

First of all, we would like to thank the reviewer for meticulously reading our article and making constructive suggestions and corrections, which helped to substantially improve the manuscript. We have responded to all comments individually.

The manuscript presents results on the extraction of metals, Si, and C from (sub) tropical soils with frequently used methods. I agree that the (sub) tropical soils under study have not intensively investigated yet so the authors aimed to fill a gap in knowledge. However, there are some major issues that must be clarified prior to potential publication.

My main concerns relate to definitions, lab procedures and data interpretation.

Several times, the authors mentioned “Fe/Al oxides” without defining this phrase. Do they mean the sum of individual Fe and Al oxides? Or do they mean mixed oxides, which contain both Fe and Al so that the “pure” Fe and Al oxides, respectively, are not included? Clarification is necessary, as it determines the interpretation of extraction data.

Response: The term Fe/Al oxides throughout the paper represent oxides, oxyhydroxides, and hydrated oxides of Fe and Al; this is indicated in the manuscript in Lines 62-64.

Several times (see below), the authors claimed that Al oxides are dissolved (extracted by) DCB. This is wrong and shown by many studies/reviews, which the authors even cited. On the other hand, sometimes the authors interpreted DCB extraction of Al oxides correctly. Again, clarification and uniform correct interpretation is necessary.

Response: Thank you for pointing this out and this has been corrected. Also, interpretations of the three extractants have been made clear in the revised Table 1.

Several times, the authors mentioned SRO and poorly crystalline minerals. Does it mean that they distinguished between SRO and poorly crystalline? If so, which minerals are SRO, but not poorly crystalline and vice versa?

Response: We did not experimentally distinguish between SRO and poorly crystalline minerals. However, technically these terms refer to slightly different phases, SRO represent minerals that have short-range three-dimensional order, while poorly crystalline may have similar or somewhat longer three-dimensional order but it is riddled with defects or disorders in the structure. Both of these forms and amorphous phase (i.e., where there is no three dimension order) are considered to be extracted by ammonium oxalate. In the manuscript, we mean to say that both poorly crystalline and SRO minerals are dissolved in the ammonium oxalate extraction.

The authors referred to Wagai et al. (2013), who suggested filtration of PP extracts with a 0.025 μm filter, but the authors used a 0.2 μm filter without explanation. Furthermore, they filtrated all extracts at 0.2 μm , except for DCB extracts, for which they applied a Whitman filter with approx. 2 μm pore size. Not only is the inconsistency of the filter pore size between the different extracts incomprehensible, but also that it does not exclude the presence of particulate species in the DCB extracts - dissolved species, and only those are at stake, are defined via a 0.45 μm filter. These are not the only examples where studies/reviews are cited but the statements in them are not considered.

Response: We have discussed this aspect in the paper (Lines 563-574). The adequacy of the 0.2 μm filter is explained on the basis acidic pH with moderate amount of Al in soils that acted as a flocculant. We believe the presence of Al, combined with the use of medium-speed centrifugation and micro-filtration mitigated the dispersion of colloidal materials in these soils. Furthermore, the

Fe_{pp} concentration data were consistent with the results obtained in other studies that used high-speed centrifugation and/or ultrafiltration (Schuppli et al., 1983; Loveland and Digby, 1984).

In the DCB procedure, dithionite is a strong reductant where all free Fe (III) oxides are reduced and the reduced Fe, i.e. Fe^{2+} , is then complexed with citrate, so there is no possibility of the presence of any fine particles of Fe phases in the extracted solution. The extractant is further added with saturated NaCl is used as a flocculant, followed by centrifugation ($3280 \times g$) and filtration (Whatman 42 filter paper). So, it is not the case of consistency, but the chemical procedure and targeted phases are important in the procedure used.

More specifically and minor concerns:

- line 41: "Soil OC carbon" Please correct. And SOM would be correct here, not SOC, which is in most cases only a measurand.

Response: Thank you and we have amended the text to make the correction throughout the manuscript.

- line 48: Similarly, SOM is associated with minerals, not SOM. Please check and correct the entire manuscript accordingly.

Response: Yes, we agree, corrected.

