Aqueous and gaseous nitrogen losses induced by fertilizer application

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[1] In recent years, concern has grown over the contribution of nitrogen (N) fertilizer use to nitrate (NO₃⁻) water pollution and nitrous oxide (N₂O), nitric oxide (NO), and ammonia (NH₃) atmospheric pollution. Characterizing soil N effluxes is essential in developing a strategy to mitigate N leaching and emissions to the atmosphere. In this paper, a previously described and tested mechanistic N cycle model (TOUGHREACT-N) was successfully tested against additional observations of soil pH and N₂O emissions after fertilization and irrigation and before plant emergence. We used TOUGHREACT-N to explain the significantly different N gas emissions and nitrate leaching rates resulting from the different N fertilizer types, application methods, and soil properties. The N₂O emissions from NH₄⁺-N fertilizer were higher than from urea and NO₃⁻-N fertilizers in coarse-textured soils. This difference increased with decreases in fertilization application rate and increases in soil buffering capacity. In contrast to methods used to estimate global terrestrial gas emissions, we found strongly nonlinear N₂O emissions as a function of fertilizer application rate and soil calcite content. Speciation of predicted gas N flux into N₂O and N₂ depended on pH, fertilizer form, and soil properties. Our results highlighted the need to derive emission and leaching factors that account for fertilizer type, application method, and soil properties.


1. Introduction

[2] Anthropogenic input of reactive nitrogen to ecosystems has led to significant environmental consequences [Galloway et al., 2003; Aber et al., 1998]. Use of nitrogen fertilizers in agriculture has a direct impact on water (NO₃⁻) and atmospheric pollution (N₂O, NO, NH₃) [Vitousek et al., 1997]. Groundwater NO₃⁻ concentrations exceed drinking water standards in many areas [Byrnes, 1990; Scanlon et al., 2007], resulting in potential human health effects (i.e., methemoglobinemia [Hill, 1996]). Elevated NO₃⁻ concentrations in leachate and surface water can also lead to eutrophication of lakes and estuaries [Lowrance et al., 1997]. Agricultural land also has been identified as the major anthropogenic source of nitrous oxide (N₂O) [Mosier, 1998; Intergovernmental Panel on Climate Change (IPCC), 2007] and an important source of nitric oxide (NO) [Yienger and Levy, 1995] entering the atmosphere. Because the formation of these N species in soils is primarily through volatilization, nitrification, and denitrification [Bremner, 1997; McKenzie and Drury, 1997; Firestone and Davidson, 1989], their release rates can drastically increase with elevated inputs of nitrogen from fertilization. Nitrous oxide (N₂O) is an important greenhouse gas and is also involved in the destruction of stratospheric ozone [IPCC, 2001]. Nitric oxide (NO) emissions contribute to the formation of tropospheric ozone and acid deposition [McTaggart et al., 2002]. NH₃ emissions affect the environment in the form of wet and dry deposition of NH₄⁺ salts, causing acidification of poorly buffered soils and eutrophication [van der Weerd and Jarvis, 1997]. Such concerns have stimulated extensive studies in recent years to identify potential mitigation options for reducing N leaching and emission from agroecosystems [Skiba et al., 1997].

[3] Several forms of N fertilizer are currently in use, resulting in different N substrates (i.e., NH₄⁺, NO₃⁻) for these loss pathways [Davidson et al., 1991] and plant uptake. Ammonium undergoes nitrification under aerobic conditions, while nitrate is reduced by denitrification under anaerobic conditions [Conrad, 1996]. There is strong evidence of a connection between the magnitude of emissions and the type of N fertilizer applied [Clayton et al., 1997; Eichner, 1990]; and also for a link between NO₃⁻ leaching and fertilizer type [Jiao et al., 2004].

[4] Understanding the effect of fertilizer type on N losses in agricultural fields is essential for developing a strategy to mitigate gaseous and aqueous losses. Although both field
and laboratory measurements have been made to examine how fertilizer type affects N loss, analysis of the plethora of factors involved in the coupled N cycle requires a mechanistic modeling framework to generalize and extend the empirical work.

[5] There are a number of published models simulating soil water dynamics and N turnover (e.g., RZWQM [Ahuja et al., 2000], DAYCENT [Parton et al., 2001], GLEAMS [Leonard et al., 1987], BIOME-BGC [Running and Gower, 1991; Thornton et al., 2005], PnET-BGC [Ghondo-Tughawa et al., 2001], DNDC [Li et al., 1992]). All these models consider soil inputs and outputs and simulate N cycle processes with varying degrees of complexity. Few existing models, however, are capable of accurately capturing the observed effects of different fertilizer types on nitrogen losses [e.g., Frolking et al., 1998]. Typically, processes such as nitrification and denitrification have been represented in models as functions of substrate and available carbon that are modified by dimensionless factors for soil water content and temperature [Li et al., 1992; Parton et al., 1996]. Such simple models have limitations, however, particularly for examining variability at fine temporal and spatial scales. For example, short-term temporal variations in N emission and leaching are too large to be explained from simple functions of soil water content, temperature, or N and C substrates [Blackmer et al., 1982; Flessa et al., 1995; Hall et al., 1996; Hutchinson et al., 1997], indicating that N losses are additionally impacted by complex interactions among N transformation and transport processes and concurrent environmental conditions. Such interactions need to be represented in models to simulate nitrogen fluxes reliably [Kroese et al., 2003]. The kinetics of NH₄ oxidation and NO₃ reduction pathways, which have been modeled individually [Grant et al., 1993; Lefler and Wessel, 1988; Mcconnaughey and Bouldin, 1985; Riley and Matson, 2000; Venterea and Rolston, 2000a], must be linked with transport processes (e.g., advection and diffusion) if they are to be used to estimate N losses under field conditions. This linkage is especially important during and immediately after hydrological events (e.g., irrigation, precipitation, spring thaw, etc.) when N transformation and transport are affected by water movement [Hutchinson et al., 1993; Scanlon and Kiely, 2003]. There are very few models that include comprehensive N transport and transformation dynamics. Some of the models, such as MIKESHE [Refsgaard and Storm, 1995] and MODFLOW-MT3D [Harbaugh and McDonald, 1996; Zheng and Wang, 1999] are transport-oriented with less mechanistic treatment of N biogeochemical processes; and some, such as DAYCENT [Parton et al., 2001], have N turnover functions but with more limited transport features.

