Interaction and spatial distribution of wetland nitrogen processes

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Abstract

A spatially-explicit, two-dimensional model was developed to evaluate the processes which determine the fate and transport of nitrogen (N) in wetland systems. The wetland soil profile was partitioned into floodwater, and aerobic, and anaerobic soil layers, with diffusion and settling accounting for the transport of N between layers. Nitrogen transformations considered in the model were: enzyme hydrolysis, mineralization, nitrification, NH4-N adsorption/desorption, NH3-N volatilization, denitrification, and vegetative assimilation and decay. Most processes were represented with first-order kinetics, except vegetative uptake, which was represented with Michaelis–Menten kinetics. STELLA® iconographic software was used to simulate processes regulating N removal from wetlands. Denitrification, ammonia volatilization, and accretion of organic N were identified as major pathways accounting for N removal. Downward flux of NO3− from floodwater to soil limited N removal through denitrification. Denitrification rates increased from 13 to 88 g N year−1 in response to augmented vertical flux of soluble N, caused by increasing diffusion coefficients two orders of magnitude. Edaphic organic N storage, through the production of inorganic N, negatively impacted N removal. Spatial simulation illustrated the phenomena of diminishing returns in the mass removal rates of N, which were in agreement with documented values. © 1997 Elsevier Science B.V.

Keywords: Wetland model; Nitrogen cycling; Wastewater treatment

1. Introduction

Present concentrations and population levels of human society require that nutrient levels in wastewater flows be reduced to preserve downstream water quality. Nitrogen (N) occurring in wastewater, due to its role in eutrophication, and
potential toxicity to aquatic species, is a nutrient of primary concern. Initial studies by Odum et al. (1977), Kadlec (1979), followed by others, have identified wetlands as a proven, low-energy method to reduce nutrient levels, including N, in wastewater. Results from wetland treatment systems have lead to a technical database quantifying nutrient removal (NATWD, 1993). Relationships, derived from this database, and other results, are the basis of current design and analysis methods of wetland treatment systems. This design approach, referred to as ‘black box’ methodology, is based upon empirical equations derived from the relationships between input and output nutrient levels. Integrative studies of the intrasystem processes leading to N removal are needed to determine the interactions of responsible processes, and possible methods to increase N removal. Singly, these processes have been researched in wetland settings (Reddy and Patrick, 1984; Bowden, 1987). However, comprehensive studies of the interactions, and resulting integrative effects of such processes are limited. Integrating N cycling processes spatially on a wetland scale through a simulation model is an approach to evaluate such effects, and provide a framework for hypothesis testing (Bakker, 1994).

The objectives of this study were to determine: (i) the interactions of N processes that affect the fate and transport of N in wetlands, and (ii) factors affecting N removal from treatment wetlands.

A mechanistic model was developed to simulate both vertical and horizontal distribution of N processes in wetlands. First, a general unit model was developed, which was then adapted for application to vertical layers of floodwater, aerobic soil, and anaerobic soil. Horizontal boundaries were determined by the hydraulic retention time (HRT). Transport between the vertical layers was simulated as diffusive flux, which was varied over 3 orders of magnitude, ranging from rates indicative of molecular to turbulent diffusion. Water was viewed as a constant medium providing horizontal transport between cells. The model follows approaches in earlier studies of vertical (Rao et al., 1984; Chapelle, 1995) and horizontal (Hammer, 1984; Dørge, 1994) distribution of N species in wetlands.

2. Description of model

2.1. Conceptual model and processes

Nitrogen transformations simulated in the model included enzymatic hydrolysis of organic N, mineralization, nitrification, NH₄-N adsorption/desorption, NH₃-N volatilization, denitrification, and vegetative assimilation and decay. Nitrogen transport was simulated vertically with diffusion and settling, and horizontally as movement due to water flow. The model was designed to determine general concepts applicable to all wetland systems, but can be applied to specific systems if required model inputs are known or can be estimated. These include basic vegetative, soil, hydrologic, and size characteristics, as well as various first-order rate constants and N loading rates. The model was developed for a southern North American climate where temperature variations have minimal effects on N removal (Knight, 1986; Gearheart, 1990) and thus, were not explicitly included in the model. The model was conceptualized and simulated using STELLA® iconographic modeling software (Richmond et al., 1987; Martin and Tilley, 1998).

Rates were described with the following differential equations: First-order rate kinetics:

\[ \frac{dS}{dt} = kS \]

Michaelis–Menten kinetics:

\[ \frac{dS}{dt} = \frac{k_m S}{k_s + S} \]

Diffusive flux following Fick’s law:

\[ \frac{dS}{dt} = D \frac{(C_1 - C_2)}{dx} \]

where \( S \) is storage; \( \frac{dS}{dt} \) is the rate of process; \( k \) is the first-order rate constant; \( k_m \) is the maximum transformation rate of storage; \( k_s \) is the saturation constant; \( D \) is the diffusion coefficient and \( C_1 \) and \( C_2 \) are the concentrations of N species in layer 1 and 2, respectively. Time units of the model were measured in days with a time step of 0.0625 days, which was necessary for the diffusion equations. The integration method was fourth order Runge–Kutta (Richmond et al., 1987).

