NITROGEN TRANSFORMATIONS IN A WETLAND RECEIVING LAGOON EFFLUENT: SEQUENTIAL MODEL AND IMPLICATIONS FOR WATER REUSE

SARA GERKE1, LAWRENCE A. BAKER* and YING XU
Department of Civil and Environmental Engineering, Arizona State University, Tempe, AZ 85287-5306, USA

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Abstract—Constructed wetlands could be components of low-tech systems to treat and reuse wastewater in arid regions. A key function of the wetland would be to provide additional N removal. To improve design criteria, a sequential model of nitrogen transformations (organic N → ammonium; ammonium → nitrate; nitrate → nitrogen gas) was successfully calibrated and verified for a wetland in Kingman, Arizona. A sequential model has the ability to “recognize” species of nitrogen in the influent and predict species of nitrogen in the effluent. Model scenarios show that increasing nitrification rates in the summer and denitrification rates in the winter would improve nitrogen removal efficiencies. Several lines of evidence suggest that wintertime denitrification may be limited by carbon supply. Winter carbon supply could be augmented by routing a portion of the water through channels planted with dryland vegetation.

BACKGROUND

Water supply is becoming a critical problem in arid regions of the world due to increasing population, increasing per capita water use and declining water quality (Postel, 1997). In the southwestern United States, including the US–Mexico border region, the problem of providing an adequate supply of pure water has generated a growing interest in the reuse of treated municipal wastewater. Treated wastewater can be used directly, generally for irrigation or industrial purposes, or indirectly, following a period of storage in surface reservoirs or underground aquifers (Bouwer, 1993).

Baker and Westerhoff (2000) suggested that a sequential system composed of aerated lagoons, constructed wetlands and infiltration basins could treat and recharge wastewater to aquifers. Recharged water would be of sufficient quality that minimal treatment would be needed following recovery. The primary objective of the wetland would be additional nitrogen removal, which would occur through a sequence of ammonification (mineralization), nitrification and denitrification. Effluent from the wetland would be sent to infiltration basins, where the treated wastewater would percolate slowly to the underlying aquifer. This type of system would be well suited for small municipalities in the southwestern United States and for the US–Mexico border region.

OBJECTIVES

Nitrogen removal is not accurately predicted with design guidelines that utilize a “black box” approach in which nitrogen loss is predicted from an overall N removal term ($k_N$) and total nitrogen (TN) in the influent. Published $k_N$ values for surface flow wetlands vary greatly (from $< 1$ to $> 60$ m/yr; Kadlec and Knight, 1996), making predictions of nitrogen removal inexact. Because of this, treatment wetlands are often designed conservatively, which means that they may be larger than necessary to achieve treatment objectives. Aside from the additional cost in overdesigning wetland treatment systems, high evaporation rates in the arid west dictate that treatment wetlands as small as possible to meet treatment objectives while minimizing evaporation. Furthermore, residence times longer than 5–10 days may result in elevated concentrations of DOC and disinfection byproduct precursors (Pinney et al., 2000).
This study had two objectives: (a) develop a more accurate design model for predicting nitrogen removal in wetland treatment systems, and (b) using the model, develop approaches to improve nitrogen removal. Data from a treatment wetland in Kingman, Arizona were used to calibrate and validate a sequential model of nitrogen transformations suggested by Kadlec and Knight (1996). A sequential model would “recognize” the reactivity of N species in the inflow and predict concentrations of individual N species in the effluent. The sequential model was used to identify several approaches to improve nitrogen removal efficiency.

STUDY SITE

The study site was a free-surface wastewater treatment wetland in Kingman, Arizona (Manthe and Ash, 1993). The 9-hectare wetland treatment system consisted of three long cells (700 m x 50 m each) connected in series (Fig. 1). The shallow zones (~0.2 m deep) were planted with Scirpus in 1994. Each cell was transected by two internal deep zones (1 m in depth) and included an open pool near the outlet. At the time of this study, wetland vegetation was a well-established mixture of Scirpus and Typha. The deep zones remained free of emergent vegetation. Wetland vegetation was deliberately burned in January 1997.

