Nitrification kinetics and modified model for the Rideau River, Canada
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ABSTRACT

Improving kinetic modeling of nitrification in rivers is of growing importance due to yearly increases in the anthropogenic release of nitrogen into rivers around the world. The use of water quality models can abate the expense of water quality monitoring while enabling the user to predict trends of variation. Data collected from a series of laboratory kinetic experiments were used to calculate the rate of nitrification in the Rideau River, Canada, and modify nitrification algorithms used in the traditional water quality model Qual2E. The modified model relates the reaction rate coefficients with a simple biomass concentration measurement of volatile suspended solids (VSS) in the river and subsequently introduces biomass growth functions directly into the kinetic algorithm. Furthermore, this modified model includes a nitrate-nitrogen assimilation pathway. The modified model demonstrates an improved correlation to nitrogen parameters observed in river water samples compared with the classical water quality model Qual2E. The inclusion of bacterial concentrations based upon the simple measurement of VSS plays a critical role in the reactions of the nitrification system and nitrate-nitrogen assimilation is an important pathway at low ammonia-nitrogen concentrations.

Key words | bacterial growth, biomass concentration, modeling, nitrification, water quality

INTRODUCTION

Human activities have significantly increased nitrogen inputs to rivers and watersheds (Vitousek et al. 1997; National Academy of Sciences 2000). Algal bloom responses to this increased release of nutrients have shown a devastating effect on surface water quality (Zhang & Zhang 2007; Nakano et al. 2008; O’Neil et al. 2011). This is of significant concern to the Rideau River, Canada, where climate change models have predicted an increased occurrence of storm events and subsequent increased risk of large runoff events and eutrophication (Zhang et al. 2000; Schernewski 2003). Eutrophication of natural waters deteriorates dissolved oxygen (DO) concentrations, kills aquatic life and generates odors and phytoxins in rivers, lakes and estuaries (Zhang et al. 2011). The improvement and subsequent validation of current water quality models are imperative tools necessary to address, predict and help restrict eutrophication events.

The flow diagram shown in Figure 1 shows the biologically mediated nitrification pathways that occur between the mineralized forms of nitrogen in natural waters. Figure 1 demonstrates that ammonia oxidation to nitrate is a two-step process, where the first step is mediated by ammonia oxidizing bacteria (AOB) that produce nitrite and the second step is mediated by nitrite oxidizing bacteria (NOB) that oxidize nitrite to nitrate. Although nitrification occurs as a two-step process, a single first-order relationship has been previously applied to nitrification kinetic models to simplify the biologically mediated oxidation of ammonia to nitrate (Di Toro & Connolly 1980; Dilks et al. 1992; Rauch et al. 1998; Park & Lee 2002; Lindenschmidt 2006; Wool et al. 2006;
Nitrification kinetics \( k_n = k_n \theta_n T^{20} \frac{DO}{K_{nit} + DO} C_{NH_4^+} \) (1)

where \( k_n \) = nitrification rate coefficient at 20 °C (time\(^{-1}\)); \( \theta_n \) = temperature coefficient (dimensionless); \( T \) = temperature (Kelvin); \( DO \) = dissolved oxygen (mass volume\(^{-1}\)); \( K_{nit} \) = half saturation constant for oxygen limited growth (mass volume\(^{-1}\)); \( C_{NH_4^+} \) = ammonia concentration (mass volume\(^{-1}\)). Note that ammonia or NH\(_4^+\)-N are used in this text to refer to the sum of the NH\(_4^+\)-N and NH\(_3\)-N that exists in the water. Although the traditional single-step model has been widely used in recent studies (Lindenschmidt 2006; Wool et al. 2006; Kannel et al. 2007), nitrite formation during the nitrification process is absent from this simplified model and as such the accumulation of this constituent and the subsequent ecotoxicological effects cannot be modeled or predicted. Several studies have thus applied a two-step kinetic system to model the nitrification process and have demonstrated the ability to predict the nitrite concentration while enabling a more accurate nitrogen balance to be applied to the kinetic system (Brown & Barnwell 1987; Wiesche & Wetzel 1998; Reichert et al. 2001; Xia et al. 2004). Furthermore, oversimplifying the kinetics of biologically mediated nitrification into a singular relationship has been shown in select studies to lead to poorly modeled results for selective natural waters, while separating the two steps of nitrification through the application of individual kinetic relationships for ammonia and nitrite oxidation individually has been shown to improve the accuracy of nitrification kinetic models in these situations (Herbert 1999; Ben-Youssef et al. 2009).

