

Biogeosciences Discuss., author comment AC1
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Reply on RC1

Timea Katona et al.

Author comment on "High-resolution induced polarization imaging of biogeochemical carbon turnover hotspots in a peatland" by Timea Katona et al., Biogeosciences Discuss., <https://doi.org/10.5194/bg-2020-438-AC1>, 2021

This hot spot geophysical investigation is definitively a hot subject area (no pun intended). My comments are minor. The paper is well-written, interesting to read, exciting and cite correctly the literature. Data quality is very good and the analysis is done rigorously. My only disappointment is that the authors remain very qualitative in their use of IP while recent works have shown how these tomograms can be used quantitatively.

We thank the first Reviewer for his evaluation and the insightful comments. We aim at incorporating all suggestions into the revised version of our manuscript. We thank the Reviewer for the references, which will be included during the interpretation of the signatures. We added the ten papers published by Revil and co-workers regarding details of the electrode polarization to the reference. Furthermore, we tried to extend our manuscript in a quantitative way.

- Perhaps the abstract is missing a physical explanation if any regarding the field and core observations. Perhaps the statement reported in Line 550 "The strong correlation between the polarization response and the DOC suggest an, as yet not 550 fully understood, causal relationship." Should be mentioned in the abstract. For me this is an exciting avenue in research !

A: We agree with the Reviewer and we have extended our Abstract, which reads as follows: "Our results reveal large variations in the electrical response, with the highest IP phase values (> 20 mrad) corresponding to high concentrations of phosphates (>4000 µM), an indicator for intensive carbon turnover. Furthermore, we found a strong relationship between the polarization response and the dissolved organic carbon."

- Lines 71-80, perhaps (up to you) it would be worth to mention that the ONLY mechanisms that explain the relaxation time is inversely proportional to the

conductivity of the material is related to a polarization mechanism inside the metallic particles. ALL the other mechanisms invoked to date in which the polarization is at the grain surface or outside the metallic grains cannot explain this fundamental observation.

A: We agree with the Reviewer and we have edited our manuscript. In the revised version of our manuscript, the line reads now: "Revil et al (2015a, 2015b, 2018b,) concluded, that to the conductivity inversely proportional relaxation time relates to the polarization mechanism inside of the metallic particles."

- Perhaps the authors will find the recent paper related to the IP signature of bioclogging relevant to their research Garcia-Artigas R., M. Himi, A. Revil, A. Urruel, R. Lovera, A. Sendrós, A. Casas, L. Rivero, 2020. Time-domain induced polarization as a tool to image clogging in treatment wetlands, Science of the Total Environment, 724, 138189, <https://doi.org/10.1016/j.scitotenv.2020.138189>.

A: We thank the Reviewer for the reference. We have included it as part of the state-of-the-art revision, and the Discussion section.

"Garcia-Artigas et al. (2020) demonstrated that clay and bacterium can form a clogging which has a linear relationship with normalized chargeability."

"Artigas et al. (2020) concluded, that bioclogging (made of fine particles and bacterium formed biofilms) coats the grain surface and can block the pore water flow. The weight of such clogging has a direct relationship with normalized chargeability as the clogging increase the specific surface area and so the CEC. However, as discussed above, we did not find relationship between the CEC and Polarization response."