The wetland received non-nitrified effluent from aerated lagoons that treat municipal wastewater from Kingman, Arizona. Flow into the wetland averaged 3710 m³/day (1.0 million gallons/day), with monthly average flows varying from 3300 m³/day to 4500 m³/day. The average hydraulic loading rate (HLR) was 4.1 cm/day and the average hydraulic retention time (HRT) was 7 days, close to the average HRT of wetland treatment systems in EPA’s Wetland Treatment Data Base (Reed, 1991). The inflow BOD of the Kingman wetland (50 mg/L) was somewhat higher than the average for Wetland Treatment Data Base (39 mg/L; Knight et al., 1992). Average TN and ammonium in the inflow to the Kingman system (25 and 22 mg/L, respectively) were considerably higher than average TN and ammonium for wetlands in the EPA’s database (14 and 7.5 mg/L, respectively). The average N loading rate to the Kingman wetland was 10 kg/ha-day.

METHODS

Water samples were collected on 10 occasions from October 1996 through September 1997. On each sampling date, grab samples were collected from 13 locations along the long axis of the wetland (Fig. 1). Because transformations of nitrogen would likely be most rapid in the first cell, seven of the sample sites were located in this cell; three sites were located in each of the other two cells. Samples were poured into 1-L HDPE bottles, stored in a cooler during transport and immediately filtered upon return to the lab. Samples for dissolved nutrient analyses were filtered through GF/C filters and preserved with H₂SO₄ to pH < 2. Samples for anion analysis were filtered but not acidified. Samples for particulate organic nitrogen (PON) were filtered using a syringe filter with Whatman GF/F filters. Filters were wrapped in aluminum foil, dried overnight at 105°C, and stored in a dessicator prior to analysis. Nitrate+nitrite was analyzed by the cadmium reduction method Standard Methods (SM) #4500-NO₃-F (APHA, 1995) using a Bran-Luebbe AutoAnalyzer and by ion chromatography (SM #4500-NO₃ C) with a Dionex Model DX 40 Ion Chromatograph. Ammonia was analyzed with an Orion Model 95 ion specific electrode (SM #4500-NH₃ D). PON was analyzed using a Leeco CHN analyzer. Suspended solids (SS), volatile suspended solids (VSS), and 5-day biological oxygen demand (BOD₅) were analyzed on several occasions following Standard Methods (APHA, 1995). Details regarding sample handling, methods of analysis, and quality assurance can be found in Gerke (1997).

Aboveground plant biomass was determined by harvesting plant material in 0.1 m² quadrants placed along transects that were perpendicular to the long axis of the wetland at distances of 10 and 20 m from the edge. Transects were established at distances of 1/3, 2/3, and 5/6 of the cell length in all three cells. Plant material was separated into live (green) and dead (brown) material. The wet weight of each quadrant was determined and a subsample was taken to determine dry weight (dried at 105°C) and loss on ignition at 550°C (Gerke, 1997).

The wetland was assumed to have plug-flow hydraulics because the cells are long and narrow (length:width ratio = 14) and are transected by deep zones, which tend to remix channeled flows and maintain plug-flow characteristics. Furthermore, the three cells were arranged in series. Travel times used in model calculations were therefore computed from the measured flow rate (Q) divided by the cross-sectional area of the wetland (A). A porosity (Φ) of 0.75 (Kadlec and Knight, 1996) was used to correct for the effect of the wetland plants (AΦ = AΦ), where A is the cross-sectional area. Travel time at the end of the wetland is the HRT.

Table 1. Aboveground plant biomass (g/m²) in the Kingman wetland during June and August 1996

<table>
<thead>
<tr>
<th>Cell #</th>
<th>June Average</th>
<th>June Std. dev.</th>
<th>August Average</th>
<th>August Std. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3489</td>
<td>2690</td>
<td>2743</td>
<td>2594</td>
</tr>
<tr>
<td>2</td>
<td>2577</td>
<td>2026</td>
<td>1510</td>
<td>782</td>
</tr>
<tr>
<td>3</td>
<td>2650</td>
<td>825</td>
<td>1448</td>
<td>373</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic of the Kingman wetland, showing numbered sampling sites. The shaded areas are shallow zones (0.2 m); the unshaded areas are deep (1.0 m) zones. The travel time through the wetland varied from about five to seven days.
RESULTS

Plant biomass

The wetland was burned in January 1996, reducing aboveground biomass to nearly zero. Plants in this region begin growing in mid-February. Aboveground biomass averaged 2905 ± 1920 g DW/m² in June 1997 and 1900 ± 1605 g DW/m² in August 1997. The difference between the two means was not statistically significant (two-sample t-test, p = 0.05). Plant biomass varied greatly among sites, but there was no statistically significant difference in average biomass among cells (Table 1).

