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# The effect of aggregates on N<sub>2</sub>O emission from denitrification in an agricultural peat soil

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## Abstract

Nitrous oxide (N<sub>2</sub>O) emissions are highly variable in time, with high peak emissions lasting as couple of days to weeks and low background emissions. This temporal variability is poorly understood which hampers the simulation of daily N<sub>2</sub>O emissions.

In structured soils, like clay and peat, aggregates hamper the diffusion of oxygen, which leads to anaerobic microsites in the soil, favourable for denitrification. In this paper we studied the effect of aggregates in soils on the N<sub>2</sub>O emissions from denitrification. We presented a parameterization to simulate the effects of aggregates on N<sub>2</sub>O, following the mobile-immobile model concept. This parameterization was implemented in a field-scale hydrological-biogeochemical model combination. We compared the simulated fluxes with observed fluxes from a fertilized and drained peat soil with grass.

The results of this study showed that aggregates strongly affect N<sub>2</sub>O emissions: peak emissions are lower, whereas the background emissions are slightly higher. Implementation of the effect of aggregates caused a decrease in the simulated annual emissions of more than 40%. The new parameterization also significantly improved the model performance to simulate observed N<sub>2</sub>O fluxes. Aggregates have more impact on the reduction of N<sub>2</sub>O than on the production of N<sub>2</sub>O. Reduction of N<sub>2</sub>O is more sensitive to changes in the drivers than production of N<sub>2</sub>O and is in that sense the key process to understand N<sub>2</sub>O emissions from denitrification. The effects of changing conditions on reduction of N<sub>2</sub>O relative to N<sub>2</sub>O production is dependent on the NO<sub>3</sub> content of the soil. It is expected that in soils with a low NO<sub>3</sub> content the influence of aggregates on the NO<sub>3</sub> concentration is not negligible. This study showed that the current knowledge of the hydrological, biogeochemical and physical processes is sufficient to understand the observed N<sub>2</sub>O fluxes from a fertilized peatland. Further research is needed to test how aggregates affect the N<sub>2</sub>O fluxes in areas or periods with little NO<sub>3</sub> in the soil.

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## 1 Introduction

Nitrous oxide (N<sub>2</sub>O) is one of the main greenhouse gases (e.g. Denman et al., 2007) and is the main ozone depleting compound of the 21st century (Ravishankara et al., 2009). Agricultural soils are the largest anthropogenic source, globally (Denman et al., 2007), in Europe (Schulze et al., 2009), and in the Netherlands (Van der Maas et al., 2008). Agricultural peatlands are major sources of N<sub>2</sub>O (Velthof and Oenema, 1995).

Time series of N<sub>2</sub>O emissions typically show long periods with low background emissions interspersed with high peak emissions lasting a couple of days to weeks. Despite their short duration, these peaks can constitute a major part of total annual N<sub>2</sub>O emission (e.g. Scheer et al., 2008; Yamulki et al., 1995). In the modeling of N<sub>2</sub>O emissions accurate simulation of peak emissions is therefore a pivotal issue (e.g. Stehfest and Muller, 2004; Lamers et al., 2007). This requires models with a small timestep of one day or less. Various process-based field-scale simulation models for daily N<sub>2</sub>O fluxes are available (Chen et al., 2008). Whereas cumulative emissions have been simulated fairly well (e.g. Li, 2000; Saggar et al., 2007; Jarecki et al., 2008) the simulation of daily emissions is still poor (Groffman et al., 2009).

In a recent simulation study with the SWAP-ANIMO model combination (Stolk et al., 2011) N<sub>2</sub>O peak emissions from peatland were simulated both too early and too high, compared to the observed N<sub>2</sub>O emissions. It was hypothesized that this misfit was due to a violation of the assumption of direct equilibrium between N<sub>2</sub>O in the gaseous and in the aqueous phase in structured soils like clay or peat. This means that the total soil concentration is not representative for the aqueous or the gaseous concentration separately. In unsaturated soils diffusion in the gas phase is the main mechanism for N<sub>2</sub>O transport to the surface. Consequently, total soil concentrations are not representative for the N<sub>2</sub>O that is available for transport to the soil surface. Support for this hypothesis is found in studies that prove a discrepancy between observed emissions and emissions calculated from soil concentrations using Fick's law for N<sub>2</sub>O (Neftel et al., 2007) and CO<sub>2</sub> (Köhler et al., 2010).

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Structured soils can contain aggregates with smaller pores and higher tortuosity, as well as disconnected or dead-end pores (Hoag and Price, 1997). These smaller or disconnected pores remain water filled longer than the larger pores in between the aggregates. The absence of air filled pores hampers the diffusion of oxygen and leads to the formation of anaerobic microsites in the soil (Currie, 1961), favourable for denitrification (Groffman et al., 2009). Diffusion of N<sub>2</sub>O, an intermediate product of denitrification, out of these microsites is hampered for the same reason, increasing the residence time of N<sub>2</sub>O in the aqueous phase. This prolonged residence time increases the chance for further reduction of N<sub>2</sub>O to nitrogen gas (N<sub>2</sub>). With regard to N<sub>2</sub>O aggregates cause both delayed and reduced emissions.

In the current N<sub>2</sub>O simulation models several concepts are used to account for these effects of aggregates on N<sub>2</sub>O reduction and transport. In the DNDC model-family (Li et al., 2000; Li et al., 1992; Li, 2000) for example, a reduction factor decreases diffusion of N<sub>2</sub>O from denitrification based on the anaerobic fraction and the clay content. In PaSim (Schmid et al., 2001) a resistance was added for N<sub>2</sub>O from denitrification to enter the total soil N<sub>2</sub>O pool and the electron affinity for N<sub>2</sub>O relative to NO<sub>3</sub> was increased empirically to get more reduction of N<sub>2</sub>O to N<sub>2</sub> and. These concepts describe the effects of soil structure on N<sub>2</sub>O without addressing the soil structure itself which makes it difficult to use the model without calibration for each new situation.

There are different concepts in use to describe soil structure in simulation models and its effects on aeration and denitrification:

- Aggregate models describe the soil as a collection of aggregates. Pore sizes can be determined from soil moisture characteristics or more in detail based on the spatial distribution of the aggregates (Arah and Smith, 1989).
- Pore models describe the soil as a collection of pores with a characteristic pores size distribution. Aggregate sizes can be determined from the spatial distribution of the pores (e.g. Groenendijk et al., 2005).

- Fractals describe soil structure in an integral way, distinguishing between air filled pores and the soil matrix, which is the combination of the solid phase and water (Rappoldt and Crawford, 1999).
- In the multi-domain approach the soil is separated in two or three zones, representing the pore space within and in between the aggregates. It is not a physical representation of the soil geometry, but the zones are conceptually superimposed over the same volume (Köhne et al., 2009). The transport between the zones is based on the shape and the size of the aggregates. In a mobile-immobile model vertical transport in the immobile zone is completely blocked (Van Genuchten and Wierenga, 1976).

