This paper addresses important issues related to N_2O emissions from peat soils. The authors show that the presence of relatively immobile water pockets in soils can significantly alter the reduction of N_2O, thereby lowering peak emissions of N_2O into the atmosphere, while increasing long-term background emissions. The proposed new modeling appears to be a major improvement over earlier models in which homogeneity is assumed in the nitrogen (especially N_2O) dynamics across all parts of the porous medium. As such, I like to see this paper being published.

At the same time I have several concerns which I believe need to be addressed. Below are a few major questions about the proposed model formulation. I also believe that the paper could be written in a more concise manner, and would benefit from some English editing. I will address both separately.

1. I have several questions about the governing equations. Equation (1) shows the transport equations used for N_2O. Some issues I am struggling with:
    a. The equation governs advective-dispersive solute transport in a soil profile. Since the air and liquid flow velocities are spatially dependent, should q_a and q_w not appear within the partial derivatives (i.e., $\partial q_w c_w/\partial z$ rather than $q_w \partial c_w/\partial z$, etc).
    b. How exactly is Q_{dr} defined? Is this the rate of vertical drainage from the bottom of the soil profile? If so, this is a boundary condition and should not be in the transport equation.
    c. Equations (1) and (8) does not contain c_a, so there seems to be no need to define the air phase concentration. Is Bunsen's coefficient used to model equilibrium partitioning between the liquid and air phase concentrations of N_2O (like Henry's constant)?
    d. Equations (3) is based only on diffusion in the liquid and air phases. Why is dispersion not included?
    e. Similar questions hold for Equations (8) and (9).
2. Equations (10) and (11) may need some explanation. Are these equations explained in Hendriks et al. (2011)? I could not find this reference on the ANIMO home page (http://www.animo.wur.nl/ANIMObibliography.htm).
3. I am confused on how the mass transfer process is implemented (section 2.1.4). Some questions here:
    a. The mass transfer dynamics and N_2O accumulation in the immobile phase is treated here independently of the dynamics in the mobile phase, perhaps in a time explicit (time-delayed manner). Should the immobile transport equation not be solved simultaneously with the transport equation for the mobile phase? This since $c_{w,MO}$ is also a function of time, like $c_{w,IM}$. An efficient way of solving the two equations simultaneously (i.e., equations (8), (12) and (14) is to (a) use finite difference schemes for the time derivatives of both transport equations, (b) solve

(12) and (14) for $C_{w,IM}$ at the new time level in terms of its value at the old time level and the values of $C_{w,MO}$ at the new and old time levels, and (c) substitute the resulting expression for $C_{w,IM}$ at the new time level in the temporal difference equation of Eq. (8). Once (8) for $C_{w,MO}$ in whatever numerical manner spatially, this value is substituted back in the equation for $C_{w,IM}$ as a function of $C_{w,MO}$ and the other variable. The approach requires only two extra lines of coding as compared to when only mobile water transport is considered (the classical transport equation). The method does not affect how the spatial terms of (8) are treated numerically (finite difference or finite element, or whatever procedure is implemented). The approach is described in more detail in the manual of HYDRUS-1D (Simunek et al., 2005).

b. Equation (15) appears to be an explicit-in-time finite difference approximation of Eq. (15). This since it likely uses values of the various coefficients (the θ's and R's) at the old time level. Perhaps the explicit approximation is considered good enough (as opposed to using a more refined Crank-Nicolson scheme? But I do not understand why the concentration of the immobile phase is evaluated at only the half time level, not at the new time level. In other words, why using a factor of 0.5 in Eq. (15)?
c. Equation (16) must have been obtained by combining equations (12), not (11), and (15), and solving for R_{tr}.
d. If the transport equations for the mobile and immobile regions are treated simultaneously, there is really no need to define θ_w in Eq. (12) as a function of the direction of the mass transfer process (i.e., being the water content of the mobile zone if the rate is positive, and the water content of the immobile zone if the rate is negative). The mobile water content should be used along with the transfer rate in the transport equation for the mobile phase, and along with the immobile water content in the transport equation for the immobile phase.
e. In conclusion, the authors here have a challenge to explain in more detail how the immobile liquid phase dynamics for N_2O was implemented in ANIMO. Or was this done in the SWAP part of the combined model? Right now it seems that - again - the dynamics of the immobile domain is treated completely independently (and explicitly in time) of the dynamics in the mobile region. Maybe it is all done correctly, but I am nevertheless a bit concerned. Inaccurate calculations usually (but not always) show up in mass balance calculations for the solute species involved (N_2O and maybe other N species considered in ANIMO). As such, where any mass balance calculations carried out for the entire profile for the various N species?

