Biogeosciences Discussions

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Reply on RC2

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-AC2, 2021

There is increasing evidence that hot spots of biogeochemical activity exert profound effects on ecosystems that are disproportionate relative to the physical footprint of the hotspots. Geophysical techniques have a role to play in locating such hotspots. Induced polarization is an interesting method as it may be sensitive to indicators of enhanced biogeochemical activity, such as the precipitation of metallic minerals where anaerobic and aerobic waters interact.

I found this paper interesting to read and it includes some nice graphics for illustration. My main concern about the work is that the attempt to correlate IP measurements with indicators of enhanced biogeochemical activity (in this case enhanced carbon turnover) is unconvincing based on the presented dataset. The paper focuses on correlating the IP-measured phase and/or imaginary conductivity with [1] vegetation patterns, [2] chemistry of soil samples, and [3] water chemistry. I could not follow the logic of the argument that the IP measurements are indicative of hotspots and I doubt that the assumed correlations are statistically significant. Figure 8 is presented to argue that the phase is correlated with the vegetation patterning – but how does that represent a hot spot? Figure 10 appears to be presented to show that phase is uncorrelated with fluid DOC, Cl- and Ftot in the pore fluid and therefore is an indicator of biogeochemical hotspots (Lines 374-381). I could not follow this logic at all. Later in the paper, the entire upper layer of the soil is identified as a 'hot spot', which seems inconsistent with the idea that there are localized zones in space of enhanced biogeochemical activity. In summary, I really struggled to understand what how the presented dataset characterizes hotspots in this paper.

Another general problem I have with the paper is that I found myself often failing to see the apparent correlations drawn between the geophysical images and the other available site information. The inferred correlations were often unconvincing at best. As an example, on lines 550-551 the significance of a correlation between polarization response and DOC is emphasized, yet the real part of the conductivity shows the strongest correlation with DOC.

I also noted some significant technical errors that suggest some misunderstanding of induced polarization. One that was particularly concerning is the statement given at Lines 297-300. This is entirely incorrect. Ulrich and Slater (2004) and Kemna et al. (2004) definitely did not say this. This statement is particularly concerning as it implies a possible misinterpretation of the IP measurements throughout the paper, which may explain why I

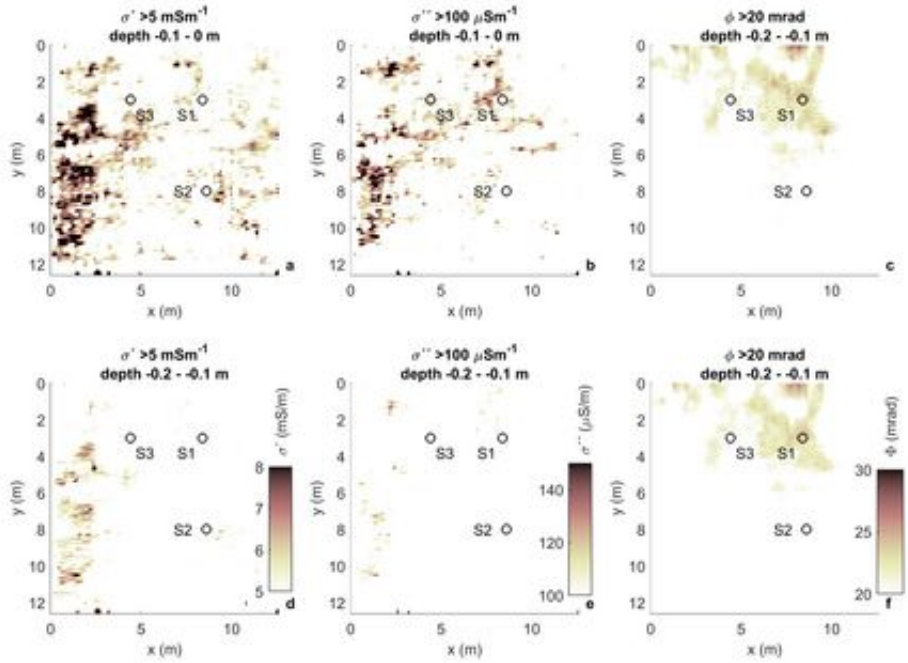
really struggled to follow the arguments being made in most places.

