nitrate loading rates on nitrate removal capacity of the wetlands should be studied further, including the effect of seasonal changes in nitrate loading rates.
REFERENCES


TABLE 1

Annual nitrate nitrogen, organic nitrogen, and total nitrogen budgets for the Des Plaines Experimental Wetlands during the 1991 operating period (April through November). Values for nitrogen in and out are in units of g N/ m²/year.

<table>
<thead>
<tr>
<th>Average Detention time</th>
<th>Nitrate Budget</th>
<th>Organic N Budget</th>
<th>Total N Budget</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in / out / % loss</td>
<td>in / out / % loss</td>
<td>in / out / % loss</td>
</tr>
<tr>
<td>EW3 12 days</td>
<td>21.6 / 4.7 / 78%</td>
<td>6.25 / 8.2 / -31%</td>
<td>27.8 / 12.9 / 54%</td>
</tr>
<tr>
<td>EW4 95 days</td>
<td>3.2 / 0.2 / 95%</td>
<td>0.94 / 0.86 / 8%</td>
<td>4.1 / 1.0 / 75%</td>
</tr>
<tr>
<td>EW5b 13 days</td>
<td>20.2 / 3.2 / 84%</td>
<td>6.15 / 7.48 / -22%</td>
<td>26.2 / 10.7 / 59%</td>
</tr>
</tbody>
</table>

^Negative % loss represents export.

bOutput for EW5 includes seepage with concentrations assumed equal to those of surface outflow.
TABLE 2

Main effects table from ANOVAs of microcosm experiments showing the effects of nitrate concentration, temperature, and location on nitrate loss rate.

<table>
<thead>
<tr>
<th>Date of Experiment</th>
<th>Treatment</th>
<th>June 17</th>
<th>June 20</th>
<th>July 3</th>
<th>July 9</th>
<th>July 25</th>
<th>July 30</th>
</tr>
</thead>
<tbody>
<tr>
<td>p value for treatment effects</td>
<td>Concentration</td>
<td>&lt;.001</td>
<td>&lt;.001</td>
<td>&lt;.001</td>
<td>&lt;.001</td>
<td>&lt;.001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>.076</td>
<td>&lt;.001</td>
<td>&lt;.001</td>
<td>&lt;.001</td>
<td>.25</td>
<td>.19</td>
</tr>
<tr>
<td></td>
<td>Location</td>
<td>.25</td>
<td>&lt;.001</td>
<td>.48</td>
<td>.56</td>
<td>&lt;.001</td>
<td>.71</td>
</tr>
</tbody>
</table>
TABLE 3

Nitrate nitrogen loss rates from microcosm experiments in relation to hydrologic loading and % sediment organic matter.

<table>
<thead>
<tr>
<th>Location</th>
<th>Hydrologic loading rate (cm/week)</th>
<th>Sediment % organic matter x (SD,n)</th>
<th>Date of experiment</th>
<th>NO$_3$-N loss rate (gN/M$^2$/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wetland 3 (upper)</td>
<td>36.4</td>
<td>28.1(.053,33)</td>
<td>6-17</td>
<td>.30</td>
</tr>
<tr>
<td>Wetland 3 (lower)</td>
<td>36.4</td>
<td>18.5(.074,11)</td>
<td>6-20*</td>
<td>.34*</td>
</tr>
<tr>
<td>Wetland 4</td>
<td>5.3</td>
<td>8.8(.017,20)</td>
<td>7-3</td>
<td>.40</td>
</tr>
<tr>
<td>Wetland 5</td>
<td>35.9</td>
<td>10.3(.027,11)</td>
<td>7-9</td>
<td>.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7-25*</td>
<td>.33*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7-30</td>
<td>.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.26*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.24*</td>
</tr>
</tbody>
</table>

* indicates significant difference (p<.001) in loss rate between locations
### TABLE 4

Velocity of deposition of nitrate from microcosm experiments in relation to hydrologic loading and % sediment organic matter.

<table>
<thead>
<tr>
<th>Location</th>
<th>Hydrologic loading rate (cm/week)</th>
<th>Sediment % organic matter x (SD,n)</th>
<th>Date of experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wetland 3 (upper)</td>
<td>36.4</td>
<td>28.1(0.053,33)</td>
<td>6-17</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6-20*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7-3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7-9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7-25*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7-30</td>
</tr>
<tr>
<td>Wetland 3 (lower)</td>
<td>36.4</td>
<td>18.5(0.074,11)</td>
<td>0.079</td>
</tr>
<tr>
<td>Wetland 4</td>
<td>5.28</td>
<td>8.8(0.017,20)</td>
<td>0.06*</td>
</tr>
<tr>
<td>Wetland 5</td>
<td>35.9</td>
<td>10.3(0.027,11)</td>
<td>0.106</td>
</tr>
</tbody>
</table>

* indicates significant difference (*p*<.001) in velocity of deposition between locations.

velocity of deposition (m^3/day)
Fig. 1. Seasonal patterns in stream flow (solid line), nitrate nitrogen (dashed line), and organic nitrogen (dotted line) for the Des Plaines River at the study site.
Fig. 2. Seasonal patterns in nitrate nitrogen concentrations in inlet water (solid line) and outlet water for EW3 and EW5 (dashed lines) and EW4 (dotted line).
Fig. 3. Seasonal patterns in organic nitrogen concentrations in inlet water (solid line) and outlet water for EW3 and EW5 (dashed lines) and EW4 (dotted line).
Fig. 4. Seasonal patterns in total nitrogen concentrations in inlet water (solid line) and outlet water for EW3 and EW5 (dashed lines) and EW4 (dotted line).
CHAPTER 3. NITRATE LOSS CAPACITY IN CONSTRUCTED WETLANDS OF DIFFERENT HYDROLOGIC AND NUTRIENT LOADS

A paper to be submitted to the journal Ecological Engineering

Richard G. Phipps. William G. Crumpton

ABSTRACT

Constructed wetlands at the Des Plaines Wetland Demonstration Project in Wadsworth, Illinois were examined for their capacity to remove nonpoint source loads of nitrate from an agricultural watershed. Three flow through wetlands received different loading rates of pumped river water with seasonably variable loads of nitrate and organic nitrogen. The nitrogen removal capacities of the wetlands were estimated using mass balance and sediment-water microcosms for the 1992 field season. Concentrations of nitrogen and flow volumes were monitored at inlets and outlets of the wetlands. Mass balance calculations revealed that all three wetlands were net sinks for nitrate and total nitrogen, but two of three wetlands were net exporters of organic nitrogen. The wetlands received high (23.3 m), intermediate (12.6 m), and low (3.3 m) rates of loading. The efficiency of nitrate removal was inversely related to hydrologic load: high flow wetland - 30.1%, intermediate flow wetland - 46.1%, and low flow wetland - 82%, and the total mass of nitrate load: high - 964 kg, intermediate - 499 kg, and low - 122 kg. In order to estimate nitrate loss capacity of a wetland, intact sediment cores (microcosms) were collected from each wetland at approximately two week intervals. Areal nitrate loss rate coefficients (k_a) were determined from laboratory incubations of the microcosms. These coefficients were expected to vary between wetlands with different loading rates, as well as over the course of the season. However, the range of k_a's was far less than the range of hydrologic load and nitrate concentrations. Mean k_a's corrected for the effect of temperature (k_{a0}) were: EW3 - .061, EW5 - .076, and EW4 - .073. Field k_a's, calculated for the period from April 15 to May 27.
when three fourths of the annual nitrogen load entered the wetlands, were on the order of .2 for all the wetlands. \( K_a \) provided a reasonably consistent parameter for estimation of the nitrate assimilative capacity in the Des Plaines wetlands.