Commonly used two-step nitrification models applied to natural waters include the nitrification models incorporated in the traditional Qual2E (Brown & Barnwell 1987) and RWQM1 (Reichert et al. 2001) models. The Qual2E model does not require many measurements or known parameter values to run the nitrification module and as such does not incorporate the growth of the nitrifying bacterial population in the nitrification module, ultimately resulting in a simplistic model but one that may be limited by its lack of growth equation. The RWQM1 model on the other hand incorporates greater complexities as it includes the growth kinetics of the ammonia and NOB separately, where each growth equation requires phosphorus measurements and subsequent phosphorus speciation based on pH measurements. These growth equations are thus not necessarily simplistic to apply to basic investigations and may be beyond the ability of certain end users. Thus a modified nitrification model that includes a simple method of incorporating nitrifier growth kinetics in natural waters may improve the accuracy of the current simplistic Qual2E model while not limiting its application because of increased measurements or complexity of use.

The purpose of this study is to quantify the kinetics of nitrification in the Rideau River and to investigate the effects of incorporating a simplistic biomass concentration and growth parameter into the Qual2E two-step nitrification kinetic relationship and subsequently evaluate the prediction of these modified nitrification rates on the N-cycle of the Rideau River, Canada. Specifically, the nitrification conversion processes widely used in water quality models are modified in this study to include biomass concentration based on the measurement of simple parameters and thus include growth parameters directly in the biochemical conversion module for nitrification. Kinetic data measured during a series of laboratory experiments performed on samples of the Rideau River in different seasonal conditions are used to develop, calibrate and validate the modified biochemical conversion nitrification module, with the results being ultimately compared with the traditional nitrification kinetic model Qual2E.

**MATERIALS AND METHODS**

**Model development and description**

The modified nitrification model developed in this study is denoted as Model B and it is based upon a two-step nitrification reaction, where the oxidation of ammonia to nitrite...
preccedes the oxidation of nitrite to nitrate (Figure 1). The modified nitrification model is based upon and compared with the traditional Qual2E model, denoted as Model A. Model A uses first-order reactions to describe the oxidation of ammonia to nitrite (Equation (2a)) and the oxidation of nitrite to nitrate (Equation (2b)). The kinetics of oxidation are a function of the first-order concentrations of ammonia and nitrite and are a function of calculated rate coefficients. The equations used to model the nitrogen concentrations, \(NH_4^+\)-N, \(NO_2^-\)-N and \(NO_3^-\)-N, of Model A are as follows:

\[
\frac{dN_1}{dt} = -\alpha N_1 \tag{2a}
\]

\[
\frac{dN_2}{dt} = \alpha N_1 - \beta N_2 \tag{2b}
\]

\[
\frac{dN_3}{dt} = \beta N_2 \tag{2c}
\]

where \(N_1 = NH_4^+\)-N concentration (mass volume\(^{-1}\)), \(N_2 = NO_2^-\)-N concentration (mass volume\(^{-1}\)), \(N_3 = NO_3^-\)-N concentration (mass volume\(^{-1}\)), \(t = \) time (time), \(\alpha = \) ammonia oxidation rate coefficient (time\(^{-1}\)) and \(\beta = \) nitrite oxidation rate coefficient (time\(^{-1}\)), the loss of \(NH_4^+\)-N being the source of \(NO_2^-\)-N, which continuously reacted to produce \(NO_3^-\)-N. The least squares method and Euler’s method were combined to optimize Model A by minimizing the differences between the experimental results measured in the laboratory and the respective model outputs while determining the optimal rate coefficient values of the model.

The kinetic pathways of the modified model (Model B) are developed to simulate nitrification in natural waters and incorporate additional relationships that improve the accuracy of models based solely on the fundamental two-step oxidation reactions of nitrification while maintaining the simplicity of the model (Figure 1). Ammonia is oxidized to produce nitrite and it may act as a nitrogen source for bacterial growth in the modified model, which would result in an accumulation of organic nitrogen. The ammonia oxidation reaction rate coefficient is thus related to the bacterial biomass concentration. Nitrite is oxidized to nitrate in the second step of the two-step nitrification process with the kinetics being a function of the bacterial biomass concentration. Nitrate is the final product of the oxidation reactions and it also acts as a nitrogen source for bacterial growth. The modified model thus includes the uptake of \(NH_4^+\)-N and \(NO_3^-\)-N for synthesis of bacterial growth. Although \(NO_2^-\)-N is thermodynamically preferential as a nitrogen source for nitrite oxidizing organisms compared with \(NO_3^-\)-N, its pathway as a nitrogen source for the system was not included in the modified nitrification module because of its traditional low concentrations in rivers.

