SOIL Discuss., author comment AC1
https://doi.org/10.5194/soil-2020-98-AC1, 2021

Reply on RC1

Maximilian Kirsten et al.

Author comment on "Aluminous clay and pedogenic Fe oxides modulate aggregation and related carbon contents in soils of the humid tropics" by Maximilian Kirsten et al., SOIL Discuss., https://doi.org/10.5194/soil-2020-98-AC1, 2021

Dear Editorial Team,

Thank you very much for accepting our manuscript for open discussion. We found the comments and questions by referee #1 (Jean-Thomas Cornelis) very useful and suggest revisions of the manuscript accordingly. All of our responses are listed below.The line number in the question, comment or clarification request always refers to the submitted pdf file. The line information in our answer always refers to a futur revised version of the manuscript.

Response to the first general comments of referee 1.

Referee 1: "In my first very general comment, it seems that there is some overlap with the study published by the same first author Kirsten et al; 2021 "Iron oxides and aluminous clays selectively control soil carbon storage and stability in the humid tropics" Scientific reports , 11, 5076."

Our response: The overlap between both studies is intentional, because it based on the used approach to indentify the influence of aluminous clay (kaolinite, gibbsite) and pedogenic Fe oxides (goethite and hematite) on aggregate distribution and associated organic carbon (OC) storage and persistence. We used the same field sites (i.e. mineralogical combinations) as in Kirsten et al. (2021) who studied the influence of mineral-organic associations on OC storage and persistence. In contrast to this previous paper, we evaluated the effects of aluminous clay and pedogenic Fe oxides as the two most important constituents of the clay-sized fraction in weathered soils on aggregation and the consequences for OC persistence after land-use change.

Referee 1: "I recommend the authors to clarify how the results of aggregates are new and add novelty compared to Kirsten et al. 2021."

Our response: In our manuscript, we went far beyond studying the effects of clay content on aggregation. We disentangled the individual role of aluminous clay and pedogenic Fe oxides for determining aggregate size distribution and aggregate stability and the consequences for OC persistence after land-use change. In contrast, Kirsten et al. (2021) focused on mineral-organic associations and how they influence OC storage and persistence.

Referee 1: "I mean here it makes sense to clarify this point as much as possible as aggregate size fraction and OC distribution in these fractions is one of the main control on soil carbon storage and stability in soils. So it makes me thinking that the data of Kirsten et al. 2021 must be presented, treated and interpreted together with the present data about aggregation."

Our response: As both studies used the same field sites (i.e. mineralogical combinations), we refer as much as possible to the study of Kirsten et al. (2021) in order to avoid any unnecessary overlap whereas all necessary data were presented and used in the discussion. In the response to the next comment of referee 1 details are given where and what data have been used already published by Kirsten et al. (2021).

Referee 1: "In my opinion, it could be great to build your research question based on what you uncover in Kirsten 2021, because their results can be a solid foundation to this study. So summarizing and building on Kirsten 2021 in the introduction could serve to expose the novelty of the present study."

Our response: We partially used the data and findings made by Kirsten et al. (2021) and will add new sentences to the text: In the introduction (Lines 129–131), material and methods (Lines 189–191; 224), and discussion (Lines 547–551; 573–575) for preparing the fundament of the study and contribute to our discussion. We further tried to use other studies conducted in the humid tropics to highlight the partially contradicting results about the mechanistic understanding of the role of clay content (mineralogy) on aggregation and its contribution to OC storage and persistence under contrasting land uses. For further clarification of our research question, we will add the following sentences (Lines 149–152: "In the precursor study, we found a positive relationship between the storage of mineral-associated OC and the ratio of pedogenic Fe to aluminous clay under forest and cropland land use, suggesting that a larger share of Fe oxides is linked to larger OC storage and persistency against land-use change (Kirsten et al., 2021). In the present study, we test whether aggregation and its contribution to OC storage follow similar patterns, or are decoupled from the individual contribution main mineral constituents. In detail, our main research goal was to investigate the individual role of aluminous clay and pedogenic Fe oxides in contrasting combinations determining...").

