Response to the referee's comments (Referee #1)

Dear Prof. André Revil. First, We appreciate your constructive comments which help to establish a more rigorous SP model. We took all comments into consideration as detailed below. We have already revised minor problems in the manuscript *(direct citation of the revised text is in blue and italics)* and made responses in the following text. For the insufficiency related to the model, we will change it later in the revision process and the response is marked in red color.

General comment

This work starts with a great promise: a physics-based model for self-potential signals in complex environments with complex chemistry including biotic processes. Once this has been stated and after reading the manuscript, I got disappointed by some aspects of the modeling, which I believe are not correct. Here my criticisms. I hope the authors will take them in a positive spirit. I thank the authors for their wish to make the code available in HYDRUS 1D but this will need to be seriously corrected or errors will propagate in the literature.

Response: Thank you for the constructive comments and encouragement. Indeed, the Hydrus 1D code will be made available directly and upon request. In each comment, we make the corresponding response as follows.

Detail comments

1. The authors called Archie's laws the conductivity equation, in which they neglect surface conductivity. Archie's law is a relationship between the formation factor and the porosity or water content whatever surface conductivity can be neglected or not. This is NOT a conductivity equation. Surface conductivity CANNOT be neglected for soils. This assumption is therefore in contradiction with the corpus of knowledge developed in the realm of hydrogeophysics.

Response: Thank you for highlighting this issue. First, we changed the expression between Archie's law and the conductivity equation to make the expression more rigorous. The revised text written as followings will be included in the revised manuscript.

The classical Archie's law (Archie, 1942) describes the relationship between the electrical formation factor and the connected porosity (Eq. 20). In sandy soil, the surface conductivity can be neglected as it is much lower than the electrolyte conductivity (Duy Thanh et al., 2019). The formulation of porous media conductivity is linked to the pore water conductivity, presented as Eq. 21.

$$F=\lim_{\sigma_s\to 0}\left(\frac{\sigma_w}{\sigma}\right)=\phi^{-m} \tag{20}$$

$$\sigma \approx \sigma_w\phi^m \qquad \sigma_w = C_f N_A e\sum_{i=1}^{N}\left|z_i\right|\beta_i C_i \tag{21}$$

Second, while you are correct in general that surface conductivity cannot be neglected for most soils, the soil in this research is packed sandy soil (and relatively coarse one), where the surface conductivity is small compared to electrolytic conductivity. In such case, surface conductivity can be neglected. In the following, we establish a triple layer model (calibrated by the stern layer polarization) to simulate the surface conductivity to confirm this.

In the triple layer model (TLM), the cations (i.e., H^+, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}) that widely exist in the solution are considered. For anions, OH^-, NO_3^-, HCO_3^-, Cl^- and SO_4^{2-} are considered due to the non-negligible amount and the importance to keep charge balance in the soil.

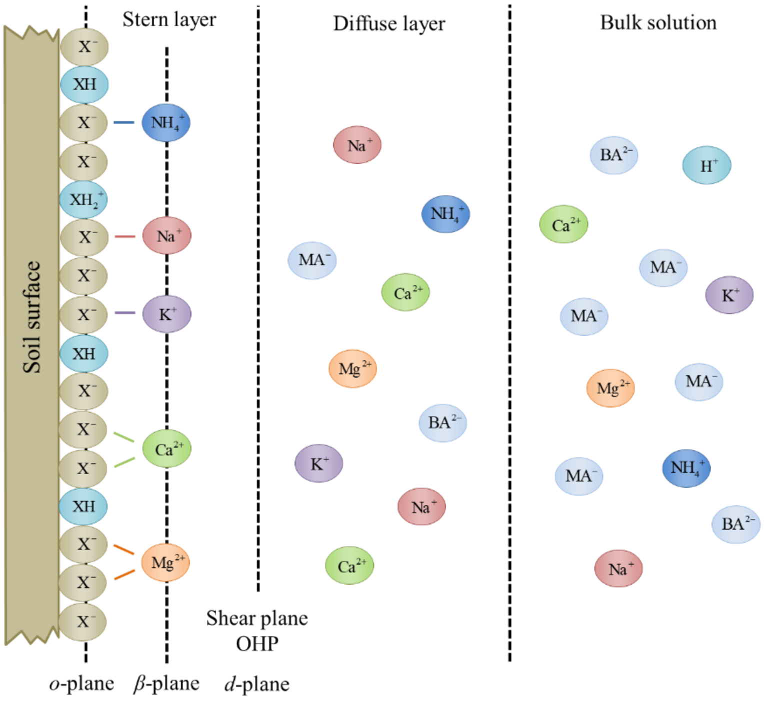

Figure 1 Schematic of the electrical double layer.