Particularly, Model B builds upon the kinetic equations of Equation (2) by adding a bacterial biomass concentration parameter \(B\), measured as volatile suspended solids (VSS). VSS was chosen as a measure of microbial biomass as a simplistic, economical and quick measurement that is readily available to many end users. Based on this chosen simplistic measurement of microbial biomass, Model B neglects microbial decay and death. Furthermore, the modified model includes an organic nitrogen rate of change equation. The bacterial biomass concentration was correlated to the rate of change of organic nitrogen and to two newly introduced parameters, the weight fraction of nitrogen in the bacterial biomass \(\left(f_B\right)\) and the specific growth rate \(\left(\mu_n\right)\). The Model B equations are as follows:

\[
\frac{dN_1}{dt} = -\alpha N_1 - \left(1 - \theta\right)Bf_B \mu_n \tag{3a}
\]

\[
\frac{dN_2}{dt} = \alpha N_1 - \beta N_2 \tag{3b}
\]

\[
\frac{dN_3}{dt} = \beta N_2 - \theta Bf_B \mu_n \tag{3c}
\]

\[
\frac{dN_4}{dt} = Bf_B \mu_n \tag{3d}
\]

where \(N_1 = NH_4^+\)-N concentration (mass volume\(^{-1}\)), \(N_2 = NO_2^-\)-N concentration (mass volume\(^{-1}\)), \(N_3 = NO_3^-\)-N concentration (mass volume\(^{-1}\)), \(N_4 = \text{Org-N}\) concentration (mass volume\(^{-1}\)), \(t = \) time (time), \(\alpha = \) ammonia oxidation rate coefficient (time\(^{-1}\)), \(\beta = \) nitrite oxidation rate coefficient (time\(^{-1}\)), \(\theta = \) fraction of nitrogen uptake from nitrate pool,
\[ B = \text{bacterial biomass concentration as VSS (mass-cells volume}^{-1}), \]
\[ f_B = \text{weight fraction of nitrogen in bacterial biomass and } \mu_n = \text{specific growth rate (mass-new-cells mass-existing-cells}^{-1} \text{time}^{-1}). \]

Equation (4) was used to calculate a specific growth rate of 0.0044 h\(^{-1}\) for the bacterial biomass in the Rideau River. The weight fraction of nitrogen in the Rideau River biomass was calculated using Equation (5) to be 0.0069 mg N/mg cells. The results of these values were used in Equation (3) above.

\[ \mu_n = \frac{\Delta \text{VSS}}{\text{VSS} \cdot \Delta t} \quad (4) \]

\[ f_B = \frac{\text{Org-N}}{\text{VSS}} \quad (5) \]

Furthermore, the kinetic rate coefficients were calculated in Model B by using the following equations:

\[ \alpha = C_1 B \quad (6a) \]

\[ \beta = C_2 B \quad (6b) \]

where \( C_1 = \text{ammonia oxidation biomass concentration factor (mass-cells}^{-1} \text{time}^{-1}) \) and \( C_2 = \text{nitrite oxidation biomass concentration factor (mass-cells}^{-1} \text{time}^{-1}) \). The least squares method and Euler’s method were combined to optimize Model B by minimizing the differences between the experimental results measured in the laboratory and the respective models while determining: (i) the concentration factors in Equations (6a) and (6b) and thus the respective rate coefficients; and (ii) the fraction of nitrogen uptake from the nitrate pool (\( \theta \)) used in Equations (3a) and (3c).