**INTRODUCTION**

Quantifying nitrate loss rates in wetlands is a step toward reducing nonpoint source nitrate runoff from agricultural watersheds. The capacity of wetlands to function as nitrate sinks is due primarily to assimilation by plant and microbial communities, and to denitrification, which is presumed to be the primary loss process in wetlands receiving external nitrate loads (Nixon and Lee, 1986; Bowden, 1987; Seitzinger, 1988; Neely and Baker, 1989). Transformations of nitrate in wetlands involve complex spatial and temporal patterns, and wetlands differ greatly in their efficiency as nitrate sinks. However, in spite of this complexity, loss rates of nitrate and a great many other contaminants in wetlands can be described as first order processes (Kadlec and Knight, 1996).

In the case of flow through wetlands receiving significant surface nitrate loads, loss rates can be described by a temperature dependent first-order areal model (Crumpton and Phipps, 1992; Kadlec and Knight, 1996):

\[
J = k_{30} \cdot C \cdot \theta^{(T-20)}
\]  

(equation 1)

where,

- \( J \) = the area-based nitrate-nitrogen loss rate, g N m\(^{-2}\) day\(^{-1}\)
- \( k_{30} \) = the area-based, first order loss rate coefficient for nitrate-N at 20°C, m/day
- \( C \) = the concentration of nitrate-nitrogen, g N m\(^{-3}\)
- \( \theta \) = the temperature coefficient for nitrate nitrogen loss
- \( T \) = the water temperature, °C

According to this model, the nitrate loss rate coefficient is assumed constant and nitrate loss rates \( (J) \) are expected to vary predictably in response to changes in nitrate concentrations and water temperature. However, it is possible that the nitrate loss rate coefficient might vary
during the season. Both Moraghan (1992, 1993) and Isenhart (1992) observed that prior exposure to nitrate had a stimulatory effect on nitrate loss in experimental wetland enclosures. Isenhart (1992) suggested that the nitrate assimilative capacity of wetlands might be enhanced by sustained nitrate loads. Prior exposure to nitrate may influence the magnitude of denitrification by increasing levels of dissimilatory reductases, reducing the capacity of assimilatory sinks, and decreasing dissimilatory reduction of nitrate to ammonia (Moraghan, 1992). These results suggest that nitrate loss rate coefficients, corrected for the effect of temperature (\(k_0\)) (Table 2), might change in response to varying nitrate concentrations and loading patterns thus reducing the predictive power of equation 1.

Effects of changing nitrate concentrations could be especially important in the case of wetlands draining agricultural watersheds. These watersheds often show dramatic seasonal patterns in nitrate loads, with concentrations typically highest during periods of high flow in the spring and fall, and declining during periods of low flow (Christensen and Sorensen, 1988; Phipps and Crumpton, 1994; W.G. Crumpton, unpublished data). The objective of the work described here was to characterize nitrate loss rate coefficients for wetlands subjected to varying hydrologic and nitrate loading regimes.

METHODS

This research was conducted at the Des Plaines River Wetlands Demonstration Project site near Wadsworth, Illinois, USA (figure 1 site map). Upstream of the site, the Des Plaines River drains approximately 520 km² of mainly agricultural land (80%) in southeastern Wisconsin and northeastern Illinois. Wetland construction and restoration at the site began in 1986 and the three experimental wetlands (EW3, EW4, and EW5) used in the research described below were completed in October, 1988. Wetlands EW3 and EW4 were 2.4 ha, while EW5 was 1.9 ha. Average depths were 61 cm for EW3, 72 cm for EW4, and 69 cm for EW5. All three wetlands had been maintained at similar water levels since construction and were at a similar developmental stage. This is important because nitrate removal capacity may be enhanced as the maturity of vegetation and litter increases (Crumpton et al., in prep). White water lilies (\(Nymphaea sp\)), milfoil (\(Myriophyllum sp\)), and
algal mats dominated open water and cattails (*Typha sp*) dominated the more peripheral emergent vegetation. Detailed descriptions of the site and the experimental wetlands, including hydrology, can be found in Hey et al. (1994a).

A pump station installed on the Des Plaines river was used to deliver controlled amounts of river water to each of the wetlands, and wetland water levels and discharge were controlled by a weir at the outlet of each wetland. During the current study, from April 15 through October 8, 1992, the wetlands were assigned low (EW4), intermediate (EW5), and high (EW3) treatments spanning approximately an order of magnitude in hydrologic loading rates. Loading rates were adjusted weekly to follow changing river flows. River stage was measured each week and flows calculated from a stage discharge formula for the site (Hey et al., 1994a). Replicate 60 ml samples were collected at weekly intervals from the Des Plaines River, from wetland inlets, and from wetland outlets, and preserved by acidification to pH <2 using H₂SO₄ (Hey et al., 1994b). Samples were assayed for nitrate and total nitrogen using second derivative spectroscopy (Crumpton et al., 1992), and for ammonium using the indophenol method (Scheiner, 1976). Organic nitrogen was calculated by difference.

Nitrate loss coefficients for all the wetlands were estimated using sediment-water microcosms at approximately two week intervals from May 1 through October 7. The microcosms were designed for both sampling and incubation so that measurements could be made of intact sediment-water systems with minimal disturbances. For each sampling date, 10 microcosms per wetland were collected from open water or lightly vegetated areas in each wetland. In EW3, cores were taken from the upper reach, 15-40 m from the inlet. In EW4 and EW5, cores were taken from middle reaches. Polycarbonate cylinders (5.1 cm ID, 30.5 cm long) with sharpened cutting edges were inserted at least 7 cm into the sediment and their tops sealed using rubber stoppers. The microcosms with intact sediment were then extracted and their lower ends stoppered. Microcosms were placed in coolers as soon as they were collected and transferred to water baths immediately upon return to the laboratory. EW4 outlet water, which was always low in NO₃⁻, was added to the baths until the tops of the microcosms were overlain by approximately 2 cm of water. Two circulating, thermostated water baths maintained constant water temperature of approximately 22°C. Water overlying
each microcosm was bubbled with air long enough to allow thorough mixing and baths were drained to 3-4 cm below the cylinder tops. Overlying water within the microcosms was then adjusted to approximately 6 cm above the sediment-water interface and microcosms were spiked with NaNO₃ to provide initial concentrations of approximately 3 or 6 mg NO₃⁻-N/liter. Microcosms were sampled by collecting 10 ml of overlying water initially and then again after a 6 hour dark incubation. Initial and final samples were preserved with HCl to pH<2 and analyzed for nitrate nitrogen using second derivative ultraviolet spectroscopy (Crumpton et al., 1992). Measured rates of decline in nitrate concentration in microcosms were used to calculate area based nitrate loss rate coefficients (kₐ) (Kadlec and Knight, 1996) according to the equation:

\[ k_a = \left(\frac{\ln (N_f/N_i)}{t}\right) \times \text{depth} \]  

\[ \text{equation 2} \]

where:

- \( k_a \) = areal nitrate loss rate coefficient, m/day
- \( N_f \) = final nitrate concentration, g NO₃⁻-N m⁻³
- \( N_i \) = initial nitrate concentration, g NO₃⁻-N m⁻³
- depth = height of water (m) overlying sediment in microcosms
- \( t \) = duration of incubation in days

In order to estimate the field nitrate loss coefficients of the different wetlands, a model with a static retention coefficient was first developed with the following differential equation:

\[ \frac{d\text{NO}_3^-}{dt} = \text{NO}_3^\text{in} - \text{NO}_3^\text{out} - \text{NO}_3^\text{ret} \]  

\[ \text{equation 3} \]

where:

- \( \text{NO}_3^\text{in} \) = mass of NO₃⁻ in the wetland, g NO₃⁻
- \( \text{NO}_3^\text{out} \) = inflow of NO₃⁻, g NO₃⁻ day⁻¹
- \( \text{NO}_3^\text{ret} \) = outflow of NO₃⁻, g NO₃⁻ day⁻¹
- \( \text{NO}_3^\text{ret} \) = retention (combined loss processes), g NO₃⁻ day⁻¹

The removal of NO₃⁻ was described by the equation:
\[
\text{NO}_3^{-\text{ret}} = k_{20} \times \text{NO}_3^- \times \theta^{(T-20)} \times \text{wetland area} \quad \text{(equation 4)}
\]

where,

\[k_{20} = \text{the areal nitrate loss coefficient at 20°C}\]
\[\theta = \text{the temperature coefficient for NO}_3^- \text{ loss}\]

For these systems, a temperature coefficient of 1.07 was used (Crumpton and Phipps, 1992, Kadlec and Knight, 1996).

The reaction rate expression for nitrate nitrogen removal was combined with a tanks in series (TIS) hydrodynamic model to simulate residence time distributions of water and chemicals entering the wetlands. A TIS model was used to represent wetland hydrodynamics since TIS models have been shown to adequately interpret tracer movement through these wetlands (Kadlec and Knight, 1996). Measured rates of inflow and measured concentrations of nitrate nitrogen in water entering the wetlands were used to provide hydrologic and nitrate loads and these loads were used as inputs to the model. Model simulations were run with a time step of one hour and nitrate nitrogen loss rate coefficients \((k_{20})\) for each wetland were found by calibration so as to minimize the deviation between observed and modeled cumulative nitrate removal.

**RESULTS AND DISCUSSION**

On an annual basis, nitrate was the predominant form of nitrogen in the Des Plaines River. Concentrations of nitrate nitrogen ranged over the course of the study from detection limits of \(<0.1 \ \text{mg/l}\) to a peak of 3.95 \(\text{mg/l NO}_3^-\)-N. Organic nitrogen was the next most prevalent form of nitrogen with concentrations which were much less variable, ranging from .31 \(\text{mg/l}\) to 1.07 \(\text{mg/l NO}_3^-\)-N. Nitrate and organic nitrogen comprised 76 and 22\%, respectively, of the total nitrogen load carried by the river. Ammonium concentrations were consistently low, ranging from .02 to .16 \(\text{mg/l}\). The relative concentrations of nitrate and organic nitrogen varied over the course of the field season (figure 2). Organic nitrogen concentrations remained relatively constant, whereas nitrate concentrations corresponded to
seasonal changes in stream flow. Spring runoff from agricultural lands in the watershed resulted in high concentrations of nitrate during this period of high stream flow (figure 2). During periods of low flow, with lower loading rates and higher rates of biological production, organic nitrogen concentrations were considerably higher than those of nitrate. Rain events in mid July and in September raised flows and nitrate concentrations to additional peaks. These patterns are typical of agricultural streams receiving significant nonpoint source inputs of nitrogen (Hill, 1983; Christensen and Sorensen, 1988; Bachmann. 1990; W.G. Crumpton, unpublished data).

The pumping regime and seasonal changes in river flow and nitrogen loads ensured that the wetlands would be subjected to a wide range of hydrologic loading rates and nitrate concentrations. The ranges of nitrate nitrogen concentration and hydrologic load encountered in these wetlands during the field season, were between 0 to 4 mg/l, and from 0 to 386 cm/week, respectively. Figure 3 shows the hydrologic load entering each wetland in meters per week and the mean water temperature, which ranged from 5 to 25°C. The overall hydrologic load for the study period was 23.3 meters for the high flow wetland, 12.6 m for the intermediate flow wetland, and 3.3 m for the low flow wetland. Most of the hydrologic load occurred during spring runoff, and in pulses following infrequent rain events. A summary of the hydrologic and nitrate loads entering and exiting the wetlands is provided in Table 1.

Hydrologic budgets of inflows and outflows were combined with nitrogen concentrations to construct mass balance budgets for organic nitrogen, nitrate, and total nitrogen. Nitrate concentrations were always lower at wetland outflows than inflows (Figure 4). In contrast, organic nitrogen concentrations at wetland outflows were nearly always higher than at wetland inflows (Figure 5). The high and low flow wetlands were net exporters of organic nitrogen, while the intermediate flow wetland was a net sink due to seepage losses from the wetland that reduced surface outflows. If seepage is assumed to transport organic nitrogen from the wetland at the same concentrations as the outflow, then the intermediate flow wetland also functioned as a net exporter of organic nitrogen. That the wetlands were predominantly exporters of organic nitrogen probably reflects high rates of
nutrient assimilation and production of aquatic vegetation and algae in the wetlands (Fennessy et al., 1992). In contrast to the case for organic nitrogen, all three wetlands were sinks for nitrate and total nitrogen on an annual basis (Table 1). However, the effectiveness of the wetlands as sinks for total nitrogen can be attributed entirely to the removal of large amounts of nitrate during periods of high flow. These results confirm the effectiveness of wetlands as sinks for nitrate, although the wetlands differed considerably in the mass and efficiency of nitrate removal (Table 1). Nitrate removal efficiency was clearly related to loading rate and residence time, with the low flow wetland having a removal efficiency nearly three times that of the high flow wetland. During the week of peak flow in April, the high flow wetland received nearly 4 meters of load (figure 3), with a residence time of just under one day, while the low flow wetland received almost .5 meters, with a residence time of nearly 5 days.

The differences in nitrate removal efficiency do not mean that the wetlands differed in nitrate removal capacity. Given the same loading rates and residence times, all three wetlands might have had an equivalent capacity for nitrate removal. Differences in nitrate removal capacity would be reflected in different nitrate loss rate coefficients ($k$). A comparison of field nitrate loss rate coefficients determined by calibration of the static retention coefficient model (equation 4) revealed that the three wetlands had nearly identical nitrate loss rate coefficients, ranging from .21 m day$^{-1}$ for the high flow and intermediate flow wetlands to .18 m day$^{-1}$ for the low flow wetland.