[6] The goal of the work presented here was to merge representations of relevant N cycle processes and thereby improve model accuracy. Our previous paper [Maggi et al., 2008] described in detail the mechanistic N model TOUGHREACT-N, which implements N biogeochemical processes into the fully distributed (three dimensional) subsurface water flow and reactive transport model TOUGHREACT [Xu et al., 2005]. Here we present some update developments to TOUGHREACT-N. The updated model includes comprehensive ion chemistry capable of simulating the application of NH₄/NO₃ forming fertilizers and associated urea hydrolysis, pH dynamics, and pH-dependent NH₃ volatilization. It also simulates dissolved organic carbon (DOC) dissolution and adsorption in order to better describe carbon substrate dynamics.

[7] TOUGHREACT-N was previously applied to a field experiment in Sacramento, CA, and successfully simulated N speciation and losses following fertilization and irrigation. Here, we applied TOUGHREACT-N to a field experiment in Burgundy, France, to simulate 31-day preemergence N losses following multiple types of fertilizer application. Transient pulse emissions and N leaching after fertilization accounted for a large portion of N loss [Eichner, 1990; Hénault et al., 1998]. Finally, after testing the model against observed soil moisture, pH, and N₂O fluxes, we examined the effects of different fertilizer and soil types on NO₂ and NO₃ leaching, and on transient NH₃, N₂O, and NO gas emissions under different fertilizer application practices and environmental conditions.

2. Materials and Methods

2.1. TOUGHREACT-N Model

[8] The multiphase flow and transport model TOUGHREACT [Pruess et al., 1999; Xu et al., 2005] was taken as the basis for the implementation of an N cycle model (TOUGHREACT-N [Maggi et al., 2008]). TOUGHREACT-N simulates the soil N cycle affected by microbial activity, water and fertilizer inputs, and soil type by coupling multiphase
2.1.2. Multiphase Transport potential and hydraulic conductivity, respectively, computed \cite{1961}.

Millington and Quirk \cite{1961} theoretically considering the effect of tortuosity based on total porosity.

Micro-organism AOB$^a$ and NOB$^b$ DEN$^c$ AOB$^a$ and NOB$^b$, and O$_2$

include effect of tortuosity based on total porosity.

the aqueous, gaseous, and solid phases as:

\[
\frac{\partial}{\partial t} \left( \theta_a C_a + \theta_g C_g + \rho_0 C_s \right) = \frac{\partial}{\partial z} \left( \theta_a D_a \frac{\partial C_a}{\partial z} + \theta_g D_g \frac{\partial C_g}{\partial z} \right) - \frac{\partial (\nu_a C_a)}{\partial z} + S
\]

2.1.4. Nitrification, Denitrification, and Aerobic Respiration

\begin{align}
S_i = B_i \tilde{m}_i \sum_{k=1}^{N_i} \frac{C_{ik}}{K_{M,k} + C_{ik}} + \frac{K_i}{K_i + I_i} f(S_0)g(pH).
\end{align}

Here, $S_i$ is the reaction rate of the $i$th aqueous species [mol m$^{-3}$s$^{-1}$], $B_i$ is biomass [mol m$^{-3}$], $\tilde{m}_i$ is maximum specific growth constant [s$^{-1}$], $C_{ik}$ is the concentration of the $k$th species [mol m$^{-3}$], $I_i$ is the concentration of the $i$th inhibitor [mol m$^{-3}$] (e.g., O$_2$), $K_{M,k}$ is the $k$th Monod half-saturation constant of the $i$th species, $N_i$ is the number of Monod terms, $K_R$ is $i$th inhibition constant, $I_i$ is $i$th inhibitor concentration, and $f(S_0)$ and $g(pH)$ are two piecewise linear functions accounting for microbial water and acidity stress.

Finally, stoichiometric production or consumption is simulated by multiplying $S_i$ by the corresponding stoichiometric coefficients based on reaction equations. Note that dissolved oxygen concentration is explicitly simulated on the basis of molecular diameter. Assuming ideal gas behavior, the tracer diffusion coefficient of a gaseous species can be expressed as \cite{Lasaga,1998}:

\[
D = \frac{RT}{3\sqrt{2\pi PN_{A,d}d_m^2}} \frac{8RT}{\pi M}
\]

2.1.3. Nitrogen Cycle

\cite{1998} A full description of inorganic N biogeochemical processes in TOUGHREACT-N is given by Maggi et al. \cite{2008}. Briefly, four main N cycle pathways (nitrification, nitrite denitrification, denitrification, and chemodenitrification) (Table 1) were implemented to model N losses and their partitioning between gaseous and aqueous phases. The reaction network and transport mechanism used in TOUGHREACT-N is depicted in Figure 1.

Table 1. Summary of N-Biogeochemical Processes Simulated in TOUGHREACT-N

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Nitrification</th>
<th>Denitrification</th>
<th>Nitrifier Denitrification</th>
<th>Chemo Denitrification</th>
<th>Aerobic Respiration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro-organism</td>
<td>AOB$^a$ and NOB$^b$</td>
<td>DEN$^c$</td>
<td>AOB$^a$ and NOB$^b$</td>
<td>HNO$_2$</td>
<td>DOC and O$_2$</td>
</tr>
<tr>
<td>Substrate</td>
<td>NH$_4^+$, NO$_2^-$, and O$_2$</td>
<td>DOC, NO$_3^-$, NO$_2^-$, NO, and N$_2$O</td>
<td>DOC, NO$_2^-$, NO, and N$_2$O</td>
<td>HNO$_2$</td>
<td>DOC and O$_2$</td>
</tr>
</tbody>
</table>

$^a$Amonium oxidizer bacteria.

$^b$Nitrite oxidizer bacteria.

$^c$Denitrifier.

$^d$Aerobes.