A: We thank the second Reviewer for the time taken to review our manuscript and his evaluation. It helps us to find some problems in the structure of the manuscript. We made changes in our introduction and the interpretation and discussion of the imaging results to improve the message. We have also made a careful revision of the citations. We have corrected most of the suggested changes, and we hope the message in the revised manuscript now is better communicated.

We found a high polarization response (quadrature conductivity) although, our chemical analysis shows negligible sulfate reduction. The biogeochemical processes might influence vegetation. Thus, some non-geophysical studies have used vegetation changes to assess biogeochemical hotspots' presence (e.g., Kleinebecker et al., 2008).

We do not believe that the vegetation controls the electrical signatures (conductivity and polarization), but we use them as an independent validation of our interpretation. As Figure 8 shows, the phase value is higher in the area where the dense vegetation is observed than in the area where the vegetation is rare. Although the phase shows a low correlation with the geochemical parameters, altogether, the phase values are high at active biogeochemical areas. Therefore, we interpret the high phase values as the hot spots. We have edited our manuscript to make this clearer.

We do not consider the entire top 10 cm as a hot spot; this was a poor formulation on our side. The manuscript will be revised to state that we observed high polarizable values within the 10 cm in well-delimited areas defined as hot spot. We propose to include the figure below at the end of our manuscript, where we indicate the hot spots' geometry at different depths.



The quadrature conductivity and phase values appear to be sensitive to variations in the peat unit's thickness (i.e., the contact to the bedrock). We agree with the Reviewer that the bedrock contact and the low polarization values do

not agree to 100%, but the depth of the contact to the low polarization response clearly reacts to variations in the depth of the peat-granite contact. We corrected our statement. Additionally, we found variations in the peat unit's electrical values, both vertical and horizontal (shown in Figure 6-8). To address these inhomogeneities, we conducted chemical analysis on soil and pore fluid samples.

It is true that, in general, the in-phase conductivity has a stronger correlation to all chemical parameters measured in the pore fluid, which is due to the increased fluid conductivity caused by the dissolved carbon. Nevertheless, we use the high DOC as a proxy to illustrate high carbon content in the solid phase, thus defining carbon turn-overs (i.e., hot-spots).

The statement at lines 297-300 was indeed poorly written. The in-phase conductivity tends to be higher at higher saturation (Tartrat et al., 2019) and the quadrature conductivity depends on the pore size and saturation (Ulrich and Slater 2004). As we do not have direct measurements at the site concerned with the saturation and pore space, we can only hypothesize based on our observation that the peat in our experimental plot is highly saturated (the deepest measured water table depth was 8 cm bgs) and the pore size is larger East-Southeast side of the experimental plot. This would explain why both the in-phase and quadrature conductivity are high at the West part of the experimental plot and why the in-phase conductivity is high, and quadrature conductivity is low East-Southeast side of the experimental plot. If we use the phase as our main parameter, we see the high phase values in the middle of the experimental plot tended to the Northside, where the quadrature conductivity is high relative to the in-phase conductivity. This difference in the quadrature and in-phase conductivity might be due to the influence of the fluid conductivity, and this is why we insisted on showing the phase values. The phase values permit a better indication of the areas where the quadrature conductivity is high relative to the in-phase conductivity furthermore (Kemna et al., 2004). Moreover, the phase values are directly resolved through the inversion scheme used in our study.

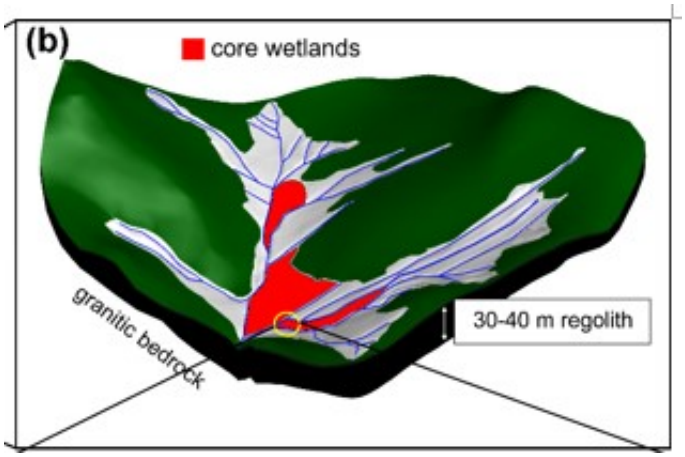
Specific comments:

Line 94: Slater and Binley (2006) is an inappropriate reference – this paper has nothing to do with IP mapping of contaminant degradation

A: Slater and Binley (2006) present changes in the electrical properties following the groundwater remediation technics in zero-valent iron permeable reactive barriers. We agree with the Reviewer. This reference is not directly relevant to the degradation of contaminants and has been removed from the citations.

Line 160: Not sure what you mean here. Fig 2d shows waterlogged/saturated soils but that doesn't mean surface runoff is occurring. Looks pretty flat as expected for a peatland

A: Yes the experimental plot is flat; however, the catchment itself has a bowl shape (Fig. 1b). Furthermore, the runoff water can be observed at the surface. We have corrected our manuscript accordingly to differentiate between the experimental plot and the catchment



Line 163: Why the difference in grid resolution?

A: This is related to the time required on the field to conduct the measurements and possible disturbance of biogeochemical conditions. We measured every 50 cm along with the selected IP profiles to have a high resolution; however, we collected data only every fifth of lines assuming relative gradual changes between the profiles.

Line 164: Unclear, what experiments are you referring to?

A: We referred to the IP survey. We modified the sentence to be clearer: "During the time IP survey, the local groundwater level was measured in two piezometers."

Lines 184-185: I cannot follow the significance of the averaging described here

A: The precision of the final spectrum is increased by increasing the number of spectrums measured per sample as it reduces noise inherent in each individual spectrum. For the instrument used here (Bruker, Vector 22 FTIR spectrometer) it is standard measurement practice to average 32 spectrums for organic rich samples (see Biester et al, 2014; Broder et al, 2012; Moore et al, 2019)

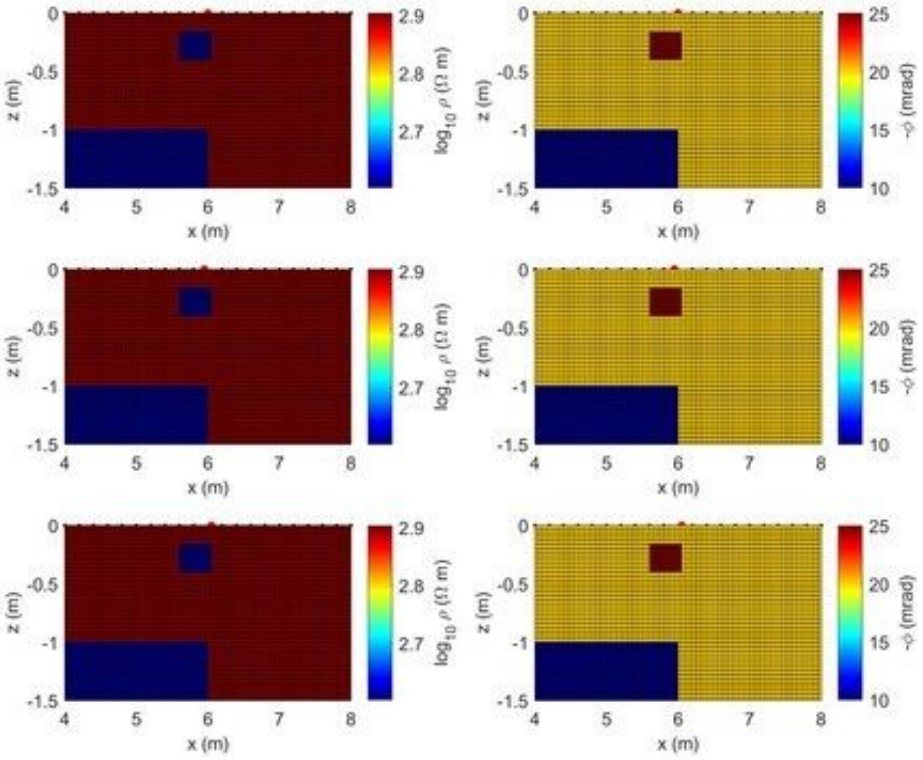
Line 210: check formatting of prime symbols on conductivity terms – currently strange