- lines 61-63: "Iron and Al oxides [...] are formed in soils from the weathering and dissolution of primary minerals (Chadwick and Chorover, 2001)." Not exclusively, but Fe oxides also in redox cycles. This has been known before 2001.

Response: The broad statement was made in relation to both Fe and Al oxides, and redox cycles are encompassed in the weathering processes. However, we agree with the reviewer that redox cycles continue to remain an important in soils. We have added an additional sentence to emphasis this "Fe oxides in soils are strongly affected by redox processes and may undergo variable periods of immobilization and mobilization over quite short terms (Schwertmann, 1985)" in Lines 64 – 66 of the revised manuscript.

Schwertmann, U. 1985. The effect of pedogenic environments on iron oxide minerals. p. 171–200. In B.A. Stewart (ed.) Advances in soil science. 1. Springer-Verlag, New York, NY.

- lines 108-111: It is good to mention these studies on drawbacks of extraction procedures, but the findings in these studies must be considered in planning and conducting the study, and interpretation of the results. For instance, these studies show issues of phase separation, and selectivity and completeness of PP extraction, which were not considered.

Response: The aim of our study was not to develop or modify procedures, as these are routinely used in research and commercial laboratories. We wanted to evaluate the role of different metal(loid)s extracted using the routinely used procedures in retaining SOM in different stabilised phases.

- line 113: Extractions cannot estimate SOM stabilisation, as they do not provide an estimate of the deceleration of SOM decomposition; they can roughly estimate the contents of stabilising phases.

Response: We agree and correction has been made in Line 116 of the revised manuscript.

- lines 113-115: The extractions used here are unable to differentiate the SOM associated with Fe or Al oxides either.

Response: Thank you and we have included this in the sentence (Lines 112-113).

- line 121-122: “the important role of poorly crystalline Fe/Al oxides and/or short range order (SRO) Fe/Al oxides” here is even a combination of incomprehensible phrases; please check my previous comment. Also, as the extractions have no proper mineralogical meaning, correlations mentioned before between extracted amounts and SOC can only indicate but never prove the importance of certain groups of minerals. Correlation is not causation.

Response: We did not distinguish between SRO and poorly crystalline Fe/Al oxides. However, oxalate-extractable Fe and Al pool were used as measure of these phases. Also, we have reworded the text (Lines 119-132). Although, we agree with the reviewer that correlation is not causation but the role of Fe and Al oxides in the preservation of SOM have been demonstrated in many studies, which show the direct role of Fe/Al phases via the observation of chemical reactions and/or spectroscopic investigations (e.g., Rasmussen et al. 2006. *Glob. Change Biol.* 12, 834–847; Gu et al. 2002. *Environ. Sci. Technol.* 28, 38–46. Schneider et al. 2010. *Geochim. Cosmochim. Acta* 74, 1606–1619. Kirsten et al. 2021. *Sci Rep* 11, 5076). However, such discussion is beyond the scope of this paper and thus we have presented the most relevant discussion in the paper.

- line 124-125: DCB-extractable Fe alone is no measure of crystalline Fe, as mentioned in the cited references, but DCB releases Fe from SRO Fe oxides, too.

Response: We agree and sentence has been revised in Lines 129 - 132.

- line 127-128: When mentioning PP extraction here, it would be good to mention the known drawbacks.

Response: We have a detailed discussion on this in the relevant part of the manuscript (Lines 526 – 530; 563 – 569 and 657 - 661), in this section the detailed discussion on various extraction procedures including PP extraction, will distract the readers from the main theme of the study.

- line 136: The selectivity of PP extraction is unknown, and some of the studies cited before indicate poor selectivity. This problematic issue is not discussed at all.

Response: We have an extensive discussion on the drawbacks and selectivity of various extracts in a latter section (Lines 526-530, 563-569 and 657-661).

- line 142: The most common methods are not necessarily the most suitable ones. Why not using citrate instead of the highly problematic PP? The studies/reviews the authors cited indicate its better suitability.

Response: We agree that perhaps citrate could have been an alternative to PP. However, PP continue to be used much more widely than citrate, and we wanted to use the extractants that are most widely used not only in research labs but also commercial labs in Australia. Pyrophosphate (at pH 10) has been considered as a good extractant for organic Fe and Al complexes and ‘active’ amorphous inorganic forms of Fe from soils (Bascomb, 1968; Loveland and Digby, 1984; Pansu and Gautheyrou, 2006).

