Response to reviewer comment 1 | Egusphere 2026-3473

The manuscript addresses an interesting topic and combines aggregate stability, microbial respiration, tracer transport, soil chemistry, and SIP measurements. In my opinion, the manuscript has potentially interesting observations, but the central mechanistic conclusions are insufficiently supported by the experimental evidence. The interpretation of SIP measurements, dual-porosity development, and the proposed conductive reservoir relies substantially on indirect inference. In addition, the limited tracer treatments, short experimental duration, and unresolved influence of soil solution chemistry substantially weaken the study. These are fundamental issues that cannot be adequately addressed through minor or moderate revision. I therefore recommend rejection in its present form.

We sincerely thank the reviewer for the constructive feedback. We have carefully considered all the comments and will revise the manuscript accordingly. Below, we provide detailed responses to each point raised:

1. *Several conclusions regarding microaggregate formation, pore-size reduction, and changes in pore architecture are inferred mainly from SIP signals. These interpretations are plausible but are not directly validated by independent measurements of pore structure. The authors should not present these hypotheses as demonstrated mechanisms.*

We thank the reviewer for this important comment. We agree that the proposed changes in pore architecture were not directly imaged, and we will revise the manuscript to present them as interpretations supported by the data rather than as demonstrated mechanisms.

We respectfully note, however, that we did not infer these interpretations from SIP alone. The SIP signatures were interpreted together with several independent measurements:

- *Tracer transport (Fig. 4), measured on the same SIP columns: by day 20, A-PAML showed pronounced tailing and a marked increase in dispersivity ($\alpha = 1.21 \rightarrow 3.78\ cm$), indicating a change in flow-path structure. ML converged to control-like behaviour.*
- *Effluent chemistry (Fig. 7), measured on the same SIP columns: in A-PAML, the increase in σ' was decoupled from the low effluent Ca^{2+}. In the control and ML, σ' tracked the rise in effluent Ca^{2+}.*
- *Aggregate stability (Fig. 3), measured on the same treated soils in parallel incubations: A-PAM produced persistent aggregation, while the aggregation induced by mucilage was transient.*
- *CO_2 emission (Fig. 2), measured on the same treated soils in parallel incubations: mucilage stimulated microbial activity, consistent with its degradation, while A-PAM did not.*

Nevertheless, we agree that the wording in several places overstates the certainty of these mechanisms. In the revised manuscript, we will soften the relevant statements in the Abstract, Discussion, and Conclusions. We will also add a statement acknowledging that the proposed structural mechanisms were not directly validated by pore-scale imaging, and that future studies combining SIP with direct pore-structure characterization are needed to confirm them.

