# Response to the referee's comments (Referee #2)

We appreciate your constructive comments which help to make the paper's expression and logic clearer. We took all the comments into consideration and made responses as follows.

## General comment

*The authors proposed a coupling model to simulate the complex bio-geochemical reactions in subsurface water flow and solte transport. The reactions are important and it is meanful to including these in a traditional model. However, I got lost in reading through the manuscript. The work is interest but I felt the authors were failed to present a clear consistent streamline from the model development to calculation, simulation and verification.*

**Response:** Thank you for the constructive comments. We will revise the paper and present a clearer consistent streamline based on your suggestion. The detailed responses are shown as follows.

## Detail comments

*1. Abstract*

*The abstract seems too long and a bit of confusing. It is kind of hard to get your main contribution from this complicated abstract. Like you state that the development of the model is your research goal, but your results focus on detailed geochemical analysis and explanations. Thus which one is your most important point? The goal and results then are not logically consistent though for sure they are related. If the model is creative, it would be better to prove its accuracy and efficiency. If the bio-geochemical processes are the problem that need to be illustrated, then it is better to describe the significance of the geochemical environment. I suggest to modify your abstract to clearly present your contribution.*

**Response:** Based on your suggestion, we will better focus the manuscript. It is probably impossible to test the accuracy of such a complex model, and our goal is primarily to present its development (innovative by itself) and to conduct a sensitivity analysis of the model over a realistic case study, even if not fully calibrated, where the physio-bio-chemical and geophysical models can successfully capture and reflect physical and biochemical processes. To make sure the main text corresponds to the abstract changes, we will also change the *results and discussion* part accordingly (see Comment 4).

Based on your suggestion, the revised abstract presented as follows will be included in the revised manuscript.

*Subsurface contamination is a significant problem due to excessive fertigation and industrial and domestic wastewater discharge. With numerical modeling and geophysical tools development, subsurface contaminant research has become easier to implement and study. However, there is still a gap in relating the biochemical processes and geophysical signals. A coupling model is needed to facilitate understanding subsurface processes and provide further theoretical basis to practice and field monitoring. Thus, this research aims to simulate the self-potential (SP) signature in response to physical and biochemical dynamics in the subsurface. For the physico-bio-chemical model, the processes of water flow, solute transport, biochemical reactions, microbial dynamics, adsorption, and gas flow are considered. Specifically, the biochemical cycles related to C, N, Mn, Fe, and S are incorporated into the model. The physico-bio-chemical model is then coupled with the SP model. The SP is the solution to Poisson's equation, contributed by streaming and redox potential. The streaming potential is calculated by the effective excess charge density and the Darcy velocity, while the Butler-Volmer equation solves the redox potential. The results show that the physio-bio-chemical model can capture the physical and biochemical dynamics (i.e. water content distribution, DOC, ammonium, and nitrate concentrations and degradation) across the capillary fringe with a high redox gradient. The redox and SP model can reflect the redox-sensitive species concentrations (i.e. oxygen and nitrate in the oxic and anoxic environment, respectively) and redox reaction rates (i.e., nitrification, denitrification, and DOC aerobic oxidation). The higher reaction rates for different redox processes correspond to their optimal redox potential ranges. The streaming potential model can reflect the water content and flux dynamics. Thus, this research can guide the geophysical detection of redox-sensitive contamination and water leakage in the subsurface, specifically around the capillary fringe.*

*2. Introduction*

*Are there any try out of embracing SP to subsurface flow and transport modeling in previous studies? I am not an expert in SP model but can you directly tranfter this signial into geochemical variables in subsurface porous media?*

**Response:** There are several references embracing SP signals to subsurface flow and transport, but there is much weaker literature relating SP to the fate of contaminants, i.e., bio-geo-chemical processes, and certainly not for both fate and transport. The introduction covers examples related to pumping tests, seepages from ditches or into sinkholes, and contaminated sites affected by hydrological dynamics **(in the manuscript: Page 3 Lines 2-6)**.

SP induced by subsurface flow can be defined as streaming potential. These signals can be directly related to the variables of hydraulic potential gradient **(in the manuscript: Page 2 Lines 23-26)**, electrical conductivity, water flux and effective excess charge density, or even water saturation in unsaturated soil **(in the manuscript: Page 3 Lines 1-2, Page 11 Line 22)**. As streaming potential signals are affected by the comprehensive factors, we need to discover the dominant factors and analyze the relationship between signature and the impact factors. For example, we mainly analyze the streaming potential in response to water flux and saturation in this research due to the variably saturated soil. However, the electrical conductivity of pore water may be the dominant factor in a high concentration gradient solution. In the *introduction* part, a general phenomenon or basic theory related to SP induced subsurface flow is usually described. The direct link between the SP signal and the geochemical variables is usually specifically described in the *model development* or *case study* parts. To make the relationship between subsurface dynamic and SP signals clear, we will first add the following figure (Fig. 1) in the *introduction* part. Then, we will also specifically discuss how the variables of the SP model are coupled with those of the physio-bio-chemical model in the *model development* and *case study* parts. This will help to better understand how the geochemical variables stimulate the SP signals, especially for the non-geophysical readers.

As for SP signal related to transport, it affects redox-sensitive species spatial distribution in our study and further influences redox reactions and SP related to redox processes. As discussed above, we will add the following figure (Fig. 1) and also a specific description of the link between SP and physio-bio-chemical model in the *model development* and *case study* parts to make our research clear.