A general unit model (Fig. 1) was first developed. Nitrogen was partitioned into five state
Fig. 1. General unit model which was amended and applied to different wetland layers. Valve symbols represent the transformation and flow of N between storages (boxes) of different N species. Clouds denote both sources and sinks outside the model boundary (Forrester, 1961; Richmond et al., 1987).

variables; particulate organic N (PON), soluble organic N (SON), ammonia N (NH₄-N), nitrate N (NO₃-N), and vegetative N. The unit model was then adapted and applied in three vertical layers consisting of a well-mixed water column, an aerobic soil layer, and an anaerobic soil layer (Jørgensen et al. (1988) used a similar approach). Diffusive flux, PON settling, and vegetative uptake and decay provided transport of the N species between the vertical layers. Adaptations to the unit model included: (a) relegating denitrification to the anaerobic soil layer; (b) relegating nitrification to water and aerobic layers; (c) adding NH₄-N sorbed storages and sorption/desorption processes in the soil layers; (d) including a PON storage in the anaerobic layer; (e) adding the process of NH₃-N volatilization in the water column; and (f) adding a vegetative N storage which assimilated N from and distributed N to different vertical layers. In addition many of the rate constants were varied to reflect differences in the layers. The anaerobic soil layer was then further subdivided into five layers which increased in thickness with depth. This resulted in the final model having seven distinct vertical layers. The depths of the layers were 30 cm for the water column, 1 cm for the aerobic soil layer, and 29 cm for the effective anaerobic soil layer (Figs. 2 and 3). Such depths are typical of wetlands and have been used in wetland models (Reddy et al., 1976; Kadlec, 1995). As the processes of interest, such as denitrification, decreased in magnitude with depth (Sørensen, 1978; Jones, 1979) the anaerobic portion of the model was divided into layers which became progressively larger as the depth increased.

Horizontal distribution of flows was accomplished by representing the wetland as a series of equal length cells, each corresponding to a 1 day HRT. For instance, if the HRT of the entire system was 1 day, the entire wetland would be simulated as one cell. If HRT was 7 days, seven cells were utilized to represent the system (this arrangement is depicted in Fig. 3). A daily exchange of water from one cell to the next, driven entirely by water flow, transported soluble and suspended N horizontally (Dørge, 1994). After testing different methods representing wetland treatment systems, Kadlec and Hammer (1988) found this approach to produce acceptable results. The effects of precipitation and evapotranspiration were assumed to be minimal and were not included in the model. With large inflows of water and N from wastewaters, such processes account for extremely low percentages of N and water entering/exiting wetland treatment systems (CDM, 1994; Kadlec and Knight, 1996).
Fig. 2. Adaptations were made to the unit model for application to the three wetland layers. Vertical diffusive flux, PON settling, and vegetative uptake and decay accounted for transport between layers. The anaerobic layer was partitioned into five sub-layers of increasing depth (1, 2, 4, 8, and 15 cm, Fig. 3). Vertical exchanges depicted between ‘Anaerobic Soil Layers 1–4’ and ‘Anaerobic Soil Layer 5’ took place between anaerobic layers 1 and 2, 2 and 3, 3 and 4, and 4 and 5. Refer to Fig. 1 for explanation of symbols.

Units of g N m\(^{-2}\) day\(^{-1}\) were selected for transformations and transport, and g N m\(^{-2}\) for storages. Such units are common in the modelling of wetland treatment systems (Kadlec and Hammer, 1988; Christensen et al., 1994; Jørgensen, 1994). Inputs of the four N species were average values taken from the North American Treatment Wetland Database (NATWD, 1993) (Table 1). A constructed surface flow wetland with predominately organic soils receiving wastewater inputs
providing storage values for time zero conditions (Table 2). While many plant species may inhabit one wetland system, constructed wetlands are often dominated by *Typha* sp., which was the case simulated in the model. At the time of simulation, the wetland system was assumed to be established with initial vegetative storage of 8 g N m$^{-2}$ (Boyd and Hess, 1970), and most of this storage was assumed to be below ground as time-zero was early January (Bernard and Fitz, 1979). The active root zone was assumed to be in the top 16 cm soil depth (Logofet and Alexandrov, 1984).

### 2.2. Process representations

#### 2.2.1. First-order processes

First-order kinetics were used to simulate the mineralization of SON to NH$_4$-N, following previous N models (Jørgensen et al., 1988; Kadlec and Knight, 1996). The tendency for mineralization to proceed at a rapid rate in aerobic environments (Reddy and Patrick, 1984) was reflected with higher rate constants in the aerobic soil layer (Table 3). Due to lower microbial activity, water column mineralization constants were less than the aerobic soil layer constants. These constants were assumed to be representative of net mineralization, therefore the process of immobilization was not represented in the model. Following the works of Reddy and Rao (1983) and Kadlec and Knight (1996) nitrification was represented with first-order kinetics, as a single step (Frissel and van Veen, 1982). Similar to mineralization constants, nitrification constants in the aerobic soil layer were greater than those of the water column. Denitrification was also simulated as a first-order process (Mehran and Tanji, 1974; Kadlec and Hammer, 1988). A list of zero-order rates and first-order constants was compiled from literature sources for the processes of mineralization, nitrification, and denitrification. Calibration runs were then performed with the average first-order constants.
Table 2
Summary of initial storage values (g N m$^{-2}$)

<table>
<thead>
<tr>
<th>Model layer</th>
<th>Layer depth (cm)</th>
<th>Organic N</th>
<th>Inorganic N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SON PON</td>
<td>NH$_4$-N soluble</td>
</tr>
<tr>
<td>Water column</td>
<td>30–0</td>
<td>0.17</td>
<td>0</td>
</tr>
<tr>
<td>Aerobic layer</td>
<td>0–1</td>
<td>0.005</td>
<td>19</td>
</tr>
<tr>
<td>Anaerobic1</td>
<td>1–2</td>
<td>0.005</td>
<td>19</td>
</tr>
<tr>
<td>Anaerobic2</td>
<td>2–4</td>
<td>0.01</td>
<td>38</td>
</tr>
<tr>
<td>Anaerobic3</td>
<td>4–8</td>
<td>0.02</td>
<td>76</td>
</tr>
<tr>
<td>Anaerobic4</td>
<td>8–16</td>
<td>0.04</td>
<td>152</td>
</tr>
<tr>
<td>Anaerobic5</td>
<td>16–30</td>
<td>0.08</td>
<td>286</td>
</tr>
</tbody>
</table>

These values were from a constructed wetland in central Florida (Gale et al., 1993a). Initial amounts of NO$_3$-N were assumed to be 0.0 g N m$^{-2}$. Initial amount of vegetative storage was assumed to be 8.0 g N m$^{-2}$.

and the resulting rates were compared to the zero-order averages. Following this iteration technique the process constants were calibrated (Table 3).