All of these model concepts have been used to simulate the effect of aggregates on nitrate ( $\text{NO}_3$ ) and  $\text{O}_2$ , but to the best of our knowledge not for the effect of aggregates on  $\text{N}_2\text{O}$ . Single-aggregate models, where the model-domain is limited to one aggregate only, have been used to study the effects of aggregates on the  $\text{N}_2\text{O}$  concentration in the inter-pore space (Leffelaar, 1988; McConnaughey and Bouldin, 1985), but this work has not been extended to models that describe the soil as a collection of aggregates.

In this paper we test the hypothesis that aggregates affect  $\text{N}_2\text{O}$  emission. We present a parameterization to simulate the effects of aggregates on daily  $\text{N}_2\text{O}$  emissions, following the mobile-immobile concept. This parameterization is implemented in SWAP-ANIMO (Soil-Water-Atmosphere-Plant; Agricultural Nitrogen Model), a combination of a field-scale hydrological and biogeochemical model. First we compare the simulated emissions with and without aggregates and we compare the simulated emissions with the observed emissions. Secondly we test the sensitivity of the model to determine how the aggregate size and shape affect production, reduction and emission of  $\text{N}_2\text{O}$  and which model parameters have most effect on these processes. Finally we make a first assessment of applicability and limitations of this model concept for  $\text{N}_2\text{O}$ .

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## 2 Method

### 2.1 Model description

#### 2.1.1 Original model

SWAP (Van Dam, 2000; Van Dam et al., 2008; Kroes et al., 2008) is a multi-layered simulation model for the transport of water, solutes and heat in unsaturated and saturated soils. The model is designed to simulate flow and transport processes at field scale level. Top, bottom, and lateral boundary conditions in SWAP allow computation of plant transpiration and interception, soil evaporation, runoff, irrigation, lateral drainage to and infiltration from drains and surface water, and seepage to or infiltration from deeper aquifers.

ANIMO (Rijtema et al., 1999; Groenendijk et al., 2005; Renaud et al., 2005; Hendriks et al., 2011) is a dynamic process-based simulation model for nutrients (N and P) and organic matter dynamics in the soil. The minimum timestep for ANIMO is one day; this timestep is used in greenhouse gas studies. It is coupled off-line to SWAP that prescribes water flow, soil moisture and soil temperature on a daily basis. In ANIMO vegetation interacts with soil moisture and nutrients. Aeration status is calculated from the average pore size, based on soil moisture content. The greenhouse gas module in ANIMO provides the simulation of  $N_2O$ ,  $CH_4$  and  $CO_2$  production, consumption in the soil and emission to the atmosphere. Transport of greenhouse gasses involves diffusion and advective transport by air and water flow. Although the SWAP-ANIMO model combination has over 100 input parameters, for most soils in the Netherlands default values are available (Wolf et al., 2003; Wösten et al., 1994), which makes it easily applicable here and in comparable soils without extensive measurement campaigns or tuning of input parameters.

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The original formulation of the conservation and transport (CT) equation in ANIMO for N<sub>2</sub>O reads (Hendriks et al., 2011):

$$\frac{\partial c_s}{\partial t} = \frac{\partial}{\partial z} \left( D_{\text{eff}} \frac{\partial c_w}{\partial z} \right) - q_a \alpha_R \frac{\partial c_w}{\partial z} - q_w \cdot \frac{\partial c_w}{\partial z} - Q_{\text{dr}} \cdot c_w + R_{\text{pr,nit}} + R_{\text{pr,den}} - R_{\text{rd}} \quad (1)$$

where

$$c_s = (\alpha_R \theta_a + \theta_w) c_w \quad (2)$$

and

$$D_{\text{eff}} = \alpha_R \rho_1 \theta_a^{\rho_2} D_{0,a} + \tau_w \theta_w D_{0,w} \quad (3)$$

Here  $c_s$  (kg N m<sup>-3</sup>),  $c_a$  (kg N m<sup>-3</sup>), and  $c_w$  (kg N m<sup>-3</sup>) are the N<sub>2</sub>O–N concentration in soil, soil air and soil water, respectively,  $t$  (d) is time,  $z$  (m) is depth,  $D_{\text{eff}}$  (m<sup>2</sup> d<sup>-1</sup>) is the effective diffusion coefficient for simultaneous diffusion in soil air and water,  $q_a$  (m<sup>3</sup> m<sup>-2</sup> d<sup>-1</sup>) and  $q_w$  (m<sup>3</sup> m<sup>-2</sup> d<sup>-1</sup>) are the vertical air and water flux in the soil, respectively,  $\alpha_R$  (m<sup>3</sup> m<sup>-3</sup>) is the reciprocal of Bunsen's coefficient,  $Q_{\text{dr}}$  (m<sup>3</sup> m<sup>-3</sup> d<sup>-1</sup>) is the drainage discharge,  $R_{\text{pr,nit}}$  and  $R_{\text{pr,den}}$  (kg N m<sup>-3</sup> d<sup>-1</sup>) are the N<sub>2</sub>O production rate by nitrification and denitrification, respectively,  $R_{\text{rd}}$  (kg N m<sup>-3</sup> d<sup>-1</sup>) is the N<sub>2</sub>O reduction rate,  $\theta_a$  (m<sup>3</sup> m<sup>-3</sup>) and  $\theta_w$  (m<sup>3</sup> m<sup>-3</sup>) are the volumetric air and water content, respectively,  $\rho_1$  and  $\rho_2$  (–) are coefficients for vertical gaseous diffusion in soil,  $D_{0,a}$  and  $D_{0,w}$  (m<sup>2</sup> d<sup>-1</sup>) are the N<sub>2</sub>O diffusion coefficient in free air and free water, respectively, and  $\tau_w$  (–) is a tortuosity factor for vertical aqueous diffusion in soil.

### 2.1.2 Mobile-immobile model concept

In the present study the mobile-immobile model concept has been implemented in the N<sub>2</sub>O module of SWAP-ANIMO. In this concept the soil is divided into a mobile and an immobile soil fraction,  $F_{\text{MO}}$  and  $F_{\text{IM}}$  (–), respectively. In the mobile-immobile model we assume that denitrification only takes place in the immobile soil fraction. Via a

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transfer term part of  $N_2O$  from denitrification is transported from the immobile to the mobile zone, or vice versa if reduction is larger than production. All vertical transport is assumed to take place in the mobile zone.

