Modeling Nitrous Oxide Emissions from Potato-Cropped Soil

Intensive agricultural land use is considered to be the major source of the anthropogenic contribution to the increase in atmospheric N₂O concentration during the last decades. A reduction of anthropogenic N₂O emissions therefore requires a change in agricultural management practices. Mathematical models help to understand interacting processes in the N cycle and state variables affecting N₂O emissions. The aim of this study was to test two modeling approaches for their ability to describe and quantify the seasonal variations of N₂O fluxes in a potato (Solanum tuberosum L.)-cropped soil. Model 1 assumes a fixed N₂O/N₂ ratio for N₂O production and neglects the transport of N₂O in the soil profile; Model 2 explicitly considers N₂O transport and assumes a dynamic reduction of N₂O to N₂. Data for model evaluation came from an experiment where N₂O fluxes were monitored during the vegetation period using a closed chamber technique. Generally, both modeling approaches were able to describe the observed seasonal dynamics of N₂O emissions and events of high N₂O emissions due to increased denitrification activity after heavy precipitation. The inclusion of a gas transport module in the modeling approach resulted in simulated N₂O emission dynamics showing a smoother transient behavior. Extremely high emission rates from the interrow soil of the potato field were underestimated by both models. The lower N₂O release from the ridge soil was mainly due to better aeriation because of a lower soil bulk density and lower water contents caused by lateral runoff and root water uptake.

In recent decades, it has become evident that arable soils contribute significantly to the increase of N₂O in the atmosphere (Duxbury et al., 1993; Mosier et al., 1998). The Intergovernmental Panel on Climate Change (2007) supported this and stated that N₂O continues to increase in the atmosphere, primarily as a result of agricultural activities. For the year 2004, N₂O was estimated to account for 7.9% of the present anthropogenic greenhouse gas emissions in terms of CO₂-equivalent emissions on a global scale. The global atmospheric concentration of N₂O increased approximately linearly (0.26% yr⁻¹) from a preindustrial value of about 270 mm³ m⁻³ to reach a concentration of 319 mm³ m⁻³ in 2005 (Intergovernmental Panel on Climate Change, 2007). Nitrous oxide is also important due to its effect on catalytic O₃ depletion in the stratosphere (Crutzen, 1981; Crutzen et al., 2008).

In the soil, N₂O is primarily produced in the presence of low O₂ concentrations by two microbial processes: nitrification and denitrification. The N₂O flux from soils, which is relatively small compared with other N fluxes, is dependent on soil temperature, soil water content, soil texture, soil pH, O₂ availability, N substrate availability (NO₃ and NH₄), and organic C substrate availability (Chen et al., 2008; Abdalla et al., 2009). The process of N₂O production during nitrification, the oxidation of NH₄⁺ to NO₃⁻, is not clearly understood. Nitrous oxide could be formed by the chemical decomposition of HNO₃ by microbial oxidation of NH₂OH, or by the reduction of NO₃⁻ at a low O₂ potential (Anderson and Levine, 1986; Papen and Rennenberg, 1990). During denitrification, the reduction of NO₃⁻ to N₂ under anaerobic conditions, N₂O is produced as an obligatory intermediate (Payne, 1981; Zumft and Kroneck, 1990). Anaerobic conditions favorable for denitrification often exist in microsites where a high O₂ demand from intense respiratory activity exceeds the supply (Parkin, 1987). Despite the increasing knowledge about cellular-level controls on microbial production and consumption of gaseous N oxides, the identification of major predictors of soil N₂O production and its exchange with the atmosphere remains a challenge (Hutchinson and Davidson, 1993; Wallenstein et al., 2006). Critical controlling factors are N availability and O₂ partial pressure, which clearly influence the total amount of NO, N₂O, and N₂ produced during nitrification and denitrification as well as the ratios of each to the others (Hutchinson and Davidson, 1993; Ruser et al., 2006). Within a cropped field, the local N and O₂ supplies that cause a variation in N₂O emissions are difficult to
determine because they strongly depend on different highly variable processes such as the growth of plant roots, the mineralization of crop residues, the application of fertilizers, and the flow of soil water.

Detailed, process-oriented simulation models that consider water, heat, and N dynamics in the soil help us to understand the interacting processes in the N cycle and state variables affecting N$_2$O emissions. Most of the simulation models that have been used to estimate N$_2$O emissions from soils under field conditions represent the underlying processes of denitrification or nitrification by first-order rates without modeling the gaseous N$_2$O transport process (Johnsson et al., 1987; Hutson and Wagenet, 1992; Cannovo et al., 2006). More detailed models considering denitrification inside aggregates and microsites (McConnaguey and Bouldin, 1985; Leffelaar, 1988; Leffelaar and Wessel, 1988) are difficult to apply at the level of soil horizons because they require information about the distribution of aggregate sizes and related solute transport parameters. Several field-scale, process-oriented simulation models were developed to simulate N$_2$O evolution from soils, e.g., DNDC (Li, 2000), NGAS-DAYCENT (Parton et al., 1996), ecosys (Grant et al., 1993, 2006), and Expert-N (Engel and Priesack, 1993; Stenger et al., 1999; Priesack et al., 2001, 2006). Both ecosys and Expert-N consider a dynamic gaseous O$_2$ and N$_2$O transport. There are only a few studies (e.g., Frolking et al., 1998) that have compared field-scale models for estimating N$_2$O fluxes from agricultural soils using field-observed data (Chen et al., 2008).

