Dear Editor and anonymous reviewers

Below, we give the details of the minor revisions as requested by the editor's decision based on our previously submitted replies to the reviewer's comments.

We give full details of:

the reviewers comments (numbered, regular font),

our replies to the comments (in bold),

our revisions (in blue) and what we have changed in *italics*.

In detailing the revisions, we make reference to the line numbers (of the non tracked manuscript version) where we have made changes. Changes can also be seen in the tracked manuscript attached to this document.

Revisions following Reviewer #1 comments

 "Characterization of peat samples: Peat soils are divers as mineral soils. Their exact characterization is crucial to classify any experimental outcome. I couldn't find any basic characterization of the investigated soil, even not the organic matter content nor the Van-Post value."
 We already did give explicit reference to previously published studies describing the structure of the peat on page 4 lines 101-106 (we will add text - refer also to comment 2)).

The paragraph now on lines 105-112 reads (changes in italics): Added text to lines 101-107 detailing the composition of the peat, its origin and disturbed nature including sample collection.

"The peat used for the fen was moderately decomposed rich fen, sedge peat with remnants of Sphagnum moss, originating from a donor fen prior to stripping of overburden material to expose the oil sands deposits (Price et al., 2011; Daly et al., 2012; Nwaishi et al., 2015). The donor fen had been drained for two years prior and the peat underwent accelerated decomposition due to exposure to oxygen (Nwaishi et al., 2015). Vegetation growth on the drained fen resulted in addition of stems and leaves to the peat. The samples were shoveled into 20L buckets from a stockpile made by the heavy machinery that removed the peat layer from the donor fen, further disturbing the peat, as it was placed in the fen. The peat has a relatively open structure (Fig. 1), compared to Sphagnum peat used in other transport studies (e.g. Hoag and Price, 1989; Rezanezhad et al., 2012)."

2) "Moreover, the peat is characterized as sedge peat, but Figure 1 shows moss with hyaline cells." —Please refer to page 15 lines 348-350, where we explicitly state that: "The peat of the Nikanotee Fen watershed was moderately decomposed sedge peat containing small amounts of Sphagnum moss (Nwaishi et al., 2015)" in the Results section. It explains Figure 1 which shows how the remnant sphagnum appears in the sedge peat. With respect to comment 1+2, we will explicitly describe the peat material in the Materials and Methods earlier on in the manuscript.

Added text to lines 105-112 detailing the composition of the peat, its origin and disturbed nature including sample collection. See item 1 for full text.

3) "The conclusion drawn is unjustified because soil structure was compromised upon sample preparation (sieving and re-packing). Relevant and recent studies clearly showed that plant residues (embedded in an intact peat structure) in undecomposed peat may serve as a preferred solute pathway (Liu and Lennartz, 2015; Liu et al., 2016)."

—We disagree. The comment correctly identifies, that we reconstituted the peat. However, the field site is characterized as a recently replaced and reconstituted site. In this respect, the laboratory protocol is similar to what has happened in the field, since undisturbed samples (i.e. naturally grown peat) does not exist in our system (See lines 102-105). More specifically, the peat had been disturbed a few years prior to sampling. It had been taken from a pile that was created using heavy machinery. We think it is very likely that these disturbances had a much greater effect on the peat properties than the lab preparation. The preparation was designed to reduce the variability caused by the disturbances. Furthermore, nowhere in the text is "sieving" mentioned. The peat was not sieved, as suggested by reviewer 1, but coarse material (leaves and twigs and stem from the aforementioned disturbances which accounted to about 2% in volume) was carefully removed and the peat was gently mixed to increase homogeneity. We don't believe this caused a change to the cellular structure of the cells. However, we do agree that we perhaps did not make it sufficiently clear to the reader that our samples are from a stockpile of heavily disturbed peat, which was replaced in the newly created artificial peatland. Thus, we will be careful to address the full characterization of the peat (also cf. comment 1) and 2) in the revised manuscript.

Lines 87-89: Added sentence: "Additionally, acknowledging that Na + and Cl- ions may interact with dissolved organic matter, inducing changes in the pore size and geometry (Ours et al., 1997; Comas & Slater, 2004) a pre-treatment was implemented (see subsection 2.3.1 - Sample preparation)."

4) "Peat soils differ from mineral soils in their ability to retain compounds that are generally considered as "conservative" or inert such as chloride anions (Hoag and Price, 1997; Caron et al., 2015). It has been likewise observed that the application of sodium-chloride to peat samples may cause a rearrangement of pore structure based on a pore dilation effect (Ours et al., 1997). Both aspects shall be discussed in a publication on sodium-chloride transport in peat soils"

—We agree with the reviewers' comment, and in recognizing the potential for sodium to cause flocculation and/or pore dilation, we flushed the column with NaCl as a pretreatment of the samples to minimize the effect during experimentation. We stated this explicitly on lines 159-162 and a lines 87-89.

No changes required.

5) "Model evaluation: The authors employed the mobile-immobile solute transport concept and the according solution of the underlying equations to obtain parameter values by running optimization algorithms. From a huge body of literature (for instance Parker and van Genuchten, 1984; Bond and Wierenga, 1990; Gao et al., 2009) it is evident that the simultaneous optimization of the pore water velocity (v) and the fraction of immobile water (β) may lead to invalid parameter values because both parameters account for the position of the BTC on the (dimensionless) time axis. Keeping v fixed at the measured values would probably have produced a different outcome and a different conclusion."

—Of course, fixing parameters will lead to different conclusions, we are aware of this. The method the reviewer proposes is for exactly that same reason a very unsatisfying method. Pre-fixing either the pore water velocity (v) or the fraction of immobile water (β) is subjective. Moreover, if parameters are fixed a priori, the inverse modeling will not provide evidence on the flow phenomena, but merely "prove" the conceptual model which was used to fix the initial parameters in the first place. For this reason, we took a different approach; we refrained from fixing parameters, and used the information content of the experiments. Thus, we attest on whether or not the mobile-immobile solute transport model is an over-parameterization or an adequate model choice. Moreover, simultaneously fitting v and β is possible and has been done previously (e.g. Zurmühl, 1998; Tang et al., 2009 and references herein). Considering the implied 1:1 representation of v for β (or vice versa) close inspection of inspection of Eq. 1 shows that what the reviewer implies cannot be the case. Division by β leads to β being part of each of the three summands on the right-hand side of the Eq. 1, and therefore contradicts the reviewer's assumption. We believe our approach is appropriate.

No changes needed

6) "In this context, the possible retardation of the "conservative" tracer needs to be considered (see above).

— We disagree that a potential Cl adsorption might be relevant on the scale of the flow through reactors. There is a theoretical potential, that an anion such as Cl- (or Br- used in other studies) might be attenuated, too, but this would contradict what is known about Cl⁻ in peat. Since no studies exists (to the knowledge of the authors) of deuterium as tracer in peat, it is very speculative to state that Cl should not be at least very close to conservative as a tracer. Hoag and Price (1997) indicated Cl was subject to physical diffusion into inactive pores as evidenced by the Cl retardation factor greater than 1 (R=1.1). The reviewer is commenting on the classical definition of retardation (by adsorption). We acknowledge that while most studies treat Cl as a conservative tracer, there is a theoretical possibility that a small anion adsorption effect may exist, which can only be distinguished by known conservative tracers like deuterium. We will add text acknowledging the possibility.

After discussion of parameter β we now additionally turn to ω : We now argue by adding: with the following sentence in line 356-358: "*This exclusion is supported by the instantaneous equilibration between the mobile and the immobile zone, as indicated by the very large* ω *which was at the upper bound during the parameter estimation*".

Table 3 now gives the estimated ω values, and we corrected the α_{MiM} of Cl to 0.9 (min⁻¹), too. By doing so, we now indicate in the table and the caption, that for the Cl break through curve using the MiM model, the coefficient of variation cannot be estimated using the classical first-order second moment approach: "*ne* – *not evaluated: the parameter is at the upper feasible bound of the parameter estimation. (Toride et al. 1995)*"

Finally, the introduction of omega required that we define it mathematically, which we now do in a footnote to Table 9: $\omega_{MIM} = \alpha * L / (\theta * v)$, $\omega_{OSA} = (\alpha (R - 1) * L) / v$

7) "For instance, how can it be explained that the optimized pore water velocity (v(fit)) showed greater values than the measured (v(measured)) employing the (single modal) convective dispersion equation? A ratio of v(measured)/v(fit) of less than 1 is a clear indication of a preferred solute transport situation."

--We think the reviewer refers to the effective pore water velocity. Of course, the comparison of v(fit) with v(measured) can be done, but differences are to be expected from normal measurement errors, experimental set up, and remaining air bubbles in the sample. In any case, ω [-], the dimensionless mass-transfer coefficient also indicated at the non-existence of mobile-immobile solute transport as it was found that $\omega > 100$ (In the paper we actually reported on the dimensioned mass transfer coefficient, α). We realize that our conclusions from our results of ω were not presented with sufficient clarity. The parameter ω could also not be identified by inverse modeling. In the inversion, ω ran into the maximum upper boundary limit of 100 in CXTFIT. This supports the conclusion, that the MIM solute transport model is an over-parameterization (corroborated by the CXTFIT results files, too), and that the CDE is sufficient for describing the observed breakthrough and solute transport. For this reason, we are convinced that our results and conclusions are not affected by this comment. In a revised manuscript, we will address this by including a brief discussion on ω , and present the values in Table 3, and hope this can strengthen the paper considerably.

No changes needed

8) "Solute concentration data shall be presented against exchanged pore volume instead of absolute time to better classify the breakthrough behavior."

---Both methods of presentation can be found in the literature (e.g. Tang et al., 2009). Moreover, we took great care in presenting and discussing our results indicating CDE solute transport, and therefore do not believe it will change the understanding of the chart or the processes. If the editor finds this change compulsory, we could consider this in a revised manuscript.

No changes needed

9) "The result section starts with the presentation of the (adjusted) bulk density etc. That clearly belongs to Material and Methods. "

- A good point. While being more elaborate on the description of the peat, (cf. comment 1-3), we will address this, too, and make the Material and Methods more concise and complete.

We rephrased the sentence now in line 291-292, to clarify the bulk density results, which now reds: "*The bulk density and porosity of the prepared peat samples in the various experiments was similar (Table 1) indicating a successful sample replication.*"

10) "There are likewise some editorial flaws: Doubling of sentences, etc. (lines101-104)."
 —We apologize for this and will make an even greater effort in addressing any potential editorial concerns, thoroughly, before submitting a revised manuscript.

We thoroughly checked and corrected the document for editorial flaws which might have slipped our attention before submission. We have now deleted the repeated sentence.

11) "Suggestion: There is some potential in the work. It is, for instance, interesting to compare saturated and partially saturated solute transport scenarios. It is likewise valuable to combine transient evaporation with tension disk measurements to obtain soil water retention and hydraulic conductivity information."