Table 2. Average concentrations of major constituents in the wetland influent and treatment efficiencies

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Influent to wetland (mg/L)</th>
<th>Wetland treatment efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD</td>
<td>50</td>
<td>87</td>
</tr>
<tr>
<td>SS</td>
<td>46</td>
<td>93</td>
</tr>
<tr>
<td>TN</td>
<td>25</td>
<td>66</td>
</tr>
<tr>
<td>NH₄-N</td>
<td>22</td>
<td>—</td>
</tr>
<tr>
<td>NO₃-N</td>
<td>0.3</td>
<td>—</td>
</tr>
</tbody>
</table>

Treatment efficiencies

For four months in which BOD₅ data were collected (February, April, May, and June) average BOD₅ removal in the wetland was 87%. Over nine sampling periods, average SS removal was 93%. Most BOD₅ and SS removal occurred in the first cell (Gerke, 1997).

The non-nitrified influent from the lagoon had an average TN (TN = NH₄-N + NO₃-N + PON) of 25 N/L, mostly in the form of ammonium (Table 2).
Average TN removal efficiency throughout the year was 66%, ranging from 16% in December 1966 to 90% in August 1977 (Fig. 2). Burning of the wetland during January 1997 may have contributed to the low N removal efficiencies in January and February. BOD and TN removal efficiencies were typical for wetland treatment systems in the United States (Knight et al., 1992).

Nitrogen transformations

Transformations of nitrogen species for nine sampling periods are illustrated in Fig. 3. Ammonium was the dominant form of N in the inflow on all occasions, averaging 85% of TN (Fig. 3). Ammonium concentrations often increased slightly during the first two days of travel time (within the first wetland cell), accompanied by decreases in PON. Ammonium concentrations then declined in subsequent cells (Fig. 3). Ammonium removal was greatest in April (97%), when plants were growing rapidly. Net ammonium removal was generally higher in summer than in winter.

PON ranged from 7 to 47% of inflow TN, averaging 14%. PON generally declined rapidly within the first wetland cell to around 1–2 mg N/L as the result of filtration and sedimentation. Very small peaks in PON (ca. 0.5 mg N/L) were sometimes observed in the pools at the end of each treatment cell. PON peaks in the pools appeared to be associated with alga blooms. Effluent PON concentrations were always <1 mg N/L.

\[
\begin{align*}
[\text{NO}_3^-] &= \frac{k_{\text{NH}_4}/h \times k_{\text{NO}_3}/h}{k_{\text{NO}_3}/h - k_{\text{NH}_4}/h} \\
&\left\{ \frac{\exp(-k_{\text{NH}_4}/h) - \exp(-k_{\text{N}_2}/h) \exp(-k_{\text{NO}_3}/h) - \exp(-k_{\text{N}_2}/h)}{k_{\text{N}_2} - k_{\text{NH}_4}} \right\} \text{PON} \\
&+ \frac{k_{\text{NO}_3}/h}{k_{\text{N}_2}/h - k_{\text{NO}_3}/h} \left\{ \exp(-k_{\text{NO}_3}/h) - \exp(-k_{\text{N}_2}/h) \right\} [\text{NH}_4]_o + [\text{NO}_3^-]_o \exp(-k_{\text{N}_2}/h)
\end{align*}
\]

where \(k_{\text{NH}_4}\) is the ammonification rate constant (m/day), \(k_{\text{NO}_3}\) the nitrification rate constant.

Fig. 4. Concentrations of nitrogen species in the effluent from the Kingman wetland, October 1996 through August 1997.
(m/day), \( k_{\text{N}_2} \) the denitrification rate constant (m/day) and \( t \) the reaction time. Rate constants are areal-based “velocity” terms normalized to depth (\( h \)), following the convention commonly used in wetland design models (Kadlec and Knight, 1996), and therefore have units of m/day.

PON degrades to yield ammonia (equation (1)). The concentration of ammonia at a given time is represented as the balance between mineralization and nitrification (equation (2)). Nitrate is gained from nitrification and lost by denitrification (equation (3)).

Calibration coefficients were determined for each month using field measurements. Coefficients were calibrated in sequence. First, PON data were used to determine \( k_{\text{NH}_4} \) (equation (1)). The calibrated \( k_{\text{NH}_4} \) value was then used to determine \( k_{\text{NO}_3} \) (equation (2)). Finally, values for \( k_{\text{NO}_3} \) were used in equation (3) to solve for \( k_{\text{N}_2} \).