The aim of this study was to test two modeling approaches of the modular N modeling system Expert-N for their ability to describe and quantify the seasonal variations of N$_2$O fluxes in a potato-cropped soil. Nitrous oxide releases from potato ridges as well as from ridge-till interrows were measured and compared with simulation results in our study. A detailed description of the field experimental results was given by Ruser et al. (1998, 2001). Due to the use of two different N-fertilization levels and different soil bulk densities of the ridge and interrow, we expected a variation of N and O$_2$ supplies in the soil and a corresponding impact on N$_2$O release to the atmosphere. The aim of the simulation study was threefold. First, we tested if a simple modeling approach based on half-saturation kinetics would be sufficient to simulate the observed N$_2$O field emissions. Second, the usefulness of including a N$_2$O gas transport model for the simulation of N$_2$O emissions was examined. Finally, we were interested in whether the modeling approaches were a useful tool to improve knowledge about the controlling factors of N$_2$O production at the field scale. The focus of our analysis was on the assessment of simulated N$_2$O emission rates in relation to measurements. First, we calibrated the modeling approaches with a data set from 1995. In the second step, the model was validated and used for a retrospective prediction of N$_2$O emission rates for the year 1996 at the same site to assess model assumptions and performance without further parameter estimation for N turnover processes. Water flow parameters were estimated anew in 1996 due to soil tillage and the formation of potato ridges.

Materials and Methods

Study Site

Nitrous oxide flux measurements were performed on a crop rotation trial plot of the Experimental Station of the Helmholtz Zentrum München (Schröder et al., 2002). Based on the already published field experimental results, we give just a brief description of the measurements necessary for model input data. The Experimental Station is situated approximately 40 km north of Munich in a hilly landscape derived from tertiary sediments, partially covered with loess. The study site is located 454 m above sea level, the mean annual precipitation is 803 mm, and the mean annual temperature is 7.4°C. The soil type is a fine, silty Dystric Eutrochrept. The total organic C and total N contents of the A horizon (0–30 cm) were 1.5 and 0.15%, respectively. Clay and silt contents were 22 and 56%, respectively (Table 1).

Nitrous oxide emission rates were measured on two differently fertilized plots planted with potato during the vegetation periods of 1995 and 1996 and were described in detail by Ruser et al. (1998, 2001). Due to the ridge culture (which is the usual cropping system for potato in Germany), potato fields show a distinct regular spatial pattern of emissions. In 1996 on 4 July, 12 August, and 9 September, bulk densities were measured on 21 June and 10 October in 1995 and showed no deviation between the two measurements. In 1996 on 4 July, 12 August, and 9 September, bulk densities

<table>
<thead>
<tr>
<th>Soil type and site</th>
<th>Horizon depth cm</th>
<th>Bulk density $g\ cm^{-3}$</th>
<th>Clay %</th>
<th>Silt %</th>
<th>Sand</th>
<th>$K_{sat}$ $mm\ d^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dystric Eutrochrept, ridge, 1995</td>
<td>0–15</td>
<td>1.2</td>
<td>21.8</td>
<td>55.6</td>
<td>22.6</td>
<td>-0.02</td>
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<tr>
<td></td>
<td>15–30</td>
<td>1.4</td>
<td>21.8</td>
<td>55.6</td>
<td>22.6</td>
<td>-0.04</td>
</tr>
<tr>
<td></td>
<td>30–90</td>
<td>1.5</td>
<td>20.9</td>
<td>51.0</td>
<td>13.0</td>
<td>-1.01</td>
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<tr>
<td>Dystric Eutrochrept, ridge, 1996</td>
<td>0–15</td>
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Table 1. Soil properties and hydraulic characteristics of the ridge soil (the second ridge layer equates to the first interrow layer). Campbell A and Campbell B denote the empirical constants of the pedotransfer function of Campbell (1985); $K_{sat}$ is the saturated hydraulic conductivity.
were measured with a standard deviation of 0.05 g cm\(^{-3}\) of the value listed in Table 1. Nitrogen fertilizer was applied as NH\(_4\)NO\(_3\)–urea solution for the extensively fertilized plot F1 (50 kg N ha\(^{-1}\)) and intensively fertilized plot F2 (150 kg N ha\(^{-1}\)) on 12 May (DOY 132) in 1995 and on 10 June (DOY 161) in 1996. Air temperature and precipitation data were recorded by the climate station at the experimental farm.

**Measurements of Nitrous Oxide Emission Rates**

Nitrous oxide emission rates were measured using the closed chamber method as described by Hutchinson and Livingston (1993). We used dark polyvinyl chloride chambers (diameter of 30 cm) that covered the plots. A detailed description of our soil chamber system and the procedure of gas sampling in the field using evacuated glass bottles was given by Flessa et al. (1995) and Ruser et al. (1998). Recently, Rochette and Eriksen-Hamel (2008) developed a system to determine the quality of trace gas sampling procedures with closed chambers. We assessed our measurement quality using this system. For the factors of chamber design, seal on the surface, and air sample handling and storage, our procedure was rated “very good.” Because we calculated the flux rates assuming a linear relationship between time and concentration change, our procedure was only rated as “good” with respect to the determination of the rate of change of N\(_2\)O concentration. According to Rochette and Eriksen-Hamel (2008), nonlinear models yield less-biased estimates of concentration change in closed chambers than linear models.

At each site, five plots for gas flux measurement were established. Measurements of N\(_2\)O flux were performed at least once a week. We periodically took four gas samples out of each chambers’ atmosphere (0, 15, 30, and 45 min after closing the chambers). The gas samples were analyzed using a gas chromatograph (GC-14 A, Shimadzu Corp., Kyoto, Japan) with a \(^{63}\)Ni electron capture detector. The configuration of the automated gas chromatographic system was described in detail by Löffler et al. (1997). We calculated the flux rates based on the following equation given by Flessa et al. (1995):

\[
F_N = k_{N_2O} \frac{273 V}{T} \frac{dc}{dt}
\]

where \(F_N\) (mg N\(_2\)O-N cm\(^{-2}\) d\(^{-1}\)) is the flux, \(k_{N_2O} = 1.25\) mg N cm\(^{-3}\) is a unit conversion factor, \(T\) (K) is the temperature in the chamber headspace, \(V\) (cm\(^3\)) is the chamber volume, \(A\) (cm\(^2\)) is the area covered by the chamber, and \(dc/dt\) (cm\(^3\) cm\(^{-3}\) d\(^{-1}\)) is the rate of change in concentration of N\(_2\)O in the chamber atmosphere with time.