Referee 1: "I also recommend to clarify the results interpretation without comparing the two ecosystems, especially because the co-variable inducing OM changes due to land use and management practices. I am saying the bottom line of the study is to compare the two ecosystems, but the current presentation of results and data interpretation make it a bit fuzzy, confusing."

Our response: The high variability in the effects of land-use changes on soil OC (e.g. Don et al., 2011) motivated us to study the controls of OC persistence to land-use changes. In the present manuscript, we aimed to improve knowledge about how the storage and persistence of OC in defined aggregate size fractions is affected by different combinations of aluminous clay and pedogenic Fe oxides and what the consequences are for OC persistence after land-use change from natural forest to cropland. Therefore, the comparison between the two land uses is an essential part of the entire study. However, we presented and discussed the results first for natural forests and second for the studied cropland sites, i.e. addressing effects of land-use change. That will be further improved (whenever possible) during the revision. With this approach, we are able to test whether aggregation and the related OC in aggregate size fractions stays constant under both land uses in the respective mineralogical combination – an important indication of OC persistence. For example, when the mean weight diameter and OC storage in aggregate size fractions within a given mineralogical combination remains similar under both forest and cropland, this would indicate that this specific mineralogical condition favors aggregate stability and OC persistence. On the other hand, once the mean weight diameter and OC storage in aggregate size fractions decline in a given mineralogical combination upon land-use change, this would rather suggest that aggregate integrity and OC persistence is less supported by the mineralogical condition.

Referee 1: "I know the sites and sampling, and some of the methodologies are already presented in Kirsten et al. 2021, but given the topic of the submitted study I strongly recommend the authors to make the site selection and soil sampling crystal clear to help the readers to understand how environmental factors are similar between the studied sites under forest (how is your vegetation homogenous) and croplands (especially here for agricultural practices)."

Our response: We agree with referee 1 that providing more information about site selection would be beneficial for the reader. We will add additional information to the material and method section to (i) describe the selection of the study sites, (ii) illustrate that the forests have similar input of fresh organic matter input, and (iii) show the similar management practices at the different croplands (Lines 190–197: "The site selection was done based on total clay content determined in the field and the associated total Fe content measured with a portable XRF device (Kirsten et al., 2021). We did not observe systematic differences in vegetation composition of the forest sites and NMR spectra showed a similar composition of litter for each of the two land uses investigated (Kirsten et al., 2021). Furthermore, several visits in the study region over the last decade (2012, 2013, 2015, and 2018) combined with personal communications with farmers and local partners working in the region, enabled us to select cropland sites with similar agricultural management (cultivation of cassava (Manihot esculenta), hand hoe tillage, biomass burning before seed bed preparation).").

Answers to detailed comments of referee 1

- **Abstract:**

Referee 1: "Line 27: could you please clarify what you mean by "positive feedbacks on soil carbon storage"."

Our response: We intended to emphasize the positive effect of aggregation on soil OC storage. We will change "feedbacks" into "effects" (Line 27).

Referee 1: "Line 30: would it make sense to use either "aluminous clays" or "aluminosilicates" for the sake of clarity? I would prefer "aluminosilicates"."

Our response: Beside the dominant aluminosilicate kaolinite ($Al_2Si_2O_5(OH)_4$), we also identified the hydroxide gibbsite (☐-Al(OH)3) in the clay fractions of the study soils (Kirsten et al., 2021). This is the reason why we summarized both mineral constituents under the term "aluminous clay" and would like to keep with this denomination. We will also correct a mistake in Line 30 ("as both secondary aluminosilicates and Fe oxides…" into "as aluminosilicates, aluminum hydroxides, and Fe oxides…"

Referee 1: "(Line 37 should be clarify, a bit wordy) ☐ and Lines 38–41: I recommend to reword this sentence as this is not clear why you oppose formation of large macroaggregates and promoted OC storage and persistence."

