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Author responses to comments of Referee #1

We would like to thank the referee for the effort and time they put in to comment on our manuscript. We are grateful for their comments and will make every attempt to fully address these comments in the revised manuscript.
In the following list, the points raised by the referee are written in bold characters, whereas our responses are shown in regular characters.

General Comments:

This study determined the gas diffusivity of forested peat and extracted the macropore networks from µCT images of peat to simulate the gas diffusion along the networks. The authors highlighted that the combination of the µCT and pore networking modeling provide reliable estimation of gas diffusivity of peat. This is a very interesting story because our understanding of the pore structure of fen peat as well as the gas diffusivity is indeed quite limited. The novelty of the manuscript is high and it is well written. But a moderate revision is necessary before publication:

My major concerns are:

1. The pore structure of peat is missing and the discussion is a little weak.

The authors analyzed the pore structure of peat but the pore features (e.g. tortuosity, pore connectivity, pore size distributions) are not shown and discussed. These parameters are quite important for gas diffusivity but were only mentioned in several sentences during discussion (e.g. line 413). I think the quality of the manuscript will be improved greatly if the authors could give solid discussion based on the parameters derived from peat soils. Maybe the authors have published this information previously, still a summary of these parameters is necessary.

We agree that macropore network connectivity and other pore network features are significant issues in the gas diffusion capability of soil. In Kiuru et al. (2022), we have determined and presented network metrics for the pore structure of the same samples that were used in the gas diffusion measurements and simulations in this study. However, because of the shrinkage of the samples and computational limitations, connectivity metrics were calculated for subsamples, which were then assumed to be representative for the corresponding total sample volumes. Therefore, the network metrics and the measured diffusivities are not directly comparable. We will summarize the results on macropore size and network connectivity metrics in Discussion (Sect. 4.1).

2. The shrinkage information is unclear.

One unique property of peat is “shrink-swell”, which is much greater than mineral soils (e.g. clay). This is also the reason that our understanding of the gas diffusivity of peat is limited. The authors indicated that the gas diffusion measurement may be affected by soil shrink. I think it is necessary to provide more detailed information on soil shrink: percent of volume change and at which pressures and for which soils the gas diffusion values are less affected by soil shrink.

The vertical shrinkage of the samples was measured after the diffusion experiment (at -10 kPa matric potential conditions), and the results are presented in Kiuru et al. (2022). The presence and amount of horizontal shrinkage could be roughly estimated from the micro-computed tomography images. The shrinkage and its effect on diffusion properties was considered negligible at higher matric potentials. We will add information on the measured sample shrinkage and on the observations of shrinkage properties in the Results section.

Specific comments:

1. line 12, this conclusion is unclear. From table 1, for top soil (0-5 cm) the gas diffusivity is high at -1 kPa, but the air-filled porosity is also high 30 vol%. This is not near saturation. For deeper peat (40-45 cm), the gas diffusivity is low though it is more near saturation.

The measured relative diffusivity values were greater than 0.01, mostly greater than 0.02, at air-filled porosity less than 0.1 $m^3 m^{-3}$. Measurements of gas diffusion in mineral soil have given lower values for relative diffusivity near saturation (Moldrup et al., 2004), and all the studied gas diffusivity models predicted a relative diffusivity of less than 0.01 at an air-filled porosity less than 0.1 $m^3 m^{-3}$. Therefore, the measured gas diffusivity was higher than the diffusivity model predictions and higher than that of many mineral soils, so we conclude that the diffusivity was relatively high compared to mineral soils or model predictions and that it was not extremely low even in wet conditions. We will clarify the wording in the text.

2. line 14, or you mean the traditional gas diffusivity models?

Yes, we mean the traditional or conventional, commonly used gas diffusivity models mentioned in line 11. We will change the wording.

3. lines 37-39, “unsaturated” is a quite wide range. I would suggest using “when soil moisture is high”.

Because the water table is rather close to the soil surface in undrained peatlands, it is often assumed that soil moisture is high in unsaturated peat, and therefore, it is not considered necessary to refer to high-moisture unsaturated peat in particular in the literature. However, near-surface peat may occasionally be drier in drained peatlands. We will clarify the wording as suggested.

4. lines 48-50, not true. Or you could refer to “natural peat” or “pristine peat”. For degraded peat, the density as well as macroporosity decreases with depth.

We will clarify the sentence.

5. line 267-268, this sentence is not necessary.

6. line 271, see above.

We will remove the sentences as suggested.

7. Figure 4, why select this pressure head, not others. At this pressure head, soil shrink occur and it affect the results the most (line 341). Also, this figure shows the only the top soils do not follow the function well. Because it has the highest macroporosity (42 vol%). This value is comparable to

the total porosity of mineral soils. I think the authors could provide more detailed information to highlight the unique structure of peat.

