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Author responses to comments of Referee #2

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.

Soil gas diffusivity and its controls are important issues in understanding greenhouse-gas dynamics of ecosystems. Knowledge gaps in this area are more obvious for organic soils than for mineral soils. Therefore the study of Kiuru et al. covers a relevant topic and principally aims and scopes of Biogeosciences. Although the study touches many several relevant aspects of the research area, nowhere a really satisfactory scientific depth is achieved. Therefore I suggest a complete revision of the manuscript with a stronger scientific focus on aspects that are well covered by the measurements and can be amended by a sufficient theoretical base.

We will revise the manuscript, extend the discussion, and highlight the connection between the experimental results and the theoretical framework and assumptions of the pore network modeling method on the basis of the comments and suggestions by both referees.

Introduction: Here I miss any review about specific soil-physical features of peats in contrast to mineral soils. The state of the art, especially considering water retention but in parts also for gas diffusion would allow to formulate specific hypotheses for the application of diffusion models.

As suggested, we will extend the Introduction to shortly summarize the specific physical properties of peat soils and to introduce the challenges in the application of the gas diffusivity models. In addition, we will revise the corresponding statements in the Discussion accordingly.

line 36: Consumption of O2 higher than the supply is not precise, you mean that diffusion cannot maintain O2 concentration above a critical level (which can be even zero in extreme cases).

We will clarify and revise the sentence as suggested.

line 52: This applies only when gas diffusion through the water is disregarded.

Earlier in the paragraph, we stated that the diffusion is significantly faster in air than in water, and therefore, we implicitly ignored the diffusion in the water phase in the following discussion in the paragraph. Also, totally isolated individual macropores or totally isolated macropore clusters (that is, with neither air-filled nor water-filled connections to the active pore network) do not contribute to any transport processes. We will remove the sentence for clarity.

Material and methods: Description of standard methods can be substantially shortened (by 50%)

We will condense the measurement descriptions in Sect. 2.2 somewhat. However, we want to keep a sufficient level of detail so that ambiguity can be prevented and the reproducibility of the measurements can be enabled.

line 87: Reference soil group Histosol, is it order from UsSoilTax or reference soil group from WRB? Anyway, classification should be done somewhat deeper (WRB principal qualifiers).

The soil classification follows the WRB classification system, and it was classified as Hemic Histosol. We will refine the classification.

line 104: Shrinkage has been measured, but not reported.

The results for vertical shrinkage are presented in Kiuru et al. (2022). The presence and amount of horizontal shrinkage at -10 kPa matric potential conditions could also 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.

line 119: I wonder about the extremely long closing times (60 and 120 minutes). With the very high Ds values this could let to high measuring errors.

Generally, the nitrogen mole fractions were well (on average approximately 8 percentage units) above the ambient value of 78 % during the second sampling about 120 minutes after closing the nitrogen tubes (the measurement data are available as stated in the "Code and data availability" section of the manuscript). Therefore, we consider the results very reliable in that sense. However, in the measurements with the highest diffusion coefficients, the top-layer samples at -10 kPa, the second samples were taken 119–123 minutes after closing the tubes. It is true that the chamber system may have been rather close to the equilibrium state during the time of the second sampling for the few samples with the highest diffusivity values. This may have resulted in too low a calculated gas diffusion coefficient. When looking at the concentrations of the second sampling, this may have been the case for three or four samples, one of which had already been discarded because of an inconsistent concentration value at the first sampling. However, we cannot definitely confirm this conclusion on the basis of the measurements because of the indefiniteness of the ambient nitrogen concentration value and other possible error sources in the measurements. We will mention the possible measurement error caused by the long measurement process time in the Discussion.

line 130: What was the exact criterion to discard measurements? How do you know that the other measurements were correct?

We compared (1) the measured nitrogen concentrations at the sampling times to the analytical concentration value (Bakker and Hidding, 1970) and (2) the measured nitrogen concentrations of the same sample between different matric potentials. The criterion (1) also compares the concentrations

of an individual pair of measurements between the two sampling times. The measurement was discarded if there was a very high discrepancy.

The temporal evolution of the chamber nitrogen concentration, C(t), is dependent on the geometry of the measurement system (which was unchanged during a measurement), the air-filled porosity a of the sample, and the soil gas diffusion coefficient D of the sample. The dependence on C(t) on a is much smaller than on D especially at higher t (approximately greater than 30 min for the scale of D and the system geometry in this study).