Our response: We will clarify our statement in Lines 37–38: "Patterns in soil aggregation were rather similar across the different mineralogical combinations (high level of macroaggregation and high aggregate stability)." Furthermore, we will add in Lines 38–39: "Nevertheless, we found some statistically significant effects of aluminous clay and pedogenic Fe oxides on aggregation and OC storage." The proposed reformulation and expansion of the abstract will lead more clearly to the following sentences, in which we explain why we assume that the mineral properties control the aggregation and storage of OC, but that the two processes (aggregation and OC storage) were not closely related to each other. Therefore, we would like to keep these important findings in the abstract and also clearly announce the threshold values to distinguish between the selected mineralogical combinations.

Referee 1: "Line 42: "low clay-high Fe" does not ease the reading. I would suggest to present it another way to read smoother"

Our response: We agree to the comment of referee 1, in order to improve readability. Therefore, we will not use these acronyms in the abstract. Furthermore, we will rephrase the sentence (Lines 43–45: "The combination with low aluminous clay and high pedogenic Fe contents displayed the highest OC persistence, despite conversion of forest to cropland caused substantial disaggregation.")

Referee 1: "Line 36: a bit awkward as mineral-organic interactions are part of the aggregation. How can you oppose them?"

Our response: We assume that the referee means Lines 45–48. We agree with the statement that mineral-organic associations are part of aggregates (building blocks) as shown e.g. by Totsche et al. (2018). Although mineral-organic associations are part of the various aggregate fractions, an additional part of (particulate) OC is also occluded within the aggregates potentially contributing to OC storage, which could be considered as an indirect effect of mineral-organic associations. With our last sentence, we want to emphasize that aggregation is less important for OC persistence in comparison to the more direct effects of mineral-organic associations. Therefore, we would like to stay with this sentence.

- ***Introduction:***

Referee 1: "Line 61: I suggest to change "reacting" by "associating"

Our response: We would be happy to keep "reacting" because that word should express the more active role of the charges for these interactions to form an association.

Referee 1: "Line 64–65: reading this sentence makes me thinking – how does it make sense to think aggregation processes in soils could be associated with one unique mineral phase? As long as soil is multiphase, it seems pretty reasonable to assume aggregation is explained by interactions between various phases. While I fully understand the need to better understand how proportion between minerals play a role in aggregation. Maybe, the sentence here needs to be rephrased."

Our response: We agree with the statement of referee 1. We will rephrase the sentences as follows (Lines 84–87): "Aggregation might be ascribed to inorganic or organic cementing agents with no consensus about the relevance of each individual agent. Understanding the effects of individual cementing agents for aggregation is needed to disentangle their potential contribution to soil aggregation.". Additionally, we already described various influencing factors on aggregation (Lines 87–111).

Referee 1: "Lines 83–86: In addition could you please clarify how you isolate the OM content and quality between your sites? This is neat the idea to choose sites with identical mineralogical context. But OM quantity and quality play also a role in aggregation, so that it could make sense to explain whether this variable is also similar between studied sites."

Our response: We analyzed the OC contents of each aggregate size fraction and bulk soil by high temperature combustion at 950°C and thermo-conductivity detection (Vario EL III/Elementar, Heraeus, Langenselbold, Germany). Furthermore, we applied 13C-NMR spectroscopy to test the composition of OM along the mineralogical combinations (Kirsten et al., 2021). We considered the quantity of OC mainly as consequence of the various mineralogical combinations as well as land-use, as OC associated with minerals often was the most prevalent carbon form in the study soils (Kirsten et al., 2021). Furthermore, reactive minerals are well-known "filters" that can preferentially retain high-affinity OM components while others, less sorptive ones are excluded from sorption (sorptive fractionation). Consequently, the contents and composition of OM in mineral-organic associations, especially in topsoils as in this study, can be very similar despite of pronounced differences in aboveground litter quality (Mikutta et al., 2019). The composition of litter varied to a certain extent as indicated by the NMR spectra but, as mentioned before, we did not consider these differences in litter composition as decisive control of OM accumulation and stabilization (cf. Schmidt et al., 2011; Lehmann and Kleber, 2015).

