

[Response to reviewer comment 2 | Egusphere 2024-2101](#)

The manuscript by Altitset et al. presents results from an experimental investigation where spectral induced polarization was applied to monitor hydroquinone oxidation in the presence of MnO₂ in an artificial soil mixture of a sandy soil amended with MnO₂. The findings are convincing and the quality of the experiments provides confidence in the results. However, the authors provide only minimal insight into the chemical reactions occurring in the system that support their conceptual model. In addition, the analysis of breakthrough curves remains qualitative, and would (potentially) benefit from mass balance calculations to better justify the findings in the solid phase characterization. Based on these general remarks and my specific comments below I recommend moderate revisions before this paper can be accepted.

We appreciate the reviewer's insightful and constructive feedback. We have thoroughly addressed each of the comments and will revise the manuscript accordingly. Below, we provide detailed responses to all the points raised:

Specific comments:

Line 20: Do you mean soil “sub”surface processes?

*Thank you for your careful reading. We appreciate the opportunity to clarify our meaning. In this context, we are referring to processes occurring on the surface of the soil particles, which are located throughout the soil profile. To clarify, the sentence in Line 20 has been revised to ensure this distinction is clear. The revised sentence reads: **"Our findings conclusively demonstrate that the noninvasive electrical method allows real-time monitoring of calcite dissolution, serving as a direct cursor to the oxidation process of hydroquinone, enabling the observation of chemical interactions in soil solution, and on soil particle surfaces."***

Methods: I suggest removing the sub-section headings “2.1 materials” and “2.3 methods”

We agree with the suggestion and will remove the sub-section headings as recommended.

Line 95: Describe the geometric factor.

*We appreciate the comment. We use the relationship $\sigma = G * Y$ to convert admittance (Y) to complex conductivity (σ), where G is the geometric factor. The geometric factor G (1/m) accounts for the geometry of the measurement setup, including electrode configuration and sample dimensions, enabling the conversion of measured electrical properties (admittance) to intrinsic material properties (complex conductivity). For our setup, G was determined by measuring the admittance of a series of electrolytes with*

known electrical conductivities, as described in lines 104-107. The value of G for our measurements is 0.0127 m⁻¹.

Line 92 – 98: The authors should also introduce alternative nomenclature e.g. real and imaginary conductivity, because this is a soil science audience. This way there is no ambiguity when readers compare with other literature.

Thank you for the valuable suggestion. We agree that introducing alternative nomenclature will enhance clarity for a soil science audience, and we have revised the manuscript accordingly.

Line 97: There are earlier references that determined the sensitivities of the quadrature and in-phase conductivities

Thank you for pointing this out. We have updated the reference in Line 97 to Vinegar and Waxman (1984)

Line 104: Was there a mesh preventing the sand sample from falling into the electrode casing?

All electrodes are tightly inserted into the casing through a rubber band that matches the electrode's diameter, preventing sand from entering. Therefore, there is no mesh in the columns. The current electrodes extend through the entire sample, while the potential electrodes do not directly contact the sample but are connected through a clay mixture salt bridge. This configuration ensures no electrode polarization while maintaining secure contact with the sample.

Lines 153 – 164: In Figure 2 you justify the “conservative” transport behavior of both hydroquinones based on the breakthrough ($C/C_0 = 0.5$) at 1 PV in panel (a). However, it is interesting that **the slope of the breakthrough curves differs between hydro- and benzo quinones**. The authors could compare their results to the Ogata-Banks solution for 1D conservative transport to highlight any deviations from the expected idealized behavior. **There appears to be a background concentration of benzoquinone in the sand-only column. Here the concentrations measurements also exhibit a large error spread when compared to the Mn-sand column.** The authors should address this in the text.

Thank you for the insightful comment. We have revisited our data and evaluated the fit of our results to the advection-dispersion equation (ADE) solution, as described in "Soil Water Dynamics", chapter 7, page 307-310 (AW Warrick). The figure attached shows the fitting of the ADE solution to the breakthrough curves, indicating a good match for both hydroquinone and benzoquinone. The deviation in the benzoquinone results is likely due to measurement errors, as you noted. One possible factor contributing to these deviations could be the reduction of benzoquinone, given the natural conditions of the system in which the experiments were conducted. Such a setting inherently introduces some variability between runs, which may explain the larger standard deviations observed. We have highlighted these points in the revised text to provide greater clarity.

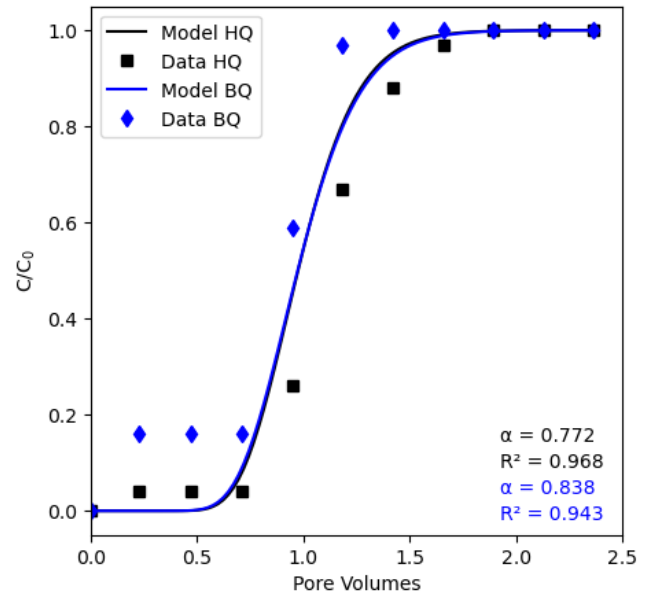


Figure 2b shows that more benzoquinone exits the column as the hydroquinone. In line 120, I interpret that the Mn-sand col was only injected with hydroquinone, but the sand only with both. Is this correct? Please highlight this point more clearly in the text.

