Reply to the referee comments on "The effect of aggregates on N2O emission from denitrification in an agricultural peat soil", by P.C. Stolk et al.

First of all, we would like to thank the referees for their detailed reviews and constructive criticism that will help to improve the manuscript. Below, we will address the comments of each referee separately. In the revised manuscript we will change the text based on the comments of the referees. Purely textual comments are not addressed here, they will be changed in the revised manuscript.

Reply to the comments by R. van Genuchten

1. a. Eq. 1: The air and liquid flow velocities are spatially dependent and should appear within the partial derivative.
   b. Eq. 1: Q_{dr} is the lateral discharge to drainage systems or surface water and is calculated for each layer separately. This will be explained in the text.
   c. We will remove c_a from the text. Bunsen's solubility coefficient is derived from Henry's constant to partition N2O between the liquid and air phase, following Sander (1999).
   d. and e. The physical dispersion term is replaced by a mathematical dispersion term. The convection/ dispersion equation with the mathematical dispersion coefficient is solved by means of a pseudo-analytical method. The computation scheme yields numerical dispersion by means of spatial discretization and temporal discretization and the assumption of time averaged constant concentration values within a time interval. A more detailed description is given by Groenendijk et al. (2005), p. 34/35.

2. The report we refer to is still in preparation. Publication is foreseen this year; therefore we would like to keep this reference. To assure that the reader has access to the information, we will add an appendix with the relevant equations for this paper, like the denitrification module and the O_2 module.

3. a. In ANIMO the transport equation in the mobile zone is solved for daily average values. Therefore also the average concentration is used in the immobile zone. From these values the concentrations at the end of the timestep are derived.
   The production and reduction in the immobile zone are calculated based on the average concentrations of N2O and NO3 of the same timestep. Therefore it is difficult to express the average concentration in the immobile zone in terms of its value at the previous timestep. Instead, we use an iterative approach: 1) estimate the average N2O concentration in the immobile zone 2) determine production and reduction of N2O 3) determine the transfer rate as a function of the average concentration in the mobile zone (Eq. (15)) 4) solve the transport equation for the mobile zone 5) determine the amount of mass transfer, based on the calculated average concentration in the mobile zone 6) determine the N2O concentration in the immobile zone, based on the amount of mass transfer. This schedule is repeated as long as the concentrations in step 1 and 6 do differ significantly.
   b. The transport equation for the mobile zone is solved based on the daily average values for all parameters. It is solved using a tridiagonal system of linear equations, with the TRIDAG routine (Press et al., 1989, p. 40/41). Therefore, the mass transfer is evaluated halfway the timestep, as is the concentration in the immobile phase. The concentrations at the end of the timestep are evaluated in a second step.
   As suggested by the second referee, we will separate more clearly between the governing equations and the numerical elaboration. we can send the full numerical elaboration upon request.
   c. It should be eqs. (12) and (15) instead of eqs. (11) and (14).
   d. The mass transfer rate is expressed relative to soil volume (kg N m^{-3} soil d^{-1}). Also, the mobile and immobile soil water content are expressed relative to the total soil volume. The mass transfer should be equally large, but with an opposite sign, for the immobile zone and the mobile zone. If we would use the immobile soil water content for the CT-equation in the

immobile zone, and the mobile water content for the CT-equation in the mobile zone, the mass transfer rate would not be equal. Therefore we cannot change this in the manuscript.
e. The mobile-immobile approach was implemented in ANIMO, only for the N2O denitrification module. Mass balance calculations for single layers and for the total soil profile showed no errors.

5. The second referee also suggests leaving out the description of various concepts to include soil structure in simulation models. Our aim was to show how our paper is related to historical work done on denitrification and soil structure, and to explain why we decided to use the mobile-immobile concept. The main reason to choose for the mobile-immobile approach is that it uses parameters that can be derived from observations, without extensive calibration. A main disadvantage is that in ANIMO, for aerobicity, a pore model is used to account for soil structure. In the revised manuscript we will shorten this paragraph and focus more on the points we mentioned above.

7. Page 8, l. 8: The maximum fraction of immobile water is determined from the immobile water in saturated soils. The amount of stagnant water in unsaturated soils does not give information about the maximum fraction of immobile water.