Table 2. Chemical Species Considered in the Model

<table>
<thead>
<tr>
<th>Group</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary species</td>
<td>H$_2$O, CH$_3$OH, H$^+$, O$_2$(aq), NH$_4^+$, NO$_3^-$, NO$_2^-$, NO(aq), N$_2$(aq), HCO$_3^-$, Ca$^{2+}$, K$^+$, SO$_4^{2-}$, CO(NH$_2$)$_2$</td>
</tr>
<tr>
<td>Aqueous complexes</td>
<td>OH$^-$, HNO$_2$, HNO$_3$, NH$_3$(aq), CO$_2^+$, CO$_2$(aq), CaCO$_3$,$^{2-}$, CaHCO$_3^-$, CaSO$_4$,$^{2-}$, HSO$_4^-$, KSO$_4$</td>
</tr>
<tr>
<td>Precipitated species</td>
<td>CaCO$_3$, CaSO$_4$</td>
</tr>
<tr>
<td>Gaseous species</td>
<td>O$_2$(g), NO(g), N$_2$(g), CO$_2$(g), NH$_3$(g)</td>
</tr>
</tbody>
</table>

\cite{1961} TOUGHREACT-N simulates chemical transport using a multiphase form of the advection-dispersion-reaction equation to describe chemical advection in the aqueous phase and diffusive transport in the gas and aqueous phases. The model conceptualizes the transient mass balance of chemical species in aqueous, gaseous, and solid phases as:

\[
\frac{\partial}{\partial t} \left( \theta_a C_a + \theta_g C_g + \rho_0 C_s \right) = \frac{\partial}{\partial z} \left( \theta_a D_a \frac{\partial C_a}{\partial z} + \theta_g D_g \frac{\partial C_g}{\partial z} \right) - \frac{\partial (\nu_a C_a)}{\partial z} + S
\]

2.1.1. Soil Moisture Dynamics

\cite{9} The model numerically simulates variably saturated water flow using Richards’ equation:

\[
\frac{\partial \theta}{\partial t} \frac{\partial}{\partial z} \left[ K(\theta) \left( \frac{\partial \psi(\theta)}{\partial z} + 1 \right) \right]
\]

where $\theta$ is the soil moisture, and $\psi(\theta)$ and $K(\theta)$ are the water potential and hydraulic conductivity, respectively, computed as functions of soil type according to van Genuchten \cite{1980}.

2.1.2. Multiphase Transport

\cite{10} TOUGHREACT-N simulates chemical transport using a multiphase form of the advection-dispersion-reaction equation to describe chemical advection in the aqueous phase and diffusive transport in the gas and aqueous phases. The model conceptualizes the transient mass balance of chemical species in aqueous, gaseous, and solid phases as:
the balance between diffusion and consumption from stoichiometric relationships. Oxygen inhibition effects on denitrification are simulated by introducing an inhibition relationship (analogous to g(pH)).

### 2.1.5. Microbial Dynamics

[14] The dynamics of each microbial biomass ($B_i$) is assumed to satisfy the Monod equation:

$$\frac{\partial B_i}{\partial t} = \sum_c S_c Y_{ic} - \delta_i B_i$$

with $Y_{ic}$ the yield coefficients for $B_i$, $S_c$ to grow upon the substrate $c$ [mg mol$^{-1}$], $S_c$, as in equation (4) for each substrate $c$, and $\delta_i$ the biomass death rate [s$^{-1}$].

### 2.1.6. Chemodenitrification

[15] Chemical decomposition of nitrite plays an important role in NO emissions from acidic soils [Venterea and Rolston, 2000b]. The contribution of chemical decomposition of HNO$_2$ into HNO$_3$ and NO was taken into account by the reaction:

$$3\text{HNO}_2 \rightarrow \text{H}_2\text{O} + \text{HNO}_3 + 2\text{NO(aq)}.$$ (6)

TOUGHREACT-N assumes first-order kinetics for this reaction on the basis of the study of Venterea and Rolston [2000b].

### 2.1.7. pH Dynamics

[16] TOUGHREACT-N simulated temporal change in soil pH by directly predicting, and consumption estimated from stoichiometric reaction equations [Maggi et al., 2008, Tables 1b and 1c].

### 2.1.8. Dissolved Organic Carbon

[17] Different sizes of organic matter pools exist in the soil. In the present study we simplified the soil carbon dynamics by taking into account a single organic matter pool, particulate organic carbon (POC). Given the long time scales of soil carbon turnover (from days to centuries), this simplification is not expected to affect predicted N dynamics over the monthly time scale considered in this study. Note that POC cannot be used directly by microorganisms. Hydrolysis and solubilization of these compounds are necessary steps of the microbial energy or growth use. This process may act as a source of labile DOC, which is later subject to transport processes (e.g., advection and dispersion). On the basis of the DOC adsorption studies of Jardine et al. [1992], a kinetic dissolution model is used to simulate the release of DOC from POC. The model has the following form

$$\frac{d\text{POC}}{dt} = \alpha \times (K_d \times \text{DOC} - \text{POC}),$$ (7)

where POC is the mass of solid organic carbon per unit mass of solids (MM$^{-1}$ solids), $\alpha$ is a first-order mass transfer coefficient (1/T), $K_d$ is a linear distribution coefficient for the layer (L$^3$ water/M solids), and DOC is the dissolved organic carbon concentration (ML$^{-3}$ water).

[18] In TOUGHREACT-N, DOC is competitively consumed by ammonium oxidizer bacteria (AOB) and denitrifier (DEN) during denitrification, and by other heterotrophic and aerobic microbes (AER) during respiration, resulting in CO$_2$ production (Figure 1).

### 2.1.9. Cation Exchange

[19] Soil buffering capacity plays a central role in regulating NH$_3$ volatilization and soil microbial metabolism. Soil pH is buffered mainly by exchangeable base cations in both mineral and organic form. In TOUGHREACT-N, cation exchange is described as an equilibrium reaction between an exchangeable cation and an exchange site. We apply the Gaines-Thomas convention as a general expression of cation exchange reactions [Appelo and Postma, 1993]. The concentration of the $j$th exchanged cation, $w_j$ (mol m$^{-3}$), is estimated from the $j$th equivalent fraction:

$$w_j = \beta_j \text{CEC} \rho_s z_i \frac{(1 - \phi)}{1000 \phi^{-1}},$$ (8)

where $\beta_j$ is the equivalent fraction, CEC is the cation exchange capacity (meq of cations per 100 g of solid), $\phi$ is the porosity (m$^2$ m$^{-3}$), $\rho_s$ is the density of the solids (g cm$^{-3}$), and $z_i$ is the cation charge (-).

