Mechanistic Modeling of Nitrite Accumulation and Nitrogen Oxide Gas Emissions during Nitrification

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ABSTRACT

Nitrite (NO\textsubscript{2}) accumulation in soil following nitrogen (N) fertilizer application has been observed under a variety of conditions. The presence of NO\textsubscript{2} together with soil acidity results in the formation of nitrous acid (HNO\textsubscript{2}), which decomposes abiotically to produce nitric oxide (NO) and nitrous oxide (N\textsubscript{2}O). These N oxide trace gases have potential effects on several atmospheric processes. Presented here is a model that describes some of the interactions between microbial, chemical, and physical processes that influence NO\textsubscript{2} accumulation and N oxide gas emissions following applications of NH\textsubscript{4}-based fertilizers. The model is applied to hypothetical and actual field scenarios. A two-step, two-population nitrification submodel is linked to gas production and transformation submodels. Transport of all chemical species occurs by diffusion. The model results suggest that some degree of transient nitrite accumulation following NH\textsubscript{4} application is a consequence of the nature of nitrification itself. Model simulations and sensitivity analysis indicate that (i) soils receiving similar fertilizer treatments but differing in their ability to buffer nitrification-induced acidity may produce dramatically different N oxide gas emissions, (ii) subsurface fertilizer placement can significantly reduce net NO emissions, and (iii) the differential responses of Nitrosomonas and Nitrobacter populations to chemical toxicities associated with the form and/or rate of fertilizer application may significantly affect the extent of NO\textsubscript{2} accumulation and corresponding gas emissions. Overall, the results contribute to our basic understanding of how multiple microbial, chemical, and physical factors can interact to control the net soil-to-atmosphere emission of nitrite-derived NO and N\textsubscript{2}O.

Nitrite accumulation in soil following N fertilizer application has been observed under a variety of conditions (Martin et al., 1942; Chapman and Leibeg, 1952; Morrill and Dawson, 1967; Bezdicek et al., 1971; Paul and Domsch, 1972; Chalk et al., 1975; Burns et al., 1995). The presence of NO\textsubscript{2} can promote abiotic reactions involving HNO\textsubscript{2}, which decomposes chemically to form NO and N\textsubscript{2}O gases (Nelson, 1982). Nitrogen losses in the form of NO and N\textsubscript{2}O are known to occur on several atmospheric processes (Crutzen, 1981). A conceptual “hole-in-the-pipe” model describing N oxide gas release from soil has been proposed by Firestone and Davidson (1989). Empirical models have also been developed based on fertilizer N inputs and soil temperature (Williams et al., 1992). The need for more mechanistic, process-based models has been identified as important for at least two reasons: (i) to assist in developing management strategies for minimizing gaseous N losses from agricultural systems and (ii) to help reduce uncertainties in regional and global assessments of the importance of soils as sources of N oxide gases (Mosier et al., 1996; Davidson and Kingerlee, 1997; Matson, 1997; Matson et al., 1998).

The phenomenon of NO\textsubscript{2} accumulation in soil has generally been attributed to the nitrification process (Van Cleemput and Samater, 1996). In order for NO\textsubscript{2} to accumulate during nitrification, the activity of Nitrobacter bacteria, which catalyze the second step of the nitrification sequence (i.e., the oxidation of NO\textsubscript{2} to nitrate [NO\textsubscript{3}\textsuperscript{-}]), must be less than that of Nitrosomonas and other bacteria that catalyze the first step of the sequence (i.e., the oxidation of ammonium [NH\textsubscript{4}\textsuperscript{+}] to NO\textsubscript{2}). Reduced Nitrobacter activity has been attributed to slower growth rates in response to N additions (i.e., lag effects) compared with NH\textsubscript{4}\textsuperscript{+}-oxidizer populations (Morrill and Dawson, 1967) and/or to the sensitivity of Nitrobacter populations to toxicity effects associated with free NH\textsubscript{3}, nitrification-induced acidity, or other chemical factors (Bezdicek et al., 1971; Venterea and Rolston, 2000).

Recent studies have quantified kinetic relationships between HNO\textsubscript{2} concentrations and NO and N\textsubscript{2}O production rates in several agricultural soils. These studies indicate that even relatively low NO\textsubscript{2} levels (<1 μg N g\textsuperscript{-1}) can promote significant rates of HNO\textsubscript{2}-mediated NO production (Venterea and Rolston, 2000b). Because pH and NO\textsubscript{2} concentrations together determine HNO\textsubscript{2} concentrations and each tend to be highly dynamic during nitrification, a model describing HNO\textsubscript{2}-driven NO emissions needs to account for transient nitrification dynamics, accompanying changes in soil pH, and HNO\textsubscript{2}-mediated gas production kinetics. In addition, NO is highly reactive and subject to transformation as it diffuses from points of production to the soil–atmosphere interface. Recent studies have also quantified the kinetics of NO-mediated N\textsubscript{2}O production under bulk aerobic soil conditions (Venterea and Rolston, 2000b). While detailed models of soil nitrification kinetics and/or biologically mediated N oxide gas emissions have been previously presented, none have described the coupling of these mechanisms (Paul and Domsch, 1972; Arakani et al., 1974; Darrah et al., 1985; Li et al., 1992; Grant, 1995).