Table 3
Constants utilized in model regulating first-order processes and diffusive flux

<table>
<thead>
<tr>
<th>First-order constants (day$^{-1}$)</th>
<th>Source</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water enzyme hydrolysis rate</td>
<td>Assumption</td>
<td>1.00 × 10$^{-5}$</td>
</tr>
<tr>
<td>Aerobic enzyme hydrolysis rate</td>
<td>Assumption</td>
<td>1.50 × 10$^{-5}$</td>
</tr>
<tr>
<td>Anaerobic enzyme hydrolysis rate</td>
<td>Assumption</td>
<td>8.00 × 10$^{-6}$</td>
</tr>
<tr>
<td>Water mineralization rate</td>
<td>1, 2, 3, 4</td>
<td>0.008</td>
</tr>
<tr>
<td>Aerobic mineralization rate</td>
<td>1, 2, 3</td>
<td>0.015</td>
</tr>
<tr>
<td>Anaerobic mineralization rate</td>
<td>1, 2, 3, 5</td>
<td>0.005</td>
</tr>
<tr>
<td>Water nitrification rate</td>
<td>5, 6, 7, 8, 9</td>
<td>0.10</td>
</tr>
<tr>
<td>Aerobic nitrification rate</td>
<td>5, 6, 7, 8, 9</td>
<td>1.20</td>
</tr>
<tr>
<td>Denitrification rate</td>
<td>5, 9, 10, 11, 12</td>
<td>2.50</td>
</tr>
<tr>
<td>PON water to aerobic settling rate</td>
<td>13</td>
<td>0.95</td>
</tr>
<tr>
<td>PON aerobic to anaerobic settling rate</td>
<td>Assumption</td>
<td>0.01</td>
</tr>
<tr>
<td>PON soil settling rate</td>
<td>Assumption</td>
<td>5.00 × 10$^{-4}$</td>
</tr>
<tr>
<td>Plant nitrogen decay rate</td>
<td>Assumption</td>
<td>0.006</td>
</tr>
</tbody>
</table>

Other processes modelled using first-order kinetics included plant decay (Hammer, 1984), settling of PON (Kadlec and Hammer, 1988), and enzymatic hydrolysis of organic N. The weight proportions of the PON particles were assumed to be constant, which resulted in a constant percentage settling out during each time step. Limited information concerning the enzymatic hydrolysis of PON lead to the assumption of first-order kinetics.

2.2.2. Vegetative uptake and decay

To represent the vegetative uptake of N, a maximum demand for N was calculated as the product of the amount of plant growth per day, represented by C fixation, and a variable stoichiometric relationship between N and C. To ensure a maximum N demand this relationship was determined using data for Typha sp., grown in eutrophic conditions (Martin and Fernandez, 1992). This demand was then utilized as a maximum uptake rate in a Michaelis–Menten equation with soluble inorganic N concentrations as the limiting parameters. The linkage between N uptake and the available concentration in regards to aquatic macrophytes has been previously described with Michaelis–Menten kinetics (McCroy and Alexander, 1975; Morris, 1980; Nelson et al., 1981). Eqs. (1) and (2) describe the vegetative uptake of NH$_4$-N and NO$_3$-N, respectively:
veguptake = $N_{\text{demand}} \times \text{layerdpth\%}$

$$= \frac{[\text{NH}_4 - N]}{K_m + [\text{NH}_4 - 4]} \times \frac{[\text{NH}_4 - N]}{[\text{NH}_4 - N] + [\text{NO}_3 - N]}$$

(1)

veguptake = $N_{\text{demand}} \times \text{layerdpth\%}$

$$= \frac{[\text{NO}_3 - N]}{K_m + [\text{NO}_3 - N]} \times \frac{[\text{NO}_3 - N]}{[\text{NO}_3 - N] + [\text{NH}_4 - N]}$$

(2)

The last term provides that the species with the greater concentration will be assimilated preferentially (Jørgensen, 1994). Ammonium N is preferred to NO$_3$-N by most aquatic macrophytes, and with a larger concentration of NH$_4$-N, which was the case in the anaerobic layers, the model followed this preference. This preference was also reflected by smaller $K_m$ values for NH$_4$-N compared to NO$_3$-N, which were calibrated based on seasonal characteristics of Typha sp. The fraction of the active root layer occupied by each layer was designated as layerdpth\%. To avoid further complications within the vegetation component, toxic effects due to high concentrations of NH$_4$-N were not considered.

Seasonal translocation of N within the vegetation was simulated to properly distribute vegetative loss of N through decay. As opposed to creating multiple vegetative N storages in the wetland profile, one storage was used and the decay was distributed mimicking seasonal changes in N allocation. Utilizing studies of Typha sp. by Bernard and Bernard (1977) and Martin and Fernandez (1992) a graphical seasonal relationship of above and below ground N allocation was derived. Eq. (3) describes vegetative decay into the aerobic soil layer. Vegbiomass is the

Aerobic decay = vegbiomass $\times$ decayk

$$\times \text{blwgrd\%}\text{N} \times \text{aerobic\%}$$

(3)

amount of N (g N m$^{-2}$) in the vegetation, decayk is the first-order decay constant, blwgrd\%N is the percentage of below ground vegetative N storage, and aerobic\% is the fraction of the active root layer in the aerobic soil layer.