Within each wetland, nitrate loss rates varied with seasonal changes in loading rate and residence time. In the case of the high flow wetland, for example, 74.1% of the nitrate load occurred during the spring runoff period between April 15 and May 27. Nitrate loss during this period accounted for 81.4% of the total, annual nitrate loss (figure 6). Nitrate loss coefficients might also be expected to vary seasonally in response to changing nitrate loads. However, the field data were not adequate to examine seasonal changes in nitrate removal capacity, especially during periods when nitrate loading rate was minimal. Nitrate loss rates in microcosms allowed the calculation of $k$ under controlled conditions of temperature and nitrate concentration throughout the field season. Loss rates in microcosms were expected to
reflect the history of recent nitrate exposure in the field, i.e., that higher \( k_\alpha \) values might be measured in the wetlands at higher nitrate loads. However, microcosm loss rate coefficients among the three wetlands were reasonably close. Figure 7 shows that the \( k_\alpha \)'s for the wetlands ranged from around 0.02 to 0.22. At any one time, \( k_\alpha \)'s between wetlands varied by a factor of less than two while within wetland \( k_\alpha \) varied over the course of the season by a factor of around three. The range of \( k_\alpha \)'s found in microcosm studies was comparable to loss rate coefficients from other studies (Kadlec and Knight, 1994). However, because of the incubation conditions, loss rate coefficients estimated from microcosms and from the field mass balance data are not equivalent measures. \( k_\alpha \)'s estimated from the field mass balance data were significantly higher than those found in the microcosms, which is expected given the lower oxygen concentrations in the field (Cronk and Mitsch, 1994). Oxygen concentrations near the sediment surface frequently dropped below 1mg/l in the field (Cronk and Mitsch, 1992), while oxygen concentrations in the microcosms were at or near saturation. Lower oxygen concentrations in the field would reduce the thickness of the oxic surface layer, thereby increasing the rate of nitrate diffusion to anaerobic sites, and result in a higher realized \( k_\alpha \) value (Christensen et al., 1990; Sweerts et al., 1989).

Nitrate loss rate coefficients in microcosms (\( k_\alpha \)'s) could be expected to vary seasonally in response to changing NO\(_3^-\) loads in the field. In early May, when river temperature was 13°C, \( k_\alpha \)'s ranged from 0.04 to 0.07 (figure 7). Peak \( k_\alpha \)'s occurred shortly after the first major inflow and leveled off following this early peak. The nitrate loading, (mg NO\(_3^-\)-N m\(^{-2}\)) (figure 4), was high through April into late May, dropped to near 0 in June, had a small peak in July, flattened in late July through early September, and rose sharply in September. Low \( k_\alpha \)'s in early May might be due to lower temperatures in the field at that time. Bacterial populations and denitrifying enzymes may not have been adequate to fully take advantage of the excess nitrate. Higher \( k_\alpha \)'s from mid May through mid June may be the result of larger, nitrate adapted populations developing at higher temperatures. The midsummer decline in \( k_\alpha \)'s may have been related to lower availability of nitrate, reduced availability of carbon for denitrifying bacteria, or possibly some other limiting factors.
More important than the variations between and within wetlands, is how little \( k_a \)'s did vary, despite the great range of hydrologic input during the year. For example, the hydrologic loading rate and nitrate concentrations for the high flow wetland varied by two to three orders of magnitude, from .04 to 3.86 meters/week, and .01 to 3.19 mg/l, while \( k_a \) ranged between .05 to .15. Nitrate loss coefficients, found in 1991 for these same wetlands, provide a year to year comparison (Table 2). Unlike the hydrology in 1992, loading rates for each wetland were held constant for the season. Mean \( k_{30} \)'s for all 1991 experiments, ranged between .062 and .077. In comparison, 1992 \( k_{30} \) values, ranged between .061 and .076 (Table 2).

In spite of this speculation regarding seasonal changes in \( k_a \), the data presents no indisputable trends. Any effect of hydrologic loading may have been obscured for a number of reasons. Unlike wetlands designed for wastewater treatment, hydrologic loads entered the wetlands in large pulses of short interval, dependent on precipitation events. For most of the summer of 1992, precipitation was minimal and nitrate concentrations very low. Even in the high flow wetland, water movement was extremely slow, with an average speed on the order of .001 ft/sec, and an intermediate flow pattern between complete mixing and plug flow (Kadlec and Hey, 1994; Hey et al, 1994a). Denitrification is known to show great spatial and temporal variability in rates, with coefficients of variation often exceeding 100% (Groffman, 1994). More frequent and intensive sampling may be required to detect any effects of loading patterns on nitrate assimilative capacity. The wetlands also differed in distribution of vegetation, litter development, flow patterns, depth of sediment, and other characteristics.

It is also important to recognize that nitrate loss coefficients can increase for several years in newly created wetlands before stabilizing (Crumpion et al., in prep). The development of vegetation and litter is likely to be an important influence in achieving this rate for several reasons. Vegetation may supply carbon for denitrifiers, provide surface area for microbial activity, act as an obstacle to flowing water that increases residence time, interfere with oxygen transfer across the air/water interface (Rose and Crumpion, 1996) and provide oxygen to oxidize reduced forms of nitrogen to nitrate in oxygenated rhizospheres (Reddy et al., 1989). However, the relative lack of variability in \( k_a \) suggests that once a
wetland has matured, $k_4$ might be a relatively stable, robust measurement useful in modeling nitrate loss.

Any effect of hydrologic loading on the nitrate removal capacity of wetlands remains speculation. In the Des Plaines River Wetlands, factors other than nitrate loading may be involved. Despite the variability of wetlands, in comparison to the wide range of hydrologic and nutrient loading, there was relatively little variation in $k_4$ within or between wetlands during the course of this study. Although $k_4$, appears to be a useful parameter for the prediction of field nitrate loss in flow through wetlands, further study is needed.

REFERENCES


Table 1. Comparison of hydrologic load in meters/year, nitrate loads in kg/year, and efficiency of nitrate removal for the three wetlands

<table>
<thead>
<tr>
<th></th>
<th>low</th>
<th>intermediate</th>
<th>high</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m) Hydrol load in</td>
<td>3.6</td>
<td>13.3</td>
<td>25.2</td>
</tr>
<tr>
<td>kg NO3-N in</td>
<td>122</td>
<td>502</td>
<td>964</td>
</tr>
<tr>
<td>kg NO3-N out</td>
<td>22</td>
<td>327</td>
<td>729</td>
</tr>
<tr>
<td>% NO3-N removal</td>
<td>81%</td>
<td>35%</td>
<td>24%</td>
</tr>
<tr>
<td>kg orgN in</td>
<td>52.2</td>
<td>166.8</td>
<td>383.9</td>
</tr>
<tr>
<td>kg orgN out</td>
<td>71.1</td>
<td>151.4</td>
<td>474.3</td>
</tr>
<tr>
<td>% orgN removal</td>
<td>-36.1%</td>
<td>9.2%</td>
<td>-23.5%</td>
</tr>
<tr>
<td>kg total N in</td>
<td>201.8</td>
<td>678.5</td>
<td>1381</td>
</tr>
<tr>
<td>kg total N out</td>
<td>88.7</td>
<td>424.4</td>
<td>1176.2</td>
</tr>
<tr>
<td>% total N removed</td>
<td>56.1%</td>
<td>37.4%</td>
<td>14.8%</td>
</tr>
</tbody>
</table>
Table 2. Temperature corrected nitrate loss coefficients (m day⁻¹) from microcosm experiments in 1991 and 1992. The calculation of $k_{20}$ uses a temperature coefficient determined from microcosm data (Crumpton and Phipps, 1992) as: $k_{20} = k_4/1.07^{(T-20)}$, where $k_{20}$ = nitrate loss coefficient corrected to 20°C, m/day; $k_4$ = areal nitrate loss coefficient at temperature of incubation, m/day; and T = temperature of incubation, degrees °C.