Yes, that is correct. We added benzoquinone only to the sand-only columns to confirm that no significant reactions occurred with benzoquinone. The primary objective of the experiment was to follow the oxidation of hydroquinone. To clarify this in the manuscript, we have revised the text: "Upon reaching equilibrium, the inlet solution was replaced either by a mixed solution of hydroquinone and benzoquinone (0.1M each in CaCl₂ 5mM solution) for the sand-only columns or by a hydroquinone-only solution (0.1M in CaCl₂ 5mM solution) for the Mn-sandy soil columns. **The mixed solution was used for the sand-only columns to ensure no interactions occurred with benzoquinone, while the primary purpose was to follow the hydroquinone oxidation.** Both solutions passed through their respective columns for 4 or 8 pore volumes (PV), respectively, until mass balance was achieved."

Line 172: Correct referencing error.

Thank you for noticing. The reference issue at Line 172 has been fixed.

Line 178 – 179: Why do you state that the Ca²⁺ concentrations were negligible? Your inflowing solution contained 5 mM Ca²⁺ and that is what you see in the outflow. Rather than being negligible the concentrations remained constant.

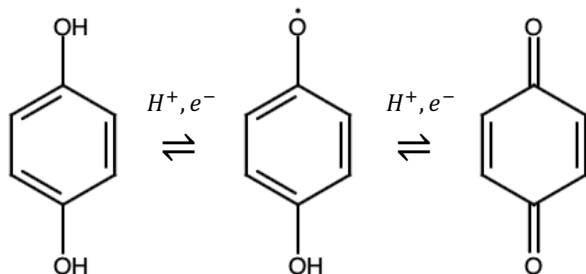
Thank you for the comment. You are correct, the increase in Ca^{2+} is negligible, and we have revised the text accordingly. The updated sentence now reads: "This was accompanied by negligible concentrations of benzoquinone and manganese, while the Ca^{2+} concentration remained constant at 5 mM in the effluent."

Line 182: How does the oxidation reaction change the surface charging properties of the MnO_2 ? This is not clearly addressed in the paper.

Thank you for your comment. In this line, we intended to indicate that the oxidation reaction leads to a reduction in available MnO_2 for further oxidation, as its concentration decreases. We address the surface properties of MnO_2 more explicitly later in the manuscript, particularly in Lines 238–239, where we discuss MnO_2 surface possible passivation due to Mn^{2+} precipitation.

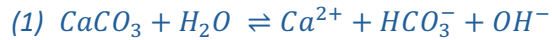
Lines 190 – 204: Here the discussion presents a plausible conceptual model that describes the reactions taking place in the Mn-sand columns and their potential effects on SIP signatures. While the differences between control and treatment columns are apparent, the text discussion requires additional information: It would be an improvement for the manuscript to present the chemical reactions that the authors propose are occurring in the system, this would allow H^+ changes to become immediately apparent.

We added the following chemical reaction equation to Figure 2.

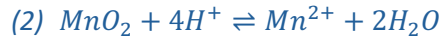


Mass balance calculations: Currently the discussion remains very qualitative. The authors should check whether their mass balance supports their conclusions. For example, the extent aqueous Mn production, the total amount of outflow Ca^{2+} and pH change should be related to the stoichiometry of the chemical reactions. How much of the 4% CaCO_3 is expected to be consumed based on the total breakthrough of calcite. Such an analysis would improve the plausibility of the conceptual model and highlight the potential of such monitoring schemes to deliver quantitative information. This would also further support the findings depicted in Figure 6.

Thank you for the insightful comment. I will first describe the chemical reactions occurring in the column: Calcite dissolution:



Manganese oxide reduction:



Hydroquinone oxidation:



Based on these reactions, I address your comments as follows:

- **Mass balance:** *Although a complete mass balance is desirable, calculating the exact extent of produced Mn^{2+} is challenging due to its likely precipitation within the system. While we have multiple measurements of pH in the column outlets, we hypothesize that the pH changes driving the cascade of reactions are mainly local, making it difficult to accurately correlate them with stoichiometric changes.*
- **Estimation of CaCO_3 dissolution:** *We estimated that CaCO_3 dissolution occurs in a 1:1 ratio with the release of Ca^{2+} into the solution. Based on our measurements, approximately 0.26 g of CaCO_3 was washed out of the column. However, it is important to emphasize that this amount likely underestimates the CaCO_3 dissolved in the system. Some of the dissolved Ca^{2+} may have been retained within the column or precipitated on the surfaces, making it difficult to determine the precise amount of CaCO_3 dissolved. Nevertheless, we have extensive supporting evidence from various measurements, which strongly supports our interpretation of CaCO_3 dissolution in this context.*