### 2.1.10. Urea Hydrolysis

[20] TOUGHREACT-N simulates the N cycle transformations of several widely used N fertilizers, including urea,

### Table 3. Initial Conditions of Water Saturation and Aqueous Concentrations of All Primary Species Other Than Fertilizer Chemicals

<table>
<thead>
<tr>
<th>Depth Interval</th>
<th>0–1.25 (cm)</th>
<th>1.25–10 (cm)</th>
<th>10–60 (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_o$ (mol L$^{-1}$)</td>
<td>0.82</td>
<td>0.82</td>
<td>0.80</td>
</tr>
<tr>
<td>pH</td>
<td>6.0</td>
<td>6.0</td>
<td>7.0</td>
</tr>
<tr>
<td>O$_2$ (aq) (10$^{-4}$ mol L$^{-1}$)</td>
<td>2.7</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>NO$_2$ (aq) (10$^{-6}$ mol L$^{-1}$)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>NO (aq) (10$^{-4}$ mol L$^{-1}$)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>HCO$_3$ (mol L$^{-1}$)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>HCO$_3$ (mol L$^{-1}$)</td>
<td>4.76</td>
<td>4.76</td>
<td>4.76</td>
</tr>
<tr>
<td>Ca$^{2+}$ (10$^{-2}$ mol L$^{-1}$)</td>
<td>2.76</td>
<td>2.11</td>
<td>2.11</td>
</tr>
<tr>
<td>POC (10$^3$ (mol L$^{-1}$))</td>
<td>1.5</td>
<td>1.5</td>
<td>0.78</td>
</tr>
<tr>
<td>AOB (10$^3$ (mol L$^{-1}$))</td>
<td>1.26</td>
<td>1.07</td>
<td>0.52</td>
</tr>
<tr>
<td>NOB (mol L$^{-1}$)</td>
<td>3.5</td>
<td>3.2</td>
<td>0.5</td>
</tr>
<tr>
<td>DEN (mol L$^{-1}$)</td>
<td>5.0</td>
<td>3.1</td>
<td>1.6</td>
</tr>
<tr>
<td>AER (10$^3$ (mol L$^{-1}$))</td>
<td>7.3</td>
<td>6.2</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*a* Water saturation ICs the same for all fertilizer treatments.  
*b* Values were calibrated with observation.  
*c* Values were assigned by steady state simulation without N species.

### Table 4. Initial Chemical N Concentrations for Four Fertilizer Types at 0–1.25 cm Depth

<table>
<thead>
<tr>
<th>Fertilizer Types</th>
<th>NH$_4$ (10$^{-1}$ (mol L$^{-1}$))</th>
<th>(NH$_4$)$_2$SO$_4$ (10$^{-2}$)</th>
<th>CO(NH$_2$)$_2$ (10$^{-2}$)</th>
<th>KNO$_3$ (10$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$ (10$^{-1}$ (mol L$^{-1}$))</td>
<td>0.77</td>
<td>1.54</td>
<td>1 $\times$ 10$^{-5}$</td>
<td>1 $\times$ 10$^{-2}$</td>
</tr>
<tr>
<td>K$^+$ (10$^{-1}$ (mol L$^{-1}$))</td>
<td>1 $\times$ 10$^{-2}$</td>
<td>1 $\times$ 10$^{-2}$</td>
<td>1 $\times$ 10$^{-2}$</td>
<td>1.54</td>
</tr>
<tr>
<td>CO(NH$_2$)$_2$ (10$^{-7}$ (mol L$^{-1}$))</td>
<td>1 $\times$ 10$^{-5}$</td>
<td>1 $\times$ 10$^{-5}$</td>
<td>0.77</td>
<td>1 $\times$ 10$^{-5}$</td>
</tr>
<tr>
<td>SO$_4$ (10$^{-1}$ (mol L$^{-1}$))</td>
<td>1 $\times$ 10$^{-2}$</td>
<td>0.77</td>
<td>1 $\times$ 10$^{-2}$</td>
<td>1 $\times$ 10$^{-2}$</td>
</tr>
</tbody>
</table>
anhydrous ammonia, ammonium, and nitrate based fertilizers. When applied to soil, urea is hydrolyzed by the ubiquitous urease enzyme, producing NH$_4$$^+$ and other inorganic C compounds whose form depends on soil pH. TOUGHREACT-N computes urea hydrolysis according to:

$$\text{CO\,(NH}_2\text{)}_2 + H^+ + 2H_2O \rightarrow 2NH_4^+ + HCO_3^-$$

(9)

TOUGHREACT-N simulates the urea hydrolysis rate ($R_u$, g m$^{-3}$ s$^{-1}$) as a function of soil pH and moisture [Youssef et al., 2005] using Michaelis-Menten kinetics.

$$R_u = f(S_0)g(pH)\mu_u \left( \frac{C_u}{K_u + C_u} \right) \left( \frac{m}{g} \right)$$

(10)

where $\mu_u$ is the maximum reaction rate (s$^{-1}$), $K_u$ is the half-saturation constant (g m$^{-3}$), and $C_u$ is the urea-N concentration (g m$^{-3}$). $f(S_0)$ and $g(pH)$ are two piecewise linear functions accounting for microbial water and acidity stress.