As we state in Sect. 3.3, the TPM model uses the relative diffusivity at −10 kPa conditions as the basis for the gas diffusivity parameterization. Therefore, we illustrate the behavior of gas diffusivity at that matric potential in the figure. As suggested, we will extend the discussion on the performance of the TPM model parameterization in Sect. 4.3 in the Discussion.

8. lines 314-323, I think the authors could discuss a little more. Generally, peat types (fen, bogs) and decomposition/degradation stages (Liu and Lennartz, 2019) are two crucial factors affecting peat structure. I think the authors could compare the gas diffusivity for fens and bogs (from previous publications) at a comparable decomposition level (e.g. bulk density values).

Unfortunately, studies on gas diffusivity in peat are very scarce especially for fens, and the sample size of most of the studies is small. Therefore, it is difficult to perform a more detailed comparison between studies or between fens and bogs. The available studies have been listed in the discussion. We will extend the discussion on the basis of available literature.

9. Line 335, the pore structure (e.g. connectivity) of the samples should be provided.

In Kiuru et al. (2022), we have determined and presented metrics for the pore structure and connectivity of the same samples that were used in the gas diffusion measurements and simulations in this study. However, because of the shrinkage of the samples and computational limitations, the connectivity metrics were calculated for subsamples, which were then assumed to be representative for the corresponding total sample volumes. We will give an overview of the network metrics in Discussion and an example of network connectivity metrics between samples from a single depth in this paragraph.

10. lines 345-354, I do not understand why it is necessary to give this discussion. Or, just concise the paragraph.

In the paragraph, we want to point out that a decrease in the gas diffusivity of peat with depth strongly affects the potential gas transfer rate in the soil. Further, we want to emphasize that it is important to take the vertical variation of gas diffusivity into account in, for example, the estimates of soil aeration rate, atmosphere–soil carbon exchange, and soil carbon budget. The calculation presented in the paragraph gives an example of the impact of the diffusivity variation on soil aeration rate, which further affects, for example, the rate of carbon degradation processes in the unsaturated layer. We will clarify the text and justify the relevance of the discussion.

11. lines 388, Actually, you could estimate the pore size according to the capillary rise equation.

We have determined, analyzed, and presented the pore sizes of the samples in Kiuru et al. (2022). The pore dimensions were determined from the micro-computed tomography images. The pore size distribution obtained from the water retention curve and capillary rise equation is more inaccurate than the image-based method because it gives the diameters of pore openings (throats) rather than pore volumes or pore body diameters and because it relies on the dynamic accessibility of pores to the invading fluid (Nimmo, 2005). Entrance of air to larger pores near the bottom of the sample can be prevented by the existence of smaller pores above them. Also, both the diameters of the pore openings and the cross-sectional diameters of the pore bodies are used in the simulations based on the pore network geometry and dimensions. The diffusional conductance between two pores is affected by the diameter of both pores as well as the diameter of the throat between them.

12. lines 389-392, Not so true. I mean, you determined the weight of the samples. The air-filled porosity could be justified according to the weight differences rather than using particle density or total porosity.

The relative volume of air as a fraction of the total pore space volume ("the degree of air saturation") can be determined from the weight differences between the samples if it is assumed that there is no air present in the sample in the saturated state. However, air-filled porosity is defined as the air volume present in the soil relative to the total soil volume, not to the total pore space volume. In addition, the air-filled porosity is usually greater than zero even in the saturated sample, and therefore, the total porosity of the sample must be calculated using the estimated particle density of the sample.

13. Section 4.3, I think the authors could explain the reasons together with highlighting the unique structure of peat.

As suggested, we will restructure the section, separating the comparisons to previous studies from the analysis of the reasons behind the observed mismatch of the gas diffusivity models.

14. Table 3. Please check the values again, especially for R2.

The determination of the performance statistic was ambiguous in the manuscript. The values for R^2 were calculated with Eq. (9) from the residuals between measured and model-estimated values and the differences between the measured values and their mean. When comparing the measured values directly to the model-estimated values instead of the linear regression between the measured and model-estimated values, it is more correct to refer to this statistic as to the Nash–Sutcliffe efficiency (Moriasi et al., 2007). In this case, the sum of squares of the model error may be greater than the sum of squares of the differences between the measurements and their mean, and therefore the value of the statistic can be negative. We will change the term for the statistic from the coefficient of determination to the Nash–Sutcliffe efficiency in Sect. 2.6 and in Table 3.

Reference:

Liu, H., & Lennartz, B. (2019). Hydraulic Properties of Peat Soils along a Bulk Density Gradient– A Meta Study. Hydrological Processes, 33, 101–114.

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Moldrup, P., Olesen, T., Yoshikawa, S., Komatsu, T., and Rolston, D. E.: Three-porosity model for predicting the gas diffusion coefficient in undisturbed soil, Soil Sci. Soc. Am. J., 68, 750–759, https://doi.org/10.2136/sssaj2004.7500, 2004.

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