—We agree this is interesting, but do not believe it is central to the manuscript; it would disrupt the flow, and in its extent is a separate study for another time.

No changes needed

12) "In any case, the experimental data base needs to be substantiate addressing the given points to draw definite conclusion. The study could be substantially upgraded if data from UNDISTURBED samples could be presented in comparison to the data from the disturbed samples. This holds true for the solute transport as well as for the hydraulic properties alike".

—We agree that comparison to undisturbed samples is always interesting; however, the peatland from which these samples were drawn was destroyed long before we began this experiment. So in that sense, we disagree, as undisturbed samples do not exist. The samples are obtained from stockpiled and heavily disturbed original material (during placement on site). Our focus here is to characterize the disturbed peat, so the implications for solute transport at the specific site can be discussed. In a revised manuscript, we will include a clear statement on the objectives, and, again, be much more precise on the nature of our samples.

Added text to lines 105-112 detailing the composition of the peat, its origin and disturbed nature including sample collection. See item 1 for full text.

References used in Reply to Reviewer #1:

Hoag, R.S., and Price, J.S. (1997). The effects of matrix diffusion on solute transport and retardation in undisturbed peat in laboratory columns. Journal of Contaminant Hydrology 28:193–205.

Nwaishi, F., Petrone, R. M., Price, J. S., Ketcheson, S. J., Slawson, R., & Andersen, R. (2015). Impacts of donor-peat management practices on the functional characteristics of a constructed fen. Ecol. Eng., 81, 471-480.

Tang, G., Mayes, M. A., Parker, J. C., Yin, X. L., Watson, D. B., and Jardine, P. M. (2009). Improving parameter estimation for column experiments by multi-model evaluation and comparison, Journal of Hydrology 376, 567–578.

Zurmühl, T. (1998). Capability of convection–dispersion transport models to predict transient water and solute movement in undisturbed soil columns, Journal of Contaminant Hydrology, 30, 101–128.

Revisions following Reviewer #2 comments

1. "Lines 9-10. This opening sentence is overly complex and confusing as written. I would advise revising the sentence by playing more careful attention to syntax and shortening the sentence. For example it can be changed to: The underlying processes governing solute transport were analyzed in peat from an experimentally constructed fen peatland by performing saturated and unsaturated solute breakthrough experiments using Na+ and Cl- as reactive and non-reactive solutes, respectively. A good rule of thumb with regard to syntax is to keep like elements of a sentence together".
—We agree and appreciate this helpful comment. In our revised manuscript, we will be careful in enhancing readability, e.g. by adopting proposed sentence.

Changed lines 11-13 to: "The underlying processes governing solute transport were analyzed in peat from an experimentally constructed fen peatland by performing saturated and unsaturated solute breakthrough experiments using Na+ and Cl- as reactive and non-reactive solutes, respectively."

2. "Line 16: Please don't begin a sentence with a stand-alone pronoun (e.g. "This"), which in this context is ambiguous. Add words or words after "This" to clarify the subject of this sentence."
—we will try to address this throughout the document.

Now line 18: We changed the instances of stand-alone pronouns to be grammatically correct. Corrected for the entire document.

"Line 17: change "(!infinity)" to "(which approaches)""
we will change this as proposed.

Changed lines 18-20 to: "Furthermore, the very high Damköhler number (which approaches infinity) found suggests instantaneous equilibration between the mobile and immobile phases; underscoring the redundancy of the MIM approach for this particular peat."

4. "Line 17: See my note about stand-alone pronouns above. It is always preferable to avoid introducing unintended ambiguity by avoiding this usage altogether."
—We agree and will change it to be decisive.

Now line 18, we changed to: "(->infinity)" to "(which approaches infinity)".

5. "Lines 27-28: Does this study have broader implications beyond the specific experimental setting and its selective process of constructing the peat columns in the lab? The concluding sentence of the abstract should address this question and point out the broader significance of these findings. Are these results specific to this experimental apparatus, study site, other reconstructed fens. Can the results provide new insights on the limitations of the dual porosity model of pristine peatlands as well?"

— We agree with both comments/questions. The study does have a broader implication, and we think we can exploit this aspect more than we have done. We will state the significance of our study/conclusions in the abstract of a revised manuscript. i.e. the mobile-immobile solute transport model cannot be selected per se.

Added to lines 29-30 and lines 455-456: "... and imply that MIM should not be automatically assumed for solute transport in peat but should rather be evidence based."

6. "Lines 32-33. The subject of this sentence is too long. Please shorten the subject and move the verb to the beginning of the sentence. "

---As stated previously, we will be more specific in the use of our language and address this in a revised manuscript.

Now lines 34-35: Shortened the subject and moved the verb to the beginning of the sentence.

7. "Line 35: Change "which" to "that""—see for previous comment.

Line 39: Changed "which" to "that".

*Line 40: Change "Generally, Sphagnum" to "Generally, in Sphagnum"
—as previous comment.

Line 40: Changed "Generally, Sphagnum" to "Generally, in Sphagnum".

9. "Lines 32-49: First two paragraphs: Some of the ideas expressed in these opening paragraphs should be reduced and incorporated into the Abstract to provide a better rationale for this study and its broader significance."

---We understand this is related to the comments on lines 27-28, and will, in a revised manuscript, carefully reassess how to make the abstract stronger. This is a good suggestion, it is logical and helps strengthen the essence of the article in the abstract, and will be addressed in the revised manuscript.

Now lines 34-49. Rewritten to be more concise.

10. "Line 64: Please avoid using (especially at the beginning of a sentence) a stand-alone pronoun. In this case the subject of this sentence is not clear."

---we agree and will check our manuscript for these instances.

Line 64: corrected standalone pronoun.

"Line 71: A dangerous assertion since any person's knowledge of the literature is always limited.
For example, the authors could also cite Comas, X. and L. Slater (2004) Low frequency electrical properties of peat Water Resources Research, Vol. 40, W12414, doi:10.1029/2004WR003534, 2004."
—We agree, and in the following, we will be more reserved in the revised manuscript by writing: "As to the current knowledge of the authors.". Additionally, we will consider the mentioned publication, and possible implications from it. We also added the suggested citation.

Now line 70: "As to the knowledge of the authors..". We also added the suggested citation.

12. "Line 77: Please add the appropriate word or words after the stand-alone pronoun "this" to clarify its meaning. Otherwise the subject of this sentence is ambiguous. "
—We will replace 'this' by stating "[...], the method of estimating n_e from photo-imagery may easily lead to a systematic miscalculation of effective pore water velocity."

Line 77: We replaced 'this' with the sentence: "The method of estimating n_e from photo-imagery may easily lead to a systematic miscalculation of effective pore water velocity."

13. "Line 85: The authors may want to consider the possibility that interactions between NaCl and dissolved organic matter (e.g. organic acids) may induce changes in the pore size and geometry as originally proposed by Ours et al. 1997 and supported by Comas & Slater 2005 or Levy et al. 2016? "
—We fully agree with this statement, and had, for this reason, explicitly included a pretreatment to equilibrate and flush the samples. This is clearly stated in lines 152-155 and see no necessity to for changes.

Added sentence in line 87: "Additionally, acknowledging that Na + and Cl- ions may interact with dissolved organic matter, inducing changes in the pore size and geometry (Ours et al., 1997; Comas & Slater, 2004) a pre-treatment was implemented (see subsection 2.3.1 - Sample preparation)."

14. "Line 88: Change "We approach this" to "We approach this objective"" —we will correct this as suggested.

Changed "We approach this" to "We approach this objective" now in line 92

15. "Lines 88-89: Were these experiments conducted in the field or lab? It would be a good idea to specify the later here."

—we are surprised that this was not clear, but will add the following sentence in the revised manuscript: "lab based experiments including" in line 88.

We added a "We approach this objective by conducting lab based experiments including saturated and unsaturated breakthrough experiments using NaCl.", now in line 92-93.

16. "Lines 109-112. I am confused. The previous text describes the peat used in this experiment was dominated by sedge remains. However, but figure caption suggests that the peat was composed of Sphagnum moss. Please provide an explanation in this figure caption if possible. "

—We realize we did not elaborate on this point sufficiently, and failed to make it clear to the reader, since also the other reviewer commented on this. Therefore, we will be more specific on the description of the peat characteristics (e.g. by repeating the findings of other researchers in a revised manuscript). We do note, that we give references to other research on the same constructed peatland, and we do present a scanning electron microscopy images of the Sphagnum remnants in the peat samples (lines 348-350).

Added text to now in lines 105-112 detailing the composition of the peat, its origin and disturbed nature including sample collection. See item 1 in answer to reviewer #1 for full text.

17. "Lines 112-125: How were these samples collected? A very brief description would be crucial since any method to secure peat samples for laboratory experiments will produce deformations to the original peat fabric, which will alter the hydraulic properties of the peat and therefore the affect results of the experiments. I realize that artifacts are unavoidable regardless of the sampling methods used but it would still be a good idea to address this issue here. It appears that the material used in this experiment were collected from a pile of peat that was excavated from an intact fen and then dumped in a pile. It would probably be a good idea to add a sentence or two to describe how peat was collected from this excavated pile. Please remember that peat is a generic term covering a wide and heterogenous range of porous media. "

—This concern was also raised by the other reviewer, and we seem to have failed to be precise in describing the a) characteristics of the peat, b) the sampling method, and c) the site description. As we have mentioned before, we will be careful to present the information more coherently in a revised manuscript. We do point out, that at several points in the manuscript we give descriptions, e.g. lines 102-105 where we state: " the peat has been disturbed for a few years prior to sampling. It was taken from a pile that was created using heavy machinery. It is therefore likely that these disturbances had a much greater effect on the peat properties than the lab preparation. Further the preparation was designed to reduce the variability caused by the disturbances.". Moreover, the peat was not sieved, as suggested by reviewer 1, but coarse material was carefully removed (<=2% in volume) and the peat was gently mixed to increase homogeneity. It is unlikely this caused a change to the cellular structure of the cells.

See item 16 above.

18. "Line 118: The authors should provide a rationale for adapting this unusual plan for packing peat into their permeameter columns. The approach will alter the fabric of the original in situ peat by preferentially removing coarser material and rearranging the packing and intra particle porosity of the finer-grained material. "

-See answer to previous comment.

Provided a rationale for sample homogenization during sample preparation as an addition to the lines 122-125 "As previously noted, the peat was sampled from the stock of disturbed peat used to construct the fen; in addition, we carefully removed woody inclusions and intact leaves to homogenize it such that we could ensure minimal variation between samples. The peat was gently, yet thoroughly mixed and packed into columns (see appendix A.1); no milling or sieving was done." Also see lines 105-112 regarding sample collection.

19. "Line 384: How can the bulk density and porosity be similar if they have different units of measure (gm/cm3 vs %)?"