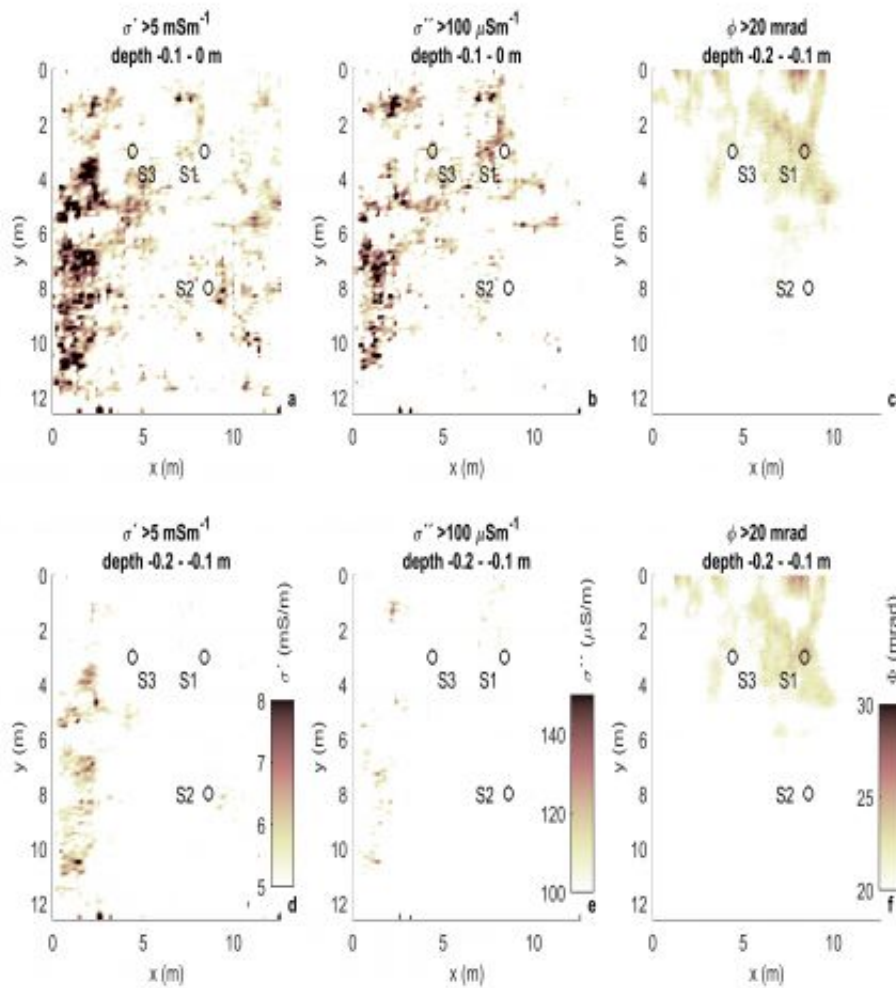
- I fundamentally disagree with the following sentence which is NOT supported by the underlying physics of IP "The phase of the complex conductivity roughly represents the ratio of the polarization ($\delta \square \square \square'$) relative to the Ohmic conduction ($\delta \square \square \square'$). Therefore, it has been argued that the phase represents the polarization effect better than the imaginary conductivity itself as it removes effects stemming from changes in fluid conductivity, saturation, and porosity (Kemna et al., 2004; Ulrich and Slater 2004)." It is quite wrong and misleading. Only the quadrature conductivity or normalized chargeability represents the polarization process. What is misleading is that in presence of metallic particles, the phase and chargeability are used because it can demonstrated that these properties are proportional to the content of metallic particles. Period.

A: This section was rewritten according to the comments of the Reviewer. What we wanted to mention here, is that the size of the pore throats influences the polarization, and the water saturation of the peat influences the in-phase conductivity. We assume that the peat in our experimental plot is almost fully water-saturated (the lowest measured water table depth at the two piezometers was 8 cm), and the pore size is larger in the area East-Southeast side of the experimental plot. This would explain why both the in-phase and quadrature conductivity are high at the western part of the experimental plot and why the in-phase conductivity is high, and quadrature conductivity is low in the East-Southeast side of the experimental plot. The phase can highlight the high quadrature conductivity values relative to the in-phase conductivity.

“The phase of the complex conductivity represents the ratio of the polarization (σ'') relative to the Ohmic conduction (σ'). Therefore the high phase values highlight the high σ'' values relative to σ' values. The phase depends on the electrolytic and surface conduction term furthermore, reveals the saturation dependence in the case the ohmic conduction changes because of drainage (Kemna et al., 2004; Ulrich and Slater 2004). Furthermore, the phase value depends on the volumetric content of metallic particles (Revil 2015a, 2015b) and therefore the phase could reveal the possible metallic content in the peat.”

- My main criticism is that IP is used qualitatively in this paper while we can do much better in terms of quantitative assessment based on field IP measurements, see for instance Abdulsamad F., A. Revil, A. Soueid Ahmed, A. Coperey, M. Karaoulis, S. Nicaise, and L. Peyras, 2019. Induced polarization tomography applied to the detection and the monitoring of leaks in embankments dams and dikes, *Engineering Geology*, 254, 89–101, <https://doi.org/10.1016/j.enggeo.2019.04.001>. Abdulsamad F., A. Revil, A. Ghorbani, V. Toy, M. Kirilova, A. Coperey, P.A. Duvillard, G. Ménard, and L. Ravel, 2020. Complex conductivity of graphitic schists and sandstones, *Journal of Geophysical Research-Solid Earth*, 124, 8223–8249. <https://doi.org/10.1029/2019JB017628>. Revil A., A. Soueid Ahmed, A. Coperey, L. Ravel, R. Sharma, N. Panwar, 2020. Induced polarization as a tool to characterize shallow landslides, *Journal of Hydrology* 589 (2020) 125369, <https://doi.org/10.1016/j.jhydrol.2020.125369>.