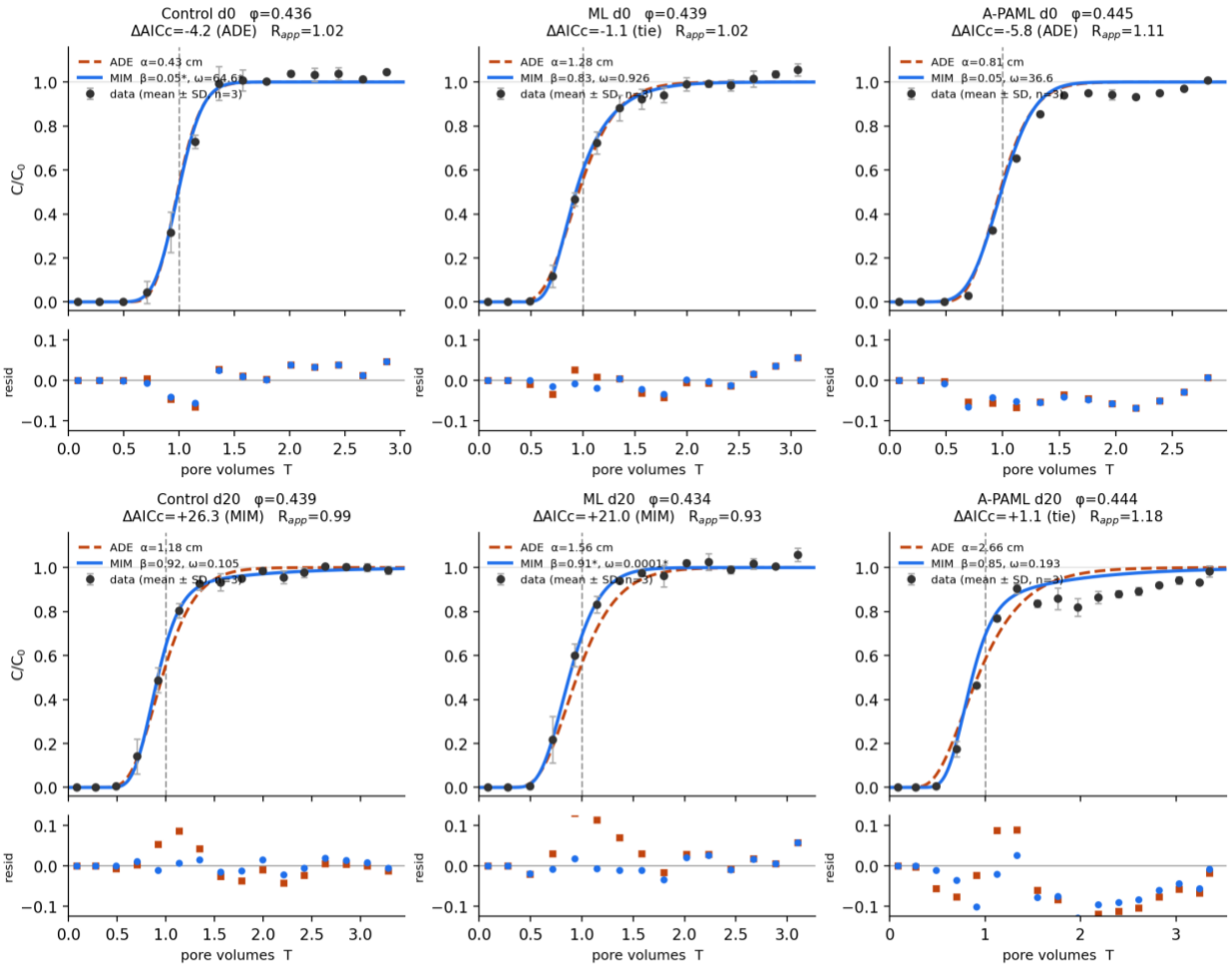
2. *The deviation of the A-PAM breakthrough curve from the ADE is interpreted as evidence of mobile and immobile water domains. However, ADE failure alone cannot demonstrate a dual-porosity system. A dedicated dual-domain transport model and quantitative comparison with the ADE would be required.*

We thank the reviewer for this valuable comment. We agree that the failure of the ADE alone cannot demonstrate a dual-porosity system. Following this suggestion, we fitted the breakthrough curves with the mobile–immobile model (MIM; van Genuchten and Wierenga, 1976), in addition to the ADE, and compared the two models quantitatively using the corrected Akaike Information Criterion (AICc) and the root-mean-square error (RMSE). In both models, the water content was fixed at the measured porosity of each column, and iodide was treated as a conservative tracer (R = 1).

The results confirm that the behaviour of A-PAML differs distinctly from that of the other treatments. After 20 days of incubation, all treatments showed some change in transport behaviour. For the control and ML, both models described the data well ($R^2 \geq 0.98$). The MIM provided a modest refinement, with a large mobile water fraction ($\beta = 0.91–0.92$), indicating

only minor physical non-equilibrium. In contrast, neither model captured the pronounced tailing of A-PAML at day 20. The MIM offered no meaningful improvement over the ADE (ΔAICc = 1.1), and the residual error of the best-fitting model was three to five times higher than in the control and ML treatments (RMSE of 0.066, compared with 0.012 and 0.022, respectively). A-PAML also showed the largest dispersivity (α = 2.66 cm, compared with 1.18 and 1.56 cm for the control and ML).