The cation concentration on the mineral surface or in the stern layer is related to the concentration in the solution, which is described by Boltzmann distribution (Davis et al., 1978) and shown as

$$C_j^0 = C_j \exp\left(-\frac{ez_j\varphi_0}{k_b T} \right) \tag{1}$$

$$C_j^\beta = C_j \exp\left(-\frac{ez_j\varphi_\beta}{k_b T} \right) \tag{2}$$

where C_j^0 and C_j^β are the concentrations of species *j* on the mineral surface and in the stern layer, respectively (mol L^{-1}), C_j is the concentration of species *j* in the aqueous phase (mol L^{-1}), e is the elementary charge ($e = 1.6 \times 10^{-19} C$), z_j is the valence of species *j* in stern layer, φ_0 is the electrical potential at the *o*-plane corresponding to the basal plane of the mineral surface (V), φ_β is the electrical potential at the *β*-plane corresponding to the mean plane of the stern layer (V), k_b is the Boltzmann's constant ($k_b = 1.381 \times 10^{-23}\,\mathrm{JK}^{-1}$), and T is the temperature ($T = 298.15\mathrm{K}$).

Then, the surface site densities for different species on the mineral surface and in the stern layer are expressed by equilibrium constants associated with half-reactions, which are shown as follows (monovalent cation as an example)

$$\Gamma_j^0 = \Gamma_{>\mathrm{SiO}^-}^0 K_j^S C_j \exp\left(-\frac{e\varphi_0}{k_b T} \right) \tag{3}$$

$$\Gamma_j^0 = \Gamma_{>\mathrm{SiO}^-}^0 K_j^S C_j \exp\left(-\frac{e\varphi_\beta}{k_b T} \right) \tag{4}$$

where Γ_j^0 is the surface site density of species *j* on the mineral surface or in the stern layer (sites m^{-2}), and K_j^S is the equilibrium constant of species *j* for surface reaction

The equivalent surface density of species *i* in the diffuse layer is expressed based on the Gouy-Chapman diffuse layer theory and Boltzmann distribution.

$$\Gamma_i^d = 10^3 N_A C_i \int_0^\infty \exp\left[-\frac{ez_i\,\varphi(\chi)}{k_b T} \right] \mathrm{d}\chi \approx 10^3 N_A C_i \cdot 2\chi_d \exp\left[-\frac{ez_i\,\varphi_d}{2k_b T} \right] \tag{5}$$

where Γ_i^d is the equivalent surface site density of species *i* in diffuse layer (sites m^{-2}), N_A is the Avogadro's number ($N_A = 6.02 \times 10^{23}\,\mathrm{mol}^{-1}$), z_i is the valence of species *i* in diffuse layer, $\varphi(\chi)$ is the local electrical potential (V) at the distance χ (m) from the mineral surface, χ_d is the Debye screening length and it can be defined as the following equation, and φ_d is the electrical potential at the outer Helmholtz plane (also known as the *d*-plane) (V).

Considering the conservation for the surface sites, we get the equation as follows

$$\Gamma^0 = \Gamma^0_{\mathrm{>SiO^-}} + \Gamma^0_{\mathrm{>SiOH}} + \Gamma^0_{\mathrm{>SiOH_2{}^+}} + \Gamma^0_{\mathrm{>SiO^-NH_4{}^+}} + \Gamma^0_{\mathrm{>SiO^-Na^+}} + \Gamma^0_{\mathrm{>SiO^-K^+}} + 2\Gamma^0_{\mathrm{2(>SiO)^-Ca^{2+}}} + 2\Gamma^0_{\mathrm{2(>SiO)^-Mg^{2+}}} \quad (6)$$

where Γ^0 is the total surface site density of the mineral surface, with a characteristic value of 5×10^{18} sites $\mathrm{m^{-2}}$ for silica (Wang and Revil, 2010).