**Laboratory batch experiments**

Two series of bench-scale batch reactor experiments were studied to: (i) develop and calibrate a modified biochemical conversion nitrification module; and (ii) quantify the rate of nitrification in the Rideau River and validate the modified nitrification module for the Rideau River (Figure 2). The calibration experiments incorporated the operation of two batch reactors. The first reactor was fed with Rideau River water, was spiked with ammonia to elevate the ammonia concentration to 1.5 mg/L NH\(_4\)\(^+\)-N and was aerated throughout the experimental phase to maintain a DO concentration above 5 mg/L. This reactor was operated parallel to a control reactor that was fed with the same spiked Rideau River water sample and was autoclaved to prevent microbial activity. The control reactor was aerated at the same rate of aeration as the first reactor to confirm that the aeration did not cause ammonia stripping in the reactors and that no other pathways of ammonia removal, other than biologically mediated oxidation, were significant in the laboratory reactors. Triplicate measurements of the nitrogen constituents, temperature, DO and pH were conducted once per day with a higher frequency at the start of the experiments. VSS was measured in triplicate at the beginning and end of each experiment. Slight variances of less than 10% relative to the triplicate measurements were observed for each of the parameters measured.

The model validation experiments were designed to measure the rate of nitrification in the Rideau River and validate the developed, modified nitrification module. This
experimental phase included three batch reactors. The first two reactors were operated under the same conditions and were used to demonstrate experimental repeatability. The water sample in the third reactor was sterilized and operated as a control to again confirm that aeration does not cause ammonia stripping and that ammonia removal by biologically mediated oxidation is in fact the dominant pathway of ammonia removal in the reactors. The three reactors were fed with Rideau River water and were aerated throughout the experimental phase to maintain a DO concentration above 5 mg/L. The control reactor was again autoclaved to prevent microbial activity. The same sampling and testing plan described for the model calibration experiments was followed for this second set of laboratory experiments. However, in this experimental phase the total nitrogen (TN) concentrations were unfortunately only measured at the start and end of the experimental phase because of instrument maintenance.

All river samples were collected 15 cm below the water surface of the Rideau River at two locations, one approximately 10 km downstream of the other, in the City of Ottawa in spring and winter conditions. Each reactor contained approximately 2 L of sample and the following parameters were immediately measured: NH4\textsuperscript{+}-N, NO2\textsuperscript{-}-N, NO3\textsuperscript{-}-N, Org-N, total phosphorus (TP), pH, DO, temperature and total suspended solids (TSS). All reactors were monitored for TP to ensure that phosphorus levels remained above a minimum concentration of 0.005 mg/L-P. Also, the reactors were shielded from light to prevent algae growth.

Analysis

NH4\textsuperscript{+}-N, NO2\textsuperscript{-}-N and NO3\textsuperscript{-}-N were measured using standard methods (Standard Methods 1995) 4500 – NH3 B & C, 4500 NO2-B and 4500 NO3-B with HACH spectrophotometry (DR5000 HACH, Colorado). TN was measured using a Teledyne Tekmar total nitrogen module (Apollo 9000, Teledyne Tekmar, Ohio) and the Org-N content of the sample was calculated using Equation (7). TP samples were measured using standard method 4500-P D (DR5000 HACH, Colorado). The microbial growth of the nitrifiers was estimated by measuring VSS of the water.

$$\text{Org-N} = \text{TN} - \text{NH}_4^+\text{-N} - \text{NH}_2^+\text{-N} - \text{NO}_3^-\text{-N} \quad (7)$$

RESULTS AND DISCUSSION

Model calibration experiments

The first set of laboratory reactors were spiked with ammonia and the subsequent experimental results were used to develop and calibrate Model B. Model coefficients of ammonia oxidation biomass concentration factor ($C_1$), nitrite oxidation biomass concentration factor ($C_2$) and fraction of nitrogen uptake from nitrate pool ($\theta$) were calibrated and are shown in Table 1. The experimental results are also compared with the simulation results of Model A and Model B (Figure 3). The 95% confidence intervals as error bars are not included in any figures in this study as the error bars are too small to be displayed about the average values plotted on the graphs (Figures 3–5). The control reactor demonstrated that nitrogen was not lost in the reactors due to aeration.