— We think the reviewer refers to line 284 (not 384): This similarity is not apparent, in Table 1 the bulk density is clearly given by 0.12 g/cm3 and porosity by 0.93 [-]. The numbers with % sign are the coefficient of variation as mentioned in the caption, which is the standard deviation of the three replicates divided by their mean. Therefore, we do not believe we need to change anything here. "Do you mean instead that they are statistically related? "

---No, it is a measure for the similarity of the replicates.

No changes needed.

20. "Lines 307-310: Is this conclusion specific to soils that have high levels of Cl and other salts?" —It is specific to the use of EC electrodes to monitor the transition of reactive ions in any solution that flows through a reactive medium. We will incorporate this explanation.

Now on Lines 315-319: Added an explanation for the use of EC electrodes to monitor reactive solute flow through a reactive medium. "The dissimilarity of the EC breakthrough curve to that of Na+ (Fig. 4) demonstrates the limitation of using EC electrodes as an indicator for solutions containing reactive solutes, flowing through reactive mediums. This limitation is due to enrichment of ions in the solution from the soil and cation exchange with the medium, which changes the solution concentration of the cation of interest; therefore, EC can be a good estimator for non-reactive solutes but is limited as an indicator for cation transport (Olsen et al., 2000; Vogeler et al., 2000)."

21. "Line 342: Place the non-restrictive clause ("which is the ratio of advective vs diffusive transfer") directly after the subject it modifies (=Peclet number). I suggest changing this sentence to: The Peclet number, "which is the ratio of advective vs diffusive transfer, was 33.9. for the fitted CI- breakthrough data." "

---Agreed. This is a sensible suggestion and will make the changes accordingly in the revised manuscript. In the next comments, we will limit our response to "agreed", indicating we will revise the manuscript accordingly.

Now in line 351: changed sentence to: "The Peclet number, *which is the ratio of advective vs diffusive transfer*, was 33.9 for the fitted Cl- breakthrough data."

22. "Line 356: change "this" to "this finding" to clarify the meaning of the stand-alone pronoun "this""

--- agreed.

Now in line 358 we changed "this" to "this finding"

23. "Lines 352-357: "Additionally, evidence found in the SEM scans of the peat used in this study (Fig. 1), shows that the cell walls have decayed, with only the skeleton of the cell remaining," I suggest clarifying this sentence since it is not clear whether the authors are specifically referring to the slender chlorophyllose cells (which I think is their intention) or the much larger hylaline cells that have rigid reinforcing structures and microfibril reinforcing structures that are resistant to decay (and will therefore retain their shape when dead). This paragraph also seems to contradict the opening description of the fine-grained peat that was packed into the lab permeameters. "

— We thank you for this helpful and knowledgeable sentence. In discussing the decomposition of the Sphagnum moss parts, we were not specific enough. Generally, the sentences (lines 352-357) relate to the decomposition of the membranes of the hyaline cells. In the presence of intact hyaline cells, the cells act as dead-end pores, where the membranes restrict the solute transport to very small openings. Once the hyaline cell membranes have decayed, solutes can be transported by advection through-out the inner-plant matrix. Thus, the dead end pores no longer exist, a fact which can serve as an explanation for why the parameterization of solute transport models does not indicate a mobile and an immobile domain. While the reviewers comment does not contradict our findings, we will elaborate carefully on the different structures in the peat in a revised manuscript. Finally, the comment does not contradict our study description and methods, since it is unlikely that the careful packing impacted cell membranes (as discussed in the answer to comment on lines 112-115).

Now in lines 363-365 we changed the expression "cell walls" to "cell membrane".

24. "Lines 354-355: Please add the appropriate citations to support the statement that "solute transport in peat has to be simulated using the MIM.""

—We will gladly address this by giving more references to the literature, by rephrasing and providing references: 'These results contradict the hitherto common finding in laboratory studies that breakthrough experiments on peat need to be described by the MIM (Hoag and Price, 1997; Liu et al., 2016; Rezanezhad et al., 2012; Rezanezhad et al., 2017; Thiemeyer et al., 2017)'

Now in line 365-369 we rephrased the section and provided references: "*These results contradict the hitherto common finding in laboratory studies that breakthrough experiments on peat need to be described by the MIM (Hoag and Price, 1997; Rezanezhad et al., 2012; Liu et al., 2016; Rezanezhad et al., 2017; Thiemeyer et al., 2017)*".

25. "Lines 358-359: Either delete the adverb "As" at the beginning of this sentence or add an appropriate verb to complete this sentence."

---Agreed.

Changed "As" to "Since".now in lines 370-371.

26. "Lines 362: Delete "these" to avoid a run on sentence. "and the robust estimates of v and D for the CDE, these were""

---Agreed.

Deleted "these" and rephrased the sentence, now in line 373-374: "Having shown that the MIM is not parsimonious in its parameters, the robust estimates of v and D for the CDE were fixed when fitting the remaining model parameters of the CDE and one-site adsorption model for Na+."

27. "Line 401: Change" With this" to "With this approach"" — *Agreed.*

We changed "this" to "*this approach*", now in line 414.

28. "Line 409: Did the authors consider chemical interactions between the ionic composition of the pore waters and organic acids as suggested by Ours et al. 1997? " *—See answer to comment on line 85.*

See answer to item 13.

29. "Line 401: I suggest changing "With this we tested if the common assumption" to "With this approach we investigated whether the common assumption""
—Agreed.

We changed "With this we tested if the common assumption [...] " to "*With this approach we investigated whether the common assumption* [...]" now in line 414.

30. "Line 410: Please add the appropriate word or words after "this" to clarify the subject of this sentence. I think they are referring to "this result" but I am not certain."
—Agreed.

We changed "this" to "*this result*", now in line 423.

31. "Line 411: Was the peat primarily composed of Sphagnum? Elsewhere in the text the peat was described as sedge peat extracted from a fen."
—See lines 348-350.

See answer on item 16.

32. "Line 419-420: How can this statement ("has decayed enough to lose the cell walls but not enough to break the cell skeleton ") be true if the cell walls provide the structural basis of all plant cells. Please revise this statement both here and elsewhere in the text. "

--- We inadvertently used the word "cell walls" while we meant "cell membranes". We will correct this in a revised manuscript.

We changed "cell walls" to "cell membranes", now in line 432-433:

33. "Line 421: Another possible reason could be the sampling plan, which selectively packed the finer-grained peat particles into the permeameters. This procedure altered the fabric of the original peat fabric, which was probably first altered by the extraction of an intact fen and the deposition of the peat into a spoil heap. "

— There is no dispute that any manipulation of a sample alters it. However, the prior disturbance, as mentioned in the comment, is likely to have had a greater impact. The peat was not manipulated in a destructive manner such as sieving or milling. The reduced variability as a result of the careful homogenization process provides the improved ability to understand the hydraulic properties of the peat. While we doubt the sample preparation had a notable effect on the value of the parameters, we are certain it did not invalidate our interpretation of the processes, and thus our conclusions. As indicated elsewhere in this reply and in the reply to the reviewer #1, we will make it clearer in a revised manuscript, that both the sampling methods and sampling treatments, in the light of the type of sampling site, are acceptable.

Now starting on line 434, we added a paragraph stating: "Although we acknowledge that any manipulation of a sample alters it, the prior disturbance (see introduction of the method section) is likely to have had a significantly greater impact. Furthermore, the peat was not manipulated in a destructive manner such as sieving or milling and handled carefully. The reduced variability as a result of the careful homogenization process provides the improved ability to understand the hydraulic properties of the peat.

34. "Lines 437-438: "From the industry perspective, choosing and peat with dead end pores would allow a potential for significant attenuation." Remove "and" from this sentence."
— Agreed.

Now in line 454-455 we removed the "and" from this sentence.

35. "Are the authors concluding that partially decomposed peat (preferentially dominated by Sphagnum) provides the best material for optimizing solute attenuation in reconstructed peatlands?" —The sentence tries to convey that the hydraulic and transport properties of the peat should be checked and match the desired function. Therefore, to answer the reviewers question, if solute attenuation is the goal then peat with a larger amount of sphagnum and a dual porosity structure would be a better choice. We will add additional text in the revised manuscript.

Now in lines 454-455 we changed sentence to "From the industry perspective, if solute attenuation is the goal then peat with a larger amount of sphagnum and a confirmed dual porosity structure would be a better choice".

References used in Reply to Reviewer #2:

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1 Saturated and unsaturated salt transport in peat from a constructed

2 **fen**

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11 Abstract. The underlying processes governing solute transport were analyzed in peat from an experimentally constructed fen

12 peatland were analyzed by performing saturated and unsaturated solute breakthrough experiments using Na⁺ and Cl⁻ as

13 reactive and non-reactive solutes, respectively. To determine the underlying processes of solute transport in peat an

14 experimental constructed fen peatland, soil hydraulic properties were measured and saturated and unsaturated solute

15 breakthrough experiments were performed using Na⁺ and Cl⁻ as reactive and non-reactive solutes, respectively. We tested the

16 performance of three solute transport models, including the classical equilibrium Convection-Dispersion Equation (CDE), a

17 chemical non equilibrium one-site adsorption model (OSA) and a model to account for physical non-equilibrium, the

18 mobile-immobile phases (MIM). The selection was motivated by the fact that the applicability of the MIM in peat soils finds

19 a wide consensus. However, results from inverse modelling and a robust statistical evaluation of this peat provide evidence

20 that the measured breakthrough of the conservative tracer, Cl⁻ could be simulated well using the CDE. This is demonstrated

21 by aFurthermore, the very high Damköhler number (which approaches \rightarrow infinity) found suggesting suggests instantaneous

22 equilibration between the mobile and immobile phases; this underscores underscoring the redundancy of the MIM approach

23 for this particular peat. Scanning electron microscope images of the peat show the typical multi-pore size distributions

24 structure have been homogenised sufficiently by decomposition, such that physical non-equilibrium solute transport no

25 longer governs the transport process. This result is corroborated by the fact the soil hydraulic properties were adequately

described using a unimodal van Genuchten-Mualem model between saturation and a pressure head of \sim -1000 cm of water.