According to the species on the mineral surface, in the stern and diffuse layers, the surface charge densities at the soil surface can be expressed as

$$Q_0 = e\left[\Gamma^0_{\mathrm{>SiOH_2{}^+}} - \Gamma^0_{\mathrm{>SiO^-}} - \Gamma^0_{\mathrm{>SiO^-NH_4{}^+}} - \Gamma^0_{\mathrm{>SiO^-Na^+}} - \Gamma^0_{\mathrm{>SiO^-K^+}} - 2\Gamma^0_{\mathrm{2(>SiO)^-Ca^{2+}}} - 2\Gamma^0_{\mathrm{2(>SiO)^-Mg^{2+}}}\right] \quad (7)$$

$$Q_s = e\left[\Gamma^0_{\mathrm{>SiO^-NH_4{}^+}} + \Gamma^0_{\mathrm{>SiO^-Na^+}} + \Gamma^0_{\mathrm{>SiO^-K^+}} + 2\Gamma^0_{\mathrm{2(>SiO)^-Ca^{2+}}} + 2\Gamma^0_{\mathrm{2(>SiO)^-Mg^{2+}}}\right] \quad (8)$$

$$Q_d = e\sum_{i=1}^{N}(\pm)z_i\Gamma_i^d \quad (9)$$

where Q_0, Q_s and Q_d are the surface charge densities at mineral surface, stern layer, and diffuse layer, respectively ($\mathrm{C\ m^{-2}}$).

Then, taking Eqs 3-6 into Eqs 7-9, we can get the surface charge densities at the mineral surface, stern layer, and diffuse layer (Eqs 7-9) that only include unknown parameters of φ_0, φ_β and φ_d.

Finally, we consider the global electroneutrality equation and relationship of electrical potential at the mineral-water surface and take the transformed Eqs 7-9 into Eqs 14-16 to solve φ_0, φ_β and φ_d.

The global electroneutrality equation for the TLM model is given as

$$Q_0 + Q_s + Q_d = 0 \quad (10)$$

The electrical potential for TLM have the relationships as

$$\varphi_0 - \varphi_\beta = Q_0 / C_1 \quad (11)$$

$$\varphi_\beta - \varphi_d = -Q_d / C_2 \quad (12)$$

where C_1 and C_2 are the integral capacities of the inner and outer parts of the stern layer, respectively ($\mathrm{F\ m^{-1}}$). The C_1 and C_2 are constant values, and we take $C_1 = 1.2\,\mathrm{F\,m^{-1}}$ (Schwartz and Furman, 2012) and $C_2 = 0.2\,\mathrm{F\,m^{-1}}$ (Wang and Revil, 2010).

The electrical potentials (i.e. φ_0, φ_β and φ_d) can be solved by numerical resolutions. Then, the surface site densities of different species in the stern and diffuse layers can also be attained.

After that, the specific surface conductivities for stern layers are shown as

$$\sum^s = e\left(\beta_{\mathrm{NH_4^+}}\Gamma^0_{\mathrm{>SiO^-NH_4^+}} + \beta_{\mathrm{Na^+}}\Gamma^0_{\mathrm{>SiO^-Na^+}} + \beta_{\mathrm{K^+}}\Gamma^0_{\mathrm{>SiO^-K^+}} + 2\beta_{\mathrm{Ca^{2+}}}\Gamma^0_{\mathrm{2>(SiO)^-Ca^{2+}}} + 2\beta_{\mathrm{Mg^{2+}}}\Gamma^0_{\mathrm{2>(SiO)^-Mg^{2+}}}\right) \quad (13)$$

For a packing of spheres of diameter d_0, the surface conductivity can be expressed as (Bolève et al., 2011)

$$\sigma_s = \frac{6\sum_s}{d_0} \quad (14)$$

where $\sum^s$ is the specific surface conductivity of stern layer (S), σ_s is the surface conductivity, and d_0 is the characteristic particle diameter (m) ($d_0 = 3.2\times10^{-4}\,\mathrm{m}$).