Models A and B both demonstrate a strong correlation to the experimental NH4\textsuperscript{+}-N data, with Model B showing a slightly better correlation compared with Model A (Figure 3(a)). This slightly improved correlation is reflected in the higher $R^2$ values for Model B ($R^2 = 0.89$) compared with Model A ($R^2 = 0.88$). Model B was able to simulate higher rates of ammonia consumption at greater ammonia concentrations and also decreasing rates with lower ammonia concentrations. This provided a stronger correlation between the experimental data and Model B at all ammonia concentrations. Model A simulated well the trend in the time period shortly after 400 h; however, it failed to predict the decrease of ammonia after 475 h, which resulted in an inaccurate long tail. Thus, Model A showed a strong correlation to the experimental data at high ammonia concentrations; however, it did not simulate well low rates of removal at low ammonia concentrations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$ (L h\textsuperscript{-1} mg\textsuperscript{-1})</td>
<td>$1.82 \times 10^{-4}$</td>
</tr>
<tr>
<td>$C_2$ (L h\textsuperscript{-1} mg\textsuperscript{-1})</td>
<td>$9.61 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\theta$</td>
<td>0</td>
</tr>
</tbody>
</table>
Early peaking and long tailing of NO$_2$-N concentrations were predicted by both models (Figure 3(b)). However, the experimental data show that the peak of nitrite occurs later in the experimental phase and that the NO$_2$-N values show insignificant tailing effects. Comparing the experimental data with Models A and B demonstrates that the error associated with early peaking and long tailing was diminished by Model B. The long tail predicted by Model A weakened the correlation with the observed experimental values ($R^2 = 0.23$) and thus Model B demonstrated a better correlation to the observed data ($R^2 = 0.56$).

Both models correlate well to the NO$_3$-N experimental data, with Model B demonstrating a superior ability to simulate the trends of the experimental data set; specifically showing an improved correlation at moderate and higher nitrate concentrations (Figure 3(c)). Particularly, Model B showed an ability to predict the NO$_3$-N concentration increase observed between 200 and 400 h and the subsequent slowed rate of increase after 500 h. The ability of Model B ($R^2 = 0.92$) to improve the simulation of the NO$_3$-N experimental data compared with Model A ($R^2 = 0.77$) is attributed to the modified model’s kinetic rate of NO$_3$-N production being a function of the biomass concentration in the reactor, as nitrate-nitrogen synthesis did not influence the simulation. The spiked ammonia concentrations in the reactors resulted in the model simulating complete ammonia-nitrogen uptake from the ammonia pool; (1–θ) value of one. Consequently,
the uptake of nitrate-nitrogen from the nitrogen uptake pool was a value of zero \( \theta = 0 \) as the synthesis of ammonia-nitrogen is thermodynamically preferential compared with nitrate-nitrogen.

Model A is not able to simulate changes in Org-N concentrations as no bacterial activity equations are included in the model (Equation (4)); consequently constant values are displayed as the overall modeling result (Figure 3(d)). The inclusion of the bacterial growth equations in Model B allows accumulation in Org-N to be simulated. The correlation of Model B to the experimental Org-N data was weak \( (R^2 = 0.002) \); however, the increase in the concentration of organic-nitrogen as the nitrifying organisms grow in the system was well predicted. The small change in concentration was a main reason for the low correlation, as the calculated Org-N fluctuations between small concentration values could not be accurately simulated by Model B.

Sensitivity analysis

Sensitivity analyses were performed for Model B to evaluate the sensitivity of the model results to the change in six main parameters of the model: biomass concentration factors \( C_1 \) and \( C_2 \); fraction of nitrogen uptake from nitrate pool coefficient \( \theta \); growth rate coefficient \( \mu_n \); initial bacterial biomass concentration \( B \); and the weight fraction of nitrogen in bacterial biomass \( f_B \). Each coefficient was changed by a factor of two (e.g. \( C_1 \) was changed to \( 2C_1 \) and \( 0.5C_1 \)) and the subsequent changes in the model predictions for nitrogen constituents were monitored (Table 2). NH4+\(-N\) was found to be moderately sensitive to \( C_1, \mu_n \) and initial \( B \). Note that in Model B, NH4+\(-N\) is not directly related to coefficient \( C_2 \) which governs the oxidation process from NO2\(-N\) to NO3\(-N\). Therefore, the concentration of NH4+\(-N\) is not very sensitive to the change in \( C_2 \). The nitrogen components NO2\(-N\) and NO3\(-N\) are sensitive to the changes of all parameters as they are intermediate products in Model B, with the concentration of NO2\(-N\) being the most sensitive to the change of coefficients. The concentration of Org-N is found to have the lowest sensitivity to \( C_1, C_2 \) and \( \theta \) as Org-N is a function of \( \mu_n \) and the initial bacterial biomass concentration \( B \) and is therefore not directly related to \( C_1, C_2 \) and \( \theta \). It should be noted that the sensitivity analysis simulations were terminated when the concentration of any of the nitrogen components became zero.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( C_1 )</th>
<th>( C_2 )</th>
<th>( \theta )</th>
<th>( \mu_n )</th>
<th>( B )</th>
<th>( f_B )</th>
</tr>
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<tbody>
<tr>
<td>NH4(-N)</td>
<td>24.64</td>
<td>&lt;1</td>
<td>6.38</td>
<td>28.19</td>
<td>29.37</td>
<td>6.37</td>
</tr>
<tr>
<td>NO2(-N)</td>
<td>54.38</td>
<td>64.87</td>
<td>6.74</td>
<td>35.41</td>
<td>42.85</td>
<td>6.74</td>
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<tr>
<td>NO3(-N)</td>
<td>32.47</td>
<td>11.39</td>
<td>11.58</td>
<td>49.38</td>
<td>47.27</td>
<td>3.63</td>
</tr>
<tr>
<td>Org-N</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>21.77</td>
<td>11.22</td>
<td>14.86</td>
</tr>
</tbody>
</table>