2.2.3. Soil adsorption/desorption of NH$_4$-N

The adsorption/desorption of NH$_4$-N by the soil cation exchange complex was modelled with a linear adsorption isotherm (Frissel and van Veen, 1982; Reddy et al., 1988) (Eq. (4)). Multiplication of the partitionk and excNH$_4$soilstorage, the amount of NH$_4$-N presently sorbed, determines the amount of soluble NH$_4$-N fulfilling equilibrium conditions. From this product the

soilexch = (partitionk $\times$ excNH$_4$soilstorage)

$- \text{NH}_4\text{storage} \times \text{spectrate}$

(4)

actual soluble NH$_4$-N storage, NH$_4$storage, is subtracted. This difference is then reduced at a rate governed by the specific constant, spectrate. This process was reversible, due to the fact that soil can adsorb, or release NH$_4$-N dependent upon the concentration. A partition coefficient of 0.5 ml g$^{-1}$ (Rao et al., 1984) was converted to 1.375 g NH$_4$-N soluble per g NH$_4$-N sorbed for use in the model.

2.2.4. NH$_3$-N volatilization

The transformation from NH$_4$-N to NH$_3$-N was regulated by the pH of the water column. After NH$_3$-N was formed volatilization was assumed to follow. The equation utilized was characterized by a large shift between NH$_4$-N and NH$_3$-N at pH values from 8 to 9 (Rao et al., 1984) (Eq. (5)).

$$\text{NH}_3 = 5.8 \times 10^{0.5 - 10} \times \text{NH}_4\text{storage}$$

(5)

A diel relationship from a Typha sp. dominated wetland (Reddy, 1983) determined the pH in the above equation.

2.3. Diffusive flux

Molecular diffusive flux occurred when a concentration gradient existed between vertically adjacent storages of soluble N species. Flux was described by the multiplication of the concentration difference between two layers and the diffusion constant, $D$, divided by the average

$$\text{flux} = \frac{D[\text{storage1/depth1} - \text{storage2/depth2}]}{(\text{depth1 + depth2}/2)}$$

(6)
Table 4

<table>
<thead>
<tr>
<th>Description</th>
<th>Source</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SON diffusion constant</td>
<td>1, 2, 3, 4, 5</td>
<td>$2.29 \times 10^{-5}$</td>
</tr>
<tr>
<td>NH$_4$ diffusion constant</td>
<td>1, 2, 3, 4, 5</td>
<td>$5.85 \times 10^{-5}$</td>
</tr>
<tr>
<td>NO$_3$ diffusion constant</td>
<td>1, 3, 6</td>
<td>$1.40 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Savant and DeDatta (1980), Rao et al. (1984), Reddy (1982), Reddy et al. (1980), Krom and Berner (1980), Krottje (1980). These are literature values and were increased 10 and 100 times in simulations testing diffusion coefficients.

The distance between the two layers (Eq. (6)). The average distance was calculated as the total additive depth of the two layers divided by two (Park et al., 1975; Chapelle, 1995). Because the water column was assumed to be well-mixed, only the depth of the aerobic soil layer was included in the denominator in calculations of flux between these two layers. Depending upon the concentration gradient diffusive flux could contribute or subtract N from any soluble storage. Molecular diffusion constants used in initial simulations were derived from literature sources (Table 4). In later simulations these diffusion constants were increased by one and two orders of magnitude to simulate turbulent diffusion.

3. Results and discussion

Following a sensitivity analysis, simulations were performed to determine general relationships and interactions which affect the fate and transport of N in treatment wetlands. The sensitivity analysis tested variances of model parameters on N output and identified the most influential parameters affecting N removal. The coefficients used for diffusive flux were found to produce large (11–35%) changes in N species outflow. Although changes in mineralization, nitrification, denitrification, and vegetative uptake constants produced large changes in the directly associated processes, their effect on N outflow was minimal (Table 5).

Predicted diffusive flux of soluble N species from simulations using initial values (Tables 3 and 4) was much lower than reported values from wetland systems. This lead to a second set of simulations which tested the effects of varying diffusion coefficients of N species. Increasing these coefficients produced results which agreed with reported process and removal rates. Large amounts of SON outflow were also predicted by these simulations. In later simulations the composition of N entering the system was varied and the N loading rate increased to ascertain: (i) the effect of N composition on total N removal; (ii) interactions between N species; (iii) dependence of processes on inflow N composition; and (iv) the applicability of first-order assumptions. Simulations were performed with 1 year durations and a timestep of 0.0625 days and a 7 day HRT, which resulted in a spatial distribution of 7 cells (Fig. 3).

3.1. Simulations based on literature values

These simulations predicted a N removal efficiency of 38% (Table 6). Others (Bavor, 1986; Gale et al., 1993a; Kadlec and Knight, 1996) have reported higher efficiencies ranging from 45 to 70% for similar systems and HRTs. A low denitrification rate of less than 2 g N m$^{-2}$ year$^{-1}$ (Fig. 4) contributed to a 90% increase in NO$_3$-N (Fig. 5 and Table 6), which was primarily responsible for the low N removal efficiency. A literature search yielded an average denitrification rate of 35 g N m$^{-2}$ year$^{-1}$ for wetland systems. High NO$_3$-N concentrations in the water column and aerobic layer indicated that the transport of NO$_3$-N to anaerobic layers was a limiting process accounting for low NO$_3$-N removal from the system. In addition, nitrification of inflow NH$_4$-N (Table 1) also resulted in increased levels of NO$_3$-N outflow. Slow diffusive flux of NH$_4$-N and SON, as well as decreased vegetative storage also indicated low rates of soluble N transport. This agreed with results from previous modelling and experimental work which identified NH$_4$-N and NO$_3$-N flux as limiting gaseous N losses in flooded soils (Rao et al., 1984).