8. Page 8, Eq. 4: The factor 0.95 is quite arbitrary indeed, and is mainly introduced to prevent zero water content in the mobile zone and subsequent numerical problems. There is evidence that water remains in the soil as films around particles, but we could not find publications that quantify the amount of water in these films. However, when water filled pore space is less than the maximum immobile fraction, it is not likely that anaerobic conditions are present for denitrification. The mobile-immobile concept is only implemented for N2O production and reduction by denitrification. Therefore the N2O emissions are not affected by this value.

10. Page 12: In this section we describe the full range of the values for the input parameters for peat soils. The values we use in the simulation are based on the soil description that is given on Page 13. The soil in the experiment in this study is a drained clayey peat soil and might have properties of both peat soils and clay soils. The mobile-immobile concept will work for both soil types and to better connect to the soil in the experiment in this study we will add the ranges for the input values for clay soils as well.

Reply to comments by J. Léonard

The referee mentions there is a similar conceptualization in DNDC. Both DNDC and ANIMO base the production of N2O by denitrification on the anaerobic fraction of the soil. There is difference regarding the residence time in the soil and the subsequent reduction of N2O: DNDC takes the effect of the extent of anaerobic microsites into account, whereas the new ANIMO version takes the effect of the physical aggregation of the soil into account. It would be interesting to compare both concepts (in another paper).

The referee suggests changing the title of the paper. We will follow the advice of the referee and change the title to “Modelling the effect of soil structure on N2O emission from a clayey peat soil with a mobile-immobile approach.”

We will follow the advice of the referee to add a figure about the model concept in section 2.1.2 where we explain the mobile-immobile approach in general. We think it is better to first introduce the old ANIMO model and the general way the transport equation and diffusion are modelled, before introducing the mobile-immobile concept. In the revised manuscript we will better separate the equations explaining the mobile-immobile concept and the numerical elaboration in ANIMO.

The report and paper explaining the original ANIMO are still in preparation. To overcome this problem and to assure the readiers will have access to all relevant background information we will add an Appendix with relevant equations and values for input parameters.

The referee requests a more in-depth comparison between the original and new model. We think all relevant aspects have been covered. Nitrification and denitrification rates have not been changed, only reduction and emission have been changed in the new model. The effect on emission is clear in Figure 1. To highlight the effect of the aggregates on reduction, we can add this as a fourth line in Figure 4.

In the period between doy 250 and 270 N2O production by denitrification takes place in the subsoil, in layers with wfps > 0.998. Nearly all N2O that is produced stays in solution and only little is released to the atmosphere. This is the same in both the new and the old model. In the new model part of the N2O is present in the mobile zone, and 'protected' against reduction. In this case the mass transfer coefficient determines how much N2O is transferred to the immobile zone, where reduction takes place, and how much N2O remains in the mobile zone. In the new model the N2O emissions in this period are slightly higher. We will address the differences between the topsoil and the subsoil in the revised manuscript.

Answers to the additional questions and comments:

- The parameters of the new model have not been changed, compared to the old model. The calibration procedure we describe in the text refers to the calibration of the old model. In the old model the N2O module was calibrated on the fluxes in between the peaks, and on the N2O concentrations. This fit was reasonably well in the old model and it was not to be expected that these fluxes would change much in the new model. To better compare the old model with the new model, we decided not to calibrate the new model. Even the new input parameters have not been calibrated based on the fluxes, but values were taken from literature or observations.

- For quantitative evaluation of the differences between simulated and observed fluxes, several measures are used. All measures have advantages and disadvantages, therefore we decided to use five different measures. R^2 and RMSE are the most common measures and are added for this reason. The modelling efficiency, r^2_{eff}, has the advantage above r^2 that it checks if the observations match the simulations, whereas r^2 only checks for linearity. $RMSE_n$ has the advantage above RMSE that you can compare this value among different datasets. The coefficient of residual mass, CRM, has the advantage that it compares the total emission. A time lag between observations and simulations has no effect on CRM.

- 3255 l. 8-10: we agree with the referee that background emissions and peak emissions are both important considering total emissions. The sentence in lines 8-10 does not exclude this, but the focus of the paper is on the peaks. For background emissions a model with a weekly or monthly timestep would be sufficient. For peak emissions however, it is essential to have a model with a timestep of a day or less.

- 3256: See referee 1, point 5.

- 3257 l.4: In the multi-domain approach several domains can be distinguished, each having a different flow velocity. A two-domain approach ("dual-porosity") is the most common one.