Then, the Duhkin number represents the ratio between surface conductivity of particle and electrical conductivity of pore water can be expressed

$$Du \equiv \frac{\sigma_s}{\sigma_w} \quad (15)$$

Based on the discussion above, the related conductivities and Duhkin number can be calculated in Table 1. Thus, the surface conductivity can be neglected ($Du < 0.01$) and the electrical conductivity can be written as (Bolève et al., 2011)

$$\sigma \approx \sigma_w \phi^m \quad (16)$$

Table 1 Related conductivities and Duhkin number.

Parameter	σ_w (S m^{-1})	$\sum^s$ (10^{-9} S)	σ_s (10^{-4} S m^{-1})	Du (10^{-4})
Value	0.145-0.156	5.86-6.05	1.10-1.13	7.27-7.58

2. The authors neglect the diffusion/membrane polarization, which is related to the gradient in the electrochemical potential of the ionic charge carriers. However, this contribution is well-established and probably the major contributor of the observed signals. It is related to the Hittorf transport numbers of the ionic charge carriers, which depends in turn on the surface conductivity. Obviously, the authors have a lack of knowledge on how to compute this contribution and it was not discussed for that reason. This is not a good practice.

Response: We are guessing that you mean diffusion/membrane potential rather than diffusion/membrane polarization. We neglected this contribution for two reasons. First, this research focuses on a capillary fringe where the redox potential changes range around hundreds of millivolts within a small distance, but the membrane potential (contributing around 5% for SP signals) is much lower by numerical modeling estimation. Thus, the membrane potential contribution is not as obvious as redox processes. Second, this study is inspired by a soil aquifer treatment scenario, and the main purpose is to detect redox-sensitive species (i.e. C and N) distribution and degradation. Thus, the redox potential contribution must be considered as expected. Although streaming potential contribution is often smaller than membrane potential, the study of streaming potential can help detect water flow or estimate the groundwater water level, which is significant to create a redox environment for C and N contaminant degradation. The study of membrane potential is of lesser importance in our case (i.e., for C and N contaminant detection), especially where multi-non-target ions (e.g. Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}) that may largely affect membrane potential in the treated wastewater. To more cater to the theme, we changed the title to *Numerical modeling of carbon and nitrogen transformation in the subsurface and their impacts on the self-potential signature*.

Moreover, we also added the explanation that we neglected the membrane potential. **(the revised text will be included in the revised manuscript:** *This research focuses on SP signature and its forming processes in a redox environment with variable water flux. Thus, the SP response to membrane potential, where ions diffuse through the narrow pores and result in the charge separation (counterions are attracted to the mineral surface but the coions are blocked at the pore entrance) (Revil et al., 1998; Jouniaux et al., 2009), is neglected.***).** Nevertheless, we do understand that considering membrane potential could make the SP signals more complete and we very appreciated your constructive suggestion.

3. The redox potential contribution exist ONLY if a biotic or an abiotic (metallic in a broad sense including semi-conductors) electronic conductor is present in the material. This point is not well-discussed in the paper. The authors seems to mix electrodic potential associated with redox chemistry at the electrodes/ medium interface (which can be avoided with agar agar gel) and what specialists called self-potential signals (remotely measured without having the electrodes in contact with the medium in which the source of current occurs). I am glad that the authors modeled electrodic potentials but they should NOT be misled with self-potentials.

Response: Thank you for this comment. Actually, our purpose is to build a creative model to simulate the redox potential which can reflect the redox measurement in the experiment. This is probably what you mentioned as the electrode potential. It is assumed versus a standard hydrogen electrode, commonly denoted as redox potential (Peiffer et al., 1992). As for the SP signals associated with redox processes, we simplify the SP model and just used the previous equation (Eq. 28) for the SP signal simulation. In Eq. 28, the redox potential is usually acquired from measurement in numerous references, but it is the simulated value in our research. Thus, we do not mislead electrode potential with SP, just simplify the SP model.