These results not only showed that N removal was limited by the vertical flux of soluble N, but the entire N cycle was functioning much slower than anticipated based on reported rates from
Table 5
Results of sensitivity analysis

<table>
<thead>
<tr>
<th>Parameters varied</th>
<th>Baseline value, tested value</th>
<th>%Change in outflow</th>
<th>%Change in transformation rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NH₄-N</td>
<td>NO₃-N</td>
</tr>
<tr>
<td>NH₄-N diffusion coefficients</td>
<td>(4.6E-4, 4.6E-5 m² d⁻¹)</td>
<td>11.8</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>(4.6E-4, 4.6E-3 m² d⁻¹)</td>
<td>−25.3</td>
<td>1.2</td>
</tr>
<tr>
<td>NO₃-N diffusion coefficients</td>
<td>(3.2E-3, 3.2E-4 m² d⁻¹)</td>
<td>−0.2</td>
<td>35.3</td>
</tr>
<tr>
<td></td>
<td>(3.2E-3, 3.2E-2 m² d⁻¹)</td>
<td>0.8</td>
<td>−31.4</td>
</tr>
</tbody>
</table>

Mineralization

| Water layer mineralization constant | (0.01, 0.001 d⁻¹) | -0.4  | −0.1 | 1.7  | −0.2 |
|                                     |                   | -89.9 | -88.5| -87.9|

Nitrification

| Water layer nitrification constant | (0.1, 0.05 d⁻¹) | 4.0   | −11.1| 0.0  | 0.0  |
|                                   |                 | -48.0 | -48.1| —   |

Denitrification

| Denitrification constant | (1.5, 0.5 d⁻¹) | 0.1   | 1.5  | 0.0  | 0.7  |
|                         | (1.5, 2.5 d⁻¹) | 0.0   | −0.8 | 0.0  | −0.4 |
|                         |                 | 58.0  | 21.5 | 11.0 |

‘Anaerobic3’ denotes rate in third anaerobic layer.

similar systems. However, mass removal rates predicted by this simulation, disregarding an increase in NO₃-N, were near ranges reported for similar systems (Table 7).

3.2. Increased diffusion coefficients

Ammonium N and NO₃-N removal efficiencies were 83 and 11%, and 79 and 100%, correspond-
Table 6
Summary results for simulations testing variances of inflow N composition and increased N loading rates used diffusion coefficients \( \times 10 \)

<table>
<thead>
<tr>
<th>Nitrogen Input/Output</th>
<th>Simulation description</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Literature values</td>
</tr>
<tr>
<td>Total nitrogen input (g N year(^{-1}))</td>
<td>350.4</td>
</tr>
<tr>
<td>Total nitrogen output (g N year(^{-1}))</td>
<td>216.1</td>
</tr>
<tr>
<td>Removal efficiency</td>
<td>0.38</td>
</tr>
<tr>
<td>Total nitrogen removed (g N year(^{-1}))</td>
<td>0.37</td>
</tr>
<tr>
<td>Denitrification (g N year(^{-1}))</td>
<td>13.5</td>
</tr>
<tr>
<td>Volatilization (g N year(^{-1}))</td>
<td>62.8</td>
</tr>
<tr>
<td>Vegetative change (g N year(^{-1}))</td>
<td>-33.0</td>
</tr>
<tr>
<td>Nitrogen soil change (g N year(^{-1}))</td>
<td>90.8</td>
</tr>
<tr>
<td>SON Input (g N year(^{-1}))</td>
<td>60.2</td>
</tr>
<tr>
<td>Outflow (g N year(^{-1}))</td>
<td>74.5</td>
</tr>
<tr>
<td>%increase</td>
<td>0.2</td>
</tr>
<tr>
<td>Total removed (g N d(^{-1}))</td>
<td>-0.0</td>
</tr>
<tr>
<td>PON Input (g N year(^{-1}))</td>
<td>60.2</td>
</tr>
<tr>
<td>Outflow (g N year(^{-1}))</td>
<td>0.1</td>
</tr>
<tr>
<td>%decrease</td>
<td>1.0</td>
</tr>
<tr>
<td>Total removed (g N d(^{-1}))</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Table 6 (continued)

<table>
<thead>
<tr>
<th>Nitrogen Input/Output</th>
<th>Simulation description</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Literature values</td>
</tr>
<tr>
<td>NH₄-N Input (g N year⁻¹)</td>
<td>178.9</td>
</tr>
<tr>
<td>Outflow (g N year⁻¹)</td>
<td>44.5</td>
</tr>
<tr>
<td>%decrease</td>
<td>0.8</td>
</tr>
<tr>
<td>Total removed (g N d⁻¹)</td>
<td>0.4</td>
</tr>
<tr>
<td>NO₃-N Input (g N year⁻¹)</td>
<td>51.1</td>
</tr>
<tr>
<td>Outflow (g N year⁻¹)</td>
<td>96.9</td>
</tr>
<tr>
<td>%decrease</td>
<td>—0.9</td>
</tr>
<tr>
<td>Total removed (g N d⁻¹)</td>
<td>—0.1</td>
</tr>
</tbody>
</table>