27 Hence, MIM is-was not the most suitable choice, and the long tailing of the Na⁺ breakthrough curve is-was caused by

chemical non-equilibrium. Successful description was possible using the OSA model. To test our results for the unsaturated case, we conducted an unsaturated steady state evaporation experiment to drive Na^+ and Cl^- transport. Using the

29 case, we conducted an unsaturated steady state evaporation experiment to drive Na^+ and Cl^- transport. Using the 30 parameterised transport models from the saturated experiments, we could numerically simulate the unsaturated transport

31 using Hydrus-1D. The simulation showed a good prediction of observed values, confirming the suitability of the parameters

32 for use in a slightly unsaturated transport simulation. The findings improve the understanding of solute redistribution in the

- constructed fen_and imply that MIM should not be automatically assumed for solute transport in peat, but rather, should 33
- rather be evidence based. 34
- 35
- Keywords: solute transport, peat, non-equilibrium, unsaturated, 36

37 **1** Introduction

38 A large pool of leachable Na, Ca and S were introduced The through incorporation of large quantities of in the tailings sand 39 into-used to construct aed fen watershed ereated as part of a novel attempt at landscape reclamation in the oil sands region, 40 introduced a large pool of leachable Na, Ca and S (Simhayov et al., 2017). The transport of these solutes in groundwater 41 derived from these tailings are likely to affect fenNear surface accumulation and potential impact of these solutes on the vegetation is controlled by the transport rate from the upland to the fen and the rate of flushing out of the system, which that 42 43 are currently under investigation (Simhayov et al., 2017). In constructed peatlands designed for oil sands reclamation landscapes, water quality is a concern due to incorporation of process affected materials (Price et al., 2011; Daly et al., 44 45 2012). In this context, thus a better understanding of the transport processes through peat, and solute accumulation in the 46 rooting zone of the fen, is needed. 47

48 The current assumption is that solute attenuation in peat is a result of solute adsorption and mass exchanges between mobile and immobile phases (Hoag and Price, 1997; Rezanezhad et al., 2012). Generally, in Sphagnum derived peat, hyaline cells 49 50 and their skeletal remnants are thought to account for a large fraction of dead end pores with distinct pore size density 51 distributions (Weber et al., 2017a, 2017b) and a volumetric moisture content (VMC) between 10 and 20% (Hayward and 52 Clymo, 1982; Weber et al., 2017a; 2017b). Additionally This, along with surface adsorption of reactive solutes (Rezanezhad 53 et al., 2012; 2016) may be present. Both effects will lead to more dilute but longer solute plumes a delayed arrival of solutes which might are likely to affect revegetation efforts community development in oil sands reclamation landscapes. The 54 55 physical and hydraulic properties of undisturbed peat changes along a continuous vertical profile (Weber et al. 2017b, 56 Limpens et al. 2008), whereby deep peat layers are generally more decomposed (Clymo, 1983). In addition to pore-scale effects, the systematic layered heterogeneity common in natural peatlands influences mixing and transport (Hoag and Price, 57 58 1995). However, in constructed peatlands this the decomposition gradient is destroyed because of the disruption caused by draining, stripping, transport and placement (Nwaishi et al., 2015). 59

60

Solute transport in the subsurface may be subject to physical and chemical non-equilibrium (Nielsen et al., 1986) 61 invalidating the use of the conventional convection dispersion equation (CDE) to simulate it. Physical non-equilibrium is 62 63 thought to be a process of a heterogeneous flow field with spatial differences in hydraulic conductivity due to dead-end pores 64 (Coats and Smith, 1964, Zurmühl and Durner, 1996), non-moving intra-aggregate water (Philip, 1968; Passioura, 1971), or

stagnant water in thin liquid films around soil particles (Nielsen et al. 1986). In this mobile-immobile model (MIM, Coats and Smith, 1964; van Genuchten and Wierenga, 1976) the liquid phase is partitioned into a mobile and an immobile region. Convective-dispersive transport occurs only in the mobile zone, while solute transport into the immobile region is by diffusion, the rate of which can be determined by experiments and inverse estimation of transport parameters (Vanderborght et al., 1997). In chemical non-equilibrium models, it is assumed that sorption at the pore-water solid particle interface is kinetically controlled (Cameron and Klute, 1977; Nkedi-Kizza et al. 1989). Both parametric non-equilibrium models may additionally account for chemical equilibrium adsorption (Toride et al. 1993).

72 To distinguish between the governing solute transport process, inverse modelling can provide the necessary information on 73 model parameter estimates, associated uncertainties, and permits the calculation of model performance and selection criteria (Iden and Durner, 2008; Vrugt and Dane, 2005, Weber et al. 2017). This-The modelling can be based on measured solute 74 75 breakthrough experiments of reactive as well as non-reactive solutes (Nkedi-Kizza et al., 1984). In the notation of the 76 convection dispersion equation the retardation factor is strictly referred and attributed to equilibrium adsorption (Toride et 77 al., 1995, Šimůnek and van Genuchten, 2008, Šimůnek et al. 2008) and is a function of bulk density, the slope of the 78 adsorption isotherm, and volumetric water content (Toride et al., 1995). A problem in deriving a numerical value for the 79 retardation factor during inverse modelling is that it is mathematical directly negatively proportional to the flow.

80 As tTo the current knowledge of the authors, To date the only literature reports with experiments of NaCl breakthrough on saturated peat columns conducted in the laboratory are from Price and Woo (1988), Ours et al. (1997), Hoag and Price 81 82 (1997), Comas and Slater (2004) and Rezanezhad et al. (2012). Ours et al. (1997) speculate that the observed prolonged 83 tailing of NaCl is a result of solutes diffusing into immobile zones. However, neither batch adsorption tests with the potential to exclude kinetic chemical sorption are presented, nor were solute transport models fitted to breakthrough curves, leaving 84 their conclusions tentative. Hoag and Price (1997) successfully described their observations with the conventional 85 86 convection dispersion equation (CDE). However, based on an effective porosity (n_e) determined by photo imagery, the 87 authors calculated the calculate pore water velocity by $v = q/n_e$, where q is specific discharge. The method of estimating n_e 88 from photo-imagery may easily lead to a systematic miscalculation of effective pore water velocity,; This results resulting in 89 higher different values of v than those calculated from total porosity, φ , or inverse estimation. By estimating CDE model 90 parameters describing non-reactive Cl⁻ breakthrough and keeping v fixed, their retardation factor (R), reflecting v_{water}/v_{water 91 v_{solute} was >1, and close to the ratio of φ to n_e . They attributed the delay in solute transport to physical non-equilibrium 92 processes, whereby solutes diffuse into inactive pores (i.e., solute transfer from the mobile to the immobile region). The 93 approach of Hoag and Price (1997) differs from the classical understanding where diffusion into the immobile zone is described by a kinetic constant, while R assumes chemical equilibrium of solutes with sorption sites (e.g. Coats and Smith, 94 95 1964; van Genuchten and Wierenga, 1976). Rezanezhad et al. (2012) concluded MIM transport is observable on small peat 96 samples. Moreover, parameter uncertainties and correlations are not shown and the performance of the MIM in comparison to the classical CDE is not given, such that a rigorous model selection is not possible. Additionally, acknowledging that Na⁺ 97

- 98 and Cl⁻ ions may interact with dissolved organic matter, inducing changes in the pore size and geometry (Ours et al., 1997;
- 99 Comas & Slater, 2004) a pre-treatment was implemented (see subsection 2.3.1 Sample preparation).
- The goal of the study is to expand our understanding of the transport processes in the vadose zone of decomposed peat by 100 101 testing various transport models and scrutinizing the common assumption that the mobile-immobile transport model best 102 reflects the processes in saturated and unsaturated peat. We approach this objective by conducting lab based experiments 103 including saturated and unsaturated breakthrough experiments using NaCl. Cl is generally uninvolved in chemical reactions in peat, except for ultra-saline conditions (Ours et al., 1997), and its counter-ion, Na⁺, is a prominent solute and potential 104 105 contaminant in the oil sands reclamation landscape (Simhayov et al., 2017). To compare the performance of models, model 106 parameters were estimated using inverse modelling with the CXTFIT v2.0 code (Toride et al. 1995). Comparison was based 107 on a statistical analysis to investigate the information content of the data collected, enabling a careful assessment of the 108 underlying processes. Subsequently, the parameterised models were used to numerically simulate the solute transport in 109 unsaturated steady state evaporation experiments with Hydrus-1D (Simunek et al., 2008). We tested if the model selection 110 and parameterization based on saturated experiments can be extended to predict unsaturated solute transport. No further 111 inverse estimation was done for the unsaturated transport of the non-reactive solute except for the Freundlich-Langmuir 112 parameters of the reactive solute. A sensitivity analyses was then carried out to estimate potential errors caused by using 113 parameters derived from saturated transport to simulate the unsaturated case.

114 2 Materials and methods

The peat used for the fen was moderately decomposed rich fen, sedge peat with remnants of Sphagnum, moss, taken 115 116 originating from a donor fen prior to stripping the of overburden material to expose the oil sands deposits (Price et al., 2011; Daly et al., 2012; Nwaishi et al., 2015). Peat samples were taken from a donor fen prior to stripping the overburden material 117 118 to expose the oil sands deposits (Price et al., 2011; Daly et al., 2012; Nwaishi et al., 2015). The donor fen had been drained 119 for two years prior to stripping and the peat underwent rapid accelerated decomposition due to exposure to oxygen (Nwaishi 120 et al., 2015). Vegetation growth on the drained fen resulted in addition of stems and leaves to the peat. The samples were 121 shovelled into 20L buckets from a stockpile made by the heavy machinery which that removed the peat layer from the donor fen, sofurther disturbing the peat-was disturbed, as it iwas when-placed in the fen. The peat has a relatively open structure 122 123 (Fig. 1), compared to Sphagnum peat used in other transport studies (e.g. Hoag and Price, 1989; Rezanezhad et al., 2012). 124



Figure 1 – Scanning electron microscope pictures of samples of the peat used in this study. a) Moss with hyaline cells, note cells with intact membrane at bottom right corner and larger pore spaces in bottom left and top right corners. b)
 Moss-Hyaline_cells, Note that with membranes are-missing: the and a view through the skeleton is evident. Modified from Rezanezhad et al., (2016).

