Response to Referee #2

We are grateful to Referee #2 for their constructive and useful comments. Our response to the reviewer's comments (original comments quoted in blue) and the corresponding revision are described in detail and separately below. The numbers of pages, lines, equations, tables and figures are those in the revised manuscript unless otherwise noted.

Comment 1:
"Abstract: Generally fine, but there is an imbalance of overall description and results. The latter needs more emphasis or details. I suggest condensing the "general introduction" and expand the key findings and implications."

Response:
We agree that the introductory section can be condensed and more implications can be added in the Abstract.

Changes in manuscript (Page numbers/Line numbers):
We have modified Abstract (P1/L10-11, L25).

Comment 2:
"L.15-17: Split in two sentences for clarity."

Response:
Agreed. This has been changed.

Changes in manuscript (Page numbers/Line numbers):
Corrected as suggested (P1/L15-16).

Comment 3:
"L.44-47: Shouldn't it be highlighted here the potential/efficiency of adding crushed basalt is somewhat dependent on the basalt composition itself, gran size, soil temperature, moisture and drainage? Furthermore, what are the possible impacts (positive or negative) of ERW for soils themselves and downstream (if/when leachates escape to the surrounding environment)?"

Response:
We fully agree that any pH shift as a result of basalt dissolution will reflect the factors suggested by the reviewer. We have attempted to emphasize this, and also cite papers that discuss potential

impacts of ERW on rivers and oceans (e.g., Zhang et al., 2022; Kanzaki et al., 2023) in lines 38-39.

Changes in manuscript (Page numbers/Line numbers):
We have modified the relevant sentence (P2/L43-44).

Comment 4:
"L.48-52: Is there comparative evidence to bridge gaps between pH(s) and pH(pw), as predicted by models?"

Response:
pH(s) and pH(pw) can be relatively close to one another, depending on soil condition and extractants used for soil pH measurements. As far as we know, however, there have been few efforts to mechanistically understand the gap between pH(s) and pH(pw), as we describe in lines 54-56.

Changes in manuscript (Page numbers/Line numbers):
We have added a sentence that further study that reports both porewater pH and soil pH is desirable in Conclusions (P11/L331-333).

Comment 5:
"L.81-82: What are the solid species involved in cation exchange?"

Response:
Clay minerals and organic matter are major cation-exchangers in soils. Accordingly clay minerals and organic matter compounds have non-zero CEC values but the rest have zero for CEC in the default setting of the model, although the code allows the user to assign any cation exchange parameterization to any solid species.

Changes in manuscript (Page numbers/Line numbers):
We have added explanations such as those above (P3/L81-82).

Comment 6:
"L.130-138: It is probably easier to follow here as a table or as single-line items instead of a running text."

Response:

We agree that a list of symbols used in this study might be useful.

Changes in manuscript (Page numbers/Line numbers):
We have added a list of symbols used in this study in Appendix (P12/L348-349, P26-27).

Comment 7:
"L.138-144: This would read best right after Eq.(11), then followed by the table/list of individual parameters (L.130-138)."

Response:
Agreed.

Changes in manuscript (Page numbers/Line numbers):
Corrected as suggested (P5/L131-138).

Comment 8:
"L.160-161: Is the pH(s) modelling a two-step process (i.e., a "normal" field run is required to provide the needed boundary conditions for the "lab" experiment.)? Can it be run stand-alone with assumed boundary conditions? Can one obtain only set depths or averaged conditions, or is it possible to calculate the pH(s) continuously along the soil profile?"

Response:
In most cases, field observations cannot be directly utilized as inputs to laboratory experiments. This is because thermodynamic constants for cation exchange are important inputs to the laboratory experiments, but cannot be directly measured in the field and must be determined by developing a model that explains the field observations (e.g., a "field simulation" as described in Section 3). Therefore, we would argue that it makes the most sense to run simulations under field conditions in order to reproduce field observations (obtaining soil physicochemical properties through tuning), and then calculate soil pH in-silico under laboratory conditions.

We attempt to explicitly clarify that "Data from the field run are retrieved at a given model field depth and/or averaged over a given depth interval" in line 160. Accordingly, soil pH can be considered a representative value either at a given depth or over a given depth interval.