**Soil Analysis**

Soil samples were taken to a depth of 30 cm from the ridges and the interrows at each date of trace gas sampling. The samples were stored overnight at 4°C and analyzed for soil moisture and soil NO\(_3\) contents the following day. The soil moisture content was determined gravimetrically after drying at 105°C. The soil NO\(_3\) content was measured by the extraction of 100 g of soil with 200 mL of 10\(^{-2}\) mol L\(^{-1}\) CaCl\(_2\) solution. The photometric analysis of the NO\(_3\) contents in the supernatant was done using a continuous flow analyzer (SA 20/40, Skalar Analytical, Erkelenz, Germany).

**Modeling Approach**

To simulate N turnover in the soil–potato system, the modular N model software system Expert-N was applied. The Expert-N system consists of different subroutines for each of the model components of soil water flow, soil heat transfer, soil N transport and turnover, and crop growth. Soil water flow was calculated by numerically solving the Richards equation and using representations of the hydraulic functions for soil water retention and unsaturated hydraulic conductivity as given by the LEACHM model (Hutson and Cass, 1987; Hutson and Wagenet, 1992). The solute transport of urea, NH\(_4\), and NO\(_3\) was described by numerical solutions of the convection–dispersion equation, following the methods of the LEACHM model (Hutson and Wagenet, 1992). Nitrogen turnover involving N mineralization of plant residues, N immobilization by soil microorganisms, and turnover of soil organic matter was modeled according to Johnsson et al. (1987) and Vereecken et al. (1990). Water and N uptake by potato roots were simulated using the potato growth model of Gayler et al. (2002). Potential evapotranspiration was calculated by the Penman model (Penman, 1948). This determined the upper boundary condition for soil water flow. For the lower boundary, free drainage, i.e., a unit hydraulic gradient condition, was assumed. Soil heat transfer was simulated using the procedure of Tillotson et al. (1980).

For this study, we used two modeling approaches to simulate N\(_2\)O emissions:

- Model 1 assumed a fixed N\(_2\)O/N\(_2\) ratio for N\(_2\)O production during denitrification and neglected the transport of N\(_2\)O within the soil profile.
- Model 2 explicitly considered N\(_2\)O transport and further reduction of N\(_2\)O to N\(_2\) during transport.

The second model approach (Model 2) had already been applied in simulation studies with Expert-N by Frolking et al. (1998) and Kaharabata et al. (2003), but the equations were not given in detail. The rewetting approach was newly implemented for the present study.

**Nitrous Oxide Production and Denitrification Model**

The model approach to denitrification followed the concepts of Johnsson et al. (1987) (Eq. [2–5]) but was modified so that a further reduction from N\(_2\)O to N\(_2\) could be also described (Eq. [6–9]). The N\(_2\)O production during denitrification and the N\(_2\)O reduction to N\(_2\) during denitrification were modeled by half-saturation or first-order kinetics.

\[
N_2O \text{ production rate } k_{den,N_2O} (\text{mg cm}^{-3} \text{ d}^{-1}) \text{ during denitrification in a soil layer was estimated by}
\]

\[
k_{den,N_2O} = k_{den,N_2O,max} \int_{0}^{T} f_{NO_3} dT
\]

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where the maximal rate \( k_{\text{den,N2O,max}} \) (mg cm\(^{-3}\) d\(^{-1}\)) is the rate for optimal conditions in the soil layer and is reduced under nonoptimal conditions by different reduction factors: \( f_2 \) (dimensionless) denotes the reduction factor for the volumetric water content \( \theta \) (cm\(^3\) cm\(^{-3}\)) (Johnsson et al., 1987), indexing \( O_2 \) availability:

\[
f_\theta = \left( \frac{\theta - \theta_d}{\theta_{\text{sat}} - \theta_d} \right)^2
\]

For volumetric water contents below a threshold value \( \theta_d \) (cm\(^3\) cm\(^{-3}\)), indexing \( O_2 \) availability:

\[
f_\theta = \left( \frac{\theta - \theta_d}{\theta_{\text{sat}} - \theta_d} \right)^2
\]

For the first model (Model 1), the N\(_2\)O reduction rate to N\(_2\) was calculated by the first-order rate constant \( k_{red,N_2} \) (mg cm\(^{-3}\) d\(^{-1}\)):

\[
k_{red,N_2} = \alpha k_{\text{den,N}_2}O
\]

Assuming additionally that N\(_2\)O from net N\(_2\)O production in the soil layers is emitted immediately through the upper soil surface, we obtained the first model (Model 1) for the simulation of N\(_2\)O emissions \( e_{N_2O} \) (mg cm\(^{-2}\)) out of a soil profile of depth \( L \) (cm) by:

\[
e_{N_2O} = \int_{z=L}^{z=0} k_{\text{den,N}_2}O (1 - \alpha) \, dz
\]

In the second model (Model 2), which was defined by a transport equation for N\(_2\)O given below, the N\(_2\)O reduction rate to N\(_2\) during denitrification was estimated by first-order kinetics and calculated by the first-order rate constant \( k_{red,N_2} \) (mg cm\(^{-3}\) d\(^{-1}\)):

\[
k_{red,N_2} = k_{\text{red,N}_2,\text{max}} f_\theta f_T f_7
\]

where the functions \( f_\theta \) and \( f_T \) are the same as for the N\(_2\)O production rate. The function \( f_T \) (dimensionless) describes the impact of high NO\(_3\) concentrations that inhibit or retard N\(_2\)O reduction to N\(_2\):

\[
f_T = \frac{I_{NO_3}^3}{(\theta_{NO_3})^3 + I_{NO_3}^3}
\]

The form of \( f_7 \) and the inhibition constant \( I_{NO_3} \) (mg cm\(^{-3}\)) of the NO\(_3\)–N concentration in the soil volume with \( \theta \) were estimated from the data of Weier et al. (1993).

In Expert-N, the production rate of N\(_2\)O during nitrification for Models 1 and 2 was assumed to be directly proportional to the nitrification rate. The nitrification rate was estimated by first-order rate kinetics (Johnsson et al., 1987). Hence, the first-order rate constant \( k_{\text{nit,N}_2O} \) (d\(^{-1}\)) of N\(_2\)O production during nitrification was given by:

\[
k_{\text{nit,N}_2O} = k_{\text{nit,NO}_3} \beta
\]

for a constant factor \( \beta \) (dimensionless) and the first-order rate constant \( k_{\text{nit,NO}_3} \) (d\(^{-1}\)) of the nitrification rate.