<table>
<thead>
<tr>
<th></th>
<th>Mean $k_{20}$</th>
<th>SE</th>
<th>Mean $k_{20}$</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1991</td>
<td></td>
<td></td>
<td>1992</td>
<td></td>
</tr>
<tr>
<td>EW3</td>
<td>.064</td>
<td>.002</td>
<td>.061</td>
<td>.003</td>
</tr>
<tr>
<td>EW4</td>
<td>.062</td>
<td>.003</td>
<td>.073</td>
<td>.003</td>
</tr>
<tr>
<td>EW5</td>
<td>.077</td>
<td>.006</td>
<td>.076</td>
<td>.004</td>
</tr>
</tbody>
</table>
Figure 1. Site Map
Figure 2. Seasonal patterns in stream flow, nitrate nitrogen, and organic nitrogen for the Des Plaines River at Wadsworth Rd.
Figure 3. Seasonal patterns of hydrologic loading rates and temperature of water pumped into the three wetlands
Figure 4. Seasonal patterns in nitrate nitrogen concentrations in inflow water and outflow water for the three wetlands
Figure 5. Seasonal patterns in organic nitrogen concentrations in inflow water and outflow water for the three wetlands
Figure 6. Seasonal pattern of nitrate load and nitrate removal for the high flow wetland
Figure 7. Seasonal patterns of nitrate loss coefficients from laboratory microcosm studies
Figure 8. Seasonal patterns of nitrate concentrations, temperature, and mean $k_a$ (3 wetlands combined)
CHAPTER 4. FATE OF NITROGEN LOADS IN EXPERIMENTAL WETLANDS

A report to the Environmental Protection Agency

William G. Crumpton, Richard G. Phipps

ABSTRACT

Agricultural applications of fertilizers and pesticides have more than doubled since the 1960s, and agrichemical contamination of surface and groundwaters has become a pressing environmental problem. One of the most promising strategies for reducing non-point source contamination of surface and groundwaters is the use of constructed or restored wetlands specifically as sinks for ag-chemical contaminants. Studies suggest that wetlands may act as sinks for a variety of compounds, and wetlands may be especially effective as sinks for nonpoint source nitrate loads. However, nitrogen transformations involve complex spatial and temporal patterns, and wetlands differ greatly in their efficiency as nitrate sinks, even when depth, area, and residence time are accounted for.

The overall objective of the work described here is to develop models of nitrate loss for wetlands receiving non-point source nitrate loads. Our approach combines field studies of nitrogen fate in the Des Plaines River Experimental Wetlands and experimental studies of factors affecting nitrate loss to develop models of nitrate flux. Field studies demonstrated the considerable capacity of the experimental wetlands as nitrate sinks, and experimental microcosm studies demonstrated the importance of nitrate concentration, temperature, and location on rates of nitrate loss. These data were used to evaluate two empirical models describing nitrate flux as a linear function of nitrate concentration and as either an exponential (metabolically limited) or linear (diffusion limited) function of temperature. The models explained approximately 75% of the variance in nitrate loss. Our results suggest that nitrate loss can be described as a first order process controlled by denitrifier activity, nitrate concentration, and the effective length of the diffusion path for nitrate to anaerobic sites.
INTRODUCTION

Agricultural applications of fertilizers and pesticides have more than doubled since the 1960s, and agrichemical contamination of surface and groundwaters has become a pressing environmental problem (Gianessi et al. 1986, Gray 1985, Keeney 1986). Nitrate and pesticides are the ag-chemical contaminants of foremost concern because of their potential impacts on both public health and ecosystem function, and because of the widespread use of nitrogen and pesticides in modern agriculture. The total amount of N applied in fertilizers far exceeds that of any other nutrient, and annual application of fertilizer-N in the U.S. has grown from a negligible amount prior to World War II to approximately nine million metric tons of N per year (USDA 1983). Substantial amounts of the chemicals applied to farm fields are lost to surface and groundwaters in agricultural watersheds (Omernik 1977, Keeney 1986). As much as 50% of the fertilizer nitrogen applied to cultivated crops may be lost in agricultural drainage water, primarily in the form of nitrate (Neely and Baker 1989). Despite our best efforts, it is unlikely that these contamination problems can be solved by chemical management alone. The best solutions will involve a combination of on-field and off-field approaches. One of the most promising strategies for reducing non-point source contamination of surface and groundwaters is the use of constructed or restored wetlands specifically as sinks for ag-chemical contaminants (van der Valk and Jolly 1992).

Studies suggest that wetlands may act as sinks for a variety of compounds (Howard-Williams 1985, Nixon and Lee 1986), and wetlands may be especially effective as sinks for nitrate loads from cultivated fields. If wetlands are to serve as long term sinks for nitrogen, differences in inputs and outputs must reflect net storage in the system through accumulation and burial in sediments, or net loss from the system through gaseous evolution of $\text{NH}_3$, $\text{N}_2\text{O}$, or $\text{N}_2$. Most of the published papers dealing with wetlands and water quality note the probable importance of denitrification, with resulting gaseous loss of $\text{N}_2\text{O}$ and $\text{N}_2$. In fact, with rare exception, denitrification is cited as the primary reason wetlands may serve as nitrogen sinks. However, there have been few actual measurements of denitrification in freshwater marshes (Nixon and Lee 1986, Bowden 1987, Seitzinger 1988, Neely and Baker 1989). As Neely and Baker (1989) note, denitrification is assumed to be an important
process in many freshwater wetlands based largely on circumstantial evidence, first that conditions in the wetlands are suitable for denitrification (anaerobic conditions and a large base of organic carbon) and second that nitrate disappears rapidly from water overlying wetland sediments. Increased nitrate loading to wetlands in agricultural watersheds might be expected to stimulate denitrification, but there are no reliable measurements of the effects of such loading or of the denitrification capacity of wetlands receiving agricultural loads.

Nitrogen transformations in wetlands involve complex spatial and temporal patterns, and wetlands differ greatly in their efficiency as nitrate sinks, even when depth, area, and residence time are accounted for. Aquatic plants (Reddy et al. 1989) and benthic invertebrates (Chaterpaul et al. 1980) may for example affect rates of microbial nitrogen transformations by altering fluxes of gases to and from anoxic sediments. In addition, seasonal and even diurnal changes in factors such as temperature, nitrate concentration, and oxygen concentration can dramatically effect nitrogen transformations in sediments (Andersen et al. 1984, Christensen et al. 1989). Understanding nitrate loss in wetlands requires consideration of process dynamics in addition to the details of system hydrology and nitrate transport.