The objective of the present study was to develop a model that describes the microbial and chemical processes influencing HNO\textsubscript{2}-driven N oxide gas emissions while accounting for chemical diffusion. The model is applied to hypothetical and actual field scenarios to examine the sensitivity of predicted NO\textsubscript{2} levels and gas emissions to key parameters and assumptions. The model provides a tool for studying complex interactions between microbial, chemical, and physical factors, while helping to identify areas requiring further investigation.
MODEL DESCRIPTION

Scope and Simplifying Assumptions

The dynamics of six chemical components (NH$_4^+$, NO$_2^-$, NO$_3^-$, H$^+$, NO, and N$_2$O) and two autotrophic bacterial populations (NH$_4^+$ oxidizers and NO$_3^-$ oxidizers) under hydrostatic and isothermal conditions are described (Fig. 1). For simplicity, the two classes of bacteria are referred to as *Nitrosomonas* and *Nitrobacter*, respectively, and diversities with respect to growth and activity rates within each population are not considered. The model is applied to conditions of moderate water content (\(<0.20\text{m}^{-3}\)) and it is assumed that levels of oxygen or carbon dioxide do not limit nitrification rates. Nitrite accumulation and/or NO gas production associated with dissimilatory NO$_2^-$ reduction to NO$_3^-$ or NH$_3^+$ are not considered, although these processes may be important under certain conditions (Firestone and Davidson, 1989; Kelso et al., 1999). While culture studies have indicated that nitrifying organisms can produce NO and N$_2$O through direct biological means (Firestone and Davidson, 1989; Kelso et al., 1999), the present model considers the primary source of NO production to be the result of abiotic decomposition of biologically generated NO$_2^-$ and HNO$_3$, based on results of recent experiments with agricultural soils (Venterea and Rolston, 2000a). The subsequent microbial reduction of nitrification-derived NO to N$_2$O, which has been shown to be important under bulk aerobic soil conditions, is considered (Venterea and Rolston, 2000b). Transport of all chemical species into and out of the soil is assumed to be governed by one-dimensional, vertical Fickian diffusion.

Process Description

Processes considered by the model are illustrated in Fig. 1. Ammonium N added as fertilizer or released from soil organic matter (SOM) is subject to nitrification and cation exchange onto soil surfaces. The first step of nitrification, mediated by *Nitrosomonas*, generates NO$_2^-$ and H$^+$ in molar ratios of 1:1 and 2:1, respectively, in proportion to NH$_4^+$ oxidized. While the primary biochemical substrate for autotrophic NH$_4^+$ oxidizers appears to be ammonia (NH$_3$) and not NH$_4^+$ (Suzuki et al., 1974; Darrab et al., 1985), the overall reaction is commonly written with respect to NH$_4^+$ (e.g., Conrad, 1995b) and kinetic dependencies are often expressed as a function of NH$_4^+$ concentrations (Paul and Domsch, 1972; Ardakani et al., 1974; Darrab et al., 1985). During nitrification, soil pH responds to the production of H$^+$ and to buffering reactions that neutralize some of the H$^+$ that is produced (Wang et al., 1998; Nye, 1972). *Nitrosomonas* populations increase as substrate is utilized (Morrill and Dawson, 1967; Ardakani et al., 1974). The NO$_2^-$ produced is oxidized to NO$_3^-$ by *Nitrobacter* populations, which also proliferate as substrate is utilized (Morrill and Dawson, 1967; Ardakani et al., 1974). The NO$_3^-$ is subject to protonation and formation of HNO$_3$ (pK$_a = 3.3$) (Van Cleemput and Samater, 1996):

$$\text{H}^+ + \text{NO}_3^- \rightleftharpoons \text{HNO}_3$$ \[1\]

Production of NO results in part from aqueous disproportionation of HNO$_2$–N:

$$3 \text{HNO}_2 \rightarrow 2 \text{NO} + \text{HNO}_3 + \text{H}_2\text{O}$$ \[2\]

or similar reactions (Van Cleemput et al., 1976). Reactions of HNO$_3$ with soil organic matter also may result in NO and/or N$_2$O production (Stevenson, 1994). Additional N$_2$O production results from microbial NO reduction, which increases with increasing water content (Venterea and Rolston, 2000b). The NO produced is subject to heterotrophic and autotrophic microbial oxidation in the liquid phase and chemical oxidation by O$_2$ in the gas phase (Fig. 1) (Conrad, 1995b).

Mathematical Description

Chemical Transport and Transformation

Each chemical component is governed by a diffusion–reaction equation, so that the system can be represented as:

$$R_i \frac{\partial C_{ij}}{\partial t} = \frac{\partial}{\partial z} \left( D_i \frac{\partial C_{ij}}{\partial z} \right) + P_i$$ \[3\]

where $i$ is the component index, with the correspondence: NH$_4^+$, $i = 1$; NO$_2^-$, $i = 2$; NO$_3^-$, $i = 3$; H$^+$, $i = 4$; NO, $i = 5$; and N$_2$O, $i = 6$; $C_{ij}$ is the concentration (g N m$^{-3}$ or g H$^+$ m$^{-3}$) of component $i$ with respect to the component’s predominant phase (i.e., $j$ refers to the gas or liquid phase of soil); $R$ is a phase partitioning parameter (m$^3$ m$^{-3}$ soil); $P$ is the net production rate (g m$^{-3}$ soil h$^{-1}$); $t$ is time (h); $z$ is soil depth (m), and $D$ is the soil diffusivity (m$^2$ m$^{-1}$ soil h$^{-1}$), which is described by Moldrup et al.’s (1997) model:

$$D_i = 0.66 D_{0i} \frac{\kappa^3}{\phi^3}$$ \[4\]

where $D_{0i}$ is the diffusion coefficient (m$^2$ h$^{-1}$) in free liquid or gas of component $i$, $\phi$ is total porosity (m$^3$ m$^{-3}$ soil), and $m = 1$ for liquid-phase diffusion and $m = 3$ for gas-phase diffusion. The parameter $\kappa$ refers to the volumetric content of the relevant phase, that is, $\kappa$ is the water content (m$^3$ m$^{-3}$ soil) or the gas content (m$^3$ m$^{-3}$ soil) for liquid- and gas-phase diffusion, respectively.

