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

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Received and published: 23 June 2020

We would like to thank reviewer 2 for the detailed comments and suggestions to improve the quality of our work. Detailed responses to the comments of R2 are given below. The original comments by R2 are between quotation marks.

“General comments” 1. “This study concerns the evaluation of the soil-related factors that dominate iodine retention and mobilization in tropical soils and solid phase sequential extraction was used to identify iodine binding forms in soils. It is interesting the evaluation of the mobilization along the nine soil profiles, however the main concern relates to the novelty of this study. Author should review the previous knowledge in detail about soil component controlling iodine mobility, and the novelty of this study
should be stressed.”

Regarding the novelty of this study, we believe that the combination of solid phase iodine binding analyses and mobilisation tests and especially the monitoring of iodine in adjacent aquatic system is novel and indicates the consequences of long-term enrichment and retention of iodine in Fe-rich tropical soils for aquatic systems and its potential bioavailability there. We recognized that this has not become entirely clear, and changed the title and put more emphasis on these novel findings in the revised manuscript. We are aware, that several previous papers have shown that iodine mobility is mainly controlled by organic matter and iodine is leached out as organic iodine from soils (e.g. Roulier et al., 2019; Xu et al., 2011a; Unno et al., 2017). Our study shows that iodine is transported as DOC-complexes from topsoil to deeper soil horizons (page 13 Line: 5), where the DOC-iodine (DOC-I) complexes are retained through binding to Fe-oxide surfaces (page 13 Lines: 12-13). The high Fe concentrations in our soils cause the low amounts of leachable iodine (and DOC). Due to the high age of our soils and the long exposure time to iodine depositions the soils had a long time to accumulate iodine in the soil during soil formation due to the process of DOC-iodine leaching from topsoil to subsoil and fixation by Fe-oxides. (page 14 Lines: 11-12)

2. “The title “Iron oxides control sorption and mobilisation of iodine in a tropical rainforest catchment” presents a problem that is repeated throughout the article.”

Based on this comment we have decided to change the title of the manuscript to “Organo-iodine sorption to iron-oxides controls high enrichment and low mobility of iodine in soils of a pristine tropical rainforest”.

3. “I would expect a focus on the effect of Fe oxides on the mobilization of iodine, but Fe oxides have not been identified in this work.”

As mentioned above previous studies showed that organic matter is a main factor controlling iodine mobility in surface soils. But we showed that Fe-oxides stabilize organically bound iodine by strong sorption in the soils and protect it against mobilisation. The
exact identification of the Fe-oxides was not part of the study and would not change the fact that some Fe phases act as the main sorbent for (organo-) iodine.

“In its current state, the manuscript is not suitable for publication in SOIL. I hope that the comments below are useful, and look forward to reading more about this work in the future.” We thank the Reviewer for his/her constructive criticism and hope to provide an acceptable revision for publication in SOIL.

“Specific comments”

4. “Page 1 Lines 27-31: please cite more recent references (Humphrey et al. (2017) Environmental Science Processes and Impacts and references therein). “

We will include the references.

5. “Page 5 Lines 1-2: the data related to “Physical soil properties for each horizon were recorded in the field including texture, aggregate type, degree of rooting, skeleton and pore volume (see Supporting Information)” are not provided in the Supporting Information. “

We will update the SI.

6. “Page 5 Lines 7-9: “The pH value of the air-dried soil was measured in water with a soil:solution ratio of 1:2.5. The water content () was determined gravimetrically for all horizons of profiles L2 and R2. Stream water temperature, pH, redox potential (Eh) and conductivity (EC) were measured in-situ using a handheld Hanna multi-parameter probe (HI 98195)”

a. “Some pH values are missing in tables S1 and S2. " The pH was only measured in selected profiles (L2, R2 and R4) because the sample amount was limited. But it can be assumed that they would be in the same range of 4.1-4.9

b. “In addition, the role of pH on organo-iodine formation and the dissolution of Fe-oxides should be clearly explained.” We agree that the pH can have an impact on
iodine speciation and mobility. But a detailed discussion on the effect of the pH on iodine speciation was not part of the manuscript and can be found elsewhere (e.g. (Schwehr et al., 2009; Kaplan, 2003; Xu et al., 2011b; Yeager et al., 2017; Sheppard et al., 1995; Yoshida et al., 1992)).

c. “The authors mention redox potential (Eh) and conductivity (EC), however, no such results are presented in the manuscript. “ Will be included in the revised manuscript.