- 3258 l. 16-17: we will include details on aeration module in an Appendix.

- 3260 l. 2-3: Vertical gas and water transport is combined, as is shown in Eqs. (1) – (3).

- 3260 l. 7-8: *T*he mobile and immobile soil fractions are determined from the average daily soil moisture content. They are assumed to be constant over a day, but can change between timesteps. If the mobile and immobile zones change, the local concentrations in the mobile and immobile zone at the start of a timestep, *$c_0(t)$*, are different from the concentration at the end of the timestep the day before, *$c_{end}(t-1)$*. However, the total soil concentration does not change between timesteps. If the immobile zone increases between timesteps, the concentrations at the start of the timestep are given by:

  $$c_{0,\mathrm{w,MO}}(t) = c_{\mathrm{end,w,MO}}(t-1)$$

  $$c_{0,\mathrm{w,IM}}(t) = \left(c_{0,\mathrm{s}}(t) - c_{0,\mathrm{w,MO}}(t)\cdot\left(\alpha_{\mathrm{R}}\cdot\theta_{0,\mathrm{a}} + \theta_{0,\mathrm{w,MO}}\right)\right)\cdot\frac{1}{\theta_{0,\mathrm{w,IM}}}$$

  If the immobile zone decreases between timesteps, the concentrations are given by:

  $$c_{0,\mathrm{w,IM}}(t) = c_{\mathrm{end,w,IM}}(t-1)$$

  $$c_{0,\mathrm{w,MO}}(t) = \left(c_{0,\mathrm{s}}(t) - c_{0,\mathrm{w,IM}}(t)\cdot\theta_{0,\mathrm{w,IM}}\right)\cdot\frac{1}{\left(\alpha_{\mathrm{R}}\cdot\theta_{0,\mathrm{a}} + \theta_{0,\mathrm{w,MO}}\right)}$$

- 3260 l. 8-9: Stagnant = not participating in vertical transport.

- 3262 eq. 10 and 11: This is outside the scope of this paper and will be addressed in the report and paper describing the original ANIMO.

- 3262 l. 12 We will address this assumption earlier in the text, in Section 2.1.2, the general description of the mobile-immobile approach.

- 3262 l. 19-24: The model calculates the potential anaerobic respiration and the potential denitrification based on NO3. These are compared, to determine if OM is limiting or NO_3.

- 3625 l. 26-28: The soil is described in a pit and on four locations with augering, following the guidelines for soil profile description from the FAO (FAO, 1990).

- 3266: The parameters are the same for the old and the new model, the calibration procedure explained refers to the old model. Calibration was done for the entire dataset. No validation was performed, because the calibration failed.

- Figure 1: This figure is used to compare the two simulations and the observations. Therefore the y-axis should match the maximum flux from either data source.

Discussion:

- We would like to stress that we did not calibrate the input value for aggregate size. We used the largest value from field observations, assuming that to be representative for wet conditions when denitrification occurs. We believe that default values for aggregate size and shape can be derived for various soil types, which makes the model easily applicable for other sites and larger scales, or to derive simplified models that take soil structure into account.

Reply to comments by R. Grant

1. The aggregate module is an extension of the existing SWAP-ANIMO model combination. The greenhouse gas module in ANIMO works with a daily time step. The main objective of the greenhouse gas module in ANIMO is to determine the budgets for longer periods or scales. A common temporal pattern for N2O fluxes is low background fluxes and a few high peaks. In general, these peaks last longer than one day. To determine the cumulative N2O flux, it is essential to capture the peaks. Because most peaks last longer than one day, using a daily timestep is appropriate to determine the flux over a longer period.

   The daily fluxes in this study are daily averages of 30 min fluxes, when more than 12 flux observations were available. The uncertainty in the 30-minute fluxes can be larger than the flux itself. This uncertainty is reduced by averaging the fluxes over a longer time span (Kroon et al., 2010a). Kroon et al. (2010b) tested this for the observations and could find a clear diurnal variation.