Changes in manuscript (Page numbers/Line numbers):
We modified Figure 1 so that the soil pH calculation procedure is clearer (P28).

We have added an explanation that soil pH in Figs. 7 and 8 are calculated at each depth point and not averaged over depth interval to the captions of Figs. 7 and 8 (P34-35).

Comment 9:

"L.180-181: Why is DIC added as labile organic matter?"

Response:

This is because of the convenience that adding labile organic matter as a source of DIC is not accompanied by adding any cations. This should be in contrast with the more complicated case where DIC is added as e.g., carbonates, where the amount of cations added as carbonates has to be subtracted from the total amount of cations that are added as oxides/salts to be consistent with the total amount of cations constrained from observations. However, this was also confusing to Reviewer 1, suggesting the need to clarify more fully the reason for this procedure.

Changes in manuscript (Page numbers/Line numbers):

We added an explanation such as above to the relevant sentence (P7/L178-179).

Comment 10:

"L.181-190: This would read better as an equation, followed by the list of components."

Response:

In the relevant sentences, we describe the procedure to determine boundary conditions for "laboratory" experiments where soil pH is calculated in multiple steps, and we do not think such multiple-step procedure can be well-formulated as an equation. However, we agree that some sort of list would be useful for readers and have added this to the revised manuscript.

Changes in manuscript (Page numbers/Line numbers):

We added a list of all symbols used in this study in Appendix A (P12/L348-349, P26-27).

Comment 11:

"L.208-209: Is such difference between pH(s) and pH(pw) systematic or predictable in any way based on boundary conditions/assumptions?"

Response:

This is a very interesting point. Very little data is currently available for attempting a systematic analysis for the relationship between the two pH measurements. Theoretical prediction might be possible with the current model but there are so many factors that can affect soil pH calculation for a given porewater pH (e.g., thermodynamic parameters for cation exchange, CEC, climate etc.). For instance, the trend found in Miller and Kissel (2010) is among soil pH measurements with different extractants and the study does not include porewater pH data.

Changes in manuscript (Page numbers/Line numbers):
We added a sentence to describe that further comparison of the model with observations will enhance our understanding of the difference between soil pH and porewater pH (P11/L331-333).

Comment 12:
"L.219: A brief description here and/or an appendix/SI is needed."

Response:
We agree that a general brief description might be useful to the reader.

Changes in manuscript (Page numbers/Line numbers):
We added a brief description (P8/L225-226).

Comment 13:
"L.245-248: Did you test the effect of not including NO3 and Cl to the lab runs?"

Response:
Yes. Without those anions, calculated electrical conductivity is lower and soil pH is higher.

Changes in manuscript (Page numbers/Line numbers):
We mentioned electrical conductivity in the relevant sentence to further justify that those anions exist as salts and should be added as salts in the laboratory runs (P9/L256).

Comment 14:
"L.250-251: The model seems to slightly underestimate Ca and Mg. Any particular reason?"

Response:
Slight offsets might have been caused by development of chemical gradients adopting two different CEC values for the two exchangers especially for the relatively strongly bound Ca and Mg.

Changes in manuscript (Page numbers/Line numbers):
We added a sentence such as above (P9/L260-261).

Comment 15:

"L.254-256: Can such variability provide any predictability of pH(s) concerning the media used to exchange cations from the solid-phase?"

Response:
This is an interesting question, and we have attempted to address the issue in our response to Comment 11 above. There are many contributing factors that are related to the exchange properties of the solid phase and thus impact prediction of soil pH (e.g., thermodynamic constants for cation exchange, CEC, concentrations of salts, etc.).

Changes in manuscript (Page numbers/Line numbers):
Please see our changes in manuscript in response to Comment 11 by the reviewer.

Comment 16:
"L.260-262: 1) The results shown here are based and compared to one mesocosm experiment. Although it looks the model performs well, there is not much to compare in terms of distinct set up conditions. Do these comparisons hold for another mesocosm conditions and natural/agricultural soils?"

Response:
We agree that studies on a variety of soil types are ideal to further validate the framework developed in this study. However, there are unfortunately not so many observations that report comprehensive soil chemistry including detailed porewater chemistry (including pH), soil pH and concentrations of exchangeable cations and thus allow validity tests of the method.

