SOIL Discuss.,
https://doi.org/10.5194/soil-2020-20-RC3, 2020

Interactive comment on "Iron oxides control sorption and mobilisation of iodine in a tropical rainforest catchment" *by* Laura Balzer et al.

Anonymous Referee #3

Received and published: 16 May 2020

This paper examines soil pools and hydrologic fluxes of iodine in a tropical forest, in conjunction with other measurements of soil and water chemistry. I concur with the authors' overall interpretation of the data, and I think that the data presented here are potentially useful for the biogeosciences / soil science community, as iodine remains an understudied element.

However, I have some significant concerns about details of data interpretation, specifically in the context of the soil extractions, but believe that these can be remedied in a revision. Specifically, the extractions used here cannot discern whether iodine was in fact directly associated with organic matter vs iron. The hydroxylamine extraction only reduces a fraction of the short-range-ordered Fe phases, a fact that is well established in the literature. To extract crystalline Fe, which is likely to be abundant in these soils as demonstrated by the high total Fe content of the subsoil, at least one (if not multiple) extractions with dithionite would be needed. Therefore, attribution of “residual” iodine following extraction by hydroxylamine to an organic-bound (as opposed to Fe-bound) iodine pool is erroneous. Second, even the iodine released by hydroxylamine may have been proximately bound by organic matter (as suggested by the authors themselves in the discussion). This needs to be made clear earlier in the paper.

Overall, interpretation of what these extractions mean needs to be more precise and cautious. However, the fact that most of the iodine was typically released in the hydroxylamine extraction is interesting and important and suggests that the iodine was associated with SRO Fe phases and/or organic matter bound with these phases. If the DOC content of the hydroxylamine extraction was measured, the authors could assess whether DOC was adsorbed or coprecipitated using the molar DOC/Fe ratios.

Second, the rationale for sampling the different soil profiles to different depths was not at all clear. Given that bedrock was not present, why were some profiles only sampled to very shallow depths? This complicates our interpretation of the data. It is difficult to interpret a depth profile of only two measurements in terms of transport/retention dynamics of an element. Some of the “A” horizons are clearly “O” horizons based on high concentrations of C.

Overall, the writing was not well-focused and often rambled. For example, the first two paragraphs of page 2 need clear topic sentences and organization to guide the reader through an argument. The rationale for studying I and Br together should be introduced, since these trends become a major part of the results.

In the introduction, it would be helpful to briefly describe the biogeochemistry of iodine in a bit more detail, because this is an uncommon topic in the literature. Some of these topics are addressed in the discussion. (e.g. differences in binding of iodine and bromine). For example, what are the major species of iodine in soil? What kinds of bonds do they form with SOM and the major mineral phases?

Specific comments: L17: “Stream water was sampled randomly over a period of five weeks”: this is haphazard, not random sampling I believe? P1 Introduction: discussion of the health impacts of iodine seems remotely linked to the focus of this paper; better to make this explicit or remove P2 L22: Avoid overgeneralizing about “tropical soils”. Note that almost all of the global soil orders (except Gellisols) can be found in the tropics. Clarify the scope of your study accordingly. P3: “(REF to the classification system)” – revise or delete Given your previous description, it seems as if this soil is really a Ferralsol? P4: Why did your sampling depth vary among soil pits (e.g. 0.5 m or 1 m) P5: The water sampling scheme is unclear. Did your sampling span both base flow and stormflow conditions? P6: Note that only a fraction of soil Fe phases are reduced with hydroxylamine. Dithionite is needed to reduce crystalline Fe. Furthermore, the hydroxylamine extraction will also extract iodine bound with organic matter, because Fe-associated organic matter is released. Therefore, the F5 fraction cannot be used to represent OM-bound iodine, as substantial iodine may remain associated with Fe (and other mineral) phases, and previous extractants (e.g. F4) likely included OM-bound iodine. See for example Coward et al. 2017 10.1016/j.geoderma.2017.07.026 Section 2.3.2: what kind of water was used for the leaching experiments? P8 L8: What kind of “temperate soils”, and how representative are these? Note the tremendous diversity in soil types and likely iodine input/output budgets among ecoystems. P9 L5: What “previous studies”? Present your data first. You need to cite specific literature if you want to compare. P9 L7: This organic C concentration is too high for a mineral A horizon. This indicates that an O (organic) horizon was sampled. P10: Note that the Fe-associated iodine is underestimated because your extractions did not release crystalline Fe phases, which likely dominated here (especially in the subsoil) Figure 4: It is concerning that three samples do not have any F5 fraction (difference between total and extracted iodine). In how many cases was this value negative (e.g. more iodine was extracted than in the total measured sample) P12 L1: Following the reasoning above, you cannot determine that F5 fraction iodine is associated with SOM. Revise. P14 L1-5: The occurrence of Fe reduction and DOC/nutrient mobilization in tropical soils has received significant recent attention, even (and especially) in systems with high rainfall and high infiltration rates. Iron reduction is widespread in these kinds of ecosystems. It would help to read and cite relevant literature here. P15 L6 “Moreover, the low mobility of iodine as DOC-I-Fe-oxide- complex was caused by the fact that Fe-oxides protect OM against degradation.” Note recent findings that challenge this notion; Fe/C/nutrient interactions can be dynamic.

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Discussion paper