The overall objective of the work described here is to develop models of nitrate loss for wetlands receiving non-point source nitrate loads. Our specific goal is to produce models of areal nitrate flux which can be combined with models of wetland hydrology and loading patterns (being developed by other researchers) to produce general models of nitrate loss and assimilative capacity. Our approach combines (1) field studies of nitrogen fate in the Des Plaines River Experimental Wetlands, (2) experimental studies of factors affecting nitrate loss, and (3) development of empirical and mechanistic models of nitrate flux.

METHODS

Experimental wetlands 3, 4, 5, and 6 (EW3, EW4, EW5, and EW6) were subjected to two hydrologic loading regimes, with two high flow wetlands (EW3 and EW5) receiving approximately five times more water per week than two low flow wetlands (EW4 and EW6). For most of the study period, EW3 and EW5 received approximately 15 to 20 inches of river
water per week while EW4 and EW6 received approximately 3 inches of river water per week. Because of excessive loss to groundwater, EW6 seldom had outflows and was dropped from the experimental design for the purposes of the analyses described below. During the study period, inlet and outlet samples were collected at weekly intervals and assayed for a range of constituents including nitrate, ammonium, and total nitrogen. Nitrate and total nitrogen were determined using the method described by Crumpton et al. (1992). A complete description of the water chemistry methods for the experimental wetlands is provided above in the appropriate section of this report. The weekly inlet and outlet monitoring data were used to assess the forms of nitrogen loaded to the experimental wetlands and the fate of different forms of nitrogen.

Experimental microcosms were used to examine the effects of temperature, nitrate concentration, and sampling location on nitrate flux. To examine these effects, experiments were run from June through November of 1991 as series of two-way and three-way ANOVAs with 4 X 2 designs (for concentration and temperature or concentration and location) and 2 X 2 X 2 designs (for concentration, temperature, and location). The microcosms used in this study were developed in our laboratory for measurements of benthic microbial processes, and consist of two-inch diameter, polycarbonate cores enclosing intact sediment and overlying water. The microcosms are designed for both sampling and incubation, so it is possible to measure processes in intact sediment-water systems with minimal disturbance. We have used these microcosms in previous studies of ammonium and nitrate flux, for 15N tracer studies of nitrogen assimilation, nitrification, and denitrification, and for studies of sediment oxygen profiles and flux rates using oxygen microelectrodes (Crumpton and Isenhart 1987, Crumpton et al. 1992, Isenhart 1988, Isenhart and Crumpton 1989, Tikkanen and Crumpton in prep.).

For the microcosm studies, cores were collected from open water or lightly vegetated areas in EW3, EW4, and EW5 every week from June through August and every 2 weeks from September through November of 1991. In EW3, cores were taken from two areas, one near the inlet and one near the outlet. Samples from the inlet area were taken from open water areas 15-40 meters from the inlet. Samples from outlet area were taken from open
water areas in the opposite third of the wetland near the outlet. Floating leaved and submersed macrophytes dominated the sampling sites but did not cover the bottom. In EW4, the region nearest the inlet was densely grown over with Typha. As a result, most of the cores were taken from middle reaches where there was more open water. Water depths were about 1/2 those of EW3, and plant growth made it more difficult to find open sediment. An effort was made to collect cores containing a minimal amount of plant material. In EW5, cores were taken from an area similar to that described in EW4. Although bottom mats of plant growth were thick, there were more patches of open sediment than found in EW4. Water depths were similar to the sampled areas of EW4.

To obtain cores, polycarbonate cylinders (5.1cm ID, 30.5cm long) were pushed into the sediment to depths of at least 7cm and their tops sealed using rubber stoppers. The cores with intact sediment were then pulled up and their lower ends stoppered. Cores were placed in coolers as soon as they were collected and transferred to water baths immediately upon return to the laboratory. EW4 outlet water was added to the baths until the tops of the cores were overlain by approximately 2cm of water. Water overlying each core was bubbled with air to allow thorough mixing and the baths drained to approximately 3-4cm below the cylinder tops. Circulating, thermostated water baths were used to maintain constant water temperature throughout the experiments. Overlying water within the cores was adjusted to approximately 6cm above the sediment water interface. Cores were spiked with 1ml additions of NaNO₃ to provide initial NO₃⁻N concentrations of approximately 0-0.2, 1, 3, 6, or 9mg/l, depending on the experimental treatment. Cores were sampled, incubated in the dark for a 6 hour period, and sampled again. Initial and final samples were preserved with HCl and analyzed for nitrate nitrogen using second derivative ultraviolet spectroscopy (Crumpton et al. 1992). Nitrate flux rates were calculated based on changes in concentration during incubation and scaled to an areal basis.

Oxygen distributions in the diffusive boundary layer and surficial sediments of microcosms were measured using Clark-style microelectrodes with tip diameters of approximately 235 um and cathode diameters of approximately 5 um. Electrode current output was measured using a picoammeter modified with the addition of a voltage regulator
circuit to supply the anode's -0.75V polarizing voltage. A micromanipulator was used to position the microelectrode, locate it at precise depths relative to the sediment surface, and advance the electrode into the sediment at precise intervals. Electrode output was recorded at .25mm intervals beginning just above the sediment water interface and continuing down into the sediment to the depth at which oxygen is no longer detected. Electrode current output was calibrated based on electrode response at the oxygen concentration in saturated water and at zero oxygen concentration in the anoxic lower sediment.

Sediment organic content was determined for the upper 2cm in sediment cores from the EW3 inlet area, the EW3 outlet area, EW4, and EW5. Two cm of surface sediment was extruded from the cylinder, collected, and wet sediment volume and weight were recorded. Sediment was then dried at 70°C for 48-72 hours and weighed. Dried sediment was mixed, ground, and subsamples were weighed before and after combustion in a muffle furnace at 550°C for 60 minutes, or until there was no further weight loss. Percent weight loss on ignition was calculated as a measure of organic content.

RESULTS AND DISCUSSION

During the study period, nitrate and organic nitrogen were the dominant forms of nitrogen entering the experimental wetlands, although as might be expected, the relative importance of these forms varied seasonally. Nitrate concentrations were highest during periods of higher flow early and late in the season and declined to near detection limits during periods of low stream flow in the summer and early fall (Figure 1). This pattern is very common in systems like the Des Plaines River which receive nonpoint source agricultural inputs, as are year to year patterns in nitrate concentrations related to variability in river flow. At Des Plaines for example, moderate river flows and elevated nitrate concentrations persisted for most of the summer of 1990, whereas river flows and nitrate concentrations declined early in the summer of 1991 and remained low until October and November. For most of the field season, the experimental wetlands act as effective sinks for nitrate. Although outlets of the high flow wetlands (EW3 and EW5) have higher nitrate concentrations than the outlet of the low flow wetland, outlet concentrations are frequently
near detection limits for all 3 wetlands. Although the experimental wetlands were clearly net sinks for nitrate, they were frequently net sources for organic and total nitrogen (Figure 2). Inlet water concentrations of organic nitrogen showed a pattern which is somewhat similar to that of nitrate, with higher concentrations early and late in the season and lower concentrations in summer and early fall. By comparison, outlet concentrations of organic nitrogen varied less during the year and exceeded inlet concentrations for most of the summer and early fall. Because of the much higher loads of nitrate early and late in the year, the wetland is still a clear sink for total nitrogen on an annual basis.

