SOIL Discuss.,
https://doi.org/10.5194/soil-2020-20-AC3, 2020
© Author(s) 2020. This work is distributed under
the Creative Commons Attribution 4.0 License.

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

Laura Balzer et al.

laura.balzer@tu-braunschweig.de

Received and published: 23 June 2020

We would like to thank reviewer 3 for the careful assessment of the manuscript and helpful suggestions to improve the quality of our work. Detailed responses to the comments of R3 are given below. The original comments by R3 are between quotation marks.

1. "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."

We agree with this comment. On page 13 Lines 14-16 we suggested that due to the high affinity of iodine binding to OM most of the iodine in the soil is likely bound to OM and the dissolution of Fe-oxides during step F4 released DOM-bound iodine to Fe-oxides similar as found by Li et al. (2013). Thus, the fraction of iodine bound to OM in deeper soil horizons was likely underestimated. (Page 13 Lines 14-16).

2. "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. "

We agree with this statement and will change this in the revised manuscript. The F5 step will be termed 'residual' including now OM and crystalline Fe-oxides. However, this does not change our main conclusion, that most of the iodine (including DOM-Iodine) was extracted during F4 with hydroxylamine and is associated to SRO Fe phases.

3. "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."

We will move this up in the revised manuscript for clarity.

4. "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."

We will include a more in-depth discussion of artifacts and misinterpretation of sequential extraction procedures in the revised manuscript. In principal, all sequential extraction procedures include (large) uncertainties arising from re-adsorption to the residue of the extraction step, cross-contamination, incomplete digestion, release of other iodine forms, volatilization or transformation of I, especially in a strong acid/base solution (Shimamoto et al., 2011; Hou et al., 2009). We have already mentioned that in the Manuscript 'In four out of twelve samples the determined sum of the iodine content extracted during F1-F4 were higher (1.4 %,5.8 %,47.7 % and 69.7 %) than the values of the total iodine content caused by cumulated uncertainties of consecutive extractions and inhomogeneity of the soil sample.' (Page 12 Lines 15-17) This probably means that Iodine dissolved during the first, second and third extractions may be re-adsorbed on the active phases/residues of F3 leading to an overestimating of iodine bound to iron oxides. However, from our data we can conclude that only a small amount of iodine is water leachable due to our low iodine concentration in the river water during base and stormflow conditions. Iodine extracted during F4 may also be reabsorbed on the remaining phase (organic matter), which would lead to an underestimation of F4. This would support our findings that most of the iodine is associated to Fe-oxides. As mentioned in the manuscript it is likely that due to the high affinity of iodine binding to OM most of the iodine in the soil is bound to OM and the dissolution of Fe-oxides during step F4 released DOM-bound iodine to Fe-oxides similar as found by Li et al. (2013). Thus, the fraction of iodine bound to OM in deeper soil horizons was likely underestimated. (Page 13 Lines 14-16). Despite all the uncertainties, most of the iodine was extracted during the hydroxylamine extraction suggesting that most of the iodine in our soils is associated to SRO Fe phases and/ or OM bound to it as also stated by the third reviewer. We also believe that the exact separation between Fe-oxide bound and organically bound iodine is not the essential point as these components never exist completely separated in soils. We try to show that the high retention of iodine through adsorption of DOM-iodine complexes to Fe-oxides is the major process of iodine enrichment in tropical soils and the resulting low iodine concentrations in adjacent

drainage systems. This is to our knowledge the novelty in this study. We will make this point clearer in the revised manuscript.

5. "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."

Unfortunately, we have not measured this to prevent instrument damage.

6. "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."

The study was conducted in a Biological Reserve in Costa Rica, which underlies stricter sample extraction regulations than national parks. Additionally, very steep slopes and heavy root penetration complicated the soil sampling. Therefore, it was unfortunately not possible to collect soil samples from greater depths. We agree that the depth profiles with only two data points are difficult to interpret and can only serve as an orientation. However, other hydrogeomorphological studies (e.g., Dehaspe et al., 2018) support the notion that only the upper soil horizons above 1m depth play a role in runoff generation that can be detected in the stream network based on biogeochemical tracers. Concerning the topsoil horizons with high C concentrations, we assume you are referring to profile L2 with 33.8 % carbon. Despite >30 % carbon, we decided to classify this horizon as an A horizon due to its low thickness (12 cm).

7. "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. "

We will improve focus in our writing as suggested.