7. “Page 5 Line 18: the sequential extraction procedure according Schmitz and Au mann (1995) is a pretty well-established procedure. The OM-bound iodine can be severely underestimated using this method. Fractionation studies have a limited scope for iodine analysis in soils as operational procedures do not necessarily yield discrete fractions. A much greater emphasis has been placed on chemical speciation analysis and various methods have been successfully developed for analyzing chemical species. In addition, the authors should underline the potential artifacts created using this extraction procedure, and should also consider limitations/problems of the analytical approach. Overall, I recommend adding a paragraph with a list and more detailed discussion about the uncertainties of the chemical fractionation. “

In Principal all sequential extraction procedures includes (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 written 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 manuscript.

8. “Page 7 Line 25: My main concern related to this work is that it is not enough to identify the major Fe concentration using an energy-dispersive X-ray fluorescence spectrometer. In addition, the method of Cheburkin and Shotyk (1996) analyzed Pb and trace elements in peats. This result should be supported by the analysis of Fe components, e.g., selective extraction methods (for tropical soils see the methods described in Coward et al., 2017 Geoderma) or XRD. “

This method is unfortunately not available in our laboratory. However, the identification of the Fe phases was not part of the study and would not change the fact that most of the iodine is associated with Fe-oxides.

9. “Page 9 Fig. 3, Page 11 Fig. 4, and Page 13 Fig. 5: please report the correlation values.” We have stated the correlation of total iodine with total carbon in the soil on
page page 12 Lines 4-5: “The correlations of iodine with C (rS= 0.42, p= <0.05) and Br with C (rS= 0.57, p= <0.01) suggest a weak association with C” and the correlation of iodine with Fe on page 10 Line 10-11: “Despite this, the correlation between iodine and Fe in the solid phase was statistically not significant (r = -0.31)”. We will add a scatter plot with this correlation. We have shown the correlation for iodine and DOC in the leachates on Page 12 Lines 27-28: “Iodine, Br and DOC were significantly correlated in the leachates (iodine-DOC: 0.7, p= <0.001, Br-DOC 0.74, p= <0.001) suggesting that water soluble iodine and Br at least partly existed as dissolved organo-halogen compounds. We will add a scatter plot with this correlation. We don’t understand the reviewer’s comment here. Which correlations are missing, especially regarding the sequential extraction?


We will include the references.

11. “Page 10 Lines 1-3 and Lines 6-8: “The solid phase SE analyses showed that between 48 and 152 % (median: 78.7 %) of total iodine (Figure 4) but only between 12.3 % and 72.1 % (median: 30.8 %) of total Br in the soils was associated with reducible components (F4; iron sesquioxides (Fe2O3), hydroxides (Fe(OH)3) and oxide hydroxides (FeO(OH)))” and “This was attributed to higher Fe contents in subsoil horizons, presumably in the form of Fe-oxides” again, the solid phase extraction and speciation of Fe oxide would be needed. “

The exact identification of the Fe-oxides was not aim of our study and would not change the fact that most of the iodine is associated with Fe-Oxides.

12. “Page 11 Fig. 4: the sum of F2, F3, and F4 fractions reaches up to 150%. Please
explain why.”

See answer above.

13. “The section about conclusions could be improved; it is rather a summary of results than a real presentation of conclusions. What are the new insights into Fe oxides mediated sorption and mobilization of iodine gained by applying the present fractionation method?”

We will change the conclusion. As stated above, we try to show that iodine is transported as DOC-complexes from topsoil to deeper soil horizons (page 13 Line: 5), where the DOC-iodine (DOC-I) complexes are retained through binding to Fe-oxide surfaces (page 13 Lines: 12-13). The high Fe concentrations in our soils cause the low amounts of leachable iodine (and DOC). Due to the high age of our soils and the long exposure time to iodine depositions the soils had a long time to accumulate iodine in the soil during soil formation due to the process of DOC-iodine leaching from topsoil to subsoil and fixation by Fe-oxides. (page 14 Lines: 11-12). The strong stabilisation by the Fe-Oxides prevent leaching from the soils leading to low iodine concentrations in adjacent drainage systems during base and stormflow conditions.

References