Figure 5 | Model validation experimental data set and Model B, (a) NH4\(+N\), (b) NO2\(-N\), (c) NO3\(-N\) and (d) Org-N.
Rideau River nitrification kinetics and model validation experiments

The model validation experiments were performed on Rideau River water samples that were not spiked with ammonia and hence were used to quantify the intrinsic rates of nitrification in the Rideau River. The average rate of ammonia removal was measured to be 0.0034 mg-N/L h at an average suspended solids value of 14 mg/L. A wide range of rates have been observed in other river studies. Xia et al. (2004) reported that the average ammonia removal rates in the Yellow River were observed at 0.00083, 0.0075 and 0.01 mg-N/L h with suspended solids concentrations of 0, 1,810 and 3,420 mg/L, respectively. Miranda et al. (2008) found nitrification rates ranging from undetectable to 0.002324 mg-N/L h in Kochi, India. A nitrogen mass balance was confirmed between the microbial consumption of NH_4-N and the production of NO_2-N and NO_3-N as the mass balance error was less than 7%.

In addition to using the second phase of laboratory experiments to quantify the rates of nitrification in the Rideau River, the experimental data were used to validate Model B and compare its simulation with Model A. The specific growth rate coefficient used for Model B was found to be similar in both laboratory experiments; however, the biomass concentration factors determined for the validation phase experiments were found to be significantly larger than those determined for the calibration phase experiments (Table 3). The larger biomass concentration factors are a result of the higher rates of ammonia oxidation at the low ammonia concentration, non-spiked validation phase experiments. Furthermore, since ammonia was consumed quickly in both reactors during the validation experiments the nitrate-nitrogen was readily used for bacterial growth in this experimental phase, resulting in high fraction of nitrogen uptake from nitrate pool values of 1.04 × 10^{-1} in Reactor 1 and 1.75 × 10^{-3} in Reactor 2 (Table 3).

Reactors 1 and 2 showed repeatable nitrogen constituent concentrations in the two reactors throughout the entire experimental phase (Figures 4 and 5). Model A simulated the general trend of the experimental NH_4-N data in Reactor 1 (R1) well; however, the steep decrease in ammonia concentrations at the beginning of the experimental phase of Reactor 2 (R2) was poorly simulated (R^2 = 0.93 (R1) and 0.87(R2)) (Figure 4(a)). This poor simulation occurred during the critical drop in ammonia concentrations. A strong correlation between Model B and the experimental NH_4-N data is observed for both reactors (R^2 = 0.95(R1) and 0.96(R2)) and an improvement over Model A is observed for one of the laboratory reactors (Figure 5(a)).

Early peaking and long tailing of NO_2-N concentrations were predicted by both models (Figures 4(b) and 5(b)). These curve attributes did not correspond well to the observed experimental data and as such the correlation between the simulated results and the experimental data was not significant for either model. Model A corresponded slightly better to the experimental data for both reactors (R^2 = 0.005(R1) and 0.26(R2)) than the respective correlation between Model B and the data (R^2 = 0.004(R1) and 0.023(R2)). Although the correlation between Model A and the data was better, the peak concentration of nitrite for both reactors was overestimated. Specifically, Model A predicted a significantly amplified peak for R2. This amplified peak for R2 was simulated as a result of the observed steep decrease in NH_4-N concentrations in R2. It should be noted that higher frequency measurements of nitrogen constituents during the peaking of the nitrite concentrations would have improved the prediction of the nitrite peak concentrations in both phases of experiments.