8. “The rationale for studying I and Br together should be introduced, since these trends become a major part of the results. “

Will be changed in the revised manuscript.

9. “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?” We will include a more detailed description in the introduction of the revised manuscript.

10. “Specific comments: L17: “Stream water was sampled randomly over a period of five weeks”: this is haphazard, not random sampling I believe?”

The sampling took place every second day or even daily in four intervals each of three until five days covering base and storm flow conditions. The time of sampling was depending on the accessibility to the research station located in a pristine rainforest.

11. “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” We decided to remove this from the revised manuscript. 12. 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. Thank you for your comment on this, we agree that the term “tropical soils” should be specified. 13. “P3: “(REF to the classification system)” – revise or delete Given your previous description, it seems as if this soil is really a Ferralsol?” The classification of the soils is difficult due to the shallow sampling depths and limited analysis of the mineral phase. However, from field observations there was no dominance of hematite (also cf. Munsell soil colour), which is a common iron mineral in ferralsols. The soils were classified using the World

Reference Base for Soil Resources (IUSS Working Group WRB, 2015). We will include the reference.

14. “P4: Why did your sampling depth vary among soil pits (e.g. 0.5 m or 1 m)” Due to strict regulations in the biological reserve, steep slopes and heavy rooting, we decided to only sample two soil pits to 1 m and sample all other soil pits to 0.5 m.

15. “P5: The water sampling scheme is unclear. Did your sampling span both base flow and stormflow conditions?”

The streamwater sampling took place every second day or even daily in four intervals each of three till five days covering base and storm flow conditions. The time of sampling was depending on the accessibility to the research station in a pristine rainforest.

16. “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 OMbound iodine, as substantial iodine may remain associated with Fe (and other mineral) phases, and previous extractants (e.g. F4) likely included OMbound iodine. See for example Coward et al. 2017 10.1016/j.geoderma.2017.07.026”

See above

17. Section 2.3.2: what kind of water was used for the leaching experiments?

MilliQ Water (18.2 MΩ.cm).

18. “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.”

Above all, we wanted to point out the climatic and age effects between soils in tropical and temperate regions. High age and continuously high rainfall resulted in long term in-

tense chemical weathering of bedrock and soils, which lead to highly weathered acidic soils with high accumulation of Fe-Oxides. The weathering of primary minerals is the same process in temperate and tropical climates, differing only in its greater intensity in the tropics.

Here a short list of some studies. âĂć (Korobova, 2010): Russian plain forest; âĂć (Muramatsu et al., 2004): Chiba Prefecture, Pacific side of Japan (Humid subtropical climate); âĂć (Roulier et al., 2018; Roulier et al., 2019): French beech forest soils; âĂć (Takeda et al., 2015; Takeda et al., 2018): pine forest, Japanese beech forest and dwarf bamboo lowland (Rokkasho, Japan (Southern Shimokita Peninsula; cold maritime climate)

19. “P9 L5: What “previous studies”? Present your data first. You need to cite specific literature if you want to compare.”

We will change the order and present our data first

20. “P9 L7: This organic C concentration is too high for a mineral A horizon. This indicates that an O (organic) horizon was sampled.”

As mentioned above, we classified the topsoil horizon in profile L2 as an A horizon instead of an O horizon due to the low thickness of the horizon (12 cm).

21. “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)”

‘In four out of twelve samples the determined sum of the iodine content extracted during F1-F4 were higher (1.4 %,5.8 %,47.7 % and 69.7 %) than the values of the total iodine content caused by cumulated uncertainties of consecutive extractions and inhomogeneity of the soil sample’. Page 12 Lines 15-17 We agree that crystalline Fe

oxides were not extracted during F4, iodine bound to crystalline Fe oxides is part of the residual fraction F5.

22. “P12 L1: Following the reasoning above, you cannot determine that F5 fraction iodine is associated with SOM.” See above, we defined the F5 fraction now as residual-fraction including now both SOM and crystalline Fe.

23. “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.”

Dehaspe et al. (2018) and Solano-Rivera et al. (2019) have shown that our catchment is rapidly responding to rain events. They found saturation excess overland flow during periods with high rainfall since soils throughout the catchment have high infiltration capacities in excess of 200 mm/h (Solano-Rivera et al., 2019) or even up to >1000 mm/h in places (Dehaspe et al., 2018). It is possible that anoxic conditions are temporarily reached (Chen et al., 2020). However, the high iodine content in our soils shows that oxic conditions or reducing conditions of nitrate and manganese reduction predominate anoxic conditions of iron reduction. Another response may be found in flatter slowly responding systems.