### 2.2. Model Evaluation

[21] For this study, we used observations from a rape-seed field on a gleic luvisol located at Longchamp in Burgundy in eastern France from March to April 1997 to test TOUGHREACT-N [Hénault et al., 1998]. The inorganic fraction of the 0–20 cm layer of this soil contained 20% clay, 69% silt, and 11% sand, which falls into silt loam textural classes. The porosity of 0.46 was adapted as a typical value of silt loam for later simulation. The organic C content, organic N content, pH and bulk density
in this depth interval were 1.1%, 0.09%, 6.0 (±0.3), and 1.40 g cm$^{-3}$, respectively. In the experiment, four different inorganic nitrogen fertilizers were applied in solid form: ammonium nitrate (NH$_4$NO$_3$); ammonium sulfate ((NH$_4$)$_2$SO$_4$); urea (CO(NH$_2$)$_2$), and potassium nitrate (KNO$_3$) on 3 March (corresponding to time zero in our simulations) at a dose of 100 kg N ha$^{-1}$, and on 18 March at a dose of 70 kg N ha$^{-1}$. Available measurements consist of soil water content (integrated from 0 to 17 cm depth), pH (mean value of 0–20 cm depth), and N$_2$O fluxes by static chamber method at various times over the subsequent five months. To focus our results on the period before plant emergence, we tested the model with the first 31 days of measurements after fertilization.

### 2.3. Simulation Description

[22] We selected a set of chemical species (Table 2) to represent the geochemical system in the field. Fifteen primary species were considered in determining the ion solute chemistry. Secondary species were produced by aqueous complexation, gas dissolution and exsolution, and precipitation and dissolution occurring under equilibrium and kinetically controlled conditions.

[23] For our numerical experiments, we used a one-dimensional vertical column 0.6 m deep divided equally into 50 layers. The column depth encompasses the dynamically active zone for N cycle reactions in the agricultural field experiment described by Hénault et al. [1998].

### 2.3.1. Initial and Boundary Conditions

[24] Prior to simulation of fertilizer application, a model spin-up was performed to calculate initial soil water chemistry, a nearly equilibrated N free water chemistry using oversaturated CO$_2$ produced by microbial respiration interacting with soil buffering capacities (i.e., ion exchange and calcite). The spin-up simulation of chemical equilibrium (i.e., CaCO$_3$-H$_2$O-CO$_2$ system) was calibrated by initial soil pH of 6.0. Next, the initial conditions were assigned according to the observed initial values, or obtained from calibration with observations (Table 3). Simulations with different fertilizer types were performed by initializing the relevant N species concentrations. Surface broadcast of fertilizer was simulated by assigning fertilizer concentrations in the topsoil control volume (0–1.25 cm depth) (Table 4).

[25] The Dirichlet boundary condition was assigned to the bottom boundary. Initial water saturation was set as 0.82 between 0 and 10 cm and 0.8 between 10 and 60 cm (Table 3) by calibration with observed soil moisture. Per reported values, the irrigation flux was set as 3.5 × 10$^{-1}$ m$^3$ H$_2$O m$^{-2}$ s$^{-1}$ for 3 h on day 15. Partial pressures of the gaseous species at the soil surface were kept constant and equal to 0.209 bar for O$_2$ (g) and to 4 × 10$^{-4}$ bar for CO$_2$ (g), and equal to zero for all other gases. Surface fluxes of NO (g), N$_2$O (g), N$_2$ (g), CO$_2$ (g), NH$_3$ (g), and O$_2$ (g) were computed from soil surface concentration gradients. N leaching flux was estimated as the product of aqueous concentrations at depth and the simulated water flux.

### 2.3.2. Model Calibration and Testing

[26] A first calibration of the flow model was performed to determine optimal soil hydraulic parameters. A stepwise calibration was taken, since the simulated N transport and transformation strongly depends on the accuracy of simulated soil moisture.

#### Figure 3.

Time evolution of observed and simulated soil pH of 0–20 cm layer over the simulation period (lines indicate simulation, and symbols indicate experiment).
[27] Calibration was assisted by PEST (Parameter Estimation, Papadopulos and Associates Inc.) to minimize the weighted least squares objective function between experimental and simulated data of liquid saturation using the Levenberg-Marquardt method. For calibration of biochemical parameters we used the weighted objective function between experimental and simulated data of pH and N2O fluxes. A classical split sampling in data type test was conducted using the data set from (NH4)2SO4 and KNO3 treatments for model calibration and the data set from NH4NO3 and CO(NH2)2 treatments for model testing.

[28] The soil was modeled as a silt loam with particle density of 2.6 g cm\(^{-3}\), porosity of 0.46, permeability of 3.82 \(\times\) \(10^{-15}\) m\(^2\), residual water saturation of 0.001, and van Genuchten parameter of 0.62. Biogeochemical parameters were taken from literatures or derived from calibration (Table 5). The remaining biogeochemical parameters are given by Maggi et al. [2008].

3. Results

3.1. Model Testing

[29] TOUGHREACT-N simulated soil moisture content accurately in the 0–17 cm depth during the observation period (Figure 2a). The soil moisture dynamics have a strong influence on predicted soil aerobicity, as indicated by the lower oxygen concentration in the pore water in the 0–5 and 5–10 cm depth intervals following both irrigation events (Figure 2b). After the first irrigation, microbes quickly consumed the available O2, turning the soil into anaerobic. As the soil drained, O2 diffused downward from the atmosphere, and the soil reoxygenated. Figure 2b indicates that the top 5 cm of soil was more oxic than the deeper (5–10 cm) soil. Relatively low oxygen availability lasted as long as 5 days in response to each irrigation event. Although soil O2 concentrations were not measured during the experiment, our predictions are consistent with Sierra and Renault [1998], who observed that the O2 concentration at 0.2 m depth of a hydromorphic soil decreased 0.09 within 3 days after a rainfall of \(\approx 40\) mm.

[30] Table 6 provides the model performance statistics for pH and N2O prediction. For soil pH predictions, the model efficiencies (NSE [Nash and Sutcliffe, 1970]) were 0.63, 0.73 and 0.73 for the calibration, validation, and total, respectively. For N2O emission predictions, the NSE for the calibration, validation, and total were 0.80, 0.46 and 0.62, respectively.

[31] TOUGHREACT-N generally captured the temporal pH patterns resulting from application of different fertilizer forms (Figure 3, \(R^2 = 0.73\); Figure 4a). Both (NH4)2SO4 and NH4NO3 fertilizer applications caused a rapid drop of pH due to nitrification followed by a gradual recovery to neutral conditions, while KNO3 application did not show significant pH decline throughout the simulation period. During the first day after a urea application, there was a rapid rise in soil pH as urea hydrolysis proceeded, followed later by a pH decrease caused by nitrification.

