Response to review - Geophysically-based analysis of BTCs and ion exchange processes in soil (Ben Moshe et al.)

Dear Dr. Stumpp,
We thank you and the two anonymous referees for the comments. We find all of the comments constructive and account for them in a revised version of the paper, as we report in the following reply:

Referee #1

Specific comments

1. *The description of fitting the "non-reactive" vs "reactive" cases is confusing. Figure 4 presents the full time series SIP dataset based on the cumulative experimental time, but figures 4b and c seem to redefine the starting time. It would be clearer if everything was plotted in relation to a single start time, but the injection of the different solutions was clearly highlighted.*
Author response - We believe that the referee misunderstood the description of the experiment represented by Fig.4. Figures 4a-c have the same starting time. Each experiment started with a 'pre-wash' stage in which the column was flushed with a background solution of $NaCl$. After the outflow EC stabilizes on the same value of the background solution, it was replaced by the inflow solution (of either $CaCl_2$ or $ZnCl_2$). The replacement of the background solution by the $CaCl_2$ or $ZnCl_2$ solutions marked $t = 0$. Since this was not clear we now state this specifically in the description of the column experiments (see Line 122-125 in the revised text).

2. *Equations 6 and 7 imply that the authors assumed linear retardation for the Ca2+ and Zn2+ ions. Is this justified for this particular loamy soil? Is there evidence to suggest that Ca and Zn sorption could exhibit a saturation-type (Langmuir/Freundlich) behavior?*
Author response - Linear adsorption patterns is assumed here for simplicity. Obviously, a non-linear (Langmuir or Freundlich-type isotherms) could have been used for the calibration. Since the values of the adsorption coefficient were not the main concern here (rather the demonstration of the model calibration using the SIP data) we see it as a reasonable approximation given the relatively narrow range of concentrations considered in this study.

3. *Are the estimated parameters from the SIP-based calibration able to capture the Na+ and Ca2+ breakthrough behavior when considering that both ions are present at the same time? (Figure 3b)*
Author response - The simple model we present here divides the SIP data into two parts (reactive and non-reactive species) and the calibration of each part is performed separately. It is correct that at this point we use only real conductivity for both the reactive and non-reactive model. To model the full SIP data, a more complex model (that includes the transport of the three species involved (Na^+, Ca^{2+} and Cl^-) and the exchange reaction between the cations) should be constructed. However, the aim of this work is limited to demonstration of the sensitivity of SIP to the BT of the different ions in the system and to the presentation of a simple and

efficient way to predict the progression of both the dissolved species and the exchange process.

4. *What subset of the Ca2+ breakthrough concentrations is plotted in Figure 4c, and how does that differ from what is shown in Figure 3b?*
Author response - The outflow Ca^{2+} concentrations in Fig.4c represent the fraction of the Ca^{2+} ions that participated in the exchange reaction (see explanation in line 184 in the revised version). In light of this comment we added an additional note in lines 214-215 of the revised version and modified the caption of the figure accordingly.

5. *Lines 224 – 225: I find the distinction between a reactive Ca2+ fraction and a non-reactive fraction misleading. An alternative, process-based approach, would be to compare the imaginary conductivity profiles to the adsorbed reactive species concentrations and attempt to calibrate the model that way, in turn validating it with the concentration breakthrough curve. For the latter case perhaps using the imaginary conductivity data presented in 6b would be best.*
Author response - We agree that such non-orthodox separation may be confusing. We have indeed considered this option. The role of σ'' as an indicator of the $Na^{+} - Ca^{2+}$ exchange progression suggests that the σ'' values can serve as a proxy for the adsorbed concentration of the retarded (reactive) species in an alternative modeling approach. In light of this comment, we now discuss this modeling approach in the paper (see lines 261-266 in the revised version). We also present in the supplementary material a demonstration of this approach. We normalized the σ'' data and used it as a proxy for the adsorbed concentration in a HYDRUS simulation. Our main concern regarding this approach is that in order to accurately model the initial increase in σ'' further investigation and modeling effort are needed, and mostly the inclusion of non-equilibrium component in the model. While this is feasible, as the supplementary information suggests), we think that including that in the main text will be somewhat confusing, and more importantly, divert the focus of the manuscript from BTC to non-equilibrium exchange.