These results indicate that the transport behaviour of A-PAML reflects a more complex form of non-equilibrium than can be represented by a single-rate exchange between mobile and immobile domains, such as multi-rate mass transfer (Haggerty and Gorelick, 1995). Such models, however, cannot be reliably constrained with the present data. In the revised manuscript, we will present the MIM analysis and model comparison, and describe the A-PAML transport behaviour as non-ideal transport consistent with physical non-equilibrium. The dual-porosity interpretation will be presented as a hypothesis supported by the combined evidence, rather than as demonstrated by the transport data.



3. *The tracer experiment included only control, ML, and A-PAML. A-PAMH was excluded because stable flow could not be maintained. This limitation considerably weakens the conclusions regarding the effect of PAM concentration and prevents a complete comparison among treatments.*

We thank the reviewer for this comment. We agree that the tracer experiments do not allow evaluation of the effect of polymer concentration on solute transport, and we will state this limitation more clearly in the revised manuscript.

It should be noted that the tracer experiments were not intended to assess concentration effects. Because stable flow could not be maintained in the A-PAMH columns, the tracer experiments were limited to the low-concentration treatments (ML and A-PAML). This allowed a comparison between the natural and synthetic polymers at equal concentration. For the same reason, MH was not included. The effect of polymer concentration was evaluated through other measurements: aggregate stability and CO_2 emission were measured for both concentrations of both polymers (Figs. 2, 3), and SIP was measured for both mucilage concentrations (Figs. 5, 6). The conclusions regarding concentration in the manuscript are based on these measurements, not on the tracer data.

In addition, the inability to maintain stable flow in the A-PAMH columns, owing to excessive backpressure, is itself an indication of a substantial reduction in permeability at the higher A-PAM concentration. This observation is consistent with a strong effect of A-PAM on the pore structure. In the revised manuscript, we will report this observation more explicitly and clarify the rationale for the choice of treatments in the tracer experiments. We will also note that the effect of polymer concentration on solute transport remains to be evaluated in future studies.

4. *The decrease in mucilage effects is mainly attributed to microbial degradation based on CO_2 emission. However, CO_2 production is not direct evidence of polymer degradation, and the manuscript itself acknowledges possible contributions from calcite dissolution. Stronger evidence is required to support this mechanism.*

We agree that CO_2 emission is not a direct measurement of polymer degradation, and that the residual mucilage in the soil was not quantified in this study.

Regarding the contribution of calcite dissolution, all treatments were prepared from the same calcareous loess, and calcite dissolution is expected to occur in all of them, including the control. For this reason, the CO_2 results were interpreted in terms of differences between treatments relative to the control rather than absolute values, as stated in the manuscript (L204-L205). The excess CO_2 emission in the mucilage treatments, reaching a 3-fold increase in MH on days 3 and 7 (Fig. 2), is therefore attributed to the added mucilage. This interpretation is further supported by the effluent chemistry of the SIP columns: the control, ML, and MH treatments reached similar Ca^{2+} and total cation concentrations by day 20 (Fig. 7), consistent with a similar extent of calcite dissolution among these treatments.

Moreover, the attribution of the decreasing mucilage effect to microbial degradation does not rely on CO_2 emission alone. It is supported by several independent observations over the same period: the decline in aggregate stability (Fig. 3), the convergence of the ML breakthrough curve toward control-like behaviour by day 20 (Fig. 4), and the convergence of σ" between ML and MH (Fig. 5). Together with the well-documented lability of mucilage polysaccharides (Nazari, 2021; Nazari et al., 2022), these observations are consistent with microbial degradation as the main driver of the transient stabilization.