However, we understand that a much better model for SP signal (associated with redox processes) is to consider the intrinsic theory that the electrons transfer through the biotic or abiotic electronic conductors. Thus, we take this issue into account and consider to improve the model in the revision process. In the meanwhile, we will also revise the introduction and results and discussion to make them more cater to the modified model. Moreover, we added the discussion that the SP contributed by redox potential is in an environment with biotic electronic conductors. **(the revised text will be included in the revised manuscript:** *The current density contributed by redox processes is associated with the redox potential gradient in the vicinity of the electronic conductor (e.g., microbial extracellular appendages) (Rittgers et al., 2013).***).**

4. The experiments are poorly described. The paper of Zhang and Furman is not related to self-potential signals so I don't have any idea on how the geophysical experiment was done. In addition, even in sand with organic matter and bacteria, surface conductivity can be strong, in contradiction with the basic assumption made in this paper. The CEC could have been estimated or measured.

Response: Indeed, the paper of Zhang and Furman only described the biogeochemical experiment, and the information related to SP signals is not included. As the information related to SP measurement was not that clear, we revised Fig. 3 to make the SP measurement clear. The revised figure that will be included in the manuscript is shown as follows. As this paper focused on numerical modeling, the surface conductivity was not measured in the experiment, but the CEC was around 2.5 meq/kg. It is a reasonable value for sandy soil, even if at the low range of the accepted range. However, we appreciate your suggestion and will measure the surface conductivity in further experiments.