Figure AR1 shows an example of the measured nitrogen concentrations and analytical concentration curves for the bottom-layer samples at -3 kPa matric potential. The analytical curves are calculated using a single value for a and different values for D, and therefore, they are not totally accurate for different samples. We can see that the concentration values for the samples number 3 and 6 do not follow the analytical curves at all. Also, the measured concentration at the first sampling, 45-50 minutes after the start of the measurement, was notably lower than the corresponding concentration for the same sample at -6 kPa and -10 kPa matric potentials for samples number 3, 5, and 6. For example, the nitrogen mole fraction for sample number 5 was 0.882 at -3 kPa at 47 minutes, whereas it was 0.977 at -6 kPa at 49 minutes and 0.928 at -10 kPa at 68 minutes. Therefore, even though the concentrations for sample number 5 follow the analytical curve, the concentrations were not consistent with the concentrations at other matric potential conditions, and the measurement has therefore been incorrect. The calculated D would have been 0.013 cm² s⁻¹ at -3 kPa, whereas it was 0.0020 cm² s⁻¹ and 0.0054 cm² s⁻¹ at the increasingly lower matric potential conditions.

In this example, no striking discrepancies were seen for samples number 1, 2, 4, and 7, and thus these measurements can be considered much more reliable than those for samples number 3, 5, and 6 when looking at the consistency of the measured concentration values. Of course, there can be many other error sources in the measurements, but the rejection of a measurement based on concentration inconsistency is a very straightforward and justified procedure. We will extend the description of the criterion in the manuscript.



Figure AR1. Measured nitrogen mole fractions and analytical concentration curves for the bottomlayer samples at -3 kPa matric potential.

line 133: Why specific models have been chosen? The Millington-Kirk models have a mechanistic base with randomly disrupted capillary systems. The TPM-model is mostly empirical. Do you have ideas, which of these models are more sound to organic material?

We have selected the gas diffusivity models on the basis of their popularity and prior performance. The simpler models have been widely used in soil biogeochemical models and other gas flux estimates because of their simple structure, and the TPM model has been shown to have good performance for many soil types. The performance of the simpler models for peat has also been assessed in previous studies as discussed in Sect. 4.1, and therefore comparison to other studies became possible in our study. We consider that the reasoning for model selection is presented clearly in Sects. 2.3 and 4.1. We discuss the structure and applicability of the gas diffusivity models quite extensively in Sect. 4.3 and conclude that none of the models significantly outperformed the other ones for peat.

Is there a reason why CO2 has been measured?

The CO₂ measurements were needed to account for respiration. We technically measured the diffusion of O₂ into the chamber (while N₂ was moving out of the chamber). However, some of this O₂ was converted to CO₂ on the way through the sample. So, effectively, we measured changes in the N₂/(N₂+O₂+CO₂) ratio rather than the actual N₂ mole fraction. This implies that we assumed a respiratory quotient (that is, CO₂ produced per O₂ consumed) of 1. For brevity, however, we will not extend the already detailed measurement description in the manuscript.

line 175 following, pore network:

It is an impressive mathematical toolbox that has been used. However, I miss any critical view (this could be also in the discussion) about the validity of the completely artifical pore network model. Peats consist of fibres, clusters with a possibly strong anisotropy due to the good compressibility. Why the throat-bubble model should reflect the pore network? Are these assumptions robust or do they easily create biases in estimations? This can be checked by simulations (sensitivity analysis) of exemplary datasets.

The pore network model is not completely artificial because it is based on the real structure of the porous object obtained from micro-computed tomography images. The model would be completely artificial if it had been constructed using a synthetic random network that was tuned to match the observed effective diffusivity. The topology of the pore network reflects very closely to that of the pore space of the porous object, and the volumes and cross-sectional areas of the network elements (the volumes and areas of pores and the areas of throats) are well-defined. Only the shapes and therefore the diffusional conductance values of the elements are approximations through the stick-and-ball simplification in the pore network representation, and the segmentation of the pore space to individual pores is always based on subjectively established distinctions. In this case, the segmentation was based on the watershed algorithm of the network extraction tool.

The structural anisotropy of the porous medium is well accounted for in the topology of the pore network. The orientation of the transport conduits is represented by the orientation of the network

edges in the three-dimensional pore network. Also, the impact of the fibric structure on the properties of the air-filled macropore network of peat is rather small in wet conditions prevailing in our study.

The "validity" or the degree of performance of the pore network modeling methodology is assessed in this study by comparing the simulated diffusivity values to the measured values. By making the comparison we can see that the integrated effect or contribution of the network elements to the diffusion capability of the peat samples was generally well reproduced. We can therefore state that the effective performance of the simulation method was rather good.

In our opinion, a thorough sensitivity analysis of the geometrical structure of the well-founded and established methodology of pore network modeling is beyond the scope of this study. The study contains the generation and assessment of an experimental dataset of peat soil gas diffusivity and the assessment of the performance of the pore network modeling methodology considering the reproduction of the measurement results. We will revise the discussion by further assessing the applicability of the simplified pore geometry used in the gas diffusivity simulations with respect to the actual structure of peat.