For NH$_4^+$ ($i = 1$), a reversible, instantaneous linear relation between solution and sorbed phase is assumed (Wagenet et al., 1977):

$$R_i = \theta + \rho K_{b1}$$ \[5\]

where $\rho$ is the soil dry bulk density (kg m$^{-3}$) and $K_{b1}$ (m$^3$ H$_2$O kg$^{-1}$ soil) is the equilibrium liquid–solid partitioning coefficient for NH$_4^+$. Analogously for NO and N$_2$O ($i \approx 5$), phase partitioning between gas and liquid phases is described by:

$$R_i = e + \frac{\theta}{K_{H1}}$$ \[6\]

where $K_{H1}$ is the Henry's law constant (m$^3$ H$_2$O m$^{-3}$ gas) for component $i$. After Wang et al. (1998) and Nye (1972), for H$^+$ ($i = 4$), a solid-phase soil pH buffering capacity term
Table 1. Parameters held constant for all model simulations.†

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D_{a,i})</td>
<td>aqueous diffusivity, (NH_4^+)</td>
<td>(7.0 \times 10^{-4})</td>
<td>m(^2) H(_2)O h(^{-1})</td>
<td>1</td>
</tr>
<tr>
<td>(D_{a,2})</td>
<td>aqueous diffusivity, (NO_2^-)</td>
<td>(6.9 \times 10^{-4})</td>
<td>m(^2) H(_2)O h(^{-1})</td>
<td>1</td>
</tr>
<tr>
<td>(D_{a,3})</td>
<td>aqueous diffusivity, (NO_3^-)</td>
<td>(6.8 \times 10^{-4})</td>
<td>m(^2) H(_2)O h(^{-1})</td>
<td>1</td>
</tr>
<tr>
<td>(D_{a,4})</td>
<td>aqueous diffusivity, (H^+)</td>
<td>(3.3 \times 10^{-3})</td>
<td>m(^2) gas h(^{-1})</td>
<td>2</td>
</tr>
<tr>
<td>(D_{g,5})</td>
<td>gaseous diffusivity, NO</td>
<td>(8.5 \times 10^{-3})</td>
<td>m(^2) gas h(^{-1})</td>
<td>3</td>
</tr>
<tr>
<td>(D_{g,6})</td>
<td>gaseous diffusivity, (N_2O)</td>
<td>(5.2 \times 10^{-1})</td>
<td>m(^2) gas h(^{-1})</td>
<td>3</td>
</tr>
<tr>
<td>(K_{H_1})</td>
<td>Henry's Law constant, NO</td>
<td>(21.2)</td>
<td>m(^3) H(_2)O m(^{-3}) gas</td>
<td>4</td>
</tr>
<tr>
<td>(K_{H_2})</td>
<td>Henry's Law constant, (N_2O)</td>
<td>(1.68)</td>
<td>m(^3) H(_2)O m(^{-3}) gas</td>
<td>4</td>
</tr>
<tr>
<td>(MR)</td>
<td>net (NH_4^+) mineralization rate</td>
<td>0.035</td>
<td>mg N kg(^{-1}) soil h(^{-1})</td>
<td>5</td>
</tr>
<tr>
<td>(B_{i})</td>
<td>initial Nitrosomonas density</td>
<td>(2 \times 10^{10})</td>
<td>cells kg(^{-1}) soil</td>
<td>6</td>
</tr>
<tr>
<td>(K_{l,1})</td>
<td>half-saturation conc., (NH_4^+)</td>
<td>2.08</td>
<td>g N m(^{-3}) H(_2)O</td>
<td>7</td>
</tr>
<tr>
<td>(K_{l,2})</td>
<td>half-saturation conc., (NO_2^-)</td>
<td>1.89</td>
<td>g N m(^{-3}) H(_2)O</td>
<td>7</td>
</tr>
<tr>
<td>(K_{l,3})</td>
<td>inhibition factor, (NH_4^+) oxidation</td>
<td>(10^{-12})</td>
<td>mole H(^+) L(^{-1})</td>
<td>8,9</td>
</tr>
<tr>
<td>(Y_1)</td>
<td>yield coef., Nitrosomonas</td>
<td>(1.7 \times 10^{-4})</td>
<td>cells biomass kg(^{-1}) N</td>
<td>7</td>
</tr>
<tr>
<td>(Y_2)</td>
<td>yield coef., Nitrobacter</td>
<td>(1.4 \times 10^{-4})</td>
<td>cells biomass kg(^{-1}) N</td>
<td>7</td>
</tr>
<tr>
<td>(d_l)</td>
<td>decay coef., Nitrobacter</td>
<td>0.01</td>
<td>h(^{-1})</td>
<td>7#</td>
</tr>
<tr>
<td>(d_{i,2})</td>
<td>rate coef. for NO reduction to (N_2O)</td>
<td>(32 + 9.2 S_o)</td>
<td>kg N kg(^{-1}) NO-N h(^{-1})</td>
<td>91†</td>
</tr>
<tr>
<td>(L)</td>
<td>depth of soil profile</td>
<td>20 cm</td>
<td></td>
<td>11</td>
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</table>

† Additional parameters that were varied for Cases 1 through 3 are shown in Table 2.
‡ = Hunik et al., 1994; 2 = Kemper, 1986; 3 = Bird et al., 1966; 4 = Wilhelm et al., 1977; 5 = Curtin et al., 1998; 6 = Morrill and Dawson, 1967; Burns et al., 1995; Burns et al., 1999; 7 = Keen and Prosser, 1987; 8 = Ventera and Rolston, 2000a; 9 = Ventera and Rolston, 2000b; 10 = Atkinson et al., 1997.
§ \(K_{l,3}\) value estimated from published data as described in text.
# Value set by authors.
†† Function of degree of saturation \((S_o)\) calculated from data in Venterea and Rolston (2000b).