130 2.1 Research approach

Four soil physical experiments were conducted to estimate the hydraulic properties and solute transport characteristics of the 131 132 fen peat material. The conducted experiments were: 1) Transient evaporation; 2) Water retention characteristics using 133 tension disks; 3) Saturated breakthrough; and 4) Unsaturated breakthrough. As previously noted, the peat was sampled from 134 the stock of disturbed peat used to construct the fen; in addition we carefully removed woody inclusions and intact leaves to 135 homogenize it such that we could ensure minimal variation between samples. Due to the highly disturbed origin of the 136 samples as detailed above, a careful homogenization of the samples was required and would not be a major disturbance 137 comparingly. Initially, the peat was carefully cleaned from woody plant material, which grew during the drainage phase, 138 such as leaves and stems, to increase replicability. Furthermore, to reduce variations in moisture content between samples 139 while preserving the cellular structure, tThe peat was gently, yet thoroughly mixed before a sample was and lightly packed 140 into columns (see appendix A.1); while no milling or sieving were was done. Prior to experimentation, samples were 141 saturated from the bottom in small increments, over a 24-hour period, using 18.2MQ cm water (ultra-pure water). All experiments were conducted at a target bulk density; (ρ_B ; g cm⁻³), of 0.12 g cm⁻³. Experiments were conducted in on 142 143 triplicates, except for the tension disk experiments, which were conducted on 4 samples. For the determination of the solute 144 transport properties, Cl⁻ was used as a non-reactive solute and Na⁺ as a reactive solute. All breakthrough experiments were performed using a solution of 200 mg l⁻¹ Na⁺ and 300 mg l⁻¹ Cl⁻ corresponding to values measured by Kessel (2016) in the 145

146 constructed Nikanotee Fen watershed. This solution was prepared by mixing 500 mg of NaCl (1.06404.055, ACS grade,

147 Merck, Germany) per <u>Hlitre</u> of ultra-pure water.

148 2.2 Soil hydraulic properties

149 To determine the peat soil hydraulic properties, we conducted transient evaporation experiments (Schindler, 1980, Peters et 150 al., 2015, Weber et al., 2017a, 2017b) for the retention properties, supplemented with tension disk experiments (Klute and 151 Dirksen, 1986; McCarter et al., 2017). Tension disk experiments are considered to be a more reliable method to determine 152 the unsaturated hydraulic conductivity in the wet range, because transient evaporation experiments contain limited 153 information at pressures heads between 0 and -60 cm for the unsaturated hydraulic conductivity curve (Peters and Durner, 154 2008). Water retention and unsaturated hydraulic conductivity data were obtained with the tension disk experiments using 10 155 cm i.d. and 5 cm high peat samples at -2.5, -5, -7.5, -10, -15, -20, -25 cm pressure head (h; cm) steps, which was also the 156 order in which the experiment was conducted. Outflow during each pressure step was monitored by scales with an accuracy 157 of 0.1 g and logged at 1-minute intervals and the unsaturated hydraulic conductivity calculated with the Darcy-Buckingham 158 equation (Swartzendruber, 1969). The transient evaporation experiments were conducted on the same samples using 159 commercial UMS HYPROP devices (UMS GmbH, Munich, Germany). The water retention and unsaturated hydraulic 160 conductivity data were then used to obtain parameters of the unimodal van Genuchten-Mualem model (van Genuchten, 161 1980; Mualem, 1976) by inverse modelling. For further details on parameters the reader is referred to appendix A.2. 162 The volumetric water content, θ , was determined as the difference between sample weight and the oven-dry mass for

163 samples dried at 80°C until no difference in weight was measured (Gardner, 1986). Bulk density was determined as the ratio

164 of dry weight to the original sample volume. Volumetric water content at saturation, θ_s , was assumed to be equivalent to the

- 165 sample total porosity. Saturated hydraulic conductivity (K_s ; cm d⁻¹) was determined with a constant head test (Freeze and
- 166 Cherry, 1979) using the flow-through chambers described below and a hydraulic gradient of 1.

167 2.3 Saturated breakthrough experiments and inverse modelling

168 2.3.1 Sample preparation

Saturated breakthrough experiments were conducted in 10 cm long, 10 cm i.d. PlexiglasTM (785 cm³) flow-through chambers, fitted at each end with 2.5x15x15 cm HDPE end-plates with silicon gaskets. A polypropylene fibre pad was placed between the plate and the sample to enhance the distribution of the solution beneath the sample (see appendix A.1). The NaCl solute source was a 20 l magnetically stirred solution reservoir pumped at a steady rate of 5 ml min⁻¹ (a flux density of 0.064 cm min⁻¹) using a peristaltic pump (WT600-3J, LongerPump, China) and the outflow solute concentration monitored continuously (e.g. Skaggs and Leij, 2002). Prior to the breakthrough experiment, the samples were flushed with 2 chamber volumes of the NaCl solution to reduce potential changes to the pore sizes as a result of swelling (Price and Woo,

- 176 1988; Ours et al., 1997) or clogging due to flocculation. Subsequently, the samples were inverted and flushed with ultra-pure
 - 6

177 water for 6 chamber volumes to remove the solutes that were introduced. To determine sampling times and the end of the experiment an EC electrode (11388-372, SympHony, VWR, USA) connected to a portable meter (SP80PC, SympHony, 178 VWR, USA) was used The EC meter was calibrated using a 2-point calibration with 84 μ S cm⁻¹ and 1413 μ S cm⁻¹ 179 conductivity calibration solutions (HI-7033 and HI-7031, respectively (Hanna instruments, USA). EC was checked every 5-180 181 10 minutes depending on the trend observed. Sampling was done with observed changes in EC and the experiment was 182 continued until 1 hour after the outflow EC value was similar to the inflow. Samples were collected in 1.5 ml polypropylene 183 micro centrifuge tubes (Z336769, Sigma Aldrich, USA) and kept frozen until analysed. Water samples were analysed for Na⁺ and Cl⁻ using an ion chromatograph (IC) (DIONEX ICS 3000, IonPac AS18 and CS16 analytical columns). Apparatus 184 185 blank corrections were done as described in Rajendran et al. (2008), where no transport model for the apparatus blank was 186 assumed but correction values generated using hermite cubic splines.

187 2.3.2 Solute transport models

Two different parametric solute transport model types were used to describe the observed breakthrough data of Cl^- and a third additional model for the Na⁺ data. We list the model in the order of testing. The first two consisted of the mobile immobile equation (MIM; Eq. (1) and (2); van Genuchten and Wagenet, 1989) and the classical convection dispersion equation (CDE; Eq. (3); van Genuchten and Alves, 1982, Nielsen et al., 1986), and the third is the one-site adsorption equation (OSA; Eq. (5) and (6); van Genuchten et al., 1974, Nielsen et al., 1986) which was only used for Na⁺.

193 The MIM for a non-reactive solute with instantaneous equilibration is given by

194

$$\beta \theta \frac{\partial c_m}{\partial t} = D \frac{\partial^2 c_m}{\partial^2 x} - v \frac{\partial c_m}{\partial x} - \alpha_{MIM} (c_m - c_{im})$$
 Eq. (1)

$$(1-\beta)\theta \frac{\partial c_{im}}{\partial t} = \alpha_{MIM}(c_m - c_{im})$$
 Eq. (2)

where β is the ratio of the water content of the mobile region to the total water content, θ (L³ L⁻³), *C_m* and *C_im* are the concentrations in the water phase of the mobile and immobile regions (M/L³), respectively, *D* is the dispersion coefficient (L² T⁻¹), *v* is the average linear pore water velocity (L T⁻¹), and α_MIM is the first order rate coefficient between the mobile and immobile region (T⁻¹).

199 The CDE is given by

200

$$\frac{\partial c}{\partial t} = \frac{D}{R} \frac{\partial^2 c}{\partial^2 z} - \frac{v}{R} \frac{\partial c}{\partial z}$$
 Eq. (3)

201

where *c* is the concentration of the total water phase (M L⁻³), and *R* is a retardation factor for equilibrium adsorption, which for a non-reactive solute is typically assumed to be 1 (but see Hoag and Price, 1997). In the classical interpretation, *R* is related to the adsorption distribution coefficient, K_d (M³ L⁻³), by $R = 1+\rho_B K_d/\theta$. The MIM reduces to the CDE equation under certain conditions, which can be analysed by the dimensionless Damkohler number (D_a ; Vanderborght et al., 1997, Wehrer and Totsche, 1995), Eq. (4), given by

207

$$D_a = \frac{\alpha_{MIM}L}{\nu(1-\beta)\theta}$$
 Eq. (4)

208

where *L* is the column length (L). Large D_a values indicate very fast equilibration between the regions. From inspection of Eq. (4) it becomes clear that $\lim_{\beta \to 1} D_a \to \infty$, and as α_{MIM} increases, D_a increases proportionally, signifying instantaneous equilibration, thus a differentiation between the two regions cannot be determined. Moreover, Parker and Valocchi (1986) showed that the CDE may also be applicable when a considerable part of the solute dispersion is caused by diffusion into the immobile region.

In physical non-equilibrium the attenuation of both reactive and non-reactive solutes is affected. However, if only the reactive solute shows long tailing, then it can be assumed that chemical non-equilibrium is affecting the flow process. In NaCl breakthrough experiments (Rezanezhad et al., 2012), only Na⁺ showed long tailings in fen peat so that the physical non-equilibrium model should not be employed. For this case, first-order kinetic chemical non-equilibrium models may be chosen. One typical model for solute transport in porous media is the one-site adsorption equation which is an expansion of the CDE with the addition of a kinetic adsorption member. It is given by

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial^2 z} - v \frac{\partial c}{\partial z} - \alpha_{OSA} [(R-1)c - \frac{\rho_B}{\theta}s]$$
 Eq. (5)

$$\frac{\rho_B}{\theta} \frac{\partial s}{\partial t} = \alpha_{OSA} [(R-1)c - \frac{\rho_B}{\theta}s]$$
Eq. (6)

where s is the kinetically sorbed concentration to the solid (M), and α_{OSA} is the first order rate coefficient between dissolved and adsorbed concentration (T⁻¹) which has been found to be a function of pore water velocity and cannot be derived by batch experiments alone (Nielsen et al., 1986).

223 Following the traditional approach for solute transport parameterization in peat (Rezanezhad et al., 2012, 2017), we initially 224 assumed the MIM model and compared it with the performance of the CDE for the non-reactive solute. For Na⁺, transport 225 parameters were additionally estimated with a one-site chemical adsorption model. The data used for the fitting were 226 averages of three replicates. Parameterization of the model was done with CXTFIT (V2.0; Toride et al., 1995), which 227 minimises the least-squares. We estimated the following parameters: v and D for the CDE, v, D, β , and α MIM for MIM, and 228 R and α OSA for the OSA model. The estimated D and v from the Cl⁻ data fit were used for the Na⁺ simulations, since 229 dispersion is a physical material property, and R can only be determined if v is fixed from knowledge of a conservative 230 solute experiment. Using various starting values, we ensured that the global minimum was found. CXTFIT calculates the 231 variance-covariance matrix, which is required for the calculation of the standard errors of the parameters and the parameter 232 correlation matrix.

233 The root-mean-squared-weighted error (RMSE) was used as an index for model performance calculated for each of the

tested models (Eq. (14) in Weber et al, 2016). The corrected Akaike Information Criterion (AICc; Eq. (2) in Ye et al. 2008)

was used as a method of model comparison where the model with the smallest AICc is to be favoured. It is a statistically robust and commonly used index to compare models in soil physics (e.g. Weber et al., 2017a).