**Rewetting Model**

To explicitly address the effects of soil rewetting (Groffman and Tiedje, 1988; Davidson, 1992), we extended the N\(_2\)O production model to account for the higher N\(_2\)O emission rates that were observed after rainfall events following a longer period of low or no precipitation. We assumed precipitation events of >10 mm of rainfall would trigger the occurrence of rewetting events. The effectiveness of such a rewetting on N\(_2\)O production and denitrification was assumed to depend on the past wet–dry cycle and was estimated using a measure \( F \) (mm) for the soil drying as given by the potential evapotranspiration \( ET \) (mm) minus precipitation \( N \) (mm) accumulated since the last rewetting event:

\[
F(t_j) = \int_{t_{j-1}}^{t_j} ET(t) - N(t) \, dt
\]

where \( t_j \) (d) is the time of the actual and \( t_{j-1} \) (d) of the formerrewetting event. The maximal effectiveness factor of rewetting, \( f_{rew,max} \) (dimensionless), at time \( t_j \) was then determined by:

\[
f_{rew,max}(t_j) = \min \left[ \frac{F(t_j)}{F_{rew,max}}, 1 \right]
\]

where \( F_{rew,max} \) is a constant describing the cumulative potential evapotranspiration since the last rewetting, assumed to be necessary for a maximal rewetting impact on N\(_2\)O production during denitrification. To account for the delay before maximal denitrification occurs (Groffman and Tiedje, 1988) and to describe the impact, assumed to last for 1 wk after the rewetting event, the actual rewetting effectiveness factor \( f_{rew} \) (dimensionless) was defined as:

\[
f_{rew}(t) = g(t - t_j) f_{rew,max}(t_j)
\]

for \( t_j \leq t \leq t_j + 7 \)

where \( t \) (d) denotes the time and \( t_j \) the time of rewetting, and the function \( g(x) \) of variable \( x \) is given by
Nitrous Oxide Transport Model

The second model (Model 2) explicitly accounts for N$_2$O transport assuming local equilibrium between gas- and liquid-phase N$_2$O concentrations. It was defined by the commonly used advection–dispersion equation for the gaseous N$_2$O-N concentration $c_{N2O}$ (mg cm$^{-3}$) in the soil air with an Expert-N specific sink term:

$$\frac{\partial}{\partial t} \left[ \varepsilon (\theta + K_H) c_{N2O} \right] = \frac{\partial}{\partial z} \left( D \frac{\partial c_{N2O}}{\partial z} - q K_H c_{N2O} \right) + \Phi$$

where $\varepsilon$ (cm$^3$ cm$^{-3}$) is the volumetric content of gas-filled soil porosity, i.e., $\varepsilon = \theta_{sat} - \theta$, $K_H$ (dimensionless) is the Henry constant representing the gas–liquid partition coefficient assuming the validity of Henry’s law, $D$ (cm$^2$ d$^{-1}$) is the diffusion–dispersion coefficient, $q$ (cm d$^{-1}$) is the average water flow velocity or Darcy flow velocity, $c_{NH4}$ (mg cm$^{-3}$) is the NH$_4$–N, and $c_{NO3}$ (mg cm$^{-3}$) is the NO$_3$–N concentration in the liquid phase, $t$ (d) is time, and $z$ (cm) is depth. The diffusion–dispersion coefficient $D$ was given by

$$D = D_{og} \left[ \frac{\theta}{\theta_{sat}} \right]^{10/3} + K_H \left( D_{eff} + \lambda \sqrt{q^2} \right)$$

Model Input Parameters

The simulation of soil N$_2$O transport and depending N$_2$O emissions from soil requires an adequate simulation of soil water flow and soil NH$_4$ and NO$_3$ transport. Therefore, not only a parameterization of the N$_2$O transport model was needed, but also input data and parameters for the model components of water flow and N turnover had to be given. For water flow, Table 1 summarizes the parameters defining the hydraulic functions for the ridge and interrow soils. To handle the soil surface geometry of the ridge-till cultivation for the simulations, the ridges were subdivided into two vertical soil layers of 15 cm each. For these ridge layers, bulk densities were measured and water retention curves were determined by laboratory experiments. Measurements of bulk densities and pore-size distributions for the interrow soil (Ruser, 1998; Ruser et al., 1998) gave the basis for the model assumption that for the upper 0–15 cm interrow soil layer the same hydraulic properties as obtained for the second ridge layer (15–30 cm depth) can be used. The Campbell constants $A$ and $B$ (Table 1) were calculated by fitting Hutson and Cass type water retention curves (Hutson and Cass, 1987) to the laboratory-determined water retention values for the soil layers 0 to 15, 15 to 30, and 30 to 90 cm of the ridge soil and for the layers 0 to 15 and 15 to 90 cm for the interrow soil using the fitting routine RETPRED (Hutson and Wagener, 1992). The unsaturated hydraulic conductivity functions were estimated from the retention curves assuming Mualem’s theory (Mualem, 1976) and using the pedotransfer function of Campbell (1985) to calculate the saturated conductivity. To get more realistic water flow simulations for the topsoil of the ridge, the saturated conductivity derived by the pedotransfer function was increased by a factor of 20 (Table 1). The parameter values for the N mineralization–immobilization–turnover model (Johnsson et
The values for the different approaches in using the first-order rate constants for the Henry constant $K_{H1} = 0.676$, for the molecular gaseous diffusion coefficient $D_{og} = 118.4 \times 10^{-5} \text{cm}^2 \text{d}^{-1}$, for the dispersivity $\lambda = 40.0 \text{mm}$, and for the effective $N_2O$ diffusion coefficient in the soil water solution at volumetric water content $\theta$, given by $D_{ef} = D_{ef,a} \exp(\theta b)$ with $D_{ef,a} = 1.20 \text{cm}^2 \text{d}^{-1}$, $a = 0.001$, and $b = 10.0$.