4. The paper needs some careful editing. I made quite a few edits on a copy I printed, but struggled with the BG web page on how to include my suggestions directly in some copy

of the paper. Should I have used the "Source" file for this? In any case, my suggestions were all seemingly a bit silly, but overall I trust should improve the readability of the paper. Here are just a few examples of the first few pages:

a. Page 2, line 3. ".. lasting a few days to several weeks, and with low background concentrations".
b. Page 2, line 7. In this paper we study .. and present…" . Use the presence, like you did on page 5, lines 21-25. ("we compare, etc.). In general in the paper, however, it is best to use <u>past</u> grammar for whatever research you did and what you found, but to use grammar in the present for what you think it means.
c. Page 2, line 11. " ..peat soil under grass."
d. I noticed several pieces of text (especially in the beginning) were taken literally from the VZJ paper by Stolk et at. (2011).
e. Page 3, line 10. "When modeling N_2O emissions, accurate…"
f. Page 3, line 12. " …with time steps as small as one day or less."
g. Page 3, line 19. "This difference was thought to be due to the incorrect assumption…"
h. Page 3, line 21. "…aqueous phase of structured soils".

Some other comments:

5. The descriptions on page 4 of the pore, aggregate and fractal models have little bearing on how simulation models can use soil structure for modeling nonequilibrium transport. I probably would leave all this out, and immediately go to the multi-domain approach (or better: the "dual-porosity" approach) on page 5, line 4.
6. Page 6, line 24. "… applicable to soils in the Netherlands, and to comparable soils, without …"
7. Page 8, line 8. I would remove this sentence. Part of water in unsaturated structured soils may also be immobile.
8. Page 8, Eq. (4). Why a factor 0.95? Seems quite arbitrary.
9. Page 10, line 19. "… two situations can be …".
10. Page 12. Peat soils are known to contain lots of immobile water. But the structure of peat soils is generally quite different than that of mineral soils (including clay soils). My experience (with organic soils from the Delta in California) is that nonequilibrium flow in peat soils occurs mostly along individual pipes (like cylindrical macropores), which would suggest very small values for β/a^2.
11. Page 13, line 11. "… the more rapid the transfer between …".
12. Page 13, line 18. Move N_2O from after " 2006" to before " fluxes"
13. Page 13, line 26. Use something like "Deeper horizons showed a more massive structure"
14. Page 14, line 3. "In that study…"

15. Page 15, line 20. I know you are very enthusiastic about the results (and probably rightly so). But I would still use a more modest term here like “dramatic”, rather than “spectacular”.
16. The discussion section (starting on page 17) is pretty long and wordy, and somewhat repetitive. Why not shorten things a bit and combine with the results part?
17. Page 20, lines 16, 20, 24. On line 16, please change “are able” to “were able”. This may seem like a small change. But it has more meaning. You were able to show significant improvements for your study involving one particular clayey peat soil. There is no guarantee that other soils or other people will find similar results. Actually, you mentioned on line 20 yourself that the model concepts should be tested on different soils and for different management practices. As such, be careful also with the first sentence of the conclusions, which generalizes too much again. The conclusions hold only for your study, your soil, your fertilization program, your climate, your …. etc, etc.

In conclusion, this paper definitely needs to be published. It constitutes a very significant contribution. However, the paper may need a bit more work in terms of the model description, and also editorially.