237 2.4 Unsaturated breakthrough experiments and sensitivity analyses

238 2.4.1 Sample preparation

239 The unsaturated solute breakthrough experiments were designed as six steady state evaporation columns 23 cm high and 10 240 cm i.d. (Fig .2). Peat samples were placed in a column constructed with a grooved HDPE base plate with an inlet, inlet; a 241 silicon washer and polypropylene fibre pad, and open at the top (see appendix A.1). The columns were slowly saturated from 242 the bottom in small increments over 48 hours to minimize trapped gas bubbles. Once saturated, the columns were flushed 243 with 2 column volumes of the NaCl solution to reduce potential changes in hydraulic properties, as previously described. 244 This-The NaCl flushing was followed by flushing 6 column volumes of ultra-pure water to remove the Na⁺ and Cl⁻, with the water overflowing from the top of the sample. Flushing of Na⁺ did not remove all solute, resulting in 40 mg l^{-1} of Na⁺ 245 246 remaining in the time 0 samples taken at the bottom 8 cm of the column. Nevertheless, these concentrations were accounted 247 for in the HYDRUS simulation. Columns were then drained overnight with 0 cm pressure head at the bottom of the sample, and connected to a Marriot device containing ultra-pure water. The water table was set to the base of the peat column, and 248 249 the columns were left to settle for 11 days, after which the columns were instrumented with the soil tensiometers and water 250 samplers (further details below).

Each Marriot device was fitted with a low flow 12-volt mini water pump to circulate the water within it for 5 minutes every 251 252 two hours, to prevent solute stratification. Three Marriot devices were filled with an 8.9 mM solution of NaCl as treatment and three with ultra-pure water. The columns were fitted with 4 unsaturated soil water samplers at 2.5, 7.5, 12.5 and 17.5 cm 253 254 above the water table (19.21.05, Rhizon, Rhizonsphere, Germany), and with 2 two tensiometers at 10 cm (LM) 23 cm (UM), 255 to determine if the water pressure deviated from hydrostatic conditions (see appendix A.3). Tensiometers were composed of 256 a porous clay cup and a flexible silicon tube, which was open to the atmosphere. The experiment was run for 120 days; 257 evaporation was calculated based on changes to the water level in the Marriot device (see appendix A.3). The experiment 258 was conducted in a room with controlled humidity maintained at \sim 45%, assisted by a fan to mix the air in the chamber. 259 Relative humidity (RH) and temperature were measured every 10 minutes (ECT, Decagon, USA) (see appendix A.3).

9



• Soil water pressure meter

262 Figure 2 – Unsaturated column experiment column and water reserve setup.

263

261

NaCl solution was introduced at the base of the column and drawn upwards by evaporation. Marriot devices were attached to supply water over the bottom boundary for each column. The pressure head at the lower boundary was fixed to a pressure head of 0 cm for the duration of the experiment. Daily <u>measurements-values</u> of the water level in the Marriot were measured with a measuring tape, and the evaporative water flux over the upper boundary was calculated by dividing the water lost by the cross-sectional surface area of the column (see appendix A.3).

269 Pore-water samples were taken weekly from each sample height through the Rhizon samplers. On average, 5.5 ml of water 270 was drawn from each sampler using a dedicated 30 ml polypropylene syringe (Z683647, Sigma-Aldrich, USA). To ensure 271 equal pull on each sampling point, 6x4x4 cm HDPE spacers were fabricated and placed within the syringe body and piston. 272 Only samples from time steps 0, 21, 42, 63, 84 and 120 days were analysed. After the experiment ended the cores were 273 frozen then sliced to ~ 2 cm thick sections using a band saw. Sections were measured with callipers, weighed and placed in 274 pre-weighed, food grade and heat resistant bags. The slices were than thawed and ultra-pure water, twice the weight of the 275 slice, was added to extract the solutes and placed on a table shaker (MaxQ 3000, Thermo scientific) for 48 hours. All 276 samples were frozen until analysed for Na⁺ and Cl⁻ via IC at the Biogeochemistry Laboratory at the University of Waterloo 277 (DIONEX ICS 3000, IonPac AS18 and CS16 analytical columns). Results were adjusted to account for the dilution effect of 278 the added water.

279 2.4.2 Numerical simulations and sensitivity analyses

280 The steady state unsaturated evaporation experiment with solute transport was simulated with HYDRUS-1D (Simunek et al.,

281 2008), which numerically solves the Richard's equation for water flow, and the solute transport equations. For the water 282 flow, the soil hydraulic properties are the necessary input and were parameterized with a unimodal van Genuchten-Mualem 283 equation using data collected in the tension disk experiments and transient evaporation experiments. The model domain

- represented the 23-cm high column with a spatial discretization of 0.5 cm.
- The lower boundary condition for the water flow was a constant zero pressure representing the water table. The upper boundary condition was a flux boundary based on measured evaporation rates. For the solute transport, the lower boundary was a fixed concentration in the liquid phase and the upper boundary condition was a zero flux. To account for the soil solution sampling (that would otherwise lead to a misrepresentation of water flow and solute transport), we used the Root Water Uptake function in HYDRUS by specifying an individual root at the height of each of the four Rhizon samplers. The applied root water uptake model (Feddes et al., 1978) assumes no salinity stress, no pressure dependent reduction of given water uptake quantity, and a quasi-infinite maximum allowed concentration for passive root solute uptake. The total water
- volume extracted per sampling day was taken to be equal at each root node.
- 293 Dispersion is dependent on the average linear velocity, which in turn is dependent on the water content (Perkins and 294 Johnston, 1963). To date, HYDRUS does not account for a water content dependency of dispersion $(D(\theta))$ in solute transport modelling. Also, this information is not available from the saturated experiment. Therefore, a sensitivity analysis of 295 296 D on the model response was done to approximate its quantitative influence on the solute transport. To gauge the range of 297 values for the sensitivity analysis, a calculation of the change in D was performed using data gathered from the unsaturated 298 columns. The calculation used the equation for D in capillary flow under unsaturated conditions in soils as a function of v, 299 by Fried and Combarnous (1971) (not shown). The equation connects D to changes in water content and allows the calculation of changes in D due to measured changes in water content. Comparison of the calculated values provided with a 300 301 range of change in D. Calculations indicated that the change in D ranged from 8% to 15%. Therefore, to add extra range the 302 sensitivity analysis for the HYDRUS model was performed using $\pm 20\%$ and a $\pm 100\%$ change in D. 303

304 3 Results and discussion

305 **3.1 Soil physical properties**

306 The bulk density and porosity of the prepared peat samples used in the various experiments was similar (Table 1) indicating

307 <u>a successful samples replication</u>. The retention curve (Fig. 3) does not have the classical shape that would point at

308 discrimination between an active and inactive porosity (Rezanezhad et al., 2016, Weber et al., 2017b). Measured water

- 309 retention and hydraulic conductivity data closely fit the van Genuchten-Mualem unimodal model with an RMSE of 0.03 and
 - 11

310 AICc value of--342 (Fig. 3; Table 2). Furthermore, the estimated Ks value of the unimodal fit (106 cm d⁻¹: Table 2) is

311 similar to the measured value (100 cm d^{-1} ; Table 1).

312 Table 1 - Soil physical and hydraulic properties of prepared peat cores from different experiments. Values are averages;

percentages in brackets are the coefficient of variation. Porosity was calculated using particle density for the constructed fen peat,
 from Ketcheson et al. (2017).

Type of experiment		ρ_{B}	Ks	Porosity	
		[g cm ⁻³]	$[\operatorname{cm} \operatorname{d}^{-1}]$	[-]	
Saturated breakthrough	3	0.12 (1.7%)	99.7 (2.1%)	0.93 (1.3%)	
Unsaturated columns	6	0.12 (4.1%)		0.93 (2.8%)	
Retention	4	0.12 (3.3%)		0.93 (2.3%)	





Figure 3 – Soil water retention and hydraulic conductivity curves with measurement results of the transient evaporation
 experiments (EEt) and Tension Disk Experiments (TDE) and parameterizations for the unimodal van Genuchten-Mualem model.
 Negative pressure was used for the retention experiment.

Table 2- Parameter results for the soil hydraulic properties function of the unimodal model saturation function; the parameter names are explained in the text.

	model	θ_{r}	θ	a 1	n ₁	Ks	τ	\mathbf{W}_2	a ₂	n ₂	n _p	RMSE0 (h)	RMSE log ₁₀ K(h)	AICc
_		[-]	[-]	$[cm^{-1}]$	[-]	$[\operatorname{cm} \operatorname{d}^{-1}]$	[-]	[-]	$[cm^{-1}]$	[-]	[-]	[-]	$[cm d^{-1}]$	[-]
	uni	0	0.93	0.015	1.6	106	10	-	-	-	5	0.03	0.19	-342

322 3.2 Saturated breakthrough experiment

323 Cl⁻ breakthrough started around ~60 minutes with $C/C_0=0.5$ arriving 97 minutes from the start of the experiment (Fig. 4). Complete Cl⁻ breakthrough (C/C₀=1) was achieved after 300 min. Similar to Cl⁻, initial Na⁺ breakthrough began ~ 60 324 325 minutes from the start of the experiment (Fig. 4). However, $C/C_0=0.5$ was not achieved until ~250 minutes, with only ~0.85 breakthrough at the end of the experiment that had prolonged tailing, indicating non-equilibrium process. The EC curve is 326 327 similar in shape to that of Cl⁻, but took longer to reach the full breakthrough. Attenuation of Na⁺ compared to Cl⁻ is evident by the greater time until $C/C_0=0.5$ (Fig. 4), is attributed mainly to the high adsorption capacity of peat (Ho and McKay, 328 329 2000). In contrast, Cl⁻ attenuation in peat is mainly due to mechanical dispersion and diffusion into dead-end pores and not 330 adsorption (Price and Woo, 1988). The dissimilarity of the EC breakthrough curve to that of Na⁺ (Fig. 4) demonstrates the limitation of using EC electrodes as an indicator for solutions containing reactive solutes, flowing through reactive mediums. 331 332 This limitation is due to enrichment of ions in the solution from the soil and cation exchange with the medium, which 333 changes the solution concentration of the cation of interest; therefore, EC can be a good estimator for non-reactive solutes but is limited as an indicator for cation transport (Olsen et al., 2000; Vogeler et al., 2000). 334



335

Figure 4 – EC, Cl⁻ and Na⁺ corrected saturated breakthrough curves in saturated peat over time. Each point is an average of 3
 samples, error bars are standard error of mean. Errors were not accounted for in the fitting.

339 3.3 Unsaturated column experiment

340 The evaporation rate of the experiment was 3 mm d⁻¹ (not shown, see appendix A.3). As expected, Cl⁻ was transported faster

341 than Na⁺ as evident by the more rapid rise of Cl⁻ in the peat profile (Fig. 5). $C/C_0=0.5$ of Cl⁻ reached 7.5 cm above water

table within 21 days (Fig. 5a) and by 42 days C/C₀=0.5 reached 17.5cm (Fig. 5a). Complete breakthrough (C/C₀=1) of Cl⁻

343 was achieved between 63 to 84 days from start of experiment (Fig. 5a).