[32] TOUGHREACT-N estimated N2O fluxes from different fertilizer forms reasonably well, including the onsets, peaks, and decreases over time (Figure 5). Generally, the simulated N2O flux matched the observations well (\(R^2 = 0.63\); Figure 4b). The second N2O peaks were relatively poorly estimated compared to the first peaks. We note, however, that the measurement frequency was relatively low, and these peaks in N2O fluxes may have been missed during sampling. TOUGHREACT-N captured observed cumulative N2O fluxes very well (Figure 6a).

[33] Peaks in N2O flux coincided with fertilizer and irrigation application. N2O emissions occurred rapidly over the first several days for NH4NO3 and (NH4)2SO4 applications (Figures 5a and 5b). These dynamics were caused by rapid microbial growth (Figure 7) and the accompanying biological reactions stimulated by water and substrate availability. In contrast, N2O fluxes remained low in KNO3 because of initially low soil denitrifier abundance. The predicted low N2O fluxes were consistent with incubation experiments at the Longchamp site, which showed poor denitrification potential [Hénault et al., 1998]. In the urea treatment, N2O fluxes were initially low and then increased strongly starting from the second application. Lower predicted initial N2O emissions in the urea treatment

Figure 4. The observed versus simulated (a) pH and (b) N2O flux.
were due to the lower availability of NH$_4^+$-N from urea hydrolysis. This reduced NH$_4^+$ availability was due to the delay of AOB growth (Figure 7).

The type of fertilizer had a large effect on predicted soil microbial dynamics. In the top 5 cm of soil in the NH$_4$NO$_3$, (NH$_4$)$_2$SO$_4$, and CO(NH$_2$)$_2$ treatments, AOB concentration increased initially in response to NH$_4^+$ supply. In the NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ treatments, the peak of AOB growth migrated downward because of NO$_2$/CO leaching. In the CO(NH$_2$)$_2$ treatment the peak AOB concentrations remained near the surface since its solid form did not migrate downward (Figure 7). The absence of NH$_4^+$ from the KNO$_3$ fertilizer caused a decline of AOB in the surface soil. DEN biomass in all treatments showed continuous growth on NO$_3$/CO coming either from the input directly (i.e., NH$_4$NO$_3$ and KNO$_3$) or from nitrification (i.e., CO(NH$_2$)$_2$ and (NH$_4$)$_2$SO$_4$) (Figure 7). DENs showed a much smaller peak than AOBs, indicating that the conditions were less favorable for denitrification. As for the AOB, the DEN biomass front migrated downward in response to NO$_3$ leaching. KNO$_3$ fertilizer application resulted in a maximum growth of DENs fueled by the large NO$_3^-$ supply.

Our results showed that cumulative NO and N$_2$O emissions following nitrate fertilizer (i.e., KNO$_3$) application were two to three times lower than from ammonium-N fertilizers. The differences were due to differences in nitrification rates with higher activity in soils receiving an NH$_4^+$ fertilizer, which is confirmed by higher AOB biomass than DEN biomass (Figure 7). To better understand the interactions and mechanisms leading to N$_2$O emissions, we performed a series of sensitivity analyses to characterize how fertilizer

Figure 5. Observed and modeled time evolution of N$_2$O (g) emissions. Two application/irrigation events occurred at day 0 and day 15, respectively, indicated by downward arrows.

The 31-day cumulative N losses were significantly affected by the form of applied N fertilizer (Figure 6). The corresponding N$_2$O emissions were 690, 879, 527, and 292 g N ha$^{-1}$ for NH$_4$NO$_3$, (NH$_4$)$_2$SO$_4$, Urea, and KNO$_3$ fertilizer, respectively, representing 0.28%, 0.36%, 0.21%, and 0.12% of the applied N, respectively. The relation between our predicted cumulative NH$_3$ emissions are CO(NH$_2$)$_2$ > (NH$_4$)$_2$SO$_4$ > NH$_4$NO$_3$ > KNO$_3$ (Figure 6b). The leachate fluxes were computed at 20 cm depth because of the short simulation period of this study. The order of cumulative N leaching from fertilizer types depended on NO$_3^-$ concentration depth. Consequently, KNO$_3$ fertilization led to the maximum leaching fluxes followed by NH$_4$NO$_3$, (NH$_4$)$_2$SO$_4$, and CO(NH$_2$)$_2$ fertilizers (Figure 6e). CO(NH$_2$)$_2$ had the least NO$_2^-$ and NO$_3^-$ leaching among all the fertilizer forms because of its slow production of NO$_2^-$ and NO$_3^-$ from nitrification.

Our results showed that cumulative NO and N$_2$O emissions following nitrate fertilizer (i.e., KNO$_3$) application were two to three times lower than from ammonium-N fertilizers. The differences were due to differences in nitrification rates with higher activity in soils receiving an NH$_4^+$ fertilizer, which is confirmed by higher AOB biomass than DEN biomass (Figure 7). To better understand the interactions and mechanisms leading to N$_2$O emissions, we performed a series of sensitivity analyses to characterize how fertilizer
type and amount, irrigation, and soil type impact cumulative N emissions in this system.

3.2. Fertilizer Amount

[37] The N biogeochemical cycle depends primarily on substrate availability and interaction among microbial populations. The increase of NH$_4^+$ and NO$_3^-$ from fertilizer induces higher rates of microbially induced nitrification and denitrification. These increases in reaction rates, however, can be different depending on the affinities of microbes to substrates. Thus, the disproportionate biogeochemical reaction rates may cause different changes in relative N losses between fertilizer-type treatments. To illustrate these relationships, we calculated the cumulative N losses for fertilizer application rates increasing from 50 to 400 kg N ha$^{-1}$ (100 kg N ha$^{-1}$ corresponds to the reference application).