Referee 1: "Line 92: need to precise here what you mean by "to which extent aluminous clay and pedogenic Fe oxides" do you mean, the proportion? The type of oxides and aluminosilicates?"

Our response: We refer to the amount (g kg-1 soil) of aluminous clay (kaolinite + gibbsite) or pedogenic Fe oxides (goethite + hematite) as proxies for the two mineralogical categories. To enhance clarity, we will rephrase the sentence (Lines: 125–127: "We are currently not aware of any studies that solve the puzzle of the extent to which the amount of aluminous clay and pedogenic Fe oxides controls soil aggregation and OC storage in highly weathered soils of the humid tropics.").

- ***Material and methods:***

Referee 1: "Line 141: I am aware fractionation methods are time consuming but could the authors explain why they do not investigate aggregate size under 250µm and also why the authors do not measure oxalate-extractable and DCB-extractable Fe and Al in each fractions, so that to be able to have direct relationships between type of mineral in aggregate fraction and its contribution to the OC pool."

Our response: With our study we aim at focusing on larger aggregate fractions because land-use change has a particularly strong impact on macroaggregates (John et al., 2005; Lobe et al., 2011; Maltoni et al., 2017). Thus, if the mineralogical composition has a distinct impact, it should be most pronounced for macroaggregates. We are not aware of any study that investigated into the distribution of individual mineral phases in aggregates > 0.25 mm compared to the bulk soil. As this would have been an extremely laborious task, we saved the resources to measure the dithionite-citrate-bicarbonate extractable-Fe and the aluminous clay for each individual aggregate fraction. However, this might provide valuable information in future studies.

Referee 1: "Regarding the specific extraction, it is not clear how the authors can relate aluminous minerals to oxalate-extractable Al which is very specific to short-range ordered minerals. Authors refer to Kirsten et al. 2021 for the method to determine aluminous clay based on DCB extraction and textural analysis. It could help to summarize here how they proceed, especially because all interpretations in the paper depend on this quantification."

Our response: We agree with referee 1 that ammonium-oxalate extractable Al is representative for short-ranged ordered Al minerals. We set this into relation with our total Al element contents determined by XRF (Kirsten et al., 2021) in order to demonstrate that nearly all Al-bearing mineral phases are crystalline ones and relate to residual primary minerals from the parent material, kaolinite and gibbsite. To clarify on that, we will provide the reader with a thorough understanding of the methodology used to distinguish between the four selected mineralogical combinations (Lines 218–224: "Briefly, 5–6 g soil pre-treated with 30% H_2O_2 were extracted with 30 g sodium dithionite ($Na_2S_2O_4$) and 1.35 L buffer solution (0.27 M trisodium citrate dihydrate ($C_6H_5Na_3O_7 \bullet 2H_2O$) + 0.11 M sodium bicarbonate ($NaHCO_3$)) at 75°C in a water bath for 15 min (Mehra and Jackson, 1958). The Fe concentration of the extracts were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a CIROS-CCD instrument (Spectro, Kleve, Germany). The residues of the extraction were then subjected to a texture analysis using the pipette method (Gee and Bauder, 1986).").

Referee 1: "I recommend this paper to be self-sufficient concerning the description of site location. As authors are dealing with aggregate processes, it is crucial to ensure all soil characteristics are strictly identical sites, except of course for the gradient in Fe and Al phases content. It could be helpful also to get some words explaining a bit what is behind the scene with regard to the mineralogical changes. What is the soil-forming processes and factors responsible for these changes?"