Figure 5 - Breakthrough curves of solutes in the unsaturated columns profile, a) of Cl⁻, and b) of Na⁺. Values presented are averages and whiskers are standard errors. "Cntl avg" represents the average of control measurements; for this aim, all measurements in a specific height were averaged with each point representing 18 measurements. For the treatment, each point is an average of 3 measurements. Each treatment curve represents a different sampling time from start of experiment. 0 cm is the water table location.

350 Comparably, Na⁺ C/C₀=0.5 reached 7.5 cm within 21 days (Fig. 5b). After 42 days, the C/C₀=0.5 was located between 12.5 351 to 17.5 cm from the water table (Fig. 5b). Complete Na⁺ breakthrough occurred later than Cl⁻, sometime after 84 days but 352 before 120 days (Fig. 5b). The accumulation of both elements above inflow concentrations (C/C0>1) at 17.5cm after 120 days (Fig. 5b), indicates evaporative accumulation occurred as water molecules left the column while solute molecules 353 354 remained (Tsypkin, 2003). Therefore, evaporative accumulation enhances the breakthrough rate as ions remain in the soil 355 while water evaporates; thus, producing a faster accumulation rate than if the breakthrough was estimated using a saturated 356 flow system where the solutes would leave the system with the solution. Nevertheless, this effect is a basic product of 357 evaporation controlled transport (Elrick et al., 1994; Tsypkin, 2003).

358 3.4 Simulations

359 3.4.1 Solute transport model selection

360 For all transport models, the fitted parameters and associated uncertainties, AICe, and RMSE values are given in Table 3.

361 The CDE and MIM model for Cl⁻ fit the data well (Fig. 6a), and have identical RMSE (0.032 mg/l). However, the AICc is

362 favors the CDE. Additionally, the MIM model estimated parameters (v, D and β) show much larger coefficients of variation,

363 with β varying by 1510% (Table 3). During fitting, α_{MIM} ran into the CXTFIT internal upper boundary, further suggesting

that the application of the MIM is an over-parameterization and therefore not suitable. Also, the MIM has two additional parameters than the CDE model, which makes the simpler CDE model preferable (Cavanaugh 1997).

The Peclet number, which is the ratio of advective vs. diffusive transfer, was 33.9 for the fitted Cl⁻ breakthrough data, which 366 is the ratio of advective vs diffusive transfer, was 33.9. In systems with values > 2 diffusion is considered negligible 367 (Huysmans and Dassargues, 2005). Moreover, with $\beta \rightarrow 1$ (Table 3), the Damköhler number, D_a , approaches infinity, so 368 369 that the equilibration between the mobile and immobile zones is considered instantaneous (Wehrer and Totsche, 2005; 370 Vanderborght et al., 1997). In other words, D_a indicates the system is not governed by physical non-equilibrium processes, 371 but rather the simpler CDE concept applies. The significance of this result is that the physical non-equilibrium approach may 372 be excluded for these samples and boundary conditions. This is supported by the instantaneous equilibration between the 373 mobile and the immobile zone, indicated by the very large ω which was at the upper bound during the parameter estimation. 374 One possible reason for this finding could be based on the inherent nature of the samples. The peat of the Nikanotee Fen 375 watershed (i.e., the peat used in this experiment) was moderately decomposed sedge peat containing small amounts of 376 Sphagnum moss (Nwaishi et al., 2015). It is the Sphagnum mosses that contain the hyaline cells (Hayward and Clymo, 377 1982), which are probably the main cause for the existence of dead end pores. Therefore, with only a small part of the peat 378 originating from Sphagnum, the potential for dead end pores was small compared to peat that originates mainly from 379 Sphagnum moss. Additionally, evidence found in the SEM scans of the peat used in this study (Fig. 1), shows that the cell 380 walls membranes have decayed, with only the skeleton of the cell remaining, while the skeleton itself is still intact so water 381 can move much more freely through these structures. These results contradict the hitherto common finding in laboratory 382 studies that breakthrough experiments on peat need to be described by the MIM (Hoag and Price, 1997; Rezanezhad et al., 2012; Liu et al., 2016; Rezanezhad et al., 2017; Thiemeyer et al., 2017) These results contradict the hitherto assumption that 383 solute transport in peat has to be simulated using the MIM. Additionally, this finding is reflected in the fact that a 384 385 multimodal retention curve was not observable, which would have been indicative for a two--domain flow of solute 386 transport.

387 As Since the CDE model provides a good description of the saturated Cl breakthrough, and physical non-equilibrium can be 388 discarded-neglected as the underlying process (Table 3; Fig. 6b). Therefore, the non-equilibrium effect observed in the Na⁺ breakthrough (Fig. 6b), must be due to chemical processes such as an interaction of Na⁺ ions with negatively charged sites 389 390 on the peat surface, whether through retardation or adsorption. Having shown that the MIM is not parsimonious in its 391 parameters and, the robust estimates of v and D for the CDE, these were fixed when fitting the remaining model parameters 392 of the CDE and one-site adsorption model for Na⁺. First, the CDE was fitted with R to the Na⁺ data; the resulting curve 393 shows that equilibrium adsorption does not fit (Fig. 6b). In comparison, the one-site adsorption model fit well (Fig. 6b) and had a lower RMSE and a considerably lower AICc value (Table 3). Based on the estimated R-value of the one-site 394 adsorption model, the K_d value of Na⁺ was 15.6 l kg⁻¹. The parameters from the CDE for Cl⁻ and from one-site adsorption for 395 Na⁺ were then used for the HYDRUS simulation of the unsaturated columns. 396







Solute	Model	v	D	R	β	ω	α	RMSE	AICc
		$(\operatorname{cmmin}^{-1})$	$(\mathrm{cm}^2 \mathrm{min}^{-1})$	-	-	<u>(-)</u>	(\min^{-1})	$(mg l^{-1})$	(-)
Cl	MIM	9.81*10 ⁻² (91%)	6.66*10 ⁻² (19%)	fixed to 1	1.00 (1510%)	100 ^{‡<u>a</u> (neN/E)}	<u>0.9</u> (<u>neN/E</u>)	0.032	-406
	CDE	$9.79*10^{-2}$ (1%)	$6.66*10^{-2}$ (7%)	fixed to 1	N <u>-/</u> A-	<u>N/A</u>	N <u>/</u> -A-	0.032	-408
NL- ⁺	CDE	fixed	fixed	2.65 (3%)	N . /A-	<u>N/A</u>	N <u>∕</u> -A-	0.145	-229
INa	OSA	fixed	fixed	3.07 (1%)	N . /A-	0.5 ^{2<u>b</u>} (3%)	1.12*10 ⁻³ (3%)	0.024	-443

403

 $3 \frac{1}{2} \omega_{MIM} = \alpha * L / (\theta * v)_{\frac{2b}{2}} \omega_{OSA} = (\alpha (R-1) * L) / v$

404 3.4.2 Unsaturated column simulations and sensitivity analyses

The HYDRUS predictions of solute concentrations at the four observation points were good for both solutes (Fig. 7), even though the solute transport model parameterization was based on the saturated experiments. Plotting of the concentrations from the solute extractions for the upper part of the core at the end of the experiment reaffirmed the models' generally good fit for both solutes (Fig. 7), although in both cases the models underestimate the measured concentration at the very top of the soil profile (Table 4).



Figure 7 - Observed values (Obs) from the unsaturated column experiment vs simulated values (Sim) of a) Cl⁻; and b) Na⁺. Observed values are averages and standard error, n=3. T stands for time and the number that follows is the number of days. Extract T120 represents values measured via extraction as part of post experiment processing. Zero (0)0 depth marks the surface of the column. Dashed reference line marks C/C0=0.5.

413 Table 4 - Unsaturated transport parameters used in or estimated by HYDRUS and models' goodness of fit data. ---<u>N/A</u> = not

414 applicable. Estimated values are presented with the coefficient of variation as percentages in brackets. Diff. W is the molecular 415 diffusion coefficient of the solutes.

_		D [cm ² min ⁻¹]	Kd [l kg ⁻¹]	[*] Diff.W [cm ² min ⁻¹]	α [1 min ⁻¹]	β	RMSE [mg l ⁻¹]
	Cľ	6.81*10 ⁻²	0	1.22*10 ⁻⁴	- <u>N/A</u>	- <u>N/A</u>	15.65
	Na^+	6.81*10 ⁻²	15.6	7.98*10 ⁻⁵	1.11*10 ⁻² (1.1%)	1.00 (8.1%)	10.19

taken from Appelo & Postma (2004).

416

417 Given that the dispersion coefficient for the unsaturated modeling was based on measurements in the saturated flow-through chambers, a sensitivity analysis was performed with HYDRUS to determine its impact on the simulations. It indicates that a 418 419 $\pm 20\%$ change in the dispersion coefficient resulted in a $\pm 1.2\%$ and a $\pm 4.1\%$ change in the final concentration of Cl⁻ and Na⁺, 420 respectively (Fig. 8). Further, an analysis with a $\pm 100\%$ change in D altered the final concentrations by -5% to 6.5% for Cl⁻ 421 and by 9% to -17% for Na⁺. The analysis demonstrates unsaturated transport is not highly sensitive to changes in the 422 dispersion coefficient under the experimental conditions used. Furthermore, since the differences in water contents were not 423 large, ranging between 0.93 at full saturation to 0.84 at the top of the column, it is likely that the actual hydrodynamic 424 dispersion did not vary significantly.

425



426

Figure 8 – Sensitivity analysis of unsaturated transport for changes in the dispersion coefficient. a) in Cl⁻ transport, b) in Na⁺.

429 Conclusions

430 Saturated breakthrough experiments on disturbed peat, sampled taken from stocks used in the Nikanotee Fen, were

431 conducted in the laboratory using conservative and reactive solutes. With this approach, we investigated whether we tested if

432 the common assumption of mobile-immobile solute transport process best reflects the transport processes in saturated and

433 unsaturated peat. Based on inverse modeling of time series of measured conservative tracer concentrations, and robust

434 statistical evaluation, we found that the MIM model was an over-parameterization for Cl^{-} , since very good results were found

435 using the simpler CDE.

For this reason, it could be deduced that the Na⁺ attenuation, expressed by prolonged tailings in the observed breakthrough in the fen peat is chemically based, as the physical non-equilibrium (i.e. MIM) approach would have had an effect on both solutes. Hence, we can conclude that Na⁺ showed distinct chemical non-equilibrium adsorption process, which could be described using the OSA model, and still fulfilling the requirement of parsimony. The results are in contrast to the

440 commonly accepted MIM behavior of solutes breakthrough in peat samples.

441 The significance of this <u>result</u> is that while reactive solutes may be heavily attenuated in peat, conservative solutes are not

442 necessarily retarded (Hoag and Price, 1997). In this-the presented case the degraded structure of the peat (Fig. 1) eliminated

443 many of the enclosed spaces commonly visible in less decomposed *Sphagnum* peat (see Hoag and Price, 1997; Rezanezhad 444 et al., 2016).