As seen in the model simulation of the calibration experimental data, both models correlate well to the NO_3-N experimental data, with Model B again demonstrating a superior ability to reproduce the trends of the experimental data (Figures 4(c) and 5(c)). The slight decrease in the nitrate experimental data in both reactors occurs as the ammonia concentration drops to zero in the

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reactor 1</th>
<th>Reactor 2</th>
</tr>
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<tbody>
<tr>
<td>θ (g new cells g cells⁻¹ h⁻¹)</td>
<td>4.41 × 10⁻³</td>
<td>4.41 × 10⁻³</td>
</tr>
<tr>
<td>B (mg L⁻¹)</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>C_1 (L h⁻¹ mg⁻¹)</td>
<td>7.50 × 10⁻³</td>
<td>5.56 × 10⁻³</td>
</tr>
<tr>
<td>C_2 (L h⁻¹ mg⁻¹)</td>
<td>9.49 × 10⁻²</td>
<td>8.09 × 10⁻²</td>
</tr>
</tbody>
</table>

Table 3 | Model B parameter values for model validation experiments
reactors and the biomass uses nitrate-nitrogen as an alternative nitrogen source for synthesis; this process was able to be simulated by Model B ($R^2 = 0.90(R1)$ and 0.91(R2)) and was not simulated by Model A ($R^2 = 0.86$ (R1) and 0.90(R2)). As previously described, Model A does not include a nitrate-nitrogen synthesis pathway and was not able to model the assimilation of nitrate and subsequent decrease in concentration. Owing to the fact that the number of TN measurements was limited in the study, the correlation between the model and the experimental data ($R^2$ values) was not calculated (Figures 4(d) and 5(d)). However, the trend in Org-N values is significantly better simulated by model B compared with model A, as the Org-N values are a function of the bacterial growth.

Overall, the validation results show that the nitrification model modified to include bacterial growth functions based upon simple VSS measurements and nitrate-nitrogen assimilation was able to better predict the ammonia, nitrate and organic nitrogen constituent concentrations compared with the conventional Qual2E nitrification model. In particular, the ability of Model B to simulate the changes in NO$_3$-N and Org-N demonstrates the value of bacterial growth functions. Furthermore, the study demonstrates that bacterial growth functions can be of value to nitrification models based on very simplistic VSS measurements.

**CONCLUSION**

A modified model (Model B) used to simulate nitrification kinetics in natural waters was investigated in the study. The modified model was based upon the traditional Qual2E model (Model A), where bacterial biomass concentrations measured as VSS are incorporated in a growth rate function and a pathway of nitrate-nitrogen assimilation is added to the traditional model. A sensitivity analysis was performed on the parameters of the modified model. The predicted nitrogen constituent concentrations were moderately sensitive to the change in the model coefficients, $C_1$, $C_2$ and $\theta$. The concentration of NO$_2$-N was found to be the most sensitive output to the change of coefficients while Org-N was shown to be the least sensitive.

Model B simulated the nitrification system of the Rideau River well and it more accurately simulated the concentrations of ammonia, nitrate and organic-nitrogen in the Rideau River compared with Model A. The modified model enables the user to adjust the reaction coefficients based upon bacteria concentration, which was found to significantly influence the kinetics of the nitrification system. Furthermore, the addition of the assimilation pathway of nitrate-nitrogen at low ammonia-nitrogen concentrations enabled slight changes in nitrate to be simulated.

Overall, this study showed that nitrification in rivers is not simply governed by constant coefficient kinetics. Indeed, the concentration of bacteria plays a critical role in the reactions and nitrate-nitrogen assimilation is important at low ammonia-nitrogen concentrations. Adding the bacterial biomass concentration based upon the simple measurement of VSS and the growth rate function of the bacteria into the model in addition to the nitrate-nitrogen synthesis pathway improved the accuracy of simulations. Although the optimized model improved concentration predictions, there are still significant inaccuracies in NO$_2$-N results. Further studies are needed to improve the model. Possible research directions include: (i) including the phosphorus kinetics in the proposed model; (ii) adding algal growth into the model; and (iii) combining the proposed model with sediment transport.

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