   The question remains if it is appropriate to simulate average daily fluxes with average daily drivers. This is only justified if the average daily driver is representative for the average daily flux. This is the case if the driver and fluxes are linearly related, or if the diurnal temporal pattern is similar. Soil water content is not linearly related to N2O emissions; denitrification will only start if the soil moisture content passes a certain threshold value. Modelling with a daily timestep is hampered when soil water content is above the threshold for only part of the day. When the peak emission lasts longer than one day, this can cause a time lag between simulated and observed emissions. When the peak emission lasts less than one day, the peak can be missed completely in the simulation. This can be the case for example during precipitation events, when the surface can be saturated for a short period of time. To account for this, ANIMO calculates the partial temporal anaerobicity in the top soil, based on precipitation surplus and hydraulic conductivity. In deeper layers this is less of a problem, because soil water content changes over a day are smaller. Another example where peak emissions last shorter than one day, is during soil thawing at daytime, when during the night the soil is still frozen. ANIMO, with a daily timestep, is not appropriate for this type of simulation, but such simulations are not performed in the present study.

2. We will add an appendix with the relevant equations for the denitrification module and the O_2 module (see replies to Ref 1 and 2 as well). The immobile zone is assumed to be completely anaerobic.

3. We will add figures of precipitation and observed and simulated soil water content to Figure 1. Also, we will add markers in the figure of N2O emissions to show the times of fertilizer application.

4. As shown in Figures 2 – 4, the model outcome is very sensitive to the value of *a*. At the fieldsite a pit has been dug to describe the soil properties. The soil structure has been described according to the FAO guidelines for soil description (FAO, 1990), like we described in Section 2.3. In the simulations the largest value for the aggregates has been used, that is found in the deeper soil layers, without any calibration. This value is thought to be representative for very wet soil conditions, when denitrification takes place.

5. In the revised manuscript we will pay attention to distinguish more clearly between model and experimental findings.

6.

Reply to specific comments:

Abstract

3254 l.12: We do mean aggregates in the model

3254 l. 15-16: The ratio of N2O reduction to NO3 reduction depends on the anaerobicity of the soil and the NO3 content. When NO3 is abundant, this ratio will not change under more anaerobic conditions, but when there is shortage of NO3, this ratio will increase.

Introduction

Method

l. 3258 l. 11-14: See point 1

l. 3259 Eq. 1: The average daily Bunsen coefficient is adapted for the average daily temperature.

l. 3260 Eq. 4: The parameter 0.95 is hard-coded. In this soil, the N2O fluxes are not sensitive to this parameter. See reply to Rev. 1 as well.

3262 Eqs. 10 and 11: The electron equivalent ratio is expressed per mole NO3-N and N2O-N. If it was expressed per mole NO3 and N2O, the ratio would have to be 2/14 and 4/14, respectively.
I will add a more extensive explanation of the O2 module in an appendix.

3262 l. 11-12: In the revised manuscript we will mention here that we will come back to this assumption in the discussion section.

3262 l. 16-19: When adopting this hypothesis, we assume that the measured effects of O2 on the N2O:N2 ratio are related to the average O2 content of the soil. Part of this effect will be explained by the division of the soil in a mobile zone, with oxygen, and an immobile zone, with less oxygen. As such, dividing the soil in a mobile and immobile zone, already captures the O2 effect on the N2O:N2 ratio.

3262 l. 22-24: The delay between NO3 reduction and N2O production is one of the steps that could contribute to the rapid onset of the emissions. Another possibility is the reduction of alternative electron acceptors that have not been accounted for in the model.

3623 Eq. 12: We adopted this equation, because the diffusion between the mobile and immobile zone is purely based on the aqueous concentration difference between the mobile and the immobile zone. The soil moisture content is there for book-keeping purposes: no more N2O can leave one zone, than there is present there. See also the reply to Ref. 1.

3623 Eq. 13: The parameters β and a are constrained by the physical appearance of aggregates, as is shown in Table 1. In the code we must prevent the concentrations to become negative. In some cases this means that less than the maximum amount of N2O is transported between the mobile and immobile phase.

3263 l. 20: we mean eqs. (12) and (15).