- lines 151-155: The highest content does not prove the most important role in stabilisation. Stabilisation refers to processes that decelerate SOM decomposition. What if a less abundant compound decelerates SOM decomposition more effectively than the most abundant compound? There are no data on the decomposition/stabilisation rates given, and they cannot be derived from extraction data.

Response: We agree in principle with the reviewer, however, the role of SRO, crystalline and other phases of Fe/Al oxides in MAOM has been well demonstrated in many controlled and field studies, some examples cited earlier. Furthermore, we changed the word stabilisation to association in Lines 156 – 159.

- lines 160-161: I can understand the decision to sample the soils by depth intervals, but I am not convinced, according to the available information, that actually exclusively top- or subsoils were studied. The thickness of an A horizon may exceed 20 cm so that the deeper sample is mixed topsoil and subsoil, or it may be less than 20 cm so that the upper sample is a mixed sample. I cannot believe that the A horizon(s) was/were always exactly 20 cm thick.

Response: Yes, we agree with the reviewer about the thickness of the A horizon and that is why we have not used or specified soil horizons in the study. In the study, we used samples from two depths, and we have called these as topsoil (0 – 20 cm) and subsoil (20-40 cm).

- Table 1: Apart from the implied difference between SRO and poorly crystalline minerals, the information is missing that OX extracts metals from organic forms. DCB does not generally dissolve metal oxides, but only those with a reducible metal cation, thus not Al oxides. These aspects are mentioned in several of the cited studies. Is it necessary to use the phrase ‘free’ oxides (even already in quotation marks) without definition? The phrase has no real mineralogical meaning then.

Response: In the Table 1, we included only targeted phases. The other unintended phases that are extracted by various extractants are discussed in the paper in relevant sections. However, based on the reviewer’s suggestion, we have now revised the Table 1 and included the other phases that are extracted along with the intended phases.

Dithionite-based methods are used to quantify total “free” Fe oxides in soil (Loeppert and Inskeep 1996). Shang and Zelazny (2008) pointed out that the term ‘free Fe oxides’ is operationally defined, representing Fe extracted by dithionite-based methods. The ‘free’ Fe oxides refers to Fe in Fe oxides (i.e., oxides, oxyhydroxides, and hydrated oxides of Fe) and excluding Fe that present in primary minerals and phyllosilicates.

- lines 207-208: OX extracts metals from organic association, too (see my comments before). Schwertmann (1964) exclusively referred to poorly crystalline Fe oxides, not “SRO and poorly crystalline minerals” like the authors claimed.

Response: Agreed. The missing information “OX extracts metals from organic association” have been added to the revised manuscript. The references (Parfitt and Childs, 1988) that referred to poorly crystalline and SRO minerals have been used to replace Schwertmann 1964 the revised manuscript in Lines 213-215.

- lines 215-216: “Dithionite-citrate-bicarbonate extraction was used to extract pedogenic Fe and Al phases in soils (Mehra and Jackson, 1960).” No. See my comments before. The reference is from 1958.

Response: The statement is corrected. For the reference – the paper was presented at the **Seventh National Conference on Clays and Clay Conference in 1958** but the conference proceedings were published in 1960, so we would like to keep the reference as it is.

- lines 239-240: “Inorganic HH extraction targets SRO and/or amorphous Fe and Al oxides (Chao and Zhou, 1983; Ross et al., 1985).” None of the studies mentioned studied the dissolution of Al oxides. Thus, the suitability of the method is unknown.

Response: We have added an additional reference (Jackson et al., 1986) that includes Al extraction for this procedure in Line 248 of the revised manuscript.

Jackson, M.L., Lim, C.H. and Zelazny, L.W. (1986) Oxides, Hydroxides and Aluminosilicates. In: Klute, A., Ed., Methods of Soil Analysis, Part 1, Physical and Mineralogical Methods, 2nd Edition, Agronomy Monograph 9, ASA and SSSA, Madison, 101-150.

lines 406-407: OX-soluble Fe oxides are not necessarily non-crystalline. The authors even mentioned later in the text the dissolution of e.g., goethite. The whole text needs a very substantial revision regarding uniform interpretation of studies and findings derived from them. It is not only here that there are contradictions. It seems like piecemeal.