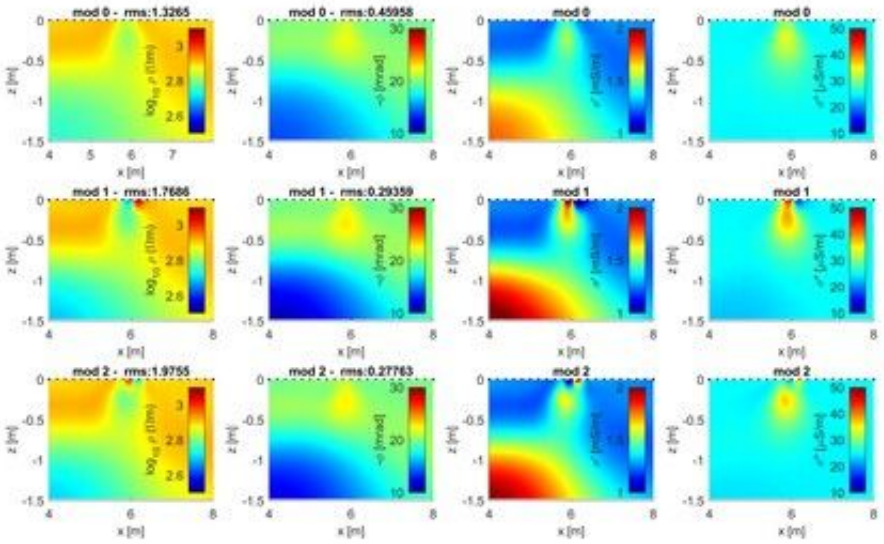
A: We modified the format in the manuscript.

Line 218: The 20 cm electrode spacing ss very hard to get right in the field conditions like those shown. What were the positioning errors and how were they incorporated into the processing?

A: We conducted careful protocol and used three measuring tapes to ensure good positioning. The electrodes were placed along with the fourth measuring tape. We estimate a maximum error of ca. 2 cm. However, we did not incorporate these errors into the processing. To address the Reviewer's concern, we present a numerical analysis to quantify deviations in the parameters using a numerical example where an electrode's position has been misplaced. We built a two-layer model reflecting our field conditions with a polarizable anomaly. Forward modeling was conducted with a regular separation between electrodes of 20 cm (mod0), followed by experiments where an electrode above the anomaly is misplaced 5cm to the left (mod1) and then 5 cm to the right (mod2) of the correct position, as seen in the attached figure. This 25% error influences

the real conductivity resolved for the polarizable anomaly (deviations in the inverted parameters are 6% and 4% by misplacing the electrode left and right of the real position), and the imaginary component of the conductivity (deviation, 9% and 6%). Simultaneously, electrodes' misplacing shows much less effect on the phase values (deviation, 3% and 2%) since the phase value is less sensitive to the geometric factor. Hence, it would support our interpretation mainly based on the phase images instead of the real and imaginary conductivity. We can present this analysis in the paper; however, we are afraid it would extend the manuscript and not engage the biogeoscience community.





Line 248 and Fig. 4: Line 248 refers to a normalized resistance but caption of Figure 4 suggests Fig 4c. is plotted as absolute resistance difference. Clarify.

A: We plotted the pseudosection of the normal and reciprocal measurement and the belonging misfit. However, we understand this may be misleading and we changed the figure to present the normalized value in Fig. 4c.

Line 264: b is shown as a percentage value but previously defined as a relative error (as needed for the equation

A: We have corrected our manuscript following the suggestion of the Reviewer.

Line 265: Why choose this value for cumulative sensitivity? No justification given.