The field studies discussed above demonstrate the considerable capacity of the wetlands as nitrate sinks but provide little insight into the processes involved in nitrate loss or the major factors affecting rates of loss. Our experimental microcosm studies were designed to examine the effects of nitrate concentration, temperature, and location on nitrate loss rates in the experimental wetlands. These were thought to be among the most significant variables affecting nitrate loss in the experimental wetlands, and experiments were conducted to facilitate development of simple models describing nitrate flux. Previous studies have demonstrated that temperature and nitrate concentrations can significantly affect nitrate loss rates in a range of aquatic systems, although most of the published literature deals with rivers, lakes, and estuaries. Location was considered a potentially important variable for the current study because the experimental wetlands differ in hydrologic and nitrate loading rate as well as in sediment characteristics. EW3 and EW5 receive approximately five times more water and nitrate load than EW4. In addition, the wetlands differ considerably in the organic content of their bottom sediment. As determined by weight loss on ignition, EW3 inlet sediments were 28.1% organic matter (S.D.=0.053%, n=33), EW3 outlet sediments were 18.5% organic matter (S.D.=0.074%, n=11), EW4 sediments were 8.79% organic matter (S.D.=0.017%, n=20), and EW5 sediments were 10.3% organic matter (S.D.=0.027%, n=11).

Between June and November of 1991, 36 separate experiments were conducted to examine the effects of temperature, nitrate concentrations, and location on nitrate loss (Phipps and Crumpton 1994). Ten of these experiments involved complete three-way ANOVAs with identical 2 X 2 X 2 designs. The results of these experiments demonstrate
that the effect of nitrate concentration was always highly significant (p<0.001) and that the
effect of temperature was significant in most experiments (p<0.005 in 6 and p<0.05 in 1 of
the ten three way experiments). The effect of location was not significant when comparing
the two high flow wetlands or when comparing the inlet and outlet areas of EW3. However,
the effect of location was significant when comparing cores from high flow and low flow
wetlands (p<0.002). At a given temperature and nitrate concentration, cores from high flow
wetlands had consistently higher rates of nitrate loss than cores from the low flow wetland.
This is a particularly interesting result since the distinction of high versus low flow
apparently was more important than the differences in sediment character among the sites.
These results are consistent with previous studies suggesting that nitrate loads might
significantly stimulate the activities and/or population densities of denitrifying bacteria
(Isenhart and Crumpton in prep.b). The seasonal pattern in nitrate loss rates is also consistent
with the idea that loading rates might affect the capacity of the system to remove nitrate.
Figure 3 illustrates the seasonal change in nitrate flux versus concentration curves for subsets
of cores taken from the inlet area of EW3. The slope of the loss rate curve can be thought of
as representing the nitrate removal capacity of the system at each point in time; the steeper
the curve, the greater the capacity. The decline in slope over time and the subsequent
increase in slope later in the study (Figure 3) parallels the nitrate loading patterns to EW3
(Figure 1). In other words, at higher loading rates early and late in the season, the nitrate
removal capacity was higher.

Results from the experimental microcosm studies were used to examine two potential
models of nitrate flux as a function of nitrate concentration and temperature. Both models
describe nitrate flux as a linear function of the nitrate concentration. In other words, the
decline in nitrate concentration over time can be described as a first order reaction. The
models differ primarily in their treatment of the effect of temperature. The first model (Cerco
1989) assumes an exponential relationship between temperature and nitrate flux. This model
takes the form

\[ F = k_1 \cdot [\text{NO}_3^- - N] \cdot k_2^{(T-20)} \]
where \( F \) is the flux rate of nitrate nitrogen in g N m\(^{-2}\) day\(^{-1}\), \( \text{NO}_3^-\text{N} \) is the concentration of nitrate nitrogen in g N m\(^{-2}\), \( k_1 \) is the coefficient for the effect of nitrate concentration, \( k_2 \) is the coefficient for the effect of temperature, and \( T \) is temperature in °C. Similar exponential models are often used to represent the effects of temperature on metabolic rates. The second model assumes a linear relationship between temperature and nitrate flux. This model takes the form

\[
F = k_1 \cdot [\text{NO}_3^-\text{N}] \cdot k_2 \cdot T
\]

where \( F \) is the flux rate of nitrate nitrogen in g N m\(^{-2}\) day\(^{-1}\), \( \text{NO}_3^-\text{N} \) is the concentration of nitrate nitrogen in g N m\(^{-3}\), \( k_1 \) is the coefficient for the effect of nitrate concentration, \( k_2 \) is the coefficient for the effect of temperature, and \( T \) is temperature in °C. This model assumes that temperature affects nitrate flux rates primarily through effects on diffusion rates of nitrate rather than on metabolic rates of nitrate users. Similar models are often used to represent the effects of temperature on diffusion rates in water. The coefficients for each of these models were estimated using an iterative, multiple regression procedure capable of nonlinear estimation.

The parameters for each of the two models are shown in Figure 4. The two models fit the data equally well, with the nonlinear model accounting for 76% of the variance in the data set and the linear model accounting for 73% of the variance. This could of course be expected given the relatively small value of \( k_2 \) in the nonlinear model, which provides a nearly flat response surface within the temperature range of the data to which the model was fit (approximately 6 to 30 °C). Nitrate concentration alone accounted for 44% of the variance in the data set. The response surfaces of the two models and the fitted data are illustrated in Figure 4.

It is our hypothesis that loss rates of externally loaded nitrate in the experimental wetlands are determined primarily by the rate of nitrate flux to anaerobic sites. The transport of nitrate to these sites can be described as a first order process whose most important controlling factors are denitrifier activities, the nitrate concentration gradient, and the effective length of the diffusion path, which is a function of water movement, sediment oxygen distribution, and porosity. We are now working to develop simple mechanistic
models of nitrate flux based on this hypothesis. Our measurements of oxygen profiles demonstrated that temperature had little effect on the depth of oxygen penetration into the sediment (Figure 5). At a given water velocity, thickness of the aerobic layer is the primary determinant of the length of the diffusion path for nitrate to anaerobic sites in underlying sediments (Christensen et al. 1990). The relatively linear nature of the temperature effect in our empirical models is therefore consistent with models for denitrification in agricultural streams which suggest that in the presence of high nitrate loads, denitrification rates are controlled by the NO$_3^-$ concentration in the overlying water and the effective length of the diffusion path between the overlying water and the primary site of denitrification in underlying anaerobic sediments (Christensen et al. 1990). In these models, the principal effect of temperature is on nitrate diffusion rates which can be expressed as linear functions.

**LITERATURE CITED**


Nixon, S.W. and V. Lee, 1986. Wetlands and water quality: a regional review of recent research in the United States on the role of freshwater and saltwater wetlands as sources, sinks, and transformers of nitrogen, phosphorus, and various heavy metals.