Calibration constants were formally optimized. For ammonification and nitrification coefficients, the optimization criterion was minimization of the sum of absolute differences between measured and predicted values. The Excel “Solver” routine was used to generate the optimum calibration value using a random guess for initiation. The absolute difference criterion produced substantially better fits to the data than least-squares minimization. For the denitrification coefficient, the absolute difference criterion produced unsatisfactory results, as determined by visual comparison of measured and modeled concentrations. Denitrification coefficients were calibrated by minimizing the relative (rather than absolute) differences between measured and modeled concentrations.

The model worked well in predicting all three nitrogen species during the summer months (Fig. 5). Calibration for the ammonification and nitrification steps was also successful during the winter, but calibration of the denitrification coefficient was problematic for several months (January, February and April). During these months, modeled nitrate peaked earlier than measured values (see Fig. 5). Several attempts were made to improve the model algorithm. In one reformulation, the denitrification rate was modified using a Monod-type substrate limitation \( \left( k = \frac{k_{\text{max}} S}{S + K_{1/2}} \right) \), where \( k \) is the rate (m/yr), \( k_{\text{max}} \) the maximum rate (m/yr), \( S \) the substrate (nitrate) concentration (mg NO\textsubscript{3}–N/L) and \( K_{1/2} \) the half-saturation concentration (mg NO\textsubscript{3}–N/L). Based on a review of denitrification literature (Seitzinger, 1988), we examined \( K_{1/2} \) values over a range of 1–5mg NO\textsubscript{3}–N/L. No combination of \( K_{1/2} \) and \( k_{\text{max}} \) values could be found to improve

![Fig. 5. Model calibration for July 1997 (left) and December 1996 (right).](image-url)
the fit of the model. A two-component model was also evaluated, where \( k_{N2} = k'_{N2} + k''_{N2}\text{BOD}_5 \). In this model, \( k'_{N2} \) represented denitrification supported by decomposing wetland plants and \( k''_{N2} \) represented denitrification supported by externally supplied \( \text{BOD}_5 \). BOD-supported denitrification declined throughout the wetland, as \( \text{BOD}_5 \) was lost. BOD degradation rate was computed from \( \text{BOD}_5 \) loss and travel time using the March 1997 data using a \( k_{\text{BOD}} = 0.12/\text{day} \) computed for this date. This too, failed to substantially improve model results. Stoichiometric calculations showed that wastewater \( \text{BOD}_5 \) entering the wetland would support no more than about 30% of the observed denitrification in the wetland, so it is not surprising that inclusion of a BOD-dependent term would not substantially improve the model fit.

Calibrated model coefficients for ammonification and nitrification did not exhibit a clear seasonal pattern (Fig. 6 and Table 3). The small (insignificant) seasonal effect on \( k_{\text{NH}_4} \) and \( k_{\text{NO}_3} \) reflects the small difference between average temperatures for winter and summer (Table 3). By contrast, the denitrification rate constant (\( k_{N2} \)) varied by more than an order of magnitude between summer and winter (Fig. 6).

### Lumped parameter nitrogen model

An overall net nitrogen removal rate constant (\( k_N \)) was also computed for each month:

\[
k_N = \frac{\ln(\text{TN}_{\text{out}} / \text{TN}_{\text{in}})}{t} \quad (4)
\]

where \( \text{TN}_{\text{in}} \) is the total nitrogen concentration in the influent (mg N/L), \( \text{TN}_{\text{out}} \) the total nitrogen concentration in the effluent (mg N/L), and \( t \) the travel time (days). Calibrated \( k_N \) values obtained using equation (4) were compared with \( k_N \) values obtained using equation (5), which uses an assumed background concentration (Kadlec and Knight, 1996). Because our minimum effluent TN concentration was 1.3 mg/L, we set the background concentration slightly lower (1.2 mg/L). This is a bit below Kadlec and Knight’s proposed 1.4 mg/L background:

\[
k_N = \frac{\ln[(\text{TN}_{\text{out}} - 1.2) / (\text{TN}_{\text{in}} - 1.2)]}{t} \quad (5)
\]

Calibrated monthly \( k_N \) values using each method are shown in Fig. 7. Although equations (4) and (5) yielded somewhat different monthly \( k_N \) values, annual average \( k_N \) values were nearly the same: 21 m/yr using equation (4) and 18 m/yr using equation (5). Winter \( k_N \) values were generally lower than summer values (Fig. 7).