In the revised manuscript, we will present this mechanism as consistent with the combined data rather than as demonstrated, and we will note that direct quantification of mucilage degradation (e.g., polysaccharide analysis or isotope labeling) would be valuable in future studies.

5. *Large changes in Ca^{2+} and total cation concentrations occur during incubation. Since SIP responses are strongly affected by pore-water chemistry, it is difficult to separate geochemical effects from structural effects. The manuscript does not sufficiently resolve this important confounding factor.*

We thank the reviewer for raising this important point. We agree that pore-water chemistry strongly affects the SIP response, and that the substantial increase in cation concentrations during incubation must be considered when interpreting the SIP signals.

The experimental design was intended to account for this effect through reference treatments. The control soil underwent the same calcite dissolution and increase in pore-water ionic strength as the polymer-treated soils, but without polymer-induced structural changes. The N-PAM treatments served as an additional reference, with minimal change in effluent chemistry (Fig. 7). Accordingly, the SIP responses of the polymer treatments were interpreted as deviations from these references rather than in absolute terms.

For the quadrature conductivity, the effect of pore-water chemistry can be largely ruled out. Quadrature conductivity is known to increase with pore-water salinity (Revil and Skold, 2011).

In the control and mucilage treatments, effluent cation concentrations increased by 2.4–3.9-fold over the incubation (Fig. 7), yet σ" decreased in all treatments except N-PAM (Fig. 5b). The decline in σ" is therefore opposite to the trend expected from pore-water chemistry, and must reflect changes at the mineral–water interface. In the N-PAM treatments, both effluent chemistry and σ" remained nearly constant.

For the in-phase conductivity, we agree that the chemical and structural contributions cannot be fully separated with the available data. Effluent chemistry was measured at only two time points (day 0 and day 20), and, as discussed in the manuscript, the effluent may not fully represent the pore water in hydraulically less accessible domains. In the revised manuscript, we will therefore present the σ'-based interpretations, namely the reduced formation factor in MH and the conductive reservoir in A-PAML, as hypotheses consistent with the data rather than as established mechanisms.

6. *The manuscript does not provide sufficiently convincing information on independent replication and statistical treatment of the temporal data. Treatment × time effects and uncertainty around the reported parameters should be analyzed more rigorously.*

We agree that the information on replication and statistical analysis should be presented more clearly, and we will revise the manuscript accordingly.

Regarding replication, all replicates in this study were independent. CO_2 emission was measured in four separate jars per treatment, and wet sieving was performed on

independently prepared soil samples. SIP and tracer experiments were conducted in triplicate, independently packed columns. Columns that developed leakage during the experiment were excluded, and results are reported for the remaining replicates.

Regarding the statistical treatment of the temporal data, the CO_2 emission data were analyzed for differences between treatments within each sampling day (Tukey HSD, $P < 0.05$), as presented in Fig. 2. In addition, we tested the temporal changes within each treatment across the sampling days (Tukey HSD, $P < 0.05$). These results confirm significant temporal changes in all treatments and will be added to the Supplementary Material.

For the aggregate stability data (Fig. 3), the results are presented as normalized distributions of the stability fractions, which do not allow error bars to be displayed clearly. We will therefore add a table to the Supplementary Material reporting the mean ± SD of each stability fraction for each treatment and sampling day.

For the SIP data, Fig. 5 presents the mean ± SD of the replicate columns, and this will be stated explicitly in the figure caption. In the revised text, the reported changes in σ' and σ" will be given with their SD.

7. *The experiment lasted only 20 days, yet the manuscript makes claims concerning persistent stabilization and long-term environmental implications of A-PAM. The available experiment cannot substantiate long-term persistence under field conditions.*

We thank the reviewer and agree. Our conclusions are limited to the 20-day incubation under laboratory conditions. In the revised manuscript, we will clarify that "persistent" refers to the stability observed over the incubation period, relative to the transient effect of mucilage, and we will present the long-term environmental implications as perspectives for future research.