A: The smallest sensitivity value resolved after the inversion is $10^{-3.6}$; with the value $10^{-2.75}$, we cut the 10% of the imaging results. We believe that using a threshold value of 10^{-3} (for instance, as suggested in Flores Orozco et al., 2013) would not justify the narrow dynamic in the sensitivity data. Weigand et al. (2017) recommend the threshold value 10^{-4}. We wanted to reach the 1.5 m as the depth of investigation, and blanking the parameters close to the boundaries, and empirically chose the value $10^{-2.75}$.

Line 281: You don't have a deep unit – maybe a 'deeper' or 'relatively deep' unit

A: We modified the text to the following: "and (iii) a "deep" unit corresponding to the granite" (see below)

Line 284: Is the porosity of the granite known or simply inferred?

A: It is not known. We inferred.

Line 288: I don't see the correspondence between the electrical imaging and the contact with the bedrock that is being inferred here

A: First of all, we realized a typo error in line 287, the contact represented by the dashed line in Fig. 6 and not the Fig. 5. The imaginary conductivity has the lowest values (below 40 µS/m) which we associated to the granite bedrock, while the peat has usually higher imaginary conductivity value (above 40 µS/m). However, the phase values resolve the granite bedrock more clearly (in our opinion). We understand the Reviewer's concern, that the border measured with the manual method and the imaging result does not give a 100% match, especially in the in-phase conductivity. Thus we modified this section.

"Figure 6 shows the imaging results of the N-S oriented profiles By 25, By 46, and the W-E oriented profile By 68 expressed in terms of the real- (σ') and imaginary (σ'') part of the complex conductivity. These images reveal three main electrical units: (i) a shallow unit in the top 10-20 cm bgs related to high σ' (>5 mSm-1) and high σ" (>80 µSm-1) values, (ii) an intermediate unit with moderate to low σ' (<5 mSm-1) and moderate σ" (40– 80 µSm-1) values, and (iii) a "deep" unit corresponding to the granite associated to the lowest σ" (<40 µSm-1) values. The second and third unit contact was measured using the metal rod (represented by the dashed line in Fig. 6). Figure 6 shows that the imaginary conductivity is sensitive to variations in the depth to the bedrock - even in areas where it is located deeper than 1 m bgs."

Lines 292-293: I don't really see this evidence for higher polarization values in the

northern part of the profiles relative to the southern parts

A: We understand the comment from the Reviewer. The variations are more evident in Figures 8b and 8h. Figure 6 shows in general higher polarization response in the northern part than the southern part although, the difference is slight. Nonetheless, we agree with the Reviewer and removed this statement.

Line 296: Why 'roughly'? At the small phase angles you measure it is almost exact – any differences are well below your measurement resolution.

A: We have corrected our manuscript following the suggestion of the Reviewer.

"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."

Line 305: What do you mean 'with higher resolution' here? Why would the phase images be higher resolution? This is unlikely given the relative errors in phase measurements relative to electrical conductivity measurements.

A: We agree with the Reviewer. We modified "higher resolution" to "higher contrast".

Line 331: what is meant by 'high electrical response'?

A: We changed the wording to more accurate expression: "high electrical conductivity values (σ'>7 mSm^{-1} and σ">100 μSm^{-1}) and phase (□ >17 mrad) values."

Line 336-337: Maybe. But could it simply be that some other common property influences both vegetation pattern and IP signal

A: Vegetation has been used in non-geophysical manuscripts to investigate biogeochemical hot-spots (e.g., Kleinebecker et al., 2008). We believe that such reference may provide independent validation to our interpretation of the IP imaging results. However, we do not imply that vegetation is related to polarization. We understand our wording is misleading and will be corrected to make this clearer. If the Reviewer recommends it, we can remove the reference to the vegetation, as this is only an independent validation but not the scope of the manuscript.

Lines 372-373: sentence is not correct as there are no phosphate results for S3

A: We agree with the Reviewer, we did not specify the phosphate to S1. We corrected our manuscript.