### Table 3. Average calibrated rate constants for the Kingman wetland, summer and winter. Summer is represented by data from April–October; winter is represented by data from November–February (no March data). Average air temperatures for the two seasons were 8°C (winter) and 22°C (summer) and average water temperatures were 11°C (winter) and 16°C (summer)

<table>
<thead>
<tr>
<th>Coefficient (m/day)</th>
<th>Winter</th>
<th>Summer</th>
<th>Annual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonification, ( k_{\text{NH}_4} )</td>
<td>0.24</td>
<td>0.25</td>
<td>0.23</td>
</tr>
<tr>
<td>Nitrification, ( k_{\text{NO}_3} )</td>
<td>0.044</td>
<td>0.066</td>
<td>0.057</td>
</tr>
<tr>
<td>Denitrification, ( k_{N2} )</td>
<td>1.04</td>
<td>1.2</td>
<td>1.14</td>
</tr>
</tbody>
</table>

![Fig. 6. Calibrated rate constants for the sequential model of nitrogen transformations (A) mineralization, \( k_{\text{NH}_4} \), (B) nitrification, \( k_{\text{NO}_3} \), and (C) denitrification, \( k_{N2} \).](image)

![Fig. 7. Monthly values for overall nitrogen removal rate constant, \( k_N \). Values were calculated using a background TN concentration of 0 mg/L (equation (4)) and 1.4 mg N/L (equation (5)).](image)
Table 4. Verification of seasonal model coefficients developed using data from 1996 to 1997 for data collected in 1998-early 1999. All concentrations are in mg N/L. Inflow ammonium and organic N were computed from measured TKN and nitrate with the assumption (based on data collected in 1996-1997) that NH$_4$-N = 0.85 TN and organic N = 0.15 TN.

<table>
<thead>
<tr>
<th>Wetland influent (measured)</th>
<th>Wetland effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
<td>Modeled</td>
</tr>
<tr>
<td><strong>Summer</strong></td>
<td></td>
</tr>
<tr>
<td>TN</td>
<td>30.7</td>
</tr>
<tr>
<td>Ammonium</td>
<td>25.5</td>
</tr>
<tr>
<td>Organic N</td>
<td>4.5</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.7</td>
</tr>
<tr>
<td><strong>Winter</strong></td>
<td></td>
</tr>
<tr>
<td>TN</td>
<td>36.3</td>
</tr>
<tr>
<td>Ammonium</td>
<td>30.5</td>
</tr>
<tr>
<td>Organic N</td>
<td>5.4</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**Verification**

The calibrated model was verified using data from a different time period (mid-1998 to early 1999). Model predictions were based on measured average influent nitrogen species and average travel time for each season and verified with average effluent concentrations (Table 4). The modeled summer effluent TN, 9.7 mg N/L, was 26% lower than measured average TN. Predicted and measured TN removal efficiencies compared well (68 and 57%, respectively). The model also correctly predicted an effluent NO$_3$-N concentration <1 mg/L.

Predicted effluent TN for the winter was within 10% of the measured average value (Table 4). Predicted and measured treatment efficiencies were 33 and 38%, respectively. The model correctly predicted higher effluent nitrate concentration in the winter than in the summer, but the predicted value of 6.5 mg NO$_3$-N/L was somewhat higher than the measured value of 3.9 mg NO$_3$-N/L.

For comparison, the lumped parameter model (with $C_0 = 0$) underpredicted effluent TN by 58% in the summer (5.4 mg N/L predicted versus 13.1 mg N/L measured) and by 11% in the winter (19.7 mg N/L predicted versus 22.3 mg N/L measured).

**DISCUSSION**

**Model evaluation**

For the verification data set, the calibrated model predicted effluent TN concentrations accurately in both seasons. During the summer, the model predicts the N composition of the effluent well. There was weaker correspondence between measured and modeled nitrate in the winter than the summer. Even in the winter, despite limitations noted above, the model reasonably approximates the distribution of effluent N species.