The values for the different approaches in using the first-order rate constants for the Henry constant $K_{H1} = 0.676$, for the molecular gaseous diffusion coefficient $D_{og} = 118.4 \times 10^{-5} \text{cm}^2 \text{d}^{-1}$, for the dispersivity $\lambda = 40.0 \text{mm}$, and for the effective $N_2O$ diffusion coefficient in the soil water solution at volumetric water content $\theta$, given by $D_{ef} = D_{ef,a} \exp(\theta b)$ with $D_{ef,a} = 1.20 \text{cm}^2 \text{d}^{-1}$, $a = 0.001$, and $b = 10.0$.

The lower the value of NRMSE, the better the agreement between simulation and observation.

$$\text{ME} = 1 - \frac{\sum_{i=1}^{n} (O_i - \bar{P})^2}{\sum_{i=1}^{n} (O_i - \bar{O})^2 + \sum_{i=1}^{n} (P_i - \bar{P})^2}$$

The maximum and ideal value for ME is 1.0, while a negative value indicates that model predictions are worse than using the observed mean as an estimate of the data points.

### Results

#### Model Calibration for the Potato Ridge and Interrow Soils

**Simulation Results for Water and Nitrate Contents**

Precise modeling of N dynamics in the soil requires correctly simulated water flow and water balance. Figure 1 shows the time course of measured and simulated water and NO$_3$ contents in the ridge and interrow soils (0–30-cm depth) of the potato field. Water and NO$_3$ contents were measured in both fertilization treatments whenever N$_2$O emissions were determined. The volumetric water content measurements of the two fertilization treatments F1 and F2 agreed well for the ridge soil (Fig. 1a) and for the interrow soil (Fig. 1c). The water content dynamics were very well described by the simulation model for the ridge soil as well as for the denser interrow soil (Fig. 1a and 1c; Table 2). In the interrow soil, the water content variability showed a smoother transient behavior, and desiccation in the summer months was diminished because no transpiration by potato plants occurred. This was also shown by the simulation results.

To simulate NO$_3$ contents, the two fertilization treatments had to be distinguished (Fig. 1b and 1d). As a result of the different fertilization management, the measured NO$_3$ contents in the ridge soil (Fig. 1b) were significantly higher (on average by 15.6 kg N ha$^{-1}$) in the intensively fertilized plot F2 than in the extensive fertilized plot F1, apart from a few exceptions (DOY 177, 191, 205, and 219). In agreement with the measurements, the simulation results showed higher NO$_3$ contents in the case of the intensively fertilized plot (on average by 7.8 kg N ha$^{-1}$). Until the sampling at DOY 170, the time course of the measured NO$_3$ contents rose and fell in parallel for the two fertilization plots (Fig. 1b). This was also shown in the model simulations, although the model underestimated NO$_3$ contents, especially for the extensive plot. After this day, differences in the measured NO$_3$ contents between the two plots were high. Model predictions were much smoother and fluctuations in NO$_3$ contents were not simulated correctly (compare NRMSE and ME in Table 2). A possible explanation may be inadequate simulated N uptake by the potato plants. For the interrow soil without N uptake of the potato plants, the NO$_3$ contents and temporal fluctuations estimated by Expert-N were in good agreement with the measurements (Table 2). In the interrow soil, the measured and simulated NO$_3$ contents were significantly higher in the intensively fertilized plot than the

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**Statistical Criteria**

To assess the adequacy of the model simulations in relation to measurements, the statistical measures of model efficiency (ME; Willmott, 1982) and normalized root mean square error (NRMSE; Wallach and Goffinet, 1989) were used. In Eq. [23] and [24], $P_i$ denotes the predicted values, $O_i$ the observed values, $\bar{P}$ the predicted mean, and $\bar{O}$ the mean observed value, and $n$ is the number of observations during the experiment times:

$$\text{NRMSE} = \sqrt{\frac{\sum_{i=1}^{n} (O_i - \bar{P})^2}{\sum_{i=1}^{n} (O_i - \bar{O})^2}}$$

$$\text{ME} = 1 - \frac{\sum_{i=1}^{n} (O_i - \bar{P})^2}{\sum_{i=1}^{n} (O_i - \bar{O})^2 + \sum_{i=1}^{n} (P_i - \bar{P})^2}$$
extensive plot, but after DOY 219, the NO₃ contents between the two fertilization treatments were nearly the same (Fig. 1d).

Simulation Results for Nitrous Oxide Emissions: Comparison of Modeling Approaches

In accordance with the measurements, the simulated time patterns of N₂O emission rates in 1995 were clearly influenced by the application of N fertilizer and by heavy rainfall events (Fig. 2). Rewetting after a longer period of dryness induced further periods of enhanced N₂O losses (sampling at DOY 198, 209, and 240). The rewetting approach in both Models 1 and 2 increased the modeling efficiency and decreased the NRMSE significantly in most cases (Table 3), confirming the importance of this process. Only for the ridge soil in the extensively fertilized plot F1 treatment were the NRMSE values higher in 1995 with implementation of the rewetting approach than without. Overall, the rewetting approach was capable of describing the rewetting effects on N₂O emission rates and its consideration clearly improved the simulation results (Table 3). In Fig. 2b, 2c, and 2d, only the results with implementation of the rewetting approach are shown.

In contrast to the measured NO₃ contents, the N₂O emission rates from the ridge soil observed during the growing period had a very similar time pattern and flux amount for both fertilization schemes (Fig. 2b and 2c). The so-called background N₂O flux rates (<50 µg N₂O-N m⁻² h⁻¹) coincided for the interrow and ridge soils and for both fertilization treatments (Fig. 2b, 2c, and 2d). The background level of N₂O emissions was well simulated for the ridge as well as the interrow soil with Model 1. Using Model 1, N₂O emissions from the total soil profile were compared with the measured N₂O emissions from the upper ridge layers. Figures 2b and 2c show that the half-saturation N₂O production model

Table 2. Modeling efficiency (ME) and normalized root mean square error (NRMSE) for volumetric water and NO₃ contents in the ridge and interrow soils for both fertilization treatments F1 and F2 and both simulation years.