References

Chen, C., Hall, S. J., Coward, E., and Thompson, A.: Iron-mediated organic matter decomposition in humid soils can counteract protection, Nature communications, 11, 2255, https://doi.org/10.1038/s41467-020-16071-5, 2020.

Dehaspe, J., Birkel, C., Tetzlaff, D., Sánchez-Murillo, R., Durán-Quesada, A. M., and

Soulsby, C.: Spatially distributed tracer-aided modelling to explore water and isotope transport, storage and mixing in a pristine, humid tropical catchment, Hydrol. Process., 110, 5089, https://doi.org/10.1002/hyp.13258, 2018.

Hou, X., Hansen, V., Aldahan, A., Possnert, G., Lind, O. C., and Lujaniene, G.: A review on speciation of iodine-129 in the environmental and biological samples, Anal Chim Acta, 632, 181–196, https://doi.org/10.1016/j.aca.2008.11.013, 2009.

IUSS Working Group WRB: World reference base for soil resources 2014, update 2015: International soil classification system for naming soils and creating legends for soil maps, World soil resources reports, 106, FAO, Rome, 181 pp., 2015.

Korobova, E.: Soil and landscape geochemical factors which contribute to iodine spatial distribution in the main environmental components and food chain in the central Russian plain, J Geochem Explor, 107, 180–192, https://doi.org/10.1016/j.gexplo.2010.03.003, 2010.

Li, J., Wang, Y., Xie, X., Zhang, L., and Guo, W.: Hydrogeochemistry of high iodine groundwater: A case study at the Datong Basin, northern China, Environ. Sci.: Process. Impacts, 15, 848–859, https://doi.org/10.1039/C3EM30841C, 2013.

Muramatsu, Y., Yoshida, S., Fehn, U., Amachi, S., and Ohmomo, Y.: Studies with natural and anthropogenic iodine isotopes: Iodine distribution and cycling in the global environment, J Environ Radioactiv, 74, 221–232, https://doi.org/10.1016/j.jenvrad.2004.01.011, 2004.

Roulier, M., Coppin, F., Bueno, M., Nicolas, M., Thiry, Y., Della Vedova, C., Février, L., Pannier, F., and Le Hécho, I.: Iodine budget in forest soils: Influence of environmental conditions and soil physicochemical properties, Chemosphere, 224, 20–28, https://doi.org/10.1016/j.chemosphere.2019.02.060, 2019.

Roulier, M., Bueno, M., Thiry, Y., Coppin, F., Redon, P.-O., Le Hécho, I., and Pannier, F.: Iodine distribution and cycling in a beech (Fagus sylvatica) temperate forest, Sci.

Total Environ., 645, 431–440, https://doi.org/10.1016/j.scitotenv.2018.07.039, 2018.

Shimamoto, Y. S., Takahashi, Y., and Terada, Y.: Formation of organic iodine supplied as iodide in a soil-water system in Chiba, Japan, Environ. Sci. Technol., 45, 2086–2092, https://doi.org/10.1021/es1032162, 2011.

Solano-Rivera, V., Geris, J., Granados-Bolaños, S., Brenes-Cambronero, L., Artavia-Rodríguez, G., Sánchez-Murillo, R., and Birkel, C.: Exploring extreme rainfall impacts on flow and turbidity dynamics in a steep, pristine and tropical volcanic catchment, CATENA, 182, 104118, https://doi.org/10.1016/j.catena.2019.104118, 2019.

Takeda, A., Tsukada, H., Takahashi, M., Takaku, Y., and Hisamatsu, S.: Changes in the chemical form of exogenous iodine in forest soils and their extracts, Radiation protection dosimetry, 167, 181–186, https://doi.org/10.1093/rpd/ncv240, 2015.

Takeda, A., Nakao, A., Yamasaki, S.-i., and Tsuchiya, N.: Distribution and Speciation of Bromine and Iodine in Volcanic Ash Soil Profiles, Soil Sci. Soc. Am. J., 82, 815–825, https://doi.org/10.2136/sssaj2018.01.0019, 2018.

Interactive comment on SOIL Discuss., https://doi.org/10.5194/soil-2020-20, 2020.