A: Following the recommendation, we suggest a new figure, which shows the active biogeochemical areas. As discussed in our manuscript, we consider that the polarization is not controlled by the iron content, as this is present in form of iron oxides which have reported low values in laboratory studies (e.g., Joyce et al., 2012). We believe the high polarization response is due to the high concentrations of Carbon inferred by the high DOC values measured in water samples. As the controls of the polarization response are still open to discussion, we decided not to apply the models proposed by Revil et al. (2015) for the quantification of metal content.



- Section 4.3 the authors wrote “The low-frequency polarization response of subsurface materials is usually attributed to either 468 electrode polarization of highly conductive metallic minerals (e.g., Pelton et al., 1978; Wong, 469 1979)”. I am quite surprised by this statement since as pointed out above, these two papers cannot explain a fundamental observation that in presence of metallic particle, the relaxation time is inversely proportional to the conductivity of the material. ONLY an intra-metallic particle mechanism can explain this observation excluding ipse factor these models, see for instance Abdulsamad F., A. Revil, A. Ghorbani, V. Toy, M. Kirilova, A. Coperey, P.A. Duvillard, G. Ménard, and L. Ravel, 2020. Complex conductivity of graphitic schists and sandstones, *Journal of Geophysical Research-Solid Earth*, 124, 8223–8249. <https://doi.org/10.1029/2019JB017628>. Similarly Line 471, the citation of Waxman and Smits is incorrect since it is dealing ONLY with conductivity and not polarization. The citation of Vinegar and Waxman (1984) would be adequate.

A: We agree with the Reviewer in so far as an important part of recent model development has been completely omitted in our first version of the manuscript. However, we are not as convinced as the Reviewer regarding the conclusion that there is only one model left, which is able to explain all experimental results. We consider that a detailed discussion of this topic is far beyond the scope of this

manuscript. As our discussion does not rely on any of the very specific/distinct predictions of the two model families (perfect conductor vs. semi-conductor), we decided to generalize our discussion and stick to those predictions, which are the same for both model families (e.g., the proportionality between polarization magnitude and volume content of metallic particles).

Reformulated paragraph:

“The low-frequency polarization response of subsurface materials is usually attributed to either polarization of conductive metallic minerals (e.g., Pelton et al., 1978; Wong, 1979; Revil et al., 2018; Qi et al., 2018; Bückner et al., 2019) or the polarization of the electrical double layer (EDL) covering charged surfaces of electrically non-conducting solid matter (e.g., Vinegar and Waxman, 1984; Revil and Florsch, 2010; Revil, 2012).

The strong polarization response of metal-bearing particles arises from the different charge transport mechanisms in the conducting solid matter (electronic or semi-conductor conductivity) and the electrolytic conductivity of the surrounding pore fluid (e.g., Wong, 1979; Revil et al., 2018; Bückner et al., 2019). This so-called charge polarization has its maximum at relatively high frequencies ($\gg 1$ kHz) unless the perfectly conducting minerals are large (Bückner et al., 2018) or if diffusion relaxation within a highly-to-moderately conducting grain is taken into account (Revil et al., 2018, Abdulsamad et al., 2020). Irrespective of which of these polarization models is considered, the magnitude of the polarization of conductive particles is always predicted to be proportional to the volume content of the conductive minerals (Wong, 1979; Revil et al. 2015a, 2015b, 2017a, 2017b, 2018; Bückner et al., 2018).”

- The explanation about electrode polarization mechanism is wrong and does not make sense. Wong is about charge transfer by redox processes and unbalances in charge transfer at the pore water / metallic particle interface. None of the models invoked in this paragraph can explain the observations in presence of metallic particles except for very small metallic particles as discussed in the series of ten papers published by Revil and co-workers in Geophysics. Lines 481-482 : All the models produces this features, not just the one by Wong.

A: We agree with the Reviewer that the extension of electrode polarization needs to be considered, as explained in the papers published by Revil and co-workers. We believe that the new version of the discussion, which includes the recent work of the Reviewer, is general enough to resolve the issue raised here.

- Line 489: this explanation is again wrong since an intra particle mechanisms has nothing to care about the concentration of Fe in the pore water. There is a lack of understanding here of the mechanisms of polarization in presence of metallic particles and how they agree or disagree with the observations.