6. *What non-reactive species concentration is being presented in Figure 4b: Cl-, Na+?*
Author response - As explained in lines 184 and 214-215, the non-reactive species in Fig. 4b are Cl_{-}, Na^{+} and the fraction of the Ca^{2+} ions that did not participate in the exchange reaction (i.e., the fraction of the Ca^{2+} ions that reached the outlet of the column together with the non-reactive species).

7. *Lines 269-280: Yes, but the SIP channels are at "earlier" locations within the columns. To better address this interpretation perhaps a comparison between imaginary conductivity and Cl-concentrations at those locations in the columns would be warranted. I find the use of "stability" vague here. Perhaps the authors could elaborate. An alternative explanation could be the interplay between the contributions of Stern- and Diffuse-layer polarization during the exchange process. The Na-Ca exchange may have released higher-mobility Na ions that temporarily remained in the diffuse layer (contributing to diffuse layer polarization) before moving into the bulk solution.*
Author response - Yes, the reviewer is suggesting in different words the same mechanism that we tried to suggest. The term "instability" is perhaps somewhat misleading and we removed it from the revised version. During the exchange process, ions that leave the stern layer are "weaker" in their connection to the soil grains and therefore are associated with higher mobility. At the same time, ions that are "on their way in" are still more mobile than they would be once they complete their journey to the Stern layer. Considering simple EDL model, this indeed suggest that ions are still at the diffuse layer, as the reviewer suggests. To address this point we have rephrased the relevant text in lines 252-255 in the revised text.

8. *Lines 297 – 300: Why not fit the "reactive" model form Zn and Ca using the imaginary*

conductivity (as the imaginary resistivity)? Figure S2 again shows that only a subset of the real conductivity dataset was used for the calibration of Ca and Zn transport, this is poorly described and also not justified.
Author response - Thanks. This point is already discussed and answered in our response to comment 5, above, including a demonstration (in the supplementary materials) of the way such an approach can be used.

Minor comments

1. *Presenting things either in PV or time makes interpreting the results confusing. Please choose one standard.*
Author response - Fig. 3 is the only relevant figure that was presented in terms of pore-volumes. To make it clearer, we changed it to time-based but added, as a secondary axis, the pore-volume presentation.

2. *Figure 2: I find the y-axis location at 1 Hz an odd way to present the data, it also partly covers the numerical values on the y-axis. I recommend moving the axis to 0.1 Hz (the left hand side limit).*
Author response - Corrected according to the comment.

3. *In general, I find the manuscript has too many acronyms, and the use of BT vs BTC is also confusing. In addition, I recommend not to abbreviate geo-electrical with GE.*
Author response - We respectfully disagree and choose to keep the use of acronyms where appropriate. We do agree however to spell-out GE as it may be wrongly interpreted

4. *"Stern layer" should be capitalized*
Author response - Corrected according to the comment

5. *Line 4: "soil profiles" to "soil profile"*
Author response - Corrected according to the comment

6. *Line 5: "The SIP signature was recorded. . . "*
Author response - Corrected according to the comment

7. *Line 9 and 11: A conductivity does not "react". Recommend to change to "changed in response to"*
Author response - Corrected according to the comment

8. *Line 139: "denoted"*
Author response - Corrected according to the comment

9. *Line 145: "Stokes" law*
Author response - Corrected according to the comment

10. *Line 152: inductively coupled plasma - optical emission spectrometer*
Author response - Corrected according to the comment

11. *Line 224: "constructed"*
Author response - Corrected according to the comment

12. *Line 235: 4b and 4b?*
Author response - Corrected according to the comment

Referee #2

Overall, the improvements of the paper are acknowledged. As a remaining minor point it is suggested to use the same loamy matrix which has been used to document Na-Ca exchanges also for the Zinc experiment. This would add to the overall logic of the paper (only one homogeneous matrix is used) and probably also emphasize differences between Ca and Zn.
Author response - Thanks. While we agree that adding an experiment with Zn and the loamy soil would make the paper more complete, we do not really see how the content (i.e., the main concepts conveyed in the manuscript) would benefit from such addition. Our approach is to be as concise as possible and therefore we choose not to include this additional data.