Table 2. Additional parameters used in simulations and sensitivity analysis.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value?</th>
<th>Units</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mu_{max,1})</td>
<td>max. growth rate, Nitrobacter</td>
<td>0.031</td>
<td>h(^{-1})</td>
</tr>
<tr>
<td>(B_{i})</td>
<td>initial Nitrobacter population</td>
<td>1 - 10 ((2) \times 10^6)</td>
<td>cells kg(^{-1}) soil</td>
</tr>
<tr>
<td>(K_{l,1})</td>
<td>inhibition factor for (NO_2^-) oxidation</td>
<td>(10^{-15})</td>
<td>mole H(^+) L(^{-1})</td>
</tr>
<tr>
<td>(\beta_s)</td>
<td>soil buffering capacity</td>
<td>0.033 - 0.045 (0.036)</td>
<td>g H(^+) kg(^{-1}) soil pH(^{-1})</td>
</tr>
<tr>
<td>(k_{p,NO})</td>
<td>NO production rate coefficient</td>
<td>(3 \times 10^{-10})</td>
<td>m(^3) NO kg(^{-1}) soil h(^{-1})</td>
</tr>
<tr>
<td>(K_{l,2})</td>
<td>(NO_2^-) production rate coefficient</td>
<td>(3 \times 10^{-10})</td>
<td>mg NO-N kg(^{-1}) N h(^{-1})</td>
</tr>
<tr>
<td>(K_{l,3})</td>
<td>(NO_3^-) phase partition coefficient</td>
<td>(3 \times 10^{-10})</td>
<td>mg NO-N kg(^{-1}) N h(^{-1})</td>
</tr>
<tr>
<td>(P_{a,1})</td>
<td>background NO production rate</td>
<td>(1.5 \times 10^{-4})</td>
<td>mg N kg(^{-1}) soil h(^{-1})</td>
</tr>
<tr>
<td>(P_{a,2})</td>
<td>background (NO_2^-) production rate</td>
<td>(6 \times 10^{-10})</td>
<td>mg NO-N kg(^{-1}) N h(^{-1})</td>
</tr>
<tr>
<td>(k_{o,s})</td>
<td>NO oxidation rate coefficient</td>
<td>(3 \times 10^{-10})</td>
<td>mg N kg(^{-1}) soil h(^{-1})</td>
</tr>
<tr>
<td>(k_{o,2})</td>
<td>(NO_2^-) oxidation rate coefficient</td>
<td>(6 \times 10^{-10})</td>
<td>mg NO-N kg(^{-1}) N h(^{-1})</td>
</tr>
<tr>
<td>(L)</td>
<td>depth of fertilizer incorporation</td>
<td>0 - 5 cm</td>
<td></td>
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</tbody>
</table>

† Values in parentheses were used in examining model sensitivity to other parameters.
‡ = Keen and Prosser, 1987; Prosser, 1989; 3 = Both et al., 1990; Degrange and Bardin, 1995; 4 = Curtin et al., 1998; 5 = Venterea and Rolston, 2000b (Case 3); 6 = Venterea and Rolston, unpublished data (Case 3); 7 = Wagenet et al., 1997 (Cases 1 and 2).
§ Initial conditions, bulk density, and water content were estimated from measured data (Venterea and Rolston, 2000b).
# Value set by authors.
* No inhibition of \(NO_2^-\) oxidation was assumed for Case 1.
and N2O, where the liquid-phase HNO2 concentration (g N m\(^{-3}\) H2O) is calculated from the NO\(_2\) concentration, soil pH, and acid dissociation constant, as described in Venterea and Rolston (2000a). The parameters \(k_{PN0}\) and \(k_{PN0,O}\) are defined below. The present formulation also assumes that NO\(_2\) and H\(^+\) in solution phase equilibrate to form HNO2, and that soil pH reflects solution phase H\(^+\) concentration. The rate of soil NO\(_2\) (\(i = 3\)) production will be controlled by the NOR as defined above. For H\(^+\) (\(i = 4\)), it is assumed that production follows the stoichiometric generation of H\(^+\) from autotrophic NH\(_4\) oxidation, and also that HNO\(_2\)-mediated reactions consume H\(^+\):

\[
P_4 = \psi \left( \frac{\partial C_{\text{HNO}_2}}{\partial t} \right)_{\text{AOR}} - \frac{1}{2} \theta k_{\text{PN0}} [\text{HNO}_2]_L
\]

where \(\psi = 2\, \text{g H}^+ \text{per} 14\, \text{g N (Wang et al., 1998)}\). The consideration of HNO\(_2\) decomposition in consuming H\(^+\) is based on experimental data showing that soil pH buffering is significantly increased during periods of high HNO\(_2\)-mediated NO production (Venterea and Rolston, 2000a) and also on Reaction [2] stoichiometry. For NO (\(i = 5\)), production is due primarily to abiotic HNO\(_2\) decomposition, while consumption occurs due to liquid-phase oxidation and reduction and gas-phase oxidation:

\[
P_5 = \theta \left( k_{\text{PN0}} [\text{HNO}_2]_L - \frac{C_{\text{NO}}}{K_{\text{H},\text{NO}}} [k_{\text{a},5} + k_{\text{red},5} (S)] \right) - \varepsilon k_{\text{red},5} C_{\text{O},5} + \rho P_{\text{S},5}
\]

where \(k_{\text{PN0}}\) is the rate coefficient for HNO\(_2\)-mediated NO production (Venterea and Rolston, 2000a), \(k_{\text{a},5}\) describes first-order NO oxidation in the liquid phase (Venterea and Rolston, 2000a), \(k_{\text{red},5}\) describes first-order microbial HNO\(_2\) reduction to N\(_2\)O as an increasing function of soil water saturation (\(S\)) (Venterea and Rolston, 2000b), and \(k_{\text{red},5}\) is a rate coefficient for NO oxidation by O\(_2\) in the gas phase with second-order dependency on NO concentration (Atkinson et al., 1997) (\(O_2\) concentration is assumed to be ambient). The additional production term (\(P_{S,5}\)) is based on data indicating that, in the absence of HNO\(_2\), aerobically incubating soils exhibit a low but steady background NO production rate (i.e., \(\leq 0.3\, \mu g\,kg^{-1}\,h^{-1}\) (Venterea and Rolston, 2000a). For N\(_2\)O (\(i = 6\)), liquid-phase production occurs through abiotic HNO\(_2\) decomposition and microbial NO reduction:

\[
P_6 = \theta \left( k_{\text{PN0}} [\text{HNO}_2]_L + k_{\text{red},5} (S) \right) \frac{C_{\text{NO}}}{K_{\text{H},\text{NO}}} - k_{\text{red},6} C_{\text{O},6} + \rho P_{\text{S},6}
\]

where \(k_{\text{PN0,O}}\) is the rate coefficient for HNO\(_2\)-mediated N\(_2\)O production (Venterea and Rolston, 2000a). The first-order reductive consumption coefficient (\(k_{\text{red},6}\) and background production term (\(P_{S,6}\)) are assumed to be mediated by denitrification processes and are therefore considered to be zero, except in comparisons with field data (Case 3, below).

**Microbial Biomass Dynamics**

Biomass kinetics are described by Monod growth with decay:

\[
dB_i = B_i \left[ \frac{\mu_{\text{max},i} C_{\text{L},i}}{K_{\mu,i} + C_{\text{L},i}} - d_i \right]
\]

where \(B_i\) is the biomass density with \(i = 1\) referring to Nitrosomonas and \(i = 2\) to Nitrobacter biomass. It is assumed that cell maintenance energy is derived fully from endogenous decay, so decay coefficients (\(d_i\)) are calculated from published maintenance and yield coefficients for Nitrosomonas and Nitrobacter (Keen and Prosser, 1987; Herbert, 1959). The common observation that nitrification rates in soil tend to decrease with decreasing soil pH (e.g., Laanbroek and Woldendrop, 1995; Prosser, 1989) was modeled using a modified formulation of Quinlan’s (1984) model describing pH effects on autotrophic NH\(_4\) oxidation activity in liquid culture. Quinlan’s (1984) complete three-parameter formulation was tested in preliminary simulations and found to significantly underestimate gross NH\(_4\) oxidation rates measured concurrently with soil pH in incubating agricultural soils (Venterea and Rolston, 2000a). This discrepancy is probably related to the observation that autotrophic NH\(_4\) oxidation proceeds in soil at much lower bulk pH than in well-mixed liquid systems, possibly due to microscale spatial variability in pH, surface effects, and/or acidophilic adaptations (Prosser, 1989; Hayatsu and Kosuge, 1993; Laanbroek and Woldendrop, 1995). The simplified one-parameter enzyme inhibition model

\[
K_{s,i} = K_{s,i} \left( 1 + \frac{10^{-\rho K_{i,i}}}{K_{i,i}} \right)
\]

was found to more adequately describe decreases in measured gross NH\(_4\) oxidation rates in soils, where \(K_{s,i}\) is an inhibition constant and \(K_{s,i}\) is the half-saturation concentration for growth in the absence of H\(^+\) inhibition. An average value for \(pK_{i,i}\) (where \(pK_{i,i} = -\log_{10} K_{i,i}\) of 6.3 was obtained by comparison with data presented in Venterea and Rolston (2000a). This \(pK_{i,i}\) value also adequately described NH\(_4\) dynamics in a separate field study (data presented below) (Venterea and Rolston, 2000b). As a preliminary model, Eq. [15] was also used to describe H\(^+\) inhibition of NO\(_2\) oxidation, and the inhibition parameter (\(pK_{i,i}\)) was evaluated over the range 6.5 to 8.0. While the above assumptions are certainly a simplification of the effects of pH on enzyme inhibition and substrate availability for autotrophic nitrifiers in soil, the formulation allows for at least a preliminary evaluation of how differential inhibition of the two classes of autotrophs can potentially affect NO\(_2\) accumulation and resulting gas emissions. Other potentially important inhibition effects not incorporated into the present model are discussed below.