Our response: As already proposed we will add more information on the study site (including agricultural management) and the applied analyses in addition to the reference of Kirsten et al. (2021). We can only speculate about the reasons for the observed differences in the amounts of aluminous clay and pedogenic Fe oxides. Possible explanations include slight spatial variations in bedrock materials (mafic biotite-hornblende-garnet gneiss in the whole area) and/or variable weathering/desilification rates and/or variable extents of soil erosion and/or different stages of clay translocation. Desilification can lead to a relative enrichment of pedogenic Fe oxides compared to aluminous minerals such as kaolinite. The "good" soil structure along the mineralogical combinations promotes downward translocation of clay/dissolved ions with soil water into deeper soil horizons. We found clear indication for clay illuviation into deeper soil horizons (cf. Kirsten et al., 2019). This process could also be selective for certain mineral fractions, because of the pH-dependent charge characteristics of dominating clay-sized mineral phases (Kleber et al., 2015). Each of these processes might have contributed to observed variations in aluminous clay and F oxide contents.

- **Results:**

Referee 1: "Line 250: which one takes over – mineralogical combination or land use?"

Our response: Our data clearly show that both factors have a combined impact on aggregate distribution. Nonetheless, mineralogical composition is the underlying determinant controlling aggregate distribution. As stated in Lines 373–375: "The conversion from forest to cropland either decreased MWD, as particularly observed for the low clay–high Fe combination, or had no effect (low clay–low Fe)."

Referee 1: "Lines 269–271: ok it makes sense, I am just wondering how agricultural practices can affect aggregate stability compared to less managed forest ecosystem. This is pretty well documented and in your study I am wondering if Fe and Al phases can take over land use management when studying parameters such as aggregate stability. I am thus wondering if it makes sense to compare the two ecosystems. What do you think about interpreting the controls of mineral phases on aggregated inside each ecosystems without venturing into comparison between ecosystems."

Our response: Please, refer to our previous comment (response to comment 5). As described above, we have tried to always choose the same order of presentation of results and discussion. We found distinct effects of certain mineralogical combinations (e.g. low aluminous clay and high pedogenic Fe) on aggregate distribution independent from land use as well as significant but very small differences for aggregate stability between land uses, i.e. land use effects. Consequently, we want to keep both aspects for interpretation of our results.

Referee 1: "Line 286: how can you directly associate a variation in soil OC content to mineral constituents as land use and management practices can significantly affect OC. Again I would separately present the results for the two ecosystems, forest and cropland."

Our response: As explained in previous comments, our study was conducted in an area with very similar natural conditions except the contents the soils' contents in aluminous clay and pedogenic oxides. Our approach is based on the reasonable assumption of similar agricultural managements at all study sites, rendering agricultural management no decisive factor to explain variations in soil OC among arable soils. Nevertheless, OC contents were quite variable in the forest soils, potentially reflecting local variations in vegetation and soil moisture. Despite of this variability, aluminous clay and pedogenic Fe oxides explained a large variability of soil OC (Kirsten et al., 2021), confirming observations in the literature (Barthès et al., 2008; Coward et al., 2017; Lawrence et al., 2015). We totally agree that land-use change has an effect on OC and we related the extent of this effect to differences in aggregation for each mineralogical setting (defined by aluminous clay and Fe oxide contents). Nevertheless, we show important results for each individual land use and in direct comparison, so that the reader gets a comprehensive overview.

Referee 1: "Line 295: linked to my previous comment (Line 286) it is pretty confusing to read that ">4mm aggregates this was significantly modified by the mineralogical combination" while OC input and quality (together with the way OM is processed in these two highly contrasting ecosystems) can also play a key role."

Our response: Please see the replies to the comments above. Here, we refer to the OC loss within this particular aggregate size fraction by conversion of forests into croplands, which depends, directly or indirectly, on aluminous clay and pedogenic Fe oxide contents.

- **Discussion and Conclusions:**

Referee 1: "Line 326: what do you mean by "did not result in entirely different""

Our response: With this introductory sentence, we would like to emphasize that all soils were well aggregated and had a high aggregate stability. The observed statistically significant differences were rather small despite a large variation in the combination of aluminous clay and pedogenic Fe oxides. We will modify this sentence accordingly (Lines: 460–462). "Our data demonstrates relatively small differences in aggregation among the generally well-aggregated study soils, being characterized by high aggregate stability despite of large variations in aluminous clay (factor three) and pedogenic Fe (factor five) contents."