[38] Cumulative N losses depended strongly on fertilizer amount (Figure 8a), primarily by impacting substrate supply. NH$_3$ volatilization from CO(NH$_2$)$_2$ increased more than those from NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ fertilizers because the alkalinity effect by CO(NH$_2$)$_2$ accelerates NH$_3$ volatilization. Negligible NH$_3$ emissions were predicted for KNO$_3$ fertilizer because of the absence of NH$_4^+$. Consequently, the differences in cumulative NH$_3$ losses for fertilizer application rates increasing from 50 to 400 kg N ha$^{-1}$ were 8.8 and 40 times more NH$_3$ than NH$_4$NO$_3$ fertilizer under the 50 and 400 kg N ha$^{-1}$ treatments, respectively.

[39] Increasing fertilizer amount diminished differences in cumulative NO and N$_2$O emissions from different fertilizer types (Figure 8b). In other words, cumulative NO and N$_2$O emissions under CO(NH$_2$)$_2$ fertilization increased with fertilizer amounts more rapidly than under NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ fertilization because the alkalinity induced by CO(NH$_2$)$_2$ relieves microbial acidity stress. Under the 50 kg N ha$^{-1}$ treatment, NH$_4^+$ fertilizer emitted 1.6 times more NO than CO(NH$_2$)$_2$ fertilizer, while only 1.2 times higher than CO(NH$_2$)$_2$ under the 400 kg N ha$^{-1}$ treatment. Similarly, CO(NH$_2$)$_2$ showed a more rapid increase of cumulative N$_2$O emissions with increased fertilizer amount than other fertilizer treatments. Consequently, at higher fertilizer application rates (i.e., > 200 kg N/ha), urea had the highest N$_2$O emissions among all fertilizers tested here.

[40] In contrast, increasing fertilizer amount exaggerated the difference of cumulative solute leaching from fertilizer types (Figure 8). For example, NO$_3^-$ leaching from KNO$_3$ is 13 and 1.7 times higher than (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$, respectively, in the 400 kg N ha$^{-1}$ treatment, compared to 7 and 1.2 times in the 100 kg N ha$^{-1}$ treatment (Figure 8e).

3.3. Effect of Soil pH

[41] Soil pH significantly impacted microbial dynamics and therefore the N cycle. Additionally, pH is subject to a feedback by which protons are consumed and produced during biogeochemical processes. One of the advantages of TOUGHREACT-N is its mechanistic representation of pH dynamics. For simplicity, we considered only calcite content among many potential buffers (e.g., ion exchange capacity, etc.) to study soil pH effect on N cycling. Soil pH and CaCO$_3$ content are coupled because of the buffering capacity of CaCO$_3$, i.e., increases in CaCO$_3$ content lead to increases in soil buffering capacity. The predicted faster microbial growth rates in high calcite fraction soils correlated to a reduction of acidity stress on microbes (not shown). Predicted relative impacts of fertilizer type on NH$_3$ emissions did not change significantly with soil buffering capacity (Figure 9a). The NO emission from the NH$_4^+$ fertilizers decreased with increasing calcite content, which we attribu-
uted to NO produced by chemodenitrification [Venterea and Rolston, 2000b] at low pH. The change, however, is small relative to the change in N₂O emissions (Figures 9b and 9c) because of the contrasting effects of increasing pH on chemodenitrification and the microbial production of NO.

[42] The dynamics of soil pH was influenced by soil buffering capacity (i.e., calcite fraction) and had significant impacts on cumulative N₂O losses, with predicted threefold and fivefold increases for NH₄NO₃ and (NH₄)₂SO₄ as calcite fraction increased from 0.02% to 0.5% (Figure 9c). Compared to the reference case, the model simulated a larger variation of N₂O fluxes at 0.5% calcite fraction (1975, 3756, 411, and 508 kg N ha⁻¹ for NH₄NO₃, (NH₄)₂SO₄, urea, and KNO₃, respectively). Thus, in soils with high calcite content, and therefore more buffered against pH changes, NH₄ fertilizer would be expected to emit much more N₂O gas than CO(NH₂)₂ and NO₃⁻ fertilizers for the same fertilizer amount.

[43] Differences in cumulative N leaching between fertilizer types decreased with increasing soil calcite fraction (Figure 9). The decreasing N leaching with increasing calcite fraction was due to enhanced denitrification that depleted the NO₃⁻ pool in the upper soil layers. The enhanced denitrification rate at 0.5% calcite content induced attenuated NO₃⁻ fronts in vertical profiles compared to those at 0.02% calcite content (not shown).

[44] TOUGHREACT-N predicted different N₂O gas emissions and N₂O/N₂ ratios as a function of initial soil pH for NO₃⁻ and NH₄ fertilizer treatments and two soil types: a clay loam (Figure 10a) and a sandy loam (Figure 10b). These simulations were run by removing the soil buffering capacities (i.e., calcite content and ion exchange capacity), which

Figure 7. Predicted vertical distribution of ammonium oxidizer bacteria (AOB) and denitrifier (DEN) over time. AOB and DEN dynamics reflected the interaction with N transport in space and transformation in time.
would otherwise mask effects of initial pH. Generally, the N$_2$O emissions and the response to pH changes for clay loam were larger than those for the sandy loam. N$_2$O emissions increased nonlinearly with soil pH with a sixfold increase for a pH change from 5 to 7 in sandy loam (Figure 10). The N$_2$O/N$_2$ emission ratio negatively correlated with pH for clay loam, and showed a maximum at pH of 6 for sandy loam soil. The N$_2$O emission and N$_2$O/N$_2$ of the NH$_4^+$ treatment were more sensitive to pH change than the NO$_3^-$ treatment.

4. Discussion

[45] Simulated NH$_3$-N loss from the Longchamp site is significantly affected by fertilizer types. NH$_3$ volatilization depended on (1) the NH$_4^+$ concentration developed at the soil surface and (2) the changes in pH that were controlled by the fertilizer application, soil buffering capacity, and microbial activity [Mkhabela et al., 2006]. The first factor, NH$_4^+$ concentration, was the dominant reason for which ammonium-N fertilizers had much higher potential for ammonia to volatilize compared to nitrate-N fertilizer. The second factor, pH, directly affected the equilibrium between NH$_3^+$ and NH$_3$. Thus, the alkaline reactions of urea hydrolysis resulted in an increase in pH and a significant NH$_3$ volatilization (one order of magnitude higher than other fertilizer types) (Figure 6b). The simulated low NH$_3$ volatilization in the current study was due to the acidic soil and high soil cation exchange capacity (CEC). Where the soil was buffered at pH values less than 7, the dominant form of ammonia-N was NH$_4^+$ and the potential for volatilization was small. Large soil CEC (i.e., high NH$_4^+$ adsorption) tended to reduce NH$_3$ volatilization potential by reducing the NH$_4^+$ soil solution concentration on exchange sites and by reducing pH (i.e., releasing H$^+$).