The units of g N year⁻¹ denote N mass based upon the entire system of 7 cells with a HRT of 7 days. To obtain a m² average for the entire system these values can be divided by 7.
Table 7
Comparison of simulated mass removal rates (g N m\(^{-2}\) d\(^{-1}\)) assuming three magnitudes of diffusion coefficients with North American Treatment Wetland Database (NATWD) and other surface flow wetlands

<table>
<thead>
<tr>
<th>N species</th>
<th>Simulation</th>
<th>Ranges from NATWD(^a)</th>
<th>Surface flow wetlands (USA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Literature diffusion coefficients</td>
<td>Diffusion coefficients (\times 10^c)</td>
<td>Diffusion coefficients (\times 100^{d})</td>
</tr>
<tr>
<td>NH(_4^+)N</td>
<td>0.09</td>
<td>0.12</td>
<td>0.10</td>
</tr>
<tr>
<td>NO(_3^-)N</td>
<td>–0.04</td>
<td>–0.02</td>
<td>0.09</td>
</tr>
<tr>
<td>Org-N</td>
<td>0.15</td>
<td>0.14</td>
<td>0.11</td>
</tr>
<tr>
<td>Total-N</td>
<td>0.20</td>
<td>0.24</td>
<td>0.30</td>
</tr>
</tbody>
</table>

\(^a\) NATWD (1993), Kadlec and Knight (1996).
\(^b\) Choate et al. (1990).
\(^c\) Walker and Walker (1990).
\(^d\) Hey et al. (1994).
\(^e\) Assume water column depth of 0.30 m.
ing to increasing diffusion coefficients 10 and 100 times (Table 6). These results demonstrate a high sensitivity of NO₃-N removal to vertical diffusion rates. A 100-fold increase in diffusion coefficients yielded a NO₃-N removal rate of 38 g N m⁻² year⁻¹ (Fig. 4), which agreed with the aforementioned values reported in the literature (Section 2.2.1). The
diffusive flux of NH₄-N and SON increased to levels which also reflected reported values. In these sim-
ulations all diffusion coefficients; SON, NH₄-N, and NO₃-N, were varied concurrently.
Larger diffusion coefficients resulted in minimal changes in total N removal due to an increase in SON outflow, which increased by 72 and 166%, when diffusion coefficients were increased by 10
and 100 times, respectfully (Fig. 5). Total N removal was 49% when diffusion coefficients were increased by 10 times, and decreased to 43% with diffusion coefficients increased 100 times. Enzymatic hydrolysis of PON in soil layers constantly produced SON. Higher diffusion coefficients increased upward flux of SON into the aerobic soil layer, and subsequently into the water column. Additionally, increased SON diffusion lead to declines in N soil storage. This was most evident when diffusion coefficients were increased 100 times, where N soil storage for the entire system declined to 33 g N year\(^{-1}\) (Table 6). Previous wetland studies have reported decreases in inorganic N accompanied by increases in SON. An N budget calculated by Cooper and Cooke (1984) revealed that removal rates of up to 67 g NO\(_3\)-N h\(^{-1}\) in a Glyceria-dominated stream were balanced by exports of PON and SON, resulting in zero net N removal (Howard-Williams and Downes, 1993). DeBusk (1984) reported NH\(_4\)-N removal rates of 0.45 g N m\(^{-2}\) d\(^{-1}\) occurring concurrently with organic N increases of 0.12 g N m\(^{-2}\) d\(^{-1}\). The trend of SON production is also supported by wetland studies (Hobbie, 1980; Howard-Williams et al., 1989) which reported SON concentrations 20–100 times higher than NH\(_4\)-N or NO\(_3\)-N concentrations, and lake studies (Reddy et al., 1988) which identified an upward flux of SON from sediments of eutrophic lakes.

Increasing diffusion coefficients resulted in greater amounts of vegetative N storage. Greater amounts of inorganic N transported into the root zone allowed increased assimilation, leading to greater amounts of vegetative N (Fig. 6). Progressing from cell 1 to 7, vegetative N storage declined, with the greatest reductions occurring when diffusion coefficients were increased by 100 times. The increased downward flux made NH\(_4\)-N and NO\(_3\)-N available to plants in cell 1, but also stimulated high rates of denitrification. As a result, inorganic N concentrations in the soil and water column decreased with distance from cell 1, which was reflected in decreased N uptake by vegetation and lower vegetative N storage in later cells (Fig. 6). The decreasing vegetative storages demonstrate a pattern of pulsing in longitudinal succession (Odum, 1996), which is characteristic of wetland systems receiving nutrient enriched inputs.

Varying diffusion coefficients caused changes in the amounts of N lost through different pathways (Table 6). With literature diffusion coefficients, which produced rates indicative of molecular diffusion, only 14 g N year\(^{-1}\) was lost from the entire system via denitrification. This represented 10% of N loss from the system. Ammonia-N volatilization accounted for 47% of the N loss and soil storage accounted for 43%. In simulations where diffusion coefficients were increased 10 and 100 times, producing rates corresponding to turbulent diffusion, denitrification accounted for greater percentages of N removal (33% (55 g N year\(^{-1}\)) and 59% (88 g N year\(^{-1}\)), respectively). As more SON moved from the soil to the water column due to increased diffusion constants, soil N storages declined from 43 to 4% of N removal (Table 6).