The two main vertical transport processes for  $N_2O$  in the soil are diffusive transport in soil air and convective flow with soil water. Based on the simplification that all air filled pores are connected, we assume that diffusive transport in air is never inhibited. Therefore all air filled pore space is assigned to the mobile zone and the immobile zone is always water saturated. In water saturated structured soils, part of the water is stagnant. This soil fraction with stagnant water represents the maximum immobile soil fraction,  $F_{IM,max}$  (-). When the water filled pore space is larger than  $F_{IM,max}$ , the immobile soil fraction,  $F_{IM}$ , is equal to  $F_{IM,max}$ . When water filled pore space is less than  $F_{IM,max}$ , the immobile soil fraction is set equal to 95% of the water filled soil fraction, assuming that always water remains in the mobile soil fraction as water films around the particles (Quinton et al., 2009):

$$F_{IM} = \min \left\{ F_{IM,max}, \frac{\theta_w}{\theta_{sat}} \times 0.95 \right\} \quad \text{and} \quad F_{MO} = 1 - F_{IM} \quad (4)$$

The total soil concentration  $c_s$  is given by:

$$c_s = c_{s,MO} + c_{s,IM} \quad (5)$$

Here  $c_{s,MO}$  ( $kg N_{MO} m_s^{-3}$ ) and  $c_{s,IM}$  ( $kg N_{IM} m_s^{-3}$ ) denote the concentrations of mobile and immobile  $N_2O-N$  in the total soil, respectively. For the mobile soil fraction, we assume that the concentration in the soil air is in direct equilibrium with the local concentration in the soil water, so we can write:

$$c_{s,MO} = (\alpha_R \theta_a + \theta_{w,MO}) c_{w,MO} \quad \text{and} \quad c_{s,IM} = \theta_{w,IM} c_{w,IM} \quad (6)$$

where

$$\theta_{w,MO} = \theta_w - \theta_{w,IM} \quad \text{and} \quad \theta_{w,IM} = F_{IM} \theta_{sat} \quad (7)$$

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Here  $\theta_{w,IM}$  ( $m_{w,IM}^3 m_s^{-3}$ ) and  $\theta_{w,MO}$  ( $m_{w,MO}^3 m_s^{-3}$ ) represent the immobile and mobile moisture content relative to the total soil, respectively, and  $c_{w,IM}$  ( $kg N m_{w,IM}^3$ ) and  $c_{w,MO}$  ( $kg N m_{w,MO}^3$ ) represent the concentrations of N<sub>2</sub>O–N in water in the mobile and immobile zone, respectively. The mobile and immobile soil fractions are constant during the timestep (= 1 day), but can change between timesteps. Consequently, although the total soil concentration stays the same, the concentrations in the mobile and immobile zone,  $c_{s,MO}$  and  $c_{s,IM}$ , can change between timesteps.

From Eq. (6) we can derive the CT-equation for the N<sub>2</sub>O in the mobile zone:

$$\frac{\partial c_{s,MO}}{\partial t} = \frac{\partial}{\partial z} \left( D_{\text{eff},MO} \frac{\partial c_{w,MO}}{\partial z} \right) - q_a \alpha_R \frac{\partial c_{w,MO}}{\partial z} - q_w \frac{\partial c_{w,MO}}{\partial z} - Q_{\text{dr}} c_{w,MO} + R_{\text{pr,nit}} + R_{\text{tr}} \quad (8)$$

where

$$D_{\text{eff},MO} = \alpha_R \rho_1 \theta_a^{\rho_2} D_{0,a} + \tau \theta_{w,MO} D_{0,w} \quad (9)$$

Here  $D_{\text{eff},MO}$  ( $m^2 d^{-1}$ ) is the effective diffusion coefficient for the mobile zone and  $R_{\text{tr}}$  ( $kg N m_s^{-3} d^{-1}$ ) is the exchange rate of N<sub>2</sub>O between the mobile and the immobile zone. This term can be a source as well as a sink for the mobile zone. The 2nd and 3rd terms at the right hand side of Eq. (8) for convective transport and the 4th term for drainage have not been changed compared to the original CT-equation in Eq. (1). In these terms soil heterogeneity has already been taken into account in the soil specific hydraulic characteristics and therefore it is reasonable to assign all convective and drainage flow to the mobile zone. Also the nitrification term has not been changed compared to Eq. (1), because nitrification, which requires oxygen rich conditions, is likely to occur mainly in the mobile zone.

### 2.1.3 N<sub>2</sub>O production and reduction

Denitrification is the sequential reduction of nitrate (NO<sub>3</sub>) to nitrogen gas (N<sub>2</sub>) with N<sub>2</sub>O as an intermediate. It requires anaerobic conditions, so it encompasses both

production and reduction of N<sub>2</sub>O. In ANIMO the ratio between production and reduction is determined by  $E_{af}$  (-), the electron affinity of N<sub>2</sub>O relative to the electron affinity of NO<sub>3</sub>, as well as by the concentrations of N<sub>2</sub>O and NO<sub>3</sub> in water,  $c_{w,N_2O}$  and  $c_{w,NO_3}$  (kg N m<sub>w</sub><sup>-3</sup>), respectively (Hendriks et al., 2011).

In the mobile-immobile model the production and reduction rates are calculated as:

$$R_{pr,den} = \frac{c_{w,NO_3}}{4/14c_{w,NO_3} + f_{pH} f_T E_{af} 1/14c_{w,N_2O,IM}} R_{pr,el} \quad (10)$$

$$R_{rd} = \frac{f_{pH} f_T E_{af} c_{w,N_2O,IM}}{4/14c_{w,NO_3} + f_{pH} f_T E_{af} 1/14c_{w,N_2O,IM}} R_{pr,el} \quad (11)$$

Here  $R_{pr,el}$  (kmol e<sup>-</sup> m<sub>s</sub><sup>-3</sup> d<sup>-1</sup>) is the electron (e<sup>-</sup>) production rate, and 4/14 and 1/14 (kmol e<sup>-</sup> kg<sup>-1</sup> N) express the electron equivalent ratio per molar mass of NO<sub>3</sub>-N and N<sub>2</sub>O-N, respectively. Functions  $f_{pH}$  and  $f_T$  (-) are response functions for pH and temperature (Hendriks et al., 2011). The NO<sub>3</sub> concentration is assumed to be equal in the mobile and immobile zones. The implicit assumption is that all reduction of NO<sub>3</sub> is located in the immobile zone and that the aggregates do not hamper NO<sub>3</sub> diffusion. With respect to the original ANIMO we left out the response function for the effect of aeration on N<sub>2</sub>O production and reduction. This response function reduces the ratio of N<sub>2</sub>:N<sub>2</sub>O production if oxygen is present (Hendriks et al., 2011). In the current mobile-immobile model we assume that most oxygen that is still present in the soil, is located in the mobile zone and that the effect of oxygen on the ratio of N<sub>2</sub>:N<sub>2</sub>O production is negligible. With regard to denitrification two statuses can be distinguished: organic matter limited or NO<sub>3</sub> limited. If the organic matter content is limiting denitrification, the electron production rate,  $R_{pr,el}$ , is known from organic matter decomposition and nitrification. If NO<sub>3</sub> is limiting, the production of N<sub>2</sub>O-N is equal to the reduction of NO<sub>3</sub>-N, which is calculated with a first order reduction constant,  $k_{rd,NO_3}$  (d<sup>-1</sup>) (Hendriks et al., 2011).

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## 2.1.4 Mass transfer

The transfer rate of N<sub>2</sub>O from the immobile to the mobile zone is approximated as

$$R_{tr} = k_{tr} \theta_{w,*} (\bar{c}_{w,IM} - \bar{c}_{w,MO}) \quad (12)$$

where  $k_{tr}$  (d<sup>-1</sup>) is a mass transfer coefficient and  $\theta_{w,*}$  (m<sub>w,\*</sub><sup>3</sup> m<sub>s</sub><sup>-3</sup>) is the moisture fraction of the zone with the highest concentration:  $\theta_{w,IM}$  if  $c_{w,IM} > c_{w,MO}$  and  $\theta_{w,MO}$  if  $c_{w,MO} > c_{w,IM}$ . The transfer in the model is constant over a day, and is approximated by using daily average concentrations. This equation is an approximation of diffusive transport in soil water and has often been used in mobile-immobile zone studies, like Gerke and Van Genuchten (1993). For the description of the mass transfer coefficient  $k_{tr}$  we follow Gerke and Genuchten (1993):

$$k_{tr} = \frac{\beta}{a^2} D_{0,w} \quad (13)$$

Here  $\beta$  (-) is a shape factor depending on the geometry of the aggregates,  $a$  (m) represents the distance from the center of the immobile zone to the interface with the mobile zone.