[46] The effects of fertilizer forms on N gas emissions and NO$_3^-$ leaching were strongly dependent on soil properties. Soil texture impacts soil moisture, which directly influenced gas diffusion and soil oxygen availability. As a result, nitrification was the predominant source of NO and N$_2$O emissions in coarse texture soils. Consequently, the availability of substrate for nitrification (i.e., NH$_4^+$) determined the magnitude of nitrogen gas emissions. N$_2$O emission...
from nitrate fertilizer (i.e., KNO₃) was shown to be lower than from ammonium fertilizers in sandy soils (Figure 10b). Our simulations also showed higher N₂O emissions associated with clay loam than sandy soil regardless of the form of N input. This prediction was consistent with experimental observations which have shown that fine textured soils and restricted drainage favor N₂O emissions [Velthof and Oenema, 1995]. The lower hydraulic conductivity of the fine textured soil (i.e., clay loam) led to slower drainage rates and higher soil moisture than in the sandy loam soils. The higher soil moisture increased the period where soil O₂ was depleted, leading to enhancements in denitrification rates and NO and N₂O emissions. Thus, nitrate-N fertilizer may reduce NO and N₂O emissions (but not N leaching) in well-aerated soils, while ammonium-N fertilizers may be more suitable to poorly drained soils.

Soil pH had a large influence on predicted N losses by impacting the three most important processes that generate nitrogen gases: nitrifier denitrification, chemodenitrification, and denitrification. On the one hand, simulations showed that cumulative NO emissions under field capacity conditions decreased with increasing calcite content. Lower initial acidity decreased abiotic NO production, which are typically more important under acidic conditions (e.g., HNO₂ decomposition). On the other hand, our study showed that the cumulative N₂O emission increased with increasing calcite content (Figure 9). This latter result is in agreement with Clough et al. [2004], who found increasing N₂O emissions in response to increasing pH at saturated soils from a urine patch. Increasing denitrification along increasing pH due to acidity stress release would exceed any effect of decreasing abiotic N gas production.

The current N-biogeochemical models are based upon the assumption of products ratios (i.e., N₂O/N₂) independent of soil pH [Parton et al., 1996; Li et al., 2000]. In contrast, our study demonstrates that N trace gas speciation depends on pH, N substrate, and soil properties. This behavior emerges because N gas effluxes depend on the substrate and the soil pH before and after fertilization. Soil pH dynamics is determined by the biogeochemical reactions (which are also a function of pH), and soil buffering capacity. Also, soil oxygen and substrate availability depend on biogeochemical reactions and soil hydrological properties that influence soil moisture and advection and diffusive

**Figure 9.** Time cumulative (a) NH₃, (b) NO, and (c) N₂O surface fluxes to the atmosphere and (d) NO₃ and (e) NO₂ leachate fluxes at depth of 20 cm for the four fertilizer types as functions of soil calcite fraction. The NH₃ volatilization from KNO₃ and the leachate fluxes from CO(NH₂)₂ were negligible and thus omitted.
transport. As a result, N gas effluxes are related nonlinearly to soil pH, soil properties, and N substrate form and concentration. Our simulation results showed that these ratios depend on soil pH, N substrate, and soil texture. Thus the validity of applying empirically derived predictive functions based on constant fraction of N species is questionable. The approach presented here allows us to mechanistically quantify the interaction of multiple N cycle controlling processes under large temporal and spatial variability.

5. Conclusions

We further developed and tested the N biogeochemical model TOUGHREACT-N by including application of different mineral N fertilizers, and water and chemical transport mechanisms (e.g., water percolation, chemical phase partitioning, advection, and diffusion, etc). We then applied TOUGHREACT-N to an agricultural field experiment in Burgundy, France. The model performed well and showed great promise in modeling NO, N\textsubscript{2}O, and NH\textsubscript{3} emissions and NO\textsubscript{3} leaching from agroecosystems undergoing fertilization and irrigation.

Model simulations showed the relation between N losses, fertilizer type, fertilization practices, and soil conditions. The results that have direct implications to fertilizer management practices include the following:

1. Soils receiving relatively small amounts of fertilizer (<100 kg N ha\textsuperscript{-1}) produced more N emissions per applied N but slightly less N leaching from NH\textsubscript{4}\textsuperscript{+} than NO\textsubscript{3} fertilizers; this difference was diminished at higher fertilization rates. Urea may produce maximum N emissions at higher fertilization rates. Consequently, the effect of a given reduction in N input on nitrogen gases emissions will be larger for urea than for other NH\textsubscript{4} and NO\textsubscript{3} based fertilizers.

2. Soil buffering capacity dramatically increased N\textsubscript{2}O emissions after fertilization; increasing alkalinity can increase NH\textsubscript{3} volatilization.

3. Soils with coarse texture produced less nitrogen gas emissions from NO\textsubscript{3} fertilizers than NH\textsubscript{4}\textsuperscript{+} fertilizers. Practically, any gains that may be made in reducing one N species loss also need to be considered in the context of possible changes to other N species. Mitigation approaches that do not include these tradeoffs may lead to unanticipated environmental problems.

Our work highlights the need for improvement of the N\textsubscript{2}O emissions inventory methodology, which currently relies on a constant emission factor irrespective of fertilizer types, environmental conditions, and soil properties. The results presented here suggest that even fertilizer-type specific emission factors need to be a function of soil type and management practice (e.g., fertilization amount).

The development of simplified mechanistic models for regional-scale application remains our goal of this research. Further coupling with atmospheric forcing (e.g., solar radiation, wind speed) and plant growth is the essential model component that needs to be accomplished. However, the current TOUGHREACT may serve as the theoretical basis for more complex large-scale models which incorporate plant growth, C and N cycling, climate, and agricultural management practices.

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