Rates of denitrification, and soluble N flux produced with 100 times greater diffusion coefficients were in the range of literature values, and mass removal rates from the system agreed with

![Fig. 6. Mass of N stored in vegetation after 1 year in each cell for simulations with varying diffusion coefficients. Initial storage for all cells was 8.0 g N m\(^{-2}\).](image)
averages from other wetland treatment systems (Table 7). The fact that these rates were the result of greatly increased diffusion coefficients raised questions about reported diffusion coefficients. Rates of molecular diffusion, leading to the determination of diffusion coefficients, can be easily measured in laboratory settings, but field measurements cannot easily distinguish between molecular diffusion and turbulent diffusion. Diffusive N flux reported from field studies is largely based on turbulent diffusion. This would partially explain why literature diffusion coefficients did not produce reported N flux and denitrification rates. If molecular diffusion was the only vertical transport mechanism in wetland soils, it would limit N removal and cycling. However, other mechanisms of soluble N transport, such as turbulent diffusion, are magnitudes greater than molecular diffusion. In the model total diffusion was represented with one equation and one coefficient. Therefore, to simulate vertical flux, diffusion coefficients had to be increased 2 orders of magnitude to produce reported diffusive flux.

What mechanisms produce the movements of water responsible for the proposed rates of turbulent diffusion? As diffusive flux increased in the model, greater amounts of N were stored in vegetative biomass. Higher rates of soluble transport in wetland systems with large amounts of inorganic N in the water column, such as wetland/wastewater systems, supply greater amounts of inorganic N to macrophytes. It is plausible that the plants themselves do not only benefit from this occurrence, but are partially responsible for causing it. High rates of evapotranspiration associated with many forms of wetland vegetation, especially *Typha* (Abtew and Obeysekera, 1995), result in large amounts of water being pulled towards the roots. This movement of water pulls NO$_3$-N, and NH$_4$-N from the water column to the soil layers, where denitrification, and higher rates of nitrification can take place. This hypothesis of turbulent diffusion augmented by vegetation explains why higher N removal efficiencies have been reported for vegetated wetlands when compared to similar unvegetated plots (Nelson et al., 1981; Gersberg et al., 1989; Kadlec, 1995). Consequently, the role of plant species in the practice of N removal from wetland systems changes from one of temporary storage to a vital mechanism stimulating water transport, leading to N removal.

### 3.3. Variances of inflow nitrogen composition

These simulations demonstrated the dependence of processes and removal rates on input N composition, and interactions between N species. Loading rates of the individual N species were identical to previous simulations (Table 1), which caused reductions in the total N loading rate when the input of certain N species were eliminated.

Denitrification rates decreased from 55 to 28 g N year$^{-1}$ for the entire system of 7 cells (Table 6) when NH$_4$-N was the only input to the system. This indicated that NH$_4$-N, through nitrification, was responsible for providing half of the NO$_3$-N for denitrification with all species entering the system. Negligible amounts of NO$_3$-N were derived from inputs of organic N, and originally present organic N in the soil column, as shown in simulations with organic N inputs only, and no N inputs (Fig. 7). The rate of volatilization with only NH$_4$-N inputs decreased only slightly, compared to simulations with inputs of all N species. Negligible amounts of N were lost due to NH$_3$-N volatilization where inputs were only NO$_3$-N and organic N (Table 6). Volatilization rates were almost completely dependent upon soluble NH$_4$-N inputs. Similar patterns and magnitudes of SON production occurred for all input compositions, including zero N inputs (Fig. 7), indicating that SON production in wetland systems relies largely upon hydrolysis of the originally present, edaphic PON storages.

Nitrate-N removal rates were dependent on N input composition, while removal of organic N and NH$_4$-N showed less sensitivity to input composition. This trend varies with the relative input amount of each N species, but identifies important differences in N removal. Transformations of SON, PON, and NH$_4$-N were not highly dependent on the previously addressed limiting soluble transport rates. Therefore, due to first order kinetics, increases to these storages lead to increased
transformation rates. Since denitrification only occurred in anaerobic layers, NO$_3$-N removal was limited by downward flux from the water column into these layers. Nitrification of the relatively large NH$_4$-N input also negatively affected net NO$_3$-N removal. Total N removal was 41 and 9% with NH$_4$-N and organic N inputs, respectively (Table 6). Low N removal efficiencies with organic N inputs were caused by continual increases of SON with progression through the wetland (Fig. 7). Inputs of only NO$_3$-N resulted in a 36% increase in total N. In this case, reduction of the relatively low NO$_3$-N inputs was overshadowed by production of SON.

### 3.4. Increased N loading rates

In previous simulations loading rates described by the NATWD (1993) were input to the first cell. This group of simulations tested increases of N loading rates to determine possible limitations of the first-order assumptions. For simplicity only two simulations, with loading rates increased 2 and 7 times, are discussed. With loading rates doubled, mass removal rates increased 2-fold to 1.1 g N m$^{-2}$ year$^{-1}$ (Table 6) as a consequence of an approximate 2-fold increase in the rates of denitrification, nitrification, and volatilization (Fig. 8). When loading rates were increased 7 times mass removal approached 5 g N m$^{-2}$ year$^{-1}$. This high rate of removal was due to elevated nitrification and denitrification rates. In these simulations denitrification rates in cell 1 approached 300 and 150 g N m$^{-2}$ year$^{-1}$ in cell 2 (Fig. 8). The literature average for annual denitrification rates is 35 g N m$^{-2}$ year$^{-1}$. This indicates that the first-order assumptions for denitrification may not apply at such high loading rates. Kadlec and Knight (1996) reported a consistent correlation between N mass removal and loading rates up to 3 g N m$^{-2}$ day$^{-1}$, while removal efficiency declined at greater loading rates. The loading rates
leading to the elevated removal rates were 6.7 and 3.4 g N m\(^{-2}\) day in cells 1 and 2, respectively. The efficiencies of these cells were similar to later cells in the system with lower loading rates. This result in comparison to literature values, suggests that the process rates and removal rates in cells 1 and 2, where 60% of the total N removal took place in these simulations, may have been over estimated by the model. However, extremely high rates of N loss (3000 g N m\(^{-2}\) year\(^{-1}\)) have been reported for the front edge of some wetland systems (Dørge, 1994) (this may be partially explained by high rates of PON sedimentation directly following input). While the maximum limit of N removal from these systems is unclear, potential over-estimation presents a problem for future spatial models of wetland treatment systems. While the first-order assumptions produce satisfactory results when mass loading rates are near literature values, the removal rates and process rates produced by these assumptions at higher loading rates were much greater than reported values. In order for future spatial models to properly simulate the dynamics of N cycling and removal at the front-end of such systems, where increased loading rates occur, other mathematical representations may be needed.