Figure 1. Inlet and outlet concentrations of nitrate nitrogen for EW3, EW4, and EW5 for 1990.
Figure 2. Inlet and outlet concentrations of nitrate nitrogen for EW3, EW4, and EW5 for 1991.
Figure 3. Inlet and outlet concentrations of organic nitrogen for EW3, EW4, and EW5 for 1991.
Figure 4. Inlet and outlet concentrations of total nitrogen for EW3, EW4, and EW5 for 1991.
CHAPTER 5. GENERAL SUMMARY

 Constructed flow through wetlands receiving periodic loads of nonpoint source nitrate nitrogen from agricultural landscapes were examined for their capacity to remove nitrate. In the three Des Plaines wetlands, nitrate removal capacities were estimated using mass balance field studies and sediment-water microcosms under controlled laboratory conditions. Microcosms were used to examine the factors affecting nitrate loss rates, and to determine loss rate coefficients under various hydrologic loads over the course of a season. Concentrations of nitrate in the Des Plaines River were highest during high flow periods, and most of the annual nitrate load was associated with spring time flows. All three wetlands were found to be significant sinks for nonpoint source nitrate nitrogen loads and two of the three wetlands were net exporters of organic nitrogen on an annual basis. The efficiency of nitrate removal was inversely related to both hydrologic load and the mass of nitrate loaded into the wetlands. Experimental microcosm studies confirmed that nitrate loss is primarily a function of nitrate concentration and temperature. At a constant temperature, nitrate loss could be described as a first order areal process. Areal nitrate loss coefficients (k_a), determined from microcosms, allow the prediction of nitrate removal for a wetland under various nitrate loads. A significant difference in loss rate coefficients between high and low flow wetlands in 1991 suggested a hydrologic loading effect, which was explored in 1992. Results from microcosm studies showed no consistent effect of loading rate on nitrate loss. The range of k_a's was far less than the range of hydrologic load and nitrate concentrations.

 The papers presented here provide reasonable estimates of nitrate removal capacity in the Des Plaines wetlands. Despite the inherent temporal and spatial variability of factors that may influence this capacity, the intrinsic loss rate coefficient (k_i) appears to be a reasonably consistent parameter. Differences in nitrate loss coefficients among wetlands at similar stages of development were not large and k_i's for all the wetlands over both field seasons were comparable. At the watershed management scale, reliable loss coefficients enable modelers to predict the effects of constructed wetlands on downstream water quality. Proper siting of constructed wetlands within watersheds requires knowledge of nitrate removal capacity under various hydrologic and nitrogen loads. The confirmation of these loss rate
model predictions, as well as the long term sustainability of nitrate removal capacity are the subject of further research.

REFERENCES


Christensen, Peter Bondo, Lars Peter Nielsen, Jan Sorensen, and Niels Peter Revsbech. 1990. Denitrification in nitrate-rich streams: Diurnal and seasonal variation related to benthic oxygen metabolism. Limnology and Oceanography, 640-651.


ACKNOWLEDGMENTS

In order to avoid weighting the contributions of anyone disproportionately, in the spirit of equality, and in no particular order, I would like to thank: Sylvia Parmley, Mike Matter, Jen Owens, Ron Sarno, Craig Davis, Dick Williams, Eric Seabloom, Jana and Greg Stenback and family, Brad Hecht, the soul of Iowa Steve Fisher, Melissa Mundt, Laura Wendling, Anne Kimber, David Brenner, Kyle Holland, Bob Matura, Craig Tikkanen, Tim Hoiman, Chuck Rose, the collective Wetzel. Taher Nejasattari, all the faithful nitrate runners. Chris Richardson, Kurt, Tom and Joanne Isenhart. my major professor Bill Crumpton to whom I owe an eternal debt, Ben Klaas, Erika Hasler, Eric Scherf, Walter Prexl. Warren Johnson, my parents Ruth and Paul, brother Rob, brother Ron, Meg, Sue, Mike, Nancy, Todd, Brian, Ada, Tanya, Gladys and Bill, Pat and Kerm, Dick and Toot, Big Al. Joanne. Steve, Kyle, Jim, Bill and Betty, Java Joe’s. Lisa and Dave, Val and Marc, Escalante. Chris and Rie, Ruth, Tom and Mary, Rick, Mike, Brad, Randy. Michael Omunyun, Bob Mangan, the Corps of Engineers, Don and Kathleen Vaillancourt, Mike Cameron, Bill Hearn. Chris Cardullo, the crazy confession, Charlie Baumgartner, Dave and Sharon White, Mark Turski, Doug Boyce, Pete and Gail Coughlan, Roger, Melita and Al Biela, John and his beloved Barnstormers. loud footed neighbors above and their ensuing silent treatment. Dan Mason at Des Plaines, Akbar, the Cronkster, Sioban Fennessy, Tom Jurik, Tony Bremholm, faithful field assistant Yumiko Plate, Kraina, Dragoslav and Nada Petrovic. Ksenija, Russian lady. Maharishi U, Chris Niemeyer, Gerry McKiernan, Prasad. Joanne Nystrom. the 91 solar eclipse in Tula, Mexico. Pat, Sharon East, Joyce Hanson, Christina, Connie Rasmussen, Lois Tiffany, George Knaphus, Steve Rodermel, Beth Middleton, Jim Raich, Jim Colbert, Harry Horner, David Oliver, Arnold van der Valk, Warren Dolphin, Janet, Kirk Maloney, John Pleasants, Jonathan Wendel, Steve Mahoney, the Rec Center, Roger Bachmann, David Cox, Sue Sprong, Greg Tylka, Gary Munkvold, Suliman al Rehianni, Tom Loynachan, Gary Atchison, fellow New Englander Fred Blackmer, Neal Harl, Al Austin, Bob Horton, Tom Tanner, David Rueger, Paul Godfrey, Bill Robertson, Joe Dever, the 100th Boston marathon, Lisa Hemesath, Shelly Gradwell, Joy Haugen, Gary, Shauna Vance, that roommate I never saw, Sue Gembara. Errol, John Mitchell, Tatti. Julia and Terry Egli-Davis. Craig, the latest in
Turkish psychiatry, Wheatsfield Grocery. Ben Nauman, Jody, Gretchen, John, Jennifer Dodge, Hillary Caffrey, Jennifer Rezek, Amy, Jennifer vdp, narcissism. Ned Crane, Paul Pruitt, Paul Mitchell, Mark Chamberlin, all the people I confused thoroughly, Jeff Worrell, Corinne, Sundogs, the Dug, Starr and Paula, Phil Dykema, Dave Higgs, all the people who politely sat through my seminars, Stomping Grounds, Andy, Frank, Brian, Barbara Haas, Nancy Preston, Bob and Neva, Cindy, Irma, Regina, Abeer, Ebru. Lorin Hatch, Spencer, Daniel, Yahyah, people who came and went, Spiritmaster, Jesus, Buddha, mud, the many students in many classes who enjoyed learning, those who tolerated me through it all, flora and fauna, and all the beautiful people of Ames, Iowa, a place I shall always remember fondly.