Response: Yes, we agree and we did not mean. We calculated the difference between the DCB extractable C minus OX extractable C to estimate the C associated only with well-crystalline forms of Fe oxides in soils.

- section 4.1: Please shorten. Everything is known, and the study using common, but partially not selective methods cannot provide new mechanistic findings.

Response: Agreed; The Section 4.1 has been substantially shortened in the revised manuscript.

- lines 519-521: It is not possible to estimate the extent of re-adsorption with the applied methods either.

Response: Agreed, and we have acknowledged this in the revised manuscript in lines 529 - 530.

- lines 524-525: “The DCB procedure is known to extract pedogenic or free Fe oxides (and Al substituted in the structure of goethite and hematite) as well as poorly crystalline and SRO Fe/Al oxides” The first part is correct regarding Al, the latter is not.

Response: We agree with the reviewer, that Al oxides are not dissolved by DCB. Correction have been made in the revised manuscript in lines 535 – 537 to read “The DCB procedure is known to extract pedogenic or free Fe oxides (and Al substituted in the structure of goethite and hematite) as well as poorly crystalline and SRO Fe oxides”

- line 533-535: “In the oxalate extraction procedure, Fe present in non-crystalline, poorly ordered and short-range ordered (such as ferrihydrite) was dissolved and a fraction in the organic complexes may also be dissolved.” Why was extraction of metals in organic complexes not mentioned and included in the interpretation before? Ferrihydrite is not poorly ordered?

Response: Thank you for spotting this out. We have included the dissolution of organic metal complexes in the revised Table 1. Ferrihydrite can be poorly ordered to SRO, for example, 2-line or 6-line ferrihydrite.

- lines 538-539: “The small ratio of $Fe_{OX}:Fe_{DCB}$, referred to as active Fe ratio, indicate the degree of crystallinity of Fe oxides in soils”. Another example of the selective interpretation of the entire literature: If OX does not only dissolve oxide Fe (lines 533-535), it is not necessarily a good indicator of oxide crystallinity.

Response: We disagree with the reviewer on this point; this is commonly used to estimate the proportion of Fe in poorly crystalline or SRO vs crystalline Fe oxides, in particular with reasonably weathered soils. Often with a good dataset, the ratio is often used for various useful measures, such as P adsorption capacity of soil. We have given few examples below: Siebers et al. (2024) Synergistic relationships between the age of soil organic matter, Fe speciation, and aggregate stability in an arable Luvisol. *J. Plant Nutr. Soil Sci.* 2024;187:77–88.

Rogeri et al. (2016). Substitution of Clay Content for P-Remaining as an Index of the Phosphorus Buffering Capacity for Soils of Rio Grande do Sul. *Rev Bras Cienc Solo.* 2016;40:e0140535.

Formeti et al. (2014) Mapping the physico-chemical properties of mineral dust in western Africa: mineralogical composition. *Atmos. Chem. Phys.*, 14, 10663–10686.

de Campos et al (2018) Degree of phosphate saturation in highly weathered tropical soils. <https://doi.org/10.1016/j.agwat.2018.05.001>;

X. Jiang, R. Bol, S. Willbold, H. Vereecken, and E. Klumpp (2015) Speciation and distribution of P associated with Fe and Al oxides in aggregate-sized fraction of an arable soil. *Biogeosciences Discuss.*, 12, 9879–9903, 2015.

Negri et al, (2024) Extreme water repellency and loss of aggregate stability in heat-affected soils around the globe: Driving factors and their relationships. *Catena* 244, 108257.

- lines 543-545: “The significant correlation between Fe_{DCB} and Fe_{OX} (Table 4), may be due to some overlap in the phases extracted by the two procedures” “Some overlap” may be between 0 and 100%. Anyway, this is known from several cited studies.

Response: We have made the assertion based on our results and cited several studies making the similar observation.

- lines 546-548: “In addition to SRO Fe oxides, oxalate is known to dissolve crystalline Fe oxides, such as magnetite, maghemite, lepidocrocite, and poorly crystalline and nano-crystalline goethite and hematite” exemplifies selective interpretation again and see my previous comment on lines 406-407.