Changes in manuscript (Page numbers/Line numbers):
We have added a sentence mentioning further comparison is desirable in the future study (P11/L331-333).

Comment 17:
"2) How does the model closely reproduce pH(s) of previously publish data? This is not shown."

Response:
This was the intention of comparing model simulations to the results from Miller and Kissel (2010) in Fig. 5, which are based on US soils.

Changes in manuscript (Page numbers/Line numbers):
We added the reference to the sentence to avoid confusion (P10/L273).

Comment 18:

“L.275: Are these target pH values for the average soil profile or at a specific depth?”

Response:

We clarify that soil pH was calculated as an average over top 15 cm in line 290. On the other hand, soil pH values shown in Figs. 7 and 8 are calculated using bulk soil composition at each depth point. We clarified this difference in the revised manuscript.

Changes in manuscript (Page numbers/Line numbers):

We added more explanations to avoid confusion (P10/L290-291, P11/L311-312, P34-35).

Comment 19:

“L.288-289: 1) Would these basalt amendments/pH correction change in any meaningful way under different environmental conditions (e.g., temperature, soil moisture)?”

Response:

Yes, we would expect that the required amount of basalt for a given target pH will change with climate and soil hydrology.

Changes in manuscript (Page numbers/Line numbers):

We modified a sentence to emphasize the importance of climate (P2/L43-45).

Comment 20:

“2) Are these predicted basalt contents in line with any expected or suggested plans of soil amendment?”

Response:

The calculated amount is consistent with the range summarized in Swoboda et al. (2022).

Changes in manuscript (Page numbers/Line numbers):

We modified a sentence to indicate that the calculated range is not inconsistent with the amendment levels examined before (P10/L301-P11/L302).

Comment 21:

“L.289-290: From Fig. 6-7, it is unclear to me when the target pH are met. Except for target pH(s) = 6.2 (Fig. 6a), after one year all pH values largely exceed the target at the surface. Is that true or am I miss-interpreting the figure? If pH values would reach > 7.0, what consequences would that bring? Either way, it's not clear. Can you indicate in each panel the target pH (vertical dotter line or so)?”

Response:
We clarify that target pH is met in 1 year in line 287. We agree that interpretation of pH from the figures might not necessarily be straightforward because target pH is evaluated based on average over top 15 cm while the figures show soil pH and porewater pH at each depth points.

Changes in manuscript (Page numbers/Line numbers):
We added more explanations to avoid confusion (P10/L276, 290-291, P11/L311-312, P34-35).
We added vertical dotted lines to show target pHs in Figs. 7 and 8 (P34-35).

Comment 22:
“L.297-298: If so, which approach would be more suitable to adopt when tracking pH, either for natural/agricultural conditions or ERW conditions? Is there a recommendation to be made here, particularly when pH(s) is a more common practice to determine pH of soil systems?”

Response:
We believe that monitoring both porewater pH and soil pH is desirable for mechanistic understanding. However, our point of showing these example simulations is not to make any recommendations but to show the potential difference between porewater pH and soil pH and its impacts on ERW. Typical field measurements will be on soil pH, while many modeling results are reported in terms of porewater pH. The key point for our purposes is to highlight this distinction and emphasize that model-data comparisons need to be mindful of this moving forward.

Changes in manuscript (Page numbers/Line numbers):
We added a sentence that indicates further observations will be desired for further understanding of ERW impacts on croplands (P11/L331-333).

Comment 23:
“L.298-300: In these basalt amendment scenarios, are there estimates of other "by products" (e.g., SiOH4 enrichment, secondary precipitation processes) and their fate?”

Response:
As stated in lines 278-280 and might be inferred from the aqueous and solid species tracked in these experiments listed in Table 11, our example experiments here are simplified as much as possible. Therefore, neither Si enrichment nor secondary precipitation is considered.

Changes in manuscript (Page numbers/Line numbers):
We modified the relevant sentence to be clearer (P10/L278-279).

Comment 24:
"L.305-310: Can these findings provide any recommendation or guidance for pH measurements in soil and/or ERW practices?"

Response:
We have addressed essentially the same point in response to Comment 22 by the reviewer.

Changes in manuscript (Page numbers/Line numbers):
Please see our change in manuscript in response to Comment 22 by the reviewer.