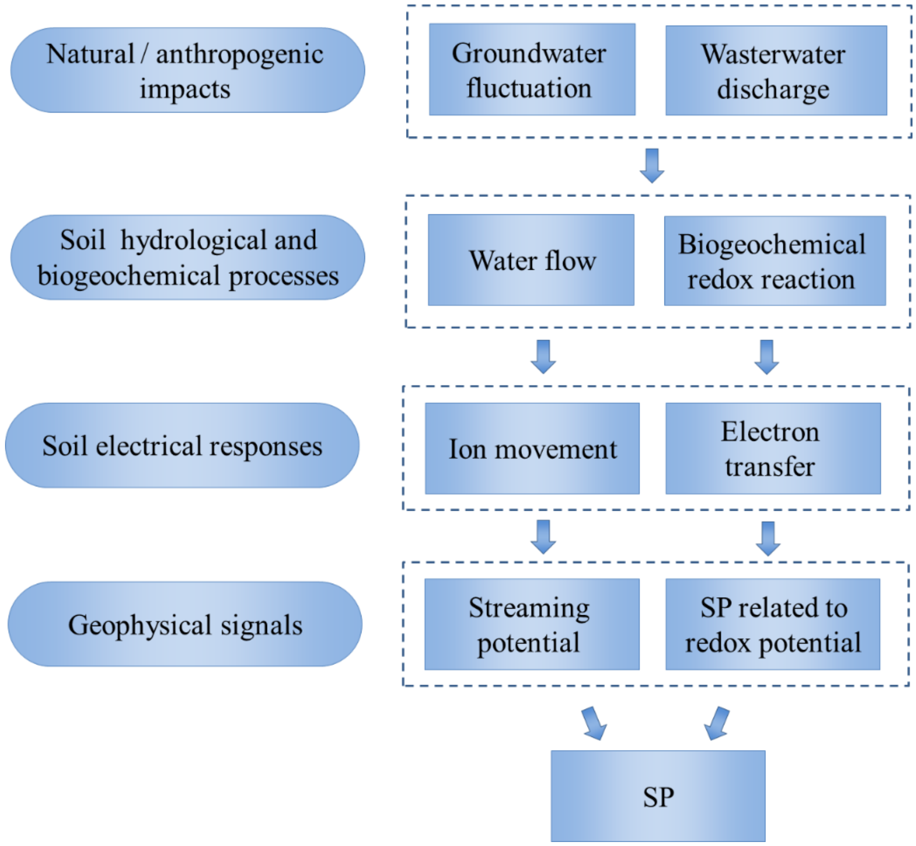


**Fig.1 Correlation between subsurface dynamics and SP**

*3. Model development*

*The authors described a bunch of equations. Are the basic water flow and solute transport... are set up by own developed code or a business code such as comsol/hydrus? I saw the authors mentioned this in the end of the manuscript, but it is better to be cleared out in the paper.*

*The same as the previous concern, is the SP code constructed by the authors or an adopted module? It is really hard to tell which equation is cited from other papers and which one is that you derived. Meanwhile, the authors introduced the flow and SP separately, but how the two parts are connected ? How the variables in the two systems are connected? A section is needed here.*

*Many paramters and observations were enrolled in the modeling but how were they obtained from the physical-based experiment? And the model then has a high degree of reedom, how did you constrain your model in the simulation and verificaiton? Also, the uncertainty is greatly increased in this process as stated in the literature: "Bayesian performance evaluation of evapotranspiration models based on eddy covariance systems in an arid region. Hydrology and Earth System Sciences. 2019, 23(7):2877-2895".*

**Response:** Thank you very much for your suggestion. We make the following three responses corresponding to each paragraph of your comment.

First, we will add the information related to the source of the code in terms of different modules.

Second, we will clarify the citation and derivation of different equations. As for the variable correlations between the biogeochemical and SP models, we have made a statement in the *case study* part **(in the manuscript: Page 21 Lines 13-17)**. To make it clear, we will further discuss the variable correlations also in the *model development* part based on your comment.

Third, we tried several models for the biogeochemical and SP processes and chose the best ones that fit the experimental data. The Nash-Sutcliffe efficiency coefficient (NSE) was used for biogeochemical model calibration and verification. As for the parameters, they are usually provided within reasonable ranges by numerous pieces of literature. We self-controlled the sensitive parameters change with small intervals and chose the best values that fit the experimental data. Thus, not only the model but also the parameters were estimated by tons of times. This could largely reduce the uncertainty of the model.

*4. Results*

*As the problem mentioned above, it is not quite clear the performance of developed model. It is hard to say whether the approach in valid or not. It would be better to show what are your inputs and what are your outputs as too many reactions are take into account here. How are the simulations compared with the observations for the most important parameters? And how the results performed by comparing to the model that ignoring the SP.*

**Response:** Thank you very much for your suggestion. In the original text, we only analyzed that the SP signals could better reflect the physical and biogeochemical processes, but neglected the analyses of soil biogeochemical characters across the capillary fringe. Based on your suggestion, we will add two parts to the *results and discussion* to test the validity of the model.

The first one is to analyze the simulated physical and biochemical results across the capillary fringe to confirm the model validity. This includes the water content and flux character in the variably saturated soil and also the redox-sensitive species reaction and distribution (i.e., DOC, ammonium, and nitrate) in a sharp redox gradient environment. These will be the factors that stimulate the SP signals. Then, the SP responses will be described as it is shown in the original manuscript.

As this research focuses on numerical modeling for the deeper subsurface and the biogeochemical observed data is hard to acquire, the results are only attained by calibrated model.

This is also the one purpose of our research that makes the subsurface biogeochemical study more available. Thus, there is no comparison between the observation and simulation. However, the sensitivity analyses related to physical and biochemical parameters could be added as a second part to further verify the model if it is needed.

Besides, there is almost no impact on the biogeochemical processes whether the SP technique is applied or not. Thus, such a comparison is not needed.