The CT-equation for N<sub>2</sub>O in the immobile zone is:

$$\frac{\partial (\theta_{w,IM} \times c_{w,IM})}{\partial t} = R_{pr,den} - R_{rd} - R_{tr} \quad (14)$$

Assuming linear change with time during a timestep,  $\Delta t$  (d), the average concentration in the immobile zone can be approximated as

$$\bar{c}_{w,IM} = c_{0,w,IM} + 0.5 \Delta t \frac{1}{\theta_{w,IM}} (R_{pr,den} - R_{rd} - R_{tr}) \quad (15)$$

Combining Eqs. (11) and (14) gives for the mass transfer rate:

$$R_{tr} = k_{tr} \theta_{w,*} \left( c_{0,w,IM} + 0.5 \Delta t \frac{1}{\theta_{w,IM}} (R_{pr,den} - R_{rd} - R_{tr}) - \bar{c}_{w,MO} \right) \quad (16)$$

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Further elaboration of Eq. (15) gives:

$$R_{tr} = \phi \left( c_{0,w,IM} + 0.5\Delta t \frac{1}{\theta_{w,IM}} (R_{pr,den} - R_{rd}) \right) - \phi \bar{c}_{w,MO} \quad (17)$$

with the mass transfer help variable  $\phi$  ( $m_{w,IM}^3 m_s^{-3} d^{-1}$ ):

$$\phi = \frac{k_{tr} \theta_{w,*}}{\left( 1 + k_{tr} 0.5\Delta t \frac{\theta_{w,*}}{\theta_{w,IM}} \right)} \quad (18)$$

5 This can be implemented in the CT-equation for the mobile zone (Eq. 8).

The transfer term has to be found with an iterative approach. The CT-equation for the mobile zone is solved numerically with a tridiagonal system of equations, conform the original ANIMO (Hendriks et al., 2011).

## 2.2 New input parameters in the mobile-immobile model

10 The mobile-immobile model has three new input parameters to describe the soil structure: the maximum immobile soil fraction of the immobile zone,  $F_{im,max}$ , shape factor  $\beta$  and the half width of the aggregate  $a$ .  $F_{im,max}$  is equal to the fraction of stagnant water in a saturated soil. Literature shows that in experimental studies this fraction in peat can be determined with nuclear magnetic resonance measurements (Culligan et al., 2001),  
15 curve fitting of measured soil water content (Price and Whittington, 2010), 2-D image analysis with resin impregnation (Hoag and Price, 1997), or 3-D X-ray tomographic image analysis (Quinton et al., 2009). In these studies values for the inactive pore fraction in peat range from 0.22–0.84. In a methane simulation model a similar parameter is used to define the immobile pore fraction for gaseous diffusion in peat, with a default  
20 value of 0.5 for non-tropical peatland (Walter and Heimann, 2000). In peat generally the immobile pore fraction increases with depth, mainly due to compression.

The value for shape factor  $\beta$  (–) depends on the type of aggregate. Values are available for a range of aggregate types and dimensions (Van Genuchten, 1985; Van

Genuchten and Dalton, 1986). Typical values range from 3 for plane-sheet type aggregates to 15 for spherical aggregates. Cubic aggregates have a shape factor comparable to spherical aggregates. Cylindrical or prismatic aggregates have shape factors around 11. Larger shape factors are calculated for cylindrical or prismatic aggregates with a limited height. Smaller shape factors are calculated for hollow cylinders.

Parameter  $a$  (m) denotes the radius of a spherical aggregate, the half-width of a plane-sheet type aggregate, or the thickness of the soil cylinder surrounding a cylindrical pore. Typical sizes for fine to coarse aggregates in the FAO soil classification (FAO, 2006) are different for the different aggregate types. Typical values for  $\beta$ ,  $a$  and  $\beta/a^2$  ( $\text{m}^{-2}$ ) are presented in Table 1, where  $\beta/a^2$  represents a combined aggregate transfer factor. The larger this factor, the more transfer between the mobile and immobile zones.

### 2.3 Observation data

Daily  $\text{N}_2\text{O}$  emission data were available for the site of Oukoop. This is a grassland site in the western part of the Netherlands used for intensive dairy farming. The annual  $\text{N}$  application is about  $350 \text{ kg N ha}^{-1}$  and is a combination of manure and fertilizer. The water level in the ditches is kept at 45 to 55 cm below the average surface level. From August until November 2006  $\text{N}_2\text{O}$ , day of year (DOY) 230 to 310, fluxes have been measured with a combination of a quantum cascade laser spectrometer and a sonic anemometer following the eddy covariance method (Kroon et al., 2007). During this period fertilizer was applied once, on DOY 257. The topsoil consists of peaty clay and clayey peat on a subsoil of eutrophic peat. In the field the soil was classified following the FAO classification system (FAO, 2006). The top layer (0–23 cm) has a fine to medium moderate granular and fine subangular blocky structure. The second layer (23–50 cm) has a coarse prismatic structure subdivided into a weak medium smooth prismatic structure. Below is a massive structure. This represents aggregate sizes of 5–20 mm in the top layer and 20–100 mm in the second layer. The main characteristics for the site are summarized in Table 2.

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## 2.4 Values for input parameters

Values for the input parameters were equal to the values used in the former simulation study for Oukoop (Stolk et al., 2011). In this study values for most input parameters were derived from observations, literature, existing databases, or the model defaults.

5 The only parameters that were calibrated were two parameters for the hydraulic characteristics, the humus and organic matter content of the start-up run in 1941, two parameters describing nitrification, and  $E_{af}$ , the electron affinity  $N_2O$  relative to the electron affinity of  $NO_3$ .

10 Values for the new input parameters of the mobile-immobile model were based on the observations of the soil structure. Shape factor  $\beta$  is set to 11 for all layers, representing a prismatic structure, with radius  $a$  of 50 mm. This set of parameters is thought to be representative for a wet soil, i.e. the conditions when denitrification occurs.  $F_{im,max}$  was set to an average value of 0.5 for all layers. At the Oukoop site peat at the surface is more humified than deeper and therefore it is not expected that immobile fraction is smaller at the surface than in deeper layers, as is the case in pristine peat soils.