Referee 1: "Line 333–335: ok, it is the observation you did concerning your results, but how can you explain soils need a mineral phase take over the other one to promote aggregation. I am curious to learn a bit more here, maybe with the help of the state-of-the-art knowledge already published in this research field?"

Our response: We agree with referee 1, but we can only speculate based on published literature. We will add additional information to the main text (Lines: 482–493: "We assume that the positive effect of increasing aluminous clay content on the aggregate mass > 4 mm is related to the hybrid electrostatic properties of kaolinite on edges (variable) and surfaces (permanent negative), which enable the formation of characteristic cards-house structures (Qafoku and Sumner, 2002). In addition to this increase in aggregation caused by the dominance in kaolinitic properties (i.e. high clay–low Fe), we also expect that, similar to the study by Dultz et al. (2019), there are mixing ratios between aluminous clay and pedogenic Fe minerals, which lead to improved aggregation (greater MWD; i.e. low clay–high Fe). This effect is probably explained by changes in the electrostatic properties of the mineralogical combinations, as was shown in the study by Hou et al. (2007) for kaolinite in different relative combinations with goethite and hematite. Nevertheless, aluminous clay is the decisive control for macroaggregation in these weathered tropical soils, confirming the often described promoting effect of increasing clay content on aggregation (Feller and Beare, 1997). Furthermore,...").

Referee 1: "Line 341: I am definitely uncomfortable with the study of land use effect on aggregate distribution through the lens of mineralogical variations. I think on top of mineralogical differences, the land use and management practice explain all the differences with regard to aggregate and OC distribution between forest and cropland."

Our response: As we discussed above, land use and management certainly have an impact on soil OC and the level of aggregation. But the magnitude of this effect − and this is what we emphasize – is modulated by the quantitative abundance of mineral constituents. Therefore, we think there is no real discrepancy in our views.

Referee 1: "Line 348: to be able to say that higher Fed/Al ratio control aggregate formation, I think you have to ensure there is no other effect concerning agricultural practices. I mean here: how are you sure that tillage, crop rotation, cover crops… are identical between your studied croplands?"

Our response: As mentioned above, we paid the utmost attention to sample cropland sites with similar tillage, cultivated crops, and a similar procedure regarding the management of crop residues. That does not mean that all of the single management operations were identical but at least they are similar − the best approximation which is feasible under field conditions.

Referee 1: "Line 385–386: it is part of the introduction, and what you are presenting from Kirsten could help to introduce your research question by presenting it in the introduction, in order to streamline the presentation of your objectives, and their novelties compared to Kirsten 2021."

Our response: We would prefer to keep this introduction into the new section of the discussion, which in our opinion eases the understanding for the readership. As stated above, we will expand the introduction by our previously published results (Kirsten et al., 2021) to better justify the objectives of this study.

Referee 1: "Line 398: taking into account land use changes as an explaining variable, compared to mineralogical changes is a bit "adventurous"."

Our response: With our data we show that land-use change has a distinct impact on OC storage, but the extent is significantly modulated by the selected mineralogical combinations.

Referee 1: "Lines 433–434: I agree but I think it could make better sense to only study the effect of mineralogical changes for each ecosystems, separately. It will help the reader to better catch your message regarding the role of Fe/Al ratios on aggregation formation for either forest ecosystem or croplands."

Our response: As outlined above, we think that the differences between forest and cropland sites in terms of the effect of aluminous clay and pedogenic Fe oxides on aggregation and associated OC is a key point of this study.

Referee 1: "Lines 435–437: I am afraid I do not understand your last conclusion sentence. Need to be rephrased, IMO."

Our response: We agree with referee 1 and will rephrase the sentence (Lines 598–603: "Hence, we must reject our initial hypothesis that the mineralogical combination that results in the greatest aggregate stability best preserves OC during the conversion from forest to cropland. Thus, the formation of macroaggregates cannot be considered as a main stabilization process for OC in strongly weathered soils of the humid tropics. We suggest that the formation of mineral-organic associations as part of the aggregate size fractions is the most important process that preserves OC during land-use change in these soils.").