A: Previous studies such as Flores Orozco et al. (2011, 2013) demonstrated that there is a correlation between the electroactive ions in the pore space and IP response, in our manuscript we argue that the electrode polarization can be explained based on these findings and the Wong model which was extended by Bückner et al. (2018). Actually, this is one of the experimental observations, which the family of semi-conductor models has not yet been able to explain and

the model by Wong (1979) (and further developments) to date (and as far as we understand) provide the only mechanistic explanation for.

- The conductivity of the metallic particle is TOTALLY irrelevant of the problem as discussed in depth by Revil and co-workers in this series of ten papers mentioned above. Actually a sediment with metallic particles is more resistive than the sediment alone at low frequency, a well-established observations that is corroborated by the underlying physics. There are therefore some flaws in your explanations of electrode polarization here.

A: We agree that in the family of models developed by the Reviewer and his co-workers, the conductivity of the particles play a secondary role (or even a smaller role). We included the possibility of a polarization of moderately conductive particles into the revised version of the discussion. In particular, the intra-grain polarization mechanism is more likely to cause a measureable polarization within other iron oxides than magnetite and within iron complexes with organic matter.

- Lines 504-509, this explanation does not explain any observations. Membrane polarization does not explain the basic observations shown by experimentalists regarding the IP effect of metallic-free porous media. Sooner or later, this will be obvious to the whole community working in this are the day people will be more quantitative in their used of IP data in the field (which is again my main criticism here).

A: We are using a membrane polarization model (Bücker et al., 2017) to demonstrate a relationship between the high carbon content in the electrolyte and a change in the polarization response. As observed by Revil and Skold (2011) the increase in the salinity leads to an early increase in the quadrature conductivity (and decrease at very high salinity). Nevertheless, we agree with the Reviewer that the membrane polarization can also be formulated in terms of grain size and the polarization around the grain in the electrical double layer. They should provide key valent results in these terms. We think the membrane polarization has to be added, even if there are doubts about whether the membrane polarization is strong enough to contribute to the polarization significantly.

- Line 510: the references are not properly cited.

A: We corrected the citation.

- Line 515, no the CEC is NOT "The product of both surface charge density and surface area". The surface charge density is the ratio of the CEC by the specific surface area. The word "specific" is missing and is very important (because of the normalization by the mass of grains).

A: We agree with the Reviewer, we corrected the line, inserted the word "specific".

- Lines 521-522, perhaps because it depends also on the water content as shown in

many models. That said, yes it is not that the CEC of zeolite and organic matter is not activated for surface conduction and polarization. This has been shown several times in the literature.

A: The ground water level was constantly 6-8 cm below the surface during the time we performed our measurements. Furthermore at the surface the peat was almost fully water saturated. Therefore we think that the weak dependence on CEC cannot be explain by the low water content.

Bücker, M., Orozco, A. F., Hördt, A., & Kemna, A. (2017). An analytical membrane-polarization model to predict the complex conductivity signature of immiscible liquid hydrocarbon contaminants. *Near Surface Geophysics*, 15(6), 547-562.

Bücker, M., Orozco, A. F., & Kemna, A. (2018). Electrochemical polarization around metallic particles—Part 1: The role of diffuse-layer and volume-diffusion relaxation. *Geophysics*, 83(4), E203-E217.

Flores Orozco, A., Williams, K.H., Long, P.E., Hubbard, S.S. and Kemna, A., 2011. Using complex resistivity imaging to infer biogeochemical processes associated with bioremediation of an uranium-contaminated aquifer. *Journal of Geophysical Research: Biogeosciences*, 116(G3).

Flores Orozco, A., Williams, K. H., & Kemna, A. (2013). Time-lapse spectral induced polarization imaging of stimulated uranium bioremediation. *Near Surface Geophysics*, 11(5), 531-544.

Joyce, R.A., Glaser II, D.R., Werkema Jr, D.D. and Atekwana, E.A., 2012. Spectral induced polarization response to nanoparticles in a saturated sand matrix. *Journal of applied geophysics*, 77, pp.63-71.

Revil, A., & Skold, M. (2011). Salinity dependence of spectral induced polarization in sands and sandstones. *Geophysical Journal International*, 187(2), 813-824.

Revil, A., Florsch, N., & Mao, D. (2015). Induced polarization response of porous media with metallic particles—Part 1: A theory for disseminated semiconductors. *Geophysics*, 80(5), D525-D538.

Wong, J. (1979). An electrochemical model of the induced-polarization phenomenon in disseminated sulfid ores. *Geophysics*, 44(7), 1245-1265.