## 2.5 Analyses

20 The simulated  $N_2O$  emissions with the mobile-immobile model for Oukoop were compared with the simulated emissions from the original model for Oukoop without aggregates. Simulated emissions were compared with the observed emissions and model performance was assessed with the generally used coefficient of determination  $r^2$  (–), the RMSE ( $g N_2O-N ha^{-1} d^{-1}$ ) (Neter et al., 1996), and , the RMSE normalized to the standard deviation,  $RMSE_n$  (–) (Kiese et al., 2005). Additionally, the modeling efficiency  $r_{eff}^2$  (–) (Nash and Sutcliffe, 1970) and the coefficient of residual mass, CRM (–), (Moreels et al. 2003) were determined. In case of skewed distributions, as is often observed for daily  $N_2O$  emissions,  $r_{eff}^2$  is a stricter measure than  $r^2$ . A positive value (0 to 1) for  $r_{eff}^2$  indicates that the predicted value is a better estimate of the observations than the mean. CRM is the difference between the cumulative simulated and observed flux,

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relative to the cumulative observed flux and is used to assess the model performance to simulate cumulative fluxes.

A sensitivity analysis was performed for the Oukoop model to determine the most important parameters for N<sub>2</sub>O production by denitrification, N<sub>2</sub>O reduction, and N<sub>2</sub>O emission and the difference in sensitivity of these processes between the top soil (0–5 cm) and the subsoil (5–300 cm). The parameters used in the sensitivity analysis and their ranges are reported in Table 3. For each parameter the minimum and maximum values were determined based on literature, specific for structured soils (clay and peat). The base values are the input values of the Oukoop model. A reference run was performed with all parameters at their base value. In an One-At-a-Time-analysis (Campolongo et al., 2001) each parameter was set alternately at its minimum and maximum value, keeping all other parameters constant. For each run the cumulative N<sub>2</sub>O emission was determined, as well as the cumulative N<sub>2</sub>O production and reduction for the top soil and the subsoil. The sensitivity is presented as the cumulative production, reduction and emission, relative to the cumulative production, reduction and emission of the reference run, respectively. The parameters  $\beta$  and  $a$  are taken together as  $\beta/a^2$ . The effect of the new model parameters on the emissions was evaluated.

### 3 Results

In Fig. 1 the simulated emissions for the Oukoop-site are plotted with and without the effect of aggregates. This figure clearly shows the spectacular improvement of the model to simulate the observed fluxes. The effect of aggregates on the emission is as expected: smaller peak emissions due to increased reduction, a delay in the highest peaks and higher emissions in between the peaks due to a longer storage time in the immobile zone. Generally the onset of the peak emissions has not changed. Table 4 shows the statistics indicating the performance of both models to simulate the observations. The positive value of  $r_{\text{eff}}^2$  (0.30) for the model with aggregates indicates that the simulation results even for the peak emissions are good. The simulated cumulative

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emissions for the simulation period is only slightly too high (CRM = 0.03). The annual emission for 2006 of the simulation ( $24.5 \text{ kg N}_2\text{O-N ha}^{-1}$ ) shows good agreement with the annual emission that is derived from observations ( $17.8 \text{ kg N}_2\text{O-N ha}^{-1} \pm 58\%$ ) (Kroon et al., 2010). This is more than 40% decrease compared to the annual emission simulated with the model without aggregates ( $42.0 \text{ kg N}_2\text{O-N ha}^{-1}$ ).

The results of the sensitivity analysis are presented in Fig. 2. The electron affinity  $E_{\text{af}}$  has the largest impact on the emission, followed by the aggregate transfer factor  $\beta/a^2$ . The other parameters have less effect on the emissions. The electron affinity and the mass transfer coefficient have hardly any impact on the production of  $\text{N}_2\text{O}$ , but a large impact on the reduction of  $\text{N}_2\text{O}$ , mainly in the topsoil. The same holds for the maximum immobile fraction  $F_{\text{IM,max}}$ , but the impact on the reduction of  $\text{N}_2\text{O}$  and on the emissions is smaller than for  $E_{\text{af}}$  and  $\beta/a^2$ . The coefficient for gaseous diffusion in the top layer  $\rho_2(1)$  affects both production and reduction of  $\text{N}_2\text{O}$  in the top soil and the subsoil. Interestingly, the effect in the topsoil is opposite to the effect in the subsoil. The rate constants for nitrification,  $k_{\text{ox,NH}_4}$  and denitrification,  $k_{\text{rd,NO}_3}$ , also affect both production and reduction of  $\text{N}_2\text{O}$ . The rate constant for denitrification has most effect on reduction on the top soil, whereas the rate constant for nitrification has the least effect on production of  $\text{N}_2\text{O}$  in the topsoil. The hydraulic conductivity of the top layer,  $K_{\text{sat}}(1)$ , has been added to the sensitivity analysis for its effect on the infiltration rate and the aeration status of the top layer. In ANIMO this parameter directly influences the time that the top soil is saturated, and anaerobic. It has a relatively large effect on reduction and production in the top soil. It is interesting to note that both the minimum and the maximum value for  $K_{\text{sat}}(1)$  result in lower emissions than the base value.

In Fig. 3a–c the simulated daily  $\text{N}_2\text{O}$  emissions are plotted for various values for the new model parameters  $F_{\text{IM,max}}$ ,  $\beta$  and  $a$ , respectively. A smaller immobile soil fraction (Fig. 3a) gives in general smaller emissions. Changes in  $F_{\text{IM,max}}$  do not affect  $\text{N}_2\text{O}$  production by denitrification. When the immobile soil fraction is smaller, this means that the  $\text{N}_2\text{O}$  concentration in the immobile zone is higher, resulting in more  $\text{N}_2\text{O}$  reduction to  $\text{N}_2$ .

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Less mass transfer between the mobile and immobile zone causes smaller peak emissions. In this case, less mass transfer can result from either a smaller shape factor (Fig. 3b) or a larger radius (Fig. 3c). The start of the peak emissions does not change, but the highest peaks occur 1 day later. The emissions in between the peaks are higher when mass transfer is less. The changes in peak emissions are caused by higher N<sub>2</sub>O reduction.

Figure 4 clearly shows that aggregate size has a large impact on N<sub>2</sub>O reduction. In soils with large aggregates there is more reduction than in soils with small aggregates. This in turn affects the emission; more reduction leads to less emission in soils with large aggregates, compared to soils with small aggregates (Fig. 3c). In soils with small aggregates, or in the absence of aggregates, peak emissions are therefore much higher. The difference in emissions from soils with a different shape factor can also be traced back to a difference in the reduction of N<sub>2</sub>O (not shown).

In the foregoing simulations  $\beta$  and  $a$  were changed in all three model layers. The effects on the emissions are mainly due to changes of  $\beta$  or  $a$  in the top layer; changes in  $\beta$  or  $a$  in the deeper layers hardly affect the emissions in this simulation.

## 4 Discussion

This study emphasized the importance of the physical transport processes and diffusional constraints on transport of N<sub>2</sub>O within and out of the soil. In this study we focused on the effects of soil aggregates on emission of N<sub>2</sub>O. For soils with spherical or prismatic aggregates with a radius >2 cm, the changes in the simulated emissions are considerable and therefore it is necessary to take aggregates into account in the simulation of N<sub>2</sub>O emissions. This is in line with Arah (1990), who states that simulation of denitrification in soils with aggregates >1 cm requires a model that takes spatial heterogeneity into account. Management practices like tillage or soil compaction, can have important effects on soil aggregation and on N<sub>2</sub>O emissions (Petersen et al., 2008). The results from this study suggest that simulation of the effect of this kind of

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management practices on N<sub>2</sub>O emissions requires a simulation model that accounts for the diffusional constraints on the physical transport of N<sub>2</sub>O in the soil.