As with any model, calibration is site-specific. The calibrated model developed in this study therefore is valid only when applied to similar types of wetlands—surface flow systems with dense emergent vegetation (maximum standing crop = 2000–3000 g/m²) located in moderate climates (mean annual temperature = 13°C). These conditions would be applicable for much of the arid southwestern US, where treatment wetlands are becoming increasingly popular (Baker, 1994). Although the model theoretically represents a variety of waste streams ranging from fully nitrified to non-nitrified, further testing is needed to validate the model using a range of waste streams, particularly for nitrified wastewater.

The sequential model is an improvement over a single parameter model, but it does not have the flexibility of an ecological process model in predicting outflow concentrations over a wide variety of conditions. Gidley (1995) developed and calibrated this type of model for a subsurface wetland in Maryland with some success. Gearheart and Finney (1996) developed an simplified ecological process model to predict BOD removal, but it did not include nitrogen processes. Jones and Stokes (1993) developed a process model for simulating removal of nitrogen and several other constituents in surface flow wetlands, but the model has not been calibrated and tested. An ecological process model would theoretically yield more accurate predictions under a wide range of environmental conditions, but complex models require large amounts of data for calibration and verification, limiting their utility for design modeling. The model developed here is intermediate in both complexity and realism between lumped parameter models and complex ecosystem models.

**Model scenarios**

We developed base cases for summer and winter using average seasonal residence times and influent compositions together with calibrated nitrogen process coefficients (Table 5). Model scenarios (Table 5) were then developed to evaluate sensitivity of the model to changes in input conditions, hydraulic residence times, and nitrogen process coefficients. Results were used to show how a sequential model could be used to guide the design and operation of a wetland treatment system in winter and summer.

For winter, the model predicts that doubling the HRT (option 1) would double the TN removal efficiency (Table 5). Nitrifying the wastewater entering the wetland (90% nitrate; 10% ammonium; option 2) would have a similar effect. Both options would reduce effluent TN to <10 mg/L. Nitrogen process coefficients were modified in the next three scenarios, simulating altered environmental conditions (see discussion below). Doubling $k_{NO_3}$ (option 3) had a modest effect on predicted TN removal but increased predicted [NO$_3$-N] and decreased predicted
Table 5. Model scenario to examine effect of treatment modifications. Winter and summer base cases were developed using average seasonal influent concentrations and HRTs and calibrated model coefficients (Table 3), all developed with data from the calibration period.

<table>
<thead>
<tr>
<th>Management option</th>
<th>[NH₄⁺-N] (mg/L)</th>
<th>[NO₃⁻-N] (mg/L)</th>
<th>[org N] (mg/L)</th>
<th>TN (mg/L)</th>
<th>% N removal</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Winter base case</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Option 1: double HRT (to 13.0 days)</td>
<td>6.0</td>
<td>2.7</td>
<td>0.0</td>
<td>8.7</td>
<td>67</td>
</tr>
<tr>
<td>Option 2: nitrify 90% of influent NH₄⁺</td>
<td>2.7</td>
<td>3.0</td>
<td>0.0</td>
<td>5.7</td>
<td>78</td>
</tr>
<tr>
<td>Option 3: double kNO₃</td>
<td>6.1</td>
<td>6.1</td>
<td>0.0</td>
<td>12.2</td>
<td>54</td>
</tr>
<tr>
<td>Option 4: double kN₂</td>
<td>12.6</td>
<td>2.4</td>
<td>0.0</td>
<td>15.0</td>
<td>43</td>
</tr>
<tr>
<td>Option 5: double kNO₃ and kN₂</td>
<td>6.1</td>
<td>2.8</td>
<td>0.0</td>
<td>8.9</td>
<td>66</td>
</tr>
<tr>
<td><strong>Summer base case</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Option 1: double HRT (to 14.5 days)</td>
<td>2.1</td>
<td>0.0</td>
<td>0.0</td>
<td>2.1</td>
<td>92</td>
</tr>
<tr>
<td>Option 2: nitrify 90% of influent NH₄⁺</td>
<td>1.8</td>
<td>0.0</td>
<td>0.0</td>
<td>1.9</td>
<td>92</td>
</tr>
<tr>
<td>Option 3: double kNO₃</td>
<td>2.2</td>
<td>0.0</td>
<td>0.0</td>
<td>2.3</td>
<td>90</td>
</tr>
<tr>
<td>Option 4 double kN₂</td>
<td>7.2</td>
<td>0.0</td>
<td>0.0</td>
<td>7.3</td>
<td>70</td>
</tr>
<tr>
<td>Option 5: double kNO₃ and kN₂</td>
<td>2.2</td>
<td>0.0</td>
<td>0.0</td>
<td>2.3</td>
<td>90.8</td>
</tr>
</tbody>
</table>