<table>
<thead>
<tr>
<th>Site</th>
<th>Water (0–30 cm)</th>
<th>NO₃ (0–30 cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NRMSE</td>
<td>ME (Wilmott)</td>
</tr>
<tr>
<td>Ridge F1 1995</td>
<td>0.08</td>
<td>0.93</td>
</tr>
<tr>
<td>Ridge F2 1995</td>
<td>0.08</td>
<td>0.93</td>
</tr>
<tr>
<td>Ridge F1 1996</td>
<td>0.23</td>
<td>0.66</td>
</tr>
<tr>
<td>Ridge F2 1996</td>
<td>0.23</td>
<td>0.68</td>
</tr>
<tr>
<td>Interrow F1 1995</td>
<td>0.07</td>
<td>0.81</td>
</tr>
<tr>
<td>Interrow F2 1995</td>
<td>0.08</td>
<td>0.79</td>
</tr>
<tr>
<td>Interrow F1 1996</td>
<td>0.12</td>
<td>0.58</td>
</tr>
<tr>
<td>Interrow F2 1996</td>
<td>0.15</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Fig. 1. (a,c) Water and (b,d) NO₃ contents measured (F1—black diamonds, F2—gray triangles) and simulated (F1—black line, F2—gray line) for the cropping period in 1995 at the 0– to 30-cm depth of ridge and interrow soils. Note that the vertical axis scales for NO₃ are different.

Fig. 2. (a) Precipitation and air temperature, and N₂O emissions from the total soil profile of the (b) ridge soil F1, (c) ridge soil F2, and (d) interrow soil F2 measured (symbols with standard deviation) and simulated (Model 1, gray line; Model 2, black line) for the cropping period in 1995 (with application of the rewetting approach). Note that the vertical axis scales for N₂O emissions are different.
overestimated the N₂O emissions during longer periods of rainfall for the ridge soil. During periods with strongly increased flux rates, the emissions from the ridge soil (Fig. 2b and 2c) and the interrow soil (Fig. 2d, results for F1 plot not shown) in the intensively fertilized plot (F2) were up to a factor of three and a half times higher than the emissions from the extensively fertilized plot (F1). Model 1 significantly underestimated the very high N₂O emission rates from the intensively fertilized interrow soil during the long rainy period after fertilizer application (Fig. 2d), although the NO₃ contents were correctly reproduced by the simulation results (Fig. 1d).

Considering the microbial nature of N₂O production (Wallenstein et al., 2006), we assumed in Model 1 that N₂O was produced only in the upper soil layer (0–30-cm depth), which is enriched by organic material, and we neglected N₂O production from lower layers. The predominance of N₂O production in the upper soil layer was also demonstrated by the simulations of the N₂O emissions by Model 2 (Fig. 2b, 2c, and 2d), which explicitly accounts for N₂O transport in the gaseous and liquid phases. If we increased the microbial activity in the model and correspondingly high gross N₂O production rates took place in the lower layers, this also resulted in higher emission rates from the total soil profile for Model 2, assuming a dynamic reduction of N₂O to N₂ in the deeper layers. For the ridge soil, the simulation results for both fertilization treatments with both modeling approaches were in very good agreement with the measurements (Table 3). Similar simulation results were achieved by Model 2 as by use of Model 1 in the case of the interrow soil. Only the underestimation of the high N₂O emission rates between DOY 158 and 177 was stronger (compare Table 3) if Model 2 was applied.

### Table 3: Modeling efficiency (ME) and normalized root mean square error (NRMSE) for N₂O emissions of the ridge and interrows soil for both fertilization treatments F1 and F2 and both simulation years: comparison of modeling approaches.

<table>
<thead>
<tr>
<th>Site</th>
<th>Model 1 NRMSE</th>
<th>ME (Wilmott)</th>
<th>Model 2 NRMSE</th>
<th>ME (Wilmott)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without rewetting approach</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ridge F1 1995</td>
<td>1.51</td>
<td>0.65</td>
<td>1.32</td>
<td>0.55</td>
</tr>
<tr>
<td>Ridge F2 1995</td>
<td>1.58</td>
<td>0.58</td>
<td>1.49</td>
<td>0.49</td>
</tr>
<tr>
<td>Ridge F1 1996</td>
<td>1.64</td>
<td>0.42</td>
<td>1.55</td>
<td>0.38</td>
</tr>
<tr>
<td>Ridge F2 1996</td>
<td>1.86</td>
<td>0.32</td>
<td>1.67</td>
<td>0.37</td>
</tr>
<tr>
<td>Interrow F1 1995</td>
<td>1.24</td>
<td>0.62</td>
<td>1.41</td>
<td>0.49</td>
</tr>
<tr>
<td>Interrow F2 1995</td>
<td>1.40</td>
<td>0.56</td>
<td>1.57</td>
<td>0.47</td>
</tr>
<tr>
<td>Interrow F1 1996</td>
<td>1.85</td>
<td>0.34</td>
<td>1.51</td>
<td>0.56</td>
</tr>
<tr>
<td>Interrow F2 1996</td>
<td>1.88</td>
<td>0.32</td>
<td>1.65</td>
<td>0.46</td>
</tr>
</tbody>
</table>

With rewetting approach

| Ridge F1 1995   | 2.11          | 0.75         | 2.30          | 0.70         |
| Ridge F2 1995   | 0.91          | 0.93         | 0.94          | 0.93         |
| Ridge F1 1996   | 1.21          | 0.86         | 0.99          | 0.90         |
| Ridge F2 1996   | 1.65          | 0.57         | 1.42          | 0.65         |
| Interrow F1 1995| 0.92          | 0.86         | 1.14          | 0.71         |
| Interrow F2 1995| 1.16          | 0.73         | 1.40          | 0.57         |
| Interrow F1 1996| 1.85          | 0.34         | 1.51          | 0.56         |
| Interrow F2 1996| 1.88          | 0.32         | 1.65          | 0.46         |

Model Validation for the Potato Ridge and Interrow Soils

### Simulation Results for Water and Prediction for Nitrate Contents

For the year 1996, the gravimetric water content measurements of the two fertilization treatments agreed very well. Also the simulated time course of water contents matched the measurements (cp. ME in Table 2). From 3 wk after potato ridge formation, however, the model predictions overestimated the measured water contents for the ridge soil (results not shown). This was presumably due to a discrepancy between the assumed total pore volume in the simulations and the actual pore volume in the soil, which is subject to temporal variability. Due to the cropping practice of potato, this was also true in the case of the ridge cultivation and after possible soil settling due to a longer rainfall period (Fig. 3a, DOY 138–148). For the interrow soil, the water content level was slightly overestimated by the model (cp. NRMSE in Table 2).