The net effect of the aggregates on the emissions can be separated in two components: (1) a decrease in the peak emissions due to more reduction of N<sub>2</sub>O and (2) an increase of the “background emissions” in between the peaks due to a longer storage time. Both components contribute to the difference between the annual emission with and without aggregates (17.4 kg N<sub>2</sub>O-N ha<sup>-1</sup>) although with an opposite sign: the annual cumulative peak emissions decrease with 22.2 kg N<sub>2</sub>O-N ha<sup>-1</sup>, whereas the annual cumulative background emissions increase with 4.7 kg N<sub>2</sub>O-N ha<sup>-1</sup>. The advantage of the mobile-immobile concept for simulation of the effect of aggregates on N<sub>2</sub>O emissions, like we did in this study, is that it takes both components, decrease and delay of emissions, in account. Another advantage of this concept is that the parameterization is based on soil characteristics and that input values can be derived from observations.

The results of the sensitivity analysis (Fig. 2) show that for this study the sensitivity of the emissions is strongly related to the sensitivity of the reduction in the top soil. It is interesting to notice that reduction of N<sub>2</sub>O is more sensitive to changes in the parameters than N<sub>2</sub>O production, and has more influence on the emissions. From this we conclude that the key to understanding N<sub>2</sub>O emissions from denitrification, is understanding the reduction of N<sub>2</sub>O. The stronger impact of reduction on the top soil than in the subsoil, can be traced back to the fertilizer application on the surface at the beginning of the observation period (DOY 257).

Another interesting aspect in the sensitivity analysis is that both the simulations with minimum and the maximum value for  $K_{\text{sat}}(1)$  gave lower emissions than the simulation with the base value. Anaerobicity in the top soil is related to the saturated conductivity  $K_{\text{sat}}$ ; a low  $K_{\text{sat}}$  hampers infiltration and enhances anaerobicity and vice versa. In ANIMO the fraction of the timestep that the soil is saturated is calculated based on  $K_{\text{sat}}$  and this is used to determine the anaerobicity of the top soil (Groenendijk et al., 2005). When we translate this to the result of the sensitivity analysis, it appears

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that both minimum and maximum anaerobicity in the topsoil result in smaller emissions than intermediate anaerobicity. This is illustrated in Fig. 5a and b, showing the simulation results with a low and high saturated conductivity in the top layer, respectively, representing more and less anaerobicity due to saturation. These figures show that anaerobicity in the top layer affects the peak emissions, but not all peaks in the same way. More anaerobicity in the top soil (Fig. 5a) can cause both an increase and a decrease in the peak emissions. Around DOY 283 and 291 more anaerobicity leads to an increase in peak emissions. In these cases there is an excess of  $\text{NO}_3$  and both  $\text{NO}_3$  reduction and  $\text{N}_2\text{O}$  reduction are higher than in the situation with shorter periods of anaerobicity (Fig. 5b), but the ratio between  $\text{NO}_3$  and  $\text{N}_2\text{O}$  reduction is not affected. Around DOY 275, 278, and 296 more anaerobicity leads to a decrease in peak emissions. In these cases there is not enough  $\text{NO}_3$  to meet the potential electron production and the ratio between  $\text{NO}_3$  and  $\text{N}_2\text{O}$  reduction is affected, in favour of  $\text{N}_2\text{O}$  reduction. So, the effect of anaerobicity on the ratio between  $\text{NO}_3$  and  $\text{N}_2\text{O}$  reduction is opposite for situations with  $\text{NO}_3$  excess or  $\text{NO}_3$  shortage.

It is also interesting to note that anaerobicity of the top soil affects the onset of a peak emission, like the peak around DOY 275. If we compare the simulated emissions in Fig. 5b to the observed  $\text{N}_2\text{O}$  fluxes, the higher conductivity significantly increases the model performance ( $r_{\text{eff}}^2 = 0.50$ ), even though the soil moisture content in the top soil has hardly changed. This example shows the importance of an accurate simulation of the anaerobicity in the top soil for accurate simulation of the  $\text{N}_2\text{O}$  emissions.

In this study we have assumed that the effect of aggregates on  $\text{NO}_3$  is negligible and that the  $\text{NO}_3$  concentration is constant throughout the soil, because the diffusion coefficient for  $\text{NO}_3$  in water is ten times higher than for  $\text{N}_2\text{O}$  (Berner, 1971; Heincke and Kaupenjohann, 1999). The good simulation results do not give cause to doubt this assumption. However, as we discussed in the foregoing, the results of this study show that  $\text{NO}_3$  content can have a large effect on the ratio between  $\text{N}_2\text{O}$  production and  $\text{N}_2\text{O}$  reduction: in case of  $\text{NO}_3$  excess this ratio is relatively stable, whereas in case of a shortage of  $\text{NO}_3$  this ratio can change. Other model studies have shown

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that aggregates do affect the NO<sub>3</sub> concentrations; NO<sub>3</sub> concentrations within the aggregates are lower than in between the aggregates (Leffelaar, 1988; Arah, 1990). In soils with NO<sub>3</sub> shortage the difference in NO<sub>3</sub> concentration within and in between the aggregates might cause a major shift in the ratio between N<sub>2</sub>O production and N<sub>2</sub>O reduction, whereas in soils with NO<sub>3</sub> excess the effect of this difference is negligible. This dissimilar effect of changes in NO<sub>3</sub> content on the ratio of N<sub>2</sub>O production and reduction were reported in a field study for a wet and a dry section of a natural peatland (Roobroeck et al., 2010). It is expected that in fertilized soils the effect of aggregates on the NO<sub>3</sub> concentration does not affect the N<sub>2</sub>O emissions, whereas in unfertilized soils fertilized soils the effect of aggregates on the NO<sub>3</sub> concentration does affect the N<sub>2</sub>O emissions. Consequently, the application of the mobile-immobile model presented in this paper is limited to fertilized soils.

Still, this study showed that the current knowledge of the hydrological, biogeochemical and physical processes is sufficient to understand the observed N<sub>2</sub>O fluxes from a fertilized peatland. With the combination of these processes in the SWAP-ANIMO model combination we are able to simulate the observed fluxes without extensive model calibration. As such this model combination is a promising tool for inventories, scenario studies or more integral scientific studies. However, model evaluation so far has been limited to data series of one site only. As a next step the model should be validated for other sites with different soil type, water management, fertilizer application, or climate. A specific question that has to be addressed is how aggregates affect the N<sub>2</sub>O fluxes in areas or periods with little NO<sub>3</sub> in the soil.

## 5 Conclusions

This study showed that the current knowledge of the hydrological, biogeochemical and physical processes is sufficient to understand the observed N<sub>2</sub>O fluxes from a fertilized peatland. The results of this study strongly confirm that aggregates affect N<sub>2</sub>O emissions. As expected, aggregates increase the reduction of N<sub>2</sub>O and decrease the peak

emissions, while at the same the background emissions are higher. Implementation of the effect of aggregates highly improved the model performance to simulate observed  $N_2O$  fluxes from a fertilized soil. Reduction of  $N_2O$  is more variable than production of  $N_2O$  and in that sense the key process to understand  $N_2O$  emissions from denitrification. The effect of the changing conditions on reduction of  $N_2O$  relative to  $N_2O$  production is dependent on the  $NO_3$  content. Therefore it is expected that simulation of  $N_2O$  fluxes from an unfertilized soil should also take the effect of aggregates on  $NO_3$  into account.

