SOIL Discuss.,
https://doi.org/10.5194/soil-2020-20-AC1, 2020

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 1 for the helpful comments and suggestions to improve the quality of our work. Detailed responses to the comments of R1 are given below. The original comments by R1 are between quotation marks.

"General comments This study deals with distribution of iodine in soils in tropical rainforest. Iodine in soils from nine profiles are investigated by sequential extraction technique. The observed data for iodine in tropical rainforest is valuable. The study is well-organized and the manuscript is well-written. But the considerable revisions for following points should be needed before acceptance."

1. "My major concern is that interruption of results from the sequential extraction may

Printer-friendly version

Discussion paper

have made erroneous conclusion. Authors concluded that iron oxide is the main factor controlling iodine mobility in soil by the fact that major fraction of iodine was F4. It is well known that iodine is highly mobilized as iodide under anoxic soil conditions. Extraction step with reducing agent (NH2OH HCl) can alter iodine form in soil resulting high percentage in F4. This is not necessarily indicating that iodine adsorbed to iron oxide."

It would be possible that NH2OH HCl reduces some iodine to iodide under the anoxic conditions in step F4. But this requires the extracted (and reduced) iodine be either sorbed to Fe phases or OM. We are not excluding, that iodine bound to DOC was extracted during F4, when Fe-oxide became dissolved. As described in the manuscript, we believe that organo-iodine is the preliminary form of iodine (DOM-I), which is then bound to Fe-oxides in the deeper soil layers. Several studies have already shown, that the main form in the soils is organic iodine (Unno et al., 2017; Xu et al., 2011) as inorganic iodine is transformed rapidly to organic forms in the soil surface (Takeda et al., 2015; Hu et al., 2012) and iodine is entering the soil to a large extent as organic iodine.

2. "In addition, sum of F1 to F4 reached up to about 150% in some soil in Figure 4, suggesting that F4 can be overestimated and F5 can be underestimated in this method. Authors should discuss in detail the potential artifact and defect of the extraction procedure for iodine fraction."

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 iodine, 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

Printer-friendly version

Discussion paper

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. The message of our study is that DOM-bound iodine is retained by the high abundance of Fe-oxides in tropical soils leading to enrichment and reduction of iodine release to the adjacent aquatic system. We will try to make this point clearer in the revised manuscript.

3. “Many previous studies indicate that soil organic matter, rather than iron oxide, control the iodine mobility in soil. “

We agree with the reviewer as this is one of our findings. We are also saying that organic matter controls iodine mobility in our soils as iodine is initially transported as DOM-iodine-complex from the upper organic rich soil layer but is retained by Fe-oxides in deeper soil horizons.

4. “Author should review the previous knowledge in detail about soil component controlling iodine mobility, and novelty of this study should be discussed. "

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., 2011; 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) 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.

5. “In addition, the manuscript lacks references of recent papers on the topics including dynamics of iodine in forest ecosystem, speciation of iodine in soil and water, and mobility of iodine in soil, for example, Roulier et al (2019) Chemosphere 224, 20; Humphrey et al. (2020) Environ. Sci. Technol. 54, 1443; Takeda et al. (2018) Soil Sci. Soc. Am. J. 82, 815; Unno et al. (2017) J. Environ. Radioactiv. 169–170, 131. Specific comments Page 3 Line 8 “

We will include the references in the revised manuscript.

6. “Refer the soil classification system exactly.”

The soils were classified using the World Reference Base for Soil Resources (IUSS

Working Group WRB, 2015). We will include the reference.

7. “Page 12 Line 5, and Page 14 Line 17-19 Scatter plot should be given to explain the correlation analysis.”

Will be included in the revised manuscript.

References 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.

Hu, Q. H., Moran, J. E., and Gan, J. Y.: Sorption, degradation, and transport of methyl iodide and other iodine species in geologic media, Appl Geochem, 27, 774–781, https://doi.org/10.1016/j.apgeochem.2011.12.022, 2012.

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.

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.

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.

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.

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.

Unno, Y., Tsukada, H., Takeda, A., Takaku, Y., and Hisamatsu, S.'i.: Soil-soil solution distribution coefficient of soil organic matter is a key factor for that of radioiodide in surface and subsurface soils, J Environ Radioactiv, 169-170, 131–136, https://doi.org/10.1016/j.jenvrad.2017.01.016, 2017.

Xu, C., Miller, E. J., Zhang, S., Li, H.-P., Ho, Y.-F., Schwehr, K. A., Kaplan, D. I., Otosaka, S., Roberts, K. A., Brinkmeyer, R., Yeager, C. M., and Santschi, P. H.: Sequestration and remobilization of radioiodine (129I) by soil organic matter and possible consequences of the remedial action at Savannah River Site, Environ. Sci. Technol., 45, 9975–9983, https://doi.org/10.1021/es201343d, 2011.

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

Printer-friendly version

Discussion paper