[NH₄⁺-N] in the effluent. Doubling kN₂ (option 4) had a modest effect on predicted TN removal, but reduced effluent NO₃⁻-N by half. Doubling both coefficients (option 5) nearly doubled predicted TN removal efficiency to 64% and reduced predicted ammonium and nitrate in the effluent by one-half. For summer, doubling the HRT increased TN removal by only 20% and decreased predicted effluent ammonium concentration to 2.1 mg/L. Nitrifying the effluent (option 2) and doubling kNO₃ (option 3) had a similar effect on effluent quality as doubling the HRT. In both cases, predicted effluent NH₄⁺-N was reduced to by two thirds compared to the base case. Doubling kN₂ (option 4) had virtually no effect on predicted effluent quality compared to the base case because denitrification rates were already very high.

**Implications for improved wetland design**

Model scenarios point to ways that might improve nitrogen removal. Conceptually, the simplest way to increase N removal efficiency for a given inflow would be to increase the size and HRT of the wetland (option 1). However, increasing the size and surface area would increase evaporative losses, which would be undesirable for a wetland intended to be part of a water reuse system. Evaporation from wetland cells at the Tres Rios Wetland Demonstration Project in Phoenix averaged 9% of inflow, even with a relatively high HLR of 8 cm/day (Whitmer and Baker, 2000). Increasing HRT would also increase concentrations of DOC and DBP precursors in the wetland effluent (Pinney et al., 2000).

Model predictions indicate that prior nitrification of the influent would increase overall TN removal in the Kingman wetland, to around 78% in winter and 92% in summer (option 2 in Table 5). Increasing the nitrification rate (represented by doubling kNO₃, option 3 in Table 5) increased predicted TN removal from 34 to 54% in winter and from 70 to 90% in summer. Nitrification rates are likely limited by oxygen availability, so increasing oxygen transfer rates would likely increase nitrification. Methods that have been used to enhance nitrification in wetland systems have included the use of open pools, cascades between wetland cells, and rock nitrification filters (Hammer and Knight, 1994; Reed et al., 1995).

Denitrification during the summer appears to be very rapid. The very high calibrated value for kN₂, the insensitivity of predicted effluent concentrations to variations in kN₂, and the near absence of nitrate in the wetland effluent lead to the conclusion that denitrification was not the rate-limiting step for summertime TN removal. These observations are consistent with observations that N removal rates in wetlands receiving nitrified influent can be as high as 40–50 kg/ha-day (Horne, 1995; Ingersoll and Baker, 1997). Doubling kN₂ in the summer (simulating improved denitrification efficiency) had no effect on TN removal or the distribution of N species in the effluent, indicating that measures to increase denitrification rates in the summer would not likely increase nitrogen removal efficiency. Doubling both kNO₃ and kN₂ in the summer (option 5) had no more effect that doubling kNO₃ only.

The mean winter kN₂ value was nearly two orders of magnitude lower than the summer value (Table 3). Doubling kN₂ in the winter increased simulated TN removal, but by only 10% (from 34 to 43%; option 4). A 10-fold increase in kN₂ was needed to achieve simulated TN removal >50%. To achieve TN removal efficiencies much greater than 50% required increases in both the denitrification and nitrification rate coefficients (option 5).