Response: We have tried to discuss all possibilities here. By no means, we are saying that these minerals made any significant contribution to the extracted fraction.

- lines 549-551: “The close relationship between Fe_{DCB} and Fe_{OX} may also suggest that both Fe forms were function of similar pedogenic processes (Rezapour et al., 2015)” See my comments before, and this knowledge was gained long before 2015.

Response: We have deleted this sentence.

- The entire section 4.2 is too extensive, only repeats existing knowledge, but does not apply this to one's own data in a critical discussion, particularly regarding PP extraction.

Response: This section is important discussion on the results obtained for extracted metals and various drawbacks of the methods; and it discuss all the points (e.g., Lines 127-128; Line 136) raised by the reviewer in the Introduction section.

- line 581: “Crystalline Al oxides are generally not dissolved during the DCB extraction” Correct, but several times the authors implied dissolution of Al oxides by DCB. Amorphous Al oxides are not dissolved by DCB either.

Response: We agree that crystalline Al oxides are not dissolved by DCB extraction, revised Table 1 makes this clear.

- section 4.3: The authors do not consider that desorption of anionic OM adsorbed on any mineral surface may be induced by the alkaline pH during PP extraction. The contribution of this fraction of the extracted SOM cannot be quantified so that it is not possible to attribute the SOM released during PP extraction to SOM formerly associated with metals. This is particularly important with the acidic soils under study.

Response: We compared the release of OC from PP at pH 10 and 7.5 for selective samples and did not find any difference. However, we can't discount the possibility of desorption of anionic groups OM; additional research may be needed on this aspect.

- lines 649-650: The large differences between Fe extracted by PP at pH 7.5 and pH 10 (factor of 2.88) clearly shows the inappropriateness of the method - what is the "correct" value for Fe in organic association? Or could this value be even higher? Or does it have to be assumed to be lower because, depending on the pH, non-targets are also dissolved?

Response: Yes, there was higher Fe extracted at pH 10 than pH 7.5, which may be due to the dissolution of Fe from phases other than Fe-organic complexes at higher pH. We believe the Fe in organic complexes was lower than we found, this part needs more work in the future.

- lines 688: “The C_{DCB} is expected to be C associated with secondary crystalline Fe oxides including SRO phases.” The pH of the DCB solution is 8 (Table 1) so that pH-induced desorption of SOM from an unknown variety of minerals surfaces occurs to unknown extent as mentioned before. DCB does not dissolve Al SRO phases completely.

Response: We tend to agree with the reviewer but there were limited minerals including Fe oxides were present in the studied soils.

- line 690: “Since DCB extracts both SRO and crystalline Fe and Al oxides” According to line 581 and several papers the authors cited, neither SRO nor crystalline Al oxides are extracted by DCB.

Response: This has been corrected in the revised manuscript (Lines 705 – 706).

- lines 692-694: The calculations do not make sense, as the SOM released during extractions cannot be attributed to certain groups of minerals because of the known drawbacks and the pH-induced SOM release mentioned before.

Response: The difference in OC extracted by the DCB and OX extracts was used as an approximate measure to evaluate the SOC association with crystalline Fe oxides; it is not an absolutely accurate measure of the contribution, but it is a reasonable measure considering the expected phases extracted by the two extractants. We agree it is likely to have some errors induced by solution pH; any chemical treatment is likely to produce some effects on the OM and mineral interactions.

- line 705: The incorporation of Al in goethite and hematite, substituting Fe, is mentioned here for the fourth time.

Response: Yes, relevant to the discussion here.

- section 4.4: Attributing metal:C ratios to mechanisms is very questionable given the known drawbacks of the methods used. For instance, pH-induced SOM release remains unknown, and so is the “correct” concentration of PP-extracted Fe and Al, depending on pH. The pH dependency of Fe and Al extraction by pyrophosphate is even reciprocal (Figure S3). In addition, the completeness of metal extraction by PP is unknown, as mentioned in cited studies.

Response: We have added some caution in Section 3.6 based on the reviewer’s plausible comments.

- section 5: The section does not provide conclusions, but a summary of the findings. At this point at the latest, the obvious problems with the application of the extractions should have been mentioned.

Response: We have made some minor changes in section 5.