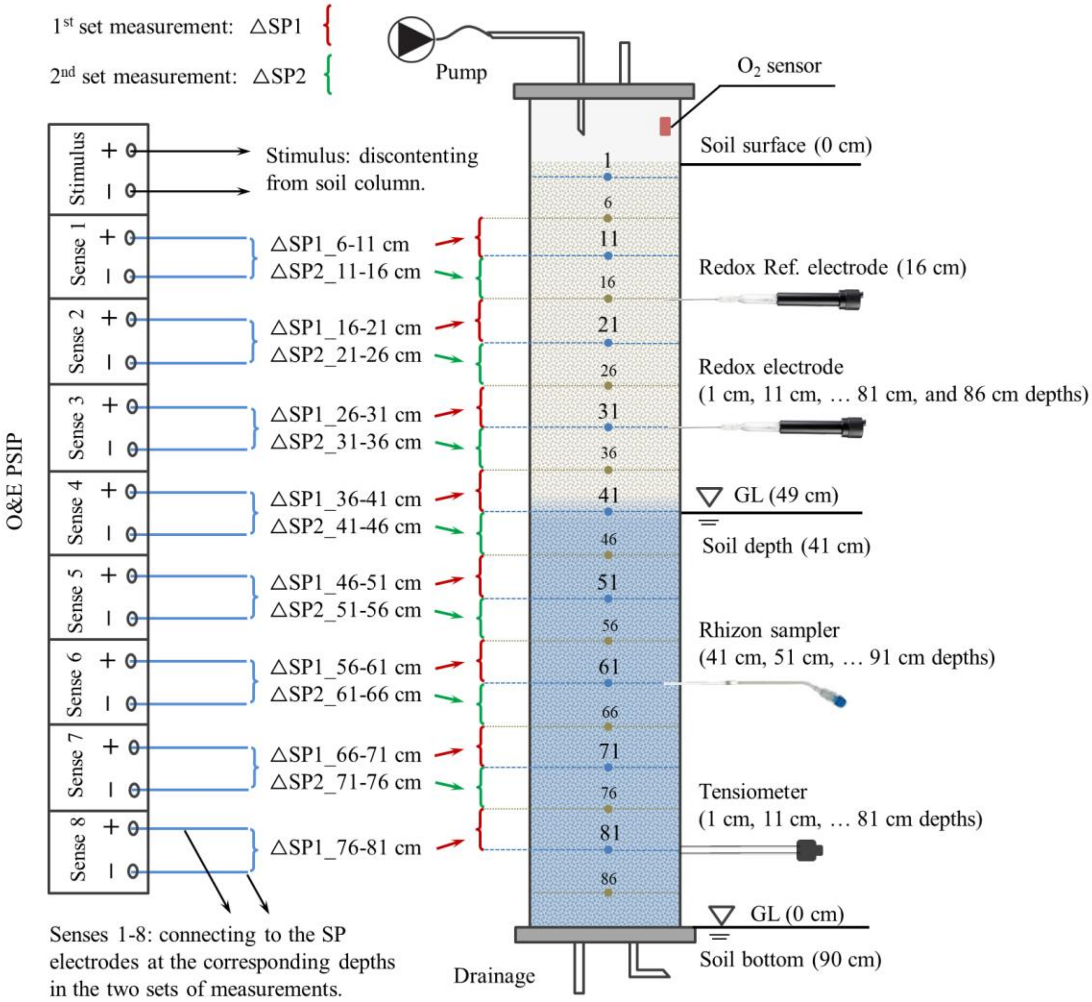

Figure 3 Schematic of soil biochemical and geophysical experiments.

5. Equation 28 is provided without any reference and associated assumptions. This is bad practice especially when this equation has already been discussed and developed in the literature. It was certainly not derived by the authors…Furthermore, equation 28 is valid ONLY in presence of an electronic conductor, this assumption is not discussed in the paper, see Rittgers J. B., A. Revil, M. Karaoulis, M. A. Mooney, L.D. Slater, and E.A. Atekwana, Self-potential signals generated by the corrosion of buried metallic objects with application to contaminant plumes, Geophysics, 78(5), EN65-EN82, 10.1190/GEO2013-0033.1, 2013, for details.

Response: Thank you very much for pointing out the issue. First, we added the associated references which the equation was used and discussed before. Second, we added the assumption that this equation is valid in the presence of electronic conductor (i.e., microbial extracellular appendages) in this research. The following revised text will be included in the revised manuscript.

The current density contributed by redox processes is associated with the redox potential gradient in the vicinity of the electronic conductor (e.g., microbial extracellular appendages) (Rittgers et al., 2013), formulated as (Arora et al., 2007; Linde and Revil, 2007)).

$$j_{rc} = -\sigma s_w^n \nabla E_h \qquad (17)$$

6. For each figure, write clearly what is measured and what is computed.

Response: We emphasized the measured or simulated values in each figure to make it more clear based on your suggestion.

7. Regarding the statement "SP associated with redox processes is induced by electron transfer, where electron donors (e.g., organic carbon) deliver electrons to acceptors (e.g., oxygen or nitrate) driven by redox potential (Jouniaux et al., 2009).", I cannot fond such statement in the cited paper. At the opposite, I am very surprise to see no citation of the excellent papers by Alexis Maineult on this subject. Also papers related to electrodic potentials should be cited as well.

Response: It is not a directly citation from Jouniaux et al., 2009. It is a rephrase after we read Section 3.2 (Jouniaux et al., 2009). Also, we added the paper citation by Alexis Maineult related to this subject. Specific revisions related to electrode potential in the introduction part will be further made in the revision stage after we modify the SP model based on the 3rd response.

8. Equation 25 is wrong. The current density is the effective charge density (defined through a dynamic volume averaging of the local current density, local charge time the local velocity) and the Darcy velocity, not the fluid velocity.

Response: Thank you for reminding this issue. We revised the fluid velocity into Darcy velocity in the model and also the corresponding result related to streaming potential. The inappropriate expressions in the abstract and introduction parts were also modified. The following revised text and figures will be included in the revised manuscript.

The Darcy velocity equals to the volumetric flux density, computed using Darcy's law (Eq. 27), which can be simulated by coupling with the water flow model (Eqs. 1-3).