Results part:

line 251 following: The database is weak and results do not contain surprising or interesting patterns, so strongly shorten!

There are few studies on gas diffusivity in peat (other studies are discussed in Sect. 4.1), and the sample sizes were generally very small in these studies. In comparison to these previous studies, our sample size is not very small. We consider that the experimental results presented for gas diffusivity in peat provide a relevant scientific contribution, and the assessment of the results is thus justified. The variability of peat properties due to its heterogeneous physical structure is also highlighted in the analysis of the results. However, we will slightly shorten the paragraph.

Shrinkage is a very critical issue but is completely disregarded in the measurements. I would suggest to correct epsilon for the reduced total volume.

The results for shrinkage are presented in Kiuru et al. (2022). The decrease in sample height was taken into account in the calculation of air-filled porosity and the soil gas diffusion coefficient at -10 kPa conditions. The description in Sect. 2.2 is therefore imprecise. We will add information on the measured sample shrinkage and on the observations of shrinkage properties in the Results section. We will also correct the text in Sect. 2.2 by mentioning the fact that the air-filled porosity was calculated from the reduced total volume at -10 kPa conditions.

Table 1: two digits are sufficient

We would prefer to present the air-filled porosity values with three significant figures as we have done for the volumetric water content and bulk density of the same samples in Kiuru et al. (2022) and for the soil gas diffusion coefficient in this manuscript.

Table 2: "significant differences" between what?

We meant that different letters in the table indicate a significant difference in the soil gas diffusion coefficient between different peat sampling depths. The same sentence structure is used in the footnote of Table 1, and we will clarify both occasions.

line 295: Hysteresis has been only modeled with a non-checked pore model with swellingshrinkage disregarded. This is no relevant scientific contribution.

The analysis of hysteresis through exactly similar pore network simulations was an important method in our earlier study on macropore networks of peat (Kiuru et al., 2022). In the study, we examined the evolution of the volume of connected air-filled peat pore space during both drying and wetting. In this manuscript, we have extended the assessment and discussion to gas diffusivity in peat using the same methodology. Thus, we consider this simulation method to be relevant. In addition, the shrinkage of the samples at the rather low maximum simulation pressure (high minimum matric potential) of 2.9 kPa can be considered rather small and thus ignored in the analysis.

Discussion:

I would expect a critical view on the scientific progress including some theoretical thoughts that support the rather weak empirical base.

We show that the simplified pore network representation of peat macropore space and the pore network simulations presented in the study are able to describe the gas diffusion properties of peat on the sample scale. We also state the benefits of the methods and the advances of this study in the Conclusions section.

As we state in the response to a previous comment ("line 175 following"), micro-computed tomography imaging reveals the real complex structure of the macropore space with a wide pore size distribution and an anisotropic nature. We also found that the simplified pore geometry applied was then sufficient to describe the effective gas diffusion behavior of the porous medium. We will highlight the connection between the results and the theoretical framework and the assumptions of pore network modeling and further discuss the applicability of the simplified pore geometry used in the simulations.

line 315 to 354: Is completely trivial and can be omitted, better is to check for critical issues in measurement quality.

Because there are few experimental studies available on gas diffusivity in peat, we think that it is justified to discuss the diffusivity measurements and to compare the results with other studies. In the section, we will extend the discussion on the variation of peat diffusivity between peat types. Following the recommendation of the other referee, we will also review our earlier results for the pore network connectivity of the peat samples, which strongly affects their diffusion capability. In addition, we will point out more issues concerning measurement discrepancies in the section, as we have described in the reply to a previous comment.

line 363: The problem is, that the pore network model does have a real theoretical foundation.

The theoretical foundation of the gas diffusion simulation, Fickian gas diffusion in tubes between pore centroids in an interconnected network, is well-established and validated in many previous studies concerning pore network modeling. The larger-scale connectivity of the pore space is captured by the pore network obtained through micro-computed tomography imaging, and the smaller-scale behavior is described semi-analytically in each network element (Blunt et al., 2013). The diameters of the pore network conduits in this study, 100 micrometers or higher, are well above the applicability threshold of Fickian diffusion. We will further justify the applicability of the pore network simulations as well as shortly discuss the theoretical foundation of the method in the Discussion.

line 393: See above, hysteresis problem/shrinkage swelling

We will add some discussion on the possible effect of peat volume changes on the hysteretic behavior. However, as stated above, we consider the shrinkage so low at higher-matric-potential conditions that its effect can be excluded from the simulations performed in this study.

References

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