After fertilizer application, the NO₃ contents in the intensive F2 plots were temporarily increased compared with the extensive F1 plots and then became similar again (after 5 wk for the ridge soil, 11 wk for the interrow soil; results not shown) with some exceptions. The earlier decrease in N contents in the ridge soil was presumably due to N uptake by the potato crop. For the ridge soil, the NO₃ simulation results agreed much better with the observed NO₃ contents than in the year before. This was also due to the fact that NO₃ measurements in 1996 showed more consistency between the two fertilization treatments. But before fertilizer application, the NO₃ contents in the ridge soil were underestimated by the model for both treatments. After fertilizer application, the measured NO₃ contents of the intensive plot (neglecting a possible outlier) were well simulated or only slightly underestimated at some dates. These discrepancies resulted in similar ME values (Table 2) as for the previous year. A slight underestimation of the NO₃ contents by the model occurred for the extensive plots of the ridge and interrow soils. For the intensive plot of the interrow soil, N contents were strongly underestimated by the model simulations after fertilizer application. A possible explanation may be the effect of lateral NO₃ movement due to runoff from the ridge to the interrow soil after rainfall.

Model Validation for Nitrous Oxide Emissions

In the same manner as during the cropping period in 1995, heavy rainfall events and N fertilizer application clearly also dominated the time patterns of N₂O emission rates in 1996 (Fig. 3). The application of the rewetting approach calibrated for the year 1995 clearly improved the simulation results for the ridge soil also in 1996 (cp. Table 3). The rewetting peak at DOY 175 was clearly reproduced by the simulation results of Models 1 and 2 (Fig. 3b and 3c). Due to the simulated smoother behavior of water content variability in the denser interrow soil (results not shown), this rewetting effect was not predicted for the interrow soil and changes in the NRMSE and ME values could be observed (Table 3) during...
the simulation period in 1996. In Fig. 3b, 3c, and 3d, only the results with implementation of the rewetting approach are shown.

Two short periods with very high N₂O emission rates occurred after N fertilizer application (Fig. 3b, 3c, and 3d). Time patterns and background flux rates coincided for the interrow and ridge soils and for both fertilization treatments and were well simulated by both modeling approaches (Table 3). Again, during periods of high emission rates, the intensively fertilized plots showed N₂O emission rates that were much higher than the emission rates at the extensive plots. For the extensive F1 plot of the ridge soil, both models achieved a good prediction of the measured N₂O emissions (Fig. 3b), which is reflected in the high ME values. For the intensive F2 plot of the ridge soil, the emission rates were also well simulated; only single flux peaks were underestimated. For all four treatments (Fig. 3b, 3c, and 3d, interrow F1 not shown), the very high N₂O peak of the second period (DOY 196) was not predicted by either modeling approach, as well as the increased N₂O flux rates between the two periods (DOY 179 and 184). Both interrow fertilization F1 plots (results not shown) and F2 plots (Fig. 3d) showed very high emission rates after fertilizer application, which was not simulated and which resulted in low ME values (Table 3). For the interrow plots, Model 2 gave slightly better simulation results than Model 1.

**Comparison of Measured and Simulated Cumulative Nitrous Oxide Emissions**

To estimate cumulative field emissions during the cropping period of the potato plants, the measured N₂O emissions were integrated by assuming that the emissions changed linearly between the sampling dates. During the same period as the measured emissions, the daily integrated Expert-N emissions (Table 4) underpredicted the observed emissions by 32% for Model 1 and by 35 to 43% for Model 2 for the ridge soil. For the interrow soil, the underestimation for Model 1 ranged between 63 and 74% and between 69 and 78% for Model 2. The standard deviations of the measurements were 33 to 41% for the ridge soil and 25 to 45% for the interrow soil. Due to the high temporal variability of the N₂O fluxes, the assumption of a linear integration between sampling dates induced further sources of uncertainty. Concerning the uncertainty in the measured integrated emissions, Expert-N provided good estimates of cumulative N₂O emissions during the cropping period for the ridge soil. Neither modeling approach could describe the high N₂O flux rates from the interrow plots, resulting in a strong underestimation of the cumulative N₂O emissions for the denser interrow soil.

**Discussion**

The aim of the simulation study was threefold. First, Model 1 was applied to test if the simulation of net N₂O production during denitrification described by a simple approach based on half-saturation kinetics (Johnsson et al., 1987) would be sufficient to model the N₂O emissions observed in a field study. Second, the usefulness of including a N₂O gas transport model for the simulations of N₂O emissions (Model 2) was examined. Finally, we were interested in whether the modeling approaches were a useful tool to improve our knowledge about the driving forces and controlling factors of N₂O production at the field scale and could lead to a recommendation for an appropriate agricultural management strategy to reduce N₂O emissions.