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**Table 1.** Typical values for the input parameters  $\beta$  and  $a$ .

aggregate type	shape factor $\beta$ (-)	radius $a$ (cm)*	$\beta/a^2$ (m <sup>-2</sup> )
plane-sheet	3	0.05	12 000 000
		0.5	120 000
sphere/cube	15	0.25	2 400 000
		2.5	24 000
prismatic/cylindrical	11	0.5	440 000
		5	4400

\*  $a$  denotes the radius of a spherical or cylindrical aggregate, or the half-width of a plane-sheet type aggregate.

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**Table 2.** Main characteristics of the Oukoop site for the year 2006 (Kroon et al., 2010).

Soil type	clayey peat
Soil class <sup>1</sup>	Fibric rheic eutric Histosol
Mean annual temperature (°C)	11.1
Annual precipitation (mm)	767
Ground water level (cm under surface level)	0–70
Fertilizer applied (kg N ha <sup>-1</sup> )	100
Cow manure applied (kg N ha <sup>-1</sup> )	253
Annual N <sub>2</sub> O emission (kg N <sub>2</sub> O-N ha <sup>-1</sup> )	17.8 ± 58%

<sup>1</sup> soil classification according to the FAO (1998).

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**Table 3.** Ranges and base values for the main N<sub>2</sub>O parameters used in the sensitivity analysis.

Parameter		Values		
		min	max	base
$E_{af}$	electron affinity N <sub>2</sub> O relative to NO <sub>3</sub> (-)	0.1	15	10
$k_{rd,NO_3}$	NO <sub>3</sub> reduction rate constant (d <sup>-1</sup> )	0.03	0.12	0.06
$k_{ox,NH_4}$	NH <sub>4</sub> oxidation rate constant (d <sup>-1</sup> )	12	50	25
$F_{im,max}$	maximum immobile soil fraction (-)	0.22	0.84	0.5
$\beta/a^2$	aggregate transfer factor (m <sup>-2</sup> )	240	1.210 <sup>7</sup>	4.410 <sup>3</sup>
$\rho_2(1)$	coefficient for vertical gaseous diffusion in soil in top layer (-)	1.5	2.5	1.5
$K_{sat}(1)$	saturated hydraulic conductivity top layer (m d <sup>-1</sup> )	0.01	0.15	0.07



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**Table 4.** Model performance regarding the simulation of the observed daily N<sub>2</sub>O emissions.

Statistic*	Units	Model with aggregates	Model without aggregates
$r^2$	–	0.42	0.11
$r_{\text{eff}}^2$	–	0.30	< 0
RMSE	g N <sub>2</sub> O–N ha <sup>-1</sup> d <sup>-1</sup>	40	198
RMSE <sub>n</sub>	–	0.83	4.09
CRM	–	0.03	1.18

\* $r_{\text{eff}}^2$ , modeling efficiency;

RMSE<sub>n</sub>, RMSE normalized to the standard deviation;

CRM, coefficient of residual mass.

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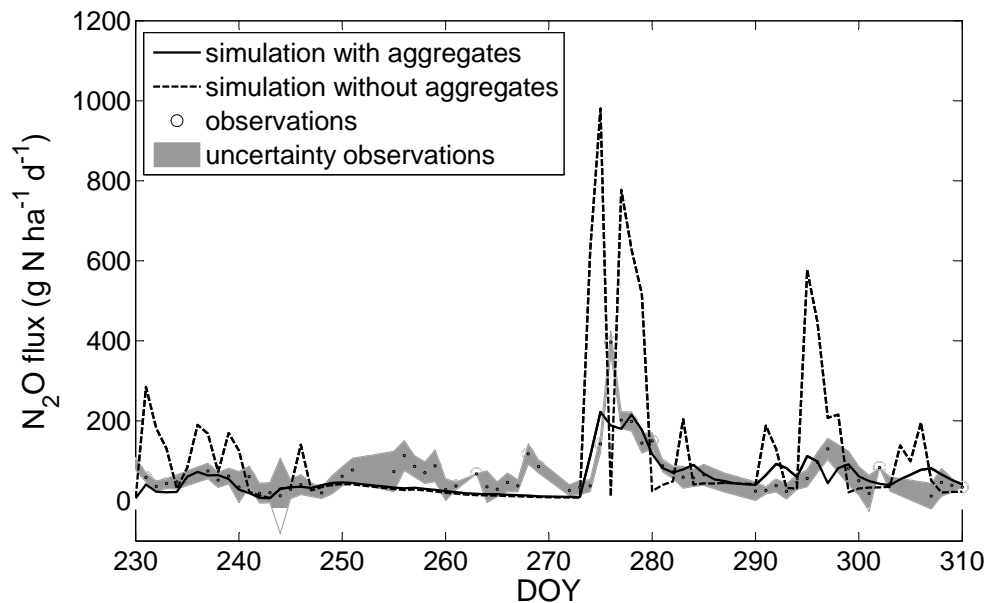


Fig. 1. Simulated N<sub>2</sub>O emissions with and without aggregates and observed emissions ± uncertainty.

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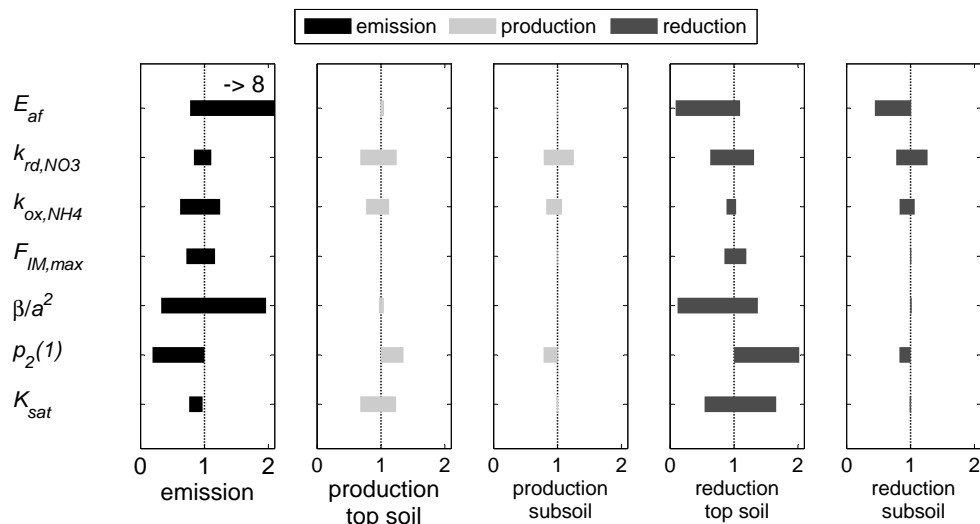
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**Fig. 2.** Results of the sensitivity analysis: range of cumulative N<sub>2</sub>O emission, production by denitrification, and reduction, relative to the cumulative N<sub>2</sub>O emission, production, or reduction of the reference run. The ranges for production and reduction are given separately for the top soil (0–5 cm) and the subsoil (5–300 cm).