Elevated concentrations of nitrate in the effluent (5–10 mg NO₃⁻-N/L) during the winter also suggest that denitrification rates were reduced, allowing NO₃ to accumulate in the water as it moved through the wetland. Three lines of evidence suggest that denitrification was limited by carbon supply during the winter. First, the total biomass of wetland plant was barely sufficient to support denitrification throughout the year. Peak aboveground biomass of emergent wetland plants was 2850 g/m² in June 1996. Root biomass may have added 50% or more to the
peak total biomass (Pullin and Hammer, 1991) but the fraction of root biomass that is lost to decomposition within a given year is probably relatively small. Furthermore, it is likely that much of the carbon from decomposing root tissue is not available to denitrifiers, which live near the oxic-anoxic interface. Thus, most of the carbon available for denitrification probably comes from shoots and stems. Assuming that wetland plants are 50% carbon on a dry weight basis, the aboveground standing stock of C was 14,250 kg/ha. Annual N loading to the wetland was 3700 kg/ha-year. The ratio of C in standing biomass: wastewater N was therefore about 4:1. Several field studies (Gersberg et al., 1983) and microcosm studies (Ingersoll and Baker, 1997), supported by theoretical calculations (Reed et al., 1995) suggest that a ratio of at least 5:1 is needed to assure an adequate carbon supply for denitrification. Even allowing for some contribution from belowground biomass and sloughing from emergent plants throughout the summer, it appears likely that the C supplied by emergent plants in the Kingman wetland was insufficient to support complete denitrification. The second line of evidence is that calibrated \( k_{N_2} \) values for the two seasons (0.14 m/day in winter and 12.9 m/day in summer) vary by nearly two orders of magnitude. Mean summer and winter water temperatures were 16 and 11°C, respectively. Using the rule of thumb that metabolic rates double with every 10°C increase in temperature, winter and summer \( k_{N_2} \) values would have differed by no more than a factor of two if a direct temperature effect on metabolism was the mechanism responsible for changes in denitrification rates. The effect of season on \( k_{N_2} \) must therefore be attributable to something other than temperature alone. Finally, effluent DOC and BOD\(_5\) values show that soluble C was in short supply by late winter. In February 1997, BOD\(_5\) in effluent from the wetland was only 3 mg/L. Measured biodegradable organic carbon (BDOC) in the effluent was only 4 mg/L in March 1997 (Pinney et al., 2000).

It is less clear whether carbon limitation was the result of the January burning or would have occurred anyway. Calibrated \( k_{N_2} \) values for November and December 1996 suggest that denitrification rates had slowed down considerably before the burn. Furthermore, the pattern of N removal was similar in 1998, when the wetland was not burned. We postulate that there was little biodegradable carbon in the dried plants that were still standing in January, so burning had little effect on wetland biogeochemistry.

The practice of burning wetland vegetation (now abandoned) would not be advisable given the likelihood that denitrification is carbon-limited in winter. To the contrary, an auxiliary carbon source may enhance denitrification during the winter. One approach for enhancing carbon supply without increasing the size of the wetland would be to grow dryland vegetation in channels parallel to the main wetland channel. During the spring and summer, these would be managed to provide high-value wildlife food crops such as Japanese millet, using a small amount of effluent for irrigation. During the winter, when extra carbon is needed for denitrification, these auxiliary channels would be part of the treatment system, with dried crop residues providing carbon for denitrification. This approach would also provide greater surface area for nitrification, at a time when evaporation rates are lower. Finally, managed auxiliary channels would provide food and cover for ground nesting birds during the summer (Baker and Westerhoff, 2000).

Implications for water reuse

Treatment wetlands could play a role in low-tech systems to treat and reuse wastewater. The key role of the wetland would be to provide additional N removal. The wetland would also remove suspended solids and BOD, reducing the potential for clogging in infiltration basins. Much of the DOC that passes through the wetland or is generated within the wetland would be removed in the infiltration system (Westerhoff and Pinney, 2000), reducing the potential for forming DBPs during subsequent chlorination. Thus, the functions of wetland and infiltration systems are complementary: together they remove nitrogen, DOC, suspended solids and pathogens.

CONCLUSIONS

The Kingman wetland, which receives non-nitrified lagoon effluent, had an average nitrogen removal efficiency of 66% with a HLR of 4 cm/day and an N loading rate of 10 kg N/ha-day. The wetland produced effluent with NO\(_3\) N consistently <10 mg/L and TN generally <15 mg/L. A sequential model of N transformations yields more information for design and management of constructed wetlands than is possible using a model based on TN alone. An advantage of the sequential model is that it recognizes the reactivity and sequence of individual nitrogen transformations. Calibration of model coefficients was generally successful and verification of the model with data from a subsequent year shows that it predicts TN removal and concentrations of nitrogen species with reasonable accuracy. Model coefficients are applicable to treatment wetlands with similar design and climatic conditions.

Wetlands can serve an important role in low-tech water reuse systems. In particular, they provide additional N removal. Model predictions suggest that enhanced nitrification alone would improve overall N removal in the summertime. Both nitrification and denitrification would have to be increased to increase winter TN removal efficiency \( \geq 50\% \). The latter could be achieved by growing wildlife crops in auxiliary channels that would be dry in the summer and then used as part of the wetland treatment system in the winter.
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