3.5. Spatial distribution

Spatial analyses is helpful in proper sizing of these systems, which have been over-designed with respect to area (Swindell and Jackson, 1990; Gale et al., 1993b). After developing a model in which the proposed wetland is divided into cells, the resulting concentrations can be analyzed and the appropriate size determined. The need for spatially explicit models that integrate ecosystem processes, especially feedbacks, which lead to improved management practices was addressed by O’Neill (1989) and Weins (1989). Spatial attributes analyzed with the model included the removal/production of N species, transformation rates, and vegetative N storage.

Removal of NH\(_4\)-N showed similar spatial patterns for all simulations in which it was input to the system. Ammonium-N removal rates decreased with distance from the inflow. This characteristic of diminishing returns was easily discernible due to the high relative amount of NH\(_4\)-N inputs compared to other N species, and showed little variance to increased diffusion coefficients, or changes in input amounts. Decreasing NH\(_3\)-N volatilization rates mirrored the pattern of NH\(_4\)-N mass removal. Total N mass removal followed a similar behavior. This species represented over half of the inputs, which partially explains the similarities between NH\(_4\)-N, and total N removal.

When NO\(_3\)-N was the only input, it was characterized by diminishing mass removal with passage through the system. However, with the addition of NH\(_4\)-N net production of NO\(_3\)-N occurred in...
the early cells, followed by NO$_3$-N reduction. Increasing diffusion coefficients pushed the change from net NO$_3$-N production to net NO$_3$-N reduction closer to the front of the system. Such changes in the middle cells represented a point in the wetland where the amount of NO$_3$-N produced through nitrification was balanced by NO$_3$-N flux into the soil.

4. Conclusions

Increasing molecular diffusion coefficients above literature values produced results similar to documented removal and process rates. This indicated that other transport processes of magnitudes greater than molecular diffusion account for the transport of soluble N in wetland systems. Based upon the concurrent increases in biomass with the increased diffusion rates, and high rates of evapotranspiration, characteristic of wetland macrophytes, it was proposed that this turbulent diffusion was augmented by vegetation induced water movement. As wetland plants draw water towards the roots, NH$_4$-N and NO$_3$-N are pulled from the water column to aerobic soil zones with enhanced rates of nitrification, and to anaerobic soil zones, where denitrification can occur. In addition to providing temporary N storage, and additional aerobic zones, wetland vegetation is a vital mechanism stimulating transport of soluble N. This implies that N removal from wetland systems without vegetation is limited by diffusive flux of soluble N, and additionally, that wetland species with greater evapotranspiration rates will promote greater N removal. This point can be further investigated by explicitly including interactions of evapotranspiration and turbulent diffusion in future models of this type.

Changes in diffusion coefficients resulted in opposing effects upon N removal. Molecular diffusion coefficients obtained from the literature resulted in slow downward flux of NO$_3$-N, resulting in large outflows of this species. Concurrently, upward movement of soluble organic N (SON) was restricted by lower diffusion coefficients. This resulted in larger storages of SON in the interstitial soil water. As diffusion coefficients were increased, resulting in flux rates in the range of turbulent diffusion, this trend reversed. Larger diffusion coefficients promoted greater downward transport of NO$_3$-N, resulting in greater amounts of denitrification. Increased diffusion coefficients lead to higher rates of SON outflow, following increased upward flux of SON to the water column.

Production of SON took place regardless of N inflow composition and loading rate. This indicated that SON production, which contributes to background levels of N in wetland systems, was dependent upon originally present, edaphic PON storages. This suggests that initial conditions for constructed wetlands should have adequate organic material to meet the demands of carbon consumptive processes, but not excessive amounts which contribute to production of SON. Less organic matter, and greater amounts of porous mineral substrate will also promote transport of soluble species in the soils, which will stimulate greater N removal.

Little change was produced in NH$_4$-N removal as a result of varying diffusion coefficients, and input composition. Ammonium-N could be lost through volatilization from the water column, or via nitrification in either the water column, or aerobic soil layer. The net effect of these processes on NH$_4$-N removal was relatively constant for all simulations. Removal rates of NO$_3$-N were greatly impacted by the input amounts of NH$_4$-N. When NO$_3$-N was the only input, a 63% reduction in NO$_3$-N resulted, but when all species were added only 11% reduction of NO$_3$-N took place due to the nitrification of NH$_4$-N. When diffusion coefficients were increased this trend did not occur, as the increased amount of NO$_3$-N was transported to anaerobic soil layers and lost via denitrification.

Spatial distribution allowed the portrayal of declining nitrogen gradients associated with N removal from wetland treatment systems. Models of this type will be beneficial in the design of future systems with regards to N, or other wetland compounds. Site specific models can be used to determine the area required to produce desired effluent characteristics, and the critical point at which background levels of N will be reached.
Spatial patterns for higher loading rates showed possible limitations of the model. At the front-end of the system, where the highest mass loading rates took place, the first-order assumptions may have yielded exaggerated removal and process rates. The same first-order representations resulted in satisfactory rates for cells with lower loading rates, characteristic of wetland treatment systems. This implies that future models may require different, and multiple kinetic assumptions to properly simulate N removal.

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