Biogeosciences
Discussions

Interactive comment on "Iron-Bound Organic Carbon in Forest Soils: Quantification and Characterization" *by* Qian Zhao et al.

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Zhao et al investigated the role of iron oxides for organic carbon storage and preservation in north american forest soils. The study is based on chemical extractions and subsequent analysis of total iron and carbon. The different carbon fractions have than further been analysed for carbon isotopic as well as molecular composition. The study covers a number of different soils from various climatic regions, which is later considered in the discussion. Overall this is a nice study and the results provide good evidence for the emerging idea that iron minerals are one of many factors that govern organic matter preservation in soils. The study is well written, clearly organized and for the most part technically sound. The results are interesting to readers from soils sciences, biogeochemistry and partly for climate scientists working on soil-climate feedbacks. However, there a few minor and some major points that I like to see revised

before the paper can eventually be published.

Major remarks: 1) I did not check the references of Obrist et al to see how soils were sampled. However, since this is basic information for the present study I suggest that the sampling should briefly be described in the paper. For example, please explain if the different soil horizons were mixed to a composite sample. If not, which horizon was sampled and used in this study? In a spodosol, iron and organic matter are enriched in the deeper horizons, while being depleted in shallow ones. The chemical composition of both likely will be different in the different horizons, which will strongly affect the outcome of this study. 2) Unfortunately, the analytical section totally misses information on data quality. For the determinations of iron, nitrogen and carbon please add information on accuracy and precision. 3) I wonder if the chemical extractions influenced the molecular properties of the organic matter? Has this been tested by the authors? I suppose that it is possible for dithionite to change the properties oxidized functional groups. What about sulfurization of organic matter? Please provide a small discussion based on literature on the effect of reducing agents on organic matter and how that might possibly affect the results of the present study.

Minor remarks: Line 19. Having this number in the abstract somewhat skews the results of this study towards a higher importance of iron minerals than it really is. Fig. 1 gives a totally different picture. Maybe report median or range here.

Lines 90-91: Coarse material was not removed? What about roots?

Lines 119-121: Are manganese oxides also affected? Has Mn been measured in addition to Fe?

Lines 130-131: This is basically the ion exchangeable organic carbon. I probably missed it, but why was this done? Was the exchangeable organic carbon subtracted from the chemically extracted carbon? If not, please discuss why.

Line 151: Why was iron only determined at a single wavelength of 259.9 nm? Using

multiple wavelengths has the advantage of identifying interferences that might occur on one wavelength, which can than easily be corrected.

Lines 160-175 and 309-331: I am not an expert on NEXAFS and FTIR. I suggest the authors and the editor to refer to another reviewer with more expertise on these methods.

Line 180: Are numbers reported as one or two standard deviations of replicates? If so, how many (eg, n = 3)? Are this analytical or sampling replicates?

Lines 187-192: This part is speculative. Since not all soil types are covered the comparison might not hold up at the global level. For example, organic rich soils such as Histosols and Chernozems were not as much considered as they should be based on their global distribution. Further, since the North American distribution of soils differs from the global distribution in that Cambisols, Regosols and iron-rich chromic luvisols are underrepresented, this section should be removed.

Lines 202-205: Why was that a surprise? Was it one the main hypothesis of the study? If so, this might be stated in the introduction or methods. After all, shouldn't non-reactive iron store more organic carbon than reactive iron?

Line 214: How do you define "most of the"? It might be better to state "2/3 of the" or some equally (quantitative) phrase.

Lines 241-262: Climate actually controls the type of soil and the type of iron minerals directly through controlling the weathering of iron-bearing primary minerals and the formation of secondary iron-phases. So 6.6°C is probably the ideal condition for soil organic matter production and the formation OM-binding FeOOH minerals. I like to hear a statement by the authors on why "Fe-OC interactions may be particularly pronounced" at 6.6 °C. Can there really be a temperature control on this type of interaction? If so, please provide references for this.

Lines 252-254: This sentence is somewhat unclear. How does temperature increase

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the amount of iron bound organic matter (see comment above)? Please re-write.

Line 258: I did expect this as these are relatively "old" soils. The long aging process accumulates old and possibly recalcitrant organic matter along with very stable iron minerals….Also, aging results in more stable iron-organic matter associations as shown by Kaiser et al 2007 (doi:10.2136/sssaj2006.0189).

Lines 282-284: … and maybe the reduced chemical potential in small pores of clay-rich soils also limits microbial degradation of soils organic matter (Riedel & Weber 2016, doi:10.2136/sssaj2015.02.0085).

Lines 304-306: This short sentence is unclear. Please explain this 'concept model' in more detail.

Lines 347-349: A nice result. We have observed a similar effect using a complementary method (ultra-high resolution mass spectrometry) in a recent study (doi: 10.1016/j.orggeochem.2014.02.003). During a leaching test a soil column had turned anoxic and the reductive dissolution of iron- and manganese oxides lead to an increase in the abundance of aromatic compounds leaching from the soil columns. Besides polyphenolic compounds we also observed a release of iron-bound condensed aromatics leading me to belief that iron minerals probably play an important role in sequestering 'black carbon'-type compounds in soils. Do the NEXAFS or FTIR data of this study allow identification of this type of organic matter?

Lines 385 and 387. "O/N-rich". This is written like a ratio, but that is not meant here, right?

Lines 382-385. This probably indicates that the lipids are derived from microbial biomass which usually has a lighter isotopic value.

Lines 391-392: But it could also be vice versa. Suppose compounds with heavier isotopic composition preferentially sorb to iron.

Lines 392: Where was this "discussed previously"?

C4

Lines 403-404. A reference would be good here.

Table 1: I had a hard time understanding table 1, because I am not familiar with the American soil taxonomy. In order to make the paper more readable to a readership beyond North America it might be a good idea if the authors could change to the international FAO soil classification standard, if this is possible. After all the paper has been submitted to a journal run by the 'European' Geophysical Union. . .

Figure 3: What was the hypothesis behind the linear regression analysis of TOC vs latitude? Did the authors suspect a linear relationship? If so, please explain why.

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