445 Measured water retention data <u>was_were</u> adequately described using a unimodal expression for the underlying pore size 446 distribution, corroborating the finding that a physical dual porosity structure was not present.

447 On a side note, we can attest that the use of EC as an indirect measurement for a reactive solute will result in overestimation448 of breakthrough if the solute interacts with the solid phase.

449 This research implies that automatically assuming mobile and immobile regions in peat is incorrect. The sedge peat with remnants of Sphagnum moss used in this experiment potentially had a limited amount of relatively few dead end pores, due to 450 451 the low content of Sphagnum moss with intact hyaline cells. Furthermore, evidence suggests that the peat used has decayed enough to lose the cell walls-membranes but not enough to break the cell skeleton, and is likely why the peat lacks the 452 453 classically assumed MIM regions. The decomposition may have been enhanced by aeration of the peat in the donor fen (Nwaishi et al., 2015). Although we acknowledge that any manipulation of a sample alters it, the prior disturbance (see 454 455 introduction of the method section) is likely to have had a significantly greater impact. Furthermore, the peat was not manipulated in a destructive manner such as sieving or milling, and was handled carefully. The reduced inter-sample 456 457 variability caused byas a result of the careful homogenization of the peat process provides the improved the certainty in our results, thus our ability to understand the hydraulic properties of the peat. Additionally, it is concluded that transport 458

459 parameters gathered in saturated breakthrough experiments can be used to simulate transport in slightly unsaturated media

460 under near steady state conditions. Data gathered show that the accumulation of solutes via evaporation causes concentration

461 to rise quickly above the initial concentration. While these results are valid for the described boundary conditions and initial

462 conditions, the fate of salt accumulation is not clear under more natural conditions such as complex meteorological evapotranspiration-precipitation cycles, with, for example, surface inundation and overland flow export of solutes. 463 464 Additionally, different salt concentration levels at the lower boundary of the experiment were not investigated, which has 465 been documented in the case of the Nikanotee Fen watershed (Kessel, 2016). As a first assessment of the effect D has on salt 466 accumulation, a synthetic parameter sensitivity analyses was carried out for Na⁺. To further understand the rates of the evaporative accumulation, a more complex numerical transport model should be used, including flushing due to precipitation 467 468 and runoff, using the parameters reported in this study along with various weather scenarios. Considering the complex 469 hydraulic retention and conductivity properties of Sphagnum mosses and peat, it is conceivable that a wide range of tested 470 water contents could affect the choice of the underlying transport process. Additionally, the experiment was carried out 471 under steady state conditions, unlike the complex meteorological patterns in the field. Finally, the implications for 472 reclamation projects are that if one of the goals is to enhance solutes attenuation, the origin and composition of the peat, its 473 water retention properties along with its decomposition state should be characterized as not all peats will perform equally. 474 From the industry perspective, if solute attenuation is the goal then peat with a larger amount of Ssphagnum and a confirmed 475 dual porosity structure would be a better choicechoosing and peat with dead end pores would allow a potential for significant 476 attenuation.

477

478 A.1 Appendix 1: Pictures of saturated and unsaturated experiments.



479

480 Figure A.1.1 - Pictures from saturated transport experiment. A) Cleaning and mixing the peat; B) flow through cells plates. The

481 green pad is below the sample, redistributing the water beneath it; C) packing cell with peat; and D) flow through experiment 482 setup, cells are connected to a pump drawing the solution from a container on a magnetic stirrer.

483



Figure A.1.2 - Pictures from the unsaturated transport experiment. A) columns with peat, note the laptop for scale; B) Marriot bottles and pumps; C) columns connected and instrumented, Blue caps are the soil pore water samplers, large tubes are the tensiometers; and D) slice of a peat column before extraction at end of experiment.

488

489 A.2 Appendix 2: Soil hydraulic properties

490 Measurements of water retention properties

491 The tension disk experiment (TDE) was conducted on 10 cm i.d. and 5 cm high peat samples at seven different pressure 492 steps under unsaturated unit gradient vertical flow conditions using a tension disk apparatus that used 15 µm Nytex screens 493 to prevent air entry below the air entry pressure (~35 cm) (Price et al., 2008, McCarter et al., 2017). Samples were initially 494 saturated for 48h and two layers of cheese-cloth covered the top and bottom of the sample to maintain the integrity of the 495 surfaces. The pressure steps (h; cm) were -2.5, -5, -7.5, -10, -15, -20, -25 cm, which was also the order in which the 496 experiment was conducted. During the experiment, outflow was monitored for each pressure step by a scale with an accuracy 497 of at least 0.1 g and logged at 1-minute intervals. The experiment stopped when there was no change from past 498 measurements over a 30-min. period. After each step the weight of the sample was determined to enable calculation of the 499 water content. From the outflow, the unsaturated hydraulic conductivity was calculated from the Darcy-Buckingham 500 equation (Swartzendruber, 1969).

501 Saturated hydraulic conductivity

- 502 The FTC were used for the determination of the saturated conductivity (K_s ; cm d⁻¹), too, which were connected to a
- 503 Marriot's bottle supplying a constant pressure head. The adopted method was a constant head test (Freeze and Cherry, 1979)
- 504 with a gradient of 0.44. Once the outflow stabilized, it was measured in a 250ml glass graduated cylinder (S63459, Fischer
- 505 Scientific, USA) every 2 min over 20 min.

506 Transient evaporation experiment

507 The transient evaporation experiment (EEt) was conducted on the same samples as the TDE. With a 0 cm pressure head at

- 508 the bottom prior to the beginning of the EEt with the commercial UMS HYPROP device (UMS GmbH, Munich, Germany).
- 509 The samples had a larger diameter than the UMS HYPROP device so that Plexiglas screens were used at the bottom to seal
- 510 and prop the sample. The pressure head was directly measured in the middle of the sample and, thus, directly related to the
- 511 calculated water content to obtain the retention information, which is a valid approximation at or near a linear pressure
- 512 distribution (Becher, 1971). With this<u>Hence</u>, the evaluation for conductivity is not reliable.

513 Inverse fitting of soil hydraulic properties

- 514 The water retention and unsaturated hydraulic conductivity data were used to parameterize soil hydraulic property (SHP)
- 515 models. We used the unimodal van Genuchten-Mualem model combination (van Genuchten, 1980; Mualem, 1976). We used
- 516 the analytical expression derived by Priesack and Durner (2006). The soil water retention function is given by

$$\theta(h) = \theta_r + (\theta_s - \theta_r) \Gamma(h)$$
 Eq.(A.1)

517 where θ_r is the residual and θ_s the saturated water content (cm³ cm⁻³) and $\Gamma(h)$ (-) the effective saturation given by

$$\Gamma(h) = \sum_{i=1}^{\kappa} \Gamma_i(h) = \sum_{i=1}^{\kappa} w_i \left[1 + (-\alpha_i h)^{n_i} \right]^{m_i}$$
 Eq.(A.2)

- where, w_i is a weighting coefficient between the modal pore size distributions, and α_i (cm⁻¹) and n_i (-) are shape parameters
- 519 with constraining, $m_i = 1 1/n_i$. The unimodal van Genuchten saturation function is obtained by k = 1. The unsaturated 520 hydraulic conductivity is expressed as
 - $K(\Gamma) = K_{s}\Gamma^{\tau} \left(\sum_{i=1}^{k} w_{i}\alpha_{i}\right)^{-2} \left(\sum_{i=1}^{k} w_{i}\alpha_{i} \left[1 \left(1 (\Gamma)^{1/m_{i}}\right)^{m_{i}}\right]\right)^{2}$ Eq.(A.3)
- 521 where K_s is the saturated hydraulic conductivity (cm d⁻¹) and τ is sometimes referred to as a tortuosity constant, which 522 should be positive-
- All parameters were estimated except for θ_s , which was set to 0.925, i.e. the porosity value. Estimation was done in R.3.2.1 (R Core Team 2015) with implementation of the differential evolution optimiser to minimise the sum of squared errors for the retention and hydraulic conductivity curves (Mullen et al., 2011). The estimation of the soil hydraulic properties of the fen peat by inverse estimation was done as described in Peters and Durner (2008). After all procedures were concluded, bulk densities for all samples were determined gravimetrically based on an oven-dry mass basis for samples dried at 80 °C until no difference in weight was measured (Gardner, 1986). From knowledge of the dry weight and experimental system weight water contents could be calculated for the soil hydraulic properties.

- 530 Statistical parameters
- 531 The root mean square error (RMSE) is used as a metric to describing the model prediction quality, such that

$$RMSE = \sqrt{\frac{1}{m} \sum_{l=1}^{m} (y_l - \hat{y}_l)^2}$$
 Eq.(A.4)

where *m* is the number of observations, y_l is the observed and \hat{y}_l the model predicted value (solute concentration, water content or hydraulic conductivity). The corrected Akaike Information Criterion (AICc; Ye et al. 2008)) was also used as a method of model comparison where the model with the smallest AICc is to be favored. Applications so soil hydrological model testing can be found in Weber et al. (2017a, 2017b).

$$AICc = m \ln\left(\frac{1}{m}\sum_{l=1}^{m} (y_l - \hat{y}_l)^2\right) + 2n_p + 2\frac{n_p(n_p+1)}{m - n_p - 1} + C$$
 Eq.(A.5)

537 where n_p is the number of parameters of a respective model.

Estimation of model parameters was done by minimising the sum of squared errors for the retention and hydraulic conductivity curves in R.3.2.1 (R Core Team 2015) with an implementation of the differential evolution optimiser (Mullen et al., 2011) by adopting the multi-objective function as described in Peters and Durner (2008).

541

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- 545

546

547 A.3 Appendix 3: Unsaturated experiment conditions

Ambient conditions in the chamber where the experiment was conducted were stable with an average temperature of $\sim 25\pm 1$ °C and an average RH of 41 ± 0.02 % (Fig. A.3.1). Additionally, water pressure profile in the soil did not vary much for each column; soil water pressure above the water table averaged -10.7 ± 0.5 cm for the low meter and -19.5 ± 0.5 cm for the high meter (Fig. A.3.2). Furthermore, data from all columns were in a similar range (Fig. A.3.2) meaning the columns were reasonable replicates in soil water pressure.



Figure A.3.1 – measured temperature and relative humidity during the unsaturated column experiment. Each point is a daily average of 144 measurements and corresponding standard error.



Figure A.3.2 – Soil water pressure measurements over time. 0 cm marks the water table. Values around the -10 cm mark are from the low pressure meters of all 6 columns; values around -20cm are from the high pressure meters.

- 559 Moreover, E data strengthen the conclusion that the columns were decent replicates with an overall low fluctuation
- 560 in values averaging at 0.27 ± 0.05 cm d⁻¹ (Fig. A.3.3).



561

562 Figure A.3.3- Calculated ET during the experiment. Data presented is for each column separately (color coded, see legend).

- 563
- 564

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