**Numerical Methods and Simulations**

The partial differential equation (PDE) describing six chemical components (Eq. [3]) and the ordinary differential equation (ODE) describing two biomass populations (Eq. [14]) were solved simultaneously using numerical techniques based on Wu et al. (1990). Algorithms were validated by (i) material balance calculations computed at each time-step, (ii) comparison with exact solutions for single PDEs and for coupled systems of ODEs with linear reaction terms (Haberman, 1998), and (iii) convergence of solutions at decreasing time-step. Simulations presented were generated with maximum time-steps of \(8 \times 10^{-3}\) h and a \(10^2\) m spatial grid. Equation [3] was solved with no flux boundary conditions (BCs) for solutes \((i \leq 4)\) at \(z = 0\) (the soil surface) and \(z = L\), where \(L\) is the depth of the soil profile. A value of 0.2 m for \(L\) was selected based on simulations that showed that use of greater \(L\) values had negligible effects on model output. For gases \((i \geq 5)\), Eq. [3] was solved with no flux BCs at \(z = L\), and constant concentration BCs with \(C_{i,j} = C_{i,0}\) at \(z = 0\), where \(C_{i,j}\) is the atmospheric concentration of gaseous component \(i\). Soil-to-atmosphere fluxes of NO and N\(_2\)O were calculated from Fick’s law with the gradient estimated by the difference be-
between $C_0$ and the concentration at the first subsurface node ($z = 0.1$ cm). The model was applied to two hypothetical fertilizer scenarios, Cases 1 and 2, to evaluate sensitivity to key input parameters (Tables 1 and 2). The initial conditions for Cases 1 and 2 consisted of uniform applications of NH$_4^+$ fertilizer within the top 0 to 5 cm of soil at 100 and 250 kg N ha$^{-1}$, and initial pH values of 6.0 and 8.0, respectively. A water content ($\theta$) of 0.20 m$^3$ m$^{-3}$ and bulk density ($\rho$) of 1200 kg m$^{-3}$ were assumed. The effect of subsurface banding vs. surface incorporation was also examined for Cases 1 and 2.

Input parameters (Tables 1 and 2) for Cases 1 and 2 are taken directly from published data except for the H$^+$ inhibition factors ($K_{H_+}$), as discussed above. A range of growth rate ($\mu_{max}$) and half-saturation ($K_{H_+}$) values have been reported for Nitro-
RESULTS AND DISCUSSION

Case 1 (100 kg N ha\(^{-1}\), initial pH = 6.0)

Concentration profiles for N solutes, gases, and soil pH shown in Fig. 2 are indicative of nitrification, which is nearly complete by 20 d. A transient accumulation of \(\text{NO}_2^-\) is predicted (Fig. 2c). The decrease in soil pH examined for initial \textit{Nitrobacter} population density \(B_{0.2} = 1\times10^8\) cells kg\(^{-1}\) soil in Case 2, where the initial soil pH was assumed to be 8.0.

For Case 3, data from a previously published field study (Venterea and Rolston, 2000b) were compared with model simulations. In this study, anhydrous NH\(_3\) was applied to a tomato field comprised of a moderately acidic (pH = 5.3) loam (11% clay) over 0 to 20 cm depth at 120 kg N ha\(^{-1}\) in 15-cm-wide bands spaced 25 to 35 cm from each row on both sides. Parameters (Table 2) were selected from within the range of values examined in the sensitivity analyses, except for values of \(k_{\text{red}}\), \(P_{\text{hs}}\), \(k_{\text{red}}\), and \(P_{\text{hs}}\), which were selected by trial and error for best fit to the data (discussed below).
Table 3. Effect of inhibition factor (K_{A2}), buffering capacity (β), and subsurface fertilizer placement on Case 2 simulation results.

<table>
<thead>
<tr>
<th>K_{A2}</th>
<th>β</th>
<th>Depth</th>
<th>Peak flux</th>
<th>Total emissions</th>
<th>Peak concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol H^+ L^{-1}</td>
<td>mg H^+ kg^{-1} pH^{-1}</td>
<td>cm</td>
<td>NO</td>
<td>N_{2}O</td>
<td>NO</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>0-5</td>
<td>2.3</td>
<td>0.12</td>
<td>0.61</td>
</tr>
<tr>
<td>10^{-6.5}</td>
<td>30</td>
<td>0-5</td>
<td>2.7</td>
<td>0.13</td>
<td>1.6</td>
</tr>
<tr>
<td>10^{-7.5}</td>
<td>30</td>
<td>0-5</td>
<td>5.5</td>
<td>0.27</td>
<td>1.6</td>
</tr>
<tr>
<td>10^{-8.5}</td>
<td>30</td>
<td>0-5</td>
<td>10.0</td>
<td>0.50</td>
<td>1.6</td>
</tr>
<tr>
<td>10^{-9.5}</td>
<td>25</td>
<td>0-5</td>
<td>23.0</td>
<td>1.20</td>
<td>1.6</td>
</tr>
<tr>
<td>10^{-10.5}</td>
<td>30</td>
<td>2.5-7.5</td>
<td>11.0</td>
<td>0.55</td>
<td>1.6</td>
</tr>
<tr>
<td>10^{-11.5}</td>
<td>30</td>
<td>1-6</td>
<td>5.5</td>
<td>0.27</td>
<td>1.6</td>
</tr>
<tr>
<td>10^{-12.5}</td>
<td>40</td>
<td>0-5</td>
<td>1.8</td>
<td>0.09</td>
<td>0.64</td>
</tr>
</tbody>
</table>

† Total integrated emissions over 20 d.
‡ 1 kg N ha^{-1} = 100 mg N m^{-2}.
§ No inhibition of N\textsubscript{2}O oxidation was assumed in this simulation.
¶ Initial vertical distribution of fertilizer at rate of 250 kg N ha^{-1}.