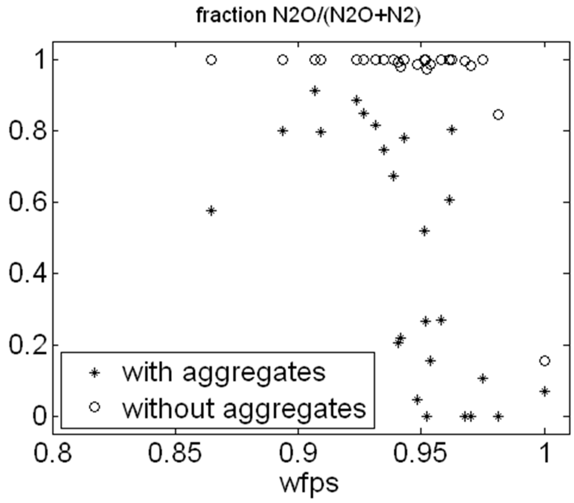
3264 l. 7: The transport equation for the mobile zone is solved based on the daily average values for all parameters. It is solved using a tridiagonal system of linear equations, with the TRIDAG routine (Press et al., 1989, p. 40/41). Therefore, the mass transfer is evaluated at a half time level, as is the concentration in the immobile phase. The concentrations at the end of the timestep are evaluated in a second step. See also the reply to Ref. 1

3265 l. 17-20: The daily fluxes in this study are daily averages of 30 min fluxes, when more than 12 flux observations were available.

Results

3267 Fig. 1: See questions 1 and 3. Total N2O + N2 production is larger in the new model with aggregates. Production of N2O in the new model is less than in the old model, but reduction of N2O is larger than in the old model.
The fraction N2O/(N2O+N2) that is formed in the top soil in the old and the new model is shown in the figure below. Note that the fraction N2O/(N2O+N2) is not only dependent on wfps, but also on the amount of N2O present. If wfps would be equal, the first day of a peak emission the fraction N2O/(N2O+N2) would be higher than the second day because no N2O is present the first day.

This fraction cannot be inferred from Figures 3- 5.



3268 Fig. 2: we agree with the referee that it is helpful to indicate the direction of the relationship between model inputs and inputs. We will add this in Figure 2 in the revised manuscript.

3269 Figs. 3, 4: See question 4.

3269 l. 7-14: A few experiments have considered the effect of aggregates on denitrification (Miller et al., 2009; Drury et al., 2004; Seech and Beauchamp, 1988), but these experiments all blocked reduction of N2O to N2. To the best of our knowledge, no experiments have been performed where N2O and N2 production have been studied in relation to aggregate size.

Discussion

3269 l. 25-27: we agree with the referee that management practices like tillage or soil compaction strongly affect diffusion. Apart from that, they also affect the aggregation of the soil, which adds to the effect on N2O emission.

3271 Fig. 5: See question 4.

References

Drury C.F., Yang X.M., Reynolds W.D., Tan C.S. (2004) Influence of crop rotation and aggregate size on carbon dioxide production and denitrification. Soil and Tillage Research 79:87-100.

FAO. (1990) Guidelines for Soil description, Food and Agriculture Organization of the United Nations, Rome, Rome, Italy.

Groenendijk P., Renaud L.V., Roelsma J. (2005) Prediction of Nitrogen and Phosphorus leaching to groundwater and surface waters; Process descriptions of the ANIMO 4.0 model, Alterra, Wageningen, p. 34/35. Available at http://www.animo.wur.nl/.

Kroon P.S., Hensen A., Jonker H.J.J., Ouwersloot H.G., Vermeulen A.T., Bosveld F.C. (2010a) Uncertainties in eddy covariance flux measurements assessed from CH_4 and N_2O. Agricultural and Forest Meteorology 150:806-816. DOI: doi:10.1016/j.agrformet.2009.08.008.

Kroon P.S., Schrier-Uijl A.P., Hensen A., Veenendaal E.M., Jonker H.J.J. (2010b) Annual balances of CH_4 and N_2O from a managed fen meadow using eddy covariance flux measurements. European Journal of Soil Science 61:773-784. DOI: 10.1111/j.1365-2389.2010.01273.x.

Miller M.N., Zebarth B.J., Dandie C.E., Burton D.L., Goyer C., Trevors J.T. (2009) Denitrifier Community Dynamics in Soil Aggregates under Permanent Grassland and Arable Cropping Systems. Soil Sci Soc Am J 73:1843-1851. DOI: 10.2136/sssaj2008.0357.

Press W., Teukolsky S., Vetterlinkg W., Flannery B. (1989) Numerical recipes, The art of scientific computing (Fortran Version) Cambridge University Press, UK.

Sander R. (1999). Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry (version 3*)*. Available at http://www.henrys-law.org (verified 10 November 2010).

Seech A.G. and E.G. Beauchamp (1988). Denitrification in soil aggregates of different sizes. Soil Sci Soc Am J 52:1616-1621.