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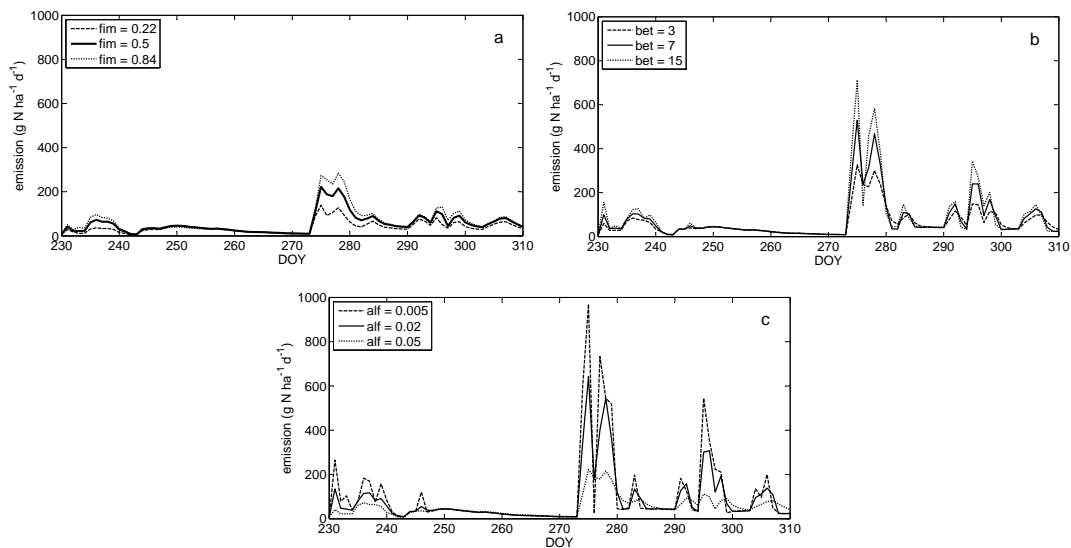
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**Fig. 3.**  $\text{N}_2\text{O}$  emission for a range of values of **(a)** the maximum immobile fraction  $F_{im,max}$  (=fim); **(b)** the shape factor  $\beta$  (=bet); and **(c)** the radius  $a$  (= alf) of a cylindrical aggregate in m. All other parameters are at their base value.

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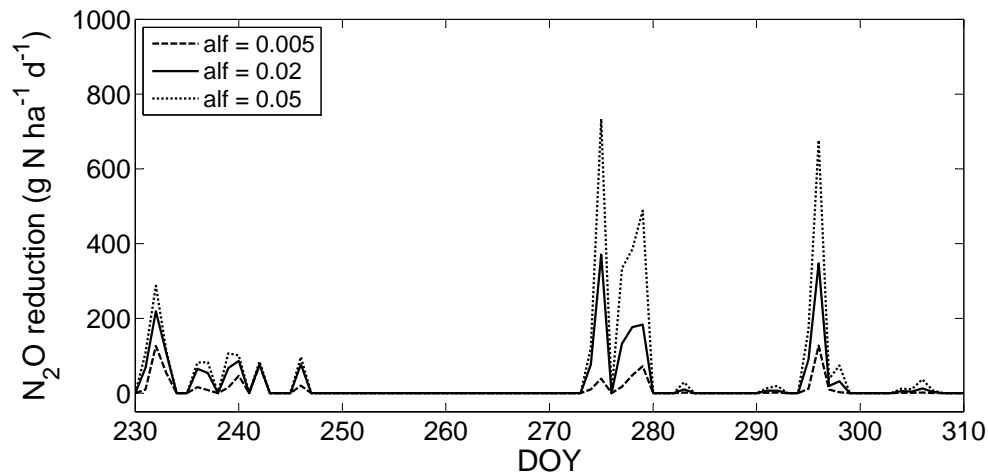
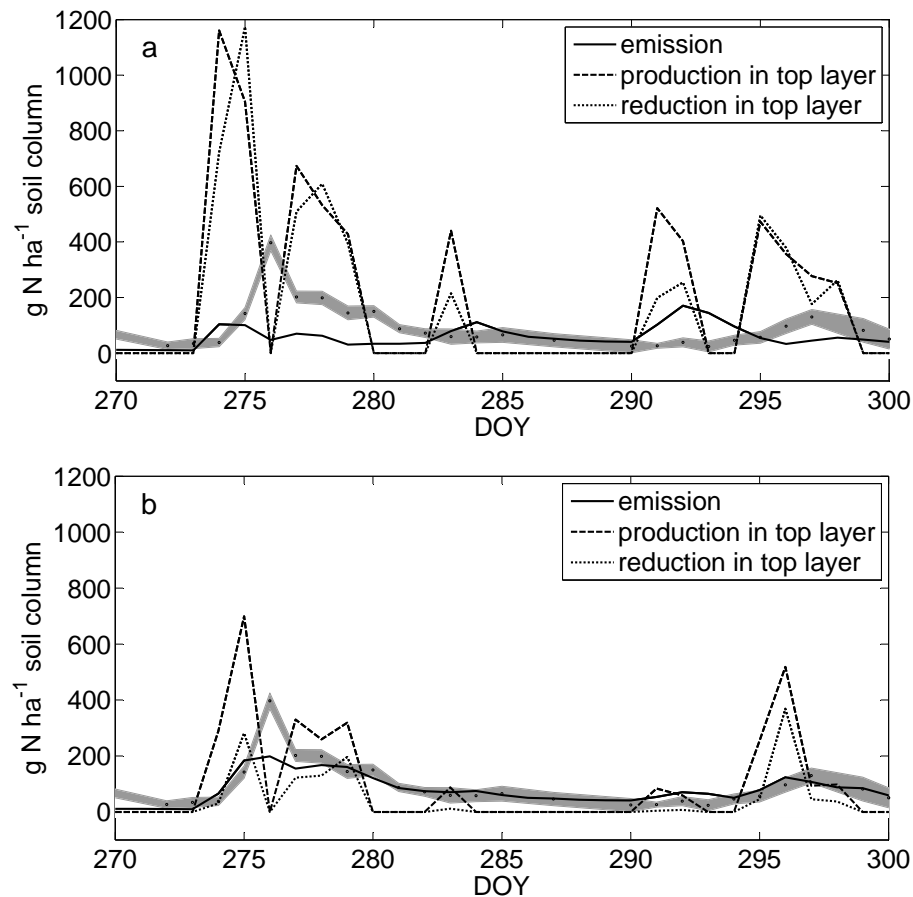


Fig. 4. N<sub>2</sub>O reduction in the top soil (0–5 cm) for a range of values for the radius *a* (=alf).

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**Fig. 5.** N<sub>2</sub>O production and reduction in the top soil (0–5 cm) and N<sub>2</sub>O emission for (a)  $K_{\text{sat}}(1) = 0.01 \text{ m d}^{-1}$  and (b)  $K_{\text{sat}}(1) = 0.15 \text{ m d}^{-1}$ .