$$v = q_w = -K(h)\left(\frac{\partial h}{\partial z} + 1\right) \qquad (18)$$

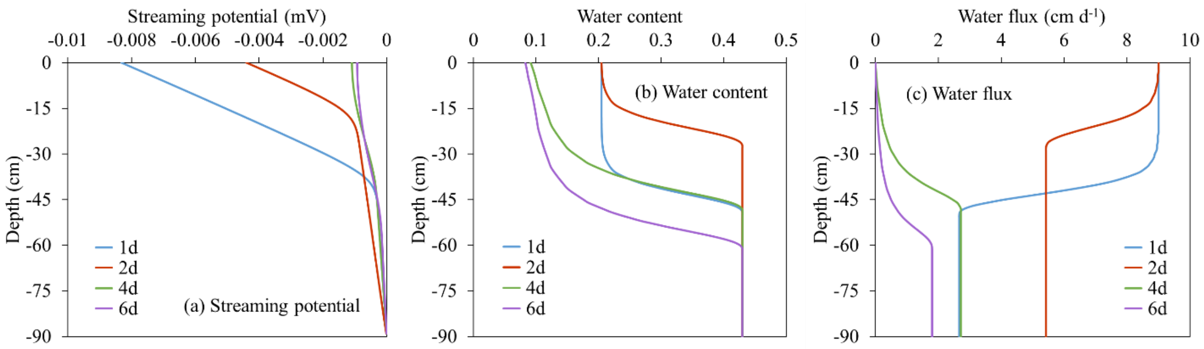

Figure 6 Streaming potential in response to water content and flux along with the soil profile (simulated). Panes (a), (b), and (c) represents streaming potential, water content, and water flux, respectively.

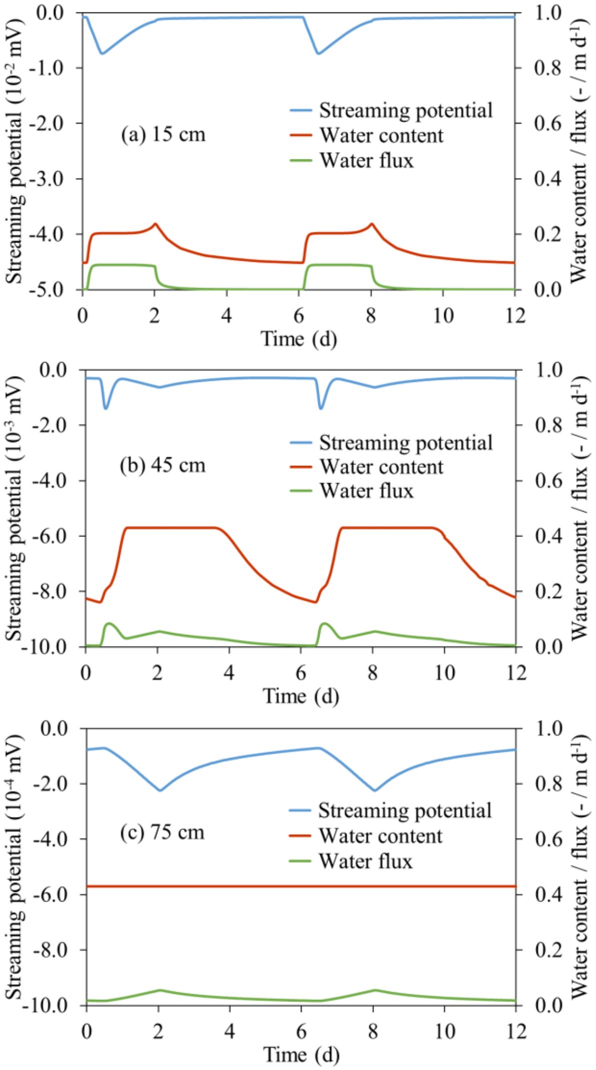

Figure 8 Streaming potential in response to water content and flux in time series (simulated). Panes (a), (b), and (c) represent 15cm, 45cm, and 75cm depths respectively.

9. In the introduction, it is written that Poisson equation for the self-potential is a continuity equation. This is a field equation obtained by combining a continuity equation (conservation of charge in the quasi-static limit of the Maxwell equations) and a constitutive equation (generalized Ohm's law). The authors should be more rigorous.

Response: Thank you very much for pointing out this inclarity. We changed the expression into a more rigorous phrasing based on your comment **(the revised text will be included in the revised manuscript:** *The SP distribution is attained by the solution to Poisson's equation, obtained by combining a continuity equation (conservation of charge in the quasi-static limit of the Maxwell equations) and a constitutive equation (generalized Ohm's law)***).**