For both years—the evaluation and prediction years—the simple modeling approach was suitable for N₂O emission simulation even if single high emission events were not predicted. For the second year, when the models were applied without further parameter optimization, the

<table>
<thead>
<tr>
<th>Site</th>
<th>N₂O emissions</th>
<th>Model 1</th>
<th>Model 1/ measured</th>
<th>Model 2</th>
<th>Model 2/ measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ridge F1</td>
<td>1.58 (0.65)</td>
<td>1.62</td>
<td>1.02</td>
<td>1.34</td>
<td>0.85</td>
</tr>
<tr>
<td>Ridge F2</td>
<td>2.91 (0.97)</td>
<td>1.98</td>
<td>0.68</td>
<td>1.65</td>
<td>0.57</td>
</tr>
<tr>
<td>Interrow F1</td>
<td>3.18 (1.42)</td>
<td>1.17</td>
<td>0.37</td>
<td>0.98</td>
<td>0.31</td>
</tr>
<tr>
<td>Interrow F2</td>
<td>5.48 (1.38)</td>
<td>1.44</td>
<td>0.26</td>
<td>1.20</td>
<td>0.22</td>
</tr>
</tbody>
</table>
As reviewed by Granli and Bøckman (1994), the water-filled pore space (WFPS) between the modeled and measured N$_2$O fluxes. Due to the high temporal variability of the N$_2$O fluxes, with highly skewed frequency distributions and coefficients of $>150\%$ at diurnal time scales (Flessa et al., 1995), accurate measurement techniques for N$_2$O emissions are essential. Manually operated surface chambers over small areas capture only small portions of the spatial and temporal variability (Grant et al., 2006; Metivier et al., 2009) and the weekly determination of emission rates can result in an error when estimating cumulative fluxes for a longer period (Flessa et al., 2002; Kaharabata et al., 2003). Therefore, it should be tested in further studies whether model performance for high N$_2$O flux rates is improved for data sets of higher temporal resolution and if data using micrometeorologic techniques at the field scale could provide a better basis for model hypotheses testing as discussed by Metivier et al. (2009).

Grant et al. (2006) and Cannovo et al. (2006) pointed out that the coupled modeling of microbiological processes and transport of gaseous reactants is required for the simulation of N$_2$O emissions. In our study, the simulated time patterns of N$_2$O emission rates were not affected by the applied modeling approach and could be simulated by either modeling approach, with a few discrepancies for single days. Time patterns were clearly influenced by the application of N fertilizer and by heavy rainfall events, which, among others, was also reported by Metivier et al. (2009). Because the simple modeling approach showed model performance similar to the modeling approach that included N$_2$O gas transport, our results suggest that nitrification and denitrification activity in the upper soil centimeters determine N$_2$O dynamics. This result was confirmed by the work of Cannovo et al. (2006). The background level of N$_2$O emissions was well simulated by both approaches if appropriate maximal N$_2$O production rates were chosen. Maximal N$_2$O production rates during denitrification as well as during nitrification should be approximately known. These optimal production rates vary among different soil horizons and soil types and are often highest within the surface layer. As reported for conventional-tillage and no-till corn (Zea mays L.) treatments by Kaharabata et al. (2003), Expert-N provided good estimates of daily N$_2$O emissions also for this study.

Nitrous oxide emission activity was highest after strong rainfall and high N amounts in the soil, i.e., after fertilizer application. This fact was reflected in the model assumptions. At limited mineral N in the soil, Expert-N simulated no response of N$_2$O emissions to rainfall distribution. The rewetting model was capable of describing increased N$_2$O emission rates after a period of low precipitation. As reviewed by Granli and Bøckman (1994), the water-filled pore space in the soil is a key factor for denitrification activity and N$_2$O emissions. They concluded that the increase in denitrification rate with increasing soil water content was most marked in soils exhibiting water-filled pore space (WFPS) $\geq 60\%$. This was supported by the study of Ruser et al. (2006). They showed that N$_2$O emission rates were generally small at soil water contents $\leq 60\%$ WFPS, while significantly higher N$_2$O emission rates were measured at soil water contents $>70\%$ WFPS, with the highest fluxes occurring at the highest soil moisture level of 90% WFPS. A threshold value of $h_d = -0.6$ kPa above which denitrification occurs proved to be appropriate for the current simulations. The accurate simulation of WFPS is a key requirement for a reliable simulation of N$_2$O (Frolking et al., 1998). This was also confirmed by our simulation results. Low NRMSE and high ME values for the water content simulations resulted in a high agreement between measured and simulated N$_2$O emissions. Especially at higher water contents, gas diffusion is severely hindered, less O$_2$ from the atmosphere enters into the soil, N$_2$O stays longer within the soil, and increasingly more N$_2$O is reduced to N$_2$ during denitrification. With decreasing water contents, gas diffusion increases, more O$_2$ becomes available, and denitrification proceeds at an increasingly lower N$_2$/N$_2$O ratio until O$_2$ diffusion is no longer impeded and denitrification ceases. Therefore, the inclusion of a gas transport module in the modeling approach resulted in simulated N$_2$O emission dynamics showing a smoother transient behavior.

As increased soil bulk densities reduce macropore space and increase WFPS, the different bulk density and pore-size distribution in the ridge soil and the denser interrow soil significantly affected the measured N$_2$O release. The Expert-N modeling approaches could not describe the high N$_2$O flux rates from the interrow plots. The underestimation by the simulations of the observed high N$_2$O emission rates from the interrow soil was probably mainly due to additional runoff water from the upslope area of the ridge soil, which increased the WFPS and was not accounted for by the simulations. Additionally, these high emission rates could be due to higher NO$_3$ concentrations after runoff from the ridges to the interrow caused by strong rainfall events after the broadcast surface N application. The NO$_3$ runoff from the ridges can increase NO$_3$ concentrations in the uppermost few centimeters and may not be detectable by the NO$_3$ measurements averaged over the 0- to 30-cm soil depth.

Comparing measured data with simulation results of N$_2$O emissions and soil water and NO$_3$ contents, it can be concluded that both modeling approaches were able to describe the observed seasonal dynamics if appropriate maximal N$_2$O production rates were chosen. In some cases, extremely high emission rates were underestimated by both models and could not be reproduced correctly, but generally Expert-N provided good estimates of daily N$_2$O emissions. The variation of N$_2$O emissions could be described by assuming denitrification to be the major source for N$_2$O production. The lower N$_2$O release from ridge soil was mainly due to better aeration than the interrow soil because of a lower soil bulk density and lower water contents as a result of lateral runoff and water uptake by the potato plants. It should be tested in further studies whether data sets of higher temporal resolution could provide a better basis for model hypotheses testing.