Lines 374-381: I don't follow the argument that what is written here means that high phase values can be interpreted as biogeochemical hotspots

A: The in-phase and quadrature conductivity show a high correlation with the DOC and other chemical parameters likely as both are sensitive (σ" is indirect) to

the chemical composition of the electrolyte (e.g., Lesmes and Frye, 2001). Accordingly, the phase is less dependent on fluid conductivity and shows the lowest correlation to the geochemical parameters measured in water samples. However, in general, the hotspots found in S1 and S3 still show higher phase values; while S2 indicates an inactive biogeochemical zone corresponding to low phase values. Therefore we interpret that high phase values as highly active areas. We updated our figures and created a new figure to prove (shown above) our findings.

Line 390: previously you refer to upper 10 cm

A: Indeed. We corrected to 10 cm.

Lines 409-411: Need to modify sentence as no phosphate levels for S3

A: We corrected the manuscript, this was a typo error.

Line 434: What do you mean by IP response here? Phase? Imaginary conductivity?

A: We modified it to imaginary conductivity. However, the phase values at S2 show similar behavior.

Line 458: What about the solid phase iron?

A: We discuss the solid phase iron under the section 4.3. The iron in the solid phase seems to be forming iron oxide complexes, which is most probably not polarizing (e.g., Abdel Aal et al., 2014, Atekwana et al., 2016).

Lines 468-482: This material belongs in the Introduction/Background to IP rather than in the Discussion

A: We think this material is necessary to be introduced in the Discussion. However, we understand the concern and changed our structure according to the suggestion.

Lines 527-528: Not necessarily the case for iron minerals. Point of zero charge for iron is around 8

Our original statement was about EDL polarization and not electrode polarization (or the polarization of other metallic minerals) and thus excludes the case of iron minerals. Furthermore, the point of zero charge for peat material is below the pH4 (e.g., Bakatula et al., 2018).

Line 534-535: Published work supports that in silica-dominated systems pH influence is indeed small

A: Our results, similar to (Slater et al., 2005), show that the pH has an insignificant influence on the measured IP. However, the point of zero charges of the peat is below 4 (e.g., Bakatula et al., 2018), the point of zero charges of the iron (-oxide) is around 8 (Stumm and Morgan, 1996). The measured pH in our case is between 4.5 and 5.8, this means the OM is charged negatively, and the iron oxide is charged positively. The pH at the S2-non hotspot is above 5. Although the pH is ideal for the DOC at the S1 and S3 top 20 cm to bond with the solid phase's iron (Vindedahl et al., 2016).

Lines 550-551. This makes no sense to me – the DOC correlation is stronger with the real

part of the conductivity.

A: The in-phase conductivity is usually high at the near-surface and decreases with depth. The real part of the conductivity indeed correlates the most to the DOC. Because the in-phase conductivity decreases with the highest rate with depth. However, as Fig. 9 shows, the in-phase conductivity curve at S1 and S2 show almost no difference although, DOC concentration is way higher at S1 than at S2. If we take a closer look, the chemistry shows a little higher activity at the surface, even at the less active areas, and the chloride content is generally higher at the surface (Fig. 9), which influences the pore water conductivity and thus, the in-phase conductivity.

Line 570-571: Is a layer really a hotspot? It rather destroys the concept

A: We understand that our wording was misleading. We rewrote the conclusion, the hot spots are located within the top layer within the first 10 cm bgs. We add a new figure (shown above), where we delineate the exact locations of hot spots.

"Figure 12. shows that the electrical conductivity values are decreasing with the depth. However, we did not conduct exact measurements, based on our on-site observation, we assume that the peat in our experimental plot is almost fully saturated (fully saturated below the groundwater table, 8cm bgs), and the pore size is larger East-Southeast side of the experimental plot. Which would explain why both the real and imaginary conductivity is high at the West part of the experimental plot and why the real part of the conductivity is high, and imaginary conductivity is low East-Southeast side of the experimental plot. The phase can highlight the high imaginary conductivity values relative to the real part of the conductivity and show the biogeochemical hot spots."

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Tartrat, T., Revil, A., Abdulsamad, F., Ghorbani, A., Jougnot, D., Coperey, A., ... & de la Vaissiere, R. (2019). Induced polarization response of porous media with metallic particles—Part 10: Influence of desiccation. *Geophysics*, *84*(5), E357-E375.

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