(Fig. 2b) results in HNO\textsubscript{2} formation and abiotic NO production (Fig. 2e). Decomposition of HNO\textsubscript{2} together with NO reduction results in N\textsubscript{2}O production (Fig. 2f). Predicted biomass and N solute dynamics at the center with NO\textsubscript{2}O production due to NO reduction results in N\textsubscript{2}O production in Table 2a). At higher (Fig. 3a) and transient NO\textsubscript{2}O accumulation (Fig. 3b). These results are very similar to patterns observed in 56 of 100 soils (all with pH <7.5) examined in soil percolation studies by Morrill and Dawson (1967). Similar temporal patterns and peak NO\textsubscript{2}O concentrations (0.2 to 10 mg N kg^{-1} soil) have been observed in several other nitrification studies under neutral to acidic conditions following N applications (Chapman and Leibeg, 1952; Jones and Hedlin, 1970; Paul and Domsch, 1972).

In the above simulation (Fig. 3), NO\textsubscript{2}O accumulates even though initial Nitrobacter and Nitrosomonas populations are equivalent and the kinetic parameters (μ_{\text{max},1}, K_{A2}) favor more rapid growth of Nitrobacter compared with Nitrosomonas (Tables 1 and 2). At higher initial Nitrobacter population densities (up to 10^9 cells kg^{-1}), NO\textsubscript{2}O still accumulates (Fig. 4a). Varying the maximum Nitrobacter specific growth rate (μ_{\text{max},1}) over the range 0.050 to 0.033 h^{-1} (Prosser, 1989) produced peak NO\textsubscript{2}O concentrations of 0.3 to 10 mg N kg^{-1}, respectively, with the same temporal patterns. Varying the decay (d_{i}) or yield coefficients (Y_{i}) over a range of literature values, or removal of the decay term from either or both of the biomass expressions had a similar range of effects (not shown).

Kinetic Basis for Nitrite Accumulation

The above results suggest that some degree of transient NO\textsubscript{2}O accumulation following NH\textsubscript{4}\textsuperscript{+} addition is a consequence of the nature of nitrification itself, that is, as a two-step sequential process carried out by distinct microbial populations. High NH\textsubscript{4}\textsuperscript{+} levels stimulate Nitrosomonas growth and NO\textsubscript{2}O production, while Nitrobacter growth rates are initially limited by lower substrate (NO\textsubscript{2}) levels. Eventually, Nitrobacter growth and activity increase to match the rate of NO\textsubscript{2}O supplied by Nitrosomonas activity (Fig. 3). The simulation results demonstrate how reductions in initial Nitrobacter population densities (B_{\text{a2}}) (Fig. 4a) and/or growth rates (μ_{\text{max},2}), which may occur in response to NH\textsubscript{3} or other chemical toxicity effects, can enhance the extent of NO\textsubscript{2}O accumulation. The results also suggest that diversity of autotrophic populations with respect to growth and substrate utilization kinetics may be responsible for observed variations in NO\textsubscript{2}O accumulation across a range of soil environments.

Transient Nitrogen Oxide Emissions

The peak NO fluxes (0.10–1.0 mg N m^{-2} h^{-1}) and the temporal patterns predicted by the model (Fig. 4b) are within the range observed in several field studies following the addition of NH\textsubscript{4} salts under acidic to slightly alkaline conditions (Johansson and Galbally, 1984; Slemr and Seiler, 1984; Shepherd et al., 1991; Slemr and Seiler, 1991; Hutchinson and Brams, 1992; Thornton and Valente, 1996). The magnitude of the predicted N\textsubscript{2}O pulses (<0.06 mg N m^{-2} h^{-1}) (Fig. 4c) is generally less than that observed following similar fertilizer applications. This is probably due to N\textsubscript{2}O derived from biological reductions of NO\textsubscript{2} and/or NO\textsubscript{2}O, which are not accounted for by the present model.

Case 2 (250 kg N ha^{-1}, initial pH = 8.0)

For Case 2, the predicted peak NO\textsubscript{2}O concentrations and gas fluxes, assuming no pH effects on Nitrobacter activity, are significantly higher than in Case 1 (Table 3). Additional simulations indicated that the more favorable (i.e., slightly alkaline) initial pH resulted in more rapid NH\textsubscript{4} oxidation rates given the same initial NH\textsubscript{4}\textsuperscript{+} concentrations, thereby leading to higher peak NO\textsubscript{2}O concentrations. For pK_{A1} values >6.5, significant increases in peak NO\textsubscript{2}O levels, peak fluxes, and total gas emissions are predicted (Table 3). The predicted maximum soil NO\textsubscript{2}O concentrations (60–160 mg NO\textsubscript{2}O–N kg^{-1}) are similar to those observed following the application of urea, anhydrous ammonia, or other N fertilizers under moderately alkaline conditions (Martin et al., 1942; Chapman and Leibeg, 1952; Chalk et al., 1975; Jones and Hedlin, 1970). The role of NH\textsubscript{3} toxicity under these conditions remains uncertain.
Fig. 5. Results of applying a mechanistic model of nitrite accumulation and N oxide gas emissions to a hypothetical uniform application of NH$_4^+$ fertilizer (250 kg N ha$^{-1}$) to the top 0 to 5 cm of soil of pH 8.0 (Case 2). Panels are (a) soil pH at center of incorporation depth and (b) surface NO flux at varying values of buffering capacity ($\beta_b$).

Buffering Capacity Effects

The dynamics of soil pH as influenced by buffering capacity ($\beta_b$) had significant effects, with predicted peak gas fluxes and total emissions increasing by >90% as $\beta_b$ is decreased from 40 to 20 mg H$^+$ kg$^{-1}$ soil pH$^{-1}$ (Fig. 5, Table 3) are also within the range of maximum fluxes observed under similar fertilizer conditions (Slemr and Seiler, 1984; Thornton et al., 1996; Matson et al., 1998).

Surface vs. Subsurface Fertilizer Incorporation

Predicted NO fluxes were increasingly attenuated with increasing depth of fertilizer incorporation for Case 1 (Fig. 6) and Case 2 (Table 3) due to microbial and chemical transformation of NO as it diffuses to the surface. This general effect has been observed in field studies (Matson et al., 1996). The present model predicts that placement over a depth of 5 to 10 cm would result in reductions in total NO emissions of >76% and >98% compared with surface applications (0-5 cm) for Cases 1 and 2, respectively. The model does not consider potential increases in denitrification-derived N$_2$O production that might occur due to the same practice.

Case 3: Comparison with Field Data

The general temporal dynamics of N solutes, soil pH, and NO and N$_2$O fluxes are described fairly well using input parameters in Table 2 (Fig. 7). Part of the discrepancy between simulated values and observed data is probably due to the assumption of spatially uniform initial conditions, especially since banded anhydrous NH$_3$ applications generally result in highly heterogeneous NH$_4^+$ distributions (Moraghan, 1980). The need for increased values of $P_{b,5}$ and $P_{b,6}$ in order to approximate the observed flux data is probably due to source processes, including denitrification, occurring at depths >20 cm. The need for increased values of the transformation parameters $k_{ox,5}$ and $k_{ox,6}$ may be due to more rapid and/or unaccounted for sinks under field conditions. For example, as discussed by Venterea and Rols-ton (2000b), horizontal subsurface gaseous diffusion resulting from lateral gradients in HNO$_2$ concentrations may have resulted in attenuated gas fluxes directly above the fertilizer band at this site. Expanding the present model to include two-dimensional transport would require a significant increase in complexity, but may be required in order to adequately predict fluxes that are driven by geometrically nonuniform processes. Additional uncertainty in modeling Case 3 arises from the unknown initial conditions and N dynamics over the 10- to 20-cm depth, since intensive sampling in the previous study was limited to the 0- to 10-cm depth. In these simulations, the 10- to 20-cm depth was assumed to provide a background source (described by $P_{b,5}$ and $P_{b,6}$) and also a sink for NO and N$_2$O. The predicted low recovery of NO$_3^-$ compared with the amount of added NH$_4^+$ (Fig. 7a,b) is due to the production, transformation, and escape of N oxide gases considered by the
model. While the predicted NO and N₂O emissions accounted for only 3.3 and 1.3%, respectively, of the NH₄⁺ initially present in the upper 10 cm, the high liquid-phase NO consumption rate ($k_{ox}=1.3 \times 10^{5} \text{hr}^{-1}$) resulted in most of the remaining discrepancy. In reality, a large fraction of the NO oxidized may well be converted to NO₃⁻ (Conrad, 1995b). This conversion was not accounted for by the model (i.e., the oxidized NO was not allocated to a specific N pool).

While the predicted N solute dynamics are consistent with data in the above-referenced studies, other data from liquid culture and soil studies suggest that enzyme inhibition kinetics of autotrophic nitrifiers are likely to be more complex than assumed here. The inhibition of NH₄⁺ oxidation due to NH₃ toxicity and/or inhibition of NH₄⁺ and NO₂ oxidation due to accumulations of NO₃⁻, HNO₃, or NO₂ are not considered in the present model. Preliminary simulations indicate that these effects may be responsible for the more prolonged duration of NO₃⁻ accumulation (up to several months) observed in some field studies (Chalk et al., 1975; Chapman and Leibeg, 1952). Quantitative models have been developed to describe some of these effects in liquid systems (Boon and Laudebout, 1962; Hunik et al., 1993). However, the applicability of these models to soil systems has not been examined, and therefore it would be premature to include them in the present model.

**CONCLUSIONS**

The model of N transformation and transport presented here describes how interactions between biological, chemical, and physical processes can regulate N oxide gas emissions under conditions favoring nitrification in soil. An advantage of this modeling approach is the capability to examine quantitative effects of multiple complex interactions under transient conditions that cannot be considered using more simple approaches. The results have direct implications with respect to fertilizer management practices. For example, the results indicate that (i) soils receiving similar fertilizer treatments, but differing in their ability to buffer nitrification-induced acidity, may produce dramatically different N oxide emissions; (ii) subsurface fertilizer incorporation can significantly reduce, and in some cases nearly eliminate, net NO emissions; and (iii) the differential responses of *Nitrosomonas* and *Nitrobacter* populations to chemical toxicities associated with the form and/or rate of fertilizer application may significantly affect the extent of NO₃⁻ accumulation and corresponding gas emissions. Further investigations are required in order to better model the behavior of autotrophic nitrifying populations in response to a range of dynamic chemical conditions. Few field studies exist, and more are required, involving simultaneous measurements of soil pH, N substrate concentrations, and gas fluxes, so that detailed mechanistic models can be compared against actual data. Models of this type will also benefit from more basic investigations of the functional diversity of autotrophic nitrifying microbes under differing ecological conditions. Consideration of additional mechanisms of NO and N₂O production not included in the present model, including microbial reduction mediated by denitrifying (and possibly nitrifying) soil bacteria, is also required in order to more fully describe the